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BY

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ASSOCIATE OF THE ROYAL SCHOOL OF MINES,
ASSOCIATE-MEMBER OF THE INSTITUTION OF CIVIL ENGINEERS, MEMBER OF THE INSTITUTION
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1900.

PREFACE.

THE Father of English metallurgical literature has said,* "Of all the branches of Metallurgy that of which Silver forms the subject is the most extensive, the most varied, and the most complicated." It will, therefore, be obvious that in order to cover the ground embraced by such a wide subject within the modest compass allotted to this volume, it was necessary to condense and summarise to the greatest possible extent. It is, however, hoped that the digest now presented will be found to combine the requirements of accuracy and "up-to-dateness" with such measure of completeness as the limitations of space have permitted.

As in the case of Part I. on "Lead," obsolete processes have received only casual mention, it being felt that the student of what may be termed "historical metallurgy" will do better to consult the pages of authorities who were more nearly contemporary with the processes they describe. The aim throughout has been to consider the subject from the practical standpoint of the working metallurgist; how far this attempt has been successful it is for working metallurgists to judge.

Among others, the Chapters on "Hyposulphite Leaching Practice" and on "Blast Furnace Matting" will be found to contain information hitherto unpublished. There can, however, be little which is absolutely novel in a volume of this character, and the freest use has been made of

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* Preface to Percy's *Metallurgy of Silver and Gold*, Part I., London, 1880.

published literature bearing on the subject so far as it has been available to the Author. The source of most of the contributions is given in the footnotes, but special indebtedness must be acknowledged to the works of Percy (already referred to), Schnabel (*Handbuch der Metallhüttenkunde*, Berlin, 1894), and Egleston (*Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., New York, 1887), to the *Transactions of the American Institute of Mining Engineers*, the *Engineering and Mining Journal of New York*, and the *Columbia College School of Mines Quarterly*; as well as to those gentlemen referred to in the body of the work who have privately, and with the greatest kindness, supplied valuable details of actual practice.

Errors have crept in here and there, principally through the fact that owing to distance it was not possible for the Author to see any of the proof-sheets. Some of these errors have been corrected in a list of "Errata," and for any which have remained undiscovered the Author begs the kind indulgence of his readers.

HENRY F. COLLINS.

MINA DE SANTA FE,
CHIAPAS, MEXICO,
December, 1899.

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Ann. de Chimie et de Physique. Annales de Chimie et de Physique.

Ann. des Mines. Annales des Mines.

Berg- u. H. Zeitung. Berg- und hüttenmännische Zeitung.

Chem. News. Chemical News.

E. M. J., or *E. and M. J.* The New York Engineering and Mining Journal.

J. Am. Chem. Soc. Journal of the American Chemical Society.

Journ. Soc. Arts. Journal of the Society of Arts.

J. Soc. Chem. Ind. Journal of the Society of Chemical Industry.

Met. Silver. Metallurgy of Silver.

Min. Ind. Mineral Industry.

Mon. U.S. Geol. Survey. Monographs of the United States Geological Survey.

Oesterr. Zeitsch. f. Berg- und Hüttenwesen. Oesterreichische Zeitschrift für Berg- und Hüttenwesen.

Oesterreich. Jahrb. Oesterreichische Jahrbuch.

Phil. Trans. Roy. Soc. Philosophical Transactions of the Royal Society.

Proc. Civ. Eng. Proceedings of the Institution of Civil Engineers.

Proc. Colo. Sci. Soc. Proceedings of the Colorado Scientific Society.

Proc. Roy. Soc. Proceedings of the Royal Society.

S. M. Q. Columbia College School of Mines Quarterly.

Trans. A. I. M. E. Transactions of the American Institute of Mining Engineers.

Trans. Aust. Inst. M. E. Transactions of the Australian Institution of Mining Engineers.

Trans. Fed. Inst. Min. Eng. Transactions of the Federated Institution of Mining Engineers.

Trans. I. M. M. Transactions of the Institute of Mining and Metallurgy.

Zeitsch. f. angewandte Chemie. Zeitschrift für angewandte Chemie.

Zeitschr. f. B. H. u. S. W. in Preussen. Zeitschrift für das Berg- Hütten und Salinen Wesen in Preussische Staate.

THE METALLURGY
OF
LEAD AND SILVER.

PART II.—SILVER.

SECTION I.—SILVER AND ITS ORES.

CHAPTER I.

PROPERTIES OF SILVER & ITS PRINCIPAL COMPOUNDS.

Since the earliest times silver has been associated with gold as a "precious metal," and although of late years it has become depreciated in value, its usefulness for coinage and ornamental purposes has been maintained.

Physical Properties—*Colour.*—Silver is the whitest of metals, and possesses a most brilliant lustre, which is unapproached by any other metal, save, perhaps, lithium.

Hardness.—Silver figures at 990 on Bottone's scale,* and is therefore harder than gold, though softer than copper.

Malleability and Ductility.—In these qualities silver is excelled only by gold. It can be hammered into leaves only $\frac{1}{10000}$ of an inch thick, and a single grain can be drawn into 400 feet of wire.

Tenacity.—The tenacity of silver according to Baudrimont † is 17·27 tons per square inch at 0° C.

Specific Gravity.—The specific gravity of rolled silver is at 13·2° C. according to Matthiessen ‡ 10·468. Cooke ‡ determined that of cast silver at 0° C. to be 10·461. The finely-divided

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* Roberts-Austen, *Introduction to the Study of Metallurgy*, 4th edition, 1898, p. 17.

† *Ann. de Chimie et de Physique* [3], vol. xxx., p. 304.

‡ Percy, *Metallurgy of Silver and Gold*, p. 4.

precipitate of silver thrown down by iron sulphate has, according to Rose, a specific gravity of 10·55 to 10·61.

Fusibility and Volatility.—According to the best concurrent evidence the melting point of silver may be taken as 954° C.[*] Silver is readily volatilised in the electric arc or under the oxy-hydrogen blowpipe; and as pointed out by Stas and confirmed by Roberts and Lockyer,[†] its vapour is blue by reflected light. The exact temperature at which volatilisation begins is not known. According to Van Riemsdijk[‡] there is sensible volatilisation at a temperature slightly above the melting point of copper (1054°), but the boiling point is certainly very much higher than the melting point of steel (1600°), probably indeed over 2000° C. The volatility of silver, however, is no doubt much increased by its admixture with other volatile metals, such as lead, zinc, and antimony, and to this cause is partly due the presence of silver in flue-dust from roasting furnaces, the temperature in which is never high enough to sensibly volatilise pure silver by itself.

When silver is melted and cooled slowly, octahedral crystals can be obtained. When melted in the air it absorbs twenty-two times its volume of oxygen, which is, however, given off on solidification. This phenomenon called "sprouting" is peculiar to silver which is nearly pure, comparatively small quantities of copper or of lead destroying its property of sprouting.

Conductivity and Expansion.—The conductivity of silver both for heat and electricity is higher than that of any other metal. Silver is always adopted as the standard for heat conductivity, being called 100; the heat conductivities of gold and copper with reference to this standard are respectively 53·2 and 73·6. The standard now usually adopted for electrical conductivity is Hg at 0° C. = 1; referred to which standard silver figures as 57·23.[§] Its coefficient of linear expansion between 0° and 100° is 0·0000192.

Latent and Specific Heat.—The latent heat of fusion of silver is generally taken as 21·07. Its specific heat between 0° and 100° is, according to Dulong and Petit, 0·056.

Other Constants.—The atomic weight of silver is 107·66, its atomic volume 10·2.

Chemical Properties.—Silver undergoes no change when placed in water, or when exposed to pure air either wet or dry, nor is it affected by caustic alkalies even in a molten condition. The tarnish formed on silver plate is caused by the presence of traces of sulphur compounds in the air, especially H_2S.

Silver is readily dissolved by nitric acid, but sulphuric acid only attacks it when concentrated and boiling. Hydrochloric

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[*] Roberts-Austen, *op. cit.*, p. 177.

[†] *Proc. Roy. Soc.*, 1875, vol. xxiii., p. 344.

[‡] Percy, *op. cit.*, p. 6.

[§] Roberts-Austen, *op. cit.*, p. 73.

acid attacks the surface only, covering it with an impervious coating of chloride. Other acids do not attack it, but chlorine, bromine, and iodine all do so, even in the cold, with formation of the corresponding haloid compound.

Alloys of Silver of Commercial Importance.—"In whatever proportions *silver and copper* are melted together comparatively homogeneous alloys are obtained, whether solidification takes place slowly or quickly."* Levol's alloy (71·89 per cent. of silver) has, according to Roberts-Austen,† a lower melting point than any other.

The silver-copper alloys have been the subject of elaborate investigation by Roberts-Austen,‡ and later by Heycock and Neville,§ who have made very accurate determinations of their melting points. Osmond ‖ has shown that Levol's alloy is the true *eutectic* alloy of the silver-copper series.

When alloys of silver and copper are roasted with free access of air both metals are oxidised, but the copper in much larger proportion than the silver. When roasted with salt, the silver is converted into chloride, the copper into black oxide, CuO. When melted with sulphur both metals are sulphurised, but the copper in much larger proportion than the silver. This process was suggested for refining the very base alloys formerly used in France and called "billon." If sufficient excess of sulphur be present, both metals are completely sulphurised and converted into a regulus. If the alloy be alternately treated with dilute sulphuric acid and exposed to the air, the copper goes into solution as sulphate, while the silver remains as metal.

Silver and Lead.—The alloys of these metals have been already described (Part I., p. 24). Lead has a powerful affinity for silver, and will remove it from all its salts and combinations with sulphur, arsenic, antimony, &c., and even from its alloy with copper. Upon this last property was founded the now extinct "Saigern" or liquation process described in all old text-books.

When silver-lead alloys are melted at a red heat with free access of air the lead is oxidised to litharge, while the silver remains unaltered.

Silver and Bismuth.—Silver alloys with bismuth in all proportions, and the latter metal may even be employed instead of lead for cupellation, though the process is then much slower and the loss of silver is stated to be greater than when lead is used.

Silver and zinc alloy in very wide proportions. The alloys are white and do not readily tarnish; those containing up to 25 per

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* Percy, *op. cit.*, p. 150.

† *Journ. Soc. of Arts*, Mar., 1897.

‡ *Proc. Roy. Soc.*, 1875, vol. xxiii., pp. 481, *et seq.*, and Cantor Lectures, Society of Arts, Session 1897.

§ *Phil. Trans. Roy. Soc.*, vol. clxxxix., 1897, p. 25, *et seq.*

‖ *Comptes Rendus*, vol. cxxiv., 1897, p. 1094.

cent. Zn are malleable; with more than this amount they are brittle. The affinity of zinc for silver is so great that the former metal at a temperature a little above its melting point will remove silver from its alloy with lead.

According to Alder Wright and Thompson there are two definite zinc-silver alloys, $AgZn_5$ and Ag_4Zn_5, the former of which is more soluble in lead than the latter, and is also more unstable when melted, resolving itself into free zinc and Ag_4Zn_5. The latter is quite stable in a molten condition, but is soluble to a considerable extent in molten lead. Fortunately, however, it is almost insoluble in lead which is already saturated with zinc, and upon this fact is based the almost universal Parkes process of lead desilverisation.

Silver and Mercury.—Silver is readily dissolved by mercury in all proportions, forming "amalgams" of all consistencies from liquid to solid (according to the relative proportions of the two metals).

A great number of amalgams have been prepared artificially, but all those which are fluid seem to be merely mixtures of the definite crystallisable compound, Ag_2Hg_2, with metallic mercury. It is probable that, as in the case of gold, the amalgam is not held in true solution, but merely in mechanical suspension. When liquid amalgams are squeezed through canvas or chamois leather the residue is always found to have about the same composition—viz., 43·7 parts of silver to 100 parts of mercury, corresponding, according to Joule, with the formula $Ag_2Hg_2 + 4{\cdot}6$ per cent. of free mercury. When silver is plunged into mercury "there is produced at the surface of the metal a very thin layer of amalgam, which arrests the ulterior action of the mercury"* and this is the reason why grinding is so necessary in the amalgamation of silver ores, because the adherent film of amalgam is removed by the friction, and fresh surfaces of silver are exposed to the mercury. In the same way, clean siliceous sand assists amalgamation, while clay and other substances which increase the viscosity of the pasty mixture hinder the amalgamation.

Interesting *triple alloys* of Au, Ag and Bi and of Au, Ag and Pb have been found by R. Pearce† formed in octahedral crystals in the furnace treatment of rich ores of the precious metals.

Other alloys of silver will be described in the volume on Alloys in this series.

COMPOUNDS OF SILVER.

Silver Oxide, Ag_2O, as prepared by adding limewater to a solution of silver nitrate, is a deep olive-brown powder which blackens in sunlight, and the specific gravity of which is 7·143.

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* Percy, *op cit.*, p. 180.

† *Proc. Colo. Sci. Soc.*, 1883 and 1885.

It may also be prepared by boiling freshly precipitated and still moist silver chloride with a strong solution of caustic potash of at least 1·25 specific gravity, grinding up the residue, re-treating in the same way, and washing. Prepared thus it is a deep black powder.

When heated, it begins to lose oxygen at 250° C., and is generally supposed to be completely reduced to metal below a red heat, though this is disproved by the experiments of Deville and Debray. In combination with oxides of zinc, lead, copper, and manganese, however, it is no longer reduced by heat alone.

Silver oxide is a strong base; it is soluble in 3000 parts of water and the solution is a powerful oxidiser, acting at once on Hg (forming an amalgam) as well as on Zn, Cd, Sn, Pb, and Cu, but not on Fe, Ni, or Co.

According to Berthier[*] finely-divided silver heated with CuO, Pb_3O_4, or MnO_2 reduces these oxides to Cu_2O, PbO, and MnO respectively, being itself oxidised; and although, on raising the mixture to the melting point of silver, the greater part of the oxide is reduced again, a portion is still retained by the other metallic oxides.

Silver oxide precipitates Hg from solutions of all its salts; when the mercuric salt is in excess the precipitate consists of a basic double salt (sulphate or nitrate); but when the silver oxide is in excess the precipitate is chiefly composed of mercuric oxide. Salts of Cu, Ni, Pb, Cd, and Zn also give precipitates of the respective oxides.

In spite of the decomposition of Ag_2O at temperatures of 300° and upwards there is little doubt that the brown powder produced by the deflagration of silver wire by the electric current, as well as that produced when the metal is boiled under the oxyhydrogen blowpipe, consist of this substance. Its existence in litharge is also probable, though by no means certain. According to Wait,[†] in a rich litharge containing about 3 per cent. silver, from 18·6 to 19·25 per cent. of the silver is soluble in acetic acid, which certainly points to the existence of that metal in the oxide condition, as metallic silver itself is quite untouched by acetic acid, even in the most minute state of subdivision. The subject of the temperature at which silver oxide is decomposable under different conditions requires further investigation.

In most of the published data on the roasting of silver ores it is stated that the loss seemed to be greatest just before the completion of the roast, and it would seem, therefore, as if the loss only begins to be heavy when the decomposition of silver sulphide commences. After all the silver has been converted into the metallic condition there is little further volatilisation, and it would almost appear that the volatile compound must be some intermediate combination, perhaps a suboxide, which,

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[*] Percy, *op cit.*, p. 19.

[†] *Trans. A.I.M.E.*, vol. xv., p. 463.

though dissociating almost immediately, remains stable long enough to volatilise.

Silver Sulphide, Ag_2S, is found native as the mineral argentite. Silver readily combines with sulphur and decomposes H_2S at ordinary temperatures. When clippings of silver and excess of sulphur are melted together the mass becomes incandescent, and forms silver sulphide, which is perfectly liquid but does not, like lead sulphide, permeate the crucible. Thus prepared, it is grey and crystalline, with a metallic lustre; it is soft, sectile, and moderately malleable. It may also be formed in the wet way. Molten silver sulphide is unaltered out of contact with air, but when heated with excess of air it is decomposed into metallic silver and SO_2.

Silver sulphide is insoluble in water, in solutions of caustic alkalies, alkaline carbonates and chlorides, hydrate and carbonate of ammonia, also in sodium thiosulphate (hyposulphite). It is, however, readily dissolved by KCy solutions, both hot and cold. Nitric acid readily dissolves it, forming nitrate of silver and liberating some free sulphur. It is not affected by dilute hydrochloric and sulphuric acids, but is decomposed by the strong acids, liberating H_2S and free sulphur respectively. The film of chloride formed on the unaltered sulphide in the former case hinders the further progress of the reaction. *Molten silver* dissolves the sulphide in all proportions up to 19·5 per cent. of its own weight.[*] *Alkaline sulphides* dissolve it, the resulting mass being decomposed by water with separation of the silver sulphide as a black powder. Many other metallic sulphides also dissolve it in a molten condition, forming argentiferous "mattes"; while metallic silver and its haloid compounds are also converted into sulphides by their agency, the silver always entering the resulting matte as a sulphide. Upon this fact is based one of the most important processes of silver extraction, the so-called "matting process."

Even in the condition of a moist precipitate, silver sulphide remains unaltered on exposure to air and moisture at ordinary temperatures. When a current of steam is passed over it at the constant temperature of 100° C. metallic silver is liberated, with production of sulphuric acid and sulphuretted hydrogen,[†] according to the equation—

$$4Ag_2S + 4H_2O = 8Ag + H_2SO_4 + 3H_2S.$$

At a red heat the sulphur of the silver sulphide is acted upon simultaneously by the oxygen and hydrogen of the steam with production of SO_2 and H_2S, free sulphur being also produced by secondary reaction between these gases.

Reactions of Metals on Silver Sulphide—*Iron.*—At a red heat iron in excess completely decomposes silver sulphide. In

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[*] Percy, *loc. cit.*, p. 26.

[†] Percy, *loc cit.*, p. 28.

presence of water at the ordinary temperature no action takes place, but on the addition of a little HCl or H_2SO_4, which liberate nascent hydrogen, H_2S is evolved and metallic silver set free.

Zinc behaves like iron.

Copper does not completely decompose silver sulphide when heated with it, for some silver sulphide remains in the copper sulphide, while the liberated silver alloys with part of the copper. With water silver sulphide is reduced by contact with copper, and the action is increased by the addition of metallic salts like ferrous sulphate or alum.

Lead, like copper, only partially reduces Ag_2S at a red heat, but the decomposition is somewhat more perfect than in the case of copper.

Mercury decomposes silver sulphide at ordinary temperatures when triturated with it, whether in presence of water or not. According to Malaguti and Durocher, quoted by Percy,* the decomposition of silver sulphide by mercury is much quicker than that of the chloride. This, however, may be easily explained by the different mechanical condition of the two substances; silver sulphide is comparatively brittle and can be reduced to the condition of a very fine powder, while the chloride forms minute malleable clots or scales which obstinately resist comminution; the actual contact between the mercury and the chloride is, therefore, not nearly so perfect as in the case of the sulphide.

The action of mercury on sulphide of silver is greatly increased by addition of solutions of ferrous sulphate, alum, or cupric sulphate. According to the authors above cited, the relative proportions of silver extracted under equal conditions are as follows:—with mercury alone 1·00, with addition of alum 1·34, of ferrous sulphate 1·80, and of cupric sulphate 2·83.

Pyrargyrite ($3Ag_2S . Sb_2S_3$) *and Proustite* ($3Ag_2S . As_2S_3$) are also acted upon by mercury similarly to silver sulphide, but the action is much slower.

It is noteworthy that natural argentiferous sulphides of other metals are much less acted upon than plain silver sulphides. In the experiments of Malaguti and Durocher, quoted by Percy,† out of eleven specimens of argentiferous galena from different localities kept in contact with mercury in a rotary machine only two gave up part of their silver contents; out of seven specimens of blende and six specimens of fahlerz only two of each were acted upon; while of four specimens of argentiferous iron pyrites not one yielded any silver. Their conclusion is that the silver exists in these minerals in two different conditions—sometimes as a true silver compound mechanically interspersed through the base metal sulphide, and sometimes as a double sulphide chemi-

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* *Op. cit.*, p. 32.

† *Id.*, pp. 33-35.

cally combined with it. In the former case mercury can attack the silver sulphide, in the latter there is no action.

Reactions of Silver Sulphide.—When it is melted with lead and cupric oxides double decomposition takes place at the temperature of fusion, the reaction being in accordance with the equation—

$$Ag_2S + 2CuO = Ag_2Cu_2 + SO_2.$$

Silver sulphate also reacts upon silver sulphide at the temperature of fusion, double decomposition taking place as follows:—

$$Ag_2S + Ag_2SO_4 = 4Ag + 2SO_2.$$

When fused with excess of *alkaline carbonates*, silver sulphide is reduced to the extent of about 90 to 95 per cent., the remainder being dissolved in the alkaline sulphide formed—

$$4Ag_2S + 4Na_2CO_3 = 8Ag + 3Na_2S + Na_2SO_4 + 4CO_2.$$

When fused with *alkaline cyanide*, about five-sixths of the silver is reduced, the rest remaining in combination with the resulting alkaline sulphide. Some alkaline sulphocyanide is formed, but no silver sulphocyanide.*

Silver sulphide is completely reduced by fusion with *nitre*. It is not acted upon by fusion with *sodium sulphate* or *lime*. With *potassium chlorate* one-third of the silver is reduced to metal, the remaining two-thirds being converted into chloride. Roasted with *common salt* sulphide of silver is partly converted by the joint action of sodium chloride and oxygen into silver chloride, sodium sulphate being formed at the same time. Another part of the sulphide is reduced directly to metallic silver with formation of sulphurous acid. By long continued roasting the metallic silver is reconverted into chloride by the direct action upon it of excess of sodium chloride, so that finally almost all the silver is converted into chloride (in which condition part of it is volatilised) even when the silver sulphide is combined with other metallic sulphides.

Silver sulphide is attacked by *chlorine*, slowly at ordinary temperatures, but more quickly at a red heat, though to some extent the film of chloride formed protects the underlying sulphide from further action. Chlorine water acts upon it slowly in the cold with formation of silver chloride and sulphuric acid.

Both the *chlorides of copper* decompose it in presence of water, slowly even in the cold, but more quickly at a boiling heat. With cupric chloride the silver is converted exclusively into chloride; with Cu_2Cl_2 nearly all of it is reduced to metal.† *Ferric chloride* acts to some extent upon silver sulphide, but only very slowly. *Ferrous chloride* and *mercurous chloride* have no action upon it.

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* Percy, *op. cit.*, p. 37.

† See the author's experiments, *Trans. Inst. Min. Met.*, vol. vii.

Sulphuric acid vapour at a red heat decomposes silver sulphide with formation of sulphate. When combined with cuprous sulphide, the same decomposition takes place, the copper being, however, converted into oxide at this temperature.

If a mixture of silver sulphide with base-metal sulphides be roasted absolutely "sweet," the silver is left as metal, while all the other metals remain as oxides.

Silver Sulphate, Ag_2SO_4.—This substance may be formed by heating granulated silver with sulphuric acid (as in the "parting" process) when the following reaction takes place:—

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

Boiling and concentrated H_2SO_4 dissolves so much silver as to become, on cooling, a solid crystalline mass of acid sulphate, $AgHSO_4 + n Aq$. Neutral silver sulphate is a slightly yellow anhydrous salt of specific gravity 5·34, which crystallises in the rhombic system. It is comparatively insoluble in cold, but very soluble in hot, water, requiring only 88 parts of the latter at 100° C. The best solvent, however, is sulphuric acid diluted to a specific gravity of 1·25. From this solution silver is completely separated as metal in a crystalline condition by Cu, Fe, Zn, Sn, and Pb. Copper is usually employed in practice for this purpose on account of its greater intrinsic value and of the greater demand for its sulphate than for that of any of the other metals. This reaction is made use of in the Ziervogel process of silver extraction. Cuprous oxide precipitates silver mixed with basic sulphate of copper.

Silver sulphate melts unchanged at a low red heat, forming a yellow liquid. At a *strong* red heat it is completely decomposed with evolution of sulphurous acid and oxygen, but it resists unchanged the somewhat lower temperature which completely decomposes iron and copper sulphates. Silver sulphate can therefore be formed by heating silver sulphide in air with either of the above sulphates, since the sulphuric anhydride evolved by their decomposition combines with the metallic silver reduced from its sulphide. Upon this reaction is based the well-known "Ziervogel" process of silver extraction, which will be described in its proper place.

At a dull red heat silver sulphate is completely reduced by charcoal according to the reaction

$$Ag_2SO_4 + C = 2Ag + CO_2 + SO_2.$$

Although dilute sulphuric acid has no effect upon silver, ferric sulphate solutions (even when neutral and in the cold) readily attack it, while the action is much quicker when hot, and is assisted by the presence of free acid. The reaction seems to be one of simple solution and reduction, as in the case of zinc—viz.,

$$Fe_2(SO_4)_3 + 2Ag = 2FeSO_4 + Ag_2SO_4.$$

Silver sulphate in crystals, on the other hand, is completely reduced to metallic silver by contact with a strong neutral solution of $FeSO_4$ at 100° C. The reaction which takes place is the exact converse of the preceding, and it is used on the large scale as an essential part of Gutzkow's process for parting gold from silver bullion as formerly conducted at the San Francisco Mint, at the Argentine works of the Con. Kan. City S. & R. Co., and elsewhere.

Silver sulphite, a colourless crystalline substance, is formed by adding a solution of sulphurous acid, or of an alkaline sulphite to one of a silver salt. It is rapidly changed under the influence of light, or of a heat below incipient redness, into metallic silver and sulphate. It forms double salts with the alkaline sulphites, which are used in electro-plating.

Silver Chloride, AgCl, is found in nature as the mineral kerargyrite, which has a specific gravity, according to Rodwell, of 5·40 to 5·50,* and crystallises in the cubical system.

It may be prepared in the wet way by adding chlorine water or a solution of a soluble chloride to a solution of silver nitrate or sulphate, and washing and drying the precipitate. In this way it is obtained as a snow-white anhydrous powder, which blackens when exposed to light, even in a hermetically sealed tube, but recovers its white colour when kept for some time in the dark.

It fuses at about 360° C., forming first a yellow liquid and afterwards a thin red one, which rapidly permeates ordinary clay crucibles. It volatilises, though slowly, but quite fast enough to give a perceptible loss in metallurgical operations. After solidification it is pale yellowish-grey in colour, waxy or horn-like, and translucent and sectile, with a crystalline fracture.

Solubility.—Silver chloride is so nearly insoluble in water that a solution containing only 1 part of silver per million as nitrate is rendered turbid by the addition of a drop of HCl. It dissolves in *ammonia* water unchanged, and dissolves also with double decomposition in solutions of alkaline and other soluble *cyanides* and *hyposulphites*. It is also dissolved by hot concentrated HCl, and by solutions of almost all the soluble chlorides.

According to Vogel † it is soluble in the *chlorides* of all the *alkalies and alkaline earths*, but insoluble in the following chlorides—viz., those of Zn, Cd, Cu, Sn, Hg, Ni, and Co.

According to Hahn ‡ the solubility of silver chloride at the ordinary temperature in saturated solutions of different chlorides is as given in the following table :—

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* *Proc. Roy. Soc.*, 1876, vol. xxv., p. 291.

† Wagner's *Jahresberichte*, 1874, vol. xxii., p. 481.

‡ *Trans. A.I.M.E.*, vol. ii., p. 99.

TABLE I.—SOLUBILITY OF SILVER CHLORIDE.

Formula of Salt.	Per cent. of Salt in Solution.	Temp. at which Saturated.	Per cent. of AgCl Dissolved.	Per cent. of Ag. in Solution.	Sp. Gr. of Solution.	Temp of Solution.	Grm. Ag. in 100 c.c. Solution.
		Deg. C.				Deg. C.	
KCl, . . .	24·95	19·6	0·0776	0·0584	1·1774	19·6	0·0688
$NaCl$, . .	25·96	,,	0·1053	0·0793	1·2053	,,	0·0956
NH_4Cl, . .	28·45	24·5	0·3397	0·2551	1·0835	30·0	0·2764
$CaCl_2$, . .	41·26	,,	0·5713	0·4300	1·4612	,,	0·6283
$MgCl_2$, . .	36·35	,,	0·5313	0·3999	1·3350	,,	0·5339
$BaCl_2$, . .	27·32	,,	0·0570	0·0429	1·3017	,,	0·0558
$FeCl_2$. . .	30·70	...	0·1686	0·1269	1·4199	20·0	0·1802
Fe_2Cl_6, . .	37·48	...	0·0058	0·0044	1·4472	21·4	0·0064
$MnCl_2$, . .	43·85	24·5	0·1996	0·1499	1·4851	30·0	0·2226
$ZnCl_2$, . .	53·34	...	0·0134	0·0101	1·6005	,,	0·0162
$CuCl_2$, . .	44·48	24·5	0·0532	0·0399	1·5726	,,	0·0627
$PbCl_2$, . .	0·99	,,	0·0000	0·0000	1·0094	,,	0·0000

It may be useful to remember that a solution of common salt saturated at 15° C. contains 26·34 per cent. of salt by weight, its specific gravity is 1·20403 at the temperature of saturation, and one litre of it will dissolve, according to the mean of the figures given by Hahn and Vogel, 1·001 gramme of silver chloride. Most of the above solutions dissolve a larger proportion of silver chloride when boiling, but the excess separates out on cooling.

Strong *hydrochloric acid* dissolves AgCl even in the cold (1 part in 336), the solubility is increased by heating and much diminished by dilution, but it is not possible to precipitate all the silver from moderately diluted acid, say 1 to 5.

Silver chloride is insoluble in cold nitric and sulphuric acids, both strong and dilute, but is decomposed by both acids in the concentrated condition; readily in the case of sulphuric, but only after long boiling in the case of nitric acid. Most nitrate solutions dissolve small quantities of silver chloride, even in the cold, the degree of solubility being much greater when the solutions are hot. Among nitrates which act thus are those of the alkalies, lime, magnesia, and copper, the solubility being much greater in the case of mercuric nitrate.

According to Stas, silver chloride in the pulverulent granular or crystalline conditions is practically insoluble in water, but when in the flaky condition (as occurs just after precipitation in the cold from a very dilute solution) it is distinctly soluble in pure or acidified water, though, curiously enough, either silver nitrate or alkaline chloride will reprecipitate it from this solution. This explains the so-called "neutral point" in the Gay Lussac method of estimating silver volumetrically.*

Certain crystalline compounds containing sodium and silver chlorides have been prepared, but they do not appear to be true double salts.

Formation of Silver Chloride from the Metal.—Silver chloride may be produced by passing chlorine or hydrochloric acid gas or vapour of NH_4Cl over metallic silver heated to redness. Conversely, the chloride may be reduced again to metal by passing over it a current of hydrogen or of NH_4Cl vapour at a slightly higher temperature.

In small quantity silver chloride is formed by simple contact of the metal with solution of sodium chloride. Thus a solution of common salt by simple boiling in a silver crucible dissolves enough silver to give a black precipitate with H_2S, but the action appears not to take place if air be excluded. In this way may be explained the occurrence of a film of chloride on silver coins which have been long buried in the ground.

When silver leaf is ground up with common salt and heated to a temperature below redness no action takes place. When the temperature is raised to bright redness and the heat maintained for three-quarters of an hour the whole of the silver is converted into chloride, some of which volatilises. Metallic silver can also be converted into chloride by melting it in ordinary crucibles with common salt and keeping it molten at a high temperature, when a portion volatilises together with part of the salt, while the remainder is found disseminated through the layer of salt. One ounce of silver treated by Rose in this way lost 2·7 per cent. of its weight in two and a-half hours by volatilisation; the presence of copper tends to prevent the formation of silver chloride and consequent loss of silver.†

Silver is slowly converted into chloride by solutions of cupric, mercuric, and ferric chlorides, which it reduces to the lower chlorides thus:—

$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2.$$

Mercuric chloride also acts upon silver at a heat below redness, calomel subliming, while silver chloride is left.

Formation of Silver Chloride from its Sulphide.—Many experiments have been made on this subject, but the published results are contradictory. Percy and Dick,‡ and Malaguti and Durocher§ have each made elaborate series of experiments with both chlorides of copper, and they conclude that both cuprous and cupric chlorides give AgCl as the product of their action

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* Percy, *loc. cit.*, p. 291.

† Percy, *op. cit.*, p. 70.

‡ *Ibid.*, pp. 73, *et seq.*

§ Quoted *ibid.*, pp. 98, *et seq.*; also in the original *Recherches sur l'Association de l'Argent aux Mineraux Metalliques*, Paris, 1850, vol. i., p. 658.

upon Ag_2S, the equation in the case of cuprous chloride being :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S.$$

Laur, Stolzel, and other authorities,* however, while concurring as to the decomposition of the sulphide, conclude that the final product when Cu_2Cl_2 is used is metallic silver and not its chloride. This is confirmed by the author's experiments,† which indicate that only one-tenth of the total amount of silver sulphide acted upon is converted into chloride, the remainder being reduced to metal, probably according to the equation :—

$$Ag_2S + Cu_2Cl_2 = CuS + CuCl_2 + 2Ag.$$

If the silver sulphide were largely in excess, no doubt the metallic silver might be partly reconverted into chloride by secondary reaction with the cupric chloride formed; but, under conditions approximating those of actual practical work, the above reaction is that which takes place.

The sulphantimonides and sulpharsenides of silver are acted upon similarly and, according to Rammelsberg,‡ the reactions which take place in the case of pyrargyrite are as follows :—

$$2(Ag_3SbS_3) + Cu_2Cl_2 = 2AgCl + Ag_2S + 2Ag + 2CuS + Sb_2S_3,$$

while in the case of proustite it is

$$6(Ag_3AsS_3) + 7Cu_2Cl_2 = 14Ag + 4AgCl + 2CuCl_2 + 2AsCl_3 + 12CuS + 2As_2S_3.$$

All of the above reactions are important and will be referred to again in connection with wet amalgamation processes.

The formation of chloride by heating metallic silver with sodium chloride has been already referred to. The same substance may also be formed by heating silver sulphide with *sodium chloride* and other substances in a current of steam. At 100° C. the formation of silver chloride is hardly to be detected when sodium chloride alone is employed, but becomes very decided when magnesium chloride is also present. At a higher temperature the reactions take place more quickly. Finely-powdered *iron pyrites* hastens the action, no doubt owing to the formation of sulphuric acid by oxidation. These reactions are of importance in connection with the subject of chloridising roasting.

Silver sulphate and *sodium chloride*, when melted together, show a perfect double decomposition, the whole of the silver being converted into chloride. This reaction is utilised in Augustin's lixiviation process of silver extraction.

Reduction of Silver Chloride.—In the dry way, AgCl is completely reduced by a current of *hydrogen* when the compound is

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* Schnabel, *Handb. der Metallhüttenkunde*, vol. i., p. 658.

† *Trans. Inst. Min. Met.*, vol. vii., p. 233.

‡ Percy-Rammelsberg, *Metallurgie des Silbers und des Goldes*, Braunschweig, 1881.

heated to about its melting point; as also by *carbonic oxide*, which is said to carry away the chlorine as phosgene gas, $COCl_2$. *Steam* does not affect it, except at much higher temperatures. *Alkaline hydrates* and *carbonates* decompose it at about the melting point of silver, the reaction being

$$4AgCl + 2Na_2CO_3 = 4Ag + 4NaCl + O + 2CO_2,$$

but part of the silver chloride escapes by volatilising or by permeating the crucible before acquiring the temperature necessary for the reaction.

Calcium carbonate decomposes silver chloride at a temperature above the melting point of silver, forming calcium chloride.

Charcoal, in the proportion of 1 part to 2 parts of the chloride, reduces it readily; but the reaction is said to be due to the hydrogen in the charcoal, for all the chlorine is evolved as HCl, and no reduction takes place when pure plumbago is substituted for charcoal.

Zinc, *iron*, *copper*, and *lead* all reduce the chloride when heated with it. In the last two cases the reduced silver alloys with the excess of reagent metal. *Mercury* also reduces it at the ordinary temperature, but the reaction is much promoted by the action of water.

In the wet way, silver chloride may be reduced by boiling it with a solution of Na_2CO_3 and its own weight of *glucose*.

Stannous chloride also reduces it, and when very dilute solutions of silver are precipitated by a soluble chloride so that the liquid is just turbid, and a few drops of stannous chloride added, the solution acquires a yellowish-brown colour like that of glass stained by silver. Percy suggests that this colour is due to the presence of finely-divided silver, and analogous to the ruby colour of gold-stained glass, which was proved by Faraday to be due to metallic gold in a very fine state of division.

In ammoniacal solution, silver chloride is reduced by *cuprous chloride* according to the equation

$$2AgCl + Cu_2Cl_2 = 2Ag + 2CuCl_2.$$

No reduction, however, takes place when both salts are dissolved in a saturated solution of common salt.* When freshly precipitated, however, both salts react upon each other in presence of water alone. Reference has been already made to the converse of this reaction, by which cupric chloride is reduced by metallic silver to cuprous chloride. Upon this point Percy remarks, "It will probably be found that an aqueous solution of cupric chloride containing a certain proportion of cuprous chloride has no effect on either metallic silver or its chloride." Such a balance of reactions is not uncommon in chemistry, but in metallurgical practice one of each pair of reactions is generally developed and the other suppressed by altering the conditions.

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* Percy, *op. cit.*, p. 91.

Among metals, *zinc* is the best reducing agent for silver chloride, and is generally employed at mints using the nitric acid and Miller processes, granulated zinc being employed at San Francisco[*] and plates at the Australian mints.[†] It is not sufficient to expose the chloride to the action of hydrogen evolved by the solution of zinc in sulphuric acid. Direct contact of the metal with the chloride is essential at first, though afterwards, the precipitated silver forming a galvanic couple with the zinc, the action proceeds throughout a thick layer of chloride.

Iron acts in a similar way to zinc in reducing silver chloride by contact in moist air or under water. The action is much promoted by additions to the liquid of common salt, ferrous sulphate, or alum. Silver chloride in ammoniacal solution is also reduced.

Copper, even with acid solutions, reduces silver chloride only very slowly at the ordinary temperature, but more quickly at 100° C. From ammoniacal and strong saline solutions, however, it reduces the silver very perfectly. This method is adopted for recovering the silver in Augustin's process.

Besides the above, silver chloride is reduced under water quickly and completely by Cd, As, and Co, slowly by Pb, Ni, and Sb, and very slowly and imperfectly by Sn, Bi, and Mn. In the case of Pb and Sn the precipitated silver forms an alloy with the reducing metal.

Mercury reduces silver chloride only slowly at ordinary temperatures with formation of calomel, according to the equation—

$$2AgCl + 2Hg = 2Ag + Hg_2Cl_2.$$[‡]

The reaction is, however, promoted by the addition of certain salts, which act as conductors and assist in the formation of a galvanic couple between the mercury and the first reduced silver. According to Malaguti and Durocher,[§] the relative proportions of silver reduced under equal conditions are as follows:—With mercury alone 1·00, with addition of cupric sulphate 1·52, ferrous sulphate 2·15, and alum 3·09.[||]

In presence of *iron* the action of mercury upon silver chloride appears to be much increased, no doubt through the current set up between the two metals, for it appears that the quantity of silver chloride reduced in a given time when the iron and mercury are together in contact is more than double that reduced when first the iron and then the mercury act each upon the chloride separately during the same number of hours.

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[*] Ninth Report Cal. State Mineralogist, 1889, p. 70.

[†] Percy, *op. cit.*, p. 418; and *private notes.*

[‡] See the reactions of the Patio Process, Chap. iii.

[§] *Recherches sur l'Association de l'Argent aux Mineraux Metalliques*, 1850, p. 369.

[||] Compare the figures given on p. 7 with reference to the reduction of silver sulphide in presence of these salts.

Silver Chloride and Base-Metal Sulphides.—Malaguti and Durocher have shown that silver chloride is directly decomposed at ordinary temperatures by contact with metallic sulphides in presence of water, chlorides of the metals being, of course, formed.* In this way CdS, Cu_2S, SnS_2, $CuFeS_2$, &c., convert the silver into sulphide with varying degrees of rapidity. The reactions take place much more completely in ammonia water and other media.

When *cuprous sulphide* is mixed with twice its weight of AgCl and shaken in ammonia water for a few minutes, the residue is found to contain a mixture of metallic silver and sulphide. The reaction may, perhaps, be:—

$$4AgCl + Cu_2S = 2Ag + Ag_2S + 2CuCl_2.$$

When *sulphides of lead* or *zinc* are employed the action is slower, but all the silver is converted into sulphide by simple double decomposition. These two sulphides, as well as *mercuric sulphide*, act upon silver chloride in exactly the same way when fused together with it out of contact with air, the resulting base-metal chlorides partly volatilising. According to Malaguti and Durocher, who have investigated the comparative action of various metallic sulphides upon ammoniacal silver chloride solutions, the action is quickest in the case of those sulphides which, like Cu_2S (see above reaction), SnS_2 and $CuFeS_2$ act by *reduction* as well as by double decomposition, and slowest in the case of those, like CdS, ZnS, FeS, HgS, and Sb_2S_3, which act only in the latter way.

$$RS + 2AgCl = Ag_2S + RCl_2.$$

Silver Bromide, AgBr, occurs native in the mineral bromyrite. Silver and bromine combine readily at ordinary temperatures; the bromide may also be prepared by precipitating a solution of silver nitrate with one of an alkaline bromide. It is a pale yellow powder of specific gravity 6·25 to 6·29, which melts to a red liquid and solidifies to a yellow semi-transparent mass with a crystalline fracture; this solid is much more brittle than the chloride. It appears to be absolutely insoluble in water and behaves to other solvents somewhat like silver chloride, but is usually less soluble in all. Like the chloride, it is decomposed by strong sulphuric acid, but boiling nitric acid, even when concentrated, does not affect it. Its best solvent is a solution of *potassium bromide*.

Silver bromide is converted into chloride when heated in a current of chlorine; conversely, when silver chloride is acted upon by a solution of potassium bromide double decomposition takes place, potassium chloride and silver bromide being produced. Its insolubility renders it a more efficient substitute

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* *Op. cit.*, pp. 268-270.

for the chloride in all assaying methods which depend upon the insolubility of that salt.*

Silver Iodide, AgI, occurs native as the mineral iodyrite, and may be prepared by precipitating silver nitrate with alkaline iodide; or by dissolving silver in cold hydriodic acid, the action being violent and accompanied by evolution of hydrogen. Strong hydriodic acid and alkaline iodides decompose silver chloride with formation of this substance. As bromides completely expel chlorine from its combination with silver, so iodides expel bromine from silver bromide. Conversely, a current of chlorine converts silver iodide into chloride.

Silver iodide melts, at 450° C., according to Rodwell,† to a red liquid which solidifies to a transparent "claret-coloured mass;" after which it becomes (1) amber-coloured and (2) pale yellow, and (finally) crystalline, brittle, opaque, and pale green.

It is insoluble in water and in dilute acids, but is decomposed by strong sulphuric and nitric acids. Its best solvent is a cold saturated solution of *potassium iodide* from which, however, it is reprecipitated on dilution. It is also soluble in a hot solution of *caustic potash*, in solutions of alkaline *cyanides* and *hyposulphites*, and in 2510 parts of *ammonia* water. It is said to be slightly soluble in saturated solutions of alkaline chlorides, but the solubility must be very slight, for a soluble iodide is employed in the Claudet process to precipitate silver dissolved in a brine solution. Silver iodide, like the bromide, may be employed instead of the chloride for assaying.

Silver Thiosulphate, $Ag_2S_2O_3$.—The thiosulphates are better known under their old name of "hyposulphites," and as the true hyposulphites are of no metallurgical importance, the old name is employed throughout this work, instead of thiosulphate. The silver hyposulphite is prepared as a white powder by dissolving out the precipitate produced by $Na_2S_2O_3$ in $AgNO_3$ with ammonia water and reprecipitating with dilute HNO_3. It is readily decomposed into Ag_2S and SO_3, and is slightly soluble in water. With the hyposulphites of sodium, potassium, and calcium it forms two series of double salts of the formulæ $2RS_2O_3 . Ag_2S_2O_3 + 3Aq$ and $RS_2O_3 . Ag_2S_2O_3 + 2Aq$, the former being readily soluble in water, while both are soluble in excess of the alkaline salt.

The double salt $2Na_2S_2O_3 . Ag_2S_2O_3$ is formed by double decomposition whenever silver oxide, chloride (or other haloid compound), sulphate, arseniate, or antimoniate is acted upon in the cold by a solution of $Na_2S_2O_3$. It is also formed slowly in the cold and much more rapidly when hot by the action of solution of the latter salt directly upon metallic silver, but the

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* Such as the combined wet and dry process for the assay of silver in copper mattes and the Gay Lussac volumetric assay of silver bullion.

† *Proc. Roy. Soc.*, 1876, vol. xxv., p. 286.

amount dissolved appears to be independent of the degree of concentration of the solution. According to Russell[*] one part of $Na_2S_2O_3 + 5Aq$ dissolves 0·4 part of AgCl (= 0·301 part Ag), forming the double salt $Ag_2S_2O_3 . Na_2S_2O_3 + 2Aq$. The solubility of AgCl in a solution of sodium hyposulphite is very injuriously affected by the presence of certain other substances as shown by the same author, a fact of the greatest practical importance in connection with the hyposulphite leaching process.[†]

From the solution of double salts, sodium and calcium sulphides completely precipitate the silver as sulphide, regenerating an equivalent quantity of sodium or calcium hyposulphite. Upon these reactions is based the series of hyposulphite leaching processes first suggested by Percy and afterwards carried out in practice by Patera, Kiss, and others.

Sodium hyposulphite forms with cuprous hyposulphite a series of double salts with formulæ 2 : 3, 1 : 1, 2 : 1, and 3 : 1, all of which act as energetic solvents of all silver compounds. The second in particular ($Cu_2S_2O_3 . Na_2S_2O_3$) acts upon metallic silver nine times as energetically as the simple sodium hyposulphite, and even dissolves to some extent silver sulphide.

Upon these facts is based the Russell process described in Chapters XI. and XII.

Silver Cyanide, AgCy, may be prepared by precipitating the nitrate with alkaline cyanide. It is a white powder of specific gravity 3·94 which, on being heated, melts and loses half its cyanogen. It is converted into chloride by chlorine water, hydrochloric acid, and by alkaline, mercuric, and some other soluble chlorides. It is decomposed by sulphuric and nitric acids, and converted into sulphocyanide by a solution of potassium sulphocyanide.

It forms double cyanides with all the alkaline cyanides, one of which, KCy . AgCy, is largely employed for electro-plating. It may be prepared by dissolving silver chloride, cyanide, carbonate, or oxide in a solution of potassium cyanide.

Compounds of Silver and Arsenic.—An artificial silver arsenide, with the formula Ag_3As (= 81·5 per cent. Ag), was prepared under the direction of Percy[‡] and slowly roasted in a muffle for three hours at a "dull black heat." Practically all the arsenic was volatilised, the silver being left as metal, and no trace of arseniate was formed.

Silver Sulpharsenide, Ag_3AsS_3, on being carefully roasted in the same way evolved, according to Plattner,[§] SO_2 and As_2O_3, while the silver was completely converted into arseniate.

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[*] Quoted by Stetefeldt, *Trans. A.I.M.E.*, vol. xiii., p. 53.

[†] Described in Chapter xi., *q.v.*

[‡] *Op. cit.*, p. 140.

[§] *Die metallurgischen Röstprozesse*, 1856, p. 160.

According, however, to Patera[*] the same substance (the mineral proustite) when roasted for five hours in a current of steam was reduced to metallic silver.

Silver Arseniate at a high temperature yields silver arsenide, oxygen, and arsenious acid, but the decomposition is incomplete, especially in presence of other metallic arseniates.

Compounds of Silver and Antimony.—Silver and antimony alloy in all proportions and a large number of the so-called alloys have been described by Cooke.[†] The best defined alloy appears to be $SbAg_4$, in which the increase in volume is most marked; but crystals corresponding to the mineral *dyscrasite*, Ag_3Sb, were also obtained.

Silver Antimoniate has been prepared by Percy, but it does not seem to possess the normal theoretical composition. It may be formed by heating together, in a current of air, the oxides of silver and of antimony in molecular proportions.

Silver Antimonide, with 47 per cent. Ag, heated in air was converted into metallic silver and Sb_2O_4. The same substance mixed with pyrites and roasted with free access of air gave only silver antimoniate, ferrous sulphate, and ferric oxide.

Silver Sulphantimonide, Ag_3SbS_3, the mineral pyrargyrite (according to both Plattner and Percy), is converted into antimoniate by roasting.

CHAPTER II.

SILVER ORES.

SILVER is found in nature both in the native condition and combined with other substances. When in combination it may be either an essential or an accidental constituent of the mineral substance containing it; in either case the latter is considered by the metallurgist as an ore of silver. It is of more importance with ores of silver to ascertain as nearly as possible the condition in which the silver occurs combined with other substances, than is the case with ores of any other metal, for upon its manner of combination chiefly depends the choice of method for its extraction. In this respect the metallurgy of silver is much more complex than that of gold, lead, or copper. It is, therefore, necessary to consider carefully such of the different mineral species containing silver as occur in quantity sufficient to render them of commercial importance.

The mineral species which contain silver as an essential con-

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[*] *Ibid.*, p. 246.

[†] Quoted by Percy, *op. cit.*, pp. 143, 144.

stituent may be considered under three heads, viz.:—(*a*) Those which are both widely distributed and occur in sufficient quantity to render them of great importance; (*b*) those which are either widely distributed in small quantities or form important ores at certain localities; and (*c*) rare minerals.

Of class (*a*) may be described:—

Native Silver, Ag. *Cubical.*—Silver is frequently found of remarkable purity, being sometimes over 995 fine, and at other times alloyed with traces of gold, copper, quicksilver, nickel, antimony, or bismuth. It forms the chief ores at Kongsberg (Norway), Batopilas (Mexico), and Silver Islet (Michigan); and has also been found in considerable quantity as an ore at Freiberg (Saxony), Broken Hill (N.S.W.), as well as in many other localities in the U.S., Mexico, Chili, Peru, and Bolivia.

Argentite, Ag_2S. *Cubical*. Ag 87·1 per cent.—It is one of the commonest of the silver ores. It is black, soft, sectile, and slightly malleable. Whether crystallised or massive it is usually very pure, but sometimes contains traces of copper, lead, and iron. It is one of the chief ores of the great Comstock Lode (Nev.), of the Morelos, Guanajuato and Zacatecas districts in Mexico, as also in the Erzgebirge (Saxony) and Upper Harz, Peru, Chili and Bolivia, Japan, Broken Hill (N.S.W.), and other places.

Stephanite, $5Ag_2S \cdot Sb_2S_3$. *Rhombic*. Ag 68·5 per cent.—This is another very widely distributed and important silver ore. Together with argentite it formed an important ore of the Comstock Lode, and is also important throughout Bohemia and Saxony, at Schemnitz (Hungary), Guanajuato (Mex.), Aspen (Colo.), and other places.

Pyrargyrite, $3Ag_2S \cdot Sb_2S_3$. *Hexagonal*. Ag 59·8 per cent.—This ore is very widely distributed and, though almost invariably accompanying argentite, stephanite, and other species, forms in the aggregate an important ore. In Europe its chief localities are Andreasberg (Harz), the Saxon and Bohemian Erzgebirge (especially Joachimsthal), and Guadalcanal (Spain). In America it is an abundant ore in the Poorman Lode (Idaho) and at Austin (Nev.), also at Zacatecas and Sombrerete (Mex.), and near Copiapó (Chili).

Proustite, $3Ag_2S \cdot Sb_2S_3$. *Hexagonal*. Ag 65·4 per cent.—This mineral is as widely distributed as the preceding, though usually occurring in smaller quantity and accompanying other species. Its chief localities are the Erzgebirge (Sax.) Joachimsthal (Bohemia), and Guadalcanal (Spain), also Morelos, Tasco, Pachuca, Catorce, &c. (Mex.), at Chañarcillo (Chili), in Peru and in Bolivia.

Polybasite, $9(Ag_2Cu)S \cdot (SbAs)_2S_3$. *Rhombic*. Ag from 64 to 72 per cent.—This species is much more widely distributed than has been commonly supposed, especially in the American continent. It forms an important ore at Guadalupe y Calvo, Guarisamey, Tasco, and Guanajuato in Mexico, at Aspen (Colo.), in the Reese River (Nev.) and Owyhee (Idaho) districts, at Tres Puntas (Chili), and other localities, and at Freiberg (Sax.) and Przibram (Boh.).

Kerargyrite, $AgCl$. *Cubical* . Ag 75·3 per cent.—This is one of the most widely distributed and important ores of silver, but it is probable that much of the so-called "chloride ore" referred to this species is, in reality, the chloro-bromide. It is always found in the upper oxidised zones of lodes which in their deeper portions carry sulphides and sulphantimonides (the so-called "colorados" of Mexico and "pacos" or "cascajos" of Peru). Reference has been already made to this subject in connection with oxidised ores of lead.[*] Many of the chief oxidised deposits are now worked out, but among the principal localities where this mineral has been an important ore may be mentioned Leadville (Colo.), Lake Valley (N. Mex.), Poorman Lode (Idaho), White Pine (Nev.), Silver Reef (Utah), Silver King and Tombstone (Ariz.), Calico (Cal.) in the U.S.; St. Eulalia, Catorce, &c., in Mexico; Tres Puntas and Chañarcillo in Chili; also at Potosi, Pasco, and other localities in Bolivia and Peru, but here as well as at Broken Hill (N.S.W.), it was not so common as embolite.

Embolite, $Ag(ClBr)$. *Cubical* . Ag 61 to 73 per cent., and AgBr from 80 per cent. down to 18 per cent. of the whole.—This ore has been very abundant in Chili, where it formed the principal ore of Chañarcillo and other mines in Copiapó. It is also found at Leadville (Colo.), Sierra Mojada, St. Eulalia, and Catorce (Mex.), Pasco (Peru), Potosi (Bolivia), and Broken Hill (N.S.W).

Fahlerz, $4(CuFeAg_2HgZn)S \,.\, (SbAs)_2S_3$. *Cubical.*—The proportion of Ag varies from 0·06 per cent. up to 31 per cent., being, generally speaking, least in those varieties where the Sb is most replaced by As, and greatest in the varieties free from As. The highly argentiferous varieties have been called *Freibergite*, and such form the principal ore at the Ontario (Utah), Huanchaca and Potosi (Bolivia), and Casapalca and other mines in Peru, besides being very important at many other mines in Nevada and Colorado (U.S.A.), and at Tasco, Cusihuiriachic, Parral, Pachuca, Charcas, and other localities in Mexico. In Europe also it is an important silver ore in all the districts of Central Europe, including the Harz, Saxony, Bohemia, Hungary, and Transylvania. Besides the localities mentioned by Dana[†] and Percy,[‡] Fahlerz containing upwards of 2 per cent. silver has been found at Collingwood (N.Z.), at Mount Lyell (Tasmania), and at Rio Tinto (Spain), associated with pyrites, chalcopyrite, and other ores of copper.

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[*] Part i., Chapter iii., p. 34.

[†] *System of Mineralogy*, New York, 1890, pp. 102, 103.

[‡] *Metallurgy of Silver and Gold*, p. 207.

In class (*b*) may be described the following less common species:—

Amalgam, Ag_mHg_n . *Cubical* . Ag 26 to 86 per cent.—Many different formulæ have been proposed for native alloys of these metals in various proportions. The most definite seems to be **Arquerite,** $Ag_{12}Hg$, which was an important ore of silver at Arqueros, Chili. Amalgams of other composition have been found in Bolivia, at Kongsberg (Norway), at Allemont (France), and in other places, but not in sufficient quantities to be of commercial importance.

Dyscrasite, Ag_3Sb . *Rhombic* . also Ag_6Sb.—There are many native alloys of silver and antimony to which formulæ have been assigned, but it seems probable that all are mixtures of native silver with the true alloy Ag_3Sb. It occurs in large masses at Chañarcillo and other places in Chili and Bolivia, at Andreasberg (Harz), also at the Australian Broken Hill Consols, Broken Hill (N.S.W.), and other places.

Stromeyerite, $Ag_2S . Cu_2S$. *Rhombic* . Ag 51·3 per cent.—While not of very wide distribution, this mineral has formed an important ore at certain mines in the province of Aconcagua, Chili, also at the Heintzelman, Silver King, and other mines in Arizona, at several localities in Colorado, and at the Australian Broken Hill Consols, N.S.W.

Castillite $(CuAg)_2S . 2(CuPbZnFe)S$. Ag 4·6 per cent.—It may be regarded as an argentiferous bornite. Though not widely distributed, this mineral forms the chief ore at Guanaceir (Durango, Mex.).

Freieslebenite, $5(PbAg_2)S . 2Sb_2S_3$. *Oblique* . Ag 22 to 24 per cent.—This, though not very widely distributed, has been an important ore at Hiendela Encina (Spain) and Przibram (Bohemia), and is also found in small quantity at Freiberg and at Kapnik and Felsobanya (Transylvania).

Cosalite, $2(Ag_2Pb)S . Bi_2S_3$. Ag 2½ to 16 per cent.—This mineral is an important ore of silver at several places in Mexico, notably at Candameña, where a variety with 15 per cent. silver forms the chief ore in the rich Loreto mine; a variety with 9 per cent. silver has also been found at the Yankee Girl Mine, San Juan Co., and at the Comstock Mine, La Plata Co. (Colo.).

Hessite, Ag_2Te . Ag 62·8 per cent., but often replaced to a considerable extent by gold, when the mineral approaches **Petzite.** Mixed with other minerals this has been an important ore of silver at Savodinski (Altai) and at Nagyag and several other localities in Transylvania and Hungary. According to R. Pearce,* "nearly all the sulphide ores of Colorado, especially those of Leadville and Gilpin Co., contain both bismuth and tellurium," and he ascribes this to the wide distribution of cosalite and hessite in small proportions.

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* *Proc. Colo. Sci. Soc.*, April, 1890.

Bromyrite, $AgBr$. *Cubical*. Ag 57·4 per cent.—It is found at Fresnillo, Plateros, Catorce, Mazapil, and other districts in Mexico; also at Chañarcillo (Chili) and in Bolivia and Peru; more recently, also at Broken Hill (N.S.W.).

Iodyrite, AgI. *Hexagonal*. Ag 46 per cent.—It is found with bromyrite at Mazapil, Catorce, and other localities in Mexico; also at Algodones, Chañarcillo, and other localities in Chili, in Arizona, and at Broken Hill, where it is an abundant ore.

Among rare species of little or no metallurgical importance may be mentioned the following, all of which are described in works on Mineralogy:—**Electrum**, $(AuAg)$; **Acanthite** and **Daleminzite**, (Ag_2S); **Naumannite**, (Ag_2Se); **Eucairite**, $(CuAg_2)Se$; **Crookesite**, $(CuAg_2Tl)Se$; **Petzite**, $(AuAg_2)Te$; **Sylvanite**, $(AuAg)_2Te_3$; **Chilenite**, Ag_6Bi; **Brongniardtite**, $PbS.Ag_2S.Sb_2S_3$; **Miargyrite**, $Ag_2S.Sb_2S_3$; **Chañarcillite**, $Ag_2(AsSb)_3$; **Sternbergite**, $Ag_2S.3FeS.FeS_2$; **Xanthoconite**, $3Ag_2S.As_2S_5+2(3Ag_2S.As_2S_3)$; **Stylotypite**, $3(CuAg_2Fe)S.Sb_2S_3$; **Jalpaite**, $3Ag_2S.Cu_2S$; **Rittingerite**, **Pyrostilpnite** (complex sulphantimonites), &c.

The following mineral species contain silver only as an accidental constituent, but from their abundance they frequently form very important ores of the metal:—**Galena**, PbS (containing from 1 dwt. up to 2000 ozs. per ton); **Blende**, ZnS (containing from 0 up to 95 ozs. per ton[*]); **Pyrites**, FeS_2 (containing from 0 up to 146 ozs. per ton[†]); **Chalcopyrite**, $CuS.FeS.FeS_2$; **Erubescite** (*Bornite*), $CuS.FeS_2$; **Chalcocite**, Cu_2S; **Mispickel**, $FeS_2.FeAs_2$; also **Bournonite**, native **Arsenic**, and many other minerals. Of the above, it is probable that as regards chalcocite, erubescite, bournonite, and, perhaps, galena, the silver most frequently occurs isomorphously replacing copper and lead respectively; whereas in the case of the other minerals it is almost invariably found as extremely thin films in the cleavage planes and not as an essential part of the mineral.

Commercial Silver Ores and their Mode of Occurrence.—The variety of associations of silver minerals is very great, and it may be convenient to enumerate here the silver minerals found at some of the principal localities in the world, together with the metallic and non-metallic minerals which accompany them. The silver minerals are given in each case under the heading **P**, the accompanying heavy minerals (frequently themselves argentiferous) under **M**, while the nature of the gangue is shown under **G**. The minerals in each class are placed roughly in order of prominence, those which are very abundant being in *italics*, while those which are rare or unimportant in quantity are put in parentheses:—

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[*] Freeland, "Iron Hill Sulphides," *Trans. A.I.M.E.*, vol. xiv., p. 181.

[†] Thomae, "Zeehan and Dundas field," *Trans. Inst. Min. Met.*, vol. iv., p. 56.

EUROPE.

Freiberg (Sax.).
P. Freieslebenite.
M. *Pyrites*, *galena*, blende, chalcopyrite, mispickel.
G. *Quartz*, chalybite, dolomite (fluor-spar).

Schneeberg (Sax.).[*]
P. *Native silver*, argentite, pyrargyrite.
M. Pyrites, galena, blende, *smaltite*, cobaltite, native bismuth, nickel, and uranium minerals.
G. Quartz, barytes, fluor-spar.

Andreasberg (Harz).[†]
P. Pyrargyrite, proustite, native silver, dyscrasite.
M. *Galena*, blende (native arsenic and antimony).
G. Calcite, quartz.

Rammelsberg (Harz).
P. No specially silver-bearing minerals.
M. *Pyrites*, *galena*, *blende*, *chalcopyrite*, fahlerz.
G. *Barytes*, quartz.

Mansfeld (Rhen. Pruss.).[‡]
P. Some argentite, Ag also in heavy minerals.
M. Chalcopyrite, blende, pyrites, galena, chalcocite (erubescite, mispickel, ores of nickel and cobalt); all as impregnations.
G. Schists.

Przibram (Bohemia).[§]
P. Fahlerz. Most of Ag, however, in galena and blende.
M. *Galena* (antimonial), *blende*, pyrites (chalcopyrite, stibnite).
G. Quartz, *chalybite*, dolomite, barytes.

Kongsberg (Norway).[‖]
P. *Native silver*, argentite (pyrargyrite).
M. Pyrrhotite, blende, pyrites, chalcopyrite, galena, native arsenic.
G. *Calcite*, quartz, chalybite, fluor-spar, barytes (steatite, prehnite).

Sarrabus (Sardinia).[¶]
P. Native silver, argentite, pyrargyrite.
M. Pyrites, mispickel, smaltite, cobaltite (chalcopyrite).
G. Calcite, *quartz*, fluor-spar, barytes.

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[*] De Launay, *L'Argent*, 1896, p. 99.
[†] *Ibid.*, p. 97.
[‡] Egleston, *S. of M. Q.*, vol. xii., p. 88.
[§] Meier, *E. and M. J.*, July 16, 1892.
[‖] Percy, *Met. of Silver and Gold*, p. 505.
[¶] De Launay, *L'Argent*, 1896, p. 82.

UNITED STATES.

COMSTOCK (NEV.).[*]

P. *Native silver* and *gold*, *argentite*, stephanite, polybasite (pyrargyrite).
M. *Pyrites*, galena, blende, chalcopyrite (cerussite, fahlerz).
G. Calcite, dolomite, iron and manganese oxides, quartz (barytes, fluor-spar).

EUREKA (NEV.).[†]

P. Little or none except a little kerargyrite and gold.
M. *Anglesite*, *cerussite*, galena, mimetite, pyrites, mispickel, blende (wulfenite).
G. *Limonite* (quartz, calcite).

ONTARIO (UTAH).[‡]

P. *Fahlerz*, argentite (kerargyrite).
M. *Blende*, galena.
G. *Quartz*, clay.

ASPEN (COLO.).[§]

P. Native silver, argentite, polybasite, stephanite.
M. Galena, pyrites (malachite).
G. *Barytes*, *dolomite*, calcite, quartz, iron oxides.

SILVER KING (ARIZ.).[||]

P. Native silver, argentite, fahlerz, stromeyerite.
M. *Blende*, galena, pyrites, stibnite (erubescite, chalcopyrite).
G. *Quartz*, *barytes*, calcite, chalybite, and "porphyry" (decomposed eruptive rock).

LAKE VALLEY (NEW MEX.).[¶]

P. *Kerargyrite*.
M. Galena, rich in silver.
G. *Flint*, *pyrolusite*, and other manganese oxides, iron oxide, limestone, and (gypsum).

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[*] Becker, "Geology of the Comstock Lode," *Monog. iii. U.S. Geol. Survey*.

[†] Curtis, *Monog. vii. U.S. Geol. Survey*. 1884.

[‡] Rothwell, *Trans. A.I.M.E.*, vol. viii., p. 551; also Almy, *Ibid.*, vol. xvi., p. 35.

[§] Hofman, *Metallurgy of Lead*, p. 39.

[||] Kemp, *Ore Deposits of the U.S.*, p. 228.

[¶] Clark, *Trans. A.I.M.E.*, vol. xxiv., p. 148.

MEXICO.

Veta Madre (Guanajuato).[*]

P. Argentite, stephanite, polybasite, gold.
M. Pyrites, chalcopyrite (blende, galena, mispickel).
G. *Quartz*, amethyst, calcite, dolomite (talc, gypsum, chalybite, fluor-spar, asbestos).
No haloid compounds of silver or heavy spar.

Veta Madre (Zacatecas).[†]

P. Native silver, pyrargyrite, stephanite, argentite (proustite), and kerargyrite.
M. *Pyrites*, *blende*, galena (stibnite).
G. *Quartz*, hornstone, calcite, barytes.

Catorce (San Luis Potosi) (colorados).[‡]

P. *Embolite*, native silver, kerargyrite, bromyrite.
M. Galena, *cerussite*, pyrolusite.
G. Quartz, calcite, oxides of iron, ferruginous clay.

Guadalcazar (S. L. P.). [§]

P. *Argentite*, fahlerz, pyrargyrite, native silver.
M. *Pyrites*, *galena*, *blende*, chalcopyrite (stibnite, smaltite).
G. Quartz, limonite, fluor-spar, calcite.

Pachuca (Hidalgo).[‖]

P. Argentite, native silver, fahlerz, pyrargyrite, stephanite.
M. *Blende*, mispickel, galena, pyrites, chalcopyrite.
G. Quartz, hornstone, amethyst, calcite, barytes.

Tasco (Guerrero).[¶]

P. Argentite, polybasite, pyrargyrite, fahlerz, proustite.
M. *Blende*, galena, pyrites, pyrrhotite (chalcopyrite, azurite).
G. Quartz, *calcite* (gypsum).

Charcas (S. L. P.).[**]

P. None, the Ag is in *fahlerz* and blende.
M. Blende, galena, mispickel, pyrites, chalcopyrite.
G. *Calcite*, clay, and quartz.

Batopilas (Chihuahua).[††]

P. *Native silver*, argentite, kerargyrite, proustite.
M. None.
G. *Calcite* (quartz).

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[*] Percy, *op. cit.*, p. 580, and *priv. notes*.

[†] *Private notes.*

[‡] Chism, *E. and M. J.*, Nov. 2, 1889.

[§] *Private notes.*

[‖] Percy, *op. cit.*, p. 584.

[¶] Halse, *Trans. I.M.M.*, vol. iii., pt. 3, p. 427.

[**] *Private notes.*

Randolph, *Trans. A.I.M.E.*, vol. x., p. 293, and *priv. communications.*

SOUTH AMERICA.

Casapalca (Peru).[*]
P. ***Fahlerz*** (very rich).
M. ***Galena***, blende, pyrites, chalcopyrite.

Pasco (Peru).[†]
P. ***Native silver***, argentite, proustite.
M. Pyrites, cerussite, galena, chalcopyrite (fahlerz).
G. Quartz, iron oxides, ferruginous clay.

Oruro (Bolivia).[‡]
P. ***Fahlerz***, native silver, pyrargyrite, proustite.
M. ***Pyrites***, chalcopyrite, galena, ***cassiterite***, blende, stibnite.
G. Slaty and small in amount.

Huanchaca (Bolivia).[§]
P. ***Fahlerz*** (var. Freibergite with 12 per cent. Ag).
M. ***Pyrites***, ***blende***, galena (chalcopyrite).
G. Chiefly quartz.

Copiapó (Chili).[‖]
P. ***Native silver***, ***embolite***, ***argentite***, pyrargyrite, proustite (polybasite, iodyrite, arquerite).
M. (Chalcopyrite, galena, native arsenic, domeykite).
G. ***Barytes***, ***calcite***, ankerite, decomposed porphyry and diabase, kaolin and asbestos.

AUSTRALASIA.

Broken Hill (N.S.W.)[¶] (*oxidised ores*).
P. ***Embolite***, ***iodyrite***, native silver (kerargyrite, pyrargyrite, fahlerz, stephanite, dyscrasite).
M. ***Cerussite***, calamine, anglesite, pyromorphite (azurite, malachite, native copper, stolzite).
G. ***Limonite***, ***kaolin***, quartz, psilomelane (chalybite, calcite).

Broken Hill (N.S.W.)[**] (*sulphide ores*).
P. Practically none.
M. ***Galena***, ***blende***, rhodonite (pyrites, chalcopyrite very rare).
G. ***Felspar*** (green and grey), ***garnet***, quartz, fluor-spar.

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[*] Pfordte, *E. and M. J.*, June 25, 1892.
[†] Hodges, *Trans. A.I.M.E.*, vol. xvi., p. 729; Pfordte, *Trans A.I.M.E.*, vol. xxiv., p. 109.
[‡] Minchin, *E. and M. J.*, Aug. 16, 1890.
[§] Peele, *S.M.Q.*, vol. xiv., p. 152.
[‖] Percy, *op. cit.*, pp. 568 and 649.
[¶] *Private notes.*
[**] *Private notes.*

ZEEHAN AND DUNDAS (TASMANIA.)*

P. Subordinate only, argentite.
M. *Galena*, blende, pyrites, chalcopyrite.
G. *Chalybite* chiefly, quartz subordinate.

Association of other Minerals with Silver.—In an interesting paper on this subject Pearce† makes the following notes:—"*Barytes* and *calcite* are common associates of silver ores, forming in some cases aim entire matrix of a silver lode. *Fahlerz*, *tennantite*, *en* d *blende* also commonly indicate richness in silver, a he above, are not kindly associates of gold." To the n nentioned by Pearce may be mentioned the following, al h are commonly associated with silver in vein fillings, an e considered as "kindly" matrices, viz.:—*Amethystine* (Guanajuato, Pachuca), *manganese carbonate* and *silica* emnitz, Hungary; Butte Mont. and Reese River, Nev. n Hill, N.S.W.), *smaltite* and other cobalt minerals (Sc g, Sax.; Sarrabus, Sard.; Guadalcanal, Spain; Arqueros, *bismuth* minerals (Erzgebirge and Sierra Madre, Mex.), *stibnite* and antimony minerals (Zacatecas, Guadalcazar, Mex.; Oruro and Huanchaca, Bol.), *chalybite* and *ankerite* (Freiberg, Przibram, Copiapó, Zeehan).

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* Thomae, *Trans. I.M.M.*, vol. iv., p. 54. † *Proc. Colo. Sci. Soc.*, 1887.

SECTION II.

AMALGAMATION PROCESSES.

INTRODUCTORY.

Amalgamation methods, though not as old as smelting, date back for three and a-half centuries. The Patio, or Mexican amalgamation process was invented by Bartolomé-Medina at Pachuca in 1557, but Biringuccio described in 1540 a somewhat similar process, and it is probable that Medina had learnt the principle of the method in Spain, and, making trial of it, developed his Patio process, for at that time the necessary quicksilver could only be imported from Spain. Those who are interested in the history of the process should consult the work of Percy so often quoted.*

The *modus operandi* in all amalgamation processes is to bring the silver ore, in a condition of finely-divided slime, into intimate contact with finely-divided globules of mercury, or with a bath of that metal. Quartzose or calcareous ores containing native silver, require no reagents other than water and mercury, but to all other kinds of ore certain reagents are added, some of which (like salt and copper sulphate) facilitate the transformation of sulphide of silver into finely-divided metal and chloride, which can be acted upon by the mercury; while others (such as iron and copper) act partly by their effect on the silver chloride, partly by regenerating mercury from its insoluble chloride, and partly by setting up a galvanic couple with the mercury, which increases the tendency of silver in solution to be precipitated upon that metal. The reactions which occur when silver compounds are brought into contact with the above reagents have been already described in Chapter I., and it has been noted that native silver, chloride, and sulphide are most easily acted upon, next the sulphantimonides and sulpharsenides (pyrargyrite, polybasite, proustite, &c.), while argentiferous fahlerz, galena, blende, pyrites, and similar ores are only acted upon with great difficulty.

All silver ores, however complex, can be treated by amalgamation after a preliminary roasting with salt, but this, while adding greatly to the expense, gives rise to an additional loss by

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* Percy, *Metallurgy of Silver and Gold*, 1880, p. 560.

volatilisation, and, in most cases, unless an ore can be amalgamated direct—*i.e.*, unless it is tolerably free from base sulphide minerals, and the gangue is mainly quartzose or earthy, it is preferable to adopt either a smelting or a lixiviation process.

In all amalgamation processes the first requisite is the crushing of the ore. This operation is a mechanical rather than a metallurgical one, and the particular appliance to be adopted will depend more upon local conditions than upon the nature of the ore. As a rule, the more primitive crushing appliances accompany the simpler methods, and more modern appliances the more elaborate ones. The various machines used for crushing silver ores will be described in the volume on Metallurgical Machinery in this series, but a short account of them are given in this work in connection with the separate processes.

Classification of Processes.—Amalgamation methods may be described under the following heads :—

(1) *Direct amalgamation processes*, in which the finely-powdered ore is acted upon direct by *mercury* in a finely-divided condition under water, without the addition of salt or any other reagent.

(2) The *Mexican*, or *Patio, process* of cold amalgamation, in which the reactions take place *at the ordinary temperature* in low flattened heaps spread out upon suitable floors.

(3) The *Cazo, Fondon, and Tina processes*, in which the reactions take place in copper pans or in wooden tubs with intervention of *cuprous chloride*, and are much facilitated by *heat*.

(4) *Pan processes*, in which the reactions are conducted in iron pans with the aid of *heat*.

(5) *Barrel processes*, in which the ore is revolved in barrels together with the reagents, of which *iron* is usually the principal.

The first is only applicable to *rich* native silver and chloride ores, and will be described here. The second, third, and fourth groups will be described in separate chapters. The fifth is practically obsolete in its original form, though the barrel principle is adopted in the Kröhnke process and has come into use again recently in connection with pan mills working on raw refractory ores. A short description of the obsolete Freiberg process will be given in Chapter VI. in treating of roast amalgamation.

The roasting of silver ores containing argentiferous metallic sulphides (sulphantimonides and sulpharsenides) as a preparation for one of the amalgamation processes will be referred to incidentally in connection with these processes, and a general discussion of chloridising roasting is contained in Chapter IX.

Composition of Ores suited to Amalgamation.—Analyses of some ores submitted to amalgamation processes (mostly after preliminary roasting) are given in Table II.

TABLE II.—Analyses of Ores Treated by Amalgamation Processes.

	Pasco, Peru. "Cascajos."	Pasco, Peru. Sulphides.	Potosi, Bolivia. Sulphides.	Huanchaca, Bolivia. Sulphides.	Knoxville, Nr. Charleston, Arizona.	Ontario, Park City, Utah.	Black Pine, Montana, Flint Creek District.
References,	1.	1.	2.	3.	4.	5.	6.
	Patio.	Tina.	Tina.	Tina.	Reese River.	Reese River.	Combination.
SiO_2,	72·00	40·05	13·50	23·00	18·10	55·21	84·09
Al_2O_3,	6·50	...	3·04	...	...	13·14	...
Fe_2O_3,	13·50	...	...	...	0·58	...	...
Fe,	1·32	26·55	29·06	11·60	...	2·77	7·05
MnO_2,	0·29	...	...	...	54·83	..	...
Mn,	0·21	...	...	...	14·97	0·45	0·35
CaO,	0·75	...	0·32	...	1·32	...	...
MgO,					0·13	...	...
K_2O and Na_2O,	...	...	...	...	1·22	...	...
Pb,	1·00	...	0·13	11·30	0·46	6·07	1·01
Cu,	0·05	2·73	5·15	1·90	0·16	1·41	1·31
Zn,	0·40	...	0·63	21·50	...	9·60	0·30
Sb,	0·25	2·40	1·45	1·80	0·66	·20	0·66
As,	Tr.	Tr.	1·30	0·35	...	0·20	0·05
Cd,	...	...	...	...	...	...	...
Ag,	Tr. to 0·10	0·13	0·358	...	0·15	...	0·08
Au,	...	...	Tr.	...	...	Tr.	...
S,	1·34	26·63	32·35	26·00	...	7·68	0·19
CO_2	...	...	...	...	1·33	...	...
H_2O,	Und.	0·95	0·32	...	1·67	...	...
SnO_2,	..	...	3·90	...	...	...	...
$BaSO_4$,	...	...	...	...	...	...	...
Cl,	...	...	...	...	0·17	...	...
O,	...	...	...	...	4·44	...	...
	97·71	99·44	91·508	97·45	100·19	97·73	95·09
		oz.	oz.		oz.		oz.
Ag per ton,	..	42·3	104·65	...	45·4	...	26·1
Au per ton,	...	...	0·045	...	...	...	...

References.—1. Hodges, *Trans.A.I.M.E.*, vol. xvi., p. 729. 2. Wendt, *Trans.A.I.M.E.*, vol. xix., p. 100. 3. Peele, *E. and M.J.*, March 25, 1893. 4. Goodale, *Trans.A.I.M.E.*, vol. xvii., p. 769. 5. Lamb, *E. and M.J.*, December 17, 1892. 6. Goodale & Akers, *Trans.A.I.M.E.*, vol. xviii., p. 247.

Simple Amalgamation in "Arrastras."—Formerly at Batopilas (Chihuahua, Mexico) all the ores containing native silver, argentite, and kerargyrite were first stamped in a battery driven by water-power to get the *stamp silver* (coarse particles of pure silver, treated by a lead scorification process). The stamped ore was then charged into 9 feet "arrastras de cuchara" (a kind of stone grinding pan driven by water-power, and fully described in the next chapter) with 2 light grinding stones. The charge for each arrastra was 1 ton of stamped ore and sufficient water to form a thick mud, to which, after eight hours' grinding at 7 to 10 revolutions per minute, from 25 lbs. and upwards of mercury were added according to the richness of the ore. Constant tests of the mud were made by washing in a horn spoon until the appearance of the mercury showed all the silver to be amalgamated; a large excess of water was then added and the grinding continued for a few hours. The motion was then stopped for a few minutes in order to enable the coarser and heavier particles to subside; the more finely-ground pulp was then run away by means of plugs at different levels, leaving the amalgam and rich concentrates at the bottom. The operation was repeated during several days until sufficient amalgam was obtained for a "clean-up," any richer ore being added with the last lot put through, so as to run less risk of loss. The tailings from the last run were saved and worked up by the Patio process, while the amalgam was washed, strained, and retorted in the same way as that from the Patio process, the treatment of which is described in Chapter VIII. The loss of mercury with pure native silver ores is said to average only 1½ ozs. of mercury per 1 lb. of silver, though in the case of chloride ores the loss is something like ¾ lb. at least for each pound of silver. The simple process just described, though obsolete at the mines of the Consolidated Batopilas Silver Mining Coy., is still in use at dozens of small mines in the same rich native silver district, which has turned out silver valued at over £40,000,000 sterling, chiefly by this primitive method.

Direct Amalgamation in "Tinas."—Like direct amalgamation in arrastras, this process is only applicable to ores in which the predominating valuable constituent is native silver, with more or less of chloride, bromide, or iodide. The process was at one time employed at *Kongsberg* (Norway); it was for many years in use for treating rich surface ores at *Copiapó* (Chili), and also at *Silver Islet* (Michigan). At the present time the author is unaware of any place where it survives, but it would be advantageously used in case of any new discovery of similar ores. The construction of the *tinas* is plainly shown in Figs. 1 and 2.*

The bottom is a cast-iron plate, 1½ inches thick in its thinnest

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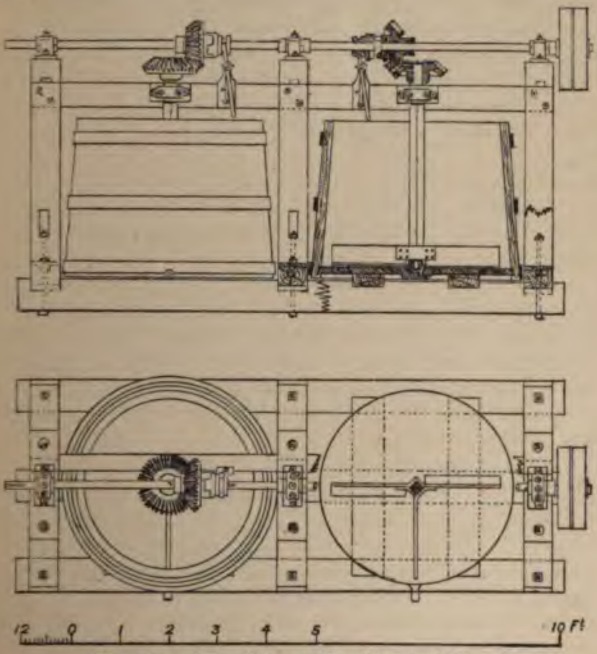
* From Percy, *op. cit.*, p. 589.

part, and strengthened as shown; the sides are wooden staves, 2¼ inches thick and 4 feet high, held together by three hoops of flat bar iron 2¾ inches by ⅜ inch. The tubs are from 4 to 6 feet in diameter at bottom and about 6 inches less at top, and arranged in line so as to be driven by clutch gear from a line shaft. The scrubbers, or agitating arms, A, are of cast or wrought iron and revolve at from ¼ to ½ inch above the cast-iron bottom plate.



Figs. 1 and 2.—Tinas (Elevation and Plan).

The ore was crushed in Chilian mills (see next chapter) and charged into the tinas with the agitators in motion at the rate of 16 revolutions per minute, together with sufficient water to make a thin mud. The charge of mercury varied according to the richness of the ore from 150 lbs. upwards. Unlike the arrastra process, in which the proportion of mercury is always kept as low as possible so as to make a "dry" amalgam and prevent loss by leakage through the chinks of the pavement, the tina process used a large excess of mercury, forming a liquid pool on the bottom of the tub. Progress of the amalgamation was followed by washing samples in an earthenware saucer; rich native silver ores would be completely amalgamated in four to six hours, while horn-silver and chloro-bromides frequently required from twenty up to twenty-four hours, owing to the difficulty of bringing the flat scales formed during grinding into complete contact with the bath of mercury. When amalgamation was completed, the contents of the tina were allowed to settle for a few moments, the mercury drawn off through a spout into an iron kettle, and the whole of the ore-mud flushed out into slime pits. The heavier parts which settled in these were called "relaves," and were re-treated by the Patio process (subsequently by smelting), while the lighter parts were commonly thrown away. The mercury was strained through canvas bags, and the resulting dry amalgam moulded and retorted under a bell similar to that used for retorting Patio amalgam; the cones of retort silver called "plata piña" averaged about 920 fine.

This process, though not now in use, is admirably suited to the amalgamation of ores carrying *only finely-divided* native silver and chlorides practically free from other argentiferous or base heavy metals; but, as such ores are of very limited occurrence, its applicability is but small. When the silver exists entirely in the metallic form the loss of mercury is exclusively mechanical and should not exceed an ounce per pound of silver produced, but when most of the silver occurs as chloride or other haloid compound, the loss may reach 10 ozs. to the pound, for in that case mercury is chemically lost through combination with the haloid element—

$$2AgCl + 2Hg = Hg_2Cl + 2Ag,$$

though a portion of the calomel formed is reduced by the iron bottom.

Argentite and other more complex silver minerals remain unaltered and are carried away in the "relaves," as well as chloride and other haloid compounds of silver in crystals, grains, and scales, which are only attacked by the mercury with great difficulty.

CHAPTER III.

THE PATIO PROCESS.

Ores Suitable to Patio Treatment.—The ores which are best suited to Patio treatment are those so common in Mexico and in parts of Peru and Bolivia which are composed of a quartzose, ferruginous, or calcareous gangue, spotted here and there with finely disseminated native silver, argentite, stephanite, pyrargyrite, polybasite, proustite, and all the powdery "chlorides" or haloid compounds, giving a total contents of 20 to 150 ozs. of silver to the ton. Considerable amounts of pyrites, galena, cerussite, and carbonates and sulphides of copper may be present without much interference with the process, but the presence of any very large quantity of blende prevents a good extraction.

Ores in which the silver exists chiefly as proustite or as argentiferous tennantite, fahlerz, bournonite, bornite, galena, blende, or mispickel must be roasted before treatment, or the extraction will be very low; and ores which contain large quantities of blende, even when the silver itself exists as stephanite or other easily reducible mineral, must be roasted before treatment, and require a large quantity of chemicals. Ores which contain crystalline or scaly varieties of chloride, bromide, or iodide of silver are quite unsuited to the process.

Crushing.—Ores for the process require to be ground so finely as not to feel gritty when rubbed between the thumb and forefinger, which may be done by any of the forms of crushing machinery. Stonebreakers are but seldom required, as the ores are usually broken by hand at the mines to sort out waste and first-class ore containing upwards of 200 ozs. per ton, which is shipped to smelting works, so that the ore which arrives at the reduction works is rarely larger than egg or fist size. Where, however, there is but little scope for sorting out first-class ore or waste, stonebreakers can be advantageously used as preliminary crushers.

The crushing to fine powder for the patio is almost invariably performed in two stages, the second of which is always done *wet* so as to yield a mud in suitable condition for the patio, while at the same time with ores containing gold advantage is taken of this wet crushing to recover most of that metal by direct amalgamation with mercury. When the ores contain no gold they may be wet-crushed with stamps or Chilian mills direct for the patio, while in cases where a preliminary roasting of the ore is found to be advantageous (as with those containing blende and proustite) the crushing must be done *dry*.

The *first stage of crushing* (down to ½-inch or less) may be performed by means of stamps (*morteros*), rolls (*rodillos*), or Chilian mills (*trapiches* or *molinos*); the *second stage* by means of stamps, Chilian mills with steel runners or arrastras.

Stamps.—Light stamps with square iron heads and iron or wooden stems, much resembling those still used in Cornwall, as well as in Germany and other parts of the Continent, are still used to some extent; they are occasionally worked by mules, but more commonly by water-wheels and, sometimes, by steam. They have, however, been largely replaced by Chilian mills, except where there is an abundance of water power.

At *Tasco* (Guerrero)* the stamps are twelve in number, with

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* Chism, *E. and M. J.*, July 20, 1889.

wooden stems and iron heads weighing about 350 lbs. each, and dropping about 24 inches at twenty-three drops per minute. They are driven, together with two arrastras, by means of an overshot water-wheel, 29 feet in diameter and 2 feet across the breast. The battery of twelve heads crushes 6 to 8 tons of ore through a 40-mesh screen. In this case no second or wet crushing is required, for the ore has to be roasted before going to the patio, which is performed in a small hand reverberatory.

Rolls.—These have largely replaced stamps for crushing. At the *Ed. Morrison Consolidated* Works (Zacatecas) rolls of 24 inches diameter and 14 inches face follow a Dodge-crusher. At *Fresnillo* a plant of geared rolls has replaced the stamps formerly in use. There are two trains, each consisting of two pairs of 27-inch rolls, 18-inch face, set one over the other and making nine revolutions per minute, the capacity of each train being about 130 tons of ore per day to 8 mesh size.

At the *Hacienda de Guadalupe* (Pachuca) the preliminary crushing plant consists of two pairs of rolls, 30 inches diameter × 24 inches face, which crush to nut-size at the rate of nearly 100 tons per twenty-four hours for each pair, the fine crushing being effected by Chilian mills.

Chilian Mills.—The simplest kind of Chilian mill, still used in some places, consists of an annular channel built of blocks of stone, 10 to 12 feet in diameter and 12 to 18 inches wide, in which a stone wheel travels. In the centre of the circle is a wooden or stone post upon which turns a pivoted wooden vertical axle having a horizontal axle passing through its centre. To this is fixed by means of wooden wedges a vertical wheel (edge-runner) of granite or, preferably, of hard porphyry, from 6 to 12 feet diameter and 9 to 15 inches face. The axle projects a considerable distance beyond the edge-runner or on the opposite side to it, and to its end are attached two or three mules. Such a mill driven by twelve mules, working three at a time in three-hour or four-hour shifts, and attended by one man and two boys on each shift, will crush from 4 to 6 tons of average ore per twenty-four hours to pea-size and less.

At the *Hacienda de Loreto* (Pachuca) of the Real del Monte Co. single-wheel Chilian mills of primitive pattern are still used for grinding. The wheel weighs 2 tons and is worked by three mules, which are relieved every six hours, the capacity per twelve-hour shift being 30 to 40 cargas (4 to 5½ tons).

Where water power is available, such Chilian mills are often driven by horizontal "hurdy-gurdy" or impact water-wheels placed in underground chambers on the same axis, and running at the rate of twelve revolutions per minute. Such are called in Peru "ingenios," and their construction is shown in Fig. 3.*

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* Pfordte, "The Cerro de Pasco Mining Industry," *Trans. A. I. M. E.*, vol. xxiv., p. 111.

Some twenty years ago, both at Zacatecas and Guanajuato, large iron-shod Chilian mills were introduced in place of the simple stone edge-runners. They consist of a large stone wheel about 4 feet 6 inches in diameter, to which is affixed, by means of wooden wedges, a heavy cast-iron tyre, 16 to 18 inches wide and 4 or more inches thick, formerly made in six segments bolted together, but now more frequently in one piece or two at most. This wheel (sometimes a pair of similar wheels is employed) rotates on a horizontal shaft, which is attached to a vertical shaft, and one end of which projects as usual so that three mules can be attached to it. The annular path on which it runs is composed of segments of cast iron, usually eight in number, a trifle wider than the runner and of about the same thickness, the outer rim being formed by blocks of stone set in the ground. The mill is built upon a strong arch so that a small passage leads to the centre of the annular space, which is covered by a conical screen of sheet iron punched with holes from ¼ to ⅙ inch in diameter. As the wheel travels over the ore a boy shovels up the latter on to the screen, through which those particles which are sufficiently fine pass, while the coarser pieces roll back again on to the wheel-path.

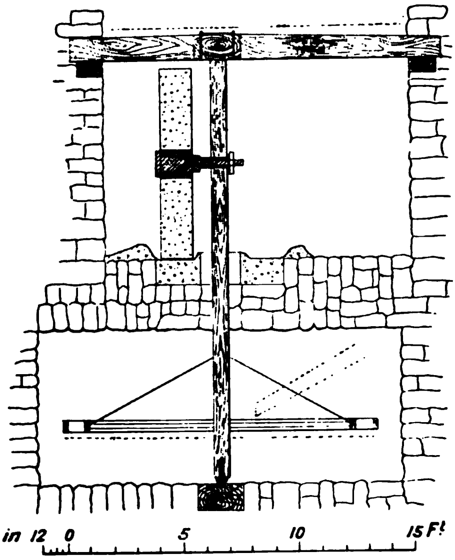


Fig. 3.—Ingenio.

The output of these mills with iron-shod runners is much greater than that of those with plain stone runners, but the presence of particles of iron in the ground ore is generally thought to be prejudicial to the progress of the reactions in the patio process, and, therefore, in some places stone runners are preferred in spite of the acknowledged smallness of their output and greater cost of working.

At the *Hacienda de Guadalupe* (Pachuca) the ore crushed to nut-size by the rolls, already referred to, is shovelled (as required) into a row of fourteen Chilian mills crushing wet, each with a pair of runners consisting of a stone centre weighing 1½ tons, with a steel tyre 1 foot face and 6 inches thick weighing about 2 tons. The runners roll upon an annular steel sectional die 2 inches thick, which gets worn out in from eight to twelve months, while the tyres last on an average three years. Each machine makes 14½ revolutions per minute, takes 6 to 8 H.P., and grinds about 7 tons per twenty-four hours.

At the works of the *Compania La Union* (Pachuca) and also at those of the *Bote Coy.* (Zacatecas), Chilian mills built entirely of iron with steel working faces, as shown in Fig. 4, are used for fine grinding at one operation. No further grinding is required; and as the ore at the *La Union* Works is treated not by the ordinary patio, but by a modification of the barrel amalgamation process, the presence of a few small particles of steel in the ground ore is not objectionable. The rollers are of cast iron, 8 feet in diameter with a steel tyre 6 inches thick, and they weigh about 10 tons each, the weight of the whole machine being about 27 tons. The runners revolve about twelve times

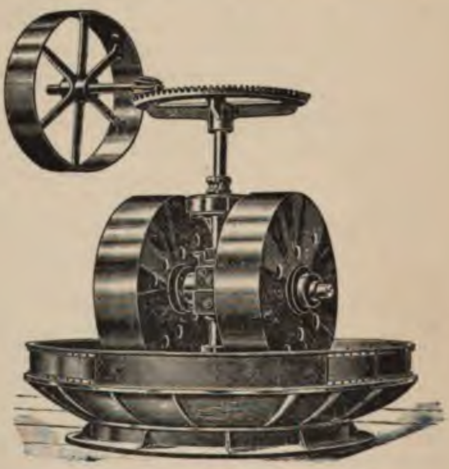


Fig. 4.—Chilian Mill.

per minute and grind about 1500 lbs. per hour of hard quartzose ore through a 120-mesh sieve. The steel tyre lasts for five to six months, during which time it grinds more than 2000 tons of ore.

Ball Mills might also be employed, as in connection with the Tina process in S. America (see next Chapter), but the author is not aware of any case where they are used for crushing ores preparatory to patio treatment.

The *second stage of crushing* is generally performed wet by means of *arrastras*, but may also be performed by means of Chilian mills, as at the *Hacienda de Guadalupe*, the pulp being in this case carried off continuously by a stream of water and settled in huge settling-pits, whereas in the more common case the whole of a charge is worked to thick slime and discharged together.

Arrastras.—The *arrastra* or *tahona* of the ordinary kind, shown in Figs. 5 and 6, is essentially a circular pavement of stone, from 9 to 16 or even 20 feet in diameter, upon which the ore is ground by means of heavy mullers, surrounded by a low wall of wood or stone. In some rude arrastras the stone pavement is composed simply of river boulders or of irregular quarried blocks laid with the flattest side uppermost and bedded in clay, but in large Haciendas it is constructed of successive circles of long deep granite, porphyry, or quartzite stones, roughly hewn to shape and set edgewise very close together so as to leave as little room as possible for mercury to filter down. When the stones are well wedged up in a good puddled clay or slime from a washed torta there is surprisingly little loss, and the pavement will last for months. In some cases natural columns of basalt have been used for paving arrastras. The outer wall is composed of long flat blocks of granite or other rock roughly hewn into shape and imbedded in the ground a couple of feet so as to stand up a foot or 18 inches. The central stone upon which the axle turns has a drillhole in its upper surface for the pivot to work in.

The stone drags, or mullers, called "voladoras," have iron ring bolts wedged into drillholes in their upper surfaces, by means of which they are attached to the cross-arms by twisted thongs of raw hide, or by chains. They may be of granite, felsite, diorite, or not too fine-grained basalt, and are two or four in number. In the latter case, those on the mule-arms are new stones, 3 to 4 feet long, 18 inches to 2 feet wide, and 12 to 15 inches thick, weighing 10 to 12 cwts., which do most of the grinding; the stones on the cross-arm are old worn stones, and serve chiefly for mixing. New stones last generally from six weeks to two months, and it has been estimated that between the drags and the pavement from 6 to 10 per cent. of the weight of the ore is ground away. The quantity of water used is about one and a-half times the weight of the ore, but it is added in small quantities at a time as the grinding proceeds.

At *Zacatecas* a 12-foot arrastra is usually worked by eight mules, which work two at a time in three-hour shifts, and grind from ½ to 1 ton per twenty-four hours. At *Hacienda La Granja* the charge for an arrastra of this size is 14 cwts., which is put in at 6 a.m. and taken out next morning at 4 or 5 a.m. One man and a boy look after five arrastras, and are paid by the piece, about 1s. 6d. per "monton" of 2000 lbs. being the usual rate.

At *Pachuca*, the arrastras are usually about the same size, but are worked by three mules at a time as they have four "voladoras" instead of two, as commonly seen at Zacatecas. The stones are of porphyry, and last from two to two and a-half months. At *Guanajuato* the ore usually contains more gold, is ground much finer, and the daily charge for a small-sized arrastra is only 600 lbs.

Fig. 5.

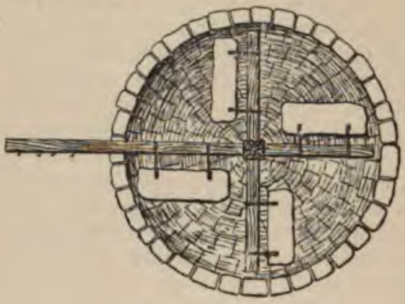
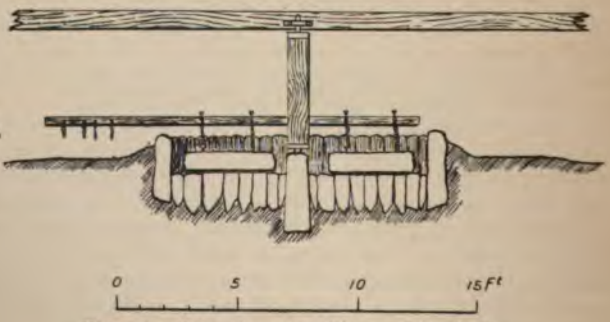


Fig. 6.



Figs. 5 and 6.—Arrastra (Plan and Section).

Arrastra de Cuchara. — Where water-power is available arrastras are sometimes driven by horizontal hurdy-gurdy wheels, either in underground chambers, on the same vertical axle, or arranged around the arrastra itself over what is ordinarily the mule-path.* In the case referred to by Chism the arrastra is 10 feet in diameter, and the charge of 1500 lbs. takes three days to grind. This method of utilising power is extremely wasteful as not more than 25 per cent. is utilised; it would be much better to put in a large wheel, or turbine, and drive each arrastra separately by means of clutch gear from a single long shaft.

Arrastras are now frequently run by steam; those at the plant of the *Ed. Morrison Consolidated Mining Coy.* (Zacatecas) are 12 feet in diameter, and grind from 6 to 10 tons per twenty-four hours with a consumption of 6 H.P. each.

Extraction of Gold in Arrastras.—Whenever the ores contain any considerable proportion of gold, as in Guanajuato, the districts of Jesus Maria and Guadalupe y Calvo (Chihuahua), San Dimas and Guanaceir (Durango), &c., this is often extracted as perfectly as possible by adding mercury in the arrastra and grinding thoroughly before passing on the ores to the patio for extracting their silver contents. The reason for this is that if the gold were left to take its chance of being amalgamated along with the silver in the patio it would be necessary to "part" the whole of the silver obtained at a very heavy expense, whereas by concentrating it in the small quantity of free or easily amalgamable silver the quantity of bullion to be parted is very small, and the "patio" bullion will be nearly free from gold.

The grinding in the arrastra is conducted as usual, except that it is more thorough, a smaller quantity of ore being treated at once. The quantity of mercury added varies, according to the supposed richness of the ore, from 2 or 3 ozs. up to 10 or 12 ozs. per day, but it is always kept as low as possible in order to ensure the amalgam produced being "dry," and to prevent loss by leakage through interstices in the floor. A proper "clean-up" of the arrastra only takes place at intervals of from one to three months, when the whole of the floor is carefully scraped, and the slime between the permanent stones dug out as completely as possible.

Use of Silver and Gold Amalgam.—In *Guanajuato* the floor of the arrastra is often plastered with a layer of *silver amalgam* before starting work, both because silver amalgam catches gold much better than pure mercury, and because it will remain spread all over the bottom, thus exposing a greater surface, instead of collecting in pools as liquid mercury would do. Subsequent additions of mercury are made every day. The auriferous amalgam obtained contains, after retorting, 4½ to 6 per cent. of gold, and the extraction is equivalent to about 60 per cent. of that contained in the ore, most of the remaining 40 per cent. being found in the silver from the Patio process and in

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* See Chism, *Trans. A.I.M.E.*, vol. xi., p. 63, for an illustration.

the concentrates from the washed torta. The amount of silver extracted is comparatively insignificant, for the Guanajuato ores contain practically no native silver or chlorides. It is found that the loss of mercury in this process is about 1 oz. for each ounce of silver extracted, and, therefore, the reduction probably takes place by the mercury combining with the sulphur of the argentite direct—

$$Ag_2S + Hg = HgS + 2Ag.$$

At the *El Bote* Mine (Zacatecas) the same process is followed, and here also the extraction of the very small quantity of gold in the ores is fully 60 per cent.—a very much better result than can be obtained by grinding these same ores in iron pans.

At some of the Guanajuato Haciendas silver amalgam has been replaced by *copper amalgam*, as first tried by Lukner at Guadalupe y Calvo (Chihuahua). This copper amalgam is frequently prepared by roasting cupriferous concentrates together with salt, and rotating the roasted mass in a barrel together with scrap iron, water, and excess of mercury. The iron precipitates the copper from solution, and it is taken up by the mercury. On subsequently straining off the excess the pasty amalgam left contains about 10 per cent. copper and 1 per cent. silver. Each arrastra has about 10 lbs. of such copper amalgam plastered over the bottom at starting, and subsequently with ordinary ores about 8 to 12 ozs. of mercury is added to each ½ ton charge (which takes twenty-four hours to grind). The method of adding is the same as in the Patio process—viz., by squeezing through a cloth so as to subdivide it as finely as possible. The copper gradually disappears from the amalgam, being, no doubt, carried away as sulphide, while a rich auriferous amalgam free from copper remains. The campaign usually lasts two months, and 18 to 20 lbs. of auriferous amalgam may be obtained from the scrapings by washing.

The washing process may be conducted in a tub-settler or in a masonry tank as described by Chism.*

Numerous arrastras are still used in remote regions of the United States, mostly worked by water-power; with fairly rich ores they yield 90 per cent. of the assay value, and when the tailings carry silver they are generally treated in pans. Sometimes, however, the arrastra itself is used to save silver as well as gold, and in that case salt and copper sulphate are ground up with the ore.

At the Scales and Wagner arrastra mill (Idaho) in 1880, according to Egleston,† 1772 tons of ore were treated in this way; the average value of the ore in gold and silver combined was $115.85, and the average assay of the tailings (chiefly silver)

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* *Loc. cit.*

† *S. of M. Q.*, vol. viii., No. 2, p. 134.

was $9.50 giving an average extraction of 91·80. The average cost was :—

Labour (including enginemen in summer), per ton,				$4.50
Fuel in summer,	0·32 cord wood	@ $7.25 =	$2.35	
Salt,	7·9 lbs.	@ 0.3 =	0.24	
Bluestone,	1·7 lbs.	@ 0.25 =	0.42	
Quicksilver,	1·7 lbs.	@ 0.48 =	0.81	
Oil, chemicals, and sundries,			0.13	
				3.95
				$8.45

or, say, 35s per ton.

Removal of Ore to the Patio.—The ground ore is either run out by means of a stream of water from the arrastras or Chilian mills into settling tanks, or is dipped out from the arrastras into slung casks, or hand barrows, and taken direct to its place on the patio; temporary dams of poles and stones being formed to keep the slimes in place until they can dry to the proper consistency.

The patio floor is usually built of stones laid as closely together as possible in stiff clay or in hydraulic mortar. Floors have been paved with rectangular blocks of hewn stone and with asphalt, but the cost of both is practically prohibitive. Wooden floors, composed of tongued and grooved planks, have also been used, but they are both expensive and troublesome, having to be kept flooded with water—often no easy matter in a dry country. Bricks laid edgewise, and as close together as possible, in hydraulic mortar make a very good floor.

When the slime has dried to the consistency of brickclay it is turned over with shovels and formed into a flat, circular, or oval cake about 12 to 24 inches thick, called a "torta" or "trilla," which may contain from 20 to 300 tons of ore,[*] but in large haciendas will usually contain about 150 tons.

Reagents used in the Patio Process.—The active reagents in the Patio process, besides *mercury*, are *salt* and *copper sulphate*. *Copper precipitate*, *lime*, and *wood ashes* are reagents sometimes used for special purposes.

Salt.—This reagent was formerly often employed in a crude form as deposited, from inland lakes, and containing, according to various authors quoted by Percy,[†] from 19 to 56 per cent. of sodium chloride, together with carbonate of lime and soda, sulphate of soda and earthy matter. At the present time, however, such inland salt is generally purified on the spot and reaches the reduction works in the form of coarse-grained crystals, similar in appearance to "bay salt"; it averages over 90 per cent. NaCl.

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[*] The latter figure is reached in the Hacienda de Guadalupe, Pachuca.

[†] *Metallurgy of Silver and Gold*, vol. i., pp. 598 and 599.

Copper Sulphate.—This substance was formerly employed exclusively in the form of *magistral*, which, of late years, has been largely replaced by bluestone imported from European and American refining works, the smaller bulk ot which renders it really much cheaper, while its uniformity of composition renders it more trustworthy, and enables more accurate control to be kept over the working.

Magistral is prepared by slowly roasting copper carbonate ores with copper or iron pyrites, or with the heavy sulphides which settle out when the "torta" is washed after amalgamation, a small quantity of salt being usually added. The mean of several analyses of average samples of magistral from different localities prepared in the above way was, as quoted by Percy,* 16 per cent. $CuSO_4$ (anhydrous), 7 per cent. $FeSO_4$, 23 per cent. Fe_2O_3, and 5 per cent. insoluble CuO; usually, however, only 50 to 70 per cent. of the total copper in the ore is converted into sulphate. The old test of the strength of magistral was to hold a handful in the closed fist under water and note the rise in temperature (piquete), caused by the hydration of the sulphates, it being formerly supposed that magistral which had become hydrated by exposure to the air, and consequently showed no rise in temperature when thus tested, was practically worthless without re-roasting. At the present time, however, amalgamation masters have more scientific knowledge, and, consequently, the additions of magistral are with greater certainty proportioned to the work to be done.

At a few places in Zacatecas, Michoacan, and elsewhere magistral is still used in preference to copper sulphate, because the near proximity of copper mines enables it to be cheaply prepared on the spot, but in other States, especially in Guanajuato, Hidalgo, Oaxaca, Guerrero, Chihuahua, and Sonora, the crystallised bluestone is used almost exclusively.

Ferric sulphate has been tried as a substitute for copper sulphate, but with poor results; in some comparative experiments reported by Laur† the extraction obtained in a torta with copper sulphate was 85 per cent., while in one with iron sulphate it was only 35 per cent.

In parts of Chili and Bolivia, where the Patio process is in use to some extent, magistral is prepared by mixing the natural ferric sulphates (coquimbite, copiapite, fibroferrite) with carbonate and oxide ores of copper, whereby a double decomposition takes place with formation of copper sulphate and hydrated iron oxide. Sometimes *atacamite* has been used with still greater efficacy, inasmuch as it already contains copper chloride and so requires less salt.

Proportions in which Reagents are Employed.—The proportions used vary according to the nature of the ores treated,

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* *Op. cit.*, p. 595.

† *Annales des Mines*, 6th series, vol. xx., p. 262.

and to a certain extent with the custom of each Hacienda or of each district.

Salt.—At *Zacatecas* the quantity varies at different Haciendas from 2½ to 6 per cent., a general average being four arrobas per *monton** of 2000 Spanish pounds (= 2029 lbs. avoirdupois) or 5 per cent. At *Guanajuato* the quantity varies between 3 and 4½ per cent.; in the State of *Durango* from 3½ to 4½ per cent. At the principal establishments in Pachuca the uniform proportion of 4 per cent. is adopted. It should be borne in mind that the quantity added is in all cases largely in excess of that required for the reactions, and, therefore, a uniform proportion may be adopted irrespective of variations in the composition of the ores.

Magistral.—The amount varies according to the nature of the ores, the least proportion being required with siliceous ores comparatively free from base-metal sulphides. At *Zacatecas*, where the ores are heavily charged with pyrites and other sulphides, the proportion of magistral added varies from 35 up to 125 lbs. per monton of 2000 lbs. (= 1¾ to 6¼ per cent.) according to the strength of the magistral and the more or less refractory nature of the ore. Generally, however, about 2 per cent. is reckoned to be amply sufficient for an ordinary 60-oz. ore of the "negro" class.

Copper Sulphate.—When this is used instead of magistral the quantity used varies from 4 up to 20 lbs. per ton (0·2 to 1·00 per cent.) according to the nature of the ore and the character of the grinding process to which it has been subjected. With ordinary arrastra-ground pulp both at *Pachuca* and *Zacatecas* the proportion used is from 4 to 5 lbs. per ton (0·2 to 0·25 per cent.). It should be noted, however, that when the pulp has been ground in mills wholly or partly of iron the proportion of bluestone employed must be very largely increased to give the same results, owing to precipitation of metallic copper, which (as will be seen hereafter) is much less active than its salts. Thus at *Hacienda de Loreto*, Pachuca, where both systems of grinding are at work side by side, the pulp from the *arrastras* (stone) requires only 0·2 per cent., while that from the *chilenos* (iron) takes 1·0 per cent. of bluestone to give the same results. It was precisely for this reason that patio amalgamators had such a rooted antipathy against the use of iron in any form, for not being able to afford sufficient "magistral" to counteract its reducing effect the results obtained on pulp ground in iron mills were necessarily inferior.

Mercury.—The proportion of mercury employed shows less variation, the general rule being to add about 6 ozs. of mercury for every ounce of silver which the torta is expected to yield.

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* The Zacatecas *monton* is 2000 lbs., that of Pachuca 3000 lbs., that of Guanajuato 3200 lbs.

Estimating the yield at 80 per cent. of the total contents, it is evident that the total quantity of mercury required is about seven and a-half times the quantity of silver in the ore as determined by fire-assay. At *Pachuca* the rule is to add seven times the weight of silver present determined by assay. The total quantity required is never added all at once.

Working of the Patio.—As soon as the "torta" has reached a proper consistency the required quantity of salt is spread over the surface with shovels, and six to twelve horses or mules, attached together by means of a long rope passed through their halters, are turned in to tread it. The end of the rope is held by one man in the centre of the heap who changes his position in such a way as to leave no part of the heap untrodden. After about an hour's treading the whole heap is spaded over by six men who turn the bottom layer to the top as thoroughly as possible, after which the string of animals is again turned on for another hour, the combination of two treadings with a spading between being called a "repaso." A sample is then taken from every portion of the heap, which is smoothed and levelled over and left till next day. The operation of adding salt is called "ensalmoro." The next thing is to add the required proportion of magistral or bluestone, which, if the ore is of known character, is determined by previous experience. If the ore is new to the amalgamator he makes several small experimental tortas of a hundredweight or so each, and is guided by the results indicated by washed samples of these. The full quantity required is, in the case of a new class of ore, never added at once, because, if too little is added, the consequence is simply a slight loss of time which can be easily remedied, whereas the addition of too large a quantity is disastrous as regards the loss of mercury and may be so as regards the extraction of silver.

Magistral is always simply sprinkled broadcast over the heap as evenly as possible and thoroughly trodden in by men or horses or both; bluestone also is usually finely powdered and sprinkled over the heap, but, occasionally, a strong solution is made with hot water and sprinkled over the heap with a watering-pot with the idea of saving time in the mixing.

The required amount of mercury is then sprinkled over the heap by squeezing it through a cotton cloth. Formerly at Zacatecas the custom was to add at first only two-thirds of the quantity of mercury estimated as necessary; the Guanajuato, Pachuca, and more common practice, however, is to add the whole quantity required at once. After adding the mercury a "repaso" or treading is given for another hour or two, and a sampler ("tentadurero") then walks all over the heap, taking at every few steps a small quantity of ore from the top and another equal quantity from the bottom after pushing away the top ore with his foot.

The sample collected in this way, weighing from ½ to 1 lb. or more, is taken to the foreman of the patio, who "vans" it in a rough horn spoon,* breaking up any lumps with his fingers as gently as possible and without rubbing the sample against the horn, as that would tend to collect the mercury into one globule and spoil the test. The test, after vanning, shows the following appearances:—At the bottom of the horn a globule of liquid mercury of the natural colour, above this a layer of metallic sulphides, and at the top a "ceja" (eyebrow) of finely-divided mercury. It is taken in the horn to the amalgamator, who judges the condition of the "torta" by the appearance of the "ceja." If the globules are of rather a large size and run together very readily into a globule of the natural colour or slightly bronzed, the torta is said to be "cold," the operation is not far enough advanced, and more magistral must be added. If, on the other hand, the extreme edge of the "ceja" appears as a fine ash-grey or dark-grey *powder*, which does not form globules on rubbing, the torta is getting too "hot," and some lime or wood ash must be immediately trodden in to neutralise the effect of the overdose of bluestone. When the operation is proceeding properly the "ceja" should consist of minute pearly-grey globules without any powder, and on gentle pressure with the thumb against the horn these very fine globules should run together and run down sluggishly in an oval shape to the bottom of the spoon, where they remain as a chain of little globules which do not readily unite except through continued rubbing The colour should always be a light pearly grey, and on pressing or rubbing some of the mercury should adhere to the ball of the thumb, indicating that it has already commenced to take up silver.

If the indications are normal as above, the torta is turned completely over so as to bring the bottom layer to the top and a treading is given as before, the operations of adding the magistral and mercury being called collectively the "incorporo."

The day after the "incorporo" a sample is taken from all parts of the heap and vanned as before by the patio foreman. This second-day sample should show at the bottom of the spoon

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* Vanning tests are made in Mexico in several different ways. For *gold*, where a large quantity has to be taken, the *batea* (a shallow bowl cut out of a block of mezquite wood) is commonly used. It is cut by hand and forms a segment of a sphere varying from 10 to 16 inches diameter and 3 to 4 inches deep. For *silver*, *mercury*, and all other heavy metallic substances the common utensil is the "cuchara" or horn spoon, made by sawing in halves longitudinally the larger end of a fair-sized bullock's horn. In some districts small saucers of red or black pottery called "platillos" are used for the same purpose, and in the hot districts, where agriculture instead of cattle raising is the staple interest of the country, a section cut from a tree-gourd and called a "jicara" is frequently used. A large well-shaped horn spoon, however, is the best of all vanning implements for finishing a test.

a large globule of clean mercury (which should be very fluid, while at the same time showing a little brilliant pasty amalgam on squeezing) and a very narrow "ceja" of finely-floured mercury. On the morning of the third day the torta gets another treading, during which, if it has become too dry (as is usually the case), water is sprinkled over it, a little at a time, taking care that the mud remains stiff enough not to obliterate the hoof prints, the right amount being about 33 per cent. moisture. After this "repaso" another assay is taken. This should now show, instead of free mercury in the "ceja" only, an edge of fine brilliant particles of pasty amalgam called "limadura," which, on pressing, exude a little mercury. If the limadura is too soft and contains much mercury more "magistral" is required; if, on the contrary, as frequently happens when only two-thirds of the mercury has been added at first, it is quite hard and dry under pressure, the rest of the mercury must be added at once. Whenever fine ash-grey powder is shown at the extreme edge, the torta is too hot, and a little slaked *lime* and *woodashes* should be trodden into the heap. This fine ash-grey or dark-grey powder is partly composed of *calomel*, or rather of minute globules of mercury coated with that substance, formed by direct action of an excess of copper chloride upon the metal.*

Instead of lime or woodashes, which actually destroy a portion of the active copper chlorides present without regenerating the mercury, some amalgamators use precipitated *copper*, which immediately reduces the excess of cupric chloride to cuprous chloride, and so prevents it from acting upon the mercury without destroying its action upon silver compounds.

Supposing everything to be going well by the third day the usual custom is to "tread" each torta on alternate days only, but this entirely depends on the indications of the daily tests. When too cold two "repasos" may be given in one day, when too hot the torta may be allowed to rest entirely for several days. The following successive appearances should be shown by the daily tests:—At first the "*limadura*" should increase in amount, in size of the individual particles and in dryness, while the globule of fluid mercury decreases in size and in fluidity. Secondly, pieces of dry amalgam ("*pasillas*") should appear in the layer of sulphides ("*asientos*"). Lastly, both limadura and globule of residual mercury disappear altogether, and nothing is left but irregular pieces of dry amalgam distri-

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* According to Egleston (*Metallurgy of Silver, &c., in the U.S.*, vol. i., p. 287), "when there is an excess of magistral the chloride of mercury acts upon the sulphide of silver and makes chloride of silver and sulphide of mercury, which latter is entirely lost." There is certainly something wrong about this remarkable statement, for sulphide of silver is absolutely unaffected by calomel and the existence of the bichloride of mercury is inconceivable in presence of an excess of the metal.

buted through the "*asiento*" and a very thin edge ("*ceja*") of floured mercury (*desecho*), which should easily run together on pressure as on the second day immediately after the incorporo. The amalgamation is now at an end, and the torta is ready to be washed.

At *Zacatecas* and in Mexico generally, as soon as the amalgamation is finished, a "baño" or addition of liquid mercury to the extent of 6 or 7 lbs. per ton of ore is made, chiefly in order to dissolve and collect the dry amalgam. At *Guanajuato* and elsewhere, where the proportion of heavy sulphides is smaller and where the ore is ground finer before going to the patio, this "baño" of mercury is omitted; but, instead, 8 lbs. extra of mercury for each pound of silver are added to the torta in the first instance, and a variable amount of extra mercury is put into the washing vats.

Time Occupied in the Process.—No general rule can be given, so much depending on the class of ore and the way in which the process is conducted.

At *Zacatecas* the average time required for small tortas is ten to twelve days in summer, and fifteen to twenty days in winter. At *Guanajuato*, and especially at *Pachuca*, where extraction is more thorough, owing chiefly to the custom of buying ores out and out instead of treating them at so much per ton, the "beneficio" of the large 150-ton tortas employed generally takes from twenty to twenty-eight and sometimes thirty days.

By far the largest part of the total silver extracted, however, is amalgamated during the first few days. Thus Percy quotes a case at *Guanajuato* of a torta which took thirty-three days altogether, in which it was found that 93 per cent. of the total extraction had been amalgamated by the twelfth day, and it is generally reckoned that at least half the silver is always amalgamated by the third day.

It is known in general terms that a high temperature accelerates, while a low temperature retards the reactions upon which amalgamation depends; and, further, that the amount of moisture present has an important effect, tortas worked too wet showing a low extraction of silver with a low loss of mercury, while the opposite results follow when worked too dry.

The frequency and duration of the "repasos" also have a great influence on the rapidity of the process. At *Guadalupe y Calvo* many years ago experiments on this point were made by Macintosh.* Two tortas of the same size having been prepared of the same ore in precisely the same way and with the same quantity of reagents and mercury, the one was given eight "repasos" of five or six hours each at intervals of three or four days, while the other was trodden continuously day and

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* Percy, *op. cit.*, p. 619.

night by relays of mules. The first took twenty-seven days to amalgamate, while the second was finished in three days six hours; but the time saved by no means paid for the extra cost.

The perfection of the mixture and intimate contact of the particles of silver mineral with finely-divided globules of mercury are the most important factors in determining the time necessary for amalgamation. For this reason none of the various appliances invented at different times as substitutes for the treading by horses and mules* have proved successful, because they do not mix the material nearly so thoroughly.

The treading, however, is very injurious to the animals, who frequently die or become permanently disabled from copper- and mercury-poisoning, following ulceration of the legs, or caused by licking up the ore mud for the salt which it contains. Care is taken to wash their legs immediately after work, while every precaution is taken to prevent their licking up the saline mud. The greater effectiveness of animal-treading, however, has enabled it to hold the field in spite of these drawbacks.

Loss of Mercury.—In Mexico the loss of mercury is considered under the two heads of *chemical* and *mechanical* loss. The former called "*consumido*" is erroneously supposed to be necessarily equal in weight to the silver recovered, ounce for ounce. Even if none of the mercury were converted into sulphide or chloride by the direct action of base-metal salts, on the supposition that the silver sulphide and chloride were reduced to metal direct by mercury the loss should be in proportion to the atomic weights—viz., 108 : 200, or nearly 15 ozs. mercury per mark (8 ozs.) of silver produced. In practice the loss varies with different ores from 7 up to 16 ozs. per mark of silver, averaging 11 to 12 ozs.

The chief loss of mercury is undoubtedly as calomel, formed by reaction of chloride of copper and of silver upon mercury, and it can be much reduced by employing *copper amalgam*, as was first done at Guadalupe y Calvo. Instead, however, of first preparing the copper amalgam (as described on a preceding page), it is now more usual to employ *precipitated copper*, which is sprinkled through the heap either at the same time with the copper sulphate or subsequently. When copper is used in this way the usual proportion is one-third, the weight of silver supposed to be present, and in this proportion, combined with 5 lbs. of copper sulphate to the ton, the total loss of mercury has been reduced to as low as 5 ozs. per mark, or, say, 63 per cent. of the weight of silver extracted. In *Chili*, where easily reducible ores are sometimes treated by the Patio process, *lead amalgam* is sometimes used for reducing the loss of mercury, which, by this means, is brought down to 4 ozs. per mark.

It should be remembered, however, that the use of all such

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* Some of which are described by Percy, *op. cit.*, pp. 610-614.

means for reducing the loss of mercury is attended by the disadvantage of increasing the time required for complete extraction of the silver with any given quantity of reagents.

Reactions of the Patio Process.*—Much has been written on this subject, but it cannot yet be said that the actual reactions are thoroughly understood, if indeed they are always the same, which may be considered doubtful.

The first reaction is undoubtedly that of salt on copper sulphate—

$$2NaCl + CuSO_4 = Na_2SO_4 + CuCl_2.$$

The cupric chloride may then in part act directly upon silver sulphide—

$$Ag_2S + CuCl_2 = 2AgCl + CuS.$$

But this reaction is slow, even if the cupric chloride could long exist in that condition (which it cannot), and it is probable that the larger part of the cupric chloride acts directly upon mercury, upon metallic copper if present, and upon small quantities of ferrous sulphate (produced by partial oxidation of pyrites in the ore during the grinding process) being reduced to cuprous chloride, which is the active agent in the process—

$$2CuCl_2 + 2Hg = Cu_2Cl_2 + Hg_2Cl_2.$$

The mercury thus transformed into calomel is the chief item of loss in the process.

Opinions differ as to the reactions between the cuprous chloride and the silver compounds. It is generally recognised, however, that any native silver present is probably taken up by the mercury direct without that previous transformation into chloride mentioned in old metallurgical text-books.

As regards the reaction of cuprous chloride upon silver sulphide most of the older text-books give

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S, \text{ and}$$
$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag.$$

It is obvious, however, that a very large part of the silver in the condition of sulphide must in some way reach the metallic state without passing through that of chloride, for, otherwise, the loss of mercury as calomel alone (to say nothing of the mechanical loss by flouring) would when dealing with a sulphide ore amount to 200 parts for every 108 parts of silver, which, as already seen, is by no means the case. The fact noted by Bowering that no silver chloride can ever be detected in the torta is, however, not convincing, because it may easily be

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* Percy-Rammelsberg, *Die Metallurgie des Silbers und Goldes*, Brunswick, 1881, p. 12; Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, New York, 1887, vol. i., p. 289; Schnabel, *Handbuch des Metallhüttenkunde*, vol. i., p. 655.

supposed that nascent chloride would be more readily acted upon by mercury than that naturally existing in the ore.

According to Laur, cuprous chloride dissolved in sodium chloride can act directly upon silver sulphide with production of metallic silver—

$$Ag_2S + Cu_2Cl_2 = CuS + CuCl_2 + 2Ag.$$

A secondary action takes place, as shown by Rammelsberg and Huntington, with re-formation of cuprous chloride—

$$CuS + CuCl_2 = Cu_2Cl_2 + S.$$

According to Bowering, Uslar, and Stolzel* the cuprous chloride acts by absorbing oxygen from the air and becoming an oxychloride—

$$[2Cu_2Cl_2 + O_2 = 2(CuCl_2 . CuO)],$$

which subsequently reduces the silver sulphide, regenerating the cuprous chloride according to the reaction—

$$Ag_2S + 3(CuCl_2 . CuO) = 3Cu_2Cl_2 + SO_3 + 2Ag.$$

According to Grützner, quoted by Schnabel,† the insoluble oxychloride is not formed, and the reaction is as follows:—

$$2Ag_2S + 2Cu_2Cl_2 + 3O = 4Ag + Cu_2S + 2CuCl_2 + SO_3.$$

The comparatively small production of calomel might be explained by either of the above reactions, but it is by no means certain that atmospheric oxygen enters into the reactions at all.

The reduction of $CuCl_2$ to Cu_2Cl_2 must, indeed, be effected by other agencies besides that of mercury, for otherwise the loss would be much greater than at present, since the $CuCl_2$ yielded by the double decomposition with salt of 5 lbs. of bluestone per ton of ore would require 4 lbs. of mercury per ton for reduction. When precipitated copper is employed this reduces the chloride at once ($CuCl_2 + Cu = Cu_2Cl_2$); when the ore has been ground with rolls or in Chilian mills with iron runners the small particles of detached iron act as reducing agents converting the chloride at once to sub-chloride ($2CuCl_2 + Fe = Cu_2Cl_2 + FeCl_2$) or even to metal when in sufficient quantity. When, however, neither metallic iron nor copper are present, it may be supposed that the metallic sulphides, or the ferrous sulphate produced by oxidation of pyrites during grinding, are the reducing agents which produce cuprous chloride.

On the much-debated question as to the reactions in the patio between Cu_2Cl_2 and Ag_2S, the author's experiments‡ lead him

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* Schnabel, *op. cit.*, p. 658.

† *Loc. cit.*

‡ "Notes on the Amalgamation of Silver Ores," *Trans. Inst. Min. Met.*, vol. vii., p. 229, *et seq.*

to conclude that the equation originally propounded by Laur—viz.:

$$Ag_2S + Cu_2Cl_2 = CuS + CuCl_2 + 2Ag—$$

more nearly represents what actually happens than any other. The bye-products of this reaction, CuS and $CuCl_2$, undoubtedly react upon each other to some extent, as pointed out by Huntington, re-forming Cu_2Cl_2, and liberating free sulphur.

Washing the Torta.—In small works the separation of the amalgam from the slimes by washing is commonly performed in a masonry tank lined with cement, called a "lavadero," the construction of which is shown in Figs. 7, 8, and 9.

Fig. 7.

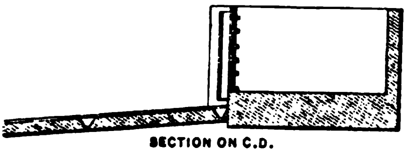


Fig. 8.

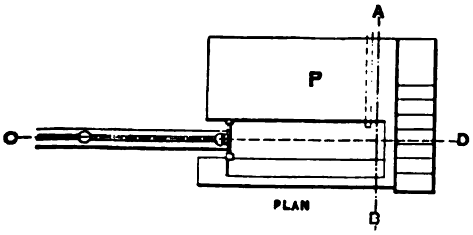
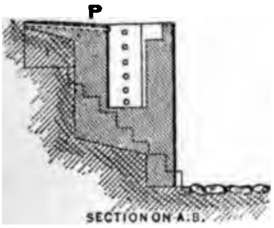


Fig. 9.



Figs. 7, 8, and 9.—Lavadero.

The tank is usually 6 feet long, 18 to 24 inches wide, and 3 feet deep. One end is closed by a plank of hardwood in which are inserted wooden plugs at different levels, which allow the tank to be emptied down a sloping channel leading to the settling tanks. The tank being half filled with water two men get in, and as the torta mud is shovelled from the platform, P, at the side they keep the mass constantly in motion by treading and jumping up and down. More mud and water are added till the tank is full, when the excess of slime is allowed to discharge at the top plug continuously, one of the lower plugs being opened at intervals to let out some of the heavy metallic concentrates if they are at all large in quantity.

In larger works, the tub-settler, worked by mules, water, or steam power, is always employed. Fig. 10* shows one of a pair of small settlers formerly used at *Fresnillo*, the capacity of which was 5000 lbs. per hour. The method of working is clearly indicated in the figure. The central wheel, *b*, with wooden teeth, was turned by four mules walking round a 23-feet circle; it drove two pinions, *c*, each of which formed the axle to which were attached four cross-arms with stirrers. The bottom of the masonry tank (*tina*), *d*, was formed of a single block of stone, *e*, hollowed out to prevent leakage of liquid amalgam. The stirrers made 16 revolutions per hour, and even at this low speed a great deal of amalgam was carried off with the slimes, to be afterwards recovered by washing on *planillas*.

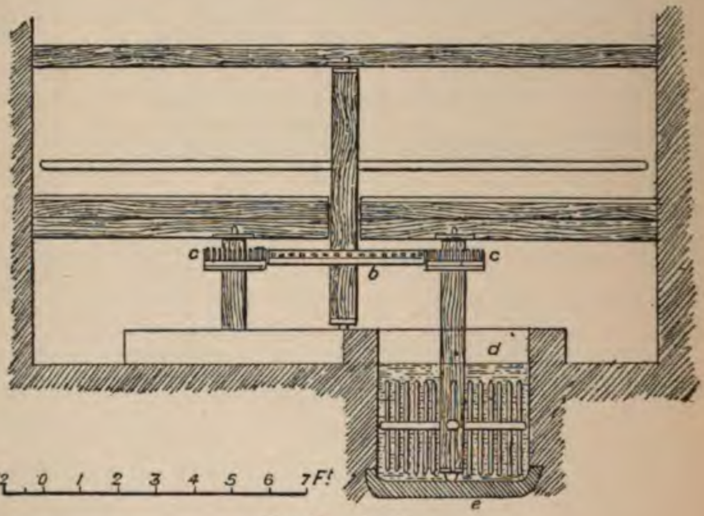


Fig. 10.—Settler.

At *Zacatecas* much larger settlers, or washing vats, are employed, though of the same construction, the bottom being formed of a single stone, or of a cast-iron pan bedded in concrete. Only one settler is worked by each team of mules, and some of

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* Copied from Percy, *op. cit.*, p. 622.

the largest measure 9 feet in diameter and 7 feet in depth, sunk in the ground, with an outlet 18 inches above the bottom, the washing capacity being 2½ tons per hour. The stuff being usually somewhat coarse at Zacatecas, and the proportion of sulphides in the ore very great, much amalgam is carried away with the concentrates and has to be separated by hand washing.

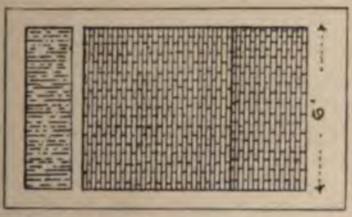
At *Guanajuato* a series of tubs is sometimes used, and the speed of rotation is very much less than in the Zacatecas district, as the finer mud comparatively free from sulphides is much more easily kept in motion. The capacity of each vat is much less, but the loss of amalgam is very small.

The heavy slimes and sand from the lavadero are run through riffled launders and caught in a series of catchpits, to be concentrated on *planillas;* the amalgam is cleaned by washing in shallow wooden bowls called *bateas*, the sulphides washed off (*relaves*) being re-washed together with the "heads" from the concentration of the slimes, after which it is strained by its own weight through large canvas bags (*mangas*) hanging from iron rings, and holding some 2000 to 3000 lbs., and afterwards retorted (see Chap. VIII.).

The *planilla* is a kind of hand buddle used throughout Mexico for the concentration of all kinds of slimes or residues containing the precious metals. It is shown in Figs. 11 and 12, and is usually paved with flat stones set in cement, but sometimes of brick set edgewise in cement or in asphalt, as shown.

Fig. 11.

Fig. 12.



Figs. 11 and 12.—Planilla (Section and Plan).

The operator begins by spreading a layer of tailings about 3 inches thick evenly over the surface of the steeply-sloping back part of the planilla. Then squatting on a board laid across the water tank he sweeps up the water with a gourd bowl or small horn, about half a pint at a time, letting it fall in a thin sheet on the lower part of the bed of tailings, travelling across the planilla, and then in lines successively up to the top. After going over the whole surface of the sloping part of the planilla in this way three or four times, nothing will be left on it but a few pounds of amalgam, floured mercury, and rich concentrates at its lower edge, which are scooped up for hand washing in *bateas*. At the front edge of the planilla floor will be found a layer of very poor sand, which for a foot or two back is scraped up and thrown away. The rest of the deposit on the planilla floor is shovelled up and spread over the slope at the back as before, and the washing repeated, when the residue at the bottom edge of the slope will be nearly clean metallic sulphides called *polvillos* or *marmajas*,* which by further repetitions of the washing process can be almost freed from the tailings (*jales*).

The process seems to be a very costly and primitive one, but as both the appliance and the labour required to work it are cheap the small output from each *planilla* is comparatively unimportant; while it possesses the unique advantage (highly important in a hot dry country) of requiring but a very small quantity of water, which is used over and over again with no loss except by evaporation.

The further treatment of the concentrates varies almost entirely according to their richness in silver, being, however, somewhat affected by the nature of the preponderating sulphide, whether pyrites alone or mixed with chalcopyrite and galena. Formerly large quantities were used in the manufacture of magistral, the rest being roasted and treated over again by patio amalgamation. Now, however, only the very poorest concentrates and middlings obtained in concentration are treated by amalgamation, the great bulk of the concentrates obtained being sacked and shipped to smelters.

In some places, at a distance from railway communication, the final cleaning of the *polvillos* for shipment is performed by "kieving"—*i.e.*, by stirring up the sulphides with water and then allowing them to settle, knocking on the side of the tub all the time with a mallet. On dipping and straining off the water with rags there is found on the top a layer of sand, then a layer of poor "middlings," which is roasted and added to the tortas, and, lower still, the rich black sulphides, with sometimes a little amalgam right at the bottom. Instead of a tub, a *boliche* is often used, hollowed out of a section of a tree, the cavity in the centre being from 24 to 30 inches in diameter and 18 to 24 inches deep.

The concentrates sometimes contain, besides more or less argentiferous base-metal sulphide, distinct scales of argentite or silver chloride, which, being sectile and semi-malleable, have escaped the grinding process and have not been sufficiently

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* The latter name being only employed when they consist almost exclusively of pyrites.

comminuted to yield to amalgamation. Ores containing fair-sized grains, scales, and nodules of argentite are not well suited to patio amalgamation, and, as already stated, the haloid compounds of silver must be in the condition of very fine disseminated powder in order to be attacked at all.

Loss of Silver.—The percentage loss of silver in the Patio process varies, not only with the nature of the ore, but also with its richness. Generally speaking, with ore of a given class the loss in tailings may be considered to be nearly constant, so that the apparent percentage of extraction rises with increased richness and *vice versâ*.

This is exemplified by the following figures from the *Hacienda de la Sauceda* (Zacatecas) quoted by Stetefeldt.[*] In treating ores of the same class from the San Acacio Mine it was found that ores containing 17 ozs. are worked with a loss of 4·4 ozs., corresponding to an extraction of 75 per cent.; those of 32 ozs. contents were worked with a loss of 3·2 ozs., showing an apparent extraction of 90 per cent.; and others of 100 ozs. were worked with a loss of only 7 ozs., showing an apparent extraction of 93 per cent.

At *Zacatecas*, according to Newall,[†] the old tailings thrown away, even when treating complex ores of 60 ozs. and upwards, rarely contained more than 12 to 14 ozs., but now they seldom run more than 6 to 8 ozs., averaging under 5 ozs. The average ores treated at Zacatecas (which are refractory) show a recovery on patio treatment alone of 75 to 85 per cent., without taking into account the silver recovered in concentrates, which is often equivalent to another 10 per cent.

Treatment of Refractory Ores in the Patio after Roasting.—At *Charcas* (San Luis Potosi), where the chief silver-bearing minerals are fahlerz and blende, according to Percy,[‡] the ore is stamped and ground in arrastras wet. then left to dry, mixed with 4 per cent. of salt, and gently roasted for twelve hours in charges of 1800 lbs. Then (sometimes) ground in arrastras to disintegrate lumps, and made into tortas with 2½ per cent. more salt and 3½ per cent. magistral. The tortas take ten or twelve days to work; the loss of mercury is more than 16 ozs. per mark, and the loss of silver 35 to 40 per cent.

At *Real del Monte*, *Sombrerete*, and other places, roasting, followed by patio treatment, was formerly in vogue for refractory ores containing large proportions of blende, galena, and other sulphides, but now the richest of such ores are commonly picked out and shipped for smelting, and the poorer ores treated raw.

At *Tasco* (Guerrero)[§] an ore containing 15 per cent. of galena, 12 per cent. of blende, and 10 per cent. of pyrites in a gangue of

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[*] *Trans. A.I.M.E.*, vol. xiii., p. 370.

[†] Quoted by Percy, *op. cit.*, pp. 647 and 648.

[‡] *Op. cit.*, p. 631.

[§] Chism, *E.M.J.*, July 20, 1889.

calcite and quartz is treated by roasting. It is stamped dry through a 40 mesh, as has already been described, and is then taken in handbarrows to a single-hearth reverberatory furnace with a hearth 12 feet wide, provided with a charging hopper above and a single rabbling and discharging door at one side. The charges are of half a ton each, and are only roasted for half an hour *without any addition of salt.* After discharging, the ore is allowed to lie in heaps for a few days in order to start decomposition of the unaltered sulphides with the help of the sulphates formed, and is then ground for a short time in arrastras in order to disintegrate agglomerated lumps. The tortas are then made up as usual, except that the salt used is from 5 to 10 per cent. and the sulphate of copper from 10 to 40 lbs. per ton, according to the nature of the ore. Only one or two treadings are given, and the amalgamation is finished in from three to eight days, averaging only five days. The loss of silver averages 12 per cent., and the loss of mercury only 10 to 12 ozs. per mark. The cost of treatment is given in Table III.

Marmajas, or pyritous concentrates, poor in silver (30 ozs.), can be roasted and treated in the patio much like ordinary ores, except that they require an extra proportion of magistral. When, however, they contain much copper pyrites the addition of magistral can be altogether dispensed with; and in such cases it is preferable to work the roasted concentrates together with ordinary ores and not separately, as loss of mercury is thereby avoided and some magistral saved.

Use of Hyposulphite.—A recent improvement in the ordinary Roast-Patio process for arsenical and antimonial sulphide ores is described by Lukis.* Like most other metallurgists who have studied the question this writer recognises that a perfect roast is not required, but only such a heating as will cause the sulphides to decrepitate and open up the cleavage planes to the action of the solutions. The great difficulty in treating roasted ore is found in the fact that the torta readily *heats*, and so causes an enormous loss of mercury by flouring. The improvement consists in adding *sodium hyposulphite* in the proportion of 1 to 1¼ lbs. per ton of ore after the treading in of salt and copper sulphate, but before the addition of mercury. It is claimed that the addition of hyposulphite enables a larger proportion of copper sulphate to be used without flouring the mercury, and so accelerates the process that on the fifth day the torta can be washed. The exact mode of action cannot be easily explained, though one may suppose that there is a formation of cuprous hyposulphite, as in the Russell process.

There is no doubt that the efficiency of the Patio process and the time taken very largely depend upon the proper proportioning of the amounts of salt and copper sulphate, and that, of

* *E. and M. J.*, May 7, 1892.

late years, the reactions have been greatly accelerated by using a larger quantity than was formerly thought advisable with the help of careful experiments on small trial tortas. It seems probable, too, that a great reduction in the loss of mercury might be effected by first thoroughly mixing salt and the required quantity (or a slight excess) of copper sulphate with the ore (say in the arrastra itself), then treading in precipitated copper or lead amalgam and leaving for a day or two, and finally adding the mercury after nearly all of the silver had been reduced to a metallic condition. Further experiments by trained metallurgists on a practical working scale seem to be urgently required.

Patio Amalgamation in S. America.—In *Peru* the Patio process is largely in use for treating the poorer ores. As regards the oxidised ores the process differs in no marked respect from that described as being in use in Mexico. The heaps usually contain only 50 to 100 tons, the quantity of mercury used is 6 to 1 of silver and the average loss is 12 to 16 ozs. per mark (1½ to 2 : 1).

The sulphide ores usually contain much fahlerz and blende and are refractory. They are roasted in small single-hearth reverberatories, which treat 8 cwts. each per day with a consumption of 20 cwts. of *taquia* or dung of various ruminating animals, chiefly llamas. Salt is used in the proportion of 5 per cent., but no magistral is required, as the roasting produces sufficient copper sulphate to carry on the reactions.

At *Cerro de Pasco* (Bolivia) * the heaps called "tortillas" are made up of raw ore inside permanent circular low walls, called "circos"; they rarely contain over 15 short tons. The charge for each heap is 40 arrobas of salt (= 6·7 per cent.), together with 15 to 30 lbs. magistral and 80 lbs. of mercury, which is trodden in as usual, the treadings being repeated once a week for two months, more mercury being added, as required, up to a total of 230 lbs. The very slow progress of the operation is no doubt partly due to the great elevation (14,000 feet), which causes a cold climate and so retards the reactions; and also partly to the proportion of magistral employed, which is very much smaller than in Mexico. The washing of the tortilla and squeezing of the amalgam are conducted as in Mexico.

At *Potosi* (Bolivia) both the poorer "cascajos" and the sulphide ores are treated by the Patio process, the latter ores being previously roasted in the way above described, except that salt is added during the roasting. Two peculiarities of patio amalgamation at Potosi are the small size of the tortas, which are trodden by men and do not generally contain above 2½ tons of ore; and the use of *tin amalgam*, instead of copper or lead, for economising mercury. One part of tin is considered as equivalent to two

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* Pfordte, *Trans. A.I.M.E.*, vol. xxiv., p. 117.

TABLE III.—COST OF

	San Dimas, Durango, 1882.		Hda. de la Granja, Zacatecas, 1889.	
Reference,	1.		2.	
Value of ore treated, per ton,	60 ozs.		23·4 ozs.	
Assay of tailings,	—		6½ ozs.	
Percentage of extraction,	70 to 80		80·5	
Motive power for crushing,	Water		Mules	
Cost for labour and general charges, per ton—	$ Mex.		$ Mex.	
Crushing (Chili mills or stamps),	1.53		...	
Grinding (mills or arrastras),	1.40		...	
Hire and keep of mules,	3.72		...	
Labour, spading, driving, &c.,	1.79		...	
,, washing torta,	0.56		...	
Concentrating sulphides,	2.06		...	
General expenses and repairs,	2.94		...	
	——	14.00		2.71
Cost for materials, per ton—				
Salt, quantity and price,	140 lbs. @ 2 c.		...	
,, cost, per ton of ore,	2.80		...	
Bluestone, quantity and price,	6⅝ lbs. @ 25 c.		...	
,, cost, per ton,	1.65		...	
Precipitate, quantity and price,	1⅓ lbs. @ 66 c.		...	
,, cost, per ton,	0.87		...	
Charcoal for retorting, &c.,	0.33		...	
	——	5.65		4.29
Total cost, exclusive of quicksilver,		19.65		7.00
Quicksilver consumed, per oz. silver,	1·7 ozs.		1·26 ozs.	
,, ,, per ton ore,	7 lbs.		1·83 lbs.	
Cost of quicksilver at 75 c., lb.,		5.25		1.37
Total cost of process, per ton,		24.90		8.37

rences.—1. Chism, *Trans. A.I.M.E.*, vol. xi., p. 76. 2. *Private Note*
*-*feldt, *Trans. A.I.M.E.*, vol. xii., p. 370. 4. Douglas, *Journ. Sc*
9. 1895. 5. Chism, *E. and M. J.*, 1889, July 20. 6. Rule, *E. an*
, 1889, p. 107.

ATMENT BY THE PATIO PROCESS.

de la Sauceda, atecas, 1883.	Cerro del Proaño, Fresnillo.	Hda. de Pedro Flores, Tasco, Guerrero, 1889.	Average. Pachuca, 1881.	Average. English money at 2/6 per $.
3.	4.	5.	6.	
7·11 ozs. 4·37 ozs. 74·5 Mules	19·2 ozs. ... 80·5 Mules	106 ozs. 8 to 12 ozs. 88 to 92 Water	About 100 ozs. ... ... Mules	... ...
$ Mex. 5.23	$ Mex.	$ Mex. 1.06 2.00 0.20 ... ... 3.26	$ Mex. 0.57 3.11 0.50 0.56 0.17 1.37 6.28	5/11 9/9½ 15/8½
bs. @ 1^{13} c. 1.93	120 lbs. ... 7 lbs.	160 lbs. @ 2 c. 3.20 15 lbs. @ 16 c. 2.40 ... ... 5.60	... 1.55 ... 0.96 ... ... 0.07 2.58	... 5/6 ... ... 4/4¾ 9/10¾
7.16	9.96	8.86	8.86	25/7¼
ozs. lbs. 1.28	1·65 ozs. 1·59 lbs. 1.20	1·25 ozs. 9·2 lbs. 6.84	... Estimated 7.00	... ... 9/6½
8.44	11.16	15.70	15.86	35/1¾

ounces in this table are Mexican ounces of 29·765 grammes = 459·382 grains 147 ounces avoirdupois, the ton being the Zacatecas monton of 2029 pounds h, nearly corresponding with the American short ton.

parts of lead. The stock of tin amalgam is added to the mercury in small quantities, stirring all the while. Amalgamation in the small heaps takes eight to twelve days, and the loss of mercury is reduced by the use of tin amalgam from 1 lb. per mark of silver to ½ lb. per mark (= 1 : 1).

In *Chili* poor ores and tailings from the Fondo and Tina processes were formerly submitted to patio amalgamation, but the Patio has now almost gone out of use since the extension of the *Kröhnke* process. Some of the Chilian ores contain *arquerite*, and in such (rare) cases the loss of mercury is largely reduced owing to the quantity recovered from the ore itself. Percy mentions one case where at one reduction works there was a positive gain of mercury in treating an easily-worked ore, which was found to contain silver in the form of *arquerite*.

Cost of Treatment.—The cost of treatment by the Patio process varies a great deal, the chief factors which influence it being the richness of the ore and the price of grain. The former affects the loss in quicksilver per ton treated; the latter affects principally and directly the cost of keeping or hiring mules for grinding and treading, while indirectly it affects the cost of materials and supplies also.

Some typical examples of patio treatment in some of the principal localities are quoted in Table III.

CHAPTER IV.

THE CAZO, FONDON, KRÖHNKE, & TINA PROCESSES.

As the Patio process originated in Mexico, so the various "copper-pan" processes originated in Peru and Bolivia. The simplest of them is the original "cazo" or "fondo" process invented by the priest Alvaro Alonzo Barba in 1609 and still in use in Bolivia, Peru, and Mexico. The "Fondon" is merely a larger Fondo, while the Tina and Kröhnke processes are only developments of the simple original.

The Fondo or Cazo Process.—The ores most suitable to this process are the oxidised ores, called in Mexico "colorados" and in Peru and Bolivia "pacos" or "cascajos," which contain chloride and other haloid compounds of silver together with more or less native silver. Argentite is commonly supposed to be irreducible and is so described by Duport and Laur, whom Percy quotes,* but the original discoverer distinctly mentions that it is to some extent affected, even in the ordinary method,

* *Op. cit.*, p. 664.

and with the addition of copper sulphate it can be worked, though imperfectly, as the author has often had occasion to see in Mexico.

Plant.—The "cazo" or "fondo" consists of two parts—first, the *fondo* proper, which is a piece of copper beaten out from a flat ingot into the shape of a huge frying-pan from 2 to 3 feet in diameter, from ¼ to ¾ inch thick, and from 4 to 6 inches deep; and, secondly, the *basin*, which is often formed (like Barba's original) of sheet copper, ⅛ inch thick, rivetted to the bottom and forming a deep basin, like the domestic boiling "copper," only wider at the top and not so deep. Sometimes the sides are formed of wooden staves resting on the edge of the fondo, hooped with iron and backed with stones and clay puddle; more rarely cut stone is alone employed. Sometimes stirring is done by means of a wooden paddle worked by hand, but often a rude mechanical stirrer worked by a handle attached to its vertical axis is employed. The copper *fondo** of the basin forms the roof of a small fireplace in which brushwood (stumps of palm trees, &c.), or, more rarely, dung is burnt; occasionally no chimney is provided, the fireplace being simply a hole dug in the bank at the side of a small rivulet. More commonly the fireplace is connected with a short chimney built of "adobe" (sun-dried brick), and grate bars are provided of the same material; in this case the fireplace is usually lengthened so as to admit two fondos, one beyond the other, and to more perfectly utilise the heat of the fuel. An aperture closed by a wooden plug is sometimes provided immediately above the edge of the bottom, through which the slime may be drawn off after amalgamation is finished.

The ores submitted to the Fondo process should contain over 40 ozs. of silver per ton as chlorides and native metal; indeed, it is but rarely that ores with less than 60 ozs. are treated. The Cazo is essentially a prospector's and working miner's appliance for rapidly extracting the larger part of their silver contents from rich ores in remote and semi-desert districts. When large quantities of ore are available it gives place to one of the more elaborate appliances which allow of the operations being carried out on a larger scale and with greater economy. Sometimes poor ferruginous or earthy gozzany materials, carrying small amounts of granular or scaly haloid compounds of silver, occur in large quantity. In such cases they are frequently concentrated on a *planilla* so as to yield a product suitable for the process. When treated direct, the ore is ground in an arrastra (usually dry) until no grittiness is observable (just as for the Patio process) or even finer. When the ore has to be concentrated it is left somewhat coarser, in order to diminish the loss in tailings; these tailings are usually treated

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* "Fondo" in Spanish means "bottom."

by the Patio process so as to recover as much as possible from them.

Mode of Working.—The process of amalgamation is conducted as follows:—The cazo is about half filled with hot water and the charge of 150 to 200 lbs. of ore according to the size of the cazo, is gradually added, stirring all the while. As soon as the resulting muddy liquid is boiling vigorously (and not before), salt is added in the proportion of from 5 to 20 per cent. of the weight of the ore and thoroughly stirred in, so as to dissolve it quickly and prevent the formation of a cake upon the bottom. Immediately the salt is dissolved mercury is added in the proportion of not more than half the weight of silver contained in the ore, as determined by inspection and by hornspoon test, or by previous experience on similar ores. This is taken up almost immediately if the ore contained much native silver and in less than half an hour (with constant stirring) when the silver existed as chloride, a part of which will have been reduced by contact with the copper, even before the addition of salt. After from fifteen to thirty minutes the first "assay" is scraped off the bottom by means of a horn fixed to a long handle; it is washed in a hornspoon or bowl and should show no mercury, but only a fine granular sand called "polveo." A second addition of mercury is now made and the boiling and stirring continued for an hour, when the second assay is taken; and so on, until the total additions of mercury amount to not more than twice the weight of silver present. Additions of hot water are made from time to time to replace that lost by evaporation. The stirring must be continuous, otherwise the amalgam is liable to stick to the bottom of the cazo and perhaps to form a cake of ore, in which latter case the "fondo" inevitably gets burnt. If the mercury were added all at once, or if excess were added, amalgamation of the copper would take place and a hole in the bottom soon result; but by keeping the additions always within the limits of 2 to 1 by weight and the stirrer in constant motion, the amalgam gradually formed becomes perfectly dry and the copper is unattacked.

Amalgamation with rich ores takes about four hours, or three hours with ores of medium richness containing only traces of argentite (which is acted upon slowly). The last test "prueba en crudo" consists of scraping up a test as before and washing off all the mineral and gangue into a pan from which the lighter slime and sand is poured away. The heavier particles of deposit are then examined with a lens, and if any scales of hornsilver remain the boiling is continued without further addition of mercury. If no scales are seen a little mercury is poured into the hornspoon containing amalgam, into which it is worked with the fingers. If the mercury appears to "dry up" and cannot be pressed out again from the stiff amalgam, more mercury is added to the charge in the fondo and the stirring continued for half an hour, as this excess of silver in the amalgam may indicate that the whole of it has not been extracted from the ore. If, on the other hand, the mercury can be squeezed out again from the amalgam and remains liquid the operation is at an end, the liquor and slimes are dipped out or drawn off by the plug into a settling tank, the heavy concentrates and amalgam dipped out, mixed with enough fresh mercury to make the latter quite pasty (say 75 per cent. of what has been already used) and washed in "*bateas.*" The tailings from the settling tank are generally rich enough to be formed into small *tortas* and treated by the Patio process, about 2 per cent. of salt being sometimes added but no magistral, as they already contain sufficient cuprous chloride for the reactions. The liquors contain a considerable quantity of salt with some cuprous chloride, and are used over again in the fondo with a fresh lot of ore until they get too full of base-metal salts.

The reactions in the fondo are simple; native silver is taken up directly by mercury, silver chloride is dissolved in the salt solution and reduced to metal, partly by the copper (even before addition of mercury), partly by the mercury itself. The calomel formed in the liquid by the latter reaction is again reduced on contact with copper. The silver as it reaches the metallic condition combines with the excess of mercury to form amalgam. The nett result of the separate action of copper and of mercury upon silver chloride may be expressed in the following equation:—

$$2AgCl + 2Cu + 2Hg = Cu_2Cl_2 + Hg_2Ag_2 \text{ (amalgam).}$$

Experiment shows that small quantities of argentite in fine powder are to some extent acted upon by the Cu_2Cl_2 formed, but the time is too short for the action to be anything like complete, and hence the tailings must be treated by the Patio process.

At *Carrizo* (Chihuahua) the author has seen ores containing considerable quantities of argentite in addition to haloid compounds of silver successfully reduced in six hours by a modification of the process. The ores consisted chiefly of heavy spar and gypsum, through which silver chloride was disseminated in very fine yellow powder, with galena in thin streaks and argentite in minute grains, shots, and streaks. The ore sometimes contained as much as 1000 ozs. to the ton, when carrying argentite, and fairly large lots of it averaged from 100 to 300 ozs. —chiefly as chloride. The treatment was identical with that above described, except that the salt (10 per cent. by weight) was first dissolved in the water and brought to a boil, the ore then added, and the mixture boiled together for half an hour; after which copper sulphate was added in the proportion of about ½ to 1 per cent. of the ore, and the whole boiled again for an hour before adding the mercury. The process then went on as above described and it was found that most of the argentite was amalgamated in from four to six hours, though the galena, of course, remained untouched. The undecomposed argentite was recovered by subsequent patio treatment, adding no copper sulphate and only a small proportion of salt. The reactions in this modified process are probably* (in addition to those already given) the following :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S,$$

the silver chloride being then reduced by copper and mercury as before.

The special advantage of this process when used on chloride ores (not to speak of the shorter time compared with the Patio process) is the very small consumption of mercury, the loss of which is exclusively mechanical and does not exceed ½ to 3 per cent. of the total quantity used, or, say, 1 to 6 ozs. for each 100 ozs. of silver. Egleston says† that the loss is "from twice to two and a-half times the total quantity of silver contained," but this may be a mistake in copying—at all events, it is totally inaccurate, as a moment's consideration of the reactions will show.

The fuel required is not very costly, for any kind of refuse bark, twigs, or worthless brushwood can be employed, or even dried cow- or llama-dung, when nothing else is to be had. The percentage of extraction, when no sulphurets are present, is very high indeed, averaging over 95 per cent., being, of course, much lower on complex ores.

Cost of Treatment.—The cost of the process varies in different localities, according to the cost of salt, copper, and to some extent with the richness of the ores; but with average oxidised ores of, say, 60 to 80 ozs. in an average dry Mexican mountain district where salt is obtainable at $40 per ton of 2000 lbs. the cost should not exceed $15 Mexican currency, or, say, at an exchange rate of 30d., 37s. 6d. per ton, made up as follows:—Grinding, $1.50 (3s. 9d.); labour, stirrers and amalgamators, $3.50 (8s. 9d.); fuel, $4 (10s.); salt, 200 lbs. at 2 c., $4 (10s.); loss of mercury, retorting, and sundries, $1 (2s. 6d.); wear and tear of fondo, 2 lbs. wrought copper at 50 c., $1 (2s. 6d.)—total, $15 (37s. 6d.). In some places the cost would be less, especially if water power were available for grinding and stirring. When copper sulphate has to be used the cost is increased, not only by the actual cost of this substance, but also by the increased loss of copper dissolved from the fondo to make Cu_2Cl_2.

The process is still largely used all over Peru and Bolivia for

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* It is quite possible that metallic silver is formed direct, according to the reaction—$Ag_2S + Cu_2Cl_2 = Ag_2 + CuS + CuCl_2$.

† *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., p. 312.

the gozzany oxidised ores, which still remain in larger quantity in those countries than elsewhere.

At *Potosi* (Bolivia), according to Wendt,* ores averaging 80 ozs. per ton, and containing fahlerz and pyrites, are first roasted in reverberatory furnaces with the addition of a small quantity of salt, and then treated in *fondos* of cast bronze 3 feet in diameter and 1 inch in thickness, the charge being 120 lbs., and from eight to ten charges being worked per day. The brine is used over and over again, with addition of fresh salt amounting to 5 per cent. of the weight of the ore. The quicksilver is added in small quantities, and the progress of amalgamation tested from time to time by washing on a small earthen plate, here called a "chua." More quicksilver is added at the end of the operation, and the amalgam is washed by hand in a small tub; after retorting, it gives silver of over 900 fine. The tailings assay 15 ozs. per ton, and, therefore, the percentage of extraction is about 80 per cent.; the loss of quicksilver is from $\frac{1}{4}$ to $\frac{5}{8}$ oz. per oz. of silver recovered.

The cost of the process is said to be between £7 and £8 per ton. It is noteworthy that the loss of silver by volatilisation in this chloridising roasting is 5 per cent., even in hand furnaces, and was much greater in revolving furnaces.

The tailings contain a large quantity of cassiterite, and when panned out give a *relave* or concentrate of 89 per cent. SnO_2, which is exported. Analyses of these ores, both raw and roasted, are given in Table II., p. 31.

The Fondon Process.—The *fondon* being only a larger *fondo* or cazo the above description applies generally to the operations carried on in it, except as regards the quantities which are larger, and the time which is a little longer. The cost is naturally decreased in proportion to the increased capacity.

The *fondon* (formerly used so largely in the districts of *Catorce* and *Matehuala* (San Luis Potosi) and still in use to some extent on hand-concentrated surface ores containing "chlorides") is shown in Fig. 13.† In this figure, *a* is the fondon or copper bottom, cast in one piece from unrefined blister copper; it is usually made about 6 feet wide, 8 inches deep, and about the same in thickness, with a boss in the centre for the stirrer axle to run on; *b*, *b* are the mullers (voladores) of cast copper, weighing 400 to 450 lbs. each, generally only two in number, attached to the lower crossbar, *c*, by rawhide thongs and driven by one mule attached to the upper crossbar, *d*; *e* is a bronze pivot on which the axle revolves, *g* the firegrate, and *f* a flue leading to a short chimney. The sides of the vat are staves resting on the rim of the copper bottom, bound with hoops and

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* *Trans. A.I.M.E.*, vol. xix., p. 94.

† Slightly modified from Laur and Percy (*op. cit.*, p. 662).

backed with a masonry wall with puddled clay between. The cost of such an apparatus, according to Laur, was formerly about $1600 (say, £200), of which the copper alone amounted to £150, but such a thick bottom should last ten years in constant use. There is always a plug in the side just above the bottom for discharging the vat.

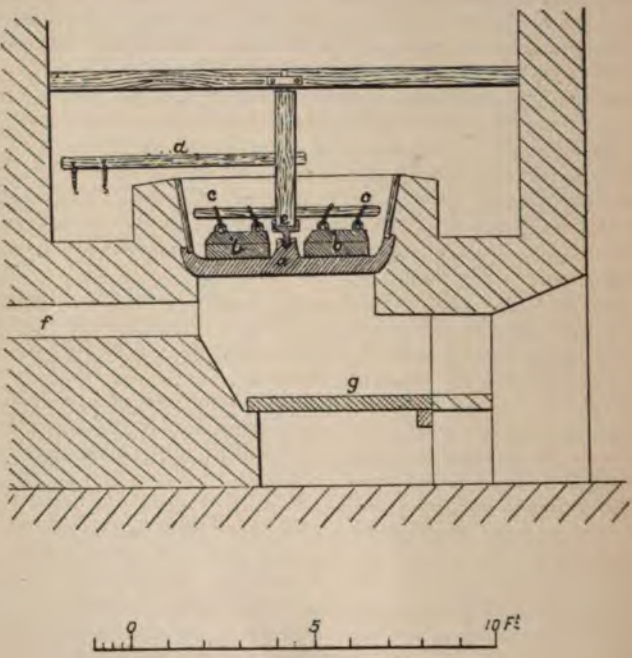

Fig. 13.—Fondon.

Mode of Working.—The working of the process is precisely th same as that carried on in the smaller *fondo*, except that th pulp is stirred by mule power, and that the ore, if of a soft kin need not be quite so finely pulverised before it is put into th *fondon*, as the copper mullers grind as well as mix. Hard ore must, however, be always finely pulverised first, or the wear copper would be too great. The *fondon* is first half filled wit water and the mule started at a slow walk, the charge of 12 lbs. of ore is then added, and the stirrer kept going at ten tur per minute for an hour, or until the muddy liquor is boiling har The salt, 5 to 10 per cent., is then added, and the first additio of mercury to the amount of one half the expected extraction o ver, just as in the cazo. Subsequent additions of mercury and the method of working tests are exactly as already described. Provided the mule is not allowed to stop and the quantity of mercury added in all does not exceed 2 to 1 of silver, there is no danger of adhesion, and at the end of the operation, which lasts from five to six hours, a small quantity of extra mercury may be added to thin the amalgam and facilitate its collection. Should adhesion occur through adding too much mercury at once or allowing the stirrer to stop, the *fondon* must be immediately emptied and the amalgam carefully scraped from the bottom and from the mullers.

The loss of mercury is somewhat less than in the *fondo*, not averaging more than 1½ per cent. of the total used, or, say, 10 ozs. per ton of ore.* The tailings at Catorce and Matehuala contain from 2 to 3 ozs. (when purely haloid ores are under treatment) up to 20 or 30 ozs. (when the ores contain much argentite or other sulphur compound). When containing upwards of 8 ozs. they are treated by the Patio process without the addition of magistral, as they already contain Cu_2Cl_2. The operation is very slow, often lasting from two to three months; but 75 to 80 per cent. of the remaining silver is recovered, with a consumption of 1¼ to 1½ ozs. of mercury per oz. of silver. In modern practice the residues from the *fondon*, instead of being treated by the Patio process, are concentrated on the *planilla* and shipped to the smelters at Monterey and San Luis Potosi. In this way the argentite, galena, and other heavy sulphides, as also the lead carbonate (which is common in all these gozzany oxidised ores) are saved.

Cost.—The cost of treatment in the *fondon* (as given by Laur) per ton of 2000 lbs. is as follows :—Labour, $1.25 ; mule, $0.32 ; wood, $2.60 ; salt, $2.50 ; loss of mercury, $0.70 ; retorting and sundries, $0.43—this gives $7.80, to which should be added, say, $1 for grinding and $0.50 for wear and tear of copper, the total being $9.30, or, say, 24s. 6d. per ton of 2000 lbs. at the present rate of exchange. Copper sulphate is now commonly used in the *fondones* at Matehuala and other places with the object of extracting a larger proportion of the silver from the less easily worked ores, but the author is not in a position to give details of the results obtained.

The Kröhnke Process.—As the *Fondo* process is chiefly used in Mexico, so this is a Chilian process invented and used in Copiapó and Antofogasta since 1862 for the treatment of the ores from the deeper workings, which, besides some native silver and chloride, carry much argentite, proustite, pyrargyrite, and polybasite. The composition of Copiapó ores is given in Chapter II.; but the process seems applicable to all which contain distinct silver minerals, except to those carrying over 1 per cent. of metallic arsenic. Argentiferous galena, blende, and pyrites are

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* Percy, *op. cit.*, p. 664.

but little affected, but it is claimed that 98 per cent. of the silver existing as pyrargyrite and proustite can be extracted, though the loss of quicksilver then rises to 12 to 35 per cent. of the silver recovered.*

In this process, as in those just described, a hot solution of cuprous chloride is the active reagent; but the operation is conducted in wooden barrels, instead of in copper-bottomed pans; and the cuprous chloride, instead of being formed *in situ*, is prepared separately, with some saving of time and of cost, as old copper can be used. Instead of copper, lead or zinc (generally the former) is used as a means of decomposing the calomel which would otherwise be formed in the process.

Plant Employed.—The ore is first crushed in Chilian mills of cast iron with steel wearing faces, the construction of which is similar to that shown in Fig. 4. The rollers weigh 4 tons each, and make ten or twelve revolutions per minute. The grinding is done wet; as soon as the ore is ground sufficiently fine it is carried off by a current of water and led into one of a pair of settling tanks, 16 ft. × 6 ft. × 3 ft deep, one of which is being filled, while the other settles during eight or ten hours. The clear water having been drawn off by a series of plug-holes, the slimes are shovelled out to dry on a platform. As soon as the ore has become thoroughly drained and half dry it is charged into the rotating barrels, the construction of which is similar to that shown in Fig. 14. The capacity of these is from 1 to 4 tons, the larger size being 6 feet long and 5 feet in diameter, while the staves are 3 inches thick.

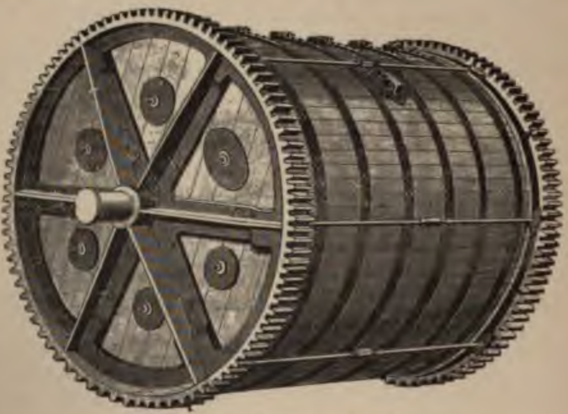

Fig. 14.—Rotating Barrel.

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* Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 638.

The solution of salt and copper sulphate is made up previously by the aid of steam, and stored in quantity; the cuprous chloride is only produced as required, in order both to avoid oxidation and to have it hot when added to the ore. Copper sulphate is first dissolved in hot water till the solution registers 20° B. and the concentrated solution filtered through salt into another vat till it will dissolve no more, the resulting saturated solution of brine, which is also nearly saturated with cupric chloride and sodium sulphate resulting from the double decomposition of the salt and copper sulphate, being stored in a third vat. As required for use this stock solution is drawn off into wooden vats containing metallic copper (old copper sheathing), where it is boiled by a current of high-pressure steam. The copper is attacked by the cupric chloride and cuprous chloride formed, which, however, does not precipitate, being held in solution by the brine. The solution is tested from time to time by dropping a pipetteful into a glass of water, when, if all the cupric chloride has been reduced, the liquid left after the white precipitate has subsided will be perfectly colourless. The solution is slightly acidulated with sulphuric acid to prevent formation of oxychloride, and used as soon as possible. The quantity of the hot solution added to each charge is ordinarily such as shall correspond to an original amount of salt equal to 5 per cent. of the weight of the ore, which on an average, for an 80-oz. ore with average gangue, is about 30 gallons per ton of 2000 lbs. This, together with the still moist ore, makes a thick mud; but ores containing much calcite require a larger quantity, or else an addition of sulphuric acid, as, without acid, the carbonate of lime decomposes some of the cuprous chloride. The barrels are turned for half an hour in order to thoroughly mix the mud and start the reactions, after which mercury (in which a small quantity of lead- or zinc-amalgam has been dissolved) is added in the proportion of twenty or twenty-five times the weight of silver contained in the ore. When the ore contains a considerable quantity of silver chloride or bromide, the lead added should be about 25 per cent. of the weight of silver present, which addition is found to reduce the loss of quicksilver from 1⅓ ozs. to ¼ oz. per ounce of silver extracted. With very rebellious ores containing proustite or pyrargyrite, zinc in the amalgam is said to give better results than lead. After the addition of the mercury the barrel is set revolving, at the rate of about four or five times per minute, for six hours; it is then filled up with water, again revolved in order to mix the contents, and the mixture turned out into a *tina* or dolly tub with wooden stirrers, where it is washed. The liquid amalgam left in the bottom of the tub is not pure, as it contains both Cu_2S (resulting from double decomposition of Cu_2Cl_2 with Ag_2S) and a hydrated cuprous oxide (produced by the action of calcium carbonate or cuprous chloride). The former impurity, together with most of the latter, is removed by stirring up the amalgam with 10 per cent. of fresh mercury in a *tina* like those shown in Figs. 1 and 2, p. 33, the stirrers of which are kept going at 16 revolutions per minute, while fresh water is run in until that left in the tub is quite clear and free from sediment. A small quantity, of cuprous oxide, retained very tenaciously by the amalgam, is removed by running off the water and adding a solution of ammonium carbonate (2 per cent. of the weight of amalgam), revolving for five hours, and again washing with water. Sometimes the amalgam contains a good deal of chemically combined copper or an excess of lead or zinc. These impurities are removed by digestion with a hot solution of cupric chloride.

The amalgam is strained and retorted in a *capellina* (*v.* Chap. VI.) giving silver, which, after melting and refining, is from 980 fine upwards. The mercury strained off is very impure, containing lead, copper, &c., and after being used five or six times will not amalgamate. It is then "quickened" by the addition of 20 grammes of dry sodium amalgam to each 100 kilos. of impure mercury.

The reactions in this process are probably the following:—

$$\begin{aligned} Cu_2Cl + Ag_2S &= 2AgCl + Cu_2S. \\ 2AgCl + 2Hg &= Hg_2Cl_2 + 2Ag. \\ Hg_2Cl_2 + Pb &= PbCl_2 + 2Hg. \end{aligned}$$

The loss of silver in tailings is not over 2 to 3 ozs. per ton on ores running 80 ozs. to the ton, an extraction of from $96\frac{1}{4}$ to $97\frac{1}{2}$ per cent., which is greater than that of any other known process on ores of a character decidedly not free milling, since they contain quantities of pyrargyrite and even proustite. The process compares very favourably with the *cazo* and *fondon* processes just described; and even with the Patio process, in which proustite is but little attacked. The fact that the Copiapó ores contain no large quantities of galena, blende, pyrites, or other base-metal sulphide, as do almost all of the Mexican ores, should, however, not be lost sight of; and it may be doubted whether—admirably as the process works on suitable ores—it would show any better results than the Patio process on ores like those of Zacatecas or Pachuca, which are full of heavy sulphides.

The cost of the process is quoted by Egleston, from Rathbone, as follows:—Crushing, 6s. 8d.; chemicals and quicksilver, 16s. 8d.; purifying, retorting, melting, and refining, 8d.; sundry expenses, 4s. 7d.; total, 28s. 7d. per ton of 2000 lbs.

The Francke-Tina Process.—This process may be considered as a modified *Fondon* process with improved appliances, which make it intermediate between the *Fondon* and the *Pan* (which will be described in the next chapter). It is the method by which the greater part of the silver production of Peru and

Bolivia is at present turned out, including that of the great Huanchaca Company, the second among the world's producers of silver and by far the greatest among those using amalgamation processes almost exclusively; hence it merits more than passing mention.

The characteristic which at once distinguishes the ores of the famous mines of Peru and Bolivia from the majority of those of Mexico is the well-nigh universal presence of rich argentiferous fahlerz (*var.* freibergite), together with proustite and pyrargyrite, as the predominating silver-bearing minerals; frequently accompanied by arsenical pyrites and cassiterite; and the comparative rarity of argentite, stephanite, and polybasite so common in Mexico. This radical difference in the quality of the ores naturally accounts for a good deal of difference in the process adopted, particularly as regards the constant necessity for *roasting* all ores except the gozzans ("pacos" or "cascajos"). It has been already observed that all minerals in which silver is the predominating constituent are much more amenable to amalgamation than those in which it is, so to speak, accidental, as, for example, *fahlerz.* Seeing that this mineral preponderates as a silver-bearing constituent of the majority of Bolivian and Peruvian sulphide ores, it follows that raw amalgamation methods would have little or no prospect of success with such ores, and that roasting must necessarily form an essential part of the process to be adopted. At all the works, therefore, where the Francke-Tina process is in use, a more or less perfect chlorodising roasting is included in the treatment. The roasting operation in use at the various works will be incidentally referred to in this chapter, but for further details and for a discussion of chlorodising roasting generally the student may consult Chapter IX.

Crushing the Ore.—At *Oruro* (Bolivia)[*] the stamps formerly in use driven by a large iron water wheel have been replaced by a battery of three No. 4 Gruson ball mills, which pulverise from 40 to 50 tons through a 25 or 30 mesh every twenty-four hours, doing more work the drier the ore is supplied to them. The screens have to be changed daily, the set of five grinding plates lasts during the crushing of 2250 tons of ore, while the side plates last about 1800 tons. The total wear and tear of the mill per ton of ore is 0·03 per cent. of its value (some £400 = 2s. 4d. per ton crushed), and each mill requires six men per twenty-four hours (two shifts of three men) to attend to it. The average work done is 140 lbs. crushed per H.P. hour.

At *Huanchaca* (Bolivia)[†] Gruson ball mills are also used for crushing the ore through a 50 mesh, and the output of each mill is 10 to 12 tons per twenty-four hours, or 130 lbs. per H.P. hour.

At the *Playa Blanca* (Antofogasta), or coast works of the

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[*] Basadre, *E. and M. J.*, Nov. 9, 1895.

[†] Peele, *E. and M. J.*, Mar. 25, 1893.

Huanchaca Co.,* which have a capacity of 250 to 350 metric tons per day, the ore is first crushed in four Blake crushers with 20-inch by 10-inch aperture, then dried in a gas-fired revolving drier and raised to the stamps-bins by a pipe screw-conveyor. The stamp mill consists of ten sets of ten heads each, fed by Challenge feeders; the stamps weigh 1000 lbs. each, and drop 7 inches about ninety-five times per minute in double discharge mortars. The construction and arrangement of this mill is similar to those described and figured in the next chapter. The average output of each stamp is 90 kilos. of ore per hour through a 40-mesh screen (=2·4 short tons per day). A pipe conveyor takes the fine ore from each battery to a separate bin, and a 6-feet Sturtevant fan sucks the fine dust from the mortars by means of an overhead 30-inch exhaust pipe running the length of the mill, and forces it through long canvas sacks, like those described for filtering flue-dust.†

Roasting the Ore.—This is always done in reverberatory furnaces, revolving furnaces having been tried and abandoned on account of the great loss of silver by volatilisation to which they give rise.

At *Oruro*‡ the furnaces are of sun-dried brick, lined with refractory stone, with a single hearth 10¼ feet by 8¾ feet, and no firebox. After spreading the charge of 1000 lbs. ore on the hearth, a small quantity of brushwood is burnt on the top of it so as to ignite the sulphur, which is the only fuel required. Continual rabbling, with the working door always open, exposes fresh surfaces and keeps up the heat. Each charge takes six hours to work through, and just before the end of the roasting 5 per cent. of salt is added. There are thirty-two of these furnaces, each of which requires one man to work it; they cost $100 to build, and last indefinitely with slight repairs. The percentage of chlorination, as determined by the hyposulphite test,§ is 86 to 96 per cent., but the loss by volatilisation is not given. The cost of roasting is $2.19 (9s. 2d.) per short ton.

At *Huanchaca* and at *Playa Blanca* long three-hearth reverberatory furnaces of the most approved type are in use, and a thorough oxidation (which involves reduction of silver to metal) with only partial chlorination (40 to 50 per cent. by hypo. test) is aimed at. Particulars of the dimensions of the furnaces and the work done by them are given in Chapter IX. After drawing the roasted ore, it is spread on cooling-floors to cool during twenty-four to seventy-two hours, so as to avoid further chlorination. The men are paid by the ton, and the ore from each shift is treated separately in the tinas, so as to fix the responsibility for bad roasting.

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* Anonymous, *E. and M. J.*, Dec. 28, 1895.

† *v.* Part i., Chap. v., p. 72.

‡ Basadre, *loc. cit.*

§ *v.* Chap. viii.

At *Potosi*[*] the ore is prepared for roasting in reverberatories by a preliminary roasting in lump form in kilns. It is then roasted in small double-hearth reverberatories with superposed hearths, and 8 per cent. of salt is added on the lower hearth. The total quantity put through each furnace is 2½ tons per twenty-four hours, and one man on each shift attends to two furnaces. The chief expense is for fuel, which is very scarce at that high altitude; brushwood and turf are used, and the cost for fuel alone is $7.09 per ton, labour being only $0.75. No attempt is made to get a thorough chlorination, as the tina, according to Wendt,[†] will extract 90 per cent. of the silver from an ore only chloridised to 20 per cent.

This most important point is too often misunderstood by practical mill men and lost sight of by metallurgical text-books. It seems to be a matter of wide experience that *good roasting* is much more important for amalgamation than *good chlorination*. A perfect dead roast without the use of salt leaves all the silver in the metallic condition, or in that of sulphate, both of which substances are acted upon in whatever amalgamating appliance may be employed. It has been seen (p. 57) that a plain roast without the use of salt is sufficient to give a good extraction from rebellious ores by the Patio process; the same holds good in the tina process, and according to "Playa Blanca,"[‡] "an ore may not contain a particle of AgCl and yet will amalgamate better than ore with a large percentage of chloride."

Construction of the Tina.—The *tina* is practically a *pan* with the bottom and mullers of copper or bronze instead of iron. The construction of the tinas used at Huanchaca is shown in Figs. 15 and 16, and those at Potosi in Figs. 17 and 18;[§] those used at Oruro are very similar; the newest tinas at Huanchaca, however, have a base and framework of iron. In all the Figs. A A are the wooden sides and bottoms of the tinas, 2 metres in diameter and 1·60 metres deep, made of 3-inch Oregon pine; B is the bottom, or "solera," which was formerly of copper in sections but is now always cast of bronze in one piece, ¾ inch thick and weighing 1100 kilos.; C is the central skeleton cone or cross, "cruzeta"; D represents the copper mullers, which, at Potosi, take the form of a copper plate in sections bolted to C, while at Huanchaca they formerly consisted of four copper shoes bolted to wooden arms (Fig. 16). Lately at Huanchaca these shoes have been cast in one piece with the central cone, out of an alloy composed of 93 per cent. Cu, 6 per cent. Sn, and 1 per cent. Zn, forming a casting weighing 1200 kilos.; while at the

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[*] Wendt, *Trans. A.I.M.E.*, vol. xix., p. 99; also Egleston, *op. cit.*, p. 393.

[†] *Trans. A.I.M.E.*, vol. xix., p. 102.

[‡] *E. and M. J.*, Dec. 21, 1895, p. 254.

[§] Rathbone, *Engineering*, vol. xxxiii., p. 173.

Playa Blanca works the bronze mullers have been entirely replaced by an iron muller and cone cast in one piece, thus making a compromise between the original copper "tina" and the iron pan; E is the bronze shaft which, in order to avoid wear and corrosion, is well marlined with hemp and red lead;

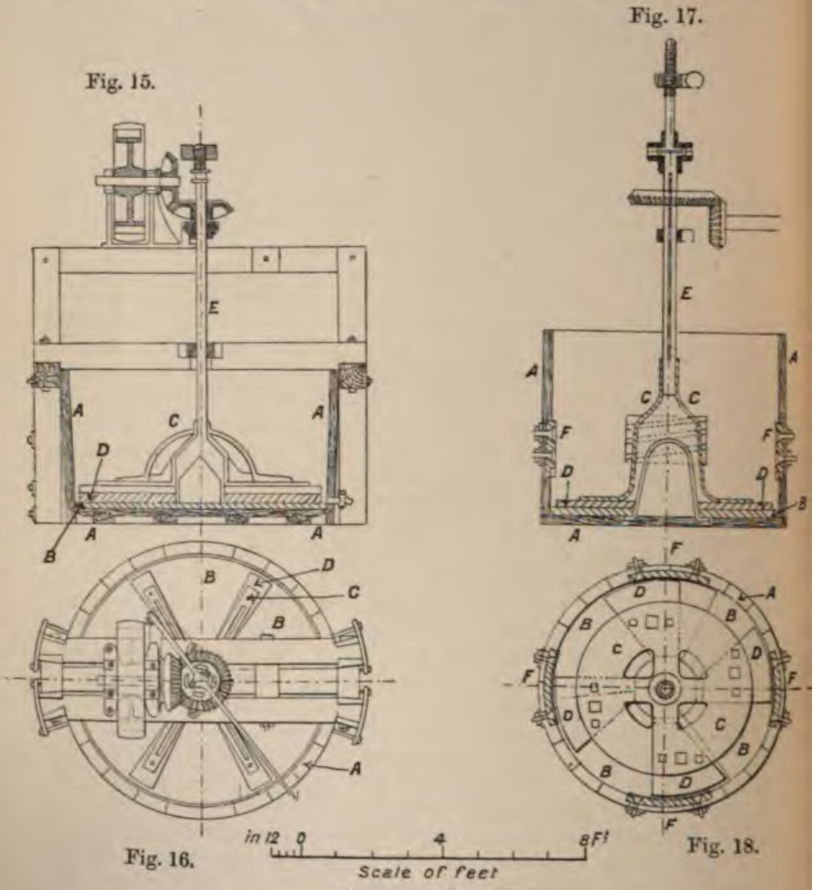

Fig. 15. Fig. 16. Fig. 17. Fig. 18.

Figs. 15 to 18.—Tina.

F shows copper plates fixed to the sides of the *tina* by means of countersunk copper bolts. These were used at Potosi, and a similar arrangement of side plates is used at Oruro, but at Huanchaca and Playa Blanca they have been discarded as unnecessary. At no place is the grinding done in the tina, as the wear and tear of copper would be prohibitive; the mullers are kept half an inch away from the soleplates, yet the loss by the reactions is so great that the average life of a bronze muller and soleplate, weighing respectively 1200 and 1100 kilos. is only three months, in which time they have been reduced by corrosion to 340 and 260 kilos. respectively, and are no longer serviceable. At Playa Blanca the life of the bronze *solera* is found to be greatly lengthened by the use of an iron *cruzeta*, which itself lasts six months and is, moreover, much cheaper in first cost—a matter which will be referred to later.

Working of the Tinas.*—At the Playa Blanca (Antofogasta) Works of the Huanchaca Company there is a battery of thirty tinas, fifteen settlers, and three agitators, besides two "clean up" tinas of smaller size; the operations as carried out at these works may be considered typical. The *tina* is charged with from 150 to 200 gallons of water by means of a hose, and the required amount of crude sea-salt (10 to 12 per cent.) added; sea water being used at Playa Blanca because it is easier to obtain, and because, incidentally, it requires a smaller addition of salt. The mullers are then started at about 45 revolutions per minute, and the ore charge added by means of hopper trucks holding 2500 kilos., which run directly over the tinas; steam is introduced through a rubber hose which reaches to 6 inches from the bottom, and then the first lot of mercury, say 10 to 16 kilos. The roasted ore always contains soluble copper salts, and hence no addition is required; further additions of mercury are made from time to time, as shown to be necessary by washing tests made in the "chua." As a rule, from four to six additions are made of 4 to 16 kilos. each, the total quantity added being reckoned at 8 kilos. for every kilo. of silver in the ore. Steam is passed during the first two hours only, and its consumption corresponds to about 2 kilos. of coal burnt per (metric) ton of ore. Amalgamation takes from four to eight hours, averaging only five to six hours. When complete the mullers are raised an inch or two, and the *tina* is discharged into a settler, making 15 revolutions per minute, the iron launder between the two having a number of depressions in it to catch most of the amalgam and mercury. The amalgam mixed with tailings is washed in one of the smaller clean-up *tinas*, and then is equivalent to silver of 980 fine; but as this is not fine enough for export it is re-fused by adding to a charge of roasted amalgam 1 to 1½ per cent. of copper sulphate and 3 to 6 per cent. of salt, thinning with mercury, heating with steam, and running hot for from six to twelve hours, which brings it up to 997 fine. It is washed in copper pans, dried, and filtered through canvas. The retorting and melting is described in Chapter VI. Each *tina* requires from 2½ to 3 H.P., or rather

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* *S. M. Q.*, vol. xiv., p. 154; also *E. and M. J.*, Sept. 14, Nov. 9, Dec. 21, and Dec 28, 1895.

more than a H.P. per ton of ore treated. The loss in mercury varies from 1 to 5 kilos. per kilo. of silver, averaging, with the all-copper tina, about one-third the weight of silver produced, while, according to "Playa Blanca,"* the loss in the new compromise tinas with iron mullers has been reduced to one of mercury for six of silver.

The following table shows slight variations in the working of the tinas at different places :—

TABLE IV.

	Oruro.	Huanchaca.	Playa Blanca.
Weight of each charge, lbs.,	8000	5500	5720
Proportion of salt used, .	12½ per cent.	10 per cent.	10 per cent.
Quantity of mercury used, lbs.,	120	120 to 160	120 to 160
Time taken in amalgamation, hours,	4 to 5	5 to 6	4 to 5
Percentage of extraction, .	80 to 85	82 to 87	90
Richness of ore treated (per ton of 2,000 lbs.), . ozs.,	80 to 100	130	75 to 90
Value of tailings (per ton of 2,000 lbs.), . . ozs.,	8 to 15	9 to 12	8 to 9
Fineness of retort bullion, .	950 to 990	990	940
Loss of mercury to 1 of silver,	...	⅓	⅙
Consumption of copper to 1 of silver, ...	...	1	0 †

The total losses of silver at Huanchaca are as follows :—‡ Transportation and grinding, 1¼ to 2 per cent. ; roasting, 3 to 5 per cent. ; amalgamation, 8 to 10 per cent. ; stealing, 0·1 per cent. ; melting, 0·6 per cent.—total, 13 to 17½ per cent.

Cost of Treatment.—The cost of the process at Oruro § is—Crushing, 4s. 9d. ; roasting, 9s. ; amalgamation, 22s. 11d. ; retorting repairs, depreciation, interest, and general expenses, 17s. 7d.—total, £2, 14s. 5d. According to the report of the Huanchaca Company for 1894, the total cost of treatment is given as £4, 18s. per ton, but this includes transportation from the mines to the reduction works on the coast and other expenses. This Company is the second largest silver producer in the world, ranking next to the Broken Hill Prop. Co. Its production for the years 1893 and 1894 was about 10,000,000 ozs. each year, but has shown a falling off since 1895.

The new modification of the Francke-tina using bronze sole

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* *E. and M. J.*, Dec. 21, 1895, p. 254.

† More copper is obtained in refining the amalgam than that lost by the "solera."

‡ Peele, *S.M.Q.*, vol. xiv., p. 154.

§ Basadre, *E. and M. J.*, Nov. 9, 1895.

plate and iron muller as described * appears to be an important innovation. The current set up between the iron and copper appears to precipitate metallic copper in the proportion of 6 per cent. of the silver, which is separated from the retorted silver by cupellation; while, curiously enough, the iron does not seem to be attacked nearly so fast as the copper in an ordinary tina. It is also claimed that the extraction of silver has been increased by the use of the compromise pan-tina and the loss of mercury diminished from one-third to one-sixth by weight of the silver present. The improved yield of silver and shortened time of amalgamation may probably be due to the electric current set up between the iron muller and the copper sole plate. The use of iron results in precipitating metallic copper and produces a poorer amalgam, which necessitates an extra refining process, but this disadvantage is much more than offset by the decreased loss of copper. The small loss of iron as compared with the previous high loss of copper is difficult to explain, and it may be that more thorough roasting, and not the mere substitution of iron for copper, is the real cause of the important results.

Reactions of the Process.—The reactions are practically identical with those which take place in the cazo and fondon processes. Any copper chloride in the roasted ore is reduced to cuprous chloride in the ordinary "tina," and ultimately to metal in the modified tina with iron cruzeta. Any silver present in the metallic condition amalgamates direct with the mercury. Unaltered silver sulphide is only partly affected, but such portion as is acted upon may be transformed partly into chloride and partly direct to metal, as shown by the equations:—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S$$
$$Ag_2S + Cu_2Cl_2 = 2Ag + CuS + CuCl_2.$$

It should be clearly borne in mind that the use of salt, though assisting the extraction, is by no means essential for the treatment of plain silver sulphide unaccompanied by the complex sulphantimonides and sulpharsenides. In some parts of Peru and Bolivia where salt is dear and sulphide copper ores plentiful, ores of silver have been treated with good results in copper "tinas" after a gentle roasting with copper pyrites alone. The reactions which take place are probably the following:—

$$Ag_2S + CuSO_4 = Ag_2SO_4 + CuS$$
$$Ag_2SO_4 + Cu = CuSO_4 + 2Ag,$$

the ultimate products being metallic silver (taken up by the mercury) and cupric sulphide, which, being in a finely-divided condition and exposed to the simultaneous action of air, water, and heat, becomes largely oxidised to sulphate.

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* "Playa Blanca," *E. and M. J.*, Dec. 21, 1895.

CHAPTER V.

THE PAN PROCESS.

THE iron pan was first applied to the amalgamation of silver ores from the Comstock Lode, Nevada, and hence the raw-pan process adapted to the treatment of ores carrying silver in the native condition, as chloride and sulphide, is called (from the name of the district where it originated) the **Washoe process.** When the ores are "refractory," containing arsenical and antimonial sulphides, and especially when they contain argentiferous fahlerz, galena or blende it is necessary to roast them with salt before they become amenable to pan treatment; this modification is sometimes known as the **Reese River process.** With the exception of the roasting operation, the appliances employed, as also the mode of operation, are substantially identical in the two processes; the ore for the Washoe process, however, is generally, though by no means invariably, crushed *wet*, while that for the Reese River process is always crushed *dry*. The Reese River process will be found described in the next chapter, while the Washoe process, and its modern development the Boss process, will be dealt with here.

The Washoe Process — Crushing.—The first step is the crushing of the ore through a mesh which varies between 24 and 80, averaging probably about 40. This is almost always done *wet*, because the capacity of a given mill is much larger when crushing with the help of a stream of water, and because the dry-crushing plant, besides being of smaller capacity, is much more complicated, requiring special drying kilns for the ore, mortars with wooden housings to prevent escape of fine dust, conveyers and exhaust fans to remove the ore as fast as pulverised, and settling chambers to collect it. When milling soft rich chloride and sulphide ores, however, it is often advantageous to crush dry in order to avoid the loss of silver in slimes and in fine scales of silver chloride and sulphide which float away on the surface of the battery water. Eissler* mentions that at White Pine (Nev.) dry-crushing mills saved 90 per cent. of the assay value of the ores, while wet-crushing mills working on the same ore could only save 80 per cent.; there can indeed be little doubt that many mills using the ordinary pan process would show a better percentage of extraction if dry crushing were employed, though it is doubtful if the increased saving would compensate for the increased cost. The slimes carried off by the water, however (as distinguished from the tailings

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* *Metallurgy of Silver*, 1891, p. 125.

thrown away or stored for re-treatment), are seldom or never systematically sampled and assayed, owing partly, no doubt, to ignorance, and partly to the reprehensible habit of making as good a "showing" as possible for the mill, quite irrespective of the real losses; and as the so-called "percentage of extraction" is generally obtained by comparing the bullion yield per ton of ore with the assay of the coarse sand "tailings," the real loss or the true value of the original ore is not known. With low-grade ores, however, the slime-losses are much less in proportion, and it is always more economical to crush wet, the greater simplicity of the plant and its increased capacity more than compensating for the loss in fine slimes. For dry crushing it is necessary to dry the ore as it comes from the mine before it can be milled. This is done by the revolving or shelf-dryers described in the next chapter.

In all well-arranged mills the ore, before reaching the stamps or other fine-crushing appliance, is passed through a stone-breaker of the *Blake* or *Gates* type.[*] These crushers should be set as fine as possible in order that the stuff leaving them may be small enough to pass a 1½-inch ring, and, preferably, even smaller, so as to relieve the stamps as much as possible and increase their capacity.

Stamps.—Some soft ores have been advantageously crushed as a preliminary to pan amalgamation by means of *rolls* and of *Huntington mills.*[†] The latter appliances, in particular, have come into use very largely in the mountainous districts of Mexico, because (although expensive for power and for wear and tear, if the ores are at all hard) they are, for equal capacity, cheaper, lighter, and simpler to erect than a stamp mill. Throughout the United States, however, and in most other places where pans are employed, *Californian revolving stamps* are the universal means of crushing employed. Five stamps work in a single mortar-box, and each such "battery" may be driven by a separate belt and pulley from a main shaft, or two such are placed side by side to form a "section" of ten heads, as shown in Fig. 19.

Space is lacking for a full description of the mechanical details of a stamp mill.[‡] There is no material difference between the stamp mills employed for crushing gold ores and those used for silver ores, except that the former invariably discharge at the front only, whereas in silver mills the principle of double discharge can be adopted, with the advantage of increased capacity,

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[*] For descriptions of these machines the student is referred to the volume on the *Metallurgy of Gold* in this series.

[†] *Ibid.*

[‡] This may be found in Rose, *Metallurgy of Gold*, 1894, pp. 99-113; Egleston, *Metallurgy of Gold, Silver, and Mercury in the U.S.*, vol. i., pp. 153-177.

as, even with wet-crushing mills, inside amalgamation is never resorted to unless the ores contain much free gold as well as silver.

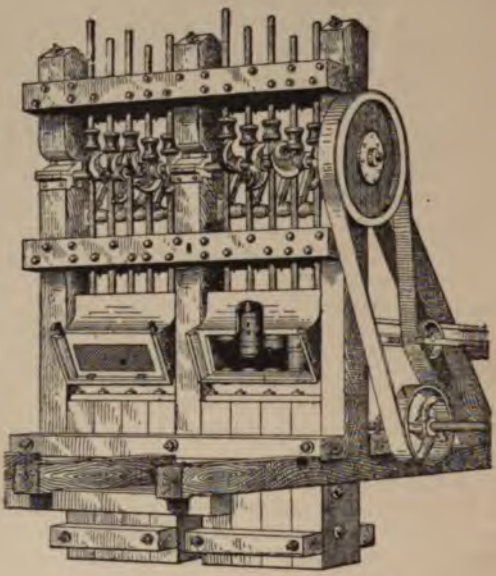
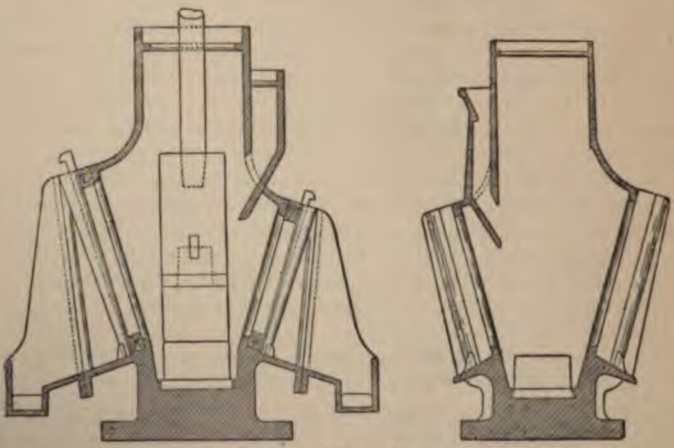


Fig. 19.—Stamp Mill.



Figs. 20 and 21.—Mortar.

There is considerable diversity in the mortars employed. Fig. 20 shows a double-discharge mortar adapted for wet crushing, and Fig. 21 one of a slightly different pattern used for dry crushing. Details of an individual stamp are shown in Figs. 22 to 26. The *stem* (not figured) is a plain rod of best wrought iron, $2\frac{3}{4}$ to $3\frac{1}{2}$ inches thick, according to the weight of the stamp, and tapered at the ends, which is wedged into the top of the *head* (Fig. 23) by means of a piece of canvas or leather, or by means of thin wooden wedges. To it is fixed the *tappet* (which is now usually made of cast steel), Fig. 22, by means of a wrought-iron gib which is pressed against the stem by two (sometimes three) steel wedges. The *shoe* (Fig. 24), or actual wearing part of the stamp, may be made (as formerly) of white cast iron or (as is more usual) of forged, cast, or chrome steel; it is wedged into the cast-iron "head" by tying thin strips of pine wood round its upper tapered portion and letting the head fall on it once or twice, which jams it tightly on. The *die* (Fig. 25), of white iron, forged or cast steel, upon which the stamp falls is circular in its upper wearing portion, but may be square, hexagonal, or octagonal below so as to better fit into the bottom of the mortar. The stamp is raised by means of a *cam* which engages with the "tappet." The most usual form of cam is keyed on to the cam-shaft by means of a keyway cut in the latter as well as in each cam; but the cutting of long keyways is an expensive job, and the replacement of a broken cam, requiring as it does a keyway to be cut in the new one and the knocking out of all the keys on the shaft, often causes hours of delay. The "Blanton" cam shown in Fig. 26 is fixed to the shaft by means of the taper bushing figured, which is jammed tight by the revolution of the

Figs. 22 to 26.—Details of Stamp and Cam.

cam-shaft and loosened when required by a gentle tap on the back of the cam. The bushing is fixed on the shaft by means of two little pins, which fit into holes in the shaft in the proper positions. The proper curve for the cam surface (in order to secure uniform velocity in raising the stamp, and, therefore, uniform wear and tear of the surfaces in contact) is the involute of a circle whose radius is the distance between the centre of the cam-shaft and that of the stamp stem. Cams are sometimes made of grey cast iron, but now more usually of cast steel. The friction of the cam on the tappet rotates the stamp as it rises, but this rotary motion ceases long before the shoe can reach the die in falling, so that the "grinding action" of the former on the latter, which some writers on the Californian stamp have claimed for it, is a myth. The rotation of the stamp is, however, essential, for it makes the contact surfaces wear evenly. The *jacks* or *fingers* for holding up each stamp when required are shown behind the cams in Fig. 19. The wooden *guides* for the stamp stems are now frequently made sectional for facility of adjustment. The *screens* used in silver mills are generally of brass wire cloth, for with these nearly double the area of discharge afforded by the punched or slot screens for any given mesh can be obtained. It is readily proved by experiment that crushed pulp which has already passed through the screens once takes nearly as long to go through a second time when fed back into the mortar, whence it may be inferred that the crushing capacity of a stamp-battery is always in excess of its discharging capacity. This is the argument in favour of double discharge for silver mills in which no battery amalgamation is attempted. In wet-crushing silver mills punched slot screens of Russia iron, like those used in gold mills, are frequently seen.

The ore is sometimes fed into the mortars by hand, in which case the feeders only work eight-hour shifts; but more generally by means of self-feeders. One of the best of these is the Hendy "Challenge," shown in Fig. 27. Whether the feeding be done by hand or automatically it is important to keep the layer of ore between the shoes and dies as thin as possible—not over 2 inches. This largely increases the crushing capacity without increasing the wear and tear, which is, in fact, frequently diminished. The wear and tear of shoes and dies, other things being equal, depends upon the hardness of the rock; with soft rock a set of shoes may last for many months, while on hard quartz they will be worn out in three to four weeks. The average wear of hard white cast-iron shoes may be reckoned at 1 to 1½ lbs. per ton of ore crushed, that of dies being usually much less, say, 10 ozs. to 1 lb. per ton of ore.

Power Required, &c.—The power required per head of stamps varies according to their weight, the number of drops per minute, and the height of drop. The weight of the whole stamp in silver mills varies from 650 up to 1050 lbs., but the most usual weight is 750 to 850 lbs., which drop from 8 to 9 inches, averaging 90 drops per minute. Supposing 850-lb. stamps drop 9 inches, and make 90 drops per minute, the theoretical H.P. required for a 20-head mill will be:—

$$\frac{20 \times 850 \times \cdot 75 \times 90}{33,000} = 37\cdot 8 \text{ H.P.}$$

Allowing 33 per cent. for friction, &c., about 50 H.P. will be required for crushing alone, or $2\frac{1}{2}$ H.P. per stamp, besides what is required for the stonebreaker.

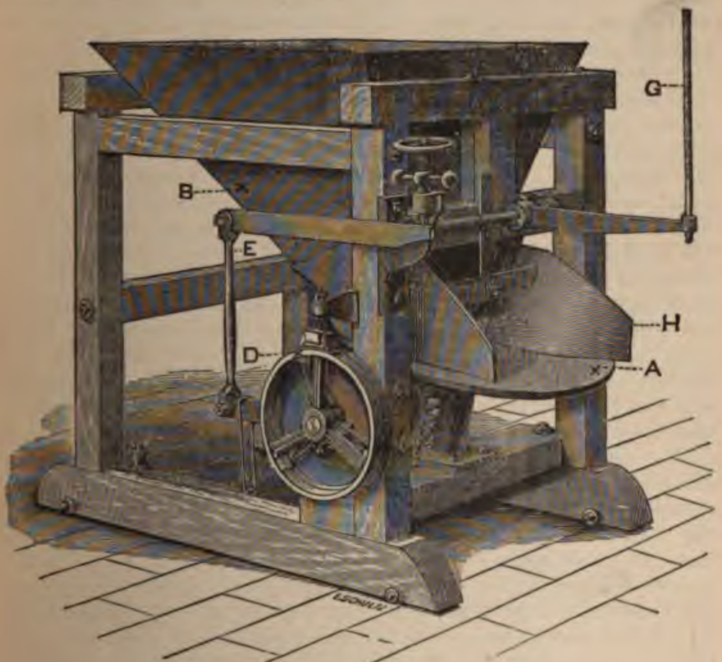


Fig. 27.—Challenge Feeder.

In crushing dry it is found advantageous to use a drop not exceeding 8 inches, and to run as fast as possible (the practical limit being reached at 96 to 100 drops per minute) so as to keep the powder under the stamps always in motion and increase the frequency of the puffs of air which serve to carry it through the screens. In crushing wet it is the splashing of the water whic carries the crushed pulp through the screens; the quantity water required is about 60 imperial gallons per stamp per hour, but frequently a much larger quantity is used.

Handling the Crushed Ore.—In dry crushing the ore dust is generally carried to bins by means of an endless belt or pipe conveyor, while the finest particles are exhausted into settling chambers by means of a fan. The pans are charged by means of a truck which runs under the hopper bottom of the settling chamber bins, and is tipped direct into the pan, already partly filled with hot water, and set in motion. In wet crushing the stream of "pulp" is received in a series of pits or tanks arranged in front of the battery, through several of which it runs so as to deposit the greater part of its solid contents. It is then led outside the building to deposit the finer slimes in large settling pits or dams, the sediment from which is occasionally removed to be worked up along with the "sand" portion of the crushed ore, or separately. On the Comstock, where the mines are controlled by milling companies (whose aim is rather to get as much as possible for themselves than the best possible returns from the ores), the "slimes" are considered a perquisite of the mill; hence they frequently amount to 10 per cent. by weight of the original ore, and are relatively much richer in metal. In most localities, however, an attempt is made to settle the slimes as thoroughly as possible, and to work them up in the pans together with the coarser pulp. Another way of diminishing the slime loss is to pump the water from the last settling tank back to a storage tank and use it over and over again in the battery and pans instead of clear water; this, while not actually resulting in a smaller production of slimes, considerably reduces the loss of silver in them.

As soon as each tank has been shut off and "settled," the remaining water is drawn off by a series of plugs, or by pumping, and the pulp baled and shovelled out on to a platform above the pans to drain, being then shovelled into the pans as required. A much more convenient and economical way of charging the pans is that described by Tatum,* who uses a portable steam-jet pump with flexible steam pipe, suction, and delivery connections, which is moved from tank to tank as required. With 1¼-inch pipe for steam supply, and 4-inch hose for suction and delivery connections, this pump will suck up in three minutes 3333 lbs. of pulp (equal to about 2000 lbs. of solid ore) from one of the settling tanks, charge it into a pan and heat it in the process up to about 110° F., thus saving time and steam afterwards.

In the pan the charge is ground with mercury and "chemicals" for four to six hours, and then passes to a "settler," in which the amalgam and surplus quicksilver separate from the pulp.

Construction of Pans.—Numerous forms of pans have been patented, and many of these have been figured and described in

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* *E. and M. J.*, Dec. 14, 1895.

books on the metallurgy of silver.[*] The oldest is the flat-bottomed *Wheeler* pan, which has been frequently figured (*v.* footnote) and is still used to some extent. Later, conical pans were adopted, which, it was believed, would require less power, but as their capacity is smaller, and as their wearing parts are more difficult to replace, they have now almost entirely gone out of use. All the conical pans, and some of those with flat bottoms, have the bottoms steam-jacketed, so as to utilise the exhaust steam from the engine for heating the pulp, but this introduces an additional complication which is an offset to the apparent saving, hence, in most cases, steam for heating is introduced into the pulp direct from the boilers. Exhaust steam cannot be used in the pulp, because the grease in it would be fatal to amalgamation. In some mills the pulp is heated by boiler steam and the temperature then kept up by exhaust steam in false-bottomed pans; this arrangement, however (though apparently a very good one), is not common. Most of the early pans had iron sides; most, if not all, of the modern ones have an iron bottom with a flange reaching above the level of the muller; the sides are of wood, which is not only cheaper in first cost but obviates loss by corrosion.

Some of the more modern pans are shown in Figs. 28 to 30, the same lettering being employed throughout to facilitate reference. Fig. 28 [†] shows the *Boss Combination* pan, which is a modification of that designed by Patton, and may be taken as typical; the bottom and flanges (to hold the 3-inch wooden staves forming the sides) are cast in one piece: *a* is the shaft rotated by bevel spur wheels underneath, *b* is the "muller-nut," into which works the screw and hand wheel, *c*, by means of which the muller is lowered on to the shoes for grinding or raised for mixing, as required, the lower hand wheel serving as a jam-nut to keep it fixed in any position. Bolted to the muller-nut is the "driver," *d*, to which the "muller," *e*, is affixed by means of stots and catches. The "shoes," *f*, are fixed to the muller, *e*, by dovetail projections and sockets, their own revolution keeping them in position, while they are readily loosened by turning the muller the other way. The sectional "dies," *g*, are fixed to the bottom of the pan in a similar way. The contents of the pan are discharged through the aperture, *i*, which is closed by a wooden plug.

The *Howell* pan, Fig. 30, is similar to that above described, except that the driver and muller are bolted together, and that the muller is thicker in proportion. The peculiarity of this pan consists in the curved "mould-boards," an idea of Stevenson's for improving the pulp currents. The natural current of the

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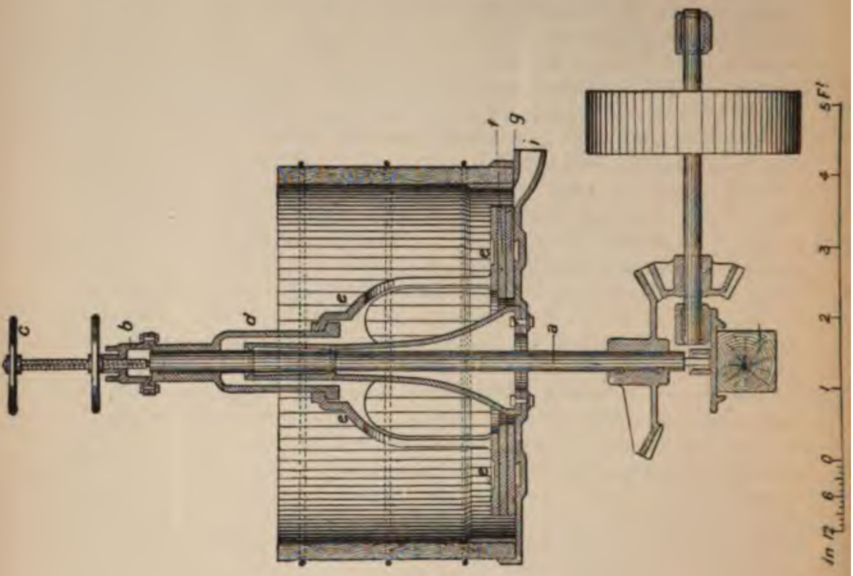
[*] *v.* Egleston, *op. cit.*, vol. i., pp. 368-379; Eissler, *Metallurgy of Silver*, pp. 64-77; Phillips, *Elements of Metallurgy*, 1891, pp. 763-769, &c.

[†] Taken from Fraser & Chalmers' catalogue.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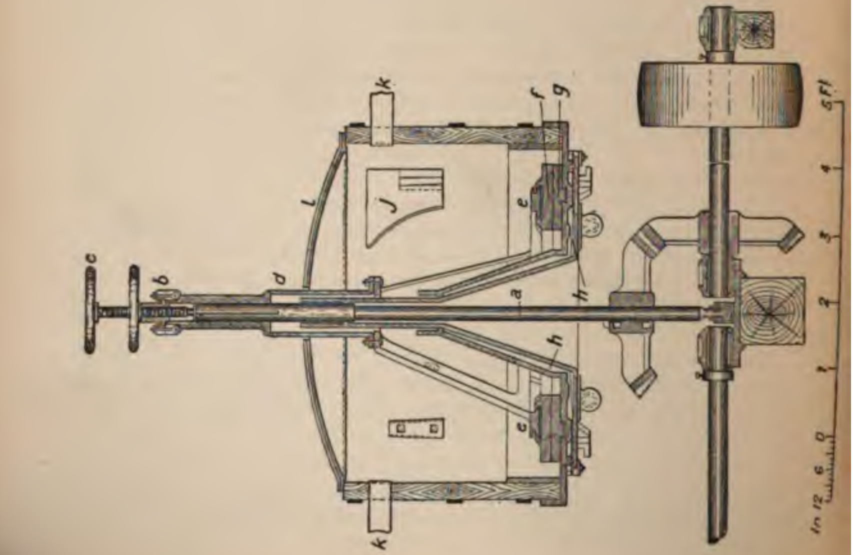
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ulp in a pan is down through the openings of the muller (which generally of tripod form), out under the shoes, up round the des of the pan and down again through the centre, but in

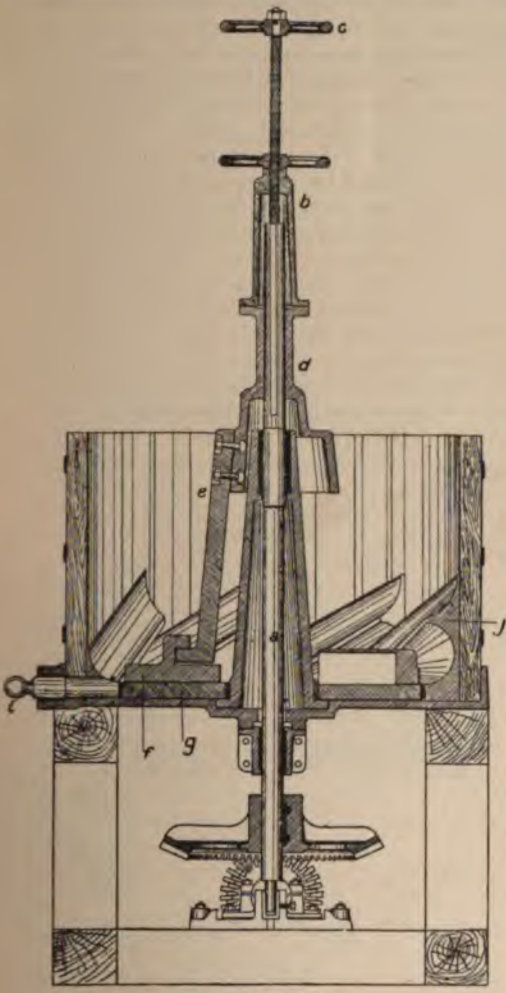

Fig. 30.—Howell Pan.

ordinary pans only a portion of the pulp takes this regular course. The object of the curved cast-iron "mould-boards" is to increase the strength of the upward current back to the centre and so increase the grinding effect; this, while lessening the area of shoe and die in contact, reduces the friction and the H.P. required to drive the pan, without diminishing the capacity.

The *Boss* pan, shown in Fig. 28, is steam-jacketed, the jacket taking the form of a false bottom extending upward round the central cone, as shown at *h*. This pan is provided with "wings," *j*, near the top to turn back the current of pulp towards the centre. Instead of being intermittent in its action like the others this pan is designed for continuous working, the pulp entering and overflowing through the pipes, *k*, and as it is not charged from the top a cover is adapted, which serves to retain the heat imparted by steam in the first pans of the series. The Boss form of pan is a good one, quite irrespective of its continuous mode of working, which will be described at length subsequently.

From the pan the pulp is drawn into a "settler," which may be considered as an extra large pan with wooden shoes and no dies. The older forms of settler, with plough-shaped shoes somewhat resembling the "clean-up" pan, Fig. 32, and often figured in metallurgical treatises, are still in use at a few mills, but most of the newer settlers are like that shown in Fig. 31,* with a continuons ring of wooden shoes, *a*. In this apparatus, which is generally 8 feet in diameter as against 5 feet for the pan, the pulp is thinned with water, and the mullers being revolved slowly (10 to 20 revolutions per minute) the globules of mercury and amalgam suspended in the pulp gradually

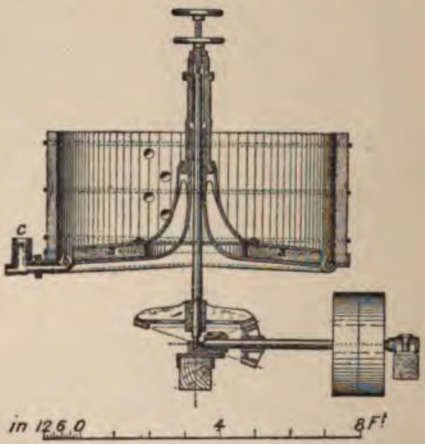

Fig. 31.—Settler.

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* From Fraser & Chalmers' catalogue.

coalesce and form a pool in the annular gutter, *b*, round the circumference; this is drawn off at intervals from the mercury cup, *c*, or is discharged continuously as it accumulates by means of goose-necks or short syphons.

In the older mills the pulp from several ordinary settlers was discharged into a single large wooden dolly-tub, 10 or 12 feet in diameter, in which a revolving cross carrying vertical arms kept the pulp in motion and allowed part of the floured quicksilver still remaining in it to settle out, together with the coarser heavier portions of the metallic sulphides. These so-called "agitators" are still in use to some extent, but in modern silver mills this device is generally replaced, or, at all events, supplemented by appliances specially suited to catching fine floured quicksilver (as copper plates) and by others for saving the sulphides, such as blanket sluices, Frue vanners, and other concentrating plant.

Working the Pan Charge.—The weight of a pan charge varies, according to the size of the pan, between 2000 and 4000 lbs., but for the ordinary 5-foot pan the charge will be from 2600 to 3600 lbs. Sufficient water is run in to the pan to form a thick pulp when the ore is added; the mullers are then set in rotation an inch or two above the dies before adding the ore, so as to prevent "packing," the usual speed being from 70 to 90 revolutions per minute. As soon as the ore charge is all in, the mullers are lowered till they all but touch the dies, and steam is at the same time introduced into the charge until its temperature reaches 160° to 180° F., or very close to the boiling point. The consistency of the pulp increases as the grinding proceeds, in spite of the condensed water from the steam jet, and it is considered important to have it quite thick, notwithstanding the greater absorption of power in rotating the mullers, because larger globules of mercury can then be carried in suspension, which, from their lessened tendency to coalesce, have a better chance of taking up the silver.* The right consistency is shown when a piece of wood dipped into the pan comes out covered with thickish mud, in which are disseminated minute globules of mercury. The grinding process usually takes from one to one and a-half hours, unless the ores be very easily worked or very fine screens have been used in the battery, in which case it may be dispensed with altogether. The usual practice now is to stamp at once to the required degree of fineness (as determined by experiment for each particular ore), and to dispense with the grinding in the pans, as in this way the same quantity of ore

* This point has been already referred to in connection with the Patio process. Another reason why thick pulp is preferred in the pan process is that in a given time larger quantities of material can be treated with the same plant and for practically the same expense, except that a little more power is required. See Hodges, *Trans. A.I.M.E.*, vol. xix., p. 238.

can be treated with a smaller number of pans, while the bullion produced is cleaner and the loss of mercury smaller.

After the grinding is finished the shoes are raised about ½ inch off the dies and mercury is added—best by pouring it through a fine strainer or squeezing through canvas. The proportion used varies within wide limits, and more in accordance with the fancy of the millman than with the richness of the ore. At various mills the quantity added varies between 150 and 350 lbs. to each pan, or from 180 to 300 lbs. per ton of ore; 300 lbs. to the charge or 200 lbs. to the ton of ore is, perhaps, an average.

Use of Chemicals.—The "chemicals" used besides mercury chiefly consist of *salt* and *copper sulphate;* if refractory sulphide ores are under treatment these substances may be advantageously added at the commencement of the grinding process so as to accelerate the reactions. In the case of some "free milling" chloride ores no additions of chemicals are made, but the use of salt has the effect of shortening the process, while in all the more refractory ores the yield is increased by adding both salt and copper sulphate. With special ores other additions are sometimes made; thus with ores containing oxide or carbonate of copper *sulphuric acid*, in the proportion of 1 or 2 lbs. to the ton, may advantageously replace part or all the copper sulphate; *lime*, in the proportion of 1 to 1½ lbs. per ton, is frequently employed with ores containing partially oxidised pyrites. *Iron borings*, in all quantities up to 20 lbs. per ton of ore, are a frequent addition to such ores as corrode the pans rapidly; *zinc shavings* are employed in the Ontario Mill in the proportion of 1 lb. per charge, partly with the object of setting up local couples with the precipitated copper (for which purpose, however, they cannot be much more efficacious than an equal amount of finely-divided iron, say in the condition of filings), but chiefly, no doubt, with the idea of keeping the precipitated copper out of the amalgam.[*] Other fanciful additions have been sometimes made, such as *potassium cyanide* (of which as much as ½ lb. per ton was used at the Black Pine Mill, Montana), *nitre*, *lye*, &c., but it is difficult to see what purpose they can serve, except that of somewhat quickening the mercury and so diminishing the loss by flouring. Practically speaking, *salt* and *bluestone* are the reagents employed in the pan, as in other amalgamation processes, but there is no general rule as to the quantities, which vary in the case of salt from 1 lb. up to 44 lbs., and in that of bluestone from ¼ lb. up to 18 lbs. per ton of ore. On the Comstock the quantity of salt varies from 2 lbs. to 16 lbs., and that of bluestone from 3 to 8 lbs. The larger amounts of both substances are required for the more refractory ores, but with such large quantities the amalgam becomes very base, carrying as much copper as silver. Some plumbiferous ores yield an amalgam

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[*] See Stetefeldt's experiments, *Trans. A.I.M.E.*, vol. xiii., p. 69.

very rich in lead, as much as 60 or even 80 per cent. in some cases. Generally speaking, the baser the amalgam the larger is the percentage of silver extracted, as the presence of a large amount of amalgamated copper is very effective in reducing from its combinations the silver in the pulp.

The time required for amalgamation is from four to six hours. In some mills, using chloride ores, the charges are completely worked off in four hours without grinding; in others, using refractory ores, the total time for each charge runs up to six or eight hours, of which, perhaps, four hours will be required for grinding.

The consumption of iron in the pan is considerable, part of the loss being mechanically worn off the shoes and dies in grinding, part being due to corrosion through the action of the copper sulphate and of metallic chlorides in the ore. The average loss varies from 3 to 7 lbs., making (with that from the stamps) a total loss of from 5 to 10 lbs. per ton of ore treated, the higher figures referring to mills on the Comstock. This iron plays an important part in the reactions of the process, as will be seen hereafter.

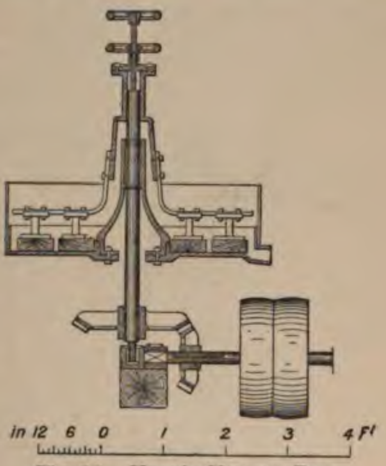

Fig. 32.—Knox's Clean-up Pan.

A small part of the iron finds its way into a peculiar hard amalgam, which settles in all the crevices of the shoes and dies and of the bottoms of the pans to the amount of 20 to 70 lbs. each pan, and which is scraped out when each pan is "cleaned up" at intervals of two to four weeks. This is collected till there is sufficient to form a charge for the Knox *clean-up pan*, shown in Fig. 32. In this pan it is worked up for several hours together with hot water (sometimes also acid and often salt) and a large excess of mercury. By working the amalgam in this way the iron and heavy sulphides are gradually floated to the top, where they can be run off with the water or skimmed off before straining out the excess mercury.

Generally the whole contents of each pan are discharged into a settler, where they are worked with water for half the time spent in the pan, thus making one settler serve two pans alternately. The speed of the settler must be regulated by the fineness of the ore and the amount of heavy sulphides it contains, for, if driven too fast, an unusual amount of floured quicksilver will be carried away in the tailings, while, if driven too slow, some of the sulphides will settle to the bottom and "pack" there. When sufficiently settled, the plugs are removed successively, beginning at the top, while a stream of clear water is allowed to flow through. Some inches of heavy sand always remain with the mercury at the bottom, but this is easily taken up by the next charge, and, if care be exercised, need not accumulate to any extent. A good deal of impure amalgam collects at the bottom of each settler, and the weekly clean-up yields, with average ores, 300 to 400 lbs., which is cleaned in the Knox pan like the hard amalgam from the pans. Most of the amalgam, however, is discharged with the excess of mercury by the goosenecks which lead from the mercury cups of the settlers into the strainers.

Clean Up, &c.—The fluid amalgam from the settlers is strained through canvas bags which are hung in a locked sheet-iron box called an "amalgam safe." One form of this, with a permanent overflow for the mercury as soon as the lower receptacle is full, is shown in Fig. 33. In large mills there is a row of these strainer-safes, all the mercury from which discharges into an iron tank, from which it is raised to the upper storage tank above the level of the pans. The mercury almost all drains through the pores of the canvas by its own weight, but straining

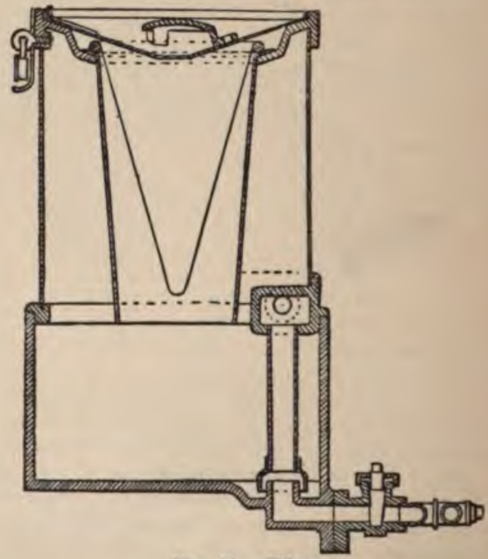

Fig. 33.—Filter.

is finished by squeezing the bag; and the pasty amalgam is taken out for retorting or for preliminary cleaning in the "clean-up" pan should it be unusually impure. In some of the Comstock mills hydraulic presses are used for squeezing out as much as possible of the excess of mercury from the amalgam; this effects a saving in the retorting, but with some base ores (especially if they contain lead) it is an advantage to have a large proportion of the mercury in use distilled, as it comes out so much cleaner and amalgamates better.

With ores which yield a very base lead-containing bullion the amalgam is often strained twice, once while hot and again after cooling. The first straining by means of a bag hung in a steam chamber removes most of the silver and copper, the lead amalgam, which while hot is perfectly fluid, running through the pores of the strainer. When cold, the lead amalgam becomes pasty and can be removed, together with the remainder of the silver and copper, and retorted separately. At *Pioche* (Nevada)[*] the hot-strained amalgam gave a bullion 550 to 680 fine in silver, the remainder being chiefly copper, whereas that from the second straining was almost all lead with a little copper and only 10 to 20 fine in silver.

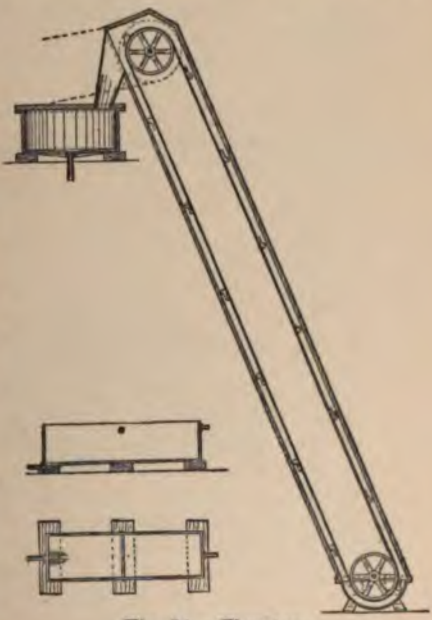

Fig. 34.—Elevator.

Handling of the Mercury.—There is always great loss in handling mercury, owing to its weight and volatility, and also to the facility with which it breaks up into minute particles. Hence it should be dealt with as much as possible automatically. One arrangement for lifting the mercury from the storage tank (into which the amalgam safes empty) to the high-level storage tank for supplying the pans is by means of an elevator (somewhat similar to those used for raising ore, but with stamped sheet-iron cups) very thoroughly housed in to prevent loss. This arrangement,

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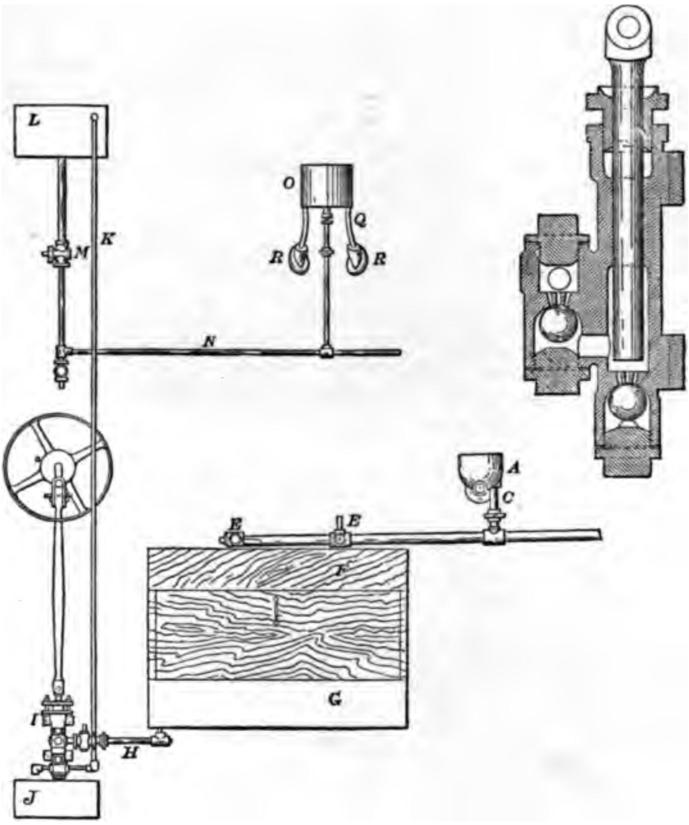
[*] Eissler, *op. cit.*, pp. 132 and 166.

shown in Fig. 34, is still in use in most small and some large mills, but in some of the latter it has been replaced by a small plunger pump with ball valves of steel and running in hydraulic packing. Limits of space render it impossible to give a detailed description of the quicksilver pump system,* but Fig. 35 shows the general arrangement, and Fig. 36 the pump itself in section.



Figs. 35 and 36.—Quicksilver Pump.

From the upper tank, L, about 4 ft. × 2 ft. × 18 in., into which the pump delivers, a ¾-inch pipe distributes the mercury to the pan reservoirs, O, each of which serves two pans, into either of which it may be emptied through the pipes, R. The reservoir is allowed to fill until the mercury reaches the required height, where it remains until one of the pans is ready for a charge.

* For which consult Egleston, *op. cit.*, pp. 399-403.

In some large mills the amalgam, instead of being carried from the strainers to the retort room, is loaded into a truck with padlocked cover running on rails. The retorting will be described in Chapter VII.

Percentage of Extraction.—Reference has been already made to the fact that the true percentage of extraction is seldom ascertainable, owing partly to bad sampling and partly to a general desire to make things look as well as possible. As a general rule, it may be said that with accurate sampling not more than 70 to 75 per cent. of the silver contents is extracted, though at Calico (Cal.), Silver Reef (Utah), Tombstone (Ariz.), and other places with rich and free-milling chloride ores the saving has risen to 85 and even 90 per cent. There is a rapid decrease, however, wherever the chlorides have become replaced to any extent by sulphides. On the Comstock the mills usually return 65 per cent. of the assay value for the Mining Companies, and retain a variable amount, estimated at from 5 to 10 per cent. more, for themselves, the tailings being afterwards worked over by other people.

The gold contents of the ores are, as a rule, much less perfectly extracted than the silver. At the silver mills of *Butte* (Montana) the percentage of gold extracted by direct amalgamation was from 50 to 60 per cent., but here the ore was roasted before amalgamation. At *Pioche* (Nev.) and *Tombstone* (Ariz.), with the ordinary process, the extraction of gold was only 40 to 50 per cent. as against 75 to 80 per cent. for silver. At *De Lamar* (Idaho), however, the extraction of gold on ores carrying about 1 oz. per ton runs as high as 70 per cent.

Loss of Mercury.—The loss of mercury in the Washoe process is chiefly *mechanical*, as pointed out by Hague,* who noted that it increases in direct proportion to the loss of iron by attrition, losses of 7 and 9½ lbs. of the latter metal per ton of ore corresponding respectively with losses of 1 lb. and 1½ lbs. of mercury per ton. The loss may vary with different ores from as little as 6 ozs. up to as much as 3 lbs. per ton, the higher figures, however, being chiefly from roast-amalgamation mills treating cupriferous ores. Part of the mercury is lost in handling, splashing, and dropping about, so much so that large quantities are usually found in the foundations of old mills; but the principal source of loss is as floured mercury which escapes with the tailings. This loss is greatly increased by grinding in the pans, so that it is preferable to crush fine in the battery and keep the pan mullers off the dies. Generally speaking, those causes which interfere with amalgamation tend also to increase the loss of mercury, for if the globules are in such a condition as not to amalgamate easily they will not readily reunite after being broken up. A fair average total loss on easily-worked ores may

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* *Report U.S. Geol. Surv. of 40th Parallel*, vol. iii., p. 292.

be taken at ½ to 1 lb. per ton, and on refractory ores 1¼ to 2 lbs. per ton.

The *chemical* loss is slight, most of the calomel formed being reduced by the excess of iron present. According to Eissler[*] some soluble sulphate of mercury is formed by direct reaction of mercury on copper sulphate, but it is difficult to believe that much mercury sulphate can exist in solution in presence of a large excess of reducing agents and of salt. The traces of mercury present in the effluent clear water from the settlers after depositing the slimes almost certainly exist in the form of calomel dissolved in excess of sodium chloride.

The loss of mercury may be greatly reduced by care in keeping the stocks of that metal in good condition, cleaning from time to time with nitric acid and keeping it "lively" by means of a little sodium amalgam or potassium cyanide.

Interference of Various Substances.—Any substance which tends to make the mercury dirty and to coat the fine globules will both interfere with amalgamation and increase the loss of mercury. Thus *grease* in any form (as in exhaust steam) is fatal to good results, while *talc*, *kaolin*, and other hydrated silicates of magnesia and alumina act similarly by coating the globules and preventing contact between them. It is essential that the pan bottom, dies, and mullers should be *clean* and not coated with a layer of graphite and iron oxide,[†] while the finely-divided iron from the batteries plays a very important part. These two reasons explain to a great extent the bad results shown by slimes as compared with sand, for, on the one hand, the particles of iron are absent in the former case, and, on the other hand, the fine mud tends to coat the mercury globules and to prevent their coming in contact with the silver.

Copper ores do not necessarily interfere with the process in any way, nor does the copper enter the amalgam unless it has first been converted into a soluble salt. When the copper is present as oxide or carbonate, sulphuric acid may be used to produce bluestone in the charge. The way in which copper enters the amalgam from its soluble salts has been already explained, and reference has been made to the fact that the more copper there is in the amalgam the better is the percentage of extraction.

Lead ores interfere by "sickening" the mercury. Under some circumstances lead ores are rapidly amalgamated, forming a pasty, readily tarnished amalgam which is very easily floured and so causes great loss. The production of low-grade lead-containing bullion from base ores at Pioche (Nev.) and other places has been referred to above, but the circumstances under which lead becomes amalgamated have not been thoroughly studied, although it is known, generally, that the higher the amount of chemicals

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[*] *Op. cit.*, p. 96.

[†] See remarks by J. K. Clark, *Trans. A.I.M.E.*, vol. xvii., p. 775.

used the greater will be the proportion of lead amalgamated. According to Austin[*] (at Tombstone, Ariz.), cerussite and galena did not seem to be affected, but the presence of wulfenite in the ore always resulted in a base lead-containing bullion being produced. Church[†] suggests that tellurides in the ore may have been the determining cause. It is certain that both cerussite and anglesite can be recovered from the pan tailings of many ores which yield no lead to quicksilver. The author would suggest that it is those ores of lead which contain $PbCl_2$ (pyromorphite, mimetesite, mendipite, &c.) which are chiefly affected by mercury and yield a lead-containing amalgam, for special experiments show that $PbCl_2$ is much more readily amalgamated than the insoluble carbonate, sulphate, or oxide. It is probable that before lead can be amalgamated it must first pass through the condition of soluble chloride, from which it is then precipitated by the iron of the pans.

Zinc ores are not amalgamated in the pan process, as might be expected from the fact that zinc is positive to iron. Blende is said to "dirty" mercury, and to some extent interferes in this way with the process.

Arsenical and *antimonial* ores are always difficult to work, for the mercury not only becomes "floured," but also "sick" and dirty, so that it will not readily amalgamate. When treating arsenical ores, the whole of the stock of mercury should be frequently cleaned with nitric acid and retorted. If the silver is combined with arsenic or antimony (*e.g.*, pyrargyrite, proustite, &c.) the ores must be roasted before pan-amalgamation is possible.

Manganese oxides froth in the pan (may this be due to escape of oxygen?), and give rise to high loss of mercury (up to even 7 lbs. per ton) and low percentage of extraction. According to Pearce, MnO_2 appears to give up oxygen, which, in a nascent condition, acts upon the mercury and forms a sub-oxide. When ores rich in MnO_2, are treated in pans the bullion is very pure, showing no trace of copper, even when as much as 100 lbs. of bluestone to the ton of ore has been added, which proves the strength of the oxidising influence.

As the effect of manganese ores is directly opposite to that of base plumbiferous and zinciferous sulphides, it is very advantageous to work the two classes of ore together, if they occur in the same neighbourhood. The best results are obtained when the mixture is made in such proportions as to yield a bullion of about 900 to 950 fine, in which case the quicksilver remains in good condition, being neither "dirtied" nor excessively "floured." Roasting is also found to minimise the bad effect of MnO_2 on amalgamation and to increase the percentage

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[*] *Trans. A.I.M.E.*, vol. xi., p. 91.

[†] *Ibid.*, vol. xv., p. 602.

of silver extracted, but it seems impossible to avoid a high loss of mercury when treating manganiferous oxidised ores alone.

Reactions of the Pan Process.—From a consideration of the fact that free-milling chloride ores will yield a very high percentage of their silver contents to mercury when treated in pans without any chemicals, it will be obvious that, besides mercury, *metallic iron* is the chief reagent in the Washoe process when treating such ores—not merely the iron castings with which the pulp comes into contact, but also the finely-divided iron from stamps and pan mullers, the total quantity of which (as we have already seen) runs from 2 to 10 lbs. per ton of ore. The action is, no doubt, direct upon the chloride, precipitating metallic silver, which is immediately taken up by the mercury, according to the equation—

$$2\text{AgCl} + \text{Fe} + n\text{Hg} = \text{FeCl}_2 + \text{Ag}_2n\text{Hg}.$$

Addition of salt greatly facilitates the reaction, principally, no doubt, on account of the solubility of silver chloride in NaCl solutions, which greatly increases the surface of attack from the particles of iron.

Addition of *copper sulphate* is found to increase the yield of silver as well as the rapidity of amalgamation, but its mode of action has been hitherto greatly misunderstood. Following Hague,[*] it has been generally supposed that the iron acts by reducing CuCl_2 to Cu_2Cl_2, which salt acts upon silver sulphide, as in the Cazo, Fondon, and similar amalgamation processes.[†] When, however, we compare the relative amounts of silver contained in the ore and of copper sulphate added, we find, from an assay of the resulting bullion, that practically the whole of the added copper has reached the metallic condition and found its way into the amalgam.[‡]

The author's experiments,[§] moreover, prove that any copper in solution, whether as sulphate or chloride, commences to be precipitated by the large excess of iron as soon as added, and that, practically speaking, within fifteen minutes, or even less, it has all reached the condition of metallic copper, which floats about in the charge more or less amalgamated with mercury. Cuprous chloride, even if formed in small proportion by the secondary action of the first precipitated metallic copper upon cupric chloride, cannot exist as such more than a few minutes, for being dissolved in salt solution it comes in contact with the

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[*] *Rep. U.S. Geol. Survey of the 40th parallel*, vol. xiii., pp. 275-293.

[†] See Egleston, *op. cit.*, p. 386; Eissler, *op. cit.*, p. 144.

[‡] Some experiments by Stetefeldt (*Trans. A.I.M.E.*, vol. xiii., p. 69) appear to contradict this, but they only prove that the addition of zinc results in keeping the reduced copper out of the amalgam, and not that the copper sulphate added was not reduced to metal, which would be incredible.

[§] See a recent paper presented to the Inst. of Min. and Metallurgy and published in their *Transactions*, vol. vii.

excess of metallic iron and is rapidly precipitated as metal, so that its opportunities of acting upon Ag_2S must be extremely limited.

Furthermore, these experiments prove that, as compared with iron, metallic copper has a far more active effect upon Ag_2S, as well as upon AgCl, which fact explains the increased yield of most ores when bluestone is employed in the pans.

Copper sulphate has the further property of driving out lead which has become amalgamated with mercury, as well as to a great extent keeping that metal out of the amalgam. In the latter case, it is in all probability first precipitated as metallic copper, which becomes amalgamated and prevents the mercury from taking up lead, just as the addition of zinc will prevent it from taking up copper. When, however, with lead-yielding ores (owing to insufficient addition of bluestone) a plumbiferous amalgam has been obtained, it may be, to a considerable extent, cleaned by digestion with a strong solution of copper sulphate, which, under these circumstances, acts directly upon the lead amalgam, forming lead sulphate.

When, therefore, bluestone is added to the pan, in addition to the reaction of *iron* direct upon silver chloride (an equation for which has been already given) the following reactions take place:—

$$\begin{aligned} CuSO_4 + 2NaCl &= CuCl_2 + Na_2SO_4 \\ CuCl_2 + Fe &= FeCl_2 + Cu \\ 2AgCl + Cu + Hg &= CuCl_2 + Ag_2Hg \end{aligned}$$

and to a small extent

$$Ag_2S + Cu + Hg = CuS + Ag_2Hg.$$

The CuS, under the combined action of water, air, and heat, is rapidly oxidised to $CuSO_4$, which then becomes available for reaction upon a fresh lot of silver compounds. When there is no more AgCl present to react upon, practically the whole of the copper remains precipitated and amalgamated with the mercury.

A consideration of the radical difference between the reactions in the patio and in the pan (hitherto lost sight of) enables us to understand the rooted aversion which skilled patio and fondo amalgamators have to the use of iron pans—an aversion, however, be it noted, which was founded originally on the debasing effect of iron upon the bullion and on the largely increased cost for bluestone, and only in a secondary degree owing to the small and indefinite lowering of the percentage of extraction which the use of iron undoubtedly does bring about.

In the Patio and Fondo processes the principal reagents (besides mercury) are $CuCl_2$ and Cu_2Cl_2. In the pan process (using the same quantities of bluestone and salt) the principal reagent, besides the iron itself, is precipitated metallic copper, which not only enters the amalgam* and lowers the grade of

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* Except in the case of oxidised manganiferous ores.

bullion produced, but is also much less active in decomposing complex sulphides than the chlorides are. On account of this difference, in the case of an ore in which the silver exists chiefly as sulphide, the tailings would be higher when worked by the pan than by the fondon, other conditions being equal.

Water Supply and H.P. Required.—Fig. 37 is a section showing the general arrangement of an ordinary Washoe mill. The number of pans required for a battery of ten stamps may be from four to eight, according to the hardness of the ore and the consequent output from the stamps. Usually six pans (and three settlers) are provided for the ten stamps, though on the Comstock and in some large mills elsewhere one pan for each two stamps is found to be an ample allowance.

A large quantity of water is required in a silver mill, less, however, being necessary with quartzose than with argillaceous ores. The following may be taken as the average:—For each stamp, 60 imperial gallons per hour; each pan, 96 gallons per hour; each settler, 54 gallons per hour; and each boiler, 6 gallons per H.P. per hour.

The skeleton specification of a twenty-stamp mill for the H.P. and water required is given in the following table, it being understood that the H.P. varies according to the amount of grinding done in the pans:—

Specification.	H.P. required.	Water required per hour.
		Galls.
1 Blake crusher, 10 × 7 inches, ...	6	...
4 Ore-feeders (Challenge), ...	...	...
20 Stamps, 900 lbs., 90 drops 8 inches, .	33	1200
12 Pans, 5 feet diameter, ...	24-50	1152
6 Settlers, 8 feet diameter, ...	18	324
Friction, say, ...	13	...
Boilers, ...	...	507-520
	94-130	3180-3396

It is usual to allow about 50 per cent. excess on the H.P. above shown.

If water be scarce the whole of the tailings stream escaping from the mill is run into a large tailings reservoir, and the water pumped back and used over again. In this case the loss by evaporation and leakage will amount to about 25 per cent.

Such a mill will treat from 35 to 45 tons of 2240 lbs. per day of twenty-four hours, according to the nature of the ore. Per ton of ore treated the H.P. required will be from 2½ to 3, and the water required from 1800 to 2100 imperial gallons, or, say, m eight to nine times the weight of the ore.

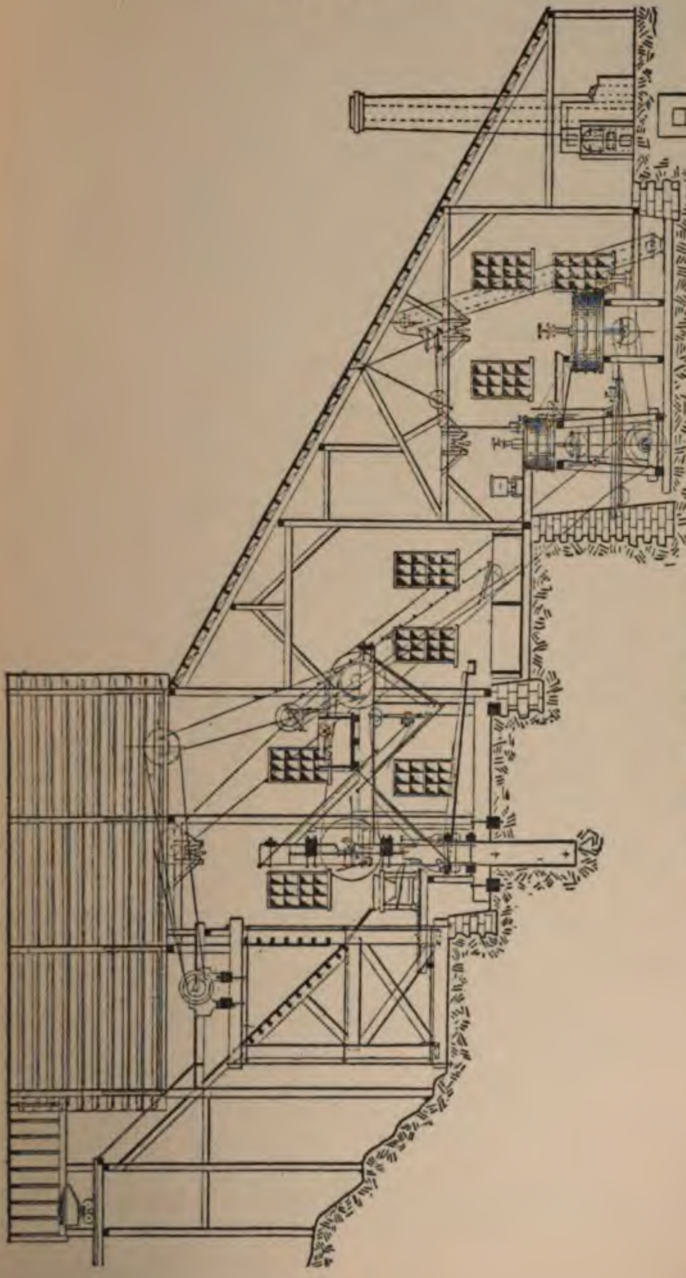

Fig. 37.—Washoe Mill General Arrangement.

TABLE V.—

	California Mill, Virginia City, Nevada.	Brunswick Mill, Nevada.	Mineral Hill, Nevada.
References,	1.	2.	3.
Crushing—	Wet.	Wet.	Dry.
Number of stamps,	80	56	15
Weight per stamp, . lbs.,	...	...	850
Drops per minute,	95	...	63
Mesh of screen,	...	...	...
Duty per stamp, . tons,	4	...	1⅛
Amalgamation—			
Number of pans,	40	26	8
Revolutions per minute,	90	88	60
Weight of pan-charge, . lbs.,	3600	...	1500
Hours charge in pan,	5	...	8
Salt used per ton, . lbs.,	6½ to 13	...	20 to 25
Bluestone used per ton, ,,	2 to 4	...	4 to 6
Loss of mercury per ton, ,,	2 to 2½	...	1½
Other chemicals per ton, ,,	...	...	...
Ore treated per day, . tons,	...	...	18
Ozs. per ton—gold,	...	...	...
,, ,, silver,	...	...	100 +
Percentage of extraction—gold,	...	...	...
,, ,, silver,	...	...	90
Fineness of bullion (bars),	937	994	920 +
Value of tailings per ton,	...	...	$16
Cost per ton—			
Labour and superintendence,	...	£0 7 2	£0 17 10
Fuel,	...	0 1 2	0 11 1
Oil and light,	...	0 0 1½	...
Mercury,	...	0 6 6½	0 8 4
Chemicals,	...	0 1 5	0 8 1
Castings and repairs,	...	0 5 5	0 4 7
Sundry expenses,	...	0 2 0	0 0 11
Total cost per ton,	...	£1 3 10	£2 10 11

References.—2. Egleston, *Met. Silver*, p. 427. 3. Eissler, *Met. Silver*, p. 1
l. *Trans. A.I.M.E.*, vol. viii., p. 558. 5. Church, *Trans. A.I.M.E.*, vol.
nderson, *E. and M. J.*, 15th Feb., 1896. 7. Report for 1894. 8. Lind

WASHOE PROCESS.

	Charleston Mills, Tombstone, Arizona, 1884.	Sheridan Mill, Mogollon Mts., New Mexico, 1893.	De Lamar Mill, De Lamar, Idaho, 1894.	Garfield Mill, Calico, California, 1886.	Gloster Mill, Montana, 1890.	Combination Mng. & Mllg. Co., Black Line, Montana, 1889.	Hda. de San Francisco, Pachuca, Mex., 1896.
	5.	6.	7.	8.	9.	10.	11.
	Wet.	Wet.	Wet.	Boss.	Boss.	Wet.	Boss.
	20	15	30	15	60	10	30
	750	1100	...	850	850	...	1050
	95	85	...	...	...	...	...
	30 to 40	25	...	...	...	40	...
	2½ to 3	2·2	4½	2·2	2·4	2·61	2·89
	...	6	...	8	...	...	...
	...	...	...	65	...	65	...
	2700	2000	...	...	...	...	...
	4 to 6	6	...	...	...	8	...
	5¼	...	...	8 to 15	...	50	44 3/10
	1¼	...	...	1 to 1½	...	$2H_2SO_4$	19 lbs.
	1¼	...	...	...	...	...	1 3/10
	...	...	...	...	...	½ KCy.	...
	55	32	...	33	...	26	86·7
	0·21	...	1·04	...	...	...	...
	33·4	17·5	10·03	...	...	22·67	32·64
	51·8	...	70·1	...	...	...	...
	77·4	69·8	90·4	80 to 90	...	47·5	87·7
-	835	...	...	850	...	800 +	...
	9 ozs.	5¼ ozs.	$7	...	...	...	4 ozs.
1½	£0 8 7	£0 8 8	£0 7 4	...	£0 4 9	£0 10 9	...
2	0 4 4½	0 3 10	0 3 7½	...	0 1 4	0 0 9¾	...
	0 0 3½	...	0 0 1½	...	...	0 0 5¼	...
5	0 2 3¼	0 3 3	0 3 6½	...	0 0 9½	0 2 0½	...
1	0 1 5½	0 3 0	0 2 0½	...	0 0 6	0 1 2¾	...
9	0 1 4½	0 2 3½	0 1 3½	...	0 0 11½	0 1 7¼	...
1½	0 0 8		0 3 10	...	...	0 1 3½	...
6	£0 19 0¼	£1 1 0½	£1 1 9½	...	£0 8 4	£0 18 2	...

., vol. xv., p. 733. 9. *E. and M. J.*, 6th Oct., 1890. 10. Goodale & Aker
I.M.E., vol. xviii., p. 249. This is a combination mill. 11. *Pr*
. P. Boss, May, 1896.

The cost of such a mill will vary from £400 to £600 per stamp erected ready for work, according to the locality, the smaller mills costing much more in proportion than the larger ones.

Cost of Working.—Table V. gives the cost of working, together with other comparative data, at several wet crushing silver mills in different parts of the world. It should be remembered that the cost of general superintendence and management is not included, and this is a very important addition to the apparent cost in a small mill. The ton to which all the figures refer is the American short ton of 2000 lbs.

The Boss Process.—The ordinary Washoe process is intermittent, inasmuch as the ore has to be collected in tanks or hoppers, and is only charged into the pans at intervals, but of late years a continuous process has been worked out by M. P. Boss, in which the pulp from the stamps runs direct through a row of pans and settlers and is discharged at the other end of the series as fast as it enters.

Plant Employed.—The particular form of pan used has been already shown in Fig. 28. The pans are covered, and each is provided with two overflow connections of 4-inch pipe, the top of which is an inch below the rim of the pan; the settlers have similar connections, but are not otherwise in any way peculiar.

Fig. 38 shows the general arrangement of the older form of plant in which the pans and settlers were on different levels. In this, A is the pipe bringing the supply of pulp direct from the battery or from the hydraulic separators, as may be preferred, which passes through the "chemical mixer" into the first two pans of the series. At B B are shown the overflows from one pan to another, made of 4-inch pipe, and at C C the similar overflows between the settlers; G G are the overflows from the last two pans, and D the pipe which takes the combined overflow into the first settler. E E are steam syphons which enable pulp to be transferred from one settler to the next but one in case it is necessary to throw out the intermediate one for repairs or clean up, and F is a similar syphon for throwing out one or more of the pans in the same way.

The chemicals, salt and bluestone, are fed into the pulp automatically at A by means of a small bucket-wheel feeder worked by a bell-crank and wire from a separate auxiliary shaft. The mercury, which overflows from the "quicksilver cups" attached to the bottom of each pan at H, is carried by a pipe to the straining box, I, after passing through which it is raised by a pump like that already figured. From the storage tank it descends to the feeding-cups, J, between each pair of pans, from which it is fed automatically as required.

As a rule, in this system the first two pans only are grinding pans, and frequently the pulp from the stamps is passed through separators so arranged that only the coarse sand passes to the grinding pans, the slimes (together with the chemicals) entering No. 3 of the series.

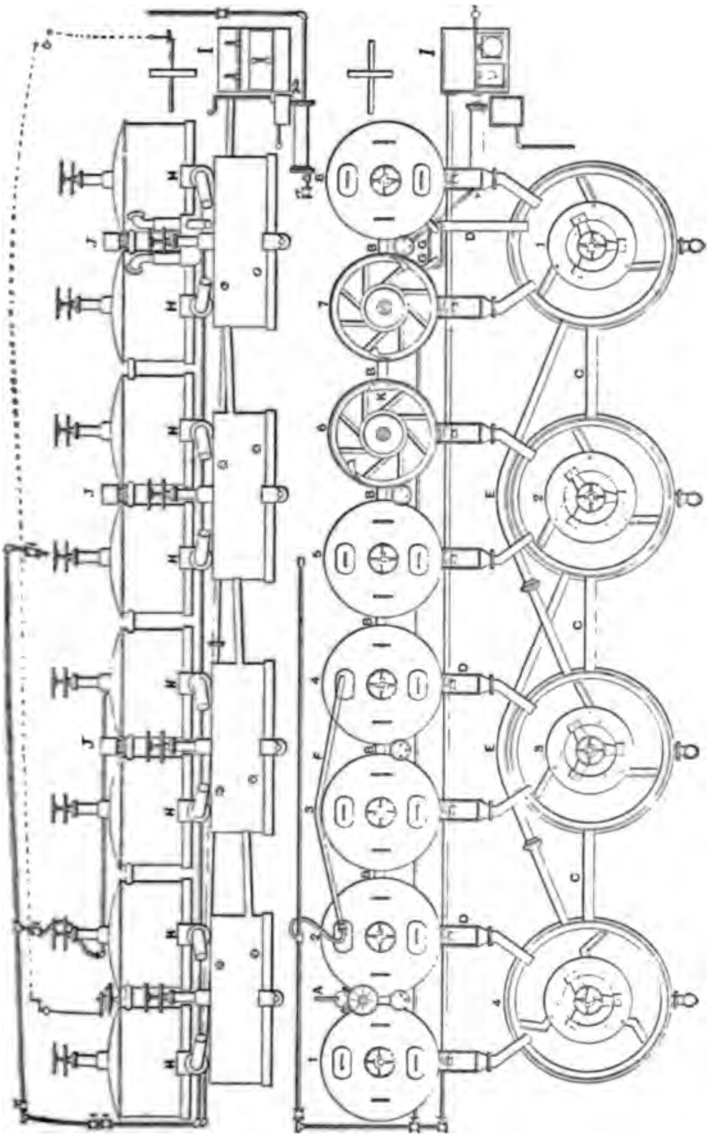

Fig. 38.—Plant of Boss Process.

A much better arrangement, employed in all the newer Boss mills, is the provision of separate flat-bottomed pans smaller than the regular amalgamating pans, running at a higher speed and constructed without a steam-bottom, whereby greater surface is secured for grinding. The pan is only 4 feet in diameter, and is provided with a muller in the form of a complete ring slotted only for a short distance from the inner edge, as is also the ring-die, so as better to admit the pulp between them. As a rule, one or two of these special grinding pans are provided for each five stamps, according to the degree of fineness to which the ore must be reduced.

One-level System.—In the newer modified plant (called the Boss one-level system) all the pans and settlers are arranged on a level and the pulp simply flows from one to the other through the entire series. Fig. 39 shows such a "one-level" plant in which the pulp from the stamps, A, passes through an upper row of special grinding pans, B, before reaching the amalgamating pans, C, which are only ten in number for thirty stamps. In a line with these are the settlers, D, the tailings of which go to Frue vanners, E, to save heavy sulphides.

One great advantage of this system is that it admits of the employment of a single main line-shaft with friction clutch gear immediately under each pan and settler, so that each machine is driven directly off the shaft without the intervention of counter-shafts and belts, enabling any individual pan or settler to be stopped and restarted in the easiest possible way.

To this latest variety of the continuous process belongs the *Garfield* Mill at Calico (Cal.) with fifteen stamps, the pulp from which passes through a series of eight 5-feet pans running at 65 revolutions, and three 8-feet settlers at 20 revolutions per minute. In the first pan the ore is ground, in the second and third mercury is added, and in the latter the chemicals—viz., 8 to 15 lbs. of salt and 1 to $1\frac{1}{2}$ lbs. of bluestone per ton. In the fifth pan a little *lime* is added to clean the mercury.

In the Boss system the quicksilver-carrying amalgam, which gradually reaches the bottom of every pan and settler and accumulates in the bowls, can be drawn off at pleasure from any of them by pulling out a plug, when it runs along an iron pipe to a central receiving tank. From here it is drawn at will into the strainers and the strained quicksilver is raised by a small chain belt elevator running in a sheet-iron housing to a storage tank, from which diverges a system of pipes supplying each pan.

In all the more recent Boss plants the chemicals are added, not to one of the pans of the amalgamating series, but in a separate "chemical mixer," which is installed between the special grinding and the ordinary amalgamating pans. This mixer may take the form either of a large settler made entirely of wood [illegible] wooden shoes and steam-bottom, or of a barrel, like that

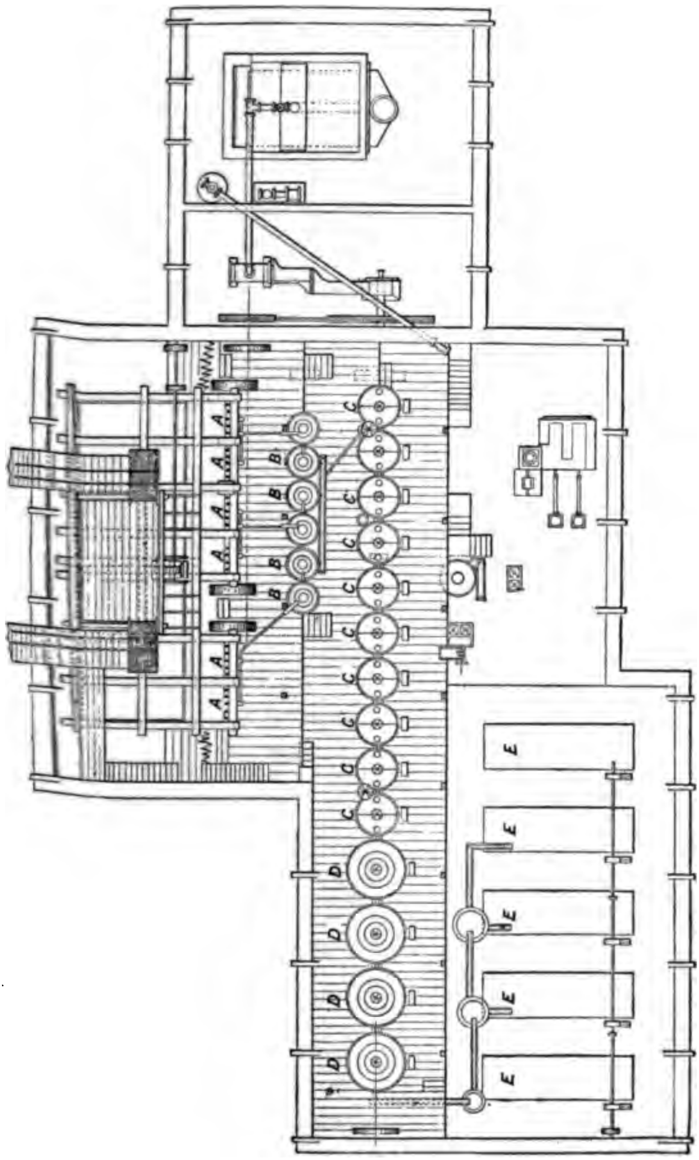

Fig. 39.—Plant of Boss Process (One-level System).

shown in Fig. 14. The former are more common in the U.S., the latter in Mexico.

Another feature of modern Boss plants, especially those treating somewhat refractory ores, is the increase in the proportion of special pans used for grinding, which relieves the stamps by permitting the employment of a coarser mesh and so enables them to be run with a smaller supply of water per ton and to deliver a thicker pulp. Thus while the plant shown in Fig. 39 has only six grinding pans for thirty stamps, the new mill at *Pachuca* contains twelve grinding pans for the same number of stamps.

The Boss System at Pachuca.—The ores of *Pachuca* are refractory, consisting mainly of argentite, fahlerz, pyrargyrite, and stephanite, with blende and other base-metal sulphides finely disseminated through a gangue, chiefly formed of quartz and hornstone.

The new mill at the *Hacienda de San Francisco* * has thirty stamps of 1050 lbs. weight each, from which the pulp passes to twelve special grinding pans making 200 revolutions per minute and thence to a steam-jacketed wooden barrel 8 ft. long × 6 ft. in diameter, similar to that shown in Fig. 14, which holds 6 or 7 ton charges and revolves ten times a minute. In this barrel the pulp and chemicals get thoroughly mixed during the hour or so that they take to pass through, and the percentage of extraction is in this way raised by an additional 5 or 6 per cent. The consumption of chemicals required to give good results on these very refractory ores is exceptionally heavy, averaging 44 lbs. of salt and 19 lbs. bluestone per ton. From the barrel the pulp passes through a series of fifteen continuous pans and three continuous settlers. Some further data with regard to the work at this mill are given in Table V.

Most of the modern pan mills built in Mexico are on the Boss system, including the new mills of the *El Bote* (Zacatecas) and *Minas Prietas* (Sonora) Companies.

Comparison of the Boss with the Ordinary Process.—The advantages of the Boss system are the following:—

(1) Doing away with double handling of sand from settling tanks into the pans, and also with the tanks themselves, which leads to considerable saving in mill buildings owing to the smaller area and fall required.

(2) Doing away with the slime-loss by passing the whole of the battery pulp through the pans.

(3) Saving of labour through automatic straining of mercury and feeding of chemicals.

(4) Facility afforded for taking accurate tailings samples.

(5) Less loss of mercury, as the thinner pulp permits of better separation.

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* *Private communication*, M. P. Boss, May, 1896.

(6) Saving of fuel, since the pulp is exclusively heated with exhaust steam.

The only disadvantages are:—

(1) Less perfect contact of flaky and finely-comminuted portions of the ore with mercury, owing to the thinner pulp which is unable to carry quite so many globules of mercury in suspension.

(2) Less facility for varying the treatment of the coarse and fine particles of the ore-pulp—*e.g.*, by giving the slimes more time or more chemicals.

The advantages, however, will in most cases far outweigh the disadvantages, and the latter can be minimised by the use of a rotating barrel between the stamps and the pans, or by the use of two barrels, one for sand and one for slimes.

CHAPTER VI.

ROAST AMALGAMATION PROCESSES IN PANS AND BARRELS.

Attention has been already called to the fact that complex sulphide ores of silver, especially the sulphantimonides and sulpharsenides, cannot be treated in pans without previous roasting. Simple roasting is frequently sufficient to bring the silver into an amalgamable condition, but the common practice is to roast with salt, by which means the silver in the roasted ore is amalgamated much more perfectly, though at the cost of a somewhat heavy volatilisation loss, varying from 2 to 20 per cent., but which, not being easily determined, is frequently ignored altogether. So widespread is this ignorance, even among practical millmen, that some writers absolutely deny the existence of any volatilisation loss of silver in roasting, Eissler,* for example, denying that there is any loss in roasting in the Stetefeldt furnace. Crude experiments are often quoted as proving this fact, but in reality they merely prove how bad was the sampling. The matter is discussed in detail in Chapter IX., where also descriptions will be found of the appliances used in chloridising roasting.

Drying.—Ores before being roasted must be crushed dry, and in order to permit of this being done they must be thoroughly dried as a preliminary, even 1 per cent. of moisture being very detrimental and greatly reducing the capacity of the battery.

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* *Metallurgy of Silver*, 2nd ed., 1891, pp. 161 and 184.

Formerly, long drying floors, composed of iron plates resting on flues and heated by the waste gases from the roasting furnaces, supplemented by separate fireplaces, were employed; but as these exercised a bad influence on the health of the workmen, besides being costly and inefficient, they have been generally replaced by *revolving dryers* or by *shelf-drying kilns*.

The *revolving dryer* is a simple wrought-iron cylinder, from 18 to 20 feet long by 3 feet in diameter at the upper and 4 feet at the lower end; it is generally similar to the Oxland and Hocking* and Howell † roasting furnaces, but without the brick lining, and is set with its axis horizontal. The capacity of such a dryer is from 30 to 40 tons per day; any automatic feeder may be used with it. Revolving dryers are in use at the *Marsac* Mill, fired with gas from a Taylor "producer" burning coal. The consumption of coal is 86·63 lbs. per ton of ore, which is 4·3 per cent., or about one-fifth more than the consumption of the shelf-dryer described below. Revolving gas-fired dryers are also in use at the works of the *Huanchaca* Co. (Bol.), at the *Granite Mountain* Mill (Mont.), at the *Ontario* (Utah), and many others.

The *Stetefeldt shelf-dryer* ‡ resembles in principle the Hasenclever roasting furnace, and is shown in transverse section in Fig. 40. Figs. 41 and 42 show in section and in plan respectively one-half of a double kiln of this pattern, and Fig. 43 shows a detail of the shelves, which are of cast-iron as the heat is never allowed to rise so high as to warp them. With this object also the kiln is not fired direct from the bottom, but the gases from the fireplaces, F, rise and enter the kiln at G, just below the top row of shelves, which is thus protected from the heat by the layer of cold wet ore upon it. The inclined shelves rest upon each other, leaving openings through which the ore can slide. The thickness of the layer of ore upon the shelves is regulated by the width of these slits and by the inclination of the shelves, which, in practice, are adjusted as nearly as possible to the natural slope of the material, on the average about 37°. The zig-zag column of ore remains stationary until a portion of roasted charge is removed from the bottom shelf, when the whole column moves down to supply its place, and the top shelf is automatically charged again by means of a hopper set above.

This form of dryer is in use at the *Lexington* Mill (Mont.), where there are two double dryers for ore, having a daily capacity of 25 tons of ore each, with a consumption of 1 cord of wood; and one single dryer for salt, with a daily capacity of 6 to 8 tons, consuming ½ cord of wood. These dryers are also in use at the Holden § Mill (Aspen, Colo.), where they are fired by

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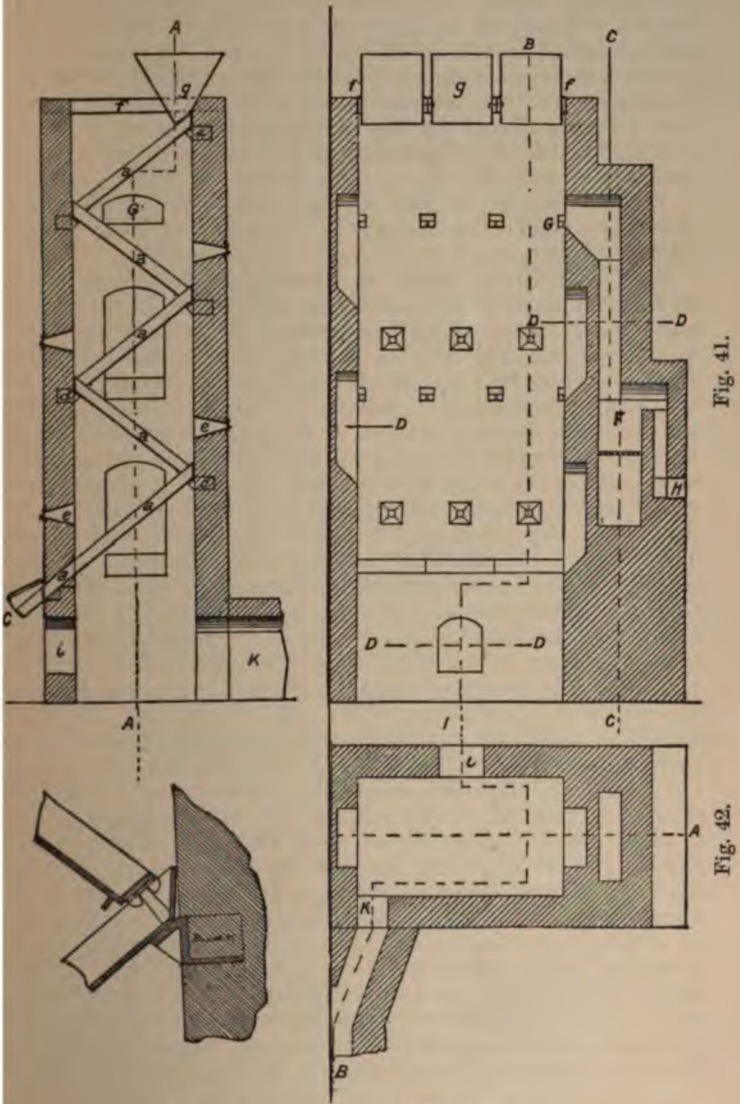
* See Part i., Chap. vi.

† See Part ii., Chap. ix., where figure and full description are given.

‡ *Trans. A.I.M.E.*, vol. xii., p. 95.

§ Morse, *Trans. A.I.M.E.*, vol. xxi., p. 920.



Figs. 40 to 43.—Stetefeldt Shelf-dryer.

Taylor gas-producers burning coal. But little heat is wasted, the perfectly dry ore being discharged at a temperature of 130° F. Four double dryers at this mill, from Nov. 10, 1891, to Jan. 1, 1893, dried on an average 82 tons of ore per day containing 6·1 per cent. moisture, besides 9½ tons of salt containing about 1 per cent. moisture. The average quantity of fuel used in this work was 3·3 tons of coal per day (or about 3½ per cent. by weight), costing 13s. 1d. per ton, so that the cost of fuel per ton dried was only about 5½d.

The advantages claimed for the Stetefeldt dryer over all others are:—(1) Durability; (2) economy of fuel; and (3) absence of dust.

Crushing Preparatory to Roasting.—Dry crushing by means of stamps has been already referred to in the last chapter, and for very *fine* crushing it is probably the best method. It is quite the common practice in amalgamation mills, especially in the U.S., where it is almost universal, and with some ores fine crushing is undoubtedly essential. With most ores, however, the process of roasting so opens up the pores and cleavage planes, besides breaking up the particles through decrepitation, that in a majority of cases ores to be roasted can be left comparatively coarse (say, a 16 or 20 mesh instead of a 30 or 40), and in this field many other machines can effectively compete with stamps. The use of *Chilian mills* and *rolls* has been referred to in Chapter III., and *ball grinding mills* in Chapter IV. One advantage that these machines have over stamps for grinding through a coarse mesh is that artificial drying, so absolutely indispensable as a preliminary to dry stamping, is much less essential; in fact, with rolls it is not required unless the ore is composed largely of actual wet clayey matter.

Rolls of the Krom pattern have been successfully used at the *Bertrand* and *Mt. Cory* mills (Nev.) and elsewhere; for descriptions of these machines and of the work done by them the student is referred to the volume on the *Metallurgy of Gold* in this series.* The capacity of two sets of Krom rolls following a stonebreaker set fine, on a moderately soft ore, has been proved to be as much as 100 tons in twenty-four hours through a 16 mesh screen, or equal to a 30 stamp mill. It is not likely that rolls will ever be able to compete with stamps for wet crushing before raw amalgamation, as with them it is difficult to crush sufficiently fine; but for dry crushing as a preliminary to roasting when a 16 or 20 mesh is sufficiently fine their small first cost and enormously greater discharge gives them an advantage. In many localities where

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* See also Curtis on "Gold Quartz Reduction," *Proc. Inst. Civ. Eng.*, vol. cviii. and Plate 3; Stetefeldt, *Trans. A.I.M.E.*, vol. xiii., pp. 109-113; Egleston, *Metallurgy of Gold, Silver, and Mercury in the U.S.*, vol. i., pp. 210-225.

[redacted]

freight is heavy and timber for framework expensive (as, for example, in many parts of Mexico and S. America) they can replace stamps very advantageously.

Chilian Mills.—Rolls answer so well for crushing before roasting that it is often assumed that no other machine can do the work equally well. So far as the author is aware only one form of machine can compete with rolls for this work, and it is the modified Chilian mill used by the *Broken Hill Proprietary Co.* (N.S.W.). The ore treated is a very hard siliceous ironstone gozzan, which has to be crushed through a $\frac{3}{32}$-slot mesh as a preliminary to roasting in revolving furnaces. The crushing plant consists of two No. 3 Gates crushers provided with manganese steel cone-sleeves on cast-iron centre, from which the crushed material passes to four Chilian mills of the type shown in Fig. 44. The annular die which forms the bed for the runners to roll upon is 52 inches outside and 30 inches inside diameter and 4 inches thick; it lasts, by turning over, for four to six months, or during the crushing of 5000 to 6000 tons of ore. The rollers,

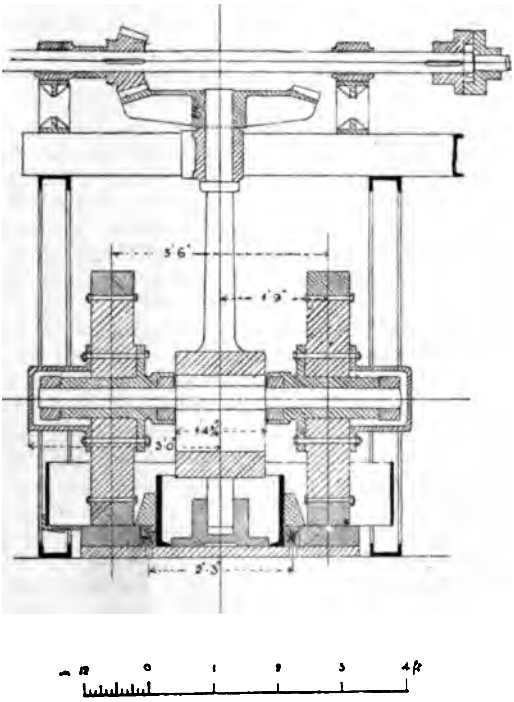

Fig. 44.—Chilian Mill.

3 feet 6 inches diameter and 8 inches face, are made of cast iron with thick steel tyres.

The crushed ore falls into hoppers, from which it is fed by self-feeders into an annular revolving hopper on the shaft provided with two spouts which deliver the ore immediately in front of the runners, while scrapers attached to the frame, so as to follow the runners, remove the crushed material at once. The mills are set so as to make 60 revolutions per minute, corresponding to a peripheral speed of the runners on the bed of 650 feet per minute or about equal to that of the modern high-speed rolls. From the mills the crushed material is carried on a belt conveyor to the elevator hutch, raised by means of an elevator with sixty-three buckets, 9-inch face and 6 inches deep, fixed to a rubber belt, and distributed to a plant of four trommels, 6 feet long and 3 feet in diameter, run at about 25 or 30 revolutions per minute, the screens being punched sheet iron with diagonal slots $\frac{1}{2}$ in. × $\frac{3}{32}$ in. The screened ore is deposited upon a belt conveyor and thence raised by another elevator to the hopper bins of the roasting plant, while the screenings are returned to the Chilian mills. The capacity of the whole plant is 180 tons per day; that of each machine is, therefore, 45 tons in twenty-four hours.

Chloridising.—A chloridising roasting may be carried out in any of the appliances described in detail in Chapter IX. Formerly, it was considered essential to convert as much as possible of the silver into chloride, and, according to Egleston,* "the whole art of chloruration consists in putting in the salt at the proper time, while there is yet some sulphur in the ore." The percentage of "chloridisation" (or "chlorination") is determined by the so-called "*chlorination assay*," which is performed by taking a sample of the ore, weighing two equal quantities, scorifying and cupelling one direct, and extracting the other with sodium hyposulphite solution till a few drops of the wash-water give no coloration with sodium sulphide, after which the residue is scorified and cupelled. Calling the weights of the two buttons a and b, the percentage of silver chloridised will be $\frac{100(a-b)}{a}$, provided the amount of soluble salts is not too great. If it exceeds 5 per cent., allowance should be made for the decreased quantity of the tailings compared with the original ore. As a rule, with furnaces such as the Howell-White and the Stetefeldt, in which salt is introduced with the ore at the beginning, the percentage of chloridisation will be roughly in proportion to the thoroughness of the roasting, and therefore the above chlorination assay will always be a useful check on the work done at the furnaces. It is certain, however, that in

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* *Op. cit.*, p. 237.

many cases more silver can be amalgamated from the roasted ore than is indicated by the chlorination assay, and this might be naturally expected from a consideration of the fact that in a perfect dead-roast without salt all the silver present would be reduced to metal or converted into sulphate, both of which are readily amalgamable. This point has been already referred to in the discussion of the *Tina* process, and deserves more attention from practical mill-men than it has hitherto received. There can be no doubt that with any type of furnace the volatilisation of silver is considerable when salt is added in roasting, and probably in many cases the saving effected by doing away with this source of loss, together with the saving of salt itself and the expense of crushing and drying it, would more than compensate for the slightly lower percentage of silver amalgamated—especially on medium and low-grade ores of 25 to 50 ozs. per ton.

Amalgamation.—The subsequent treatment of the roasted and chloridised ores may take place in copper tinas (see Chap. V.), in iron pans (Reese River process), or in barrels (Freiberg or European amalgamation).

The Freiberg Barrel Process.—This, though now obsolete, is most interesting, because it foreshadows the modern pan process, the reactions in both processes being identical. A good description of the process is given by Phillips,* to whose work the student is referred for details. Briefly, the ore, after crushing and mixing with 10 per cent. of salt, was roasted by hand in single-hearth reverberatories, and then charged into revolving barrels in charges of about ½ ton each, together with water and from 80 to 100 lbs. of scrap iron. After revolving for some time the chloride of iron in the roasted ore was reduced to ferrous chloride, and the cupric chloride (in part, perhaps, transiently) into cuprous chloride, but chiefly direct to metallic copper, even before the whole of the iron salts had been reduced.† This finely-divided metallic copper acted upon the silver chloride dissolved in the excess of sodium chloride present, precipitating metallic silver, while the large excess of metallic iron also precipitated silver in the same way. After two hours' rotation the barrels were opened and 5 cwts. of mercury added to each, after which rotation was continued for sixteen to eighteen hours and the contents of the casks turned out into dolly-tubs for washing and separation of the amalgam, which was then strained and retorted. The retort silver obtained from the amalgam averaged, at Freiberg, about 800 fine, and the loss of mercury was about 3 ozs. for every lb. of silver produced, which, as the ores averaged about 80 ozs., is equal to ¾ lb. per ton of ore treated—a fair average loss with roasted ore in the pan process. The percentage

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* *Elements of Metallurgy*, 1874, pp. 635-641.

† As shown by the author's experiments, see *Trans. Inst. Min. and Met.*, vol vii.

of extraction is said to have averaged from 90 to 95 per cent. on the raw ore, which is certainly a wonderful return. The cost is said to have been about £2 per ton.

In the United States the barrel process was tried for a time on the Comstock and in Colorado, but in the first-named locality never got a fair trial,* as under American conditions quick processes of large capacity which turn out the maximum of product with a minimum of labour—to a considerable extent irrespective of losses of valuable material—have always been preferred to slow but more thorough processes of limited capacity, which require to be spread over a greater area and demand more attention. It is quite probable, however, that had the same amount of attention and inventive skill which has been lavished on the pan, been devoted to improving the mechanical appliances of the barrel process, the latter would have shown itself capable of holding its own, especially for the richer ores. As compared with the pan process, it has the advantage of a much less expensive plant, which, moreover, can be renewed and repaired at very much less cost in those silver-mining districts where wood is plentiful and castings expensive.

A good description of the long-abandoned barrel mill at Georgetown (Colo.) is given by Egleston,† from which it appears that the percentage of extraction was 87 to 93 per cent. and the loss of mercury 2½ to 6 lbs. per ton. The cost is stated at the extraordinary figure of $31 (over £6) per ton, of which roasting cost £4, but this was chiefly due to bad management and is no criterion of what the process ought to cost with large barrels and suitable arrangements.

The Reese River Process.—In this process the roasted and chloridised ore is treated in iron pans exactly as in the Washoe process; it is, in fact, merely the combination of chloridising roasting with Washoe amalgamation, which has given the practice its distinctive name from the district where it originated.

When the ores contain enough copper, as is frequently the case, no addition of bluestone is required in the pan. With some ores, however, especially those which are almost free from copper and rich in lead or in manganese, it is necessary to add considerable quantities. Although much sodium chloride remains undecomposed in the roasting furnace, it is usual to add about 1 per cent. more to the pan charge. This is, however, merely a "rule of thumb" practice with millmen, as the roasted ore almost always contains an ample excess of salt for all the reactions.

The results obtained differ in the following respects from those shown by pan amalgamation:—

(1) The percentage of extraction on the roasted ore is much

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* Douglas, *Journ. Soc. Arts*, Aug. 19, 1895, p. 817.

† *Op. cit.*, pp. 334-348.

higher than that shown on the raw ore, running up to 85 or 90 per cent.

(2) The consumption of iron in the pans is usually greater, owing to the action upon it of the base metal chlorides formed during roasting.

(3) The loss of quicksilver is, as a rule, higher with cupriferous and plumbiferous ores, often running up to 3 or 4 lbs. per ton of ore treated. It can, however, be much reduced by running the pans for some time before adding the quicksilver.

The general arrangement of a roast-amalgamation silver mill is shown in Fig. 45,* which represents a mill in which the ore is dried in revolving dryers (not shown) and roasted in Howell-White cylinder roasters. The ore hoppers and dryers are in front of the plane of section.

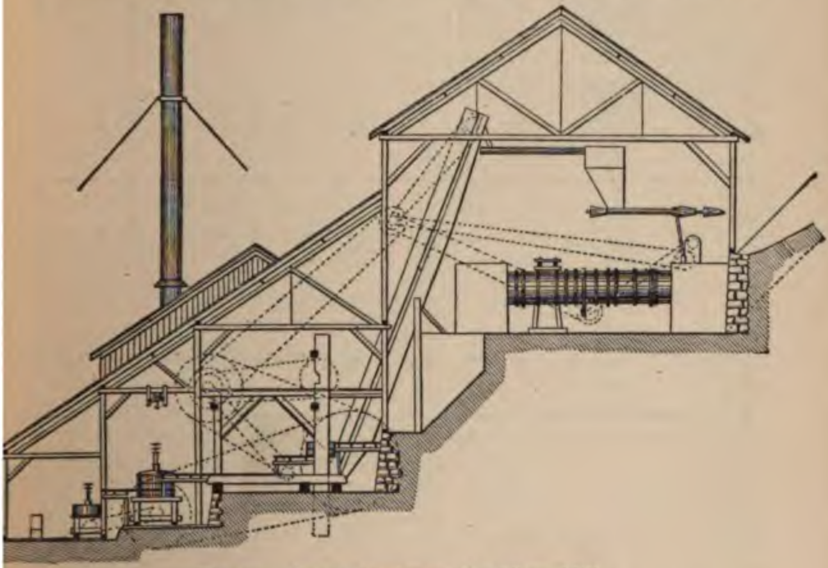

Fig. 45.—Roast-Amalgamation Silver Mill.

At the *Lexington* mill (Butte, Montana) the ore is crushed by a Blake stonebreaker and dried in a Stetefeldt kiln, the hot dry ore passing direct to the stamps, which are fifty in number, besides ten kept for stamping salt. The mortars have double discharge, and the screens are of brass wire, 24 mesh. Each stamp crushes 1·7 tons of ore per day; the salt is crushed hot. like the ore, but only through a 20 mesh screen and with lighter stamps. The ore is mixed with 10 per cent. of salt, and roasted

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* From Messrs. Fraser & Chalmers' catalogue.

TABLE VI.—The Roast Milling Process.

	Alice, Butte, Montana, 1897.	Elkhorn, Montana, 1892.	Granite Mountain, Montana, 1890.	Lexington Mill, Butte City, Montana, 1890.	Palmarejo Mill, Zapote, Chihuahua, Mexico, 1891.	Ontario, Park City, Utah, 1891.
References, ...	1.	2.	3.	4.	5.	6.
Crushing—						
Number of stamps, ...	60	25	153	50	50	40
Weight per stamp, ... lbs.,	950	...	...	1000	...	...
Drops per minute, ...	92	...	...	94	...	...
Mesh of Screen, ...	24	...	...	30	20	26
"Duty" per stamp, ... tons,	1·33	1¼	...	1·7	1·3	1·87
Roasting—						
Number of roasters, ...	4	...	10	1	4	2
Kind of roaster, ...	Howell	Howell	Howell	Stetefeldt	W. Howell	Stetefeldt
Hours roasting each charge, ...	...	...	...	...	...	...
"Duty" of each furnace, ... tons,	30–35	...	...	30	15	38
Salt used per ton, ... lbs.,	200	260	...	200	100	284

[redacted]

Hours charge in pan,		8	...	...	8	...	8
Salt used per ton,	lbs.,	...	20	...	...	...	...
Bluestone used per ton,	,,	...	...	...	...	...	...
Wear and tear of castings per ton,	milles.,	...	...	...	...	...	5·5
Loss of mercury per ton,		...	...	...	7 to 8 ozs.	¾ lb.	...
Grade of ore treated—gold,		...	...	...	0·58	...	0·044
,, ,, silver,		...	39	50·6	28·5	31	39·50
Percentage extracted—gold,		...	...	...	60	...	47·1
,, ,, silver,*		92	93 (?)	90·7	93	86·3	90·8 †
Fineness of bullion,		600	...	...	980	...	425
Value of tailings,	ozs.,	...	3½	...	2·1	...	...
Costs—							
Labour and superintendence,		...	£0 13 11	£0 14 5	...	...	...
Fuel, including roasting,		...	0 4 10½	0 6 10	...	...	...
Oil and light,		...	0 0 2	...	...	...	...
Mercury,		...	0 1 8	0 4 8	...	...	£0 5 5½
Chemicals and salt,		...	0 7 5½	0 9 6	...	...	
Castings and repairs,		...	0 3 6	0 2 7½	...	...	...
Sundry expenses,		...	0 2 3	0 3 7½	...	...	...
			£1 13 10	£2 1 8	£1 4 9	£1 3 0	£1 17 0

* Calculated on the roasted ore. † Calculated on raw ore.

References.—1. *Private notes.* 2. Company's report for 1893. 3. Company's report for 1891. 4. Company's report for 1891. 5. Company's reports for 1892, &c. 6. Lamb, *E. and M. J.*, 17th Dec., 1892.

in Stetefeldt furnaces (see Chap. IX.) in charges of 40 tons in each furnace, with a fuel consumption of about 10 cubic feet of wood per ton. The ore, as it leaves the furnace, is chloridised up to 80 per cent., which is increased to over 90 per cent. on the cooling floors, but the loss of silver by volatilisation is probably near 8 per cent., and that of gold at least 20 per cent. From the furnaces the hot ore is tipped on cooling floors, where the chloridising continues for thirty-six to forty-eight hours. There are twenty pans, each of which is charged with 3000 lbs. of ore, which is first ground for two hours, then 300 lbs. of quicksilver and 1 lb. of zinc are added, and the further manipulations are conducted precisely as in the Washoe process described in the last chapter. In this mill, owing to the comparative absence of lead from the ore treated and partly also to the use of zinc, the loss of quicksilver is very small and is said not to exceed 6 or 7 ozs. per ton of ore treated. The percentage of extraction (calculated on the roasted ore) is very high, averaging 93 per cent., but no account is taken of the loss by volatilisation; the extraction of gold is only 60 per cent. The tailings averaged in 1891, 2 ozs. of silver and 3 dwts. of gold per ton, practically all of which was in the sulphides.

A number of comparative data as to work done and cost in different mills employing the roast-amalgamation process in pans will be found in Table VI.

Reactions in the Amalgamation of Chloridised Ores.—The reactions in the barrel have been sketched above, and those in the pan are no doubt identical, the conditions being practically the same. Besides the reduction of Fe_2Cl_6 to $FeCl_2$ by excess of iron, which is non-essential, we have:—

$$1.\quad 2AgCl + Fe = FeCl_2 + 2Ag,$$

and, simultaneously,

$$2.\ \begin{cases} CuCl_2 + Fe = FeCl_2 + Cu \\ 2AgCl + Cu = CuCl_2 + 2Ag. \end{cases}$$

Both these reactions are facilitated by the excess of sodium chloride, which keeps a portion of the silver chloride always in solution; the liberated metallic silver is taken up by the mercury, the loss of which is purely mechanical.

Cost and Results.—In Chapter IX. the loss by volatilisation in chloridising roasting and the cost of the process are discussed in detail, and it there appears that the average loss may be put at not less than 8 per cent. of the total silver contents, while the cost will average at least 10s. per ton, or 4 ozs. of silver at 2s. 6d. per oz. In the case of a 50-oz. ore, therefore, the total cost of the chloridising roast is no less than 16 per cent., and, in the case of a 30-oz. ore, 22 per cent. of the total value; the extraction by roast amalgamation must, therefore, exceed by at least these amounts the extraction by raw amalgamation, in order to compensate for the increased cost. The figures usually reported as regards extraction are calculated on the assay of the roasted ore, and, therefore, an average of 8 per cent. must be deducted from them in order to show the true percentage of extraction on the original ore treated. If, for instance, we take the figures of the *Palmarejo* and *Lexington mills*, in which the mean percentage of extraction is 90 per cent. (corresponding with 80 to 85 per cent. of the value of the raw ore), and then consider that the true cost (including loss) of the chloridising roast alone is 23 to 26 per cent. of the total value of the ore, it will be obvious that raw amalgamation may only extract 65 per cent. of the true value of the raw ore and yet be as economical as, and more profitable on low grade ores than, the more complex Reese-River process. This is undoubtedly the reason why roast-amalgamation mills are becoming less common, few new ones being erected, while several of the old ones have been converted into lixiviation mills or have given way to smelting processes. It is, however, probable that many ores would yield about as large a percentage of their values after a quick plain roast as they now yield after an expensive chloridising roast with its attendant high loss; this is a point deserving of investigation by careful experiments on a variety of ores

The same progress of improvement which led to the replacement of barrel amalgamation at Freiberg in 1857 is, with better transportation facilities, fast advancing over Western America, and it is a safe prophecy that in a few years roast-amalgamation processes will become in the United States, as in Europe, things of the past, the combination of raw amalgamation with smelting, to be described in the next chapter as the Combination process, largely taking its place where raw smelting is not practicable. The conditions in S. America and Mexico are, however, different (especially on account of the scarcity of fuel and lack of transportation facilities in the Andean and Plateau districts), and it is probable that tina and patio amalgamation in their various forms may long continue to satisfy the prevailing conditions better than any other processes.

CHAPTER VII.

TREATMENT OF TAILINGS AND THE CONCENTRATION OF SILVER ORES.

Composition and Classification of Tailings.—The tailings from an amalgamation mill, in which the ore has been crushed wet, consist of two very different substances, known as *battery slimes* or *slums*, and *tailings*.

The former are the overflow from the settling tanks; they contain a large proportion of those particles of the ore which were originally finely disseminated, as well as of those more brittle constituents which fly into fine powder under the stamp. As a rule, though not invariably, these battery slimes are richer than the original ore, because most of the silver minerals are brittle or very finely divided; and their silver contents are often to a large extent amalgamable, though their clayey condition tends to coat the globules of mercury and so renders amalgamation both slow and imperfect. In the early days of milling on the Comstock these slimes were run away with the tailings; now they are for the most part caught in reservoirs near the mills, and worked up, either in the same plant, or in "annexes" which do nothing else. Although much richer than the sand tailings they form lumps impenetrable to the action of water and mercury, and it is found preferable to mix with them a considerable quantity of sand, which assists in cutting up the lumps and allowing free access of chemicals and mercury to every particle of the charge. On the Comstock the battery slimes assay from 20 to 60 ozs., and tailings from 17 to 18 ozs., and they are invariably treated by pan amalgamation, using a larger quantity of chemicals than for ore-working. Costly experiments have been made in the direction of chloridising roasting, but the additional yield was never large enough to pay for the extra expense. A very large proportion of the finest battery slime (usually the richest part) can be recovered by running the slime water into reservoirs, from which it is pumped up and used instead of clear water both in the mortars and the pans.* This is, however, not practicable in the case of very

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* Goodale, *Trans. A.I.M.E.*, vol. xviii., p. 250; Tatum, *E. and M. J.*, Dec. 14, 1895.

clayey ores, as the fine clay soon accumulates in the water and renders it too thick for use. When the ore has been dry-crushed there are no battery slimes, although the total proportion of slime in the pulp is greater.

The "tailings" from amalgamation mills consist partly of *sand*, which includes the larger particles of metallic sulphides as well as of waste which have escaped grinding, and partly of *pan slimes*, including all that part of the ore pulp which has become disintegrated in the pans, as well as the whole of the slimes in dry-crushing plants. These pan tailings, unlike the battery slimes, contain very little that is amalgamable, but, on the other hand, they contain large quantities of floured mercury and amalgam, a part of which is saved in the subsequent treatment by amalgamation.

Treatment of Tailings by Amalgamation.—The Comstock practice * may be taken as typical. Very large special "tailings pans," 9 to 10 feet in diameter by 6 feet deep, and holding charges of 6 to 10 tons at a time, were tried in some of the tailings mills, but it was found that they gave a lower yield with higher loss of quicksilver, to say nothing of greater cost for power and repairs; so that they were soon thrown out and combination pans with wooden sides (Fig. 29) 5 feet 6 inches in diameter reverted to. For treating slimes, strips of wood were nailed on to the interior of the pan vertically, so as to present a corrugated surface to the pulp-currents, which assisted materially in breaking up lumps of slime. The slimes, collected in "tailings dams," were spread out over as large an area as possible in order to disintegrate the lumps by drying, and it was found that the increased porosity thus secured had an important effect on the yield.

At the *Lyon* mill the pan-charge was 3 tons (6000 lbs.) of sand tailings, or 1½ tons (3000 lbs.) of slimes, which take more water to give the same consistency of pulp. The amount of chemicals used was 10 lbs. of copper sulphate per ton for sand, and 20 lbs. per ton for slimes; the salt used in each case being from two to two and a-half times the weight of bluestone, or, say, 25 lbs. of salt for sand and 50 lbs. for slimes. Careful experiments on a large scale at the Lyon mill proved that it was not safe to use less salt, and that a larger quantity gave no increased yield. Elaborate experiments on 19,000 tons of sand and 2000 tons of slimes showed that the best results were given by running the pulp so thick that it would drop slowly from a stick dipped into it, instead of running off in a stream.† The quantity of quicksilver used was, at *Janin's* mill, 200 lbs. to the ton; at the *Lyon* mill, 50 lbs. to the ton of material treated, whether sand or

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* Hodges, *Trans. A.I.M.E.*, vol. xix., p. 195.

† See table quoted by Hodges, *loc. cit.*, p. 229.

slimes. The method of operating was as follows:—While the pans were being charged boiler steam was turned on until the temperature reached 120° to 150° F., and as soon as the charge was all in the required amount of salt was added. After running for half an hour (without grinding) the copper sulphate was added, and then the running was continued without quicksilver for ½ hour (*Lyon*) to 1½ hours (*Janin*) in order to allow the reactions to take place. Frequently (more especially with slimes) it was found advantageous to add a pint or so of dilute sulphuric acid to the pan charge to assist the reactions, and this was also found to keep down the loss of mercury when it showed a tendency to rise. The action upon the clay of the slimes may have been chemical or mechanical—probably both—but it was effectual. The quicksilver was then added, and the pans run for the remainder of the four hours allowed for each charge before turning it into the settler. A special feature in the Lyon mill was the provision of one 8-foot settler to each pan, whereby the pulp could separate out during four hours, instead of during two only, as in the common practice, and a large part of the floured mercury became re-united. So successful was this slow settling that the loss of mercury was reduced to only 8 ozs. per ton for sand and 12 ozs. to 1 lb. for slime, in spite of the fact that the slimes and tailings treated had been previously freed from mercury and amalgam; whereas at the *Janin* mill losses of as high as 5 lbs. per ton were experienced, and from 3 to 4 lbs. was the average at all the tailings mills—except those treating blanket concentrates exclusively, which often *gained* mercury.

The amalgam yielded, after retorting, a bullion of only about 150 fine from sand and 200 to 250 fine from the richer slimes, the impurity being chiefly copper, and it was found that whenever the bullion rose above this standard of fineness the percentage of extraction fell below 60 per cent., which was about the average. The retorting and refining of this base bullion is described in Chapter VIII. A bye-product of the refining was copper sulphate, which was thus regenerated for use over and over again with a comparatively small loss.

As in all amalgamation processes, cleanliness of the mercury was found to be a most important feature, and frequent small additions of sodium or of KCy, together with repeated spongings of the mercury bath, were found necessary. The Lyon mill enjoyed the advantage of water power, and the cost of amalgamating all kinds of tailings was by suitable arrangements brought very low. The following figures are given by Hodges[*] as the average cost per ton of treating 46,500 tons in 1876:—

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[*] *Loc. cit.*, p. 231.

					s.	d.
Superintendence, assaying, legal and general expenses, taxes, insurance, freight, and sundries, . . .					0	11
Collecting, spreading, and drying tailings, . . .					1	3½
			s.	d.		
Labour,	113 shifts,	at 14s. 3d. per shift, .	1	7¼		
Quicksilver,	0·45 lb.	,, 2s. 6¼d. per lb., .	1	2		
Salt,	23·7 lbs.	,, 4s. 2¼d. per 100 lbs.,	1	2½		
Bluestone,	12·3 ,,	,, 2d. per lb., .	2	0½		
Castings,	3·1 ,,	,, 3⅓d. per lb., .	0	10¼		
Fuel,	·0276 cord	,, 26s. 1d. per cord, .	0	8¾		
Sundry supplies, ...			0	6		
					8	1¼
					10	3¾

These figures compare very well with those of the best managed ore mills, even if we add the cost of crushing by stamps, which would not be much more than that of collecting and drying tailings. The comparatively small consumption of pan castings is particularly to be noted in connection with the large quantity of bluestone employed, and is to be accounted for by the complete absence of all grinding, so that the loss was in this case almost entirely chemical. Comparing the chemical equivalents we find that 1 lb. of cast iron (supposed 95 per cent. Fe) should completely precipitate the copper of 4·23 lbs. pure copper sulphate ($CuSO_4$, 5Aq), so that the consumption of iron was very little more than that required by theory to precipitate the copper.*

The average percentages of extraction were :—On sand tailings containing a value of 15s. 3d. in silver and 4s. 8½d. in gold, 76 per cent. of the silver and 25 per cent. of the gold, or a total value of 12s. 9d. per ton; on slimes containing a value of £2 14s. 2d. in silver and 9s. 5½d. in gold, 86 per cent. of the silver and 42 per cent. of the gold, or a total value of £2 11s. 5d. per ton, out of £3 3s. 7½d. in all.

Such satisfactory results being obtained from the treatment of this comparatively poor material, it may be asked why the slimes and tailings were not more thoroughly treated and their values extracted, at the mills which originally treated the ore. Some of the reasons are the following :—

(1) The capacity of the ore mills was almost always behind the output of the mines, and with the shareholders urging a large bullion output the mills could not waste time in working over tailings or in treating the ore more thoroughly.

(2) In their unaltered condition, as discharged from the tailings sluices of the mills, the sulphides in the slimes and tailings yielded only a small percentage of their value on re-amalgamation;

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* Attention has been already drawn to the fact that all the copper added in the form of bluestone is very soon reduced to the metallic condition and ultimately enters the bullion.

whereas in their gradual passage down the valleys they underwent partial oxidation, as well as other chemical and physical changes, which rendered them more amenable to treatment.

(3) All the water power available in the upper part of the valleys was fully utilised for crushing ore, and only in the lower reaches could water power be acquired cheaply for working tailings.

Treatment of Tailings by Lixiviation.—The earlier attempts to work tailings by the Kiss process were unsuccessful, but since about 1884 at *Bullionville* (Nev.), at the *Ontario* (Utah), *Blue Bird* and *Bimetallic* (Montana), and other places, the Russell process has been used successfully. At *Broken Hill* a modification of the Patera process gives very satisfactory results on lead carbonate tailings after roasting. For details of the work done and results obtained Chapters XI. and XII. should be consulted.

Treatment by Partial Concentration.—Attention has been already called to the fact that a large part of the values in amalgamation tailings exist as "sulphides"—*i.e.*, not only in the form of complex sulphantimonides and sulpharsenides, but also in argentiferous galena, blende, mispickel, chalcopyrite, and other minerals. In almost every case where amalgamation methods are employed for treating ores of the precious metals, they are advantageously supplemented by more or less perfect attempts at dressing the tailings; so as to separate the heavy minerals in which the larger part of the valuable metals occurs, from the particles of waste.

The concentration of tailings from the Patio process on "planillas" and other simple appliances has been already described in Chapter III. The process has its advantages where labour is cheap and water very scarce, but would be utterly unsuited to American (*i.e.*, United States) or Australian conditions.

Another method largely in use everywhere for saving the heavier portion of the metallic sulphides is that of "blanket sluices." A *blanket sluice* consists of a number of wide shallow troughs of great length set side by side, at an inclination of from 6 to 10 inches in each 12 feet length, the bottom of the troughs being covered by blankets or canvas nailed to the bottom planks. A common size for the individual troughs is 20 inches wide and 1½ to 6 inches deep, and from six to as many as twenty are placed side by side, their length being anything from 50 to as much as 1200 feet (*Woodworth* sluice). The stream of pulp being divided, so that an equal proportion goes to each trough, the heavier metallic particles fall to the bottom where the velocity is least and get stranded upon the surface of the blankets or canvas, while the lighter waste is carried down by the stream and falls into a tailings sluice or launder. Either underneath the main sluice or beyond the cross sluice which carries away the tailings, is a concentrate sluice to carry the concentrate into settling tanks. At intervals of from two to four hours the stream of pulp is turned off from each blanket sluice in succession, connection is made with the concentrate sluice, and the blankets are either swept or, better, washed down with a strong jet of water from a hose into the concentrate launder.

The value of concentrates obtained by either of the above methods may vary, according to the richness of the ore, from $25 upwards. At the *Woodworth* sluice,[*] where the tailings from a number of Comstock mills were run over the largest plant of this kind ever constructed—viz., 1700 ft. long × 22 ft. wide, the concentrates collected averaged over 25 ozs. to the ton. In this case they were treated by ordinary pan amalgamation, which recovered 70 per cent. of their value, and was the most economical process in consequence of the distance to the nearest smelting centre. In most cases where the concentrates are richer, and especially if they contain gold, it will be more advantageous to treat them by smelting (which extracts practically all the silver and gold present); or by chloridising roasting, chlorination to get out 95 per cent. of the gold, and subsequent lixiviation by the Russell process, which extracts from 60 to 85 per cent. of the silver.

Concentration after Amalgamation.—In the cases thus far considered the concentration is only partial, and the percentage recovered low, a large amount being lost in the final tailings. In order to effect a closer saving of the valuable heavy minerals, while at the same time doing the work cheaply under ordinary conditions, it is necessary to put in an automatic plant comprising percussion tables and revolving buddles, or the shaking travelling belt machines which can, to a considerable extent, fill the places of both. It is not proposed to give here any description of such concentrating devices or of the mode of using them,[†] but only to mention some of the results obtained by their use at certain mills.

At the *Charleston* mills [‡] (Tombstone, Ariz.) about 90,000 tons of an ore containing hornsilver, together with small quantities of metallic sulphides and large quantities of cerussite and iron and manganese oxides, were treated by the Washoe process during the years 1881 to 1884. The ores had originally contained about 46·5 ozs. of silver and 0·20 oz. of gold per ton, of which an average of 77·4 per cent. of the silver and 51·8 per cent. of the gold had been extracted by pan amalgamation, leaving in the tailings an average of 10·5 ozs. of silver and ·098

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[*] Egleston, *Metallurgy of Gold, Silver, and Mercury in the U.S.*, vol. i., p. 453.

[†] Rose, *Metallurgy of Gold*, 1st edition, chap. ix., pp. 163 *et seq.*

[‡] Church, *Trans. A.I.M.E.*, vol. xv., p. 601.

oz. of gold per ton, worth at the then prices about £2, 9s. The concentrating plant consisted of agitators and mixers for making pulp of the tailings, trommels and spitzkasten for sizing, jigs for treating the coarser sand. Frue vanners for the intermediate sizes including the rounded grains which roll off a table, and a series of round tables with cement surfaces and successively gentler slopes for the fine slimes. The latter proved the most successful part of the whole mill, retaining the finest slimes of hornsilver and lead carbonate. The actual saving in treating about 17,000 tons during the year 1883-4 was 53 per cent. of the silver, 55½ per cent. of the gold, and 77½ per cent. of the lead shown by assay in the tailings, equal to 14 per cent. of the silver and 23·4 per cent. of the gold contents of the original ore, thus bringing up the total saving on the original ore by amalgamation and concentration combined, to 91·4 per cent. of the silver and 75·2 per cent. of the gold, which from its small amount was of only secondary importance. The cost of concentration amounted to 5s. 1½d. per ton of tailings treated, of which 1s. per ton was for steam power; and on a larger scale this could no doubt have been reduced. The concentrates contained over 50 per cent. lead, nearly 50 ozs. of silver, and about ½ oz. of gold, and were smelted in round water-jacketed furnaces,[*] yielding lead which carried practically all the gold and silver. The cost of smelting was 40s. per ton.

At the *Standard Consolidated* mill[†] the tailings from free gold plate amalgamation are run over Frue vanners, yielding concentrates which in 1892 averaged $58.97 in gold and $30.86 in silver, or $89.63 total. Treated by pan amalgamation, these concentrates yielded 80·6 per cent. of their value. The tailings from the concentrates, still containing $18 in gold and silver, are allowed to oxidise for a time, and are then re-amalgamated by the Boss continuous process, yielding this time 67 per cent. of their value (or $12.47 per ton) as a very base bullion only 100 fine.

Concentration before Amalgamation.—There are many localities in which a method of concentration after amalgamation similar to that above described can be introduced with advantage, the most suitable conditions being:—

(1) That the greater part of the silver in the ores should be amalgamable.

(2) That the concentrates should be comparatively small in quantity (not over 5 per cent. by weight of sulphides), and not too rich (say, 50 ozs. per ton as a maximum).

When the heavy minerals in an ore (consisting, as is most usual, of base metal sulphides) amount to more than 5 per cent. by weight, they will more or less interfere with amalgamation in

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[*] Described in part i., chap. xi.

[†] *Report of the Standard Consolidated Mining Co. for 1892.*

the pan, increasing the losses of quicksilver and yielding a base bullion. In such cases, therefore, it is preferable to concentrate the original battery pulp and take out as much of the sulphides as possible before passing on the remainder (in slightly diminished quantity) to the pans. This plan has the great advantage that the heavy sulphide minerals are much coarser in grain before passing through the pans than afterwards, and are, therefore, much more easily saved, it being well known that the heaviest losses in concentration occur on the finest slime material. It offers the further advantage that if the ore carries gold a considerable portion of it can be saved by battery and plate amalgamation before the pulp passes to the concentrators; and this is an important matter since many silver mines which are very rich near the surface become poorer in depth, retaining, however, the same proportion of gold per ton, and thus approximating more to the character of gold than of silver mines. As examples may be mentioned the *De Lamar* (Idaho) and the *Drumlummon* mine of the *Montana Co., Ltd.*

Other advantages of concentration before working in pans are the diminished loss of quicksilver by flouring, reduced wear and tear of pans, and doing away with pulp tanks to receive the tailings as discharged intermittently from the settlers, and with agitators to mix the tailings with a uniform quantity of water. Concentration of the battery pulp is performed more thoroughly, because it is easy to secure that even flow of pulp of uniform density without which close saving in concentration is an impossibility, whereas with tailings discharged at intervals from settlers, or delivered in trucks from a tailings dam, it is almost impossible to secure sufficient uniformity in the pulp to enable the best results to be obtained.

The so-called **combination process** in its entirety consists of three separate operations:—(1) Stamping and amalgamating on copper plates to save free gold; (2) concentrating (usually on Frue vanners) to separate the rich heavy sulphides containing non-amalgamable gold and silver; and (3) pan amalgamation of the tailings to save silver existing as chloride, and in other amalgamable forms. Sometimes a second concentration follows the pan amalgamation, in order to save a little more sulphide material from the now finely ground pulp.

Examples of the Combination Process.—The *Montana Company, Ltd.*, has, besides a 60-stamp mill treating low grade gold ores, one of 10 and one of 50 stamps, which work on the combination system. Erected as ordinary pan amalgamation mills, they had to be supplemented with concentrating appliances as the ores in depth became at once poorer and more refractory. Twenty-four Frue vanners, erected at a cost of £4000, yielded in a single twelvemonth concentrates to the value of over £70,000. Concentration before amalgamation was subsequently found to be still more advantageous, and the method of procedure in the 50-stamp mill is now as follows:—

(1) The ore is crushed and run over copper plates to amalgamate free gold.

(2) The pulp is then passed over twenty Frue vanners, which take out high grade concentrates.

(3) The tailings from the vanners, deprived of their free gold and of the richer portion of their sulphides, are amalgamated in pans in charges of about 1 ton, with the usual additions of salt and copper sulphate, and also a little sulphuric acid.

(4) From the settlers the pulp is again passed over twenty Frue vanners, which catch a small quantity of inferior concentrates.

(5) Last of all, the pulp is caught in dams to undergo a process of oxidation, with a view to subsequent treatment.

During the year 1895 the Company's mills treated 37,790 tons of ore, the average assay of which is not given. The average total yield in bullion and concentrates was, however, $7.45 (31s.) in silver and $2.64 (11s. 2d.) in gold, or a total value of 42s. 2d. The average total cost of mining and treatment was 31s. 4d. (of which milling alone came to 12s.), leaving a nett profit of 10s. 10d. per ton, so that the silver extracted just paid expenses, leaving the gold as profit. The advantages of concentration before amalgamation at this mine have been:—

(1) Raising the fineness of the silver bullion from 550 to 930 and upwards, with corresponding diminution in cost for refining and less loss in the process.

(2) Reducing the loss of quicksilver from 1·55 lbs. to 0·1 lb. per ton—which alone means an annual saving of £2500.

At the *Webster* mill (Utah) ores containing 8 per cent. of lead, 20 ozs. of silver, and $\frac{1}{2}$ oz. gold per ton are concentrated before amalgamation, the concentrates carrying 50 per cent. lead and £20 per ton in gold and silver, the tailings are then treated by pan amalgamation to get out the rest of the silver. The total percentage of the precious metals extracted is 85 per cent. by value, and the pan bullion is very fine.

At *Black Pine* (Montana)* a siliceous ore, carrying sulphides and averaging 17·5 ozs. silver per ton,† was treated during 1887 by the Washoe process in a 10-stamp mill, and yielded only 46 per cent. of its value. The mill was then altered, four Frue vanners being placed between the battery and the tanks, with the result of increasing the percentage saved to 83 per cent. The concentrates assay 136 ozs. per ton and form about 6 per cent. of the total weight of the ore, containing, roughly, about 36 per cent. of its gross value; 47 per cent. more was extracted in the pans, running for a total of eight hours—viz., four hours with

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* Goodale and Akers, *Trans. A.I.M.E.*, vol. xviii., p. 248.

† The composition of this ore is given in Table II., p. 31.

[redacted]

chemicals alone (50 lbs. salt, 2 lbs. sulphuric acid, ½ lb. potassium cyanide), and four hours more after addition of quicksilver. During the year 1889 the following results were shown :—

	Tons.	Ozs. Silver.	Value.	
			Per Ton.	Percentage
			Ozs.	
Ore crushed, dry weight,	9062	205,435	22·67	...
Concentrates produced, ,,	541·8	73,777	136·2	35·9
Bullion produced,	...	97,661	...	47·5
Total silver extracted,	...	171,438	...	83·4
Tailings,	8520	33,997	4	16·6

Cost of milling, $4.36 = 18s. 2d.

Details of the cost of milling are given in Table VI., Chapter VI.

The concentrates carry 8 per cent. Cu, 9 per cent. Pb, and 32 per cent. SiO_2, the rest being principally iron pyrites.

At *Huantla* (Morelos, Mexico)* ores averaging about 98 ozs. per ton are concentrated on vanners, which yield 8 per cent. of their weight as concentrates, with about 720 ozs. of Ag per ton, or 60 per cent. of the silver contents of the ore. The tailings from this operation, still containing about 40 ozs. of silver, are treated by a modified Patio process and yield over 90 per cent. of their value. The final tailings assay under 4 ozs. per ton, so that the total extracted by the combined process is 96 per cent. of the total contents of the original ore. The total cost of treatment is under 30s. per ton and the yield is very much higher than could be obtained by any process involving roasting, not to speak of the volatilisation loss which is avoided.

It may be remarked that the Frue vanner as a concentrator is certainly not better suited to most ores than a combination of two other machines would be; but its automatic action and adjustability, coupled with its fairly close saving, production of clean concentrates, and wide range of adaptability to variations in the ore, enable it in most cases to do better work than any other single machine.

Applicability of the Combination Process.—The advantages of concentration before amalgamation may be recapitulated as follows :—

(1) Easier and more perfect saving of sulphides.
(2) Lower final tailings
(3) Cleaner bullion from the pans.
(4) Less loss of quicksilver.

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* W. S. Morse, *Private communication*, Feb., 1897.

The process is applicable to all ores carrying argentiferous or auriferous sulphides, but more particularly to the following :—

(1) Those in which the sulphides, though comparatively small in amount, are rich, say 50 ozs. to the ton or upwards.

(2) Those in which the sulphides, though poor, are yet worth treating, and where they constitute more than 5 per cent. of the weight of the ore.

These cases are far commoner than is usually supposed, not only in the United States but also in Mexico and S. America, and as silver lodes are worked in depth the ore almost invariably becomes more refractory, carrying a larger percentage of its values in non-amalgamable forms. It is probable, therefore, that the field of this combination process will be largely extended in future years, certainly at the expense of roast-amalgamation processes which are fast losing ground, and possibly, in some cases, of lixiviation processes. There are many instances where concentration might advantageously precede lixiviation on somewhat light or medium heavy ores, but for the drawbacks involved in having to settle and dry the tailings prior to chloridising roasting, and in having to leach the fine slimes raw together with the roasted coarse sand, so sacrificing somewhat in percentage of extraction. There are, however, probably many cases in which the extra yield obtained from, say, 10 per cent. of rich concentrates shipped to a smelter, would more than compensate for the cost of redrying coarse sand, and for the trifling loss of extraction through having to leach the fine slimes raw. In some cases the tailings would not require chloridising and could be leached raw after separation of the sulphide concentrates. At anyrate, there would seem to be a promising field for experiment here.

It is evident that the adoption of the combination method need add but little to the cost of amalgamation processes, for all the operations are automatic, and this is, moreover, proved by the milling costs for the combined concentration and amalgamation at the *Montana* and *Combination Co.'s* mills, which are only 12s. and 18s. 2d. respectively, or not higher than the average cost of pan amalgamation alone throughout the United States.

Concentration in Place of Amalgamation.—There are many cases in which silver-bearing ores, containing practically all their metallic value as sulphides, none of which are amenable to amalgamation or lixiviation without a preliminary chloridising roast, can be concentrated so as to yield a very rich product for smelting and almost worthless tailings.

At the *Silver King* mine (Ariz.) the ore (its argentiferous constituents being chiefly of metallic silver and chlorides) was treated by raw pan amalgamation ; then, as base minerals developed themselves, roast amalgamation and, subsequently, lixiviation were adopted. Now, however, all these processes have given place to simple concentration.* The ore consists of streaks and spots of fahlerz and stromeyerite with some barytes in a decomposed basic eruptive rock and averages 25 ozs. of Ag per ton. It is stamped dry through a 30-mesh screen, ten stamps putting through 35 tons per day, and the pulp passes to six Frue vanners, 4½ feet wide. The concentrates assay 500 to 600 ozs. of silver and are shipped for smelting to San Francisco, while the tailings assay only 3 to 4 ozs. per ton, so that this very simple and incomplete concentration plant saves quite 85 per cent. of the silver.

This result is, however, quite impossible to obtain when the ore carries any quantity of heavy base-metal sulphides, for then these become chiefly concentrated, while any particles of true silver minerals, originally much smaller as a rule, pass away to a great extent with the fine slime. If no true silver minerals are present, and that metal is only found isomorphously replacing lead in galena the concentration may be very fair, but, as has already been seen, even with galena a proportion of its silver contents is usually in the form of a true silver mineral disseminated between the cleavage planes,† a large part of which inevitably finds its way into the slimes, while finely-disseminated polybasite and ruby silver exhibit even a more strongly marked tendency to pass away.

At *Silver Plume* (Colo.), for instance, the ores carry from 10 to 25 per cent. of metallic sulphides, chiefly galena and blende, with a little pyrites in a gangue of quartz, decomposed granite, and a little calcite. Both the galena and the blende carry silver, but there is also a good deal of finely-disseminated argentite, polybasite, and ruby silver. The nett result of concentration is that the galena and heavy concentrates sent to the smelters only carry from 30 to 40 per cent. of the silver value of the ore, while the waste blende from the third hutch of the jigs often carries as high as 40 ozs. per ton, and most of the true silver minerals go into the slimes.

In such a case as this it is obviously necessary to treat the tailings from the concentration mill by some other process (*e.g.*, by chloridising roasting and hyposulphite lixiviation), provided that they are sufficiently rich to bear the cost of the operation, which is not always the case.

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* *Private communication*, A. L. Collins, Oct. 20, 1896.

† See part i., chap. iii., p. 36.

CHAPTER VIII.

RETORTING, MELTING AND ASSAYING SILVER BULLION.

Composition of Amalgam.—The pressed amalgam obtained by the amalgamation processes described in Chapters III. and IV. varies in composition only within narrow limits, the relative proportions of silver and mercury being affected rather by the nature of the ores than by the process adopted. Native silver ores always give a rich amalgam. Amalgam obtained by the *Patio* and *fondo* processes usually contains 20 to 22 per cent. of silver, that by the *Francke-Tina* process at Huanchaca[*] 16·6 per cent. of silver. Amalgam from the *pan* process, which is always much more base than that obtained by the other processes, yields a smaller proportion of silver in spite of its containing, to begin with, a smaller proportion of mercury. According to Eissler[†] seven parts of cupriferous and only four parts of plumbiferous amalgam are required to furnish one part of retorted bullion, though five parts of patio amalgam are required; this is in accordance with the respective atomic weights of copper, lead, and silver.

Retorting Amalgam.—The simplest method of retorting amalgam is that in use in out-of-the-way places in Mexico and S. America, by miners working on a very small scale, or for the small quantities of auriferous amalgam obtained by treating auriferous silver ores in the arrastra. An earthen water-bottle with a long neck is employed, into which the amalgam is rammed with a stick. The bottle is then inverted in a sheet-iron box or brazier, with its neck dipping below the surface of a vessel of water, and glowing charcoal is heaped above it. When no more mercury is seen to run, the bottle is broken and the cake of silver taken out. An old quicksilver flask with a short length of gaspipe screwed into the neck, is also sometimes used as a makeshift.

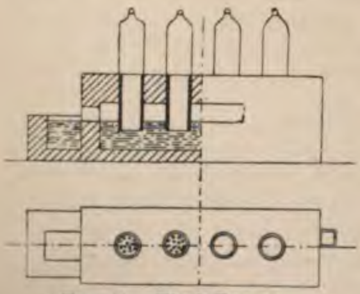

Fig. 46.—Flask Retort.

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[*] *E. and M. J.*, Dec. 28, 1895.

[†] *Met. of Silver*, p. 133.

The most common method of retorting at small reduction works in Mexico is shown in section and plan in Fig. 46.[*] A number of quicksilver flasks are taken, and the necks are cut off one-half of the number while the bottoms are cut out of the remainder. The former are built into a small brick arch in a vertical position, so that their lower ends dip into a tank of water. The flasks from which the bottoms have been cut are lined with paper, and the amalgam is then rammed into them in quantities of about 65 to 75 lbs. each. The stoppers are tightly screwed in and these flasks are then placed in position upon those which have been built in; a perforated plate is placed between each pair so as to prevent the amalgam from falling out, and the joints are luted with clay, each flask being also plastered with a thin layer of clay to protect it from the fire. A rough brick wall is then built round the upper flasks, a few embers are scattered round them to dry the clay, and the whole space is filled with glowing charcoal. Water is continually added to the tank beneath to replace that lost by evaporation, and if possible a current of water is allowed to circulate through it so as to keep it cool. There is not much danger of melting the amalgam unless the fire be allowed to get too hot, but the resulting retort silver usually contains about 1 per cent. of mercury. The operation usually lasts about four hours. Furnaces on this plan may contain as many as eight or ten retorts, in which case the total charge may be 500 to 700 lbs. of amalgam. In larger distillation furnaces on this plan the double flasks are often set into the hearth of a small reverberatory furnace; the heat is then much more even and more easily regulated, and the flasks last longer.

Capellina.—Formerly in almost all large Mexican and S. American reduction works the "*capellina*" or bell was exclusively used for retorting. The amalgam being first formed into a conical pile of little cakes with paper between, the bell (of copper, bronze, or iron) was let down over the pile and glowing charcoal heaped about it.[†] In Northern Mexico, however, this apparatus has been to a great extent replaced by the Californian retort described below, or by the above arrangement of flasks. A modern form of "capellina" used at *Potosi* (Bolivia) is shown in Fig. 47.[‡] A is a circular furnace lined with firebrick, built over an arched chamber, and provided with holes, B B, for admission of air and for raking out the ashes; C is the cast-iron "capellina," which may be raised when it becomes cracked by a chain hooked to the ring at the top; when in use it is permanently bolted to a cast-iron pipe, D, built into the arch.

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[*] Chism, *Trans. A.I.M.E.*, vol. xi., plate ii.

[†] *v.* Percy, *Metallurgy of Silver and Gold*, p. 627.

[‡] Egleston, *op. cit.*, p. 328, quoted from Rathbone, *Engineering*, vol. xxxviii., p. 174.

This pipe dips into water contained in an iron tank, E, supported by a cross-beam, F, resting on screw-jacks. The furnace is closed by a cast-iron cover, G, which is raised by means of a chain as required, and immediately below it is a ring of holes, H, for the escape of the products of combustion. Inside the "capellina" is a series of shelves supported by a stand of iron rod, which rests on the bottom of the water tank. After each operation the tank is lowered, together with its stand of shelves, and the sectors of spongy silver on each shelf replaced by similar sectors of hard amalgam, moulded into shape by a hydraulic press. The tank with its stand of amalgam is then lifted up into its place, and the fire replenished. The fuel used is dried llama dung, which costs about $9 (Bol.) per ton, and gives a steady smouldering fire. The loss of mercury in distillation varies from $\frac{1}{10}$ to $\frac{1}{4}$ per cent. when properly conducted, but may easily reach $\frac{1}{2}$ per cent. if carelessly done.

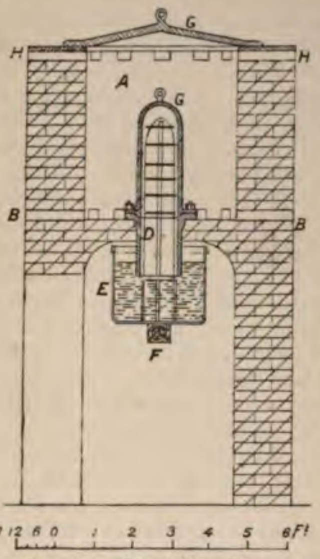

Fig. 47.—Fixed Capellina.

At the *Haciendas de Loreto** and other *Pachuca* reduction works, the capellina is provided with an iron "capote" to protect it. The charge is from 500 to 1500 lbs. of dry amalgam, which, after firing for eight hours, during which 6 cargas of wood are consumed, yields 22 per cent. by weight of retorted silver. If taken care of, and allowed to cool slowly, a capellina so arranged should last from two to five years.

Tube Retort.—At all silver mills in the United States, and at most of the larger ones in Mexico and S. America, the horizontal retort is employed. The construction of this is shown in Fig. 48 and needs no explanation. Dampers, not shown in the figure, distribute the heat evenly over the whole length of the retort, which is set in a firebrick firebox with cast-iron front, while the condensing tube passes out through a brick wall at the back. The bottom of the retort is covered with a clay wash, and occasionally the balls of amalgam are charged direct upon it. Generally, however, the amalgam is charged into little sheet-iron trays fitting the bottom of the retort, and about a foot to 18 inches long, with a partition in the centre; these are washed

* *Private notes*, 1897.

with lime or clay, or lined with several thicknesses of paper, to prevent the spongy silver from sticking. The retorts vary from 4 to 5 feet in length and 10 to 14 inches inside diameter, the metal being usually 1½ inches thick. The condenser is usually of the Liebig form, as figured, but sometimes consists of a mere inclined tube set in a long tank of water. A bladder is tied on the free end of the tube, after all the air has been expelled, to prevent danger of explosion through water being sucked back. The lid is carefully luted with wood ashes and salt or other mixture before being tightly clamped.

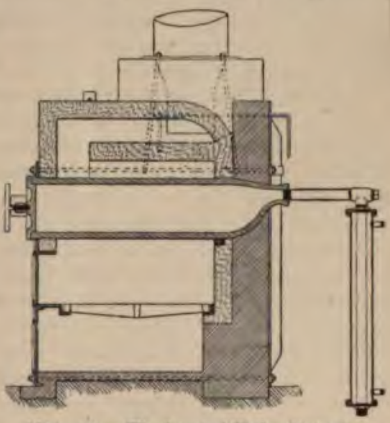

Fig. 48.—Horizontal Tube Retort.

The charge of one of these retorts is from 1000 to 2200 lbs. of amalgam, but it is found best never to fill them more than half full. The heat is increased gradually at first, most of the mercury coming off at a low temperature; but the last traces can only be driven off at a bright yellow heat, which causes distortion and sagging of the retort bottom. It is best to provide a few extra supports, either of cast or wrought iron, fitting the curve of the retort bottom, as those provided by the makers are rarely sufficient. The wear and tear, however, on the retort when it is attempted to distil off all the mercury is so great that it is preferable to stop when about 1 to 1½ per cent. is still left in the bullion. The process of distillation usually takes from ten to fourteen hours, and the consumption of fuel is 3½ to 6 lbs. of wood or 1½ lbs. of coal per lb. of retorted bullion produced. A retort should last for two hundred to three hundred operations if placed in suitable curved supports, turned round from time to time and not fired too fiercely. There is always some loss of quicksilver vapour on opening it, and to avoid this loss and the consequent danger of salivation, the retort has been exhausted by means of a steam jet in the condensing pipe at the *Lexington* mill,* the steam being condensed, together with the mercury, in a kind of "surface condenser." In this case there was no loss even on opening the retort hot, but it is usually better to allow the latter to cool off for, if possible, twelve hours before opening, and when this is done the common Liebig condenser is amply sufficient to condense the vapours.

* *Eng. and M. J.*, vol. xxxiv., p. 255.

Very base bullion is liable to "froth" in the retort, boil over the trays, and so cause great trouble in removing the spongy retort metal, besides danger of choking up the exit pipe with condensed volatile metals. Special care must be taken with such amalgam to increase the heat very gradually, which is indeed always preferable.

Retorting Cupriferous Amalgam.—When much copper is present a spongy mass, which is very rich in that metal, forms on top of the retort bullion, while poor in silver and brown from oxidation. This is particularly the case when old tailings are amalgamated with the addition of a large excess of copper sulphate, as described in the last chapter. At the *Lyon* mill* the charge for a retort was 1700 lbs. of amalgam, which, by raising the heat gradually, took fourteen hours to distil off, after which the retort was allowed to cool all night. Next morning, on opening, it was found to contain a shell of dense, compact, semi-fused, slightly reddish-white material called "white bullion," surmounted by a red-brown brittle and spongy mass known as "base bullion," which was readily chipped away from the underlying shell. For each 100 lbs. of amalgam taken, the average yield of retort bullion over a period of two years was 14·8 lbs., of which 3·1 lbs. were "white," and 11·7 lbs. "base" bullion. The former averaged during the same period 565 fine in silver and 0·4 in gold; the latter 37 fine in silver and 1·16 in gold. The concentration of gold in the upper part of the mass is somewhat remarkable, in view of the fact that in pigs of lead bullion it seems to accompany the silver, and is concentrated towards the bottom; it affords another instance of the great mutual affinity of gold and copper exemplified in the gold-copper crusts of the Parkes process† and in the "smelting for bottoms" of the Argo matting process.‡ The liquation of silver to the bottom of the mass is only to be anticipated, as its melting point is 100° C. below that of copper. The mass was taken out in one lump, and samples taken by chiselling slices clean across it before separating the two kinds of bullion.

Melting and Refining Retort Bullion.—Retort silver from the *Patio* process is very pure, often running 998 or 999 fine and seldom going below 995. It therefore requires no refining, but is simply melted (usually in plumbago crucibles) without any fluxes, and poured into ingot moulds.

The ordinary **wind melting furnace** requires neither figure nor description, being simply an enlarged example of the common crucible assay furnace with which all students of metallurgy are familiar. Formerly large iron crucibles holding from 150 to 1500 lbs. each, and handled by small cranes were very widely

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* Hodges, *Trans. A.I.M.E.*, vol. xiv., p. 735.

† *v.* Part i., chap. xvii.

‡ Part ii., chap. xvii.

employed. At *Pasco* (Peru)* 150-lb. crucibles are in use, and last about forty melts.

At the *Haciendas de Loreto* (Pachuca) † the large iron crucibles hold about 1500 lbs. of molten silver (twenty-five bars of 30 kilos. each), which takes six hours to melt down completely, being, of course, charged in gradually. When all is melted the crucible is not lifted, but its contents are dipped out into moulds by means of iron ladles, an operation which takes forty minutes. The crucibles cost $350 to $500 each, but are very economical, lasting on an average for twenty-eight melts or seven hundred bars.

Plumbago crucibles holding from 1 to 2 gallons and pouring 1000 to 2000 ozs. are most commonly used. Sprouting is prevented by putting a little charcoal powder or chaff into the mould before pouring, and by covering it immediately so as to let it cool slowly.

The Boss melting furnace for bullion which requires no refining is shown in Figs. 49 and 50. It consists of a double-tuyered brazier-shaped forge, with a cast-iron pan lined with a mixture of fireclay and boneash about 2 inches thick; the tuyeres at the back pass through a water-jacket. A fire being lighted and the pan and brazier filled with charcoal, the blast is let on; and as soon as the whole mass is thoroughly glowing, lumps of retort bullion are gradually charged at the top, together with charcoal to supply the waste. When sufficient metal has been melted down to give a bar, the discharge spout is tapped with a steel rod direct into the ingot mould and stopped again with a boneash plug, a succession of bars being then melted and cast at intervals of fifteen to twenty minutes only. It is claimed for this furnace, that the flame being reducing there is less loss in melting than with a reverberatory. It is certainly more convenient and economical of fuel owing to the localisation of the heat, but it seems likely that the violent draught coupled with the rapid expulsion of whatever quicksilver might be left in the bullion, would cause loss by volatilisation considerably greater than in the reverberatory.

Retort silver from the *Kröhnke* process (Chili) is generally less pure, containing in addition to copper, arsenic from the ores. This is removed by stirring on the hearth of a small reverberatory furnace, by which means it combines with the iron of the tools to form a speiss-slag which can be skimmed. The melted silver resulting is 980 fine.

Retort silver from the *Francke-Tina* process would be only about 980 fine, but that the amalgam before retorting is refined as already described (Chap. IV.), which brings it up to 990 fine, and to 996 after refining in charges in 5500 lbs. at a time on

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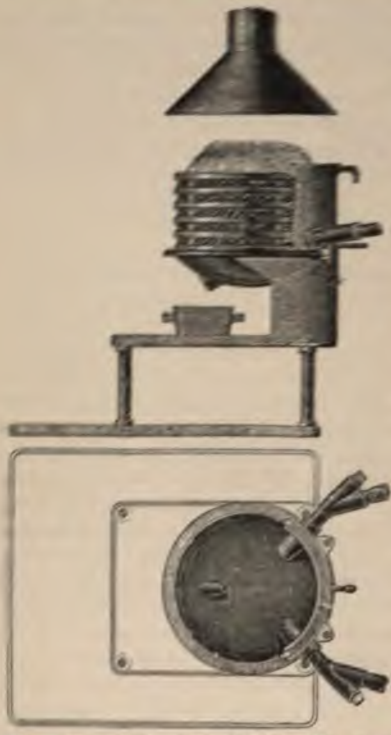
* Pfordte, *Trans. A.I.M.E.*, vol. xxiv., p. 119.

† *Private notes.*

the hearth of a reverberatory furnace, the consumption of coal in which operation is proportional to that of the silver refined.

The amalgam from the modified tinas with iron mullers used at *Playa Blanca*, gives a retort metal of only 940 fine, the impurity being copper, which is removed by cupellation, and recovered by smelting the resulting litharge and cupel bottoms.



Figs. 49 and 50.—Boss Melting Furnace (Elevation and Plan).

Retort silver from the *pan* process may vary, according to the nature of the ores and of the manipulation, from less than 200 to over 970 fine, but generally runs from 700 to 900.

At the *Ontario* mill the retort bullion (which is 500 to 600 fine) is melted down upon a small gas-fired reverberatory hearth, built of fireclay and pounded firebrick mixed with borax-water, and resting upon a layer of Portland cement in a wrought-iron pan. The hearth is 3 ft. 6 ins. × 2 ft. 9 ins. × 6 ins. deep, and it takes four to six hours to melt down the first charge of 1400 lbs., which when molten is cast into bars of about 100 lbs. apiece. Subsequent charges in the hot furnace are melted down at intervals of about three hours each. The total cost including fuel, borax, and repairs is under 37 cents (say 1s. 6½d.) per 1000 ozs. of bullion melted.

On the *Comstock* the retort bullion from ore treatment is from 930 to 960 fine, and is in most cases simply melted down in large plumbago crucibles in a wind furnace, without any attempt at refining, a little borax being used as flux. Each crucible pours a single ingot of 80 to 100 lbs., but as the bullion is bulky only 30 to 40 lbs. are packed in the crucible at first, the remainder being added afterwards with a pair of long tongs as in all crucible melting.

When it is desired to slightly refine nearly pure silver bullion, nitre is added together with the borax. Fusion of the charge in a well-built furnace should take about one and a-half hours; the bath is then skimmed, and more nitre and borax thrown on till the metal is pure enough to pour. Just before pouring the pot is skimmed, stirred with a red-hot iron or plumbago rod, and in some places a sample is dipped out in a small iron cup and poured into water. The molten metal is then poured into a warmed oiled mould (for 1000 ozs., 11 ins. long × 4½ ins. wide × 4 ins. deep), which is immediately covered with another hot mould to prevent too rapid cooling.* As soon as the interior of the ingot is quite set, the mould is inverted and the ingot plunged into a vessel of water (which in the case of somewhat base bullion should have a little sulphuric acid added to it), by which it acquires a brilliant lustrous surface. It is then chipped free from any adhering slag, trimmed up if necessary, and numbered with steel punches. When the bullion contains lead, bone-ash is added in refining together with the nitre and borax, so as to absorb the litharge and prevent it from "cutting" the crucible. When much nitre is to be used, it should always be added in the centre of a ring of bone-ash which protects the pot.

When melting very base, plumbiferous, and ferruginous bullion from tailings, Eissler † found it advisable to "liquate" out most of the lead and silver, and to take up the residual sponge containing most of the iron and copper, mix it with the skimmings from the lead pigs, and melt it down with sulphur at a white heat to form an argentiferous matte which was sold to lead smelters.

Refining Very Base Cupriferous Bullion.‡—The tailings bullion on the Comstock consisted, as already mentioned, of two parts—a "white bullion" 565 fine in silver and 0·4 in gold, and a "base bullion" which was mostly copper and averaged 37 fine in Ag and 1·16 fine in Au. The base bullion being brittle could be readily crushed and roasted and dissolved in sulphuric acid; the white bullion being dense and metallic could neither be crushed nor roasted, and it was necessary to "matt" it first. The operations (except that of matting) were identical on the two kinds of bullion, but they were kept separate throughout; the treatment being as follows:—

(1) **Preliminary calcination** (12 hours) to loosen up the bullion and partially oxidise it, for which purpose it was simply charged into the roasting furnace at night after drawing the roasting

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* Silver which has been refined with nitre is always more inclined to sprout than when no nitre has been used. The remarks in part i., chap. xviii., on the pouring of silver bullion at Port Pirie should be referred to in this connection.

† *Metallurgy of Silver*, 1891, p. 314.

‡ Hodges, *Trans. A.I.M.E.*, vol. xiv., p. 731, where drawings are given of the plant employed.

charge, so as to utilise the waste heat. The gain in weight owing to oxidation was 2·5 per cent. on the white and 17·4 per cent. on the base bullion.

(2) **Matting** of the white bullion together with metallic lumps from the crusher, assay bars, &c., in a 3-foot parting-kettle with a cast-iron cover, which was luted and bolted on. About 450 lbs. of bullion and lumps, together with 18 to 20 per cent. sulphur, were charged in layers, with thin refuse wood between in order to facilitate removal. The kettle was fired with refuse wood for four to five hours, and left till next day, when the cakes of matted bullion were broken up with hammers and sent to the crusher.

(3) **Crushing** in a 3 ft. 6 in.-diam. Chilian mill through a 20-mesh screen, the capacity being about 100 lbs. of sulphurised white and 200 lbs. of calcined base bullion per hour, and the wear and tear only 0·07 per cent. on the weight crushed, or, say, 1½ lbs. per ton. The percentage of uncrushed lumps was 0·55 per cent. on the base, and 6·86 per cent. on the white bullion. All lumps were returned to the matting-kettle.

(4) **Roasting to Sulphate.**—The furnace used was a small reverberatory, the hearth of which was formed of a cast-iron pan 7 ft. × 4 ft. 6 ins. and 1½ ins. deep, made in two pieces bolted together through the cheeks, the metal being 1½ inches thick. The fireplace was 4 ft. 6 ins. × 16 ins. and burned wood, the chimney being 9 ins. × 15 ins. and 24 ft. high. The whole cost of the furnace was £120. It treated charges of 450 lbs. of base bullion in ten hours, or, when roasting continuously, in six to eight hours, with a fuel consumption of one-fifth cord of wood per charge. The bullion gained 6½ per cent. more in weight by roasting, and was passed through a 10-mesh sieve yielding 1·3 per cent. of lumps. Of matted white bullion 300 lbs. were treated in six to seven hours, and on sifting through an 8-mesh screen gave an average of 17½ per cent. of unroasted lumps. The lumps in each case accumulated until there was enough for a separate charge, when they were re-roasted. The average sulphatisation reached was 60 per cent. of the silver, the rest remaining in the metallic condition.

(5) **Dissolving in Chamber Sulphuric Acid.**—This was performed in tubs 6 ft. diameter and 4 ft. deep, with 3-inch staves and flat iron hoops 2¼ ins. × ⅜ in. The bottom of the tubs, and up to 12 inches above the bottom, was lined with 14-lb. lead, and the remainder with 8-lb. lead; a ¾-inch lead steam pipe was fixed in the tub as well as water and acid pipes, and the cost of each tub was £60. The normal charge of each tub was 1200 lbs. of base, or 1000 lbs. of white, bullion, and the consumption of acid was 3 per cent. more than that required by theory to form $CuSO_4$ with the copper present, a small amount being consumed by metallic silver, part of which went into solution. The tubs being filled with acid and brought to the boiling point, the roasted

ullion was fed in slowly, while the bath was stirred vigorously vith a wooden paddle until the residue looked white; when it was settled for four hours and the solution (of 40° to 42° B.) was syphoned into the precipitating tanks. The residue, after washing with dilute acid and then with hot water till the washings showed no trace of silver, was dried in iron pans and melted in plumbago crucibles to doré bullion, 950 fine in Ag and 17 in Au—that from the base bullion often running up to 25 and even 30 in gold.

(6) **Precipitating the Silver on Copper Bars.**—The tanks used were old mill settlers, 10 feet diameter, lined with lead, and provided with steam pipes for heating. Precipitation took four to five hours at nearly boiling heat with occasional stirring, and the solutions at a specific gravity of 36° to 37° B. were syphoned into the crystallising vats.

(7) **Crystallising out the Bluestone.**—The crystallisers were lead-lined wooden vats, 7 ft. long × 3 ft. wide at top × 2 ft. high, with flaring sides of plank strongly bolted together. As each crystalliser was filled it was covered with planks to prevent too rapid cooling, which would produce small crystals. The crystals were washed, dried, and packed in barrels, the mother liquors of 23° to 25° B. were concentrated and again crystallised, he acid liquors being used over again. Wash waters and second nother liquors under 15° B. and containing very little acid were iluted and run through scrap-iron vats to precipitate the copper, hich was utilised in the silver precipitation.

Cost of the process on 89,394 lbs. retorted bullion (in United ates currency).

	Wages.	Fuel.	Acid.	Sulphur	Sundries.	Total.	Per lb
	Dols.	Dols.	Dols.	Dols.	Dols.	Dols.	Cents.
g, crushing, atting .	1629.96	676.14	...	60.94	...	2367.04	2·65
ng and con- ting, . .	2262.75	2488.25	4038.15	...	...	8789.15	9·83
sing and g, . .	847.12	...	...	...	115.20	962.32	1·07
. .	319.65	...	...	...	243.22	562.87	0·63
xpenses, .	2951.19	...	...	...	...	2951.19	3·30
. .	8010.67	3164.39	4038.15	60.94	358.42	15,632.57	17·48

oss of the precious metals, as shown by careful assaying pling, was under 0·1 per cent. of the silver and 0·8 per he gold. Calculating the whole of the expenses on to stone produced, and charging the refinery at market th the copper contained in the bullion, the total expens of the bluestone produced ready packed for market was 7·65 cents per lb.; but if no allowance be made for the copper contained in the bullion the total cost of the bluestone produced was less than its current selling price, so that the nett cost of refining under the above conditions was nil.

It may appear that undue prominence has been given to this wet method of refining; but an almost identical process was adopted and highly recommended by Stetefeldt for refining lixiviation sulphides,[*] and a modification of it may often prove useful for working up bye-products containing silver and copper, where acid is not too dear.

Assaying of Silver Bullion.—The cupellation of silver being attended by such high volatilisation and absorption losses it will be readily understood that wet methods are preferable and are, indeed, now universally adopted.

Practically speaking, only three methods are at all used—viz., (1) The *gravimetric* method, estimating as AgCl, in use at the Indian mints; (2) the *Gay Lussac* volumetric method with the use of standard normal and decinormal solutions of salt, which is employed at all British mints and assay offices, and at most of those in the United States; and (3) the *Volhard* volumetric method, in which a standard solution of potassium sulphocyanide with a ferric salt (iron alum) as indicator is adopted.

The latter method has been decried a good deal as inaccurate, but is capable, in practised hands, of giving very accurate results in less time than the Gay Lussac method; it has been accordingly adopted by the Broken Hill Proprietary and by other large refineries. For information as to the special precautions required with this method the student may consult an article by Torrey,[†] and for those necessary with the ordinary Gay Lussac method a recent article by Whitehead and Ulke [‡] in the same journal. Other detailed descriptions of the manipulations involved in both methods will be found in the works mentioned in the footnote.[§]

What would seem to be an improvement is the combination method described by Knorr,[||] using the normal salt solution of the Gay Lussac and the decinormal sulphocyanide solution of the Volhard methods. The very tedious shaking of the Gay Lussac method is thus obviated, and the results are at least as accurate.

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[*] *Trans. A.I.M.E.*, vol. xx., p. 37; vol. xxi., p. 286; vol. xxiv., p. 221.

[†] *Eng. and Min. Journ.*, Jan. 6, 1883.

[‡] *Ibid.*, Feb. 26, 1898.

[§] Percy, *Metallurgy of Silver and Gold*, part i., pp. 283-292 (Gay Lussac), p. 293 (Indian mint gravimetric), p. 294 (Volhard's method). Furman, *Manual of Practical Assaying*, 1st ed., pp. 240-244. Balling, *Manuel de l'Art de l'Essayeur*, pp. 389-410.

[||] *Journ. Amer. Chem. Soc.*, Oct., 1897, vol. xix., No. 10, p. 814; also abstract in *Eng. and Min. Journ.*, Oct. 30, 1897.

CHAPTER IX.

CHLORIDISING-ROASTING.

Drying and Crushing.—Chloridising-roasting is, generally speaking, a necessary preliminary to the treatment by wet processes (either amalgamation or lixiviation) of all those silver ores in which that metal occurs as a sulphide, sulphantimonide, or sulpharsenide, as well as of those in which silver sulphide occurs not merely intermingled but isomorphously associated with galena, blende, or other sulphide.

Ore for chloridising-roasting requires to be reduced so as to pass through a mesh of between 16 and 40 holes to the inch before it can be properly chloridised. Pyritic ores, and others which decrepitate on heating, will chloridise well if crushed only to 16 mesh, and when the silver-bearing mineral is brittle even a coarser mesh will sometimes serve; but ores which are dense and do not decrepitate, and especially those which consist largely of blende or galena, require to be crushed to 40 mesh in order to give good results. At *San Francisco del Oro*, O. Hofmann found that a heavy galena ore was chloridised satisfactorily when crushed through a 40-mesh screen, in which condition 90·5 per cent. passed a 90-mesh sieve; while when crushed through a 20 mesh, although 67·2 per cent. of the pulp was still fine enough to pass the 90 mesh, the percentage of chlorination was reduced by no less than 27 per cent.

The preliminary operations of drying and crushing have been already discussed in Chapter VI. (*q. v.*). The choice of crushing machinery for a given plant should be governed entirely by the degree of fineness to which it is requisite to reduce the ore prior to roasting. If a 12 to 20 mesh will do, *rolls* or *Chilian mills* are to be preferred if the ore is to be leached, as they give a more granular pulp with a smaller proportion of slime. Where, however, the ore will not chloridise well unless crushed through a 30 or 40 mesh, *stamps* must be employed, as the capacity of the other machines is very small for such fine crushing and the amount of screen "returns" is enormous.

Chloridisation of Sulphides.—The chloridising-roast aims at the conversion of as much as possible of the silver present into chloride, together with as little as possible of other metals, the agency employed being common salt, which at a high temperature is decomposed by sulphates or by silica, evolving chlorine with which the silver combines. It has been already seen[*] that at a temperature of bright redness metallic silver readily and completely decomposes salt, becoming converted into chloride, a large part of which volatilises. It is necessary to diminish this volatilisation loss by working at as low a temperature as possible; hence other reactions must be sought. With ores which contain from 3 to 8 per cent. of *metallic sulphides* (especially of pyrites) there is no difficulty, as by roasting at a low temperature they are converted into sulphates, the sulphuric acid of which being liberated by raising the heat decomposes the salt and sets free chlorine. Lead and zinc sulphates, however, neither decompose salt so readily as do those of copper and iron, nor are they so easily formed, and when an ore consists principally of galena and blende with fahlerz, as at the *Silver King* (Ariz.), *Huanchaca* (Boliv.) and many other places, roasting becomes very difficult and the losses are largely increased. In the case of ores which contain only a very small percentage of sulphides, especially if there is much calcite in the gangue, it is usual to add a small quantity (1 to 4 per cent.) of pyrites before roasting in order to form sufficient sulphates to act upon the salt. The addition of pyrites to ores containing sulphantimonides and sulpharsenides of silver is also advantageous in another way, for it assists the expulsion of antimony and arsenic in the cooler part of the furnace as sulphides,[†] in which form they appear to carry off very much less silver than when they are volatilised as oxides or chlorides. In place of pyrites, *sulphur* or *copperas* (ferrous sulphate) may be used; but although the latter has been termed by some writers "a cheap substitute for pyrites," there are but few silver-mining districts where pyrites would not be both more readily obtainable and cheaper. When the ore contains more than about 8 per cent. of sulphur, decomposition of the salt takes place so early that large quantities of base-metal chlorides are formed, and therefore, with such ores, it is advisable to burn off most of the sulphur by an oxidising roast before adding salt.

In the case of ores which contain *oxide of manganese* chlorine is also evolved at a low red heat, but the reactions which take place are somewhat obscure. According to Clark[‡] admixture of oxidised manganese ores diminishes the loss of silver by volatilisation in the roasting of ores containing much zinc.

Chloridisation without Sulphur.—With ores already roasted sweet and consisting chiefly of ferric and cupric oxides, chloridisation can be effected rapidly by stirring in a mixture of *fine sand* and salt moistened with water, which at a red heat yields sodium silicate and HCl. This method is, however, out of the question except with ores free from zinc, lead, antimony, and

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[*] Chap. i., p. 12.

[†] *v.* also part i., chap. vi., where this and other reactions of the ordinary roasting process are referred to.

[‡] *Trans. A.I.M.E.*, vol. xvii., p. 775.

other volatile metals, as the temperature required for the reactions is so high that the volatilisation loss of silver would be very great in presence of such constituents.

The active chloridising agent, whether free Cl or HCl, acts vigorously, not only upon metallic silver, but also upon silver combined as sulphide in isomorphous admixture with other metals, and upon sulphantimonides and sulpharsenides.

Chloridisation on the Cooling Floor ("*Heap chlorination*").—In many cases the ore as drawn from the furnace still retains a large proportion of its silver in an insoluble form unaffected by sodium hyposulphite and presumably non-amalgamable.[*] It is usual with most ores to allow the roasted ore to lie in heaps on the cooling floor for periods of from twenty-four to sixty hours, which frequently increases the chloridisation 10 to 40 per cent., while by subsequent sprinkling sufficient water over the cooled heaps to thoroughly moisten them an additional chlorination of 3 to 6 per cent. is often reached. By these means the "percentage of chlorination" may be increased from 10 to 45 per cent., and in some cases this slow chloridisation carried out on the cooling floor without any volatilisation loss can be almost entirely relied upon, in place of that effected in the furnace quickly but at the expense of a considerable loss of silver. At the *Ontario* mill the "percentage of chlorination" is increased on the cooling floor from 3 to 8 per cent. only, at the *Lexington* mill the increase is 12 to 15 per cent., at *Cusihuiriachic* 26 per cent., at *San Francisco del Oro* 13 per cent., and at the *Aspen* mill 26 per cent. as shown by hypo. test, and 11 per cent. by actual extraction. The more thoroughly chlorination is effected in the furnace the less is the increase shown by lying on the cooling floor.

Although, however, "wetting down" some ores, especially those containing copper, increases the percentage of chlorination, other ores are not affected by moistening whether during cooling or afterwards; while with most ores wetting down *while hot* seriously affects the percentage of chloridisation (Cusi, Yedras, Sombrerete, and Lake Valley).[†] This is particularly noticeable in the case of ores containing much lime or zinc, but even when neither is present there is a decidedly injurious effect—due no doubt to the action of steam upon AgCl. It is always best not to wet down till the ore is fairly cool, and not to leave it long in a moist condition unless it contain a considerable amount of copper and not much zinc, for copper chloride assists the formation of AgCl while zinc sulphide decomposes it.

The reactions which take place in this "heap chlorination" are various. Base-metal chlorides (especially those of copper) no

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[*] The method of ascertaining the proportion of silver which has been converted into chloride is described in chap. vi.

[†] Daggett, *Trans. A.I.M.E.*, vol. xvi., p. 389.

doubt react upon insoluble and undecomposed silver sulphide, converting it into chloride, but this reaction is strongest after wetting down. While still red hot the chief action is probably the formation of SO_3, through slow oxidation of undecomposed metallic sulphides producing SO_2 which is then further oxidised to SO_3 in contact with the higher oxides of iron, manganese, and copper present in the heap; this SO_3 then liberates chlorine from unaltered salt, as pointed out by Stetefeldt. The necessity for heap chlorination is greater the shorter the time the ore remains in the furnace; hence it is most necessary in the case of ores roasted in a Stetefeldt furnace.

Influence of Various Substances on Chloridisation. — *Lime* appears to exercise an unfavourable influence on chloridisation, and ores which contain calcite and but little heavy sulphides are usually roasted with considerable additions of pyrites so as to convert most of the lime into sulphate. The Aspen ores, for example, which contain 11 per cent. CaO and 4 per cent. MgO, require additions of pyrites sufficient to bring up the total S contents (irrespective of $BaSO_4$, which remains inert) to 8 per cent. The evil influence of lime, however, is not felt so much in the furnace as on the cooling floor, where, especially if the ore be wetted down, the caustic lime acts powerfully on the silver chloride already formed, reducing it to metallic silver. The presence of much calcite in an ore is, therefore, incompatible with that full development of heap chlorination which is so valuable in other cases, and such ores should be treated as soon as sufficiently cool to handle, especially if they are to be leached. Both *lime* and *magnesia* are disadvantageous in another way, since their chlorides, being distinctly volatile, may help to carry off silver chloride.

Cupric chloride has a very beneficial effect upon the process both in the furnace and on the cooling floor, but it is important to convert as little as possible of the base metals other than copper into chlorides, because these other chlorides are equally objectionable in amalgamation and in lixiviation. The *iron* present, therefore, should be converted as fully as possible into ferric oxide, *zinc* into oxide and basic sulphate, *lead* into sulphate, *arsenic* and *antimony* into volatile oxides and chlorides, and *copper* partly into oxide and partly into chloride. These objects are attained more perfectly on heavy sulphide ores when an oxidising roast precedes the addition of salt, and, therefore, both on this account and because of the lower volatilisation loss, much more perfect results are usually obtained in hand furnaces where the salt can be added at any required stage of the process.

Furnaces Employed. — The various furnaces in use for chloridising-roasting may be classified as follows:—(1) Reverberatories worked by hand; (2) mechanical reverberatories; (3) revolving cylinders; and (4) shaft furnaces.

Hand Reverberatories—*Three- and Four-Hearth Furnaces.*—The construction of reverberatory roasting furnaces has been already dealt with in Part I., Chapter VI.; the long three- and four-hearth furnaces there described are equally well adapted to chloridising-roasting. With anything like a high percentage of sulphur, furnaces for chloridising should be built longer than for simple roasting as it is of vital importance to keep the temperature low at first, in order to avoid sintering, and to delay the volatilisation of salt till nearly all the sulphur has been expelled. This requires long furnaces containing four or even five hearths, 12 feet long. Owing to the low temperature employed, firebrick is only required for the interior lining of the firebox and bridge, and for that portion of the arch which covers them. Both bridge and arch should be perforated to admit a separate supply of air for oxidation, previously heated by passage through the firebox walls, which are purposely built hollow. This provision is the more important when wood fuel is employed.

Eight four-hearth furnaces are in use at *Yedras*,* each 48 feet long by 10 feet wide, with working doors along one side only. The hearths are arranged under a horizontal arch, with steps of 3 inches from one to the next. In these furnaces the steep slope of the ground permitted the construction of a large vaulted discharge chamber or bin underneath the firebox end of the furnace, in which the ore gradually cools off and completes its chlorination—an arrangement decidedly to be recommended where the configuration of the ground is suitable.

Superposed Hearths.—The employment of reverberatories with superposed hearths offers the advantage of some economy in fuel. Of this type are the furnaces erected at *San Francisco del Oro* (Chihuahua, Mexico) by Hofmann.† The upper hearth with an area of 210 square feet was used exclusively for oxidising-roasting, and held two charges at a time of 1 ton each. The area of the lower hearth was 220 square feet, and it also held two charges, 4 per cent. salt being added to each charge as it was dropped from the upper to the lower hearth. Every two and a-half to three hours a charge was finished, and all the others were pushed forward a step to admit a fresh charge on the top hearth; the total output of each furnace was therefore from 8 to 10 tons per day, and each charge remained in the furnace ten to twelve hours, one-half the time being spent in oxidising and the remainder in chloridising. The ore treated in this furnace contained 11 per cent. Pb, 25 per cent. Zn, 6 per cent. Fe, 21 per cent. S, and small proportions of Cu, Sb, and other metals in a gangue of quartz and calcite. The loss of silver in roasting

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* Clemes, *Proc. Inst. Civ. Eng.*, vol. cxxv., p. 95.

† *E. and M. J.*, Feb. 23, 1889. For details of newer hand-worked reverberatories erected by Mr. Hofmann for this work *v.* "Lixiviation at Sombrerete" in chap. xii.

averaged from 10 to 13 per cent., most of which took place at the end of the oxidising roast before the addition of salt, and even this loss was increased directly the temperature was allowed to rise above a dull red. According to the chlorination assay only 59 per cent. of the silver present was soluble in hyposulphite as the charge was drawn from the furnace, of which 25 per cent was as chloride, the remainder being antimoniate. Owing to the low temperature employed the consumption of fuel was small, being only one cord of wood per day for each furnace, or about 20 per cent. by weight of the ore roasted. The cost of roasting is given in Table VIII., pp. 164-5.

Reverberatory furnaces seem to be exclusively used in Peru and Bolivia for the chloridising-roasting of ores as a preliminary to tina amalgamation; the furnaces used at *Potosi* and *Oruro* have been briefly described in Chapter IV.

At the *Playa Blanca** Works of the Huanchaca Co., eleven gas-fired reverberatories are used, each of the three-hearth type, 49 feet long by 15 feet wide. Each is worked by four men on each twelve-hour shift, paid by piecework. The average charge is 1400 kg. (3080 lbs.), and five to eight of these charges are put through in twenty-four hours, making the daily capacity of each furnace 7 to 12 tons. The gas producers are of the Taylor pattern, six in number, and 6 feet diameter by 15 feet high; the pressure of air to the producers is 2½ inches of water, that of the gas near the producers ⅜ inch, and at the end of the long pipe line near the furnace ⅛ inch of water. Using very poor quality Chilian coal the consumption averages about 14 per cent. by weight of the ore roasted, which is not bad considering the length of the pipe to the furnaces.

At *Kosaka* (Japan)† an earthy ore containing 2½ per cent. S and 8½ ozs. Ag per ton is dried in a shelf drier and roasted with salt in long three-hearth reverberatories as a preliminary to lixiviation. Each hearth is 9 feet long by 12 feet wide and contains a charge of 1700 lbs., which is only one hour passing through the three hearths with constant stirring, so that the capacity of the furnace is about 50 tons per day. The back hearth is kept dark on account of the continual absorption of heat by cold charges; the front or finishing hearth is kept at a bright red. The ore is mixed with 4 per cent. salt and a little iron pyrites, and is chloridised to an actual extraction of 84 per cent. on the roasted ore, or 78 per cent. on the raw ore, allowing for a loss of 7 per cent. by volatilisation. Further data are given in Table VIII.

The chloridising-roasting of low grade copper ores (burnt pyrites) preparatory to the extraction of their silver contents by the Claudet process is conducted in stationary muffle or rever-

* *E. and M. J.*, Dec. 28, 1895.

† Kuwabara, *S.M.Q.*, vol. xv., p. 364.

beratory furnaces, or in reverberatories with circular revolving hearths, the percentage of salt used being from 7½ to 10 per cent. As the principal object in this case is the extraction of copper the temperature is kept lower than in the roasting of silver ores. At the *Bede Metal Works* Gibb revolving hearth furnaces are used; at those of the *Tharsis Co.*, and in most of the German pyrites works, large muffle furnaces are preferred, as permitting more perfect utilisation of the chlorine and sulphuric acid fumes in the manufacture of alkali. For details of these furnaces, as well as of the subsequent lixiviation, the student may refer to standard treatises on the metallurgy of copper.*

Where labour is cheap, and the workmen can be easily taught, there can be no doubt of the advantages of hand reverberatories, in which the necessary salt can be added at any given stage of the process. The roasting operation is, however, one of some delicacy, and requires a large amount of labour which must be of a fairly-skilled character. Under North American and Australian conditions, therefore, where labour in mining districts is for the most part unskilled and always very dear, it is preferable to adopt one or other of the types of mechanical furnace in which adjustments can be made once for all by the superintendent or foreman, after carefully experimenting with each particular class of ore, and where subsequent results are much less dependent upon the care and attention of the workmen.

Mechanical Reverberatories.—Several furnaces of this type have been used for chloridising-roasting, notably the Ropp, Pearce, and O'Hara, for particulars of which *v.* Part I., Chapter VI.; but no data as to performance have been published. Like the hand furnaces, all these furnaces permit of the addition of salt at any required stage of the process. A Brown-Allen-O'Hara furnace in use at the *Cortez* mill (Nevada) is said to perfectly roast and chloridise 30 tons of ore per day. This is a double-hearth furnace; the upper hearth is used for roasting and the lower for chloridising.

Revolving Cylinders.—There are, as already stated,† two types of these—viz., the intermittent, with horizontal axis and partially closed ends, and the continuous, with inclined axis and open ends. To the first belong the *Brückner* and *Hofmann*, and to the second the *Oxland-Hocking* and *Howell-White* furnaces.

The Brückner Cylinder.—This furnace, a modification of the old black-ash barrel, is shown in Figs. 51 and 52.‡ It consists, in brief, of a somewhat barrel-shaped wrought-iron cylinder, lined with firebrick or sometimes with good red brick, and provided with two chilled cast-iron friction rings, *b*, resting upon

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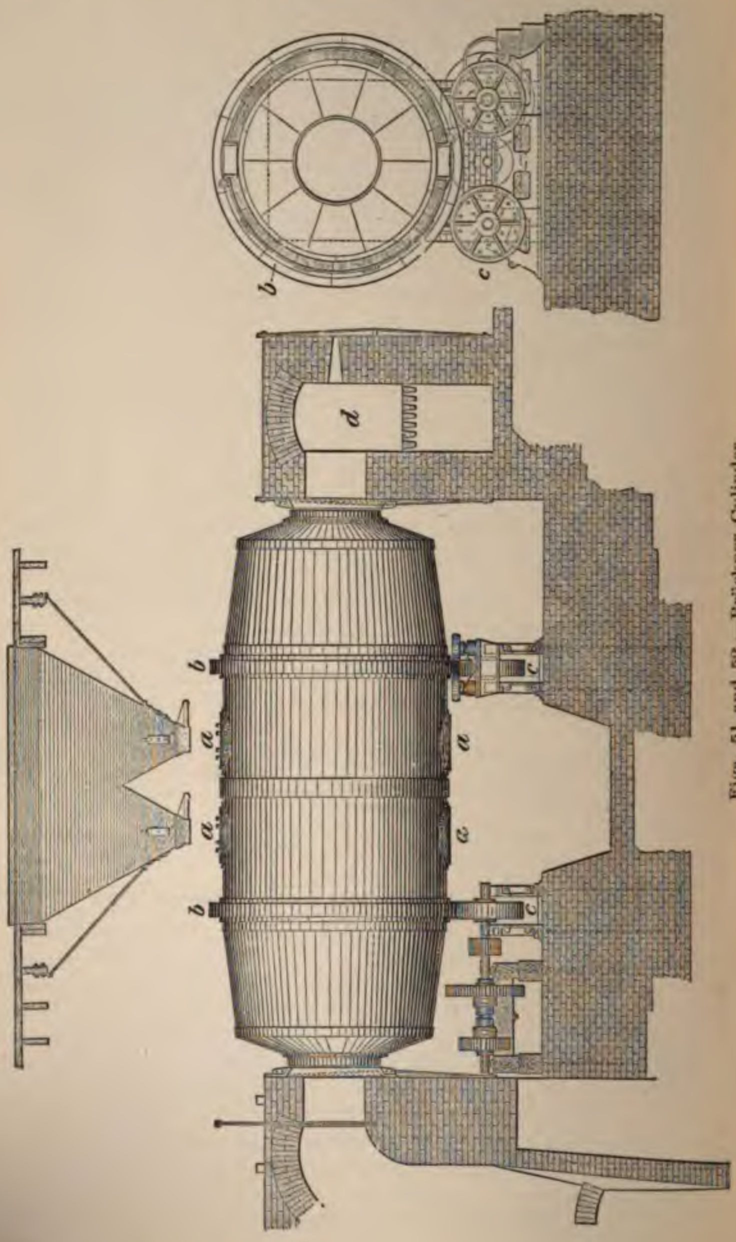
* Also to Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., pp. 223-249.

† Part ii., chap. vi.

‡ From Messrs. Fraser & Chalmers' catalogue.



Figs. 51 and 52.—Brückner Cylinder.

four chilled iron rollers, *c*, by means of which the cylinder is rotated. The ends of the cylinder are partly closed, leaving openings only about 2 feet in diameter, and in the central portion are four openings closed by hinged doors in pairs opposite each other, two being for charging and two for discharging. From the doors to the openings in the throat, the firebrick lining of the cylinder is made conical, which greatly assists the mixing of the charge and the exposure of fresh faces to oxidation. The cylinder is connected with a fireplace at one end, and with a series of dust-chambers at the other end. The earlier cylinders were only 12 ft. × 6 ft.; but the later cylinders, such as those in use at the General Custer Mill, Idaho, and figured above, are all 18 ft. × 7 ft. diameter. The principle of the intermittent revolving cylinders would seem to be inferior to that of the continuous cylinders for simple oxidation, but the advantage which they possess for chloridising-roasting is that a charge can be left in them until the result of a test proves it to be sufficiently roasted. This is attended, however, by a great disadvantage—namely, that the continuous rolling motion of the charge tends (especially in the case of ores containing calcite and galena) to form hard balls in the ore, varying in size from the finest gravel up to that of a man's head. This difficulty became so serious at the *Silver King* (Ariz.) and *Yedras* (Sinaloa) mills that the furnaces had to be replaced by hand furnaces, as the balls proved almost impervious to solutions. At the latter place the percentage of extraction on 60 ozs. ore with 7 per cent. salt was only 51 per cent., whereas on the same ore roasted in hand reverberatories it was 72 per cent.* The consumption of wood may vary from $\frac{3}{10}$ to $\frac{3}{4}$ of a cord per ton of ore, or, say, 50 to 100 per cent. of the weight of the latter. The weight of charge treated in the 12 × 6 ft. cylinders was 2 to 4 tons, but the large 18 × 7 ft. cylinders take 6 to 8 ton charges. As the time taken in roasting and chloridising varies from five to twenty-four hours, the output of the small furnace is 3 to 10 tons, and of the large furnace 8 to 28 tons per day, according to the amount of sulphur present. The lower figures, however, refer only to very pyritic ores, and it may be said that with ordinary silver ores which are to be chloridised, a small furnace will treat 6 to 10, and a large furnace 15 to 20 tons per day. The cost of a pair of large cylinders erected ready for work may vary from £1800 to £2250. Brückner cylinders are in use at a few mills in the U.S. and Mexico, and some data referring to their performance at the *Niederland* mill will be found in Table VIII.

The *Hofmann* furnace resembles the Brückner, except that it is fired from both ends alternately, by which means the heat at both ends is equalised. With this system it is possible to employ longer cylinders, and the more even regulation of the

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* Daggett, *Trans. A.I.M.E.*, vol. xviii., p. 466.

heat is said to render the furnace more suitable than the Brückner for ores which require either a very high or a very low temperature for chloridisation. The furnace has been already described and figured in this series.*

The *Howell-White* roasting furnace is a modification, in cast iron, of the *Oxland-Hocking*† calciner introduced so many years ago for roasting "tin whits," and since employed for every kind of roasting, the principal modification consisting in the provision of an auxiliary fireplace in the dust-flue. It is shown in Fig. 53. The outer cylinder is of cast iron 24 to 27 feet long and 4 to 5 feet in diameter, supported on friction rollers. Unlike the original Oxland and White furnaces, which are lined with fire-brick throughout, and in which, therefore, the outer casing is of the same diameter from end to end, the Howell furnace originally was intended to have only the enlarged part next the firebox so lined, the remainder of the cylinder having no lining, as the bare cast iron was not expected to wear very

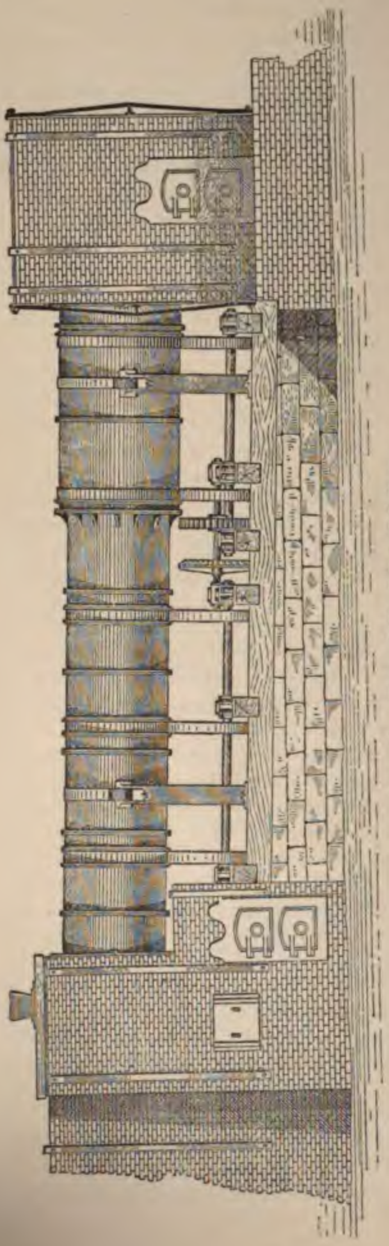

Fig. 53.—Oxland-Hocking Calciner.

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* Rose, *Metallurgy of Gold*, 3rd edition, p. 256.

† Foster, *Ore and Stone Mining*, 1897, p. 615.

The fine battery of furnaces erected for the *Broken Hill* *ary Co.*, however, are lined throughout, so that presum- s feature had to be abandoned. A series of cast-iron arranged spirally lifts the powdered ore a short distance, drops it through the flame. A great deal of dust is pro- these furnaces, and this is sometimes roasted by means uxiliary fireplace in the downtake flue, but more fre- it is taken out at intervals from the dust chambers and ed into the furnace together with fresh ore, automatically wise. The feed being continuous and the inclination of ider being usually adjusted once for all on setting it up, spent by the ore in the furnace can only be regulated asing or decreasing the number of turns per hour— enerally average about fifteen to thirty, though Roth- ommends a 36-foot cylinder which revolves once per

trong draught in this furnace carries away a large pro- of the finely-pulverised particles continually falling into ider from the feed hopper. Several forms of diaphragm en invented with the object of protecting the falling feed strong draught, and so keeping the fine dust inside the long enough for chloridisation. One of the best is the diaphragm * in use at the Granite Mountain Mill since id shown in Fig. 54. The powdered ore, fed into the the curved pipe by means usual worm conveyor, falls it and is deposited on the surface of the cylinder; e draught passes out through racted nozzle which is bolted linder and projects inwards so, its sectional area being lf that of the cylinder itself. nis diaphragm or with the which is somewhat similar in action, the proportion ust carried into the dust chambers is not more than er cent., instead of 20 per cent. or more without any m.

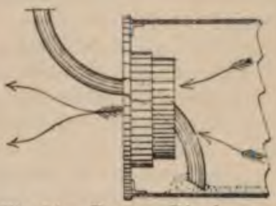

Fig. 54.—Rumsey Diaphragm.

idising-roasting this furnace has many advantages over kner type, in spite of requiring somewhat more power, avier and more expensive to set up and more readily ut of order owing to the inclined axis. For chloridising- the White type of furnace is much more largely used Brückner, having in particular the following advan- (1) Larger capacity per unit of cost; (2) smaller fuel tion; and (3) absence of "balling," which is so great

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le, *Trans. A.I.M.E.*, vol. xviii., p. 226; a somewhat similar ent is in use at Broken Hill.

a drawback on certain ores (Silver King, Yedras, Cusi). Furnaces of this type are, therefore, much more largely used in silver mills, and are to be found at *Granite Mountain* and other mills in Montana, *Palmarejo* and others in Mexico, and at *Broken Hill*, N.S.W.

The consumption of wood may vary from $\frac{1}{8}$ to $\frac{1}{4}$ cord per ton of ore, or, say, 20 to 30 per cent. by weight. The quantity of ore treated daily per furnace varies from 8 to 30 tons, according to the amount of sulphur contained; but the smaller figure only refers to very heavy ores, and of ordinary silver ores a furnace 27 feet by 4 feet should chloridise upwards of 15 tons per day.

At *San Francisco del Oro* Hofmann found that ore containing 25 per cent. of zinc and 12 per cent. of lead, both as sulphides, with very little pyrites, could not be chloridised above 67 per cent. in a furnace of this description. He, therefore, supplemented it by a small reverberatory hearth with separate fireplace and one working door, and added the salt in this hearth, treating charges of 1400 lbs. at a time as often as this amount accumulated in the drop pit. The results were satisfactory, the chloridisation being increased to 81·6 per cent.; some data of the work done and its cost are given in Table VIII.

At the works of the *Broken Hill Proprietary Co.* (N.S.W.), eight Howell furnaces, 33 feet long by 4 feet 3 inches inside diameter, are in use for chloridising siliceous iron ores too poor in lead and silver for smelting. These ores average about 4 per cent. Pb and 10 to 18 ozs. Ag per ton, mostly in the condition of iodide and chlorobromide, neither of which is readily attacked by lixiviation solvents. About 180 tons per day of this ore* are mixed with 50 or 60 tons per day of tailings from the concentration of lead carbonate ores, which contain 6 to 8 per cent. Pb and 8 to 10 ozs. Ag per ton. To the ore 7 to 8 per cent. of salt is added, and to the tailings only $5\frac{1}{2}$ per cent. The mixture is unloaded from trucks into the charging hoppers, and thence fed automatically by worm screws into the charging pipes connected with the furnaces. The furnaces have 15 inches fall in their whole length (slightly under $\frac{1}{2}$ inch per foot), and generally revolve about twenty-four to thirty times per hour, being arranged in pairs which revolve in opposite directions. Of the eleven cast-iron rings forming each cylinder only the three at the fire end are lined with firebrick, the remaining eight having a red brick lining. At 30 revolutions each particle of ore passes from end to end in about forty-five minutes, and as the total quantity of ore in the cylinder at one time is about 2 tons (forming a layer 9 inches deep at the thickest part), the daily output of each furnace is 30 tons. The fuel is coal, costing 37s. 6d. per ton, the consumption of which is 9 per cent., and the chlorination test of the roasted ores shows 75 to 80 per cent., as

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* The crushing of this ore has been referred to in chap. vii.

against 40 to 50 per cent. before leaching. The flue-dust produced, owing to the diaphragms employed, averages only 1 per cent. of the ore charged, and the volatilisation loss of silver is under 6 per cent. The roasted ore is discharged from the bottom of the hot ore bins into iron trucks, which run underneath each, and the bodies of these trucks are lifted from their carriages by a travelling crane, swung, and tipped upon a cooling floor, where the ore is wetted down and remains from three to four days. "Heap-chlorination" does not appear to come into play, for tests of freshly roasted ore show about the same percentage of chlorination as is given by the same ore charged into the vats. Further particulars are given in Table VIII.

These furnaces do very good work, but on such ores it is probable that the Stetefeldt furnace would give equally good results at less cost for fuel and power.

Shaft Furnaces.—Practically only one furnace of this class is used in chloridising-roasting.

The Stetefeldt furnace is more widely used in large establishments than any other type. It is shown in section in Fig. 55,* and consists in brief of a perpendicular shaft slightly tapering upwards, and varying in height from 30 to 45 feet, according to the amount of sulphur in the ores to be treated. The section of the shaft is square, from 4 to 6 feet in width, giving an area of 16 to 36 square feet, according to the capacity desired. The shaft is heated by gas produced in independent generators at the sides, and the finely pulverised ore (40 to 60 mesh usually) mixed with salt is showered down through the flame by means of a special feeder at the top. The powerful upward draught carries off a large proportion of the fine dust (from 20 to 50 per cent. averaging, perhaps, 40 per cent.), which is roasted and chloridised in the downcast flue by means of an auxiliary gas fire as it passes to the series of dust chambers. The walls of the shaft are hollow enclosing a sealed non-conducting air space to keep the heat uniform, and the discharging of the furnace and dust flue is effected on the side opposite the gas generators. Referring to the figure, A is the Stetefeldt feeder referred to in more detail below, B is the shaft, C the hopper in which the roasted ore accumulates and from which it is discharged at intervals into a hot ore truck; G G are the two gas ports connected with the generators, and M M air ports, the mixture of gas and air burning in the fireboxes, O O. At Q Q are doors to admit air and for cleaning the hoppers, at R R doors through which the firebridges can be cleaned. The gases and dust descend through the flue, H (which is heated by the auxiliary gas fire, E, and can be cleaned through the doors, S), and passing through the enlarged dust flue, D, a large part of the dust settles out and is collected

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* For other views of this furnace *v.* *Trans. A.I.M.E.*, vol. xxiv., pp. 5 and 6.

in the hoppers, F F. From D the gases pass to a long series of dust chambers before being allowed to escape by the stack.

The Stetefeldt feeder is composed first of a hollow water-cooled

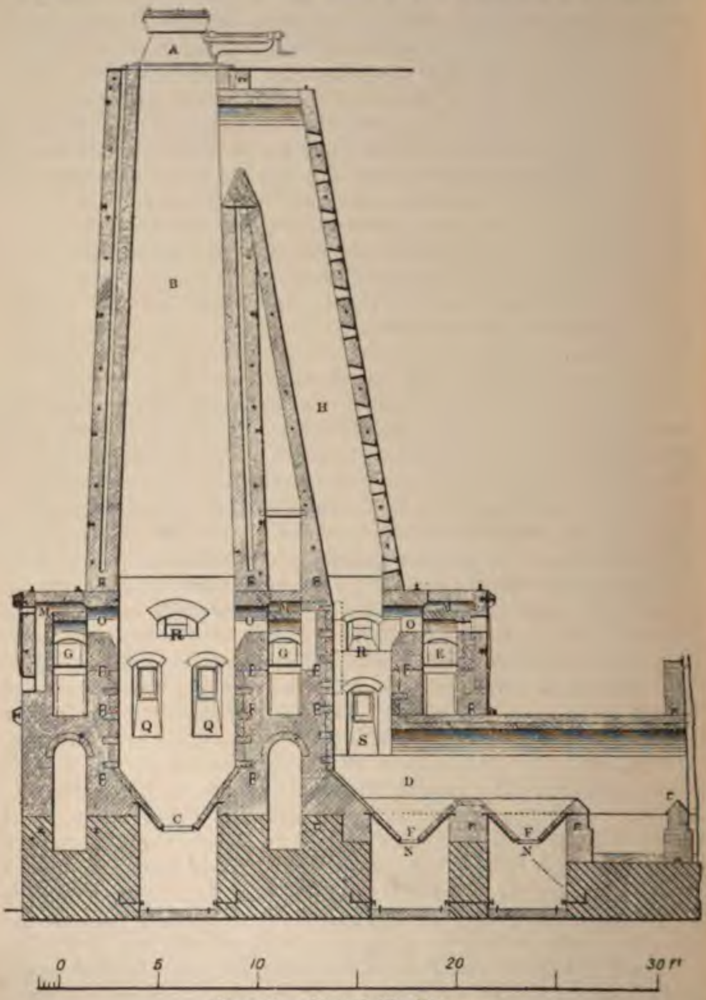

Fig. 55.—Stetefeldt Furnace.

cast-iron base, covered by a fine punched screen supported on a coarse cast-iron grating. Above the screen is a wrought-iron box, the bottom of which is a wire-mesh screen of about $\frac{1}{4}$ inch meshes, and which, resting on friction rollers, is made to oscillate by means of eccentrics a distance of about 3 inches from twenty to sixty times per minute. This box is full of pulp, the upper layers of which are prevented from moving with the box by means of a series of blades fixed to brackets connected with the cast-iron base, their lower edges reaching down nearly to the moving screen. As soon as the driving shaft is set in motion the meshes of the coarse wire screen cut through the lowest stratum of ore, and drive it through the openings of the fine-punched screen.

The gas generators, firebox, and bridges, and the hot ore hoppers of the Stetefeldt furnace are lined with firebrick, all the remainder being of common brick, except the foundations. The ironwork of the furnace is elaborate, old 30-lb. rails being liberally used in the walls, while anchor rods are laid in 6-inch by 3-inch holes left in the brickwork for that purpose at short intervals; the total weight of ironwork in a large furnace being about 22 tons. The total cost of a large furnace erected ready for work will not be less than £2000, and may reach £3000 or £4000, according to locality, cost of freight, price of bricks, &c.

The amount of fuel required by the Stetefeldt is less than by any other type of furnace treating similar ores, $\frac{1}{14}$ to $\frac{1}{10}$ of a cord of wood per ton of ore (12 to 16 per cent. by weight) being usually found sufficient when burnt in a suitable gas producer. Stetefeldt* prefers the Taylor producer, and uses spiral-weld steel tubes without any lining, but provided with expansion joints, for making connection between the producer and furnace. *Goetz* and *Blauvelt*† recommend sheet-iron pipes with a firebrick connection, so as to allow of burning out the tar which settles there; they also recommend the Wellman producer as costing 50 per cent. less than the Taylor and working better. The amount of fuel required rapidly decreases with larger furnaces and increased tonnage, as shown by the following figures from different mills:—

Name of Mill.	Tons per day.	Cords Wood per ton.	Lbs. Coal per ton in Taylor Producer.
Ontario, . . .	40	0·19	225 = 11·5 per cent.
Marsac, . . .	70	0·13	142 = 7·1 ,,
Holden, . . .	90	not tried.	117 = 5·8 ,,

Ore for the Stetefeldt furnace does not require to be pulverised any finer than for good work in a revolving furnace; the degree of fineness will depend entirely on whether the silver-bearing minerals occur as distinct granules or as fine impregnations. The Ontario ore, for example, in which the chief silver-bearing

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* *Trans. Fed. Inst. Min. Eng.*, vol. viii., part i., p. 93.

† *Trans. A.I.M.E.*, vol. xxiii., p. 587.

mineral is fahlerz in bunches with other sulphides, yields over 90 per cent. of its silver to the Russell process when crushed only through a 10 mesh before roasting, and it is not found advisable to crush it finer than 16 mesh. This ore, however, is exceptional,* and very few ores can be as successfully roasted with so coarse a crushing.

Quartzose and earthy ores usually require for chloridisation a high temperature and large fuel consumption; leady and antimonial ores a low temperature. Heavy ores containing a large proportion of galena, blende, or pyrites require the feeder to be driven slowly while a high temperature and strong draught (which means high dust losses) are kept up in the shaft; and even then the oxidation, and therefore the chloridisation of the ore as withdrawn from the furnace, is very incomplete. It may be said that approximately complete oxidation of ores containing upwards of 15 per cent. S is not possible in the Stetefeldt furnace, which is only really suited to the treatment of the so-called "light ores" containing less than 8 per cent. of S as sulphides.† This coincides with the experience of O. Hofmann at Parral, who found that with ores rich in lead and zinc most of the ore particles were, owing to the high temperature, slagged into minute black globules, which were only partially chloridised (17 per cent.) and which were very difficult to re-roast. This is opposed to the claim made by extreme advocates of the Stetefeldt furnace that it is applicable to every kind of ore, and that the principle of a short exposure to a high temperature is the right one for chloridisation.

As the ore reaches the bottom of the shaft it is only imperfectly chloridised, but the percentage of chloridisation increases the longer it is allowed to remain in the hopper before withdrawal. At the *Lexington* Mill the ore on reaching the bottom of the shaft only shows 60 to 65 per cent. of the silver to be chloridised, whereas after two hours in the hoppers the percentage rises to 75 or 80 per cent., and after thirty-six to forty-eight hours on the cooling floor to 92 or 93 per cent. of the total. It is perhaps not remarkable that the finer particles of the ore which are carried over with the draught and taken out of the first flue-hopper, besides being richer, should show a higher percentage of chloridisation than the ore which collects in the shaft-hopper. The deposit from the dust chambers is usually, though by no means invariably, poorer than the original ore (owing partly to condensation of volatile bodies, including salt and compounds of lead); but the percentage of chloridisation appears to be also higher. The following figures show the relative weights, assays, and percentages of chloridisation in the shaft and flue

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* Its composition is given in Table IX.

† Godshall, *Proc. Colo. Sci. Soc.*, May, 1893; also *Trans. A.I.M.E.*, Pittsburgh Meeting, Feb., 1896.

respectively, at the *Ontario*,* *Holden*,† and *Marsac*‡ mills; the percentage of chloridisation at the second of these does not show up very well because the assays were taken as drawn from the furnace, whereas the Ontario figures refer to ores taken from the cooling floor :—

TABLE VII.—WORK DONE BY THE STETEFELDT FURNACE.

	Ontario after cooling.		Holden as drawn.			Marsac.		
	Shaft.	Flue.	Shaft.	Flue.	Chamber.	Shaft.	Flue.	Chamber.
Percentage of total roasted ore, . .	...	...	53·1	33·0	13·9	31·7	56·1	13·2
Assay in ounces per ton, ...	69·7	86·0	27·8	25·0	18·3	...	...	...
Percentage of assay of raw ore, . .	...	...	99·5	89·5	65·6	89·0	109·0	113·0
Chloridisation by hypo. test, . .	87·7	91·8	43·5	59·1	64·2	...	...	...

There is little danger of sintering even plumbiferous ores in this furnace, owing to the fact that the particles of ore while exposed to the heat are separated from each other; and once the conditions (proportion of salt, amount of draught, rate of feed, &c.) have been determined by experiment for any given ore, the furnace manipulation demands no special skill or attention on the part of the workmen, except as regards the firing, which should be as uniform as possible. But little labour is required. As the ore is raised by an elevator to the charging floor and tipped direct into the feed-hopper, one man per shift can easily attend to the charging as well as to the firing. Two men per shift are required for the work of discharging the roasted ore and spreading it on the cooling floor. When treating "heavy ores," the output being small, 12-hour shifts are worked; but with "light ores," which can be roasted at a greater rate, the shifts are only eight hours each.

The perfection of the oxidation depends entirely on the composition of the ore. At the *Holden*§ mill, a mixture of Aspen ores containing 8 per cent. S as sulphides is roasted down to 0·2 per cent. of S, whereas at *San Francisco del Oro*‖ an ore containing 21 per cent. S still contained after roasting 8½ per

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* Egleston, *op. cit.*, p. 257.
† Morse, *Trans. A.I.M.E.*, vol. xxv., p. 142.
‡ Stetefeldt, *Trans. Fed. Inst. Min. Eng.*, vol. viii., part i., p. 93.
§ *Trans. A.I.M.E.*, vol. xxv., p. 139.
‖ *E. and M. J.*, Feb., 1889.

TABLE VIII.—CHLORIDISING-

	San Fr'cisco del Oro, Chihuahua, Mexico.	Kosaka Reduction Works, Japan.	Sombrerete, Zacatecas, Mexico.
Reference, ...	1.	2.	3.
Type of roasting furnace, ...	Reverberatory	Reverberatory	Reverberatory
Dimensions—Length or height, . . feet,	42	27	30
,, Width or diameter, . ,,	10	12	10
Quantity of ore in furnace at once, . .	4 tons	5100 lbs.	3 tons
Time each charge in furnace, . hours,	10-12	1	24
Weight of each charge, ...	1 ton	1700 lbs.	1 ton
Total output of furnace per 24 hours, tons,	8-10	51	3
Percentage of salt employed, . . .	4	4	6
Average contents of raw ore, ozs. silver,	28·85	8·5	41·9
Silver contents of roasted ore, . . ozs.,	26·10	...	42·6
Percentage of sulphur in raw ore, . .	21·0	2·6	26·4
Percentage of chlorination by assay, . .	83	75	90
Loss of silver by volatilisation, . per cent.,	10-13	7	4·8
,, gold ,, . ,,	...	...	...
Cost of salt per ton of 2000 lbs., . .	£3 3 6	...	£3 0 0
Percentage of wood required for roasting, .	19·5	13	33
,, coal ,, ,, .	...	...	...
Cost—Labour, ...	£0 3 3	No details	£0 3 6
Power, ...	nil		...
Fuel, ...	0 2 5½		0 3 9½
Oil, light, and tools, ...	0 0 6½		0 0 2½
Salt, ...	0 2 6		0 3 7¼
Superintendence, repairs, &c., .	0 0 6		...
Total per ton of 2000 lbs., .	£0 9 3	£0 5 1	£0 11 1¼

¼ per cent. sulphur is added to this ore before roasting.

—1. Hofmann, *E. and M. J.*, Feb. 23, 1889. 2. Kuwabara, *S.M.Q.*, p. 363. 3. *Private communication*, O. Hofmann, Nov., 1896. d *M. J.*, Feb. 23, 1889. 5. Goodale, *Trans. A.I.M.E.*, vol.

[redacted]

ROASTING. 1 TON = 2000 LBS.

San Fr'cisco del Oro, Chihuahua, Mexico.	Knoxville Mill, Tombstone, Arizona.	Broken Hill Proprietary, Broken Hill, N.S.W.	Niederland Mill, Caribou, Colorado.	Manhattan Mill, Austin, Nevada.	Marsac Mill, Utah (Daly).	Holden Mill, Aspen, Colorado.
4.	5.	6.	7.	8.	9.	10.
White-reverb.	Howell	Howell (mod.)	Brückner	Stetefeldt	Stetefeldt	Stetefeldt
24	24	33	12	...	50	...
...	4	4′ 3″ dia.	5′ 6″	...	6′ × 6′	6′ × 6′
...	1½ tons	2 tons	3700 lbs.	...	...	...
12	...	¾	8	...	...	...
...	...	...	3700 lbs.	...	...	...
8½	...	30	5	...	70	82
4·7	6	7	5	7	8·0	12·2
26·85	50	11	...	...	37·28	27·92
26·10	...	...	...	...	36·03	24·63
21·0	0·1	...	3·0	...	0·7 *	8·10
81·6	86	80	...	90	92·4	79·0
7·9	...	under 6	...	...	...	9·16
..	...	...	...	...	...	...
£3 3 6	£6 2 6	...	£12 1 0	£8 6 8	...	£1 9 8½
27	26	...	...	17·6	...	...
...	...	9	...	...	15	5·8
£0 1 10	...	No details	£0 2 2½	£0 4 2	£0 1 0	£0 1 4
0 2 2	...		0 2 3½	nil	nil	nil
0 3 7	£0 8 4		0 2 11	0 3 8	0 1 9½	0 0 9
0 0 7	...		0 0 1	0 0 2	...	0 0 3
0 2 7	0 7 6		0 14 7	0 11 8	0 3 0	0 3 7½
0 0 6	...		...	...	...	...
£0 11 3	...	£0 5 2+	£1 2 1+	£0 19 8+	£0 5 9½	£0 5 11½+

xvii., pp. 771 and 773. 6. *Annual report*, 1896, and *Private notes*. 7. Egleston, *op. cit.*, p. 238. 8. Egleston, *op. cit.*, p. 259, &c. 9. *Private communication*, R. B. Watson, Nov., 1896. 10. Morse, *Trans. A.I.M.E.*, vol. xxiii., pp. 6 to 10 of paper.

cent. S in the sulphide condition, the chloridisation being very incomplete, and similar results are reported from Sombrerete.[*]

The advantages and disadvantages of the Stetefeldt furnace may be summarised as follows:—

ADVANTAGES.	DISADVANTAGES.
1. Very large capacity on ores containing less than 6 per cent. sulphur.	1. Very heavy first cost.
2. Small amount of fuel required.	2. Small capacity and imperfect oxidation when treating ores with over 10 per cent. sulphur.
3. Practically no power required as compared with the revolving furnaces.	3. Inapplicability to ores consisting principally of galena and blende, the particles of which melt on the outside and form an impenetrable skin almost as soon as they enter the furnace.
4. Possibility of leaving the roasted ore in the hoppers as long as convenient, whereby the percentage of chloridisation is largely increased without any further volatilisation loss.	4. Clogging and crusting of the screens and passages when using a heavy percentage of salt.
5. The dust produced is well chloridised.	5. Volatilisation loss much higher than in reverberatory furnaces in which the heat is kept low and salt added only after complete oxidation.
6. Probably lower volatilisation loss than in any of the revolving furnaces.	

The Stetefeldt furnace was designed for the chloridising-roasting of non-pyritic silver ores containing under 10 per cent. sulphur to fit them for amalgamation or lixiviation processes, and practically is only suitable for this work.[†] Pyritic ores should always be roasted fairly well prior to chloridisation, either in heaps as at Sombrerete (Mex.) and Potosi (Peru) or in some other type of furnace. Galena ores should never be roasted in the Stetefeldt furnace.

A number of figures relating to the performance of different roasting appliances under different conditions are given in Table VIII.

Composition of Chloridised Ore.—Stetefeldt gives the composition of Ontario ore roasted in a Stetefeldt furnace. Before

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[*] *E. and M. J.*, April 8, 1893.

[†] Stetefeldt, *Trans. Fed. Inst. Min. Eng.*, *loc. cit.*; witness also its utter failure at Sombrerete and other places.

roasting the ore contains blende, 15 per cent., galena 7·6 per cent., fahlerz 4·55 per cent., pyrites 3·50 per cent., and gangue (with 9 per cent. total sulphur) 69·35 per cent. After roasting it contains* copper chlorides 0·25 per cent., $ZnCl_2$ 1·38 per cent., Al_2Cl_6 1·51 per cent., NaCl 3·68 per cent., $PbSO_4$ 3·26 per cent., $Al_2(SO_4)_3$ 0·56 per cent., Na_2SO_4 4·62 per cent., together with traces of other metallic chlorides and sulphates, the remainder being metallic oxides and gangue.

Percentage of Salt Required.—The percentage of salt employed varies within very wide limits according to the nature of the ore, from 2½ up to 18 per cent. At *Panamint* (Cal.) only 3 per cent. was used in a Stetefeldt furnace, and the percentage of chloridisation reached 95 per cent., but the ores were very docile. At *San Francisco del Oro* 12 per cent. gave the best results in a Stetefeldt furnace, a larger quantity not only giving trouble with crusts but actually *lowering* the degree of chloridisation; the same ores, however, in the reverberatory and in a White-reverberatory required only 4 per cent. of salt. At the *Ontario* mill experiment proved that the percentage of silver chloridised was increased, with augmented proportions of salt, up to 15 per cent. At *Yedras*, *Promontorios*, and other Sonora mills from 3 to 6 per cent. salt is found sufficient. It is quite probable that in many mills too much salt is being used, and that better results would be shown by slower roasting at a lower temperature with a smaller percentage of salt.

Loss of Silver by Volatilisation.—To this most important point too little attention has hitherto been paid, owing partly to the fact that in many cases the loss of weight in roasting more than balances the loss of silver by volatilisation, so that the roasted ore assays nearly or quite as high as the raw ore. Some of the best experiments on the subject of the volatilisation of gold are those of Stetefeldt† and Christy,‡ but the published experiments on the volatilisation of silver appear to be fewer and less systematic; some valuable results, however, are those of Russell§ and Godshall.‖ The chief factors which determine the loss of silver are:—(1) Time involved; (2) temperature; (3) amount of surface exposed and proportion the latter bears to the volume of gases brought into contact therewith; and (4) the presence of As, Sb, Se, Te, and other volatile elements.

Roasting tests are commonly made by mixing a weighed quantity of ore with the necessary amount of salt, and exposing in a muffle for a given time, with or without stirring. As a rule, the volatilisation loss shown in this way is much higher than that experienced on the large scale, because the surface exposed

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* *Trans. A.I.M.E.*, vol. xxiv., p. 17.

† *Trans. A.I.M.E.*, vol. xiv., p. 336. ‡ *Id.*, vol. xvii., p. 3.

§ Stetefeldt, *Trans. A.I.M.E.*, vol. xiii., p. 70.

‖ *Trans. A.I.M.E.*, Pittsburgh Meeting, Feb., 1896.

is not only greater but the volume of air brought into contact with each particle is larger, and the atmosphere is more oxidising. With gold, an oxidising atmosphere, except in presence of tellurium, gives rise to scarcely any volatilisation, which, however, is considerable as soon as the atmosphere becomes chloridising, while the loss of gold is found to be directly proportional to the time during which the ore is exposed to chloridising influences. It is, therefore, always advantageous on purely gold ores to first roast to complete oxidation and then chloridise. Silver behaves a little differently inasmuch as there is usually much volatilisation before the end of the oxidation period, but experiments on the question of subsequent volatilisation after addition of salt are inconclusive; in some cases a large percentage of salt appearing to result in lower volatilisation losses than a smaller quantity. This if well authenticated can only be explained on the supposition that silver chloride is actually less volatile in an atmosphere containing a large proportion of chlorine and salt vapour than in one consisting chiefly of air.* With silver ores consisting largely of earthy or siliceous gangue and poor in sulphur the loss of silver is usually greater when the salt is added after an oxidising roast, whereas with heavy sulphide ores it is generally less, owing no doubt to the quantity of sulphates and of undecomposed sulphides left after roasting. The sulphates decompose the salt very completely, and although the actual amount of silver volatilised on the finishing hearth may be greater, it is largely re-condensed and re-absorbed by the ore on the cooler hearths through the reducing action of the SO_2, as shown by Christy. Thus Wendt found at Potosi † that the loss when using Howell revolving furnaces was from 10 to 15 per cent. on a 100-oz. ore, whereas when these furnaces were replaced by 3-hearth (superposed) gas-fired reverberatories and the salt added on the lowest hearth the loss was kept down to 5 per cent. A smaller quantity of salt suffices when added in this way after an oxidising roast than when added at the beginning.

Influence of Time.—That *time* is an important factor in determining the volatilisation loss is well shown by a series of experiments due to Russell,‡ who roasted typical ores from six leading Western mines, without salt, in a muffle at a dull red heat, during periods which increased by half-hours from thirty minutes up to three hours. The samples showed a gradually increasing loss, which was, however, much more regular in some cases than in others, and a summary of the results was as follows :—

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* *v.* the remarks on the volatilisation of silver in chap. i., p. 2.

† *Trans. A.I.M.E.*, vol. xix., p. 101.

‡ Quoted by Stetefeldt, *Trans. A.I.M.E.*, vol. xiii., p. 70.

	Highest.	Lowest.	Average.
After half-hour's roasting, . .	4·8	0·7	2·6
,, three hours' ,, . .	17·6	2·1	8·5

Time, however, only increases the volatilisation of silver when both heat and air are in excess. There is no volatilisation in heap-chloridisation, and very little in a reverberatory when, after an ore has been roasted, it is retained in the furnace for several hours at a low temperature, all the dampers and working doors being closed. It is probable, therefore, that time only becomes a factor in so far as it increases the frequency of contact between the molecules of oxygen and other gases present and the particles of ore, since when the draught is stopped there is no volatilisation.

Influence of Temperature.—Temperature seems to be a much more important factor. Thus Clemes * quotes some experiments at a Sonora mill, where, with temperatures on the final hearth of cherry-red, red, and dull red respectively the furnace losses of silver on the same ore during the same periods of time were 15·9 per cent., 13·7 per cent., and 11·6 per cent., of which fully one-half occurred in the final chloridisation stage, while in another case when the ore was discharged before chloridisation the loss was only 6·3 per cent. This suggests the advantage of completing the chloridisation whenever possible outside the furnace, preferably in some form of masonry bin in which the cooling of the ore can be utilised to yield a supply of hot air for the furnace. Russell's experiments,† already referred to, also show volatilisation losses on Ontario ore of 8·3 per cent. at a "dark red," and of 17·6 per cent., or more than double, at a cherry-red. Hofmann ‡ mentions that at Yedras the volatilisation loss varied between 2 per cent. and 18 per cent. in reverberatories, a high temperature being accompanied by a high loss and *vice versâ*. It is worth noticing that on this heavy ore the percentage of chloridisation was inversely proportional to the temperature, a loss by volatilisation of 2 per cent. corresponding with a chloridisation of 81·5 per cent., and a loss of 18 per cent. with a chloridisation of 72·5 per cent. The two losses, therefore, give a combined result equal to 25 per cent. in favour of low temperature. According to the same author the results at San Francisco del Oro in the combined White-reverberatory also prove the loss to increase in proportion with the temperature, the extreme variations being 2 to 15·5 per cent. and the

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* *Proc. Inst. Civ. Eng.*, vol. cxxv., p. 107.
† Stetefeldt, *Trans. A.I.M.E.*, vol. xiii., p. 70.
‡ *E. and M. J.*, Feb., 1899.

average 7·9 per cent. Temperature, therefore, must be looked upon as a more important factor than time in determining the volatilisation loss on any given ore, though the contrary was always taught by the late C. A. Stetefeldt.

Influence of Volatile Elements.—The influence of As, Sb, Bi, Se, Te, and other volatile elements on the volatilisation of silver, though known to be very important, has not been systematically studied. The very high losses sometimes shown by muffle tests at a comparatively low temperature are no doubt in many cases attributable to the presence of traces of Se, Te, and other elements.

At the *Holden*[*] Mill (Aspen), where over 30,000 tons of ore were put through during the year 1892, it was found, by means of careful weighing, assaying, and sampling throughout the entire process, that the ore gained weight to the extent of 2·97 per cent., including the sodium sulphate formed during roasting, but that the loss of silver by volatilisation averaged 9·16 per cent. Stetefeldt claimed[†] that the loss in the Stetefeldt furnace is lower than in revolving furnaces, and referred to his own experiments which prove a smaller loss in roasting Ontario ore in a Stetefeldt than in a Howell furnace. The former also has the advantage over other automatic furnaces that the dust is perfectly chloridised, whereas in revolving furnaces it must be chloridised either in a separate auxiliary fireplace or by returning it to the same furnace. The claim, however, that the volatilisation loss of silver is usually lower than in the reverberatory is untenable, and, in particular, is contrary to the experiments quoted by Godshall,[‡] which show that on Aspen ores the loss in reverberatories averages only 4·2 per cent., as against 9 per cent. in the Stetefeldt and 29 to 70 per cent. experimentally on the small scale of the muffle.

Diminution of Volatilisation Loss.—The volatilisation loss may be somewhat diminished by various expedients. A jet of *steam* through the firebridge, as first suggested by Percy, is found in some cases to greatly diminish volatilisation.[§] Steam acts by decomposing volatile metallic chlorides, which carry off silver chloride with them, forming hydrochloric acid which tends to keep the silver chloridised. Steam may also assist in keeping the temperature even inside the furnace, heat being in the hottest part absorbed by dissociation and evolved by recombination at a distance from the firebridge. According to Clemes[‖] the use of steam in Sonora plants has been abandoned as it is not found to give any increase in chlorination; he says, however, nothing

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[*] Morse, *Trans. A.I.M.E.*, vol. xxv., p. 137.

[†] *Ibid.*, p. 147; also *Trans. A.I.M.E.*, vol. xxiv., p. 10.

[‡] *Trans. A.I.M.E.*, Pittsburgh Meeting, Feb., 1896.

[§] *v* some tests by Clark, *Trans. A.I.M.E.*, vol. xiv., p. 399.

[‖] *Proc. Inst. Civ. Eng.*, vol. cxxv., p. 103.

about the diminished volatilisation, so possibly no experiments have been made on this point.

In the case of ores containing much zinc at the *Moulton** mill volatilisation of silver was checked by a liberal addition of oxidised *manganese ores*. These act, no doubt, by decomposing metallic chlorides and liberating chlorine which tends to keep the silver chloridised. At *Ontario* it was similarly found that the loss was less with a high proportion of salt.

In spite of the various precautions taken, it is probable that the loss of silver by volatilisation during chloridising-roasting, taking a general average of all the various plants and localities, is little, if any, under 8 per cent. The extra cost of a chloridising roast may be reckoned at between 5s. and 15s. per ton, according to the percentage of S, cost of fuel, and the amount and cost of salt required; so that taking 10s. per ton as an average figure this is equal to 4 ozs. of silver (at 2s. 6d. per oz.) or 16 per cent. on a 25-oz. ore. Adding the volatilisation loss of 8 per cent., the extra cost of roasting in the case of a 25-oz. ore is no less than 24 per cent. of its total gross value; so that an extraction of 60 per cent. by any process of raw treatment would be as economical as one of 84 per cent. by the roast-chloridising process.† It may well be doubted, therefore, whether "the game" is always "worth the candle," and whether it would not be preferable in many cases to adopt some other process for treating such ores. Practically speaking, few ores under 30 ozs. per ton will pay for treatment if they have to undergo the processes described in this chapter, unless the conditions are exceptionally favourable as regards cost of mining and facilities for obtaining supplies. It should be understood, however, that where roasting has to be adopted it is actually the crucial point of the whole process, especially with heavy sulphide ores; and that no attention in the subsequent lixiviation can compensate for want of care in obtaining a *perfect* chloridisation, the extra cost of which over a partial roasting is very small, while its results are of the first importance.

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* Clark, *Trans. A.I.M.E.*, vol. xvii., p. 775.

† Or, in other words, a raw extraction of 78 per cent. of the assay of the raw ore is, under these conditions, exactly equivalent to the so-called extraction of 91·3 per cent. on the roasted ore, allowing for the volatilisation loss, and the whole extra cost of roasting plant and of crushing and drying the salt is saved.

SECTION III.—LIXIVIATION PROCESSES.

INTRODUCTORY.

The object of lixiviation processes is to extract the silver from ores or metallurgical products in the form of a solution, from which the metal may, by appropriate means, be subsequently precipitated in a convenient form. Practically, there are only two salts of silver which can be employed, viz.—the chloride and the sulphate; the latter requires only hot water for its solution, while the former may be simply dissolved out by means of brine or decomposed by sodium hyposulphite (thiosulphite), with which silver forms a series of soluble double salts.[*] From the aqueous solution of its sulphate, silver may be precipitated in the metallic form by copper;[†] from the brine solution of its chloride it may be precipitated either as metal or, in very dilute solutions, as iodide (*Claudet* process). From the solution of double hyposulphites, silver is always precipitated as a bulky sulphide, which is afterwards refined in various ways. There are thus three main series of processes for the lixiviation of ores, viz.:—The *Augustin* process based upon the solubility of silver chloride in brine, the *Ziervogel* process based upon the solubility of silver sulphate in hot water, and the *Patera* (Kiss and Russell) processes in which silver chloride is decomposed and taken into solution by sodium hyposulphite, commonly called "hyposulphite," or simply "hypo."

The ready solubility of silver chloride in *ammonia* has suggested attempts at an ammonia process which was actually experimented with at Broken Hill, for treating the Kaolin ores rich in haloid salts of the metal. As might have been anticipated, however, the loss of ammonia was altogether too great, to say nothing of other inconveniences connected with its use.

Silver chloride ores can sometimes (though rarely) be submitted to lixiviation without any preliminary preparation other than crushing, and in this case the solution employed is generally the hyposulphite, on account of the much greater solvent power of this medium.[‡] In most cases, however, both ores and metallurgical products have to be first subjected to a chloridising

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[*] *v.* chap. i., p. 17.

[†] Also by zinc or iron, but copper is in practice found preferable.

[‡] The solubility of silver chloride in brine and in hypo. respectively is very nearly as 1 : 100.

			1888.		1891.		1891.		
References,	1.	2.	3.	4.	5.	6.	7.	8.	9.
Process,	Augustin	Patera	Kiss	Patera	Russell	Russell	Russell	Russell	Russell
SiO_2,	27·00	50·25	25·81	29·6	76·60	64·4	20·06	21·66	55·21
Al_2O_3,	1·85	...	2·82	...	...	...	1·35	...	13·14
Fe_2O_3,	...	...	...	...	...	...	...	...	...
Fe,	7·41	8·06	10·4	16·8	1·65	3·74	13·56	10·02	2·77
Mn,	...	...	...	...	...	5·21	...	...	0·45
CaO,	0·50	4·92	5·48	0·2	1·32	...	22·20	11·00	...
MgO,	0·35	2·40	...	...	0·23	...	2·58	4·24	...
K_2O and Na_2O,	...	...	...	...	...	...	...	...	...
Pb,	4·42	4·64	9·17	9·5	3·50	4·22	1·78	2·28	6·07
Cu,	0·23	...	0·58	2·4	0·39	0·20	...	0·16	1·41
Zn,	2·44	7·62	22·45	8·9	5·30	12·80	4·92	2·85	9·60
Sb,	trace	1·35	0·73	...	...	...	...	...	1·20
As,	trace	0·73	...	...	...	...	6·16	...	0·20
Ag,	0·036	0·17	0·09	...	...	...	...	...	...
Au,	...	...	...	...	...	...	...	...	...
S,	2·66	0·96	21·00	26·4	0·70	0·50	12·90	8·10	7·68
CO_2,	...	8·30	...	...	...	...	19·30	...	..
H_2O,	...	3·80	...	...	...	...	...	...	...
$BaSO_4$,	49·28	...	...	...	...	...	...	20·92	...
Cl,	...	...	...	...	...	...	...	...	...
Cd,	...	...	0·10	...	...	...	...	...	...
Average value :—									
Ag oz. per ton, 2240 lbs.	11·46	56·0	32·31	46·93	43·8	...	61·6	31·26	...
Au oz. ,, 2240 ,,	...	...	...	0·09	0·049	...	...	...	...

References.—1. Kuwabara, *S.M.Q.*, vol. xv., p. 361. 2. Egleston, *Metallurgy of Silver*, &c., vol. i., p. 486. 3. Hofmann, *E. and M. J.*, 1889. 4. Hofmann, *Private communication*, Nov., 1896. 5. Lamb, *E. and M. J.*, Dec. 17, 1892. 6. Hoyt, *E. and M. J.*, Jan. 7, 1893. 7. Letts, *E. and M. J.*, Feb. 25, 1893. 8. Morse, *Trans. A.I.M.E.*, vol. xxv., p. 139, b, *E. and M. J.*, Dec. 17, 1892.

roast in order to bring the silver into a soluble condition. The *Ziervogel* process is characterised by an almost dead roast without salt conducted in a peculiar manner.

Analyses of Lixiviated Ores.—Analyses of some ores subjected to lixiviation after a chloridising roast are given in Table IX.

It will be convenient to describe first the *Augustin* process, which is the oldest of all, together with the *Ziervogel* process which has replaced it for the treatment of argentiferous mattes. The various modifications (*Patera*, *Kiss*, and *Russell*) of the important hyposulphite process will then be discussed in two separate chapters, one referring chiefly to the principles, chemical reactions, solutions, precipitants, and theory of the processes involved, while the other will give details of plant, and examples from practical work.

CHAPTER X.

THE AUGUSTIN, CLAUDET, AND ZIERVOGEL PROCESSES.

The Augustin Process.—This process was invented at Mansfeld as a substitute for the barrel-amalgamation of argentiferous mattes. The matte was crushed, roasted with salt, leached with brine, and the silver precipitated upon metallic copper, the latter being reprecipitated upon scrap iron. The process was also introduced at Freiberg for treating similar material, but at both places it has been superseded, at Mansfeld by the cheaper Ziervogel process, and at Freiberg by a sulphuric acid leaching process which will be described in connection with the treatment of silver-bearing mattes.

The operations as formerly carried out at Freiberg have been well described in many metallurgical text-books,* so that a short sketch will be sufficient here. Lixiviation and precipitation alike took place in a series of wooden tubs provided with false bottoms and arranged in five rows, one beneath the other. The top row consisted of a large number of tubs used for lixiviation, running on wheels so as to be brought above the precipitation tubs, or taken away to be emptied. Each contained 8 cwts. of roasted matte, and the solution of brine heated by steam pipes was run on from a general storage tank. The silver solution was received in a settling tank, from which it continuously percolated through cement copper contained in two series of tubs, the copper in the solution being recovered by passing it

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* *v.* Phillips, *Elements of Metallurgy*, 1891, pp. 782-784.

through two other series of tubs containing scrap iron. The refuse brine containing $FeCl_2$ was pumped back into the brine storage tank. The percentage of extraction in the process was from 88 to 92 per cent., the remainder being left in the copper oxide residues which were smelted to metal.

Lixiviation at Kosaka.—At *Kosaka* (Japan)* the Augustin process is employed for the treatment of an earthy ore containing 10¼ ozs. of silver, the composition of which is given in Table IX. The ore is first roasted with salt (*v.* Chap. IX. and Table VIII.), by which means, after moistening on the cooling floor, something like 80 per cent. of the silver is converted into chloride.

The lixiviation vats are of wood, twenty-one in number, and elliptical in shape, their dimensions being 7 feet long, 5 feet wide, and 2 feet 6 inches deep, and the capacity of each 2 tons of roasted ore. The false bottom is a wooden grating with 1 inch holes, and the filter cloth is composed of two sheets of straw matting. The vats are filled with ore, and hot brine containing 18 per cent. of NaCl by weight is run on from the storage tank by means of a launder which runs the whole length of the row. The leaching is continued until a polished plate of copper held at the discharge tap shows no further trace of silver, when the flow of brine is cut off and the effluent stream turned away from the precipitation tanks into the brine sump, the brine in the tailings being washed out by a stream of warm water. The operation of silver leaching takes ten and a-half hours, and requires 41 cubic feet of brine (20½ cubic feet per ton); the washing with water taking about one hour. The tailings are shovelled out into trucks and run away to the waste heap.

Precipitation.—The precipitation tanks are built of brick lined with cement instead of wood, as is usual; a section through the system is given in Fig. 56, in which *a* is the brine launder, *b* the wash-water ditto, *c* the leaching vats, *d* the top settling tanks, and *e*, *f*, and *g* successive rows of precipitation tanks. The upper settling tanks, *d*, serve only to settle out fine ore slimes and basic salts of iron in the liquors, which would also separate out in the silver tanks, *e* and *f*, were they not prevented from contaminating the precipitate by wooden frames let into the tanks a few inches below the surface of the liquid, over which straw matting is stretched to form a filtering bottom. The silver tanks *e* and *f* are provided with false bottoms like those of the leaching vats, and over which a 2-inch bed of bean-shot copper is spread to form a filter bottom. Upon this bed rest a number of "tiles" of copper, 8 inches by 6 inches by 1 inch, bent like roofing tiles and laid similarly. The lowest tank, *g*, is filled with scrap iron for precipitating the copper. Each precipitating tank is 125 feet long, divided into eight compartments, so as to permit of cleaning up without interference with the regular work, each silver tank

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* *S. of M. Q.*, vol. xv., p. 355.

being cleaned up once a month and each copper tank once in four days. The brine from the last tank flows to the brine sump, where its strength is kept up by addition of fresh salt, generally 19·6 lbs. per ton of ore, or a ton per day on the scale of 102 tons of ore daily.

The lixiviation works require only two shifts of eight men each for all work except discharging the vats, which is contracted for separately.

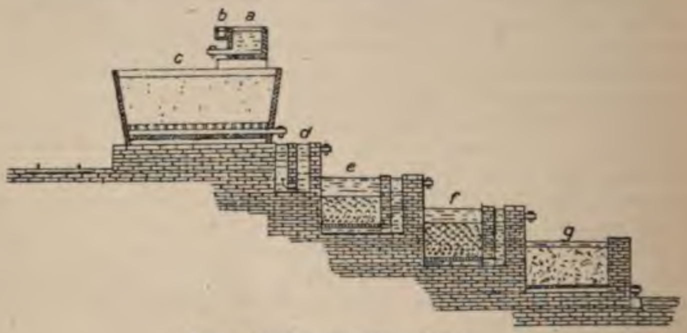

Fig. 56.—Precipitation Tanks.

Refining the Cement Silver.—The cement silver is squeezed by a screw-press into discs 1 foot diameter by 3½ inches thick, and varies from 150 to 750 fine. The discs are dried and refined in charges of 125 to 170 lbs. on English cupellation hearths with Portland cement hearths, together with 300 lbs. of lead to each charge. Each campaign lasts ten hours, and the life of a "test" is only three campaigns. The refined silver is granulated, melted in plumbago crucibles, and cast in moulds 14 inches by 5 inches by 4 inches, yielding bars of 1000 ozs. each, which average 985 fine, and are sent to the Osaka Mint for coinage.

The *cement copper* is melted down with charcoal in small open hearths, some sand and lime being added as fluxes. It is cast into ingots 17 inches by 7 inches by 1 inch, which weigh 50 to 60 lbs. each, and average 80 per cent. Cu., the impurities being chiefly lead and iron. Each hearth, with two men working one shift, only melts down half a ton of cement copper per day with a consumption of 400 lbs. charcoal. The copper for the silver precipitating tanks is further refined before use to prevent contaminating the silver precipitate with too much lead, &c.

During the year 1891 32,182 tons of ore were treated by the above process, yielding 211,809 ozs. of silver and 88·72 tons of ingot copper, the actual percentage yield being 78·6 per cent. of the silver, and 70·4 per cent. of the copper contents—a good result on such very low-grade ore. The cost was :—Drying and crushing, 1s.; roasting (including salt), 5s. 1d.; lixiviation, 2s. 8d.; refining and casting of cement silver and copper, 1s. 1d.—total, 9s. 10d. per ton. This compares remarkably well with the cost of raw amalgamation, though the very low rate of wages in Japan should be borne in mind; the total cost of mining and development, for example, was only 6s. 3d. per ton. Such ore could hardly be treated profitably in the United States by any known process.

Lixiviation at Kapnik.—At *Kapnik* (Hungary)* a peculiar combination of the Augustin and Patera processes is employed, the object being to extract as much silver as possible by the former process, which yields a clean, concentrated metallic precipitate with little trouble and loss in refining, and to take advantage of the more perfect extraction of hyposulphite solution (especially for gold) on the residues. The ores are pyritic slimes and second-class ores mixed in about equal proportions, the mixture containing on an average 16 per cent. blende, 1½ per cent. copper, and 2 per cent. lead, besides 17 ozs. silver and 2 dwts. of gold per ton. After drying the ore it is mixed with 8 per cent. salt and roasted on a 4-hearth Malétra furnace, 4 per cent. more salt being added on the third hearth. The roasting is incomplete, owing to the high percentage of zinc, and about 30 per cent. of the charge forms into balls, which, after sifting out, are re-crushed and re-roasted in a small reverberatory with 3 per cent. more salt.

The roasted ore is charged into wooden vats with false bottoms, holding 2½ to 3 tons each, and leached with brine at 80° C. containing 22 to 25 per cent. NaCl, which extracts about 60 per cent. of the total silver contents. The silver-bearing liquors are run as usual through a series of tubs containing copper, which are in this case kept warm by steam-pipes to facilitate precipitation.

The residues are lixiviated during two days with cold, strong hyposulphite solution at about 3° to 5° B., and the silver and gold extracted are precipitated as sulphides with sodium sulphide, as described in Chapter XI. The total extraction by the combined processes is brought up to 90 per cent. of the silver and 80 per cent. of the gold contents of the ore. Both cement silver and sulphides are worked up by scorification with lead, as described in Chapter XIII.

At *Tajova* (Hungary)† up to the year 1893 this process was in use for treating various black coppers from Schemnitz and elsewhere, containing 70 to 84 per cent. Cu, 2 to 15 per cent. Pb, 0 to 7 per cent. Sb, and 0·2 to 0·36 per cent. Ag (65 to 108 ozs. per ton). The black copper was broken up gradually

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* Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 735.

† *Ibid.*, p. 737.

with hammers and stamps till it all passed through a sieve of about ⅛ mesh, after which it was roasted with 15 per cent. salt on the upper hearth of a small double-hearth reverberatory for seven to ten hours. It was then dropped on to the lower hearth, and 4 per cent. fine coal raked in during three hours in order to decompose antimoniates; the heat was then raised for a couple of hours to decompose all basic salts, and the charge left to cool in the furnace for five hours. The roasted charge was re-sifted, the residues on the sieve being ground and added to a new charge.

The roasted mixed oxides were charged hot into jars holding 130 kilos. each, and lixiviated with *cold* brine (in order to dissolve out as little as possible of the chlorides of antimony and lead and cuprous chloride, all of which would contaminate the silver precipitate) for thirty to thirty-six hours. The residues were washed out with hot water, and contained only 1½ to 3 ozs. silver per ton. The solutions were precipitated on refined copper, the cement silver washed with hot water, with dilute HCl, and again with hot water, and finally pressed, dried, and melted in plumbago crucibles yielding a bullion 982 fine. The copper was precipitated on metallic iron as usual, and then the lead in the solutions was precipitated by zinc, after which they were pumped up to be used over again.

The Claudet Process.—The extraction of silver from low-grade roasted copper ores (burnt pyrites) can scarcely be considered as belonging to the metallurgy of silver since copper is the most valuable constituent of such residues, and silver merely a bye-product. The process by which the copper is extracted by means of a roasting with salt followed by a leaching with water will be found fully described in other works.

The roasted ore undergoes a series of six or seven washings, first with brine mother-liquor, and then with water to extract its copper contents; the first two washings with brine mother-liquor contain most of the excess of salt in the charge and 75 to 80 per cent. of the silver. These washings are collected after settling out the fine ore slimes in lead-lined wooden tanks holding 3500 gallons each and placed above the level of the copper precipitation vats, and samples are taken to be assayed for gold and silver, the average contents of the latter being 3 to 6 grains per gallon. As soon as the quantity of silver has been determined, the theoretical quantity of zinc iodide required to form insoluble silver iodide, together with a much larger quantity of lead acetate, is added and thoroughly stirred in. The reaction is

$$2AgCl\ (nNaCl) + ZnI_2 = 2AgI + ZnCl_2 + nNaCl.$$

The object of adding lead acetate is to form a precipitate of lead sulphate, which helps to collect the silver iodide as well as the gold present in the solution, which is almost all found in the precipitate. It is difficult to imagine that this gold can be in any way affected by the reagents added, or that their addition determines its separation in an insoluble form. In all probability the gold which has been transformed into chloride during the roast is leached out by the liquors and instantaneously reduced to metal by the ferrous and cuprous chlorides contained in the brine solution, so that it already exists as minute particles of metal in suspension which become entangled by the comparatively bulky lead sulphate. The precipitate is very light and flocculent, taking a long time (at least forty-eight hours) to settle, but its settling is much facilitated at *Oker*[*] by the addition to each tank of 7 or 8 gallons of oakbark decoction and 1 lb. of glue dissolved in hot water, when twenty-four hours is found sufficient for subsidence. The liquors are drawn off by a syphon and pass to the copper precipitating vats. Generally speaking, the precipitate is allowed to accumulate in the vats until twenty or thirty successive precipitations have taken place; it is then washed out into a small precipitate vat immediately below by removing a plug in the bottom, and there washed seven or eight times with hot water to remove iron, copper, and lead chlorides. After washing, the mass is stirred with water and pumped into a filter press, the cakes being reduced by zinc in hydrochloric acid solution to regenerate part of the zinc iodide. The waste of iodine is made up by adding potassium iodide to the zinc chloride solution, so completing the cycle and transforming the whole of the zinc into iodide again.

The composition of the precipitate is very variable, but generally it contains about 50 to 60 per cent. Pb, 3 to 5 per cent. Ag, and from 0·05 upwards of gold.

The Ziervogel Process.[†]—This process was invented at Mansfeld as an improvement on the Augustin process for extracting the silver from argentiferous copper mattes, and has been carried out there ever since. The process seems only adapted to the treatment of rich copper mattes comparatively free from arsenic, antimony, and bismuth,[‡] which all tend to form insoluble compounds with the silver, the latter forming, after roasting, an insoluble double sulphate, while the two former form arseniates and antimoniates. Ores are not well adapted to the process, chiefly because their silver contents, even if existing as sulphide, are not in that condition of intimate mixture with cuprous sulphide which quick cooling of an actual igneous solution of Ag_2S in excess of copper and iron sulphides necessarily produces. The best results are obtained when the matte is cooled *quickly*

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[*] Egleston, *Trans. A.I.M.E.*, vol. xiv., p. 111.

[†] *v.* Pearce, *Trans. A.I.M.E.*, vol. xviii., p. 55; also Egleston, *S. of M. Q.*, vol. xii., p. 207; Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 767.

[‡] Bismuth is the most harmful of all; *v.* Pearce, *loc. cit.*, p. 67.

by being cast into thin plates on a cooling floor or granulated in water, the reason being that slow cooling gives rise to a segregation and crystallisation of the very fine particles of metallic silver which separate out on cooling and form distinct filiform growths visible with a magnifying glass in masses of the matte which have been slowly cooled. A certain quantity of iron greatly facilitates the roasting, and therefore a low-grade blue to white metal of 60 to 70 per cent. is better adapted to the Ziervogel process than a high pimple metal of 75 to 80 per cent. Success of the process, even on appropriate material, depends entirely on the care with which the roasting operation is conducted; for while too low a temperature prevents the formation of silver sulphate, and too great haste and insufficient rabbling result in incomplete oxidation, with production of cuprous oxide which re-precipitates metallic silver from its sulphate solution, too great a heat or high temperature too long continued bring about decomposition of the silver sulphate already formed and leave part of the metal in the residues.

Though comparatively difficult of solution in the cold, silver sulphate is very soluble in hot water, the solution being sometimes aided by addition of sulphuric acid; this may also assist in the leaching by forming ferric sulphate, which to some extent acts on any metallic silver present and dissolves it as sulphate.*

Extraction of silver by the Ziervogel process, as carried out at Mansfeld (Rhen. Pruss.) and at the Argo Works (Denver, Colo.), comprises two main series of operations—viz., roasting for silver sulphate, and leaching out and precipitation of the silver.

Roasting.—This operation is one of the most delicate in the whole range of metallurgy, and is never attempted except on fairly pure copper mattes, even lead interfering to a considerable extent. Analyses of mattes treated by this process at *Argo* and *Mansfeld* are given in Table X., and it will be seen that while the *Mansfeld* matte is a fairly pure high-grade white metal containing 75 per cent. copper and 0·44 per cent. silver (144 ozs. per ton), that at *Argo* is a very low-grade blue metal containing 40 to 45 per cent. Cu, with a large percentage of impurities and about 1¼ per cent. Ag (over 400 ozs. per ton). The roasting operation is always performed in two stages in separate furnaces, the first being to expel the larger part of the sulphur, while the object of the second is to finish the oxidation to sulphate, decompose the sulphate of the base metals and sulphatise the silver.

The matte must be crushed previous to roasting, and this also is usually performed in two stages, the fine grinding coming after the first roasting, as it is easier to grind roasted matte than raw. At *Mansfeld* both coarse and fine grinding are conducted in No. 5 Ball mills, the capacity of which for

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* *v.* Chap. i., p. 9.

coarse crushing (down to 12 or 16 mesh) is about 14 to 16 tons per twenty-four hours. At *Argo* the coarse crushing preparatory to the first roasting is only to 6 mesh, the subsequent crushing to 60 mesh being performed in Chilian mills.

Preliminary Roasting.—At *Mansfeld* this takes place in Steinbeck shelf furnaces, which are somewhat similar to the Spence furnaces * used for calcining pyritic fines, in being worked with reversing rabbles and entirely without fuel. Each furnace comprises four superposed hearths, but the upper pair of hearths works quite independently of the lower pair, so that each particle only passes through two out of the four hearths. The combustion of the sulphur in even this high-grade matte affords sufficient heat for igniting the cold charge as it enters and for carrying on the roasting process, while the gases being very rich in SO_2 are utilised for the production of sulphuric acid. Each hearth holds 1 ton of matte at a time and each charge stays from four to six hours on each of two hearths, so that the daily output of each double furnace with four hearths is 10 tons.

At *Argo* the first roasting is conducted in Pearce turret furnaces (already described and figured in Part I., Chapter VI.), which seem to be admirably adapted to this purpose. The capacity of each furnace on this material is about 16 tons per day, the raw matte carrying about 21 per cent. and the roasted matte 6 per cent. of sulphur. The fuel consumption is about 25 per cent. by weight of coal, and the cost of roasting is about 80 cents (3s. 4d.) per ton made up as follows:—Labour, 6d.; fuel, 2s. 2d.; power and repairs, 5d.; and interest, 3d. No attempt is made to save the sulphurous acid fumes, but the actual cost of roasting on this material is considered to be less than with any other type of mechanical furnace.

Crushing.—The roasted matte, still containing 5 or 6 per cent. sulphur and much Cu_2O, besides sulphates of iron and copper, is then ground to pass a 60 mesh, which is done at *Mansfeld* in Ball and at *Argo* in Chilian mills. After grinding it passes to the second or sulphate roasting.

Roasting for Silver Sulphate.—At *Mansfeld* this is conducted in reverberatory furnaces with double superposed hearths fired by gas, so as to more effectually secure an oxidising flame and facilitate the conversion of Cu_2O into CuO. The manipulation is identical with that described below. The charge is about 8 cwts., and the total time spent in roasting varies from six to nine hours, about half of which is spent on each hearth.

At the *Argo* Works roasting takes place in small single-hearth reverberatories, hand rabbled, and provided with a separate air supply in the roof above the bridge. The charge of each is about 1600 lbs. of matte roasted in the turret furnaces, and

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* *v.* Peters, *Modern Copper Smelting*, 7th edition, 1895, p. 215, where the similar Keller furnace is figured.

the roast is conducted so as first to convert all the remaining sulphides into sulphates, and then to decompose all the copper sulphate except about 1 per cent., the SO_3 thus given off acting powerfully upon metallic silver and silver sulphide, and bringing practically all the silver present into the condition of sulphate. The addition of 2 per cent. of sodium sulphate (salt-cake) to the charge is found to greatly assist the sulphatisation of the silver.[*] Table X. (to which has been added an analysis of the Mansfeld matte for comparison) shows the composition of the raw matte at *Argo*, of the matte roasted in turret furnaces, and after roasting for silver sulphate; the matte produced from day to day varies greatly in composition, so that the samples do not correspond exactly. The insoluble material recorded in three of these analyses is silica derived from the sand beds in which the matte is cast.

TABLE X.—Analyses of Mattes Treated by the Ziervogel Process.

	Mansfeld.	Argo.		
	Raw Matte.	Raw.	Roasted in Turret Furnace.	Roasted for Sulphate.
Insoluble, . . .	...	0·65	4·05	3·75
Copper, . . .	75·34	47·30	44·92	40·60
Lead, ...	0·69	8·07	8·62	8·52
Zinc, ...	0·95	2·73	5·47	5·24
Iron, ...	1·74	17·67	17·99	18·02
Silver, . . .	0·44	1·38	1·25	1·148
Gold, ...	...	0·088	0·07	0·07
Nickel and cobalt, .	0·61	...	...	...
Sulphur, . . .	20·50	21·58	6·29	...
SO_3, ...	...	...	...	9·09
Oxygen (by diff.), .	...	...	11·34	13·562
	100·23	99·468	100·00	100·000

References.—Mansfeld—Egleston, *S. M. Q.*, vol. xii., p. 204. Argo—*Private communication*, H. U. Pearce, Nov., 1896.

Trippel gives[†] the analysis of another sample of sulphatised matte somewhat poorer in silver which contained 4·048 per cent. of sulphates soluble in water made up as follows, viz.:—$FeSO_4$ and $ZnSO_4$, 2·486 per cent.; Ag_2SO_4, 0·980 per cent.; $CuSO_4$, 0·582 per cent. In this sample the soluble silver was 213·89 ozs. per ton; the insoluble, 32·13 ozs. per ton, or 13 per cent. of the total contents.

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[*] Trippel, *E. and M. J.*, June 23, 1888.

[†] *Loc. cit.*

Progress of the Operation.—The roasting process is described by Pearce [*] as consisting of four stages :—

First Stage.—The dampers are kept closed and the working doors open, and a low temperature is maintained during one and a-half hours. The charge becomes evenly heated throughout, and glows from the oxidation of Cu_2S and Cu_2O.

Second Stage.—The temperature is slightly raised during one and a-half hours with constant rabbling. Sulphates of iron are decomposed, and all sulphur not previously driven off forms $CuSO_4$. The charge swells and becomes porous and spongy from the formation of this salt.

Third Stage.—The temperature is again raised for about one hour until tests show the silver to be "out" (*i.e.*, in the condition of sulphate soluble in water). During this stage of increased temperature $CuSO_4$ is decomposed into CuO and SO_3, which latter acts upon the metallic silver as well as upon any Ag_2S present, forming silver sulphate of both.

Fourth Stage.—The dampers being closed to keep the temperature constant, the charge is collected from all parts of the hearth and bruised down with a heavy paddle to break up the lumps; it is then vigorously stirred and turned over so as to thoroughly oxidise any remaining cuprous oxide and decompose almost all of the remaining copper sulphate.

The tests by which the progress of the roasting is ascertained are made by throwing a sample of the hot charge into a small porcelain dish containing water, which is raised to boiling and dissolves the soluble sulphates out of the charge. Early in the third stage the solution is deep blue with copper sulphate, while as the silver sulphate begins to form in the charge and to be dissolved out in the test, it is immediately reduced to metallic spangles by the cuprous oxide present.[†] As this stage proceeds the solution becomes less blue owing to decomposition of copper sulphate, while the spangles first reach a maximum and then begin to diminish. During the last stage the Cu_2O becomes completely oxidised to CuO and the spangles disappear, while the solution still remains of a very pale blue colour, about 1½ per cent. of copper and other soluble sulphates being always left in order to be sure that the silver sulphate is not itself undergoing decomposition. As soon as the spangles finally disappear the charge is drawn.

Leaching.—At *Mansfeld* the leaching with hot water takes place in a series of wooden tubs shown in cross-section in Fig. 57.[‡]

A is a series of ten leaching tubs provided with false bottoms,

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[*] *Trans. A.I.M.E.*, vol. xviii., p. 66; also Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., p. 133.

[†] According to the equation $Ag_2SO_4 + Cu_2O = CuSO_4 + 2Ag + CuO$.

[‡] From Phillips' *Elements of Metallurgy*, 1891, p. 787.

the capacity of each of which is ½ ton of roasted matte, *b* is a leaden pipe by means of which the charge is first moistened with hot water, and *a* is another larger leaden pipe through which the leaching solution of copper sulphate mother-liquors, acidulated with sulphuric acid, flows constantly on to the surface of the charge at the rate of about 30 gallons per hour for one and a-half to two hours, or until the escaping liquors give no precipitate with NaCl. B is a settling-box, and the compartment, C, serves to distribute the hot liquors to ten precipitating tubs, D, which contain first a 3-inch layer of cement copper and then copper bars for precipitating the silver. The trough, E, and tubs, F, contain respectively sheet- and shot-copper to precipitate the last traces of silver, after which the liquors are run off, and pumped to a leaden pan where they are re-heated to 87° C., with the addition of ½ lb. of sulphuric acid to each 420 gallons of solution, which both facilitates the solution of silver sulphates and prevents the separation of basic salts. The copper in the liquors steadily accumulates and is precipitated at long intervals. The leached residues generally contain from 8 to 13 ozs. per ton; they are dried, re-roasted, and again leached, which brings their silver contents down to from 5 to 6 ozs. per ton. Altogether from 5 to 5½ per cent. of the silver contents of the matte (144 ozs.) is lost by volatilisation, from 3½ to 4 per cent. remains in the residues, and about 92 per cent. is recovered as cement silver.

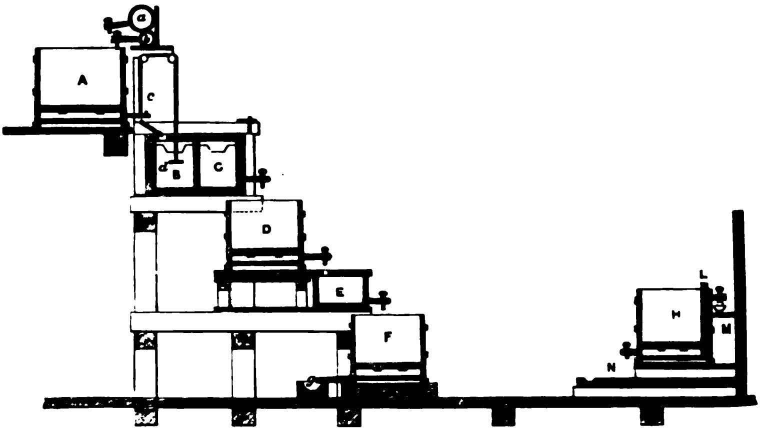

Fig. 57.—Leaching Tubs.

At *Argo* the leaching is conducted very similarly except that no sulphuric acid is used in the leaching water, and that the precipitation of silver takes place exclusively on copper plates, which are prepared at the works from the cement copper precipitated in the scrap-iron tanks so as to recover promptly any silver which escapes precipitation in the proper tank. As a rule, about 40 ozs. of silver remain in the residues out of, say, 400 contained in the original matte, or 10 per cent. Formerly, after re-smelting these residues with gold ores to copper bottoms and matte, by which the gold became concentrated in the former, the residual matte or "finished metal," containing 40 ozs. per ton, was treated by the Augustin process,* but now the Ziervogel process is repeated on it with the result of bringing down the silver contents to under 10 ozs. per ton, after which the cupric oxide residues are chiefly sold to the petroleum refiners, though a small part was until recently made into copper sulphate.

Treatment of the Cement Silver.—At *Mansfeld* the precipitated silver, besides particles of metallic copper and Cu_2O, contains gypsum. It is leached for a week in the series of tubs, H, with dilute sulphuric acid (1 : 8) in order to remove as much as possible of these impurities, and is finally washed with hot water which brings it up to 995 fine. It is then moulded into blocks, dried, and melted on a reverberatory hearth to be refined, yielding bars 999 fine.

At *Argo* the cement silver containing metallic copper and Cu_2O is refined in a tub with a false bottom, below which is the opening of a pipe through which a mixture of steam and air can be forced by an injector. The tub contains about 3000 ozs. of cement silver at a time, together with dilute sulphuric acid (about 1 : 100), and when charged the steam jet is at once turned on. The bubbling up of the air through the perforations in the false bottom oxidises the copper to CuO, which is dissolved by the acid, while the steam keeps the solution boiling, and in this way the whole of the copper is dissolved in about two or three hours. The copper sulphate solution is drawn off, and the silver washed with clean water and steam until the washings show no trace of copper, when it is dried in a long iron pan set on flues and melted down in plumbago crucibles, giving bars 999 to 999·5 fine.

Residues of the Ziervogel Process.—The treatment of these is referred to in Chapter XVII.

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* *v.* Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., p. 147, where the old process is described at length.

CHAPTER XI.

HYPOSULPHITE LEACHING PROCESSES.

The Patera and Kiss Processes.

History.—The solution of silver chloride in sodium thiosulphate (hyposulphite) and its precipitation from the solution by sodium sulphide was first suggested by Percy in 1850, and first carried into practice by von Patera at Joachimsthal (Bohemia) in 1858. Kiss, at Schmollnitz (Hungary), in 1860 first substituted calcium hyposulphite and sulphide for the corresponding sodium salts on account of their greater cheapness and because calcium hyposulphite was at that time supposed to be a better solvent for gold than the sodium compound. This, however, later researches have proved to be a fallacy,* and the use of calcium thiosulphate has certain other disadvantages (*e.g.*, readier oxidation with production of insoluble gypsum and greater consumption of sulphur) which have led to its being largely abandoned. Hofmann,† however, strongly advocates a combination of the Patera and Kiss processes, using sodium hyposulphite for the solution and calcium polysulphide for the precipitant. The advantage of this is that while sodium sulphide generally destroys more hyposulphite than it generates ‡ and so causes a consumption of that salt varying from ¼ up to 7 lbs. per ton of ore, the calcium polysulphide not only decomposes no hyposulphite but is itself oxidised so rapidly to hyposulphite as actually to increase the strength of the stock solution, and so do away with all loss of hypo.

Solubility, &c.—According to Russell's experiments § one hundred parts of $Na_2S_2O_3 + 5Aq$ dissolve forty parts of AgCl (= 30·1 parts Ag) to form the double salt $Ag_2S_2O_3, Na_2S_2O_3 + 2Aq$, while the solubility of AgCl in calcium hyposulphite
cent. of its solubility in sodium salt solutions of
Hyposulphite processes thus start with
the Augustin process, for one hundred
dissolve 0·4 part of AgCl, so that
for silver is about one hundred
salt. Russell further found
hyposulphite could dissolve

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* Stetefeldt, *Tran*

† *E. and M. J*

‡ Stetefeldt

§ *Ibid.*,

mg. of precipitated silver and 2 mg. of gold,* that the degree of solubility of both gold and silver was increased about three times by using a solution at 50° C., but not by increasing the strength of the solution.

The solubility of AgCl in sodium hyposulphite is injuriously affected by the presence of small quantities of certain other substances as shown in the following table compiled from Russell's experiments quoted by Stetefeldt.† The headings to each column show percentage addition of each salt added to a normal hypo. solution of 1½ per cent. strength, and the figures show percentage reductions in solubility.

Percentage Addition.	0·1.	0·2.	2·0.	5·0.
Lead sulphate, . . .	9	24	...	...
Sodium sulphate, . .	...	...	6	8
Caustic soda, . . .	30	90	...	...
Caustic lime, . . .	...	11 to 24	...	...

The presence of these impurities has, therefore, a most important bearing upon the lixiviation process.

Interference of Various Substances.—Ores which are to be treated by the Patera process should be comparatively free from *copper* and *lead*, also from *calcite* unless *sulphides* are present at the same time. The two former give soluble chlorides which pass into solution together with the silver and are precipitated by the sodium sulphide, thus debasing the silver precipitate.‡ The soluble salts of the base metals are leached out from the roasted ore by plain water before commencing the leaching with hyposulphite, but the excess of NaCl in the roasted ore dissolves out more or less AgCl, which has to be precipitated together with the base metals. *Lead* is also particularly injurious on account of the easy fusibility of its compounds, which are liable to sinter up and protect particles of silver chloride from the action of the lixiviating solutions. Lead also consumes hyposulphite to a notable extent as well as sulphide for precipitating, and it has been found that the economical limit of lead in ores to be treated by this process is about 10 per cent. Such part of the lead as goes into solution can, however, be recovered in a marketable form by precipitating as carbonate, as will be seen hereafter. *Zinc* chlorides and sulphates do not appear to interfere with the extraction of silver chloride, but in the case of ores

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* The double salt of gold has the formula $3Na_2S_2O_3 + Au_2S_2O_3 + 4Aq$.

† *Trans. A.I.M.E.*, vol. xiii., p. 53; also pp. 1 and 2 of Discussion.

‡ In quantities under about 3 per cent., however, copper is positively advantageous since it assists in keeping the silver chloridised, and so increases the percentage of that metal extracted.

containing much zinc, part of the zinc invariably remains unaltered as sulphide in the roasted ore, and this, as shown by Morse,[*] reacts upon silver chloride during the base metal leaching as well as in the subsequent leaching with hyposulphite and re-converts part of the silver to the condition of insoluble sulphide. Lead sulphide probably acts in the same way, although less vigorously. *Calcite* in raw ore, unless converted into gypsum by evolution of SO_2 and SO_3 from sulphides present, becomes *caustic lime* in the roasted ore which, besides tending to decompose AgCl during cooling, hinders the leaching out by precipitating insoluble oxychlorides of lead, &c., in the ore. *Arsenic* and *antimony*, so harmful in the Augustin and Ziervogel processes, do not materially interfere with the Patera process, for the arseniates and antimoniates of silver formed, though insoluble in water and brine, are readily dissolved by the hyposulphite solution.

Patera Process without Roasting.—Ores which contain a large proportion of their silver in the condition of haloids (AgCl, AgBr, or AgI) or carbonates (isomorphously replacing lead carbonate in cerussite) can be lixiviated without roasting, and yield variable proportions of their silver contents. In a series of tests on raw ores quoted by Stetefeldt[†] the percentage of extraction varied between 2 and 81 per cent.

This process was tried at Broken Hill in 1890 for the treatment of raw tailings from the concentration of lean siliceous lead carbonate ores carrying silver chiefly as chlorobromide and iodide. The chloride was extracted fairly well, but the iodide was attacked only with great difficulty. Lixiviation was, therefore, abandoned for the time and only adopted again in 1894 with the addition of a chloridising plant, the function of which is to convert AgI into AgCl and incidentally to chloridise any metallic silver present. The working of the new plant is described in the next chapter.

A somewhat similar process was in use at Cerro Gordo (Chili)[‡] for poor chloride ores containing 32 ozs. Ag and about $\frac{1}{2}$ dwt. Au per ton. The ores were crushed in ball mills, and quickly roasted, together with 8 per cent. salt, in Howell furnaces in order to render the particles more easily permeable to the solvent and to convert iodides and bromides into chloride. The cylinders were 26 feet long by 4 feet 6 inches wide, and roasted from 35 to 38 tons per day. The roasted ore was leached, in charges of 8 tons each, six times, with a 1 per cent. solution of sodium hyposulphite, and the extraction was 60 to 80 per cent. of the silver and 60 per cent. of the gold.

Preliminary Roasting.—A thorough chlorodising roast, however, is required for the majority of ores which have to be submitted

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[*] *Trans. A.I.M.E.*, vol. xxv., p. 587.

[†] *Trans. A.I.M.E.*, vol. xiii., p. 66.

[‡] Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 744.

to a leaching process, and details of the operation, as well as of the appliances in which it is carried out, have been already given in Chapter IX. The chloridisation of the silver, however, must be much more perfect when the ore has to be treated by lixiviation than when treated simply by amalgamation, for metallic silver, while readily amalgamable, is attacked only very slowly by hypo. solution. It is also necessary that the flue-dust shall be very thoroughly chloridised, especially as it is very much more difficult to leach than the ordinary ore, owing to its slimy character.

Method of Working.—The usual method of leaching the roasted ore is in false-bottomed wooden vats similar to those employed in the Augustin or Ziervogel process, though of much larger size. The ore is charged into these vats and leached with hot water until the soluble base metal salts are removed, after which lixiviation with hypo. begins and is continued so long as the escaping solutions show any trace of silver. The lixiviation always comprises two distinct operations—viz., *base metal leaching* and *silver leaching*, which, however, in tank lixiviation always follow each other in the same vat.

Base Metal Leaching.—In order to shorten the time required for base metal leaching about 2 feet of water is frequently run into the vat before charging the ore. The strong solution of brine and base metal chlorides (especially cupric chloride) dissolves a considerable amount of silver, which is carried away into the base metal precipitate, but the amount so dissolved can be much lessened by leaching from below upwards, whereby the more concentrated solution at the bottom of the vats passes up through the partially exhausted ore and so re-deposits part of its dissolved silver. This method was first introduced by Hofmann, and has the advantage of being quicker and of causing less packing of the ore, besides requiring less water. It involves, however, somewhat greater complication in the vat connections and piping, and consequently is but seldom used. When the ore leaches badly, or when it contains a large proportion of base metals, hot water is commonly employed for leaching in spite of the greater amount of silver dissolved, but when comparatively free from base metals cold water may be used. In the former case the solutions may be diluted underneath the filter with fresh water, producing a precipitate of lead, antimony, and silver chlorides which dissolves in the hyposulphite solution. In "bottom leaching" the most usual way is to fill the tank with water from the bottom, then shut off the water, open the outlet and let the level of the water sink to the top of the ore, and then continue leaching from the top. By this means comparatively little silver actually leaves the tank in the first wash-water.

The rate at which water will percolate through the ore varies according to the composition of the latter and its degree of fineness, and is from 1 inch (Bertrand, Nev.) up to 16 inches (Broken Hill, N.S.W.) per hour. The quantity of water required depends upon the amount of soluble base metal salts present, and may be as little as 12 (Broken Hill) or as much as 100 (San Francisco del Oro) cubic feet, the average being perhaps 25 or 30 cubic feet per ton of ore, and the duration of the process from two to as long as twenty-four hours. In any case it should be continued until the addition of sodium or calcium sulphide gives no further black precipitate but with the latter only a white cloud of gypsum due to the obstinate presence of sodium sulphate in the last washings. Sometimes the hyposulphite solution is turned on as soon as this point is reached, as recommended by Hofmann,* for by this means time is saved and the access of sodium sulphate to the hyposulphite solution does not matter when calcium sulphide is used as precipitant. Daggett,† however, points out that this plan risks the carrying away of silver into the base metal precipitate through carelessness in not turning the escaping solution into the silver precipitating tanks at just the right moment, besides diluting the stock solution, and recommends draining out the first wash-water before adding the stock solution.

The amount of the total silver dissolved out of the ore by the first wash-water (base-metal solution) varies according to the ore, from 1 per cent. at Blue Bird (Mont.), 7 per cent. at Marsac (Utah), and 10 per cent. at Yedras (Sinaloa, Mex.), up to as much as 19 per cent. at the Holden mill (Aspen, Colo.). At least 90 per cent. of this is contained in the first washings, and is dissolved out in the first fifteen minutes after leaching commences.

The copper, lead, and silver in the base metal solution may be precipitated (*a*) by means of sodium (calcium) sulphide, or (*b*) by means of scrap iron. The first method is not adapted to very base ores as the precipitate is then too bulky and too much precipitant is required. The first portion of the precipitate is always much richer in silver, and, therefore, it is more usual to aim at precipitating only sufficient copper to make sure of carrying down all the silver, the remainder of the copper being precipitated on scrap iron, but in this case precipitation of the silver as sulphide is always incomplete, and some is always found in the cement copper. Precipitation by means of iron is, of course, slower than with sulphide, even if acid be added to the extent of 1 or 2 lbs. per ton of ore, and it requires a large number of precipitating tanks, but the precipitate is not so bulky and is in a more saleable condition. The value of the precipitate with sodium sulphide may vary according to the baseness of the ore in copper and lead, from a few hundred ozs. up to 14,000 ozs. per ton, or nearly one-half silver after drying.

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* *E. and M. J.*, vol. xlvii., p. 236, &c.

† *Trans. A.I.M.E.*, vol. xvi., p. 405.

Silver Leaching.—After the base-metal leaching the hyposulphite solution is run on, the outlet below the filter is connected with the silver tanks, and leaching is continued until a sample of the escaping liquor gives no black precipitate with sodium sulphide, a process which may take from twenty-four hours up to four days. Most of the silver goes into solution quickly, but that portion contained in galena is most difficult to leach out, so that an ore containing 15 to 17 per cent. of lead as galena frequently takes as long as five to six days to leach completely. The volume of hyposulphite solution required varies from 63 cubic feet (Broken Hill) up to 226 cubic feet (Yedras) per ton of ore. At first the leaching should be conducted as rapidly as possible, since the larger part of the silver is extracted in the first few hours of leaching. When tests show the solution to be much more dilute, the rate of leaching is diminished by partly closing the discharge outlet. When the ore contains large quantities of lead, copper, or zinc, it is advantageous to circulate a large quantity of leaching solution through the ore rapidly, instead of shutting off the discharge and allowing the ore to leach slowly, as this plan gives the same rate of extraction in a shorter time, besides tending to yield a richer precipitate—probably owing to the "selective action" of dilute hyposulphite solutions for silver in preference to base metal.*

After the hyposulphite will extract no more silver, a second wash-water is added to expel the remaining hypo. solution contained in the pores of the ore. This is done by allowing the hypo. solution to sink down to the level of the ore, adding 10 to 20 cubic feet per ton of water above (say, 2 to 4 feet deep), and allowing it to leach down to the level again, all that leaches through being run into the stock solution up to this point, and the remainder run to waste or through the scrap-iron tanks. Where water is scarce the whole of the solution is *drained* out, and then about 5 cubic feet per ton (or, say, 6 to 9 inches deep) of clean water is run on top of the charge and leached through into the stock solution.

The Stock Solution.—Either sodium or calcium hyposulphite may be used for dissolving silver chloride, their relative dissolving energy being as already stated, as 100 : 91·5. The hyposulphite solution used at different works varies in strength from 0·5 per cent. (Sombrerete) to 1·8 per cent. (Holden), a 1 per cent. solution being used at Broken Hill. At starting, solutions are very commonly made up to 1½ per cent. (94 lbs. of the sodium salt to each 100 cubic feet of water), but after a little practice much weaker solutions may be used. The disadvantage of a strong solution is that it dissolves out much larger quantities of lead sulphate and other base-metal salts than double the amount of a weak solution would do. The decomposition of

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* Clemes, *Proc. Inst. Civ. Eng.*, vol. cxxv., p. 113.

hypo. is also very much more rapid in the case of a strong solution, so that simple oxidation of the precipitant is not sufficient to maintain its strength as is the case with weak solutions; furthermore, the loss of hypo. carried away in tailings is very much greater in the case of a strong solution. On these grounds Hofmann very strongly recommends the use of stock solutions containing only 0·50 to 0·75 per cent. of hypo., for which he claims the following advantages :—

(1) The extraction of silver can be completed quite as rapidly as with a stronger solution.

(2) The extraction of base metals is smaller, and, therefore, the precipitate is richer.

(3) Both the loss of hypo. in tailings and the loss by oxidation are very small, and, therefore, the strength of the solution is easily kept up by the natural oxidation of the precipitant.

These claims seem to be well founded, and the practice, at present unusual, of working with very weak solutions deserves to be much more widely practical. A somewhat larger quantity of stock solution would have to be kept and used, but this is of small moment.

The total quantity of stock solution required in works treating a given number of tons per day will depend partly on the strength of the solution and partly on the size of the tanks, large tanks requiring a less total quantity of solution than smaller ones. A works with capacity of 100 tons per day using large vats holding 50 or more tons each requires about 3500 cubic feet of stock solution, while a 25-ton works requires 1500 cubic feet. The solution, if of the sodium salt, may be used either hot or cold, the latter being mostly employed for ores containing calcite, which give an alkaline reaction to the wash-water, owing to the decomposing action exercised by hot caustic lime solutions upon silver chloride. With most ores, however, and especially heavy sulphide ores which give acid wash-waters, it is advantageous to heat the solutions to about 80° to 120° F. This precludes the use of calcium hyposulphite, which begins to decompose at about 100° and at 140° F. splits up into calcium sulphate and sulphur, which, however, re-combine to a considerable extent at a lower temperature to re-form hyposulphite.

Sodium hyposulphite is always purchased, but the calcium salt is manufactured on the spot from the polysulphide employed as a precipitant, either by means of spontaneous oxidation, which is sufficiently rapid, or by passing sulphurous acid (generated from charcoal and sulphuric acid, or from burning sulphur) through it. In the latter case the polysulphide is completely converted into hyposulphite according to the following reaction—

$$Ca_2S_5 + 3SO_2 = 2CaS_2O_3 + 4S.$$

In most cases a calcium hyposulphite solution prepared in this way will be much cheaper than a solution of equal strength of the sodium salt,* but, as already seen, it deteriorates rapidly and cannot be used hot.

The loss of hypo. when using the sodium salt has to be made good, either by adding fresh salt or by allowing the precipitant to oxidise spontaneously and so balance the loss. Stetefeldt has shown † that in most cases the latter is considerably more economical, as caustic soda and sulphur are relatively much cheaper than hypo. Sodium sulphide oxidises much more slowly than the calcium salt, but sufficiently fast to make up for the waste of hypo. The loss, when using a very weak solution, is so small that the 5 or 6 per cent. of hypo. naturally present in the sulphide as manufactured is usually sufficient to keep up the strength of the solution.

However prepared, the stock solution suffers deterioration from three sources, viz.:—(1) Decomposition by oxidation; (2) by becoming caustic; and (3) by accumulating sodium chloride and sulphate.

(1) The loss by oxidation is considerable, even in the case of sodium hyposulphite, for, according to experiments at the Ontario mill, a tank of solution oxidised in thirty-five days to the extent of 17·4 per cent.‡ The oxidation of calcium hyposulphite is much more rapid, for, according to the same author, comparative experiments on shallow layers of equal strength of the two salts proved that during one week the deterioration of the sodium salt was 1·4 per cent., and that of the calcium salt 16·1 per cent., or eleven and a-half times as great. In both cases sulphates are formed and free sulphur liberated.

(2) The effect of caustic alkalies in the solution is to decrease the extraction of silver except in those cases where, after roasting, a considerable proportion of that metal exists in the condition of arseniate or antimoniate. The extent of this unfavourable influence has been already referred to. More or less caustic alkali is almost always introduced into the stock solution by oxidation of the precipitants, but fortunately there is an easy remedy in the addition of a little sulphuric acid, say in the proportion of ½ to 1 lb. per ton of ore. Bluestone may be used instead of this, when the process becomes assimilated to the Russell process. When calcium sulphide is used as a precipitant the solution does not so readily become caustic.

(3) The accumulation of sodium chloride and sulphate in the stock solution is somewhat inconvenient, because the latter diminishes the solvent action of the solution. In Hofmann's combined Patera-Kiss process, using calcium sulphide as a

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* This is of much less importance where freight is cheap.

† *Trans. A.I.M.E.*, vol. xx., p. 22.

‡ Stetefeldt, *Trans. A.I.M.E.*, vol. xiii., p. 97.

precipitant, the accumulation of sodium sulphate in the stock solution is completely obviated.

The Precipitants—*Sodium Sulphide.*—The best way of preparing this precipitant is as follows*:—A 6-cwt. drum of caustic soda is broken up into lumps not larger than 6 to 8 lbs. and placed in a cast-iron tank 6 or 7 feet deep and not more than 3 feet diameter, together with 2 or 3 cubic feet of water, and dry steam is turned on. After thirty to forty minutes the whole should be dissolved and should measure 10 cubic feet at most, the temperature being not less than 200° F. If these conditions are fulfilled the sulphur may be added, a shovelful at a time, crushed up roughly so as to pass a 1-inch mesh, and the resulting mass is so thick that if allowed to cool without dilution it would solidify. If, however, the lye be too cold or too weak, combination is not complete, and the mass must be boiled with steam for about two hours, which, however, yields in any case an inferior product. The liquid mass is diluted with hyposulphite stock solution until it contains the equivalent of 12 lbs. of original caustic soda used per cubic feet of solution. Russell recommends that the weight of sulphur added should be two-thirds the weight of the caustic, which gives a sulphide of the formula $Na_2S + Na_2S_2$. The reaction which occurs is—

$$6NaHO + 2(x+1)S = 2Na_2S_x + Na_2S_2O_3 + 3H_2O,$$

so that there is always one equivalent of hyposulphite formed for two of sulphide.

As regards the quantity of sulphur to be added, Stetefeldt shows† that the nearer the composition of the sulphide approaches the formula Na_2S_2 the better the result, for Na_2S in the inevitable oxidation during storage yields NaHO, while higher polysulphides yield free sulphur, and only Na_2S_2 is completely oxidised to the hyposulphite which is utilised. The following formulæ show the reactions which take place during oxidation:—

$$\begin{aligned} 2Na_2S + 2O_2 + H_2O &= Na_2S_2O_3 + 2NaHO \\ 2Na_2S_2 + 3O_2 &= 2Na_2S_2O_3 \\ 2Na_2S_3 + 3O_2 &= 2Na_2S_2O_3 + 2S. \end{aligned}$$

Moreover, it is impossible to avoid the formation of some polysulphide, and, therefore, in aiming at the production of Na_2S, some caustic soda is left free to exercise its injurious effects upon the lixiviation, though it soon absorbs CO_2 from the air and becomes harmless Na_2CO_3.

The use of a pure crystallised Na_2S prepared in Germany is now becoming very common, as a solution of this salt can be freshly prepared which oxidises but little, while being free

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[*] Daggett, *Trans. A.I.M.E.*, vol. xvi., p. 428.

[†] *Trans. A.I.M.E.*, vol. xx., p. 24.

from polysulphides, the precipitate which it produces is almost devoid of free sulphur and is correspondingly richer in silver.

Calcium Sulphide.—It is not possible to prepare aqueous solutions of the lower sulphides CaS to CaS_3, and, therefore, the sulphides made are CaS_4 or CaS_5, according as lime or sulphur is in excess. Caustic lime having a deleterious effect, it is sought to produce CaS_5. The method of preparation is to boil with dry steam two parts of freshly-slaked lime with one part of sulphur crushed fine. The low solubility of calcium hydrate renders it necessary to boil for a long time (at least three and a-half to four hours), and hence the use of lime as a precipitant requires more iron tanks and greater expense for fuel and labour. The reaction which takes place is—

$$3CaH_2O_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

As in the case of sodium sulphide, one equivalent of hyposulphite is formed for two of sulphide. Reference has been already made to the fact that the calcium sulphide oxidises much more readily than the sodium sulphides, the first stage of oxidation being represented by the equation

$$2CaS_5 + 3O_2 = 2CaS_2O_3 + 8S,$$

and, therefore, there is always a large accumulation of sulphur in the storage tanks which can, however, be used over again.

Calcium sulphide is less effective than sodium sulphide, because in precipitating metals by polysulphides of the formula RS_x, $(x-1)S$ is always liberated as free sulphur, and, therefore, the neutralising equivalent of calcium pentasulphide is only that of CaS, the remaining free sulphur being precipitated with the metallic sulphides. Practical experience confirms this theoretical reasoning, for it is found that the sulphide precipitate is of lower grade, and, in particular, contains over three times as much sulphur when CaS_5 is used as a precipitant as when using Na_2S_2 or Russell's sulphide. The bulk of the free sulphur can, however, be boiled out with caustic soda or lime and so utilised over again, but this means a troublesome additional operation in the mill routine.

As regards the relative cost of the two precipitants for the same work done there would seem to be a conflict between the leading authorities. Hofmann states[*] that a test of 2011 tons of Cusi ore containing 45 ozs. per ton showed the consumption of sulphur per ton of ore to be 3·92 lbs. per ton, equal to 3·02 lbs. per ton on a 35-oz. ore. On the other hand, Stetefeldt quotes[†] the result

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[*] *E. and M. J.*, vol. xlvii., p. 236.
[†] *Trans. A.I.M.E.*, vol. xx., p. 29.

of a comparative test at the Cusi mill which lasted fifty-nine days, from which it appears that the consumption of sulphur, using calcium sulphide as precipitant, was no less than 9·3 lbs. per ton; while using sodium sulphide the consumption was only 2·9 lbs. per ton. As the ore was of much the same character, the two sets of figures are quite irreconcilable, but those reported by Hofmann are probably the more correct, since he had a longer experience with Cusi ores. From Russell's figures Stetefeldt attempts to prove that, even allowing for the gain in hyposulphite at current market value, the nett cost of precipitation is considerably greater with calcium sulphide than with the sodium salt.

The nett result of the Hofmann combined process (starting with sodium hyposulphite and using calcium sulphide as precipitant) is also somewhat doubtful. The usual opinion, as expressed by Stetefeldt,* is that the sodium hyposulphite becomes gradually converted into calcium hyposulphite, and this is no doubt true when ores are treated which contain an excess of lime. Hofmann, however, states that although calcium hyposulphite is formed at first, the sodium sulphate produced during the roasting of a sulphide ore, and still retained obstinately after base-metal leaching, is sufficient to effect a complete double decomposition, whereby gypsum is deposited in the ore, and the stock solution remains practically one of sodium salt. It is to be noted, however, that gypsum is soluble in such a solution to the extent of about 15 per cent. of the weight of sodium hyposulphite present; and that according to Schnabel † the solution is accompanied by a partial double decomposition, with formation of sodium sulphate and a double sodium-calcium hyposulphite. On this supposition, when treating very calcareous ores the stock solution would never be free from calcium hyposulphite, even if sodium sulphide were used exclusively as a precipitant; whereas with non-calcareous sulphide ores, even the exclusive use of calcium sulphide as a precipitant would not suffice to change all the sodium hyposulphite into the calcium salt, as the sodium sulphate in the roasted ore would undoubtedly precipitate some lime as gypsum. In all ordinary cases of calcareous ores, therefore, the relative affinities of lime and soda for sulphuric acid will balance according as more lime or more soda is introduced, and the stock solution must be a mixture of the two hyposulphites.

Relative Advantages.—The advantages and disadvantages of calcium sulphide as compared with the sodium salt may be summarised as follows:—

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* *Trans. A.I.M.E.*, vol. xiii., p. 90; and vol. xx., p. 18.

† *Handbuch der Metallhüttenkunde*, vol. i., p. 752.

Advantages.

1. Greater economy of chemicals, especially in inaccessible places where lime is cheap, for then only one chemical (sulphur) has to be imported instead of three — viz., caustic, sulphur, and hypo.

2. Solutions do not so readily become "caustic," thus calling for no bluestone or sulphuric acid as "remedy."

3. Gain of the stock solution in hypo. more than compensates for the total loss of that substance from all causes.

4. Sodium sulphate is to a great extent removed from the stock solution instead of accumulating there.

5. Lead may be separately precipitated from the silver solution by means of sodium carbonate.

Disadvantages.

1. Precipitating power of one equivalent of sulphur as CaS_5 only one-third of that which it possesses as Na_2S_2, hence enormously greater initial consumption of sulphur, a large part of which, however, can be recovered.

2. Greater cost of preparation both for fuel and labour, as well as larger plant required.

3. Less solubility, hence a greater volume of precipitant is added to the stock solution, which becomes more diluted.

4. Greater loss by oxidation — which has the same effect as the last.

5. Production of a larger bulk of precipitate which is contaminated with $CaSO_4$ as well as with free sulphur, which means increased cost for boiling, drying, and also for freight and refining.

6. Production by oxidation of such a large quantity of hypo. that the stock solution becomes in many cases too strong as well as too bulky, and part has to be run to waste.

7. If caustic lime be used to separate lead, it produces a very impure precipitate.

8. Formation of scale of gypsum in filters and false bottoms, as well as in all pipes, tanks, and launders.

On the whole, it may probably be said that the disadvantages outweigh the advantages, except in a few cases where transport is expensive and lime obtainable locally at a cheap rate.

Precipitation.—The silver solution must be stirred or agitated vigorously during the addition of the precipitant, excess of which must be carefully avoided, a few inches of space being always left in the tank so as to run in a little more silver solution if necessary. Excess of precipitant is indicated by turbidity in the solution, smell of H_2S, and discolouration of the sides of the tank. Over-precipitation is attended by the very grave result of actually re-forming and re-precipitating silver sulphide in the next charges of ore upon which the stock solution is used. The precipitated silver sulphide should not be allowed to accumulate too long in the tank, as every time it is stirred up it becomes more slimy and settles with greater difficulty. At least, every other day it should be pressed and thoroughly washed in the press to remove sodium sulphate and other soluble salts, which increase its bulk and interfere more or less with the subsequent drying, roasting, and refining.

Chemical Reactions.—The formation of sodium and calcium sulphide, and their oxidation to hyposulphites, has been already described. The oxidation of hyposulphite to sulphate in use is a simple replacement of sulphur by oxygen (thiosulphuric acid itself being a sulphuric acid in which one atom of oxygen in the hydrogen radical is replaced by sulphur) and may be expressed by the equation—

$$2SO_2NaONaS + O_2 = 2SO_2(NaO)_2 + 2S.$$

The reactions by which silver and gold in the ore pass into solution are :—

$$2AgCl + 2Na_2S_2O_3 = 2NaCl + Na_2S_2O_3 . Ag_2S_2O_3$$
$$2Ag_3SbO_4 + 6Na_2S_2O_3 = 2Na_3SbO_4 + 3(Na_2S_2O_3 . Ag_2S_2O_3)$$
$$2Au + 4Na_2S_2O_3 + O + H_2O = 2NaHO + Au_2S_2O_3 . 3Na_2S_2O_3.$$

The reaction in precipitating by CaS_5 is :—

$$Ag_2S_2O_3 . Na_2S_2O_3 + CaS_5 = CaS_2O_3 . Na_2S_2O_3 + Ag_2S + 4S$$

and in part, at least,

$$CaS_2O_3 . Na_2S_2O_3 + Na_2SO_4 = CaSO_4 + 2Na_2S_2O_3.$$

The reactions for the precipitation of gold, copper, and lead as sulphide are similar, and Na_2S_2 acts similarly to CaS_5, except that there is only one-fourth the amount of free sulphur liberated, thus—

$$CuS_2O_3 . Na_2S_2O_3 + Na_2S_2 = 2Na_2S_2O_3 + CuS + S.$$

Reversion of Silver Chloride.—With some ores, especially with those which are "light," the actual extraction of silver is equal to that indicated by the chlorination test performed on the roasted ore as charged into the tanks, but this is exceptional, the rule (especially with "heavy" ores containing much galena and blende) being for the mill extraction to show a deficiency of from 10 to 20 per cent. below the results indicated by laboratory tests. The reason for the discrepancy has been the subject of much speculation, but the explanation given by Morse * seems to be quite satisfactory. At the *Holden* mill (Aspen, Colo.) where, during the year 1892, over 30,000 tons were treated under a most careful system of checkweighings and assays, it

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* *Trans. A.I.M.E.*, vol. xxv., p. 587.

was found that the percentage of silver soluble in hypo. as charged into leaching vats was 78·93, whereas after twelve hours base metal leaching the percentage soluble was only 64·33, a difference of 14·60 of the total silver present. It is obvious that the silver must have been reconverted from the condition of silver chloride to some other combination insoluble in hyposulphite (though soluble in Russell's solution, as will be hereafter seen), and Morse proves by experiment that the unaltered blende in the ore is an agent capable of effecting the transformation, a fact, indeed, long ago pointed out by Dubois * and Aaron †; the reaction supposed to take place being the following:—

$$2AgCl + ZnS = Ag_2S + ZnCl_2.$$

In the same paper by Morse it is shown that the corresponding reaction with lead may be utilised for enriching the base metal sulphide precipitate which is so expensive to refine. Instead of using sodium sulphide for the silver solution, after the first few precipitations as an experiment, the base sulphides at the bottom of the vat (at Holden, chiefly PbS) were stirred up for about two hours by means of compressed air, with each successive tankful of fresh wash-water. The silver of the base metal wash-water was found to be completely precipitated without adding fresh alkaline sulphide, and with the advantage of constantly enriching the precipitate first formed, the reaction being:—

$$2AgCl + PbS = Ag_2S + PbCl_2.$$

It is not, however, stated how far the enrichment of the precipitate could be carried. An extension of this method might, perhaps, be possible, especially with cupriferous ores, whereby the base metal sulphides precipitated from the first wash-water should be utilised exclusively for the precipitation of silver from the stock solution in place of employing fresh alkaline sulphides. This would have the advantage of yielding only one lot of enriched precipitate for refining instead of two lots of larger aggregate bulk and different quality as at present, while, if the precipitation of silver proved to be incomplete, the last traces might be precipitated together with part of the copper in a second series of tanks before pumping back the solution, this precipitate also serving as precipitant on a fresh lot of strong silver solution. The resulting presence of cuprous hyposulphite in the stock solution would be a positive advantage on most ores as the process would then become a sort of modified Russell process without its increased cost.

According to Godshall ‡ the reversion of silver chloride is due to other agents besides the presence of metallic sulphides, and he

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* *Min. and Scient. Press*, May 11, 1889, p. 334.
† *E. and M. J.*, June 22, 1889, p. 563.
‡ *Trans. A.I.M.E.*, vol. xxv., p. 1027.

supposes that in the case of imperfectly roasted sulphide ores which sometimes show no improvement in chlorination on being left in heaps on the cooling floor, a reduction of $AgCl$ to metallic silver may take place through the direct action of SO_2 evolved during the slow oxidation of the heap.

Percentage of Extraction.—The percentage of silver extracted by the Patera-Kiss process varies from 70 up to about 85 per cent., as will be shown in the next chapter. Generally speaking, the percentage extraction is much higher on rich ores than on poor ones, though at Candameña (Mex.) in 1885 the tailings from rich refractory 180-oz. ore treated by this process averaged from 18 to 20 ozs. per ton.

Hofmann mentions [*] that the percentage of extraction on badly roasted charges of San Francisco del Oro ore (which contains no copper) was improved to the extent of 30 to 40 per cent. of the previous extraction by the addition of about 2 lbs. per ton of $CuCl_2$ in solution (prepared by boiling a mixture of bluestone and salt in suitable proportions with steam). The $CuCl_2$ is either added to the water in the vat before charging, or, it is added, a little at a time, during the whole duration of the base metal leaching process. The solution which left the ore was colourless, showing that the $CuCl_2$ had been decomposed in passing through it according to the equation $CuCl_2 + ZnS = CuS + ZnCl_2$. By this modification the ordinary Patera process is brought very near to the Russell process, but, however advantageous the addition of $CuCl_4$ might be to ores containing no copper such as those of San Francisco del Oro and Yedras, it is difficult to see how any possible benefit could arise in the case of cupriferous ores.

The Russell Process.[†]—Reference has been already made [‡] to the fact that salts of copper yield, with alkaline hyposulphites, double salts soluble in water and more so in excess of alkaline salt. The best known of these (the two-third salt of Lenz) has the formula $2Na_2S_2O_3 . 3Cu_2S_2O_3$, and is a yellow powder which can be dried at a temperature of 40° C. and is stable up to 80° C., above which it rapidly decomposes, yielding Cu_2S and free sulphuric acid. It is soluble in 352 parts of cold water, but in only eight parts of a 5 per cent. solution of sodium hyposulphite. These double salts exercise an energetic action upon all silver salts as well as on the metal itself, "which can only be compared to the action of Cu_2Cl_2 upon these salts, though the parallel is by no means close." [||] The most noteworthy point, however, in

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[*] *v.* also chap. ix., where the influence of $CuCl_2$ in increasing chlorination on the cooling floor is referred to.

[†] *v.* Stetefeldt "On the lixiviation of silver ores with hyposulphite solutions"; also *Trans. A.I.M.E.*. vol. xiii., p. 47; vol. xv., p. 355; vol. xx., pp. 3 and 15; also Daggett, *ibid.*, vol. xvi., p. 362, &c.

[‡] In Chap. i. on the properties of silver and its compounds.

feldt, *Trans. A.I.M.E.*, vol. xiii., p. 56.

connection with the dissolving energy of these double salts is that it seems to be to a great extent independent of the degree of concentration of the solution, so long as the double salt itself does not become decomposed by substances present in the ore and so lose its activity. Russell in working out the relative proportions of the salts found that the best results were given by mixing two parts by weight of sodium hyposulphite with one part of copper sulphate (both in the crystallised condition), and the resulting solution probably contained the salt $Na_2S_2O_3 . Cu_2S_2O_3$ formed in accordance with the equation

$$4Na_2S_2O_3 + 2CuSO_4 = Na_2S_2O_3 . Cu_2S_2O_3 + 2Na_2SO_4 + Na_2S_4O_6.$$

The double cuprous-calcium hyposulphites are about equal in effect to the corresponding sodium salts, but the potassium salts are much less energetic.

Action of Russell's Solution.—It was found by Russell that the above solution (which he calls the "extra solution") has, when used cold and in large excess, nine times the dissolving energy of simple hypo. for *metallic silver*. At a temperature of 50° C., however, its relative energy is only three and a-half times as great, and at a higher temperature the difference is still less marked. On *metallic gold* the "extra" has no more effect than ordinary solution. On freshly-precipitated *silver sulphide* ordinary solution has little or no effect, but extra solution in all conditions of dilution attacks it readily, a 10 per cent. solution being only 40 per cent. more powerful in its effect than one of 1 per cent. This explains why extra solution should give a better result than the ordinary on ores of a refractory nature, except those which contain much substance of a character capable of decomposing the double salt. *Gold sulphide* is attacked in a similar manner to silver sulphide, Cu_2S being precipitated as the precious metal goes into solution as hyposulphite. All silver-bearing minerals are attacked with greater or less rapidity by excess of extra solution, the order being chloride, bromide, iodide, metallic silver, argentite, stephanite, pyrargyrite, and polybasite. Fahlerz appears to be the most refractory of all silver-bearing minerals properly so called. From a valuable series of experiments on raw ores, all of a "base" or refractory character quoted by Stetefeldt[*], it would appear that the maximum percentage of extraction under experimental conditions with a large excess of extra solution varied from 32 per cent. (Ontario) up to 68½ per cent. (Lexington), 72·8 per cent. (Custer), and 81 per cent. (Tombstone), compared with 7, 26, 28, and 70 per cent. respectively by ordinary solution, part of the silver in the last-mentioned ore being as chloride. In another series of experiments by Watson[†]

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[*] *Trans. A.I.M.E.*, vol. xiii., p. 66.

[†] Daggett, *ibid.*, vol. xvi., p. 460.

three different raw ores from Sombrerete showed extractions by extra solution of 70, 81, and 86 per cent., as compared with extractions on the same ores by ordinary solution of 25, 3, and 8 per cent. respectively. It should, however, be understood that these results are merely those of laboratory experiments with excess of solvent, and cannot be taken as indicative of similar working results on the large scale. A further series of experiments by Russell proved that on many raw ores the percentage of extraction was materially greater where they had passed a 90 mesh than where they had passed one of 40 mesh only, but that with roasted ores the percentage of extraction seemed to be but little affected by the degree of fineness. This is a most important practical point, for the rapidity of leaching is inversely proportional to the degree of fineness, and hence it is advisable to keep the ore as coarse as possible, having regard to the facility of roasting; *e.g.*, a 16 or 20 mesh will serve for many ores, especially those of light character, while a 30 or 40 mesh will be required for sulphide ores containing much lead or zinc. Still another series of experiments[*] in roasting Yedras ore with 7 per cent. salt in a muffle for a gradually increasing length of time varying from a half to two and a-half minutes showed that from 67 to 86 per cent. of its silver value was converted into a form soluble in extra solution, though with ordinary solution the percentage extracted remained constant at about 64·5. This result indicates the remarkable effect of momentary roasting in a Stetefeldt furnace on all *light* ores, especially those containing sulpharsenides and sulphantimonides of silver disseminated through a gangue of quartz and calcite. Such ores are particularly well adapted to the Russell process after a short roasting with only a small proportion of salt, because any metallic silver formed in roasting, together with the arseniate and antimoniate, is attacked and dissolved by the extra solution, while the solubility of Ag_3AsO_4 and Ag_3SbO_4 is actually increased by the presence of caustic alkalies in the solution, their behaviour in this respect being directly contrary to that of AgCl.

It should be clearly borne in mind that although the extra solution is so energetic in its action upon all silver compounds, the solvent *capacity* of a given volume of it for AgCl is less than that of an equal volume of ordinary solution containing the same total amount of hyposulphites. In most cases, therefore, it is advisable to dissolve out as much as possible of the AgCl by ordinary solution, and then act upon the residual metallic silver and sulphide by "extra."

With the object of diminishing the consumption of copper salts as well as of purifying the precipitate, it is advantageous in many instances to make the extra solution which has already

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[*] Daggett, *Trans. A.I.M.E.*, vol. xvi., p. 463.

done its work upon one charge of ore, and still retains copper in solution, to pass through a second charge of ore, by which means it becomes freed from copper as well as enriched in silver. An extra solution used the second time is called a "special extra," and when used always precedes the regular extra solution. The advantages of this procedure are, however, often offset by the additional complications involved.

Separate Precipitation of Lead.—Besides the use of extra solution, which forms the principal feature in the Russell process, there is another patented improvement which can be adopted with great success on certain ores—namely, the precipitation of lead from the solution by means of sodium carbonate.

Separate precipitation of lead as hydrate from a hyposulphite solution by means of caustic lime was practised at the *Mt. Cory* mill (Nev.) in 1884, but it has the following disadvantages:—(1) The solubility of calcium hydrate is so slight that milk of lime must be used, and there is no means of ascertaining when precipitation is complete except by employing some other reagent; (2) accidental addition of an excess of caustic lime redissolves part of the precipitate, besides impairing the solvent capabilities of the solution; (3) the precipitate is contaminated with gypsum and with all the insoluble impurities of the lime and therefore fetches a low price. Russell was the first to discover the fact that $PbCO_3$ is almost insoluble in sodium hyposulphite solution while the carbonates of silver and copper are very soluble. The carbonates of iron, manganese, zinc, and calcium are also insoluble in hyposulphite solution, but all the salts of these metals which are soluble in hypo. are also more soluble in water than lead sulphate, and should be removed by the first wash-water. The advantages of using sodium carbonate for separate precipitation of lead are only attainable by employing a sodium hyposulphite stock solution and using sodium sulphide exclusively as a precipitant; they are the following:—

(1) Saving in cost of refining silver sulphides through decreased bulk and increased richness.

(2) Obtaining the greater part of the lead product in a clean, heavy, and compact form, free from Cu, Fe, Zn, &c., and readily marketable.

(3) Greater adaptability to the use of a hot stock solution, one of the chief objections to which formerly was the large amount of $PbSO_4$ dissolved by it.

(4) Saving in caustic soda and sulphur required to make sodium sulphide.

As regards the silver contents of the precipitate, Russell claimed that by washing in fresh, rather strong hypo. solution the precipitate might be so freed from silver as to carry only 2 ozs. per ton and to serve for the preparation of high grade litharge or red lead; but this degree of purity does not seem to be attainable in practice, as the average contents of the carbonates obtained during a year's work at the *Holden* mill was 432 ozs. per ton,* and of those produced at *Marsac* from 600 to 1400 ozs. per ton.†

Scheme of Operations.—The Russell process in its complete form being somewhat more complex than the ordinary Patera process the accompanying scheme of operations may be found useful.

THE RUSSELL PROCESS, GENERAL METALLURGICAL SCHEME.

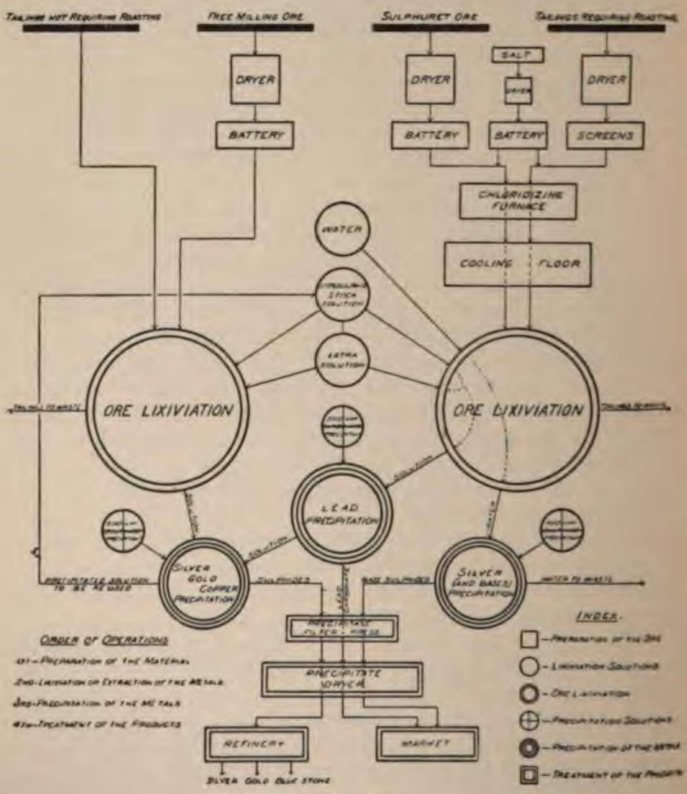

Fig. 58.

Method of Leaching.—The treatment of ores by the Russell process is varied according to their nature, three principal classes being distinguished, viz.:—(*a*) "acid," (*b*) "alkaline," and

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[*] Morse, *Trans. A.I.M.E.*, vol. xxv., p. 145.

[†] Stetefeldt, *ibid.*, vol. xxi., p. 286.

'alkaline arsenical" ores, according to the reactions of the ; wash-water.

ı) "*Acid*" ores are those the first wash-water of which has ıcid reaction owing to the presence of sulphates of the heavy als. This is by far the largest class, in it are included the ; of the *Ontario*, *Cusi*, *Sombrerete*, and other mills, as well as ost all tailings from amalgamation processes, especially if ghly concentrated before treatment. This class is treated— r the first wash-water, which is universal except in the case aw ores and tailings—first with ordinary solution, then with rong extra solution, which is often circulated through and ough the charge by means of the ejector or montejus pump, then again with ordinary solution, which is, of course, hed out by the second wash-water. Sometimes the ordinary extra solutions are alternated, but this is unusual with acid s. The applicability of the Russell process, except in the e of ores which contain a considerable amount of copper, ıot very evident.

b) "*Alkaline*" ores are those with a calcareous gangue, which r roasting contain an excess of caustic lime, and the first h-water of which gives an alkaline reaction. Of this class the ores of Lake Valley and those treated in the *Marsac** *Holden* mills. After the first wash-water, which is always l, the charge is treated with alternations of weak extra and inary solutions in large volume; the extra solutions being quently applied cold, the ordinaries always warm. The rather nplex series of alternations employed at the Marsac and lden mills respectively are described in detail in the next pter.

c) "*Alkaline arsenical*" ores are those calcareous ores which tain considerable quantities of arsenic and yield an alkaline sh-water. Practically the only ore of this class is that of dras. This class of ore is treated first with cold wash-water, n with cold ordinary solution, and then with a strong extra ıtion, which is allowed to soak into the ore during twelve ırs, being followed by a large volume of ordinary solution and wash-water as usual.

Strength of Solutions and Consumption of Chemicals.—The inary stock hypo. solution used in the Russell process differs no respect from that used in the Patera process, and varies in ength from 0·8 up to 1·8 per cent. The loss of hypo. has been eady referred to, but it may be here stated that the consump- n of hypo. varies† (1) directly as the total volume of the ck solution; (2) directly according to the strength to be intained; (3) inversely with the capacity of the works; (4) ersely with the richness of the ore; and (5) according as the

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* This ore though *slightly* alkaline may be regarded as neutral.

† Daggett, *Trans. A.I.M.E.*, vol. xvi., p. 396.

ore is acid or alkaline. The average consumption of hypo. for acid ores is greater than for alkaline ores.

The extra solution employed varies in strength from 1·5 to 2·3 per cent. of hypo. and from 0·5 to 1·1 per cent. of bluestone. It is almost invariably made up on top of the ore charge by adding the required amount of bluestone to a small quantity of ordinary solution, together with the amount of hypo. found by experiment to be the consumption per ton treated. The whole of the required hypo. is added to the extra solution because—(1) The full amount of hypo. is required in order to dissolve the copper salt and keep it in solution, whereas the ordinary solution will do its work even if temporarily much lower in strength. (2) The "extra" solution after doing its work becomes ultimately converted into "ordinary" solution, part of its copper remaining in the ore and the rest going into the precipitate. When making up the extra solution on the surface of the charge the weighed quantity of chemicals is placed in a perforated wooden box and the stream of stock solution allowed to flow through. Making up the solution in a separate tank, however, saves a little time, and is, therefore, sometimes adopted, especially with some alkaline ores which leach best when treated with a large volume of weak extra solution, which, running through the ore, leaves all its copper behind, becoming converted into ordinary solution. In the case of "acid" ores the function of the extra solution is to dissolve silver as sulphide and other combinations not acted upon by ordinary solution. It is, therefore, necessary to employ a strong solution, and advisable to "circulate" it through the ore particles by pumping it back, so as to dissolve out as much silver as possible and to remove most of its copper from the solution, as otherwise waste of copper and debasing of the silver precipitate would result. Frequently after circulation, even for five or six hours, the solution still contains so much copper as to be capable of serving as a "special extra" solution on the next tank charge immediately before the regular extra, by which means not only is the "special" freed from copper, but the following regular "extra" mixes with a solution of its own strength instead of becoming diluted with water or ordinary solution.

In the case of a simple alkaline ore, comparatively free from metallic sulphides, there is little danger that silver will remain in the sulphide condition after roasting, and therefore the chief use of the extra solution is not to attack insoluble compounds, but to protect the silver chloride from the action of caustic lime, which throws it back into the comparatively insoluble metallic condition. It is, therefore, quite possible and in many cases advantageous to add all or part of the required bluestone in the first wash-water, by which means its copper contents are precipitated upon the ore particles as carbonate, and then the ordinary olution, on being turned on, together with a slight addition of ypo., forms extra solution in the pores of the ore.

Decomposition of Extra Solution.—Extra solutions of whatever trength, and however prepared, should not be stored for more han a few hours, as they are liable to two special sources of eterioration which do not affect the ordinary solution. The irst is a spontaneous decomposition much aided by heat (as, for xample, by the use of a Körting ejector pump), according to the ollowing equation :—

$$Na_2S_2O_3 \,.\, Cu_2S_2O_3 = Na_2SO_4 + Cu_2S + SO_2 + S.$$

he SO_2 takes up oxygen and water to form sulphuric acid, hich, if the solution had been made up with fresh water, would emain free. Seeing, however, that the "extra" solution is lways made up with the stock solution, which contains more r less sodium and other soluble chlorides, the ultimate result ay be considered to be the liberation of free hydrochloric acid ccording to the following equation :—

$$Na_2S_2O_3 \,.\, Cu_2S_2O_3 + 2NaCl + H_2O + O = 2Na_2SO_4 + Cu_2S + 2HCl + S.$$

he second process of deterioration is a peculiar slow oxidation o tetrathionate, particularly noticeable when a geyser (air-) ump is employed, from which the ordinary solution, for some eason, appears to be exempt, and which may be represented as ollows :—

$$2SO_2 \left\{ \begin{array}{l} NaO \\ NaS \end{array} \right. + O + H_2O = \begin{array}{l} SO_2 \\ SO_2 \end{array} \left\{ \begin{array}{l} NaO \\ S \\ S \\ NaO \end{array} \right. + 2NaHO.$$

The Precipitants.—The composition and preparation of the *odium sulphide* has been already described in connection with he Patera process. Frequently, however, the pure crystallised a_2S is used instead, and this appears to avoid bringing traces f caustic soda into the solution.

The *sodium carbonate* solution is best prepared by dissolving olvay soda in stock solution, so as not to dilute the latter too uch. Common soda-ash may be used, but it must first be reed from traces of Na_2S (which would precipitate Ag_2S with bCO_3) as well as from traces of NaHO, which would impair he dissolving energy of the stock solution. Both impurities re removed from the strong carbonate solution by first digest- g it with a little sulphur so as to convert traces of NaHO into a_2S, and then removing the whole of the sodium sulphides by dding copper sulphate as long as a brown precipitate is pro- uced. When using the sodium carbonate precipitant it must e added cautiously as long as a precipitate forms, and care ust be taken to avoid excess—not, however, on account of any njurious effect upon the solution, but simply because when any caustic soda has to be neutralised in the stock solution the carbonate would also have to be neutralised, using more acid and producing more sodium sulphate.

Precipitation of Lead and Silver.—The precipitate of *lead carbonate* is much less bulky than that of the sulphide, and being crystalline in character, provided the contents of the precipitation tank are thoroughly stirred during the addition of sodium carbonate and for a minute or so afterwards, settles rapidly, so that in half an hour the solution can be syphoned off into the silver precipitation tanks. On calcareous ores, however, containing only small quantities of lead, separate precipitation of this metal is not worth the additional expense, as the small amount of precipitate obtained is too much contaminated with gypsum.

Silver sulphide precipitation in the Russell process should be conducted with the same precautions as in the ordinary Patera process. It has been claimed that over-precipitation is of less importance than in the ordinary process, since any silver sulphide precipitated in the pores of the ore charge by an excess of sulphide in the stock solution, would be re-dissolved by the extra solution, especially if a trifle stronger than usual; but this is a very dangerous sort of belief to work by, and it is always safer to leave a small part of the metals unprecipitated than to add excess of sodium sulphide.*

Chemical Reactions.—The reactions common to the Patera and Russell processes, as well as those which take place in the formation and oxidation of extra solution, have been already referred to in this chapter.

The mode of action of extra solution upon metallic silver and sulphide is probably a replacement of copper by silver in the double hyposulphite, as shown by the following equations:—

$$Na_2S_2O_3 . Cu_2S_2O_3 + Ag_2S = Na_2S_2O_3 . Ag_2S_2O_3 + Cu_2S.$$
$$Na_2S_2O_3 . Cu_2S_2O_3 + 2Ag + O + xH_2O = Na_2S_2O_3 . Ag_2S_2O_3 + Cu_2O . xH_2O.$$

In the case of an ore containing excess of caustic lime this cuprous hydrate at first re-dissolves in the excess of sodium hyposulphite, forming another double salt richer than the normal salt which acts upon refractory silver compounds more energetically than the simple sodium salt, though much more slowly than the normal double salt. The reaction may, perhaps, be as follows:—

$$5(Na_2S_2O_3 . Cu_2S_2O_3) + Cu_2O = 2(2Na_2S_2O_3 . 3Cu_2S_2O_3) + 2NaHO.$$

Ultimately, however, by the continued action of the caustic lime practically all the copper remains precipitated in the pores

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* Except for the definite purpose mentioned on p. 210, and even then the excess must be neutralised before running the solution into the storage sumps.

of the ore, while the silver present is fairly well extracted. It seems likely that with ores of this class some benefit would be derived by adding, together with the first wash-water, a sufficient quantity of free sulphuric acid to convert the free caustic lime present into sulphate. The chief drawback, however, to this is the increased difficulty of filtration caused by the formation of additional gypsum at such an early stage of the leaching, besides the expense. Practically speaking, the chief functions of extra solution in an alkaline ore are to prevent reaction of caustic lime upon AgCl and to re-dissolve any metallic silver formed by this reaction during the base metal leaching. With such ores a considerable quantity of bluestone is required to act upon them for a long time in order that the cuprous salts may thoroughly penetrate to every particle.

In the case of a thoroughly roasted quartzose ore containing no free caustic lime and little or no unaltered zinc and lead sulphides, the free hydrochloric acid formed by spontaneous decomposition of the double salt, as already seen, complicates the reaction by re-dissolving any cuprous hydrate separated as follows :—

$$Cu_2OxH_2O + 2HCl = Cu_2Cl_2 + (x + 1)H_2O.$$

Most of the copper thus remains in the leaching solution in a form which actively attacks silver both in the metallic and sulphide conditions, and transforms it into chloride, which is dissolved by the hyposulphite solution. On such ores the extra solution retains its activity for a long time, and only a small amount of bluestone is, therefore, required.

When, however, a heavy ore is only partially roasted (as, for example, in the Stetefeldt furnace) so that it still contains undecomposed zinc and lead sulphides, the Cu_2Cl_2 formed as above is almost instantaneously decomposed according to the equation :—

$$Cu_2Cl_2 + ZnS(PbS) = Cu_2S + ZnS(PbCl_2).$$

Similarly, it is probable that unaltered sulphides may act directly upon the cuprous double salt as follows :—

$$Na_2S_2O_3 . Cu_2S_2O_3 + PbS(ZnS) = Cu_2S + Na_2S_2O_3 . PbS_2O_3(ZnS_2O_3).$$

At any rate, whether in accordance with the above equation or not, it is a fact that such ores within a very short time precipitate the whole of their copper contents from extra solution so that the latter is no longer able to exercise any but a very weak solvent action upon silver compounds; less, indeed, than an equal volume of ordinary solution.

Reference has been made to the loss of hyposulphite through conversion into tetrathionate during the formation of the extra solution (no less than 1 lb. for each 1 lb. of bluestone dissolved), and to the continued formation of this salt through oxidation of the extra solutions. The tetrathionate is not a solvent for silver compounds, and, therefore, it is fortunate that it can be reconverted into hyposulphite by simply adding sodium sulphide, when the following reaction takes place :—*

$$Na_2S_4O_6 + Na_2S_x = 2Na_2S_2O_3 + xS.$$

This reaction only comes into play when all the silver has been precipitated; it is, therefore, advisable when using the Russell process to *always* throw down all the metals in solution by adding the full amount of sulphide, even at the expense of somewhat debasing the precipitate, and now and then it is well to over-precipitate a few tanksful of solution so as to convert all the tetrathionate present into hypo., running in a little fresh silver solution afterwards to neutralise the excess of sodium sulphide added. The free sulphur added to the precipitate in this way can be easily roasted off.

Consideration of Reactions.—From a consideration of the above reactions we might conclude *á priori* that the addition of a small quantity of bluestone to the hyposulphite leaching solution (which, practically speaking, is the only essential feature of the Russell process) would result in a notably increased extraction of silver only in the case of thoroughly oxidised† ores composed principally of quartz and of earthy gangue with calcite; that ores containing a very large proportion of calcite would require a proportionately larger amount of bluestone and a longer time in order to show any useful effect; and finally, that ores containing any large quantity of zinc or lead sulphides (as, for example, badly roasted galena ores) would show practically no effect from the use of Russell's solution in any ordinary or reasonable quantity. These conclusions are confirmed by the results of practical experience, the ore so successfully treated at the *Marsac* mill being an example of the first class; the Aspen ores treated at the *Holden* mill of the second; while the ores of *Cusihuiriachic*, *San Francisco del Oro* and *Sombrerete*, which are not suitable to the Russell process, are examples of the third class. Further reference to the claims put forward on behalf of the Russell process will be found in the next chapter.

Percentage of Silver Extracted.—On the average the percentage of silver extracted from chloridised ores by the Russell process is higher than by the ordinary Patera process, and it also compares very favourably with pan-amalgamation as regards almost all base ores. The following table shows actual mill results obtained on the various ores mentioned. It is to be understood that each ore was subjected to chloridising roasting with the percentage of salt found to give the best results, and the actual percentages of extraction given are (except those of the last column) calculated on the contents of the roasted ore.

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* Stetefeldt, *Trans. A.I.M.E.*, vol. xx., p. 26.

† *i.e.*, freed from sulphur by roasting, or originally "light" ores.

TABLE XI.—COMPARATIVE EXTRACTION OF SILVER BY AMALGAMATION AND LIXIVIATION.

	Alkaline.			Acid.				Average.
	Lake Valley, New Mex., 1885.	Marsac,[*] Park City, Utah, 1890.	Yedras, Sinaloa, Mex., 1886-87.	Ontario,[*] Park City, Utah, 1887.	Cusi, Chihuahua, Mex., 1888.	Blue Bird, Montana, 1885-90.	Sombrerete, Zacatecas, Mex., 1890-95.	
Reference, .	**1.**	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	
Amalgamation,	70·6	82·2	65·0	82·1	75·4	70·3	...	74·3
Patera process,	53·0	82·5	71·1	82·5	78·3	...	82·5	75·0
Russell process,	83·0	92·7	87·5	92·5	84·8	76·1	58·1	82·1

References.—1, 2, 4, and 5. Daggett, *Trans. A.I.M.E.*, vol. xvi., pp. 475, *et seq.* 3. Letts, *E. and M. J.*, Jan. 4, 1893. 6. Hoyt, *Private communication.* 7. O. Hofmann, *Private communication.*

It is to be remarked that mill results by the amalgamation and Patera processes often fall very far short of the percentage indicated in the assay office by a "chlorination test" with ordinary solution, whereas with the Russell process the percentages indicated by laboratory experiments can generally be realised, and occasionally slightly exceeded in practical working results on a large scale, provided the roasting be efficient. Further, it is found by experience that with "light" ores low in lead and zinc the results obtained in the mill are, to a certain extent, independent of the perfection of the roasting, whereas in the ordinary process a badly-roasted charge will frequently show a falling-off in extraction of 20 to 40 per cent. The bad influence upon extraction of the "reversion" of $AgCl$ to Ag_2S or to Ag which is disastrous in the ordinary process is also much less important in the Russell process, so that generally speaking the results are more uniform.

The questions of arrangement of plant, consumption of chemicals, and cost of operation by the Patera and Russell processes, together with comparative data of the work done at different mills, and detailed descriptions of the practice at certain typical localities, will be dealt with in the next chapter.

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[*] The Marsac ore is practically neutral, and the Ontario ore, which much resembles it, is only slightly acid.

CHAPTER XII.

HYPOSULPHITE LEACHING PRACTICE.

Preliminary Treatment.—The crushing of ores as a preliminary to their treatment by lixiviation is generally performed by means of stamps, rolls and other mills only proving successful where coarse crushing is found to be sufficient, as at Broken Hill and Sombrerete. The following table shows the crushing plant, &c., in use at some well-known lixiviation mills:—

TABLE XII.—CRUSHING PREPARATORY TO LIXIVIATION AT VARIOUS MILLS.

	Blue Bird.	Marsac.	Holden.	Sombrerete.	Broken Hill.
Number of stamps, .	80	30	30	Two sets of rolls, 26" × 16"	Four Chilian mills.
Weight per head, . .	900 lbs.	750 lbs.	850 lbs.		
Drops per minute, . .	90	92	92		
Height of drop, . .	7 ins.	8 ins.	...		
Mesh of screen, . .	30	20	...	8	6
Duty, tons per 24 hours,	...	2·3 tons	3·3 tons	...	...
Class of dryer, . . .	Rotary	Rotary	Shelf	Rotary	none
Class of roaster, . .	Stetefeldt	Stetefeldt	Stetefeldt	Reverb.	W. Howell
Number of roasters, .	2	1	1	6	8
Total crushing capacity tons per 24 hours, .	150	70	100	110	180

For a description of the chloridising-roasting of these and other ores see Chapter IX.

Construction of Leaching Plant.—The plant for the Russell process does not necessarily differ in any respect from that required for the older Patera process. The details of Russell plants, however, have been so admirably worked out by the late C. A. Stetefeldt* that they have become, with few alterations, the standard for lixiviation plants everywhere, whether using the Russell process or not. A general plan of a Russell plant is shown in Fig. 59, in which A A are leaching vats, B B

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* *v.* Stetefeldt "On the Lixiviation of Silver Ores with Hyposulphite Solutions"; also same author, *Trans. A.I.M.E.*, vol. xx., p. 3; Daggett, *Trans. A.I.M.E.*, vol. xvi., p. 432, *et. seq.*; Hofmann, *Trans. A.I.M.E.*, vol. xvi., p. 662, &c.

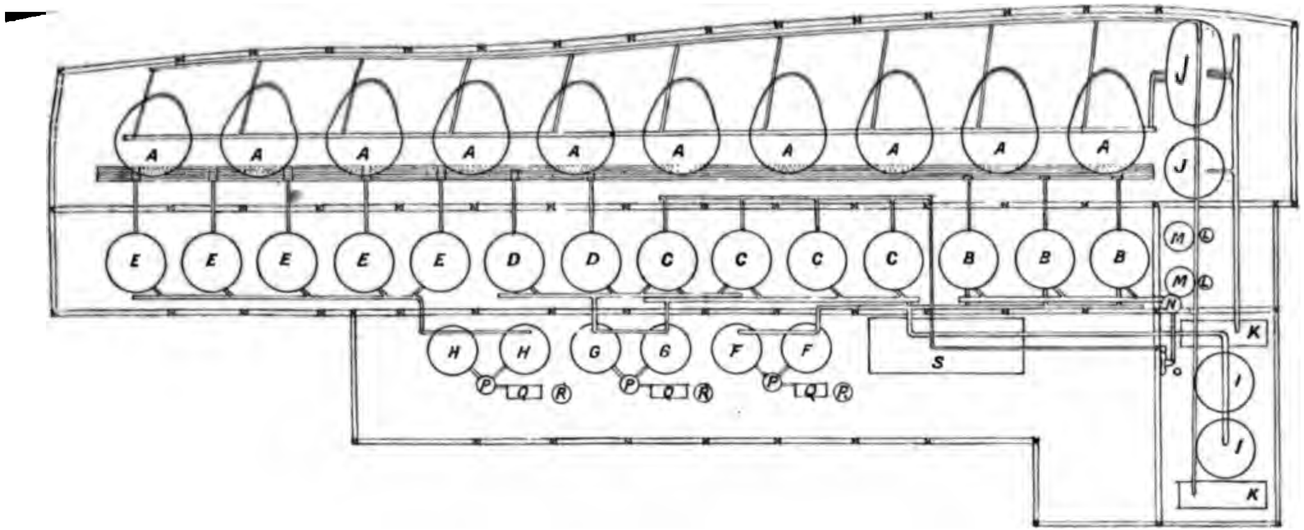

Fig. 59.—Plan of Russell Process Plant.

Index to Letters.

A	Ore vats.	K	Montejus air-pumps for raising stock solution.
B	Lead precipitation tanks.	L	Sodium sulphide mixing tanks.
C	Silver precipitation tanks for strong solution.	M	,, ,, storage tanks.
D	,, ,, ,, ,, weak solution.	N	Sump for silver solution.
E	,, ,, ,, ,, wash-water.	O	Centrifugal pump for returning silver solution.
F	Storage tanks for lead precipitate.	P	Precipitate press tanks.
G	,, ,, ,, silver precipitate.	Q	,, filter presses.
H	,, ,, ,, wash-water precipitate.	R	Sumps for drainage from filter presses.
I	Solution sumps.	S	Sulphide precipitate dryer.
J	,, high-level storage tanks.		

lead precipitation tanks, C C and D D silver precipitation tanks, and E E wash-water precipitation tanks. F, G, and H are precipitate storage tanks. O O press tanks, and P P filter presses, while Q, R, and S are respectively the drying furnace, grinder, and sampler for the precipitates; I I and J J are respectively the solution sumps and solution storage vats, K being the Montejus or air-pressure cylinder for raising the solution from the former to the latter.

Leaching Tanks.—These, often called "ore vats," are shown in plan and section in Figs. 60 and 61. The best material is clear well-seasoned Oregon pine, white cedar, or other straight grained soft wood. Both staves and bottom should be from 3 to 4 inches thick according to size of tanks, which nowadays in large plants is seldom less than 17 feet diameter. The staves must be carefully cut to the radii of the finished circle, nothing being placed between the joints but a thin coat of white lead, which many experienced metallurgists omit altogether. The bottom planks are grooved, the grooves filled with white lead and tight tongues driven in; the bottom is cut 2 inches larger in diameter than the tank and is gained 1 inch into the stowes all round, a chime of 9 inches being usually left for security. When finished the tanks are hooped up with 1⅛-inch round iron rod provided with threaded ends passing through forged lugs and fastened with nuts, or flat iron may be used. The tanks are given three good coats of white lead paint inside and out to prevent absorption of solution, and all the iron work is coated with asphalt varnish to avoid corrosion, while the heads of bolts, &c., should be well imbedded in white lead, though oak dowels should be used wherever possible instead of bolts.

Mode of Working.—The false bottom should be close down upon the bottom of the vat, both so as to secure greater resistance to the strain on the filter cloth and in order to leave as little space as possible below the ore in which solutions can collect and mix. The circular framework of 1½ by 1 inch slats crossing at right angles should rest upon the bottom of the tank, leaving a ⅜-inch annular space all round. The slats are covered with one thickness of cocoa-nut matting, and the canvas filter cloth, 6 inches larger in diameter than the tank, is fastened into the annular groove by driving in a ½-inch rope. The threaded flange forming the solution outlet is bolted through the bottom, both bolts and heads being imbedded in white lead. The tanks should always be filled from the top by means of a small track running over the whole series.

The tank here figured, which is the ordinary Stetefeldt form, is about 7 feet 9 inches deep, permitting a charge of ore 6 feet 6 inches deep. Daggett strongly recommends* these and even **deeper tanks,** pointing out that increased depth does not mate-

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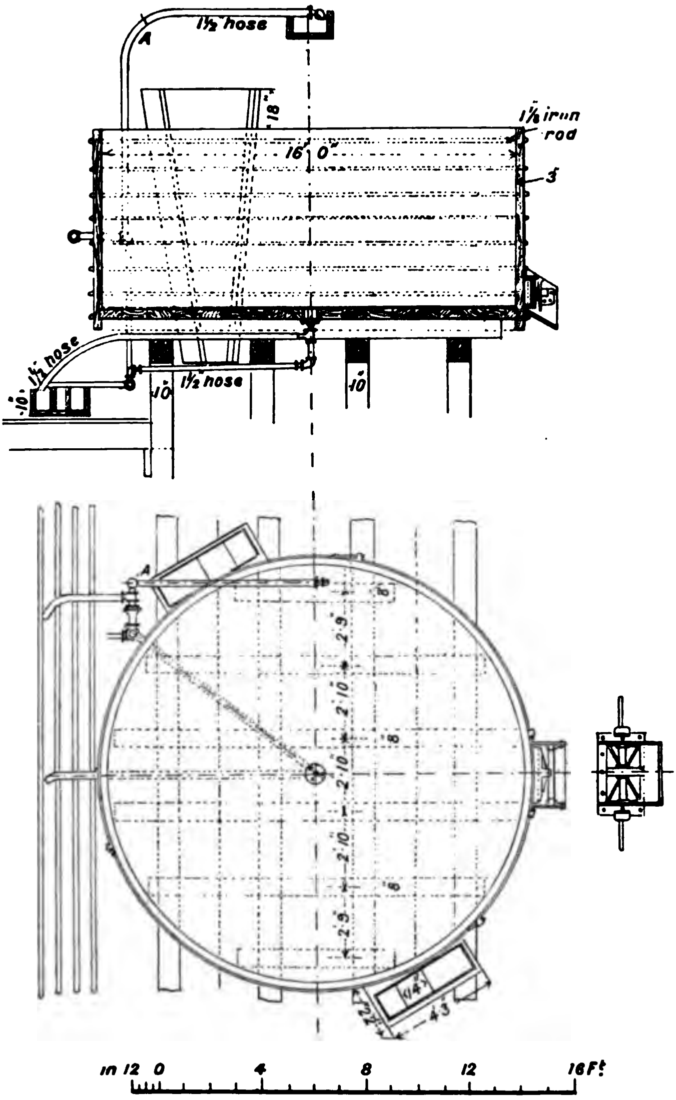
* *Trans. A.I.M.E.*, vol. xvi., p. 394.



Figs. 60 and 61.—Leaching Tanks.

lead precipitation tanks, C C and D D silver precipitation tanks, and E E wash-water precipitation tanks. F, G, and H are precipitate storage tanks, O O press tanks, and P P filter presses, while Q, R, and S are respectively the drying furnace, grinder, and sampler for the precipitates; I I and J J are respectively the solution sumps and solution storage vats, K being the Montejus or air-pressure cylinder for raising the solution from the former to the latter.

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Mode of Working.—The false bottom should be close down upon the bottom of the vat, both so as to secure greater resistance to the strain on the filter cloth and in order to leave as little space as possible below the ore in which solutions can collect and mix. The circular framework of $1\frac{1}{2}$ by 1 inch slats crossing at right angles should rest upon the bottom of the tank, leaving a $\frac{5}{8}$-inch annular space all round. The slats are covered with one thickness of cocoa-nut matting, and the canvas filter cloth, 6 inches larger in diameter than the tank, is fastened into the annular groove by driving in a $\frac{1}{2}$-inch rope. The threaded flange forming the solution outlet is bolted through the bottom, both bolts and heads being imbedded in white lead. The tanks should always be filled from the top by means of a small track running over the whole series.

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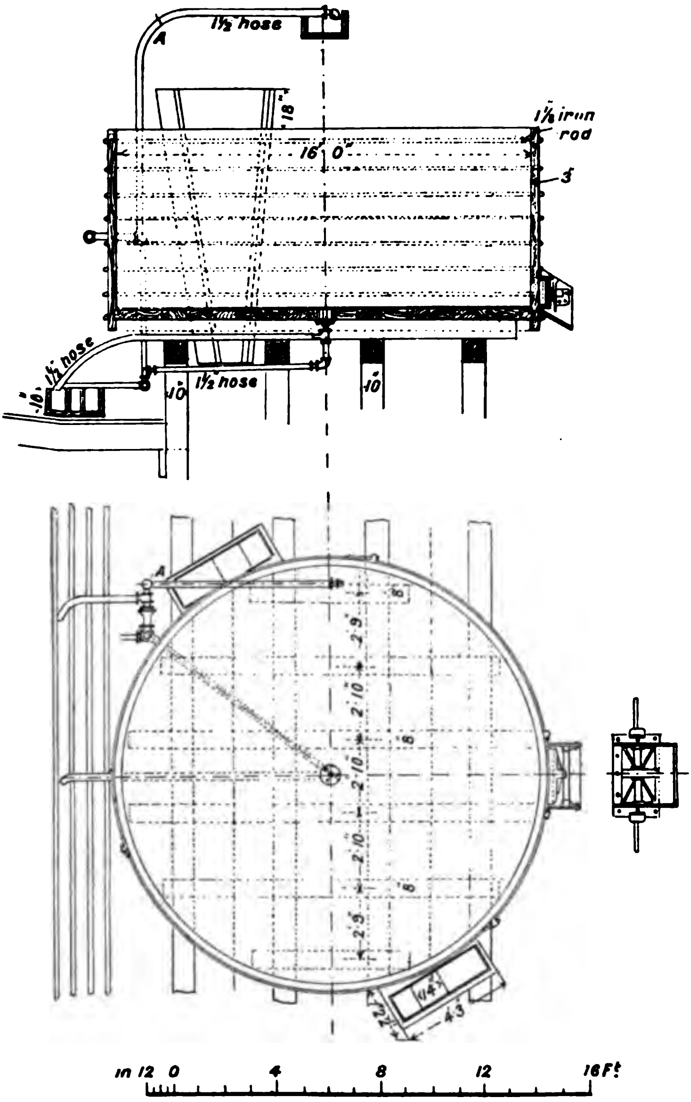
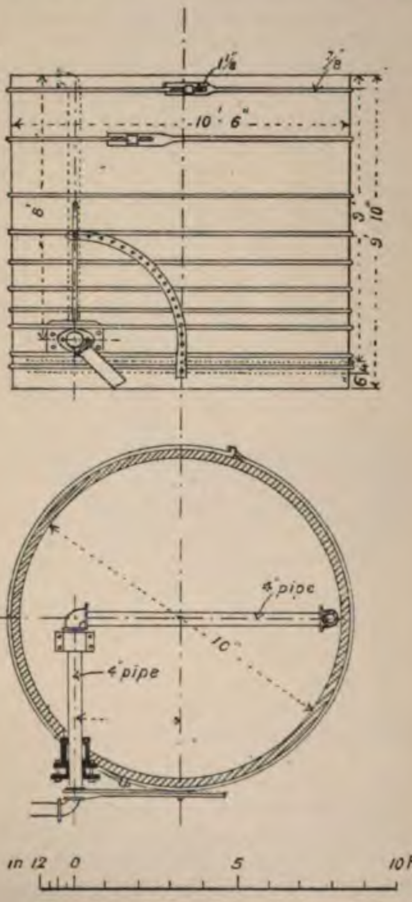
* *Trans. A.I.M.E.*, vol. xvi., p. 394.



Figs. 60 and 61.—Leaching Tanks.

with holes, through which the solution can make its exit without disturbing the surface of the charge. In the case of most ores the natural rate of filtration is fast enough for leaching, but with some finely-pulverised ores, and others which filter very slowly, as well as with tanks charged by the system of trough-lixiviation shortly to be described, it is necessary to accelerate the speed of leaching by artificial means. This may be done either by the use of a Körting ejector connected with the solution outlet (which, however, has the disadvantage of diluting the solution with condensed steam) or by means of a Montejus tank connected with a vacuum pump, in which case a single pump can be connected with a long series of tanks by means of a pipe, and any given tank shut off as required.



Figs. 63 and 64.—Precipitating Tank.

Precipitating Tanks and other Plant.—The precipitating tanks are constructed in the same general fashion as the ore vats, but they are made smaller and deeper, as shown in Figs. 63 and 64, which represent the usual form of tank with the addition of the Stetefeldt quadrant and arrangement for drawing off the solution, which is now quite obsolete. In its place stiffened hose, which is lowered as required, is usually hung the solution, with its mouth just below the surface. Former precipitating tanks were frequently provided with mechanic stirrers, either in the form of vertical rods hanging from horizont cross arms in dolly-tub fashion as recommended by Hofmann,* or in the form of a propeller blade revolving in a horizontal plane about 1 foot from the bottom of the tank as recommended by Stetefeldt.† Usually, however, the stirring was done by hand with an oar, ten minutes or so for each tank being found sufficient. Stirring with a jet of compressed air partially shut off so as to produce only a stream of bubbles was first introduced by Hofmann and proved very effective, the decomposition of hyposulphite by oxidation being only very slightly increased; this method of stirring is now in general use.

After the precipitate has been allowed to settle, the clear solution is syphoned off by means of a hanging hose, as above stated; the precipitate is run through a 2-inch cock (not shown in the figure) into the precipitate storage tank, which communicates with the press tank. This should be done at least every other day, as fresh precipitate settles readily, whereas that which has been stirred up with fresh solution several times becomes slimy and difficult to settle. The precipitates are forced through the filter-presses by means of wrought-iron press tanks on the Montejus system, provided with floating wooden pistons, above which steam or, preferably, compressed air is admitted, as shown in Fig. 65.

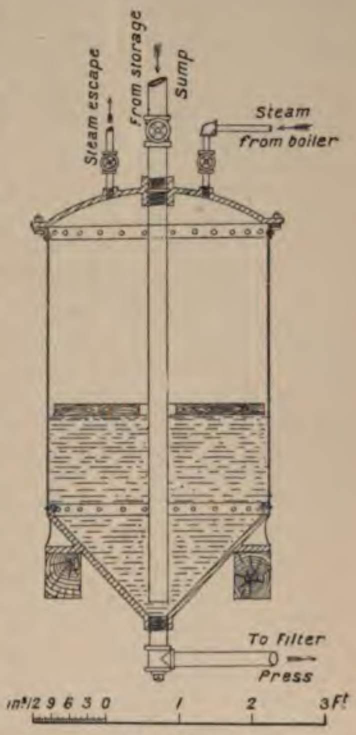


Fig. 65.—Filter Press.

The solution sumps and storage tanks for making up and heating the solutions must be, like the leaching vats, carefully put together to prevent leakage. The heating is usually done by passing steam through a coil of 1¼-inch lead pipe (about 100 feet) supported on blocks about 4 inches above the bottom.

The solutions are raised from the various solution sumps by means of Geyser pumps or Montejus tanks, as plunger and

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* *Trans. A.I.M.E.*, vol. xvi., p. 676.

† *Trans. A.I.M.E.*, vol. xx., p. 6.

centrifugal pumps would be too much corroded by them. The Montejus system is decidedly preferable, as the same tank then serves for suction of the solution through the ore vats and for forcing it up to the precipitation vats, being connected as required either with the vacuum pump or with the compressed air pipes.

The other principal appliances required are cast-iron lead-lined tanks for preparing the alkaline sulphide precipitant, plain india-rubber piping and stiffened hose, and ejector or Montejus pressure pumps worked by steam, or preferably by compressed air. Johnson filter-presses of gun-metal are commonly used for the semi-fluid sulphide and carbonate precipitates, and a steam drying-room is required for the cakes of pressed and washed precipitates. None of these appliances require illustration here.

Trough Lixiviation.—This plan was proposed by Hofmann[*] for leaching galena ores which percolate very slowly (San Francisco del Oro), and others which set hard on the addition of water, like those of the North Mexican Mine (Cusi). The rate of extraction in hypo. solution, other things being equal, depends upon the rapidity with which the solvent passes between the particles of ore, and, therefore, it is the volume of solvent brought into contact with the ore rather than the time during which it acts which is the important factor in determining the rate of leaching as distinguished from the rate of filtration. The ore is shovelled or delivered by a worm-conveyor into a V-launder or trough through which a stream of the solvent is flowing, and the mixture of ore and liquid falls into a leaching tank like that shown in Fig. 62, but with a top overflow, in order to settle. The troughs may be about 150 feet long, with a fall of ¾ inch to the foot; they may be arranged in zigzag, and must have an outlet, consisting of a square box provided with a plug, corresponding to each tank. The quantity of solvent required is always, at least, equal to the total quantity required in tank lixiviation, and in practice varies from three times up to fourteen times the weight of ore treated. When the quantity is sufficient, extraction in the short space of three-quarters to one and a-quarter minutes is found to be so nearly complete that it cannot be materially improved by several hours of ordinary tank leaching. The separation of ore from liquid is the weak point as regards raw ores and tailings, but ores which have been chloridised become so granular that they settle much more readily than might be expected. In any case the actual leaching is so much quicker that, even if very large tanks are required for complete settling of the stream of pulp, the total number of tanks

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[*] *E. and M. J.* (1887), Sept. 10, p. 185; Nov. 26, p. 393; and (1889), March 16, p. 255; also *Trans. A.I.M.E.*, vol. xvi., p. 662, where a general description of the process is given, together with plans, &c.

required for a given daily capacity of the works is practically no greater. Ores containing much galena are more especially adapted to the process, for lead sulphate, as already stated, greatly reduces the solvent energy of hypo. solution for silver, and, therefore, in ordinary tank lixiviation the solution which percolates through the charge and takes up that substance becomes comparatively inert for silver before it reaches the bottom of the tank, which explains the very long time required to leach such ores in the ordinary way. In trough lixiviation, however, the solvent is not in contact with the ore sufficiently long for much lead to be dissolved out by it, and, therefore, the slowly soluble lead sulphate cannot retard solution of the more readily soluble silver chloride.

The great advantage of trough lixiviation, however, only comes into play when it is employed for base-metal leaching of the ore as well as for the silver leaching, for by the employment of a large quantity of water in contact with the ore, the solution of brine and base-metal salts, which takes up some silver chloride, becomes instantaneously diluted, re-precipitating the silver chloride upon the finer ore particles, whence the hypo. easily dissolves it. The quantity of silver carried away in the base-metal leach is thus less than in tank lixiviation.

In a Hofmann automatic trough lixiviation mill at *Cusi* (Chihuahua, Mex.) now no longer at work, the hot ore from the furnace bins was fed by a worm-conveyor into a closed spraying apparatus, where a spray of water instantaneously cooled it, and the hot stream then passed through a kind of double-cone coffee-mill to break up the lumps. The stream of ore and water then flowed through a V-launder into the first of the series of four base-metal leaching tanks, in which it deposited most of its sand, then through the remaining empty tanks in succession, and finally left the last tank as a clear base-metal solution nearly free from silver, which was run into scrap-iron tanks. As soon as the first precipitating tank was filled the stream was turned into the second, while the first was allowed to drain off, rinsed with clean water, and leached for silver by opening the bottom valve and sluicing out the whole of its contents with hyposulphite solution in the required proportion. This should be determined by small scale experiments for each particular ore, and the required capacity of pumps, pipes, and hose for any given size of tank calculated in accordance with experimental results. The stream of hypo. and ore was carried in a V-launder, at least 150 feet long, to a second series of tanks similar to the first set in which the leached ore settled out, while the clear solution charged with silver was precipitated as usual. The solution in the leached ore being drained off and rinsed out with clear water, the tailings were sluiced to waste.

The time saved by trough lixiviation over the tank system on the very base plumbiferous ores of San Francisco del Oro is very great, only fifteen hours being required for the whole process as against one hundred and nine hours by the ordinary method. The quantity of solution required on this difficult ore was also less, being only 108 cubic feet per ton as against 658 cubic feet per ton by tank lixiviation. It must not be supposed, however, that these advantages would be shown with all ores—indeed the contrary is the case with a great number.

The relative advantages and disadvantages of trough lixiviation are :—

Advantages.	*Disadvantages.*
1. Simplification of the tank manipulation and of the precipitation process owing to the solutions being more uniform in strength.	1. Greater fall required and larger area which the mill plant occupies.
2. Less loss of silver in diluted base-metal solutions.	2. Impossibility of using weights and assays of ore charged into tanks as a means of checking volatilisation losses.
3. Saving of time in leaching and consequent saving in cost of plant for a given capacity of works.	3. Larger volume of solution required on most ores.
4. Great saving in labour through making the process automatic.	4. Greater deterioration of the stock solution by oxidation.
5. Adaptability to every kind of ore and possibility of immediately adjusting the quantity of solution employed to suit changes in the ore —*e.g.*, an increase in the percentage of galena.	5. Contamination of the silver sulphide precipitate with fine ore-slime, and consequent heavier expense for freight and refining of the sulphides.
6. Less quantity of solution required for leaching difficult plumbiferous ores.	6. Partial separation of the fine and coarse particles of ore in the settling tanks whereby the mass of pulp becomes impermeable to water. The loss of time in draining and rinsing would on some ores nearly equal the saving of time in leaching, while the tailings obstinately retain some solution, and so the loss is higher.

On the whole it may perhaps be said that the trough system is preferable for low-grade heavy plumbiferous and such other roasted ores as resist percolation without being specially refractory. For all light ores and ores free from lead, as well as for those which leach rapidly, and for all refractory ores which contain any considerable proportion of their silver in the condition of metal, arseniate, or antimoniate, the tank system would seem to offer greater advantages. For raw tailings it is indispensable.

Distribution of Silver in Products.—The total percentage of extraction at various lixiviation plants has been referred to in the last chapter, and the following table shows the percentages of the total silver extracted in the different stages of the process. Where there is no separate precipitation of lead carbonate, the silver which would be precipitated in it is all found in the "regular" sulphide precipitate.

Proportion of Total Silver Extracted.	*Yedras.*	*Blue Bird.*	*Holden.*	*Marsac.*
In base-metal sulphides, . .	10·0	1·14	18·52	7·25
,, lead carbonates, . . .	...	1·84	1·04	2·98
,, mill cleanings, . . .	...	...	...	0·65
,, "regular" or silver sulphides,	90·0	97·02	80·44	89·12
	100·0	100·00	100·00	100·00

Cost of Lixiviation.—The cost of hyposulphite leaching—apart from the cost of preliminary crushing and roasting—is greatly dependent upon local conditions, and particularly upon freight rates and the distance from manufacturing centres which affect the price of chemicals.

According to Stetefeldt and Daggett the average cost of leaching by the Russell process in a mill of the capacity of 100 tons per day should be—

					s.	d.		s.	d.
Labour, ...	$0.33	to	0.39	=	1	4½	to	1	7½
Fuel, ...	0.10	,,	0.21	=	0	5	,,	0	10½
Chemicals, . . .	0.56	,,	1.00	=	2	4	,,	4	2
Repairs, . . .	0.05	,,	0.15	=	0	2½	,,	0	7½
Assaying, &c., . .	0.07	,,	0.08	=	0	3½	,,	0	4
	$1.11	,,	1.83		4	7½	,,	7	7½

The former figure is somewhere about the cost actually attained at Broken Hill with the ordinary process, but there is no Russell process plant in existence working so cheaply. The figure quoted by Stetefeldt as a maximum is about the actual cost of leaching at the Marsac mill in 1892 to 1895, but it does not, of course, include the cost of crushing and roasting. The cost of the Russell process, however, should never be much greater than that of the ordinary process, the only additional item being the bluestone and an extra allowance of all other chemicals, while the extraction is in some cases much higher than by the ordinary process, especially in the case of ores rich in lime.

Tables XIII. and XIV. give data as to costs and results at mills using the ordinary Patera and Russell processes respectively. It should be understood that the figures given as the cost of lixiviation do not include anything for treatment of

TABLE XIII.—PATERA AND KISS PROCESSES.

	Bertrand Mill, Eureka, Nev., 1883.	San Francisco del Oro, Parral, Mexico, 1888.	Cusihuiriachic, Chihuahua, Mexico, 1887.	Broken Hill Proprietary, N.S.W., 1896.	Sombrerete, Zacatecas, Mexico, 1895.
Reference, ...	1.	2.	3.	4.	5.
Assay of raw ore treated, ... ozs.,	?	23·85	?	13	41·9
Type of roasting furnace, ...	Brückner	White-Reverb.	Howell	Howell	Reverberatory
Time charge in furnace, ...	9 hours	4 hours	35 mins.	45 mins.	24 hours
Percentage of salt used in roasting, ...	5½	4·7	8	6½ to 8	6
Loss by volatilisation, ... per cent.,	?	7·9	?	under 6	4·8
Assay of roasted ore per ton, ... ozs.,	32	26·1	35·1	12·9	42·6
Average percentage of chlorination, ...	...	81·6	...	...	90·9
Percentage of soluble salts, ...	...	...	...	6·5	11·5
Capacity of plant per day, ... tons,	50 to 60	...	...	230	...
Number of leaching vats, ...	24	...	...	12	9
Diameter and depth of each, ...	6′ × 3′	...	...	16′ × 9′	15′ 6″ × 7′ 6″
Weight of each vat charge, ... tons,	6	8½	...	50	55 to 58
Rate of leaching per hour . . . . . ins.,	8	8½	...	16	10
Time in base metal leaching, ... hours,	10½	9	66	1½	12
,, silver ,, ... ,,	25½	97		48	96
Total time each vat charge, ...	...	...	...	...	...
First wash-water used, . . cubic feet per ton,	...	100	...	12	...
Stock solution used, . . . ,, ,,	...	...	...	63	...
Total quantity of water, . . . ,, ,,	...	...	...	...	...
Percentage strength of hypo. used, ...	...	...	...	1	0·50 to 0·75
Temperature of hypo. used, ...	...	...	...	80° to 90° F.	...
Average assay of tailings, ... ozs.,	4½	4·76	7·3	2·48	3·9
Apparent percentage of extraction on roasted ore, .	86	82	78·3	80·79	86·6

True percentage of extraction on raw ore,	?	74·9	?	76·9	82·5
Consumption of hypo., in lbs. per ton,	...	...	?	3	...
" sulphur, " "	...	7	2·9	1·6	...
" caustic soda, " "	...	...	4·4	2·5	...
" lime, " "	...	21	...	...	...
" sodium carbonate, " "	...	...	...	19	...
Value per ton base metal precipitate, ozs.,	...	...	...	750	1500 to 3000
" " silver " "	...	6500	...	16,000 +	10,000 to 15,000
" of silver precipitate in gold, "	...	...	...	...	9 to 10
Precipitant employed,	CaS_5	CaS_5	Na_2S_2	Na_2S_2	Na_2S_2
Value per ton of lead carbonate precipitate, ozs.,	...	...	...	85	...
Total cost per ton:—					
Crushing,	?	?	...	£0 5 2*	£0 5 7¾
Roasting (including salt),	£0 6 3½	£0 9 3	...		0 11 1¼
Labour in lixiviation,	0 5 11	0 0 10½	...	0 3 1*	0 1 1½
Chemicals,	0 14 10½	0 1 6½	...		0 1 3
Tools, light, pumping, heating, &c.,		0 0 3½	...		0 0 4
Superintendence and repairs, &c.,		0 0 11½	...	?	0 4 3
Total,	£1 7 1+	£0 12 11 +	...	£0 8 3 +	£1 3 8½

In this table all figures refer to the short ton of 2000 lbs., except those of the Broken Hill Works, which refer to the English ton of 2240 lbs.

* These figures are taken from the annual report for 1896.

References.—1. Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., pp. 487-515. 2. Hofmann, *E. and M. J.*, Feb. 23, 1889. 3. Various. 4. *Private notes*, 1896. 5. O. Hofmann, *Private communication*, Nov., 1896.

TABLE XIV.—The Russell Process.

	Las Yedras, Sinaloa, Mexico, 1892.	Blue Bird, Montana, 1891.	Holden Mill, Aspen, Colorado, 1892.	Marsac Mill, Park City, Utah, 1895.	Tailings.		
					Bullionville, Nevada, 1885.	Blue Bird, Montana, 1893.	Las Yedras, Sinaloa, Mexico, 1889-90.
References, ...	1.	2.	3.	4.	5.	6.	7.
Assay of raw ore treated, . . . ozs.,	?	?	27·92	37·28	...	..	16·73
Type of roasting furnace, ...	Reverb.	Stetefeldt	Stetefeldt	Stetefeldt	...	...	...
Quantity roasted per furnace—per day, tons,	7	50	90	70	...	...	...
Percentage of salt used in roasting, ...	7	13	12·2	8·9	...	...	...
Loss by volatilisation, . . . per cent.,	...	...	9·2	...	...	...	...
Assay of roasted ore per ton, . . . ozs.,	?	?	24·63	36·03	...	...	...
Average percentage of chlorination, . . .	...	90	79	92·4	...	...	...
Percentage of soluble salts, ...	...	...	14·08	...	...	...	...
Leaching:—							
Capacity of plant, . . . tons per day,	...	70	100	70	175	100	...
Number of leaching vats, ...	...	4	7	7	...	4	...
Diameter and depth of each, ...	...	17′ 6″ × 9′	17′ × 9′	17′ × 8′ 7″	12′ 6″ × 3′ 6″	17′ 6″ × 9′	...
Weight of each vat-charge, . . . tons,	18	70	58·2	72	...	70	...
Rate of leaching per hour, . . . ins.,	3	8	13	3·7	...	8	...
Time in base-metal leaching, . . . hours,	12¼	...	9	19	...	...	...
,, ordinary solution, . . . ,,	97¾	...	...	81	18	24	...
,, extra solution, ... ,,	19	...	...	27			
Total time each vat-charge, . . . ,,	138	101	100	130-150	...	...	...
First wash-water used, . . c. ft. per ton,	21·6	...	44	18·3	...	...	...
Ordinary solution used, . . ,, ,,	226	...	120	68	30	...	...
Extra solution used, . . . ,, ,,	13	...	40	10·5	6½	30-40	...
Total volume of water required, ,, ,,	37	56	69	40	13	...	...

					...	...	...
Average assay of tailings, . ozs. per ton,	...	...	3·8	2·65	...	3·4	7·3
Percentage of extraction on roasted ore, . .	87·6	87·3	94·2	93·8	...	...	...
True percentage extraction on raw ore, . .	?	?	85·6	?	...	50 ±	56·6
Consumption of hypo., . . in lbs. per ton,	0·85	3·50	9·98	8·55	2·0	...	1·59
,, bluestone, . ,, ,,	6·16	7·2	13·45	5·66	3·0	...	5·10
,, caustic soda, . ,, ,,	3·64	4·2	18·86	5·55	2·0 *	...	3·38
,, sulphur, . ,, ,,	2·50	2·8		3·65	3·0	...	2·57
,, sodium carbonate, ,, ,,	None	4·6	4·04	5·17	...	...	none
Total chemicals, ... ,, ,,	13·15	22·3	46·33	28·58	10·0	...	12·64
Value per ton base-metal precipitate, ozs. Ag.,	16,300	2025	2875	1238	...	...	...
,, lead carbonate precipitate, ,,	...	137	432	526	...	...	...
,, silver precipitate, . ,,	20,200	6600	3790	10,293	...	...	...
,, ,, ,, . . ozs. Au.,	...	...	...	11·3	...	...	...
Precipitant employed, ...	Na_2S_2	Na_2S_2	Na_2S	Na_2S_2	CaS_5	NaS_2	Na_2S_2
Total cost per ton:—							
Crushing, ...	...	...	£0 6 4½	£0 18 6	...	...	...
Roasting (including salt), ...	...	...	0 5 11½				
Labour in lixiviation, ...	...	...	0 4 9	0 3 4	£0 2 3½	£0 2 11	£0 2 9½
Chemicals, ...	£0 5 9	£0 4 1	0 7 9	0 3 8	0 2 7½	0 1 9½	0 4 8½
Tools, light, pumping, and heating, . .	...	...	0 0 5	0 0 6	0 0 7	0 0 3	0 0 6½
Superintendence, repairs, &c., . . .	...	...	0 4 8	0 0 9	0 1 2½	0 1 4	0 2 1
	...	£1 9 2	£1 9 11	£1 6 9	£0 6 8½	£0 6 3½	£0 10 1½

In the above table all figures refer to the ton of 2000 lbs.

* Lime in this case.

References.—1. Letts, *E. and M. J.*, Feb. 24, 1893, and reprint of same by Russell Process Company. 2. C. A. Hoyt, *E. and M. J.*, Jan. 7, 1893; and *private communication*, Oct., 1896. 3. Morse, *Trans. A.I.M.E.*, vol. xxv., p. 141. 4. Lamb, *E. and M. J.*, 17th Dec., 1892; also *private communication*, R. B. Watson, Nov., 1896. 5. Egleston, *Met. of Silver, Gold, and Mercury in the U.S.*, vol. i., p. 533, *et. seq.* 6. Hoyt, *E. and M. J.*, July 7, 1894, and *private communication*. 7. Letts, reprint by Russell Process Company, 1893.

the sulphides, the total cost of which may vary considerably; at *Marsac* it amounted to about 5s. 2d., at *Holden* (Aspen) to about 5s. 8d. per ton of ore, when the sulphides were shipped to smelters. The total average cost of treating ores by the Russell process in a well-equipped mill is thus brought up to about 32s. to 36s. per ton. It will be well to describe in detail some typical examples of each process before drawing up a general comparison between the two. For this purpose the *Yedras*, *Marsac*, and *Holden* mills will be chosen as typical of the Russell process in its ordinary application to roasted ores; and reference will then be made to the successful treatment of tailings by this process at various places. The *Sombrerete* and *Broken Hill* Works (at both of which the Russell process has been abandoned) will then be described as typical of the ordinary Patera process.

Examples of the Russell Process.—The most conspicuous successes achieved by the Russell process are in the case of calcareous ores in which silver chloride formed by roasting is again decomposed on cooling and during the leaching process.

Las Yedras (Sinaloa, Mex.).*—The analysis of average ore from this mine has been already given in Table IX. The ore was formerly worked by roast-amalgamation, the extraction being only 60 per cent. Lixiviation by the Patera process was then tried, but after a chloridising-roasting, in which no less than 17 to 25 per cent. of the silver was volatilised, the extraction only averaged 67·1 per cent. calculated on the roasted ore, or, say, 50 to 56 per cent. of the contents of the raw ore. For the Russell process a less perfect roast, involving a volatilisation loss of only 7 per cent., is sufficient, and of the remaining silver no less than 82·4 per cent. is extracted, or 76·3 per cent. of the contents of the raw ore. The extra expense of the Russell treatment is only about one-sixth of the value of the additional product obtained.

The washing at Yedras is conducted as follows, the figures referring to total depth in the tank measured above the top of the ore; there being, however, no room for the total quantity to be added at once, each kind of solution is added in several stages, making up the total depth required.

The scheme is as follows:—(1) 40 inches of cold wash-water (2) 150 inches of cold "ordinary" solution; (3) 24 inches strong "extra" solution, which is allowed to sink down throug the ore and stand in it for twelve hours; (4) 190 inches of col ordinary solution; (5) 24 inches of second, or final, wash-wate The base-metal sulphides at this mill are unusually rich—no however, because the first wash-water carries off any very exce tional proportion of dissolved silver chloride, but because th actual quantity of base metals in solution is very small.

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* Letts, *E. and M. J.*, Jan. 14, 1893.

Since the introduction of the Russell process at Yedras, some 40,000 tons of old amalgamation and Patera tailings, averaging 16·7 ozs. silver have been treated with extra solution without re-roasting, the percentage of extraction on this material averaging 56·6 per cent. The mill results on both ore and tailings are detailed in Table XIV.

Marsac (*Park City, Utah*).*—One of the most successful plants now working the Russell process is that of the Daly Mining Company called the Marsac mill, analysis of the ore treated in which is given in Table IX. Besides stonebreakers and revolving dryers, the plant has thirty stamps crushing dry through a 30-mesh screen at the rate of 2⅓ tons each per day, together with 9·5 per cent. of salt. The salted ore is then roasted in a single Stetefeldt furnace and leached in six ore vats of the usual type, 17 feet wide by 9 feet deep. Most of the working data are to be found in Table XIV., but it may be well to give here in full the leaching programme or sequence of operations, which is much more complex than that at Yedras, the figures as before referring to the total number of inches deep in the tank measured by each kind of solution. The sequence is as follows:—(1) 40 inches of cold wash-water; (2) 30 inches of "extra" wash-water, with $\frac{1}{10}$ per cent. bluestone; (3) 120 inches of warm ordinary solution; (4) 20 inches of warm strong "extra" solution, with ¾ per cent. bluestone; (5) 40 inches of warm ordinary solution; (6) 20 inches of warm strong extra; (7) 100 inches of warm ordinary; and (8) 75 to 90 inches of cold wash-water.

The "extra" solution is made up on top of the charge as usual, the whole of the "wastage" of hypo. being added to it, so that its actual strength is about 2¼ per cent. hypo. and ¾ per cent. bluestone. The base-metal sulphides of this mill are comparatively poor in silver, and they amount to only 3·8 lbs. of dried precipitate per ton of roasted ore. The lead carbonate is still poorer, and the amount is only 3·1 lbs. per ton of roasted ore. The composition of the different classes of precipitate produced at the Marsac mill is as follows:—

	Silver.	Gold.	Lead.	Copper.
	Ozs.	Ozs.	Per cent.	Per cent.
Base sulphides, . .	2200-5200	1·6- 3·9	38-45	2·6-5·2
Lead carbonates, . .	600-1400	0·6- 1·9	23-41	...
"Regular" sulphides, .	11,200-12,000	11·1-12·1	trace to 1	23-28

The total percentage of extraction *calculated on the roasted ore* is 93·84, but the loss by volatilisation in roasting, if determined,

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* Lamb, *E. and M. J.*, Dec., 1892; also Stetefeldt, *Trans. A.I.M.E.*, vol. xxi., p. 286, and vol. xxiv., p. 221.

is not made known. As in most other Russell process mills the loss of silver by volatilisation and dusting is ignored, and the loss of weight in roasting, if determined, is not published, while it is assumed that the loss of silver in roasting is *nil*. How erroneous is this unwarrantable assumption is proved by the experience of Morse* and of most other metallurgists unconnected with the Russell Process Co., who have had experience with hyposulphite leaching.

It should further be noted that the silver contents of the sulphides are determined by the so-called "corrected" assay, making allowance for loss in slag and cupel, while the silver in the ore is determined by the ordinary scorification assay, which gives results at least 3 or 4 per cent. too low. The loss by volatilisation is probably at least 5 or 6 per cent., so that adding this to the loss in assaying the *true* percentage of extraction calculated on the real contents of the raw ore would probably not exceed 85 per cent. at most.

For further details about this plant Table XIV. should be consulted.

Holden Mill (Aspen, Colo.).†—Analysis of an average sample of the ores treated by this mill has been given in Table X., from which it will be seen that the gangue is principally barytes and dolomite with some quartz. By mixing with the ores a small quantity of pyritic ore the sulphur is raised to 8 per cent., which is sufficient to convert practically all the lime in the ore into sulphate. As withdrawn from the furnace the ore only showed 52·5 per cent. of silver in the state of chloride extractable by ordinary solution and 78·4 per cent. extractable by Russell solution, but after lying on the cooling floor for an average of 102 hours the silver extractable by ordinary solution is raised to 78·99 per cent., and that by "extra" solution to 89·78 per cent. The leaching programme is as follows:—(1) 60 inches of water in tank followed by 60 inches more, or a total of 120 inches of first wash-water; (2) 150 inches of warm ordinary solution (1·8 per cent. hypo.); (3) 50 inches of cold extra solution (0·5 per cent. bluestone); (4) 50 inches of warm ordinary solution; (5) 50 inches of cold extra solution; (6) 100 inches of warm ordinary solution; (7) 70 to 80 inches of second wash-water.

The actual extraction on the roasted ore was no less than 94·21 per cent., of which 51·4 per cent. was extracted by the first ordinary solution, the remaining 42·8 per cent. coming out gradually through the alternation of extra and ordinary solutions. In this case the loss by volatilisation and dusting was found to be 9·2 per cent., so that the true percentage of extraction on raw ore as ordinarily assayed was only 85·58 per cent. The silver in sulphides being determined by "corrected," and that in the ore

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* *Trans. A.I.M.E.*, vol. xxv., p. 137.

† Morse, *Trans. A.I.M.E.*, vol. xxv., p. 137.

by "commercial," assay, the true extraction on the real contents of the raw ore would not exceed 82 per cent. For further details as to the working of this plant reference should be made to Table XIV., and to the original paper by Morse already cited.

Treatment of Tailings by the Russell Process.—At *Bullionville* (Nev.)* in 1885 and subsequent years a large quantity of amalgamation tailings was treated by the Russell process in 12 feet tanks at the rate of over 100 tons per day. These tailings required per ton 6½ cubic feet of extra solution (1·6 per cent. hypo. and 0·5 per cent. bluestone), 30 cubic feet of weak ordinary solution (0·9 per cent.), and 13 cubic feet of wash-water. In this case CaS_5 was used as a precipitant with the idea that more gold might be extracted. The consumption of chemicals and cost of process are given in Table XIV.

At the *Blue Bird* mill (Butte, Mont.) from June to December, 1893, 16,000 tons of tailings from roast-amalgamation by pans were treated raw by the Russell process at the rate of 100 tons per day, but as the tailings did not average over 7 ozs. per ton the process, with silver at a low price, was not a commercial success. Particulars of the work done are given in Table XIV.

The *Bimetallic Mill* (Mont.) has a lixiviation tailings plant with twelve large tanks 22 feet diameter by 10 feet deep, holding 150 tons each; particulars of the work done are not published.

At *Sala* (Sweden)† tailings from the concentration of a silver lead ore containing 1·4 per cent. Pb and 0·018 per cent. Ag (=5⅞ ozs. per ton) are successfully treated by a modified Russell process in small vats 6½ feet diameter and 3½ feet deep. A weak extra solution containing 1·43 per cent. hypo. and 0·28 per cent. bluestone is exclusively used; it is run in till it stands about 4 inches above the surface of the charge, a small quantity of sulphuric acid being added to neutralise calcite in the gangue. The solution at 40° C. is circulated through the charge by means of a Körting ejector for several hours, after which it stands for other four hours in the ore; it is then drawn off, the tank drained, and then washed with a small quantity of hot water. The silver solution is precipitated in deep tanks with sodium sulphide, enough being added to throw down all the silver but only a part of the base metals, by which means a richer precipitate is obtained with a less consumption of precipitant. The precipitate dried in a filter press and subsequently at 100° C. contains Cu 40 per cent., Pb 9 per cent., Fe 6 per cent., Hg 0·04 per cent., and Ag 9 per cent. (2940 ozs. per ton); being somewhat low-grade for "sweating" on a lead bath, it is generally smelted together with lead matte for a rich bullion.

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* Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., p. 536.

† Asbeck, Abstracts *Proc. Inst. Civ. Eng.*, vol. cxvi., p. 469.

Examples of the Patera Process—Broken Hill Proprietary Co. (N.S.W.).*—At the works of this company low-grade siliceous and ferruginous oxidised ores and tailings containing silver chiefly as iodide and chlorobromide are crushed and chloridised and then treated by a process, which, to the ordinary Patera process using sodium hyposulphite for leaching and sodium sulphide for precipitation, adds separate precipitation of lead as carbonate retained from the Russell process, the essential feature of which proved unsuccessful after a thorough trial. The special value of this separate precipitation of lead is simply that it very largely reduces the bulk of the silver precipitate the treatment of which is comparatively expensive, whereas the lead carbonate precipitate is simply sent to the lead blast furnaces to be smelted with siliceous ores. If the ores contained more copper no doubt a smaller proportion of lead would be dissolved, but in the comparative absence of copper a very large proportion of lead goes into the solution from which it is advantageously separated.

The crushing of these ores to $\frac{1}{8}$ or $\frac{3}{8}$-inch mesh has been described in Chapter VI., and their chloridisation in Howell furnaces in Chapter IX. (to both of which reference should be made), and only the actual lixiviation remains to be described here. The plant is essentially a Stetefeldt plant, the general arrangement and details being substantially as described in the present chapter.† It consists of twelve leaching vats ranged in a double row on the upper level of the plant, and resembling in their construction that shown in Fig. 59, the dimensions being 16 feet diameter by 9 feet deep, and the capacity 50 tons when filled to within 1 foot from the top. The usual form of filter (canvas stretched on matting and fixed with rope) was found to clog badly, and has been replaced by one of coarse quartz sand resting on one layer of matting supported by the usual false-bottom of slats and covered by a layer of old sacks. The bottom is so set as to have 1 inch fall towards the solution pipes, which is found to be ample for draining; and the discharging doors for the roasted ore are on both sides, instead of on one side only as shown in Fig. 62. Below the leaching vats are twelve precipitation tanks, each 10 feet diameter by 9 feet deep, arranged in two rows of six, one below the other, the upper row being employed for lead carbonate and the lower row for sulphide precipitation. The remainder of the plant, precipitate and press tanks and filter presses, &c., are exactly as described and recommended by Stetefeldt, compressed air being employed for pressing the precipitates as well as for stirring and raising solutions. The

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* *Private notes*, 1896.

† *v.* also Stetefeldt *On lixiviation with hyposulphite solutions*, and the me author's papers in *Trans. A.I.M.E.*, already referred to.

precipitant for silver is sodium sulphide, prepared as described in the last chapter.

The chloridised ore treated averages about 4 per cent. Pb and 12 ozs. Ag per ton, and contains from 6 to 8 per cent. moisture as received from the cooling floors. An analysis of it showed as follows[*]:—SiO_2 78·40 per cent., Al_2O_3 0·14 per cent., Fe_2O_3 8·62 per cent., MnO 5·07 per cent., ZnO 1·25 per cent., $PbCl_2$ 3·76 per cent., AgCl 0·042 per cent., NaCl 2·48 per cent. It is charged direct from the tramway running over the vats upon the sand filter, only a few old bags being interposed, and when the tank is full to within about 1 foot from the top (50 tons) it is levelled off. Base-metal leaching is then started by running on hot jacket water from the smelter plant, the temperature of which is about 120° F.; as soon as the level of the water reaches the top of the tank the exit is opened and the base-metal wash-water is allowed to run away into a series of cemented scrap-iron tanks. The quantity of wash-water employed is only about 12 cubic feet per ton, for it is found impossible to wash out anything like all the $PbCl_2$ on account of its insolubility; and as the natural leaching rate of the material is 16 inches per hour, only one and a-half hours are taken up with the first washing. The wash-water on its way to the scrap-iron tanks cools and deposits large quantities of $PbCl_2$ in the launders. The precipitate obtained from the first tank runs as high as 70 per cent. Pb and 800 ozs. Ag per ton, that from the last tanks being, of course, more contaminated with iron oxides, basic salts, dust, &c., so that the general average of all the wash-water precipitate assays 60 per cent. Pb and over 500 ozs. Ag per ton. The escaping liquors do not contain above ½ grain of lead to the cubic foot (1 part per million).

After the requisite quantity of water has percolated down through the charge, sodium hyposulphite solution (1 per cent. strength) at a temperature of 80° to 90° F. is run on. The silver leaching is conducted by simple percolation through the charge, and the natural leaching rate of 16 inches per hour is reduced to a rate of only 4 inches per hour by means of a clamp on the solution exit hose. As a rule, about 63 cubic feet of hypo. are used per ton, taking forty-eight hours to pass through. Great difficulty was caused in the early days of the plant[†] by the formation of lead hyposulphite, which separated out in the solution pipes, in the filter bottom, and even in the ore itself, rendering the silver insoluble, choking the filter, and so causing

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[*] *Private notes*, Nov., 1896.

[†] For the information here given about the special features of this thoroughly well-managed plant the author is indebted to Mr. A. E. Savage, late assistant metallurgist of the Proprietary Company, who conducted most of the experiments and worked out the problems which presented themselves. The author has also made observations personally.

great waste of time and an enormous consumption of hyposulphite in order to give even an imperfect extraction of silver. It would appear that lead hyposulphite, though not very soluble in hypo., is formed in large quantity by the action of sodium hyposulphite on lead chloride; when freshly formed in an amorphous condition this lead hyposulphite is readily decomposed by sodium carbonate, but when once in the crystalline condition it is not perceptibly affected by some days' exposure to strong sodium carbonate solution. After considerable experimenting a remedy was found in the addition of $NaCO_3$ to the charge, and now after ten hours of silver leaching 360 lbs. of Solvay soda (7 lbs. per ton of ore) are spread upon the surface of the charge and the leaching finished as usual. The consumption of hypo. has been by this means reduced from 25 to 4 lbs., and the formation of crystallised lead hyposulphite in the ore and filters to a great extent prevented, but it still settles out in the launders as a hard, tough stalagmitic crust containing 36 ozs. silver to the ton. It is advantageous to allow the lead hyposulphite to be formed in this way and then to decompose it by sodium carbonate rather than to add the latter salt at first, because a larger extraction of lead is thus secured, and because the instantaneous decomposition of the lead salt surrounds each particle of ore momentarily with a strong solution of sodium hyposulphite by which the extraction of silver is supposed to be notably increased.

No second washing is given, the charge being merely drained as thoroughly as possible and discharged; the saving in time thus effected, coupled with the abolition of all handling of dilute solutions, quite compensates for the loss of hypo.

In discharging a tank the top layer ½ to 1 inch thick is carefully skimmed off and returned to the chloridising plant, as it is found to assay from 6 to 50 ozs. per ton. The condition of the silver in this layer is not known with certainty; it cannot be sulphide precipitate brought back in turbid solution, for the stock solution after decantation from the precipitate is carefully filtered before being raised to the storage tank. Some light is thrown upon its nature by some experiments of Mr. Savage upon the froth which is observed floating upon the surface of the solution above the charge. This froth was found to assay over 200 ozs. per ton, and to contain much amorphous silver iodide in the condition of an impalpable powder. It is probable, therefore, that the surface layer of charge owes its richness to the presence of silver iodide undecomposed in the chloridising furnaces. After skimming off this top layer a trench is cut in the tank charge from door to door, and samples are taken separately of the upper, middle, and lower thirds, and of the bottom layer, say, 6 inches thick, besides a general sample of the whole the material removed in the trench or cross-cut. The bottom layer is found generally to contain up to double the average quantity of silver, but if the assay rises above that limit it shows that longer leaching or more solution is required. Lastly, a general truck sample is taken as the tank is shovelled out, and the mean of all the samples except the bottom layer is taken for the books as the true tailings sample.

The silver solution comes out quite milky with lead carbonate, which though formed by the action of sodium carbonate upon lead hyposulphite does not seem to have had time to settle out in the ore, and is in particles too fine to be retained by the filter. It is collected in one of the precipitating tanks of the upper row, and precipitated with more Na_2CO_3, stirring being effected by means of compressed air introduced through an india-rubber hose to the bottom, which gives rise to no appreciable loss of hypo. through oxidation. The precipitate is allowed to settle for three to four hours, and the solution is syphoned off into one of the precisely similar sulphide precipitation tanks on the next level by means of a vacuum hose[*] suspended by a string with its mouth just below the surface of the liquid. In these the silver (with a good deal of copper and some lead) is precipitated by means of Na_2S_2 prepared from caustic soda and sulphur in the usual way, and stirring as before is done with compressed air. The stock solution is then syphoned off, run through a filter, and raised to the storage tank, while the accumulated precipitate from several precipitations is run into the precipitate storage tank, thence to the press tank, and then into the filter press. The dried cakes of sulphide are roasted in a small reverberatory furnace, bagged and shipped to the refinery for treatment upon the cupel.

The lead carbonate precipitate (amounting to no less than 700 tons per annum) goes to the blast furnaces; the lead contained in it is equivalent to 0·63 per cent. of the total weight of ore treated; and, including that from the first wash-water collected in the scrap-iron tanks, from $\frac{3}{4}$ to 1 per cent. by weight is recovered, or 20 per cent. on the total lead contents of the ores submitted to the process. It is not known how perfect is the extraction of gold, but the roasted lixiviation sulphides contain 21 per cent. Ag and 26 per cent. Cu, with an average of 5 ozs. gold to the ton, which is separated in the refinery.[†] Some further data with respect to the process here carried on are given in Table XIII.

Various experiments were made with this plant with Russell's extra solution, but the use of copper sulphate was found not to afford any better yield, and, therefore, the Russell process for which the plant was designed was discarded altogether, with a

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[*] India-rubber hose with a spiral of copper wire inside to prevent collapse.

[†] *v.* Chap. xiii., where a description of the process is given.

consequent gain in simplicity of working, besides the saving in copper sulphate and in the production of a richer precipitate.

Sombrerete (Zacatecas, Mexico).—To Mr. Ottokar Hofmann, the greatest living authority on silver lixiviation, the author is indebted for an elaborate and exhaustive account of the vicissitudes of lixiviation practice experienced at Sombrerete, of which the following is a summary *:—

The ore of the Sombrerete mine is complex, consisting of galena and black zinc blende (which two minerals carry most of the silver), iron and copper pyrites, with occasionally gray copper and ruby silver, all in a quartz gangue. The galena is as far as possible sorted out by hand for shipment to smelting works, notwithstanding which there is always sufficient present to raise the percentage of lead to 9 or 10 per cent.† Though heavy it is not very dense, and decrepitates on heating owing to the large percentage of pyrites; coarse crushing is, therefore, admissible, steel wire screens of 8 mesh being used.

The first process used was the common Patera process, the capacity of the works being 10 tons per day, and the results satisfactory. A company was then organised, and a new lixiviation mill of the capacity of 50 to 60 tons per day erected according to the plans of Messrs. Stetefeldt and Russell, with Stetefeldt furnaces. The results were as follows:—

TABLE XV.—THE RUSSELL PROCESS AT SOMBRERETE, MEXICO.

Month.	Tons of Raw Ore Worked.	Assay of Raw Ore.	Total Contents of Ore.	Total Returns.	Per cent. of Extraction.
		Ozs. per ton.	Ozs. Silver.	Ozs. Silver.	
June, 1889,	545·10	40·2	22,665·52	8,777·4	...
July, ,,	925·62	36·87	33,143·33	19,695·8	...
August, ,,	466·45	30·5	14,149·22	8,336·5	...
September, ,,	866·61	32·6	28,156·30	19,764·5	...
October to December, 1889, shut down for alterations.					
January, 1890,	1019·20	31·45	32,051·70	13,055·1	...
February, ,,	670·20	34·15	23,079·22	12,393·0	...
March, ,,	961·90	29·95	28,438·96	18,989·8	...
April, ,,	322·50	30·75	9,852·75	7,615·7	...
General clean-up of mill, . .	...	...	...	2,673·9	...
	5777·58	33·16	191,536·99	111,301·7	58·1

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[*] As a large number of details referring to the Sombrerete practice are to be found in Table xiii., they need not be repeated here.

[†] Analysis of an average sample of the ore going to the leaching works is given in Table ix.

New proprietors, under the advice of Mr. Hofmann, discarded the Russell process, replaced the Stetefeldt furnaces by reverberatories, and are now treating 60 or 70 tons per day in the same leaching plant by the ordinary Patera process with very satisfactory results. A description of the plant as now worked is as follows:—

Crushing.—The plant consists of two shelf dryers and two revolving ditto, two large Blake crushers and two sets of rolls 26 inches diameter and 16 inches face, working at 75 to 80 revolutions per minute, and fed by hand from a shoot, as self-feeding was found to be too slow. Under these conditions as much as 2,558 tons have been crushed in 23 days' running time, or 111 tons per 24 hours, but the average crushing rate is limited by the mill capacity, and is only 2000 to 2500 tons per month.

Roasting.—Hand reverberatories built of sun-dried bricks are in use, each unit consisting of 3 hearths 10 feet by 10 feet, two such long hearths of 300 square feet, each being put back to back so that the same tie-rods serve for the two furnaces. Thirteen such double furnaces are in use, and some of them have been lately converted into two-storey furnaces with the object of increasing the capacity of the works. The ore in charges of 1 ton each is placed into the hearth farthest away from the fire-box, and moved forward at 8- or 10-hour intervals, so that after 16 to 20 hours it arrives at the last hearth pretty thoroughly oxidised. Six per cent. of salt is then added and vigorously stirred in, so as to mix it as thoroughly as possible with the ore; it is then left undisturbed for one and a-half to three hours according to the thoroughness of the previous oxidising roast, further stirring being avoided, as it increases the loss by dusting and volatilisation. The charge is then drawn and placed in a separate pile on the cooling floor to cool, after which it is tested for percentage of chlorination, deduction being made from the normal price of $1.25 (say 5s. 3d.) paid to the roasting contractor in case the percentage falls below 90, which is the average. No water is used to assist cooling, as this often results in decomposing AgCl; the ore is allowed to cool as slowly as possible on a cooling floor of ample size, not, however, in order to secure any material increase in chlorination, which, when the ore is properly roasted in the first instance, is hardly noticeable, but rather as a safeguard against loss through carelessness in drawing insufficiently roasted charges, and because slow cooling appears to give a higher extraction of gold.

Each particle of ore usually remains in the furnace twenty-four hours, the length of the roasting operation being due partly to the coarseness of the mesh, but chiefly to the very high percentage of sulphur. Finer crushing on this ore would not result in better chlorination, and, although it would lessen the roasting time, it would considerably reduce the crushing capacity, of the works. It is, therefore, cheaper to add a few additional roasters than to crush finer. The average loss by volatilisation, conducting the roasting in the manner above described, was only 4·8 per cent.*

Base-metal Leaching.—The plant is the ordinary Stetefeldt plant already described. Over the usual false bottom of slats is stretched the filter cloth of common cotton sheeting, which is fastened by pressing it into a groove cut in a piece of board, nailed, around the inside of the vat, a little above the false bottom.

The ore is not wetted down on the cooling floor but is brought to the vats in iron trucks while still rather hot and charged into about 3 feet of water, which it soon heats, so dissolving the base-metal chlorides more readily and shortening the base-metal leaching time. The charge is 55 to 58 tons, and, as soon as it is all in, cold water is allowed to flow on top and leach through till the effluent liquor gives no more discoloration on addition of sodium sulphide. The first liquors are hot and dark green in colour, and so strong that before the practice of charging into 3 feet of water was introduced they used to crystallise out and block up the filter and outlet pipes. Such strong solutions dissolve much silver chloride, and Hofmann considers that, for ores so rich in heavy metals, shallow tanks would, on this account, be far preferable.

The base-metal liquor is equally divided between two precipitation tanks (each 9 feet 9 inches diameter by 9 feet deep), so that the last weak solutions may precipitate most of the dissolved silver chloride in the first strong liquors. Then 5 to 10 gallons of sodium sulphide solution is added, and the whole agitated with compressed air in order not only to carry down most of the silver remaining in solution, but also to change the finely-divided silver chloride suspended in the liquid into the sulphide which rapidly subsides together with part of the precipitated base metals. The resulting precipitate, after washing and drying, contains 1500 to 3000 ozs. of silver per ton. The clear solution passes to a series of shallow masonry tanks filled with scrap iron arranged upon wooden benches, through which the liquors flow in the usual zig-zag manner and deposit their copper. The cement copper removed once a month contains, after washing and drying for shipment, 60 to 70 per cent. Cu and 500 to 600 ozs. Ag per ton.†

Silver Leaching.—As soon as the effluent wash-water gives no precipitate on testing, stock solution is turned on. A very weak

* For some details of the cost of roasting, &c., see table viii., chap. ix.

† For the volume of base-metal wash-water, &c., *v.* table xiii., where all such data are given.

solution is used, in accordance with the well-known views of Hofmann,* and with the undoubted fact that with such solutions the loss of hypo. in tailings and in wash-waters is very much less. The average strength employed is only 0·5 to 0·75 per cent., at which it is readily kept by the normal oxidation of precipitant. The effluent wash-water is frequently tested, and as soon as it begins to show the slightest coloration the liquor is turned into the silver precipitation tanks. Leaching with hypo. is continued until a beaker-full of solution gives, with sulphide, a precipitate which, filtered off, well washed, dissolved with nitric acid, and again filtered, yields a solution which remains clear on addition of HCl. When this point is reached the solution is allowed to drain away until the surface of the ore is just exposed, and water is then run on in order to press out the remainder of the stock solution in the pores of the ore. Only sufficient of the effluent washed-out solution is run to the solution sumps to keep up the same total volume of stock. The residues, after draining, have to be shovelled out by hand, as sluicing out through the side doors proved unsuccessful in these deep tanks.

Precipitation is conducted as usual, compressed air issuing from a ½-inch nozzle at the end of a hose being used for agitation, as first introduced by Hofmann. After decanting the solution into the sumps, the precipitate is run into a precipitate vat, from which it is forced into a Johnson filter press and washed. The washed precipitate is dried in chambers at a temperature low enough to prevent ignition of the sulphides and shipped, together with the base-metal sulphides, to the smelting works at San Luis Potosi.

The cost of treatment is $9.48 Mexican silver, which at the arbitrary rate of exchange adopted throughout this book is equivalent to £1, 3s. 8½d., details of which are given in Table XIII. At the present rate of exchange the total expense does not exceed £1 per ton. Details of the cost of chemicals, &c., are also given in the table.

Mr. Hofmann remarks †—"The Cusi Company went through a similar experience. The old lixiviation process was for years in successful operation on a scale of 50 to 60 tons per day," when the Company was induced to adopt the Russell process, "but, after one and a-half years' trial, resulting in a heavy loss, the process was discarded, and lixiviation with sodium hyposulphite alone again resumed."

Comparison between the Russell and Patera Processes.—The literature of the Russell process is voluminous, and upon the strength of undoubted successes at *Yedras* and at *Marsac* claims of universal applicability and of superiority to the old

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* *v.* Chapter xii., p. 220.

† *Private communication*, dated Nov. 16, 1896.

process are set up. There have, however, been instances of failure on the base sulphide ores of *Cusihuiriachic*, on the heavy pyritous and lead-containing ores of *Sombrerete* and *San Francisco del Oro*, and on the siliceous and ferruginous carbonates of *Broken Hill*.

The claims made on behalf of the Russell process by its advocates in comparing it with the Patera process are as follows:—*

1. Admissibility of coarser crushing.
2. Less perfect chloridising-roasting required; consequently less salt need be used.
3. The roasting may be accomplished in a suitable furnace instantaneously, whereas the roasting for the ordinary process requires time.
4. Results less dependent upon the perfection of chloridisation.
5. More uniform and regular results produced by extra solution.
6. Results not affected by the presence of caustic alkali in the solution as those of the ordinary process.
7. Greater applicability to ores containing lime or lead.
8. Production of sulphides comparatively free from lead and recovery of lead as a bye-product.
9. Enormously greater extraction on raw ores, hence ores which require chloridisation for treatment by the ordinary process can often be treated raw by the Russell process, saving the additional expenses and losses.

With the exception of 6 and 7 the validity of all these claims appears to be more or less questionable.

The undoubted saving in cost of roasting and improved extraction shown even on such ores as are suited to the process is offset by the following disadvantages:—

1. Additional cost of the much larger amount of chemicals required as shown by a comparison of Tables XIII. and XIV. The average cost of the chemicals used by the four mills treating ore under the Russell patents is no less than 5s. 4d. per ton of ore, whereas on the three mills using the ordinary process the cost is stated to have averaged only about 1s. 6d. per ton.

2. Greater complication in working and the increased number of operations required leads to the employment of a larger amount of skilled labour.

3. Additional plant required corresponding to the increased time taken during lixiviation.

Comparison of Lixiviation (Hypo.) with Amalgamation.—The advantages and disadvantages of hyposulphite lixiviation as compared with roast-amalgamation processes may be summarised as follows:—

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* Daggett, *Trans. A.I.M.E.*, vol. xvi., p. 494.

Advantages.	*Disadvantages.*
1. Smaller first cost of plant.	1. Greater deterioration of plant if run intermittently.
2. Coarser crushing possible.	2. Much closer supervision and accurate testing are required, involving a larger amount of assaying and other skilled labour.
3. Smaller amount of power required, and consequently lower consumption of fuel.	3. Much more danger of loss by leakage, and through carelessness in manipulation or in testing.
4. Lower working costs, and with anything like base ores a higher percentage of extraction.	4. Inconvenient condition of the product (sulphides), the refining of which requires more skill, involves larger losses, and is much more costly than the retorting of amalgam and the refining of retort silver.
5. Utilisation, as bye-products, of part of the lead and copper contents of the ores treated.	
6. Smaller total quantity of water required.	
7. Cost of chemicals used is usually less than that of those used in amalgamation, including quicksilver and pan castings.	
8. Small value of necessary stock of chemicals compared with £2000 to £8000 worth of quicksilver locked up in an amalgamation mill.	

The extraction of gold by lixiviation is also, in most cases slightly greater, besides which small quantities of gold in the sulphides are paid for, whereas, in the pan bullion, they are not.

At the *Ontario* and *Marsac* mills a good opportunity was afforded during 1891 for comparing the two systems of treatment since both mills ran uninterruptedly on substantially the same ore.* The comparative results are summed up by Lamb † as proving that to treat about the same quantity of ore per day the Ontario (roast-amalgamation) mill required 39 per cent. more labour, 30 per cent. more stamps (in consequence of finer mesh of screen), 48 per cent. more salt, 40 per cent. greater cost in chemicals, double the number of furnaces and very much more power, while the extraction of both gold and silver on the roasted ore is slightly less.

On the whole, therefore, the advantages of the Russell process for ores which need roasting as compared with amalgamation far outweigh its disadvantages. It is, however, still doubtful whether it can compete with smelting for heavy ores containing less than 30 per cent. SiO_2, except where the ores contain excessive quantities of zinc, or in very inaccessible localities where the price of fuel would be prohibitive, and even in these latter pyritic smelting will ere long prove a formidable rival.

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* *v.* Analyses in Tables iii. and ix.

† *E. and M. J.*, Dec. 17, 1892.

CHAPTER XIII.

THE REFINING OF LIXIVIATION SULPHIDES.

Composition of Lixiviation Sulphides.—The sulphides from hyposulphite lixiviation vary considerably in composition, the variations depending more upon the nature of the ore and the precipitant employed than upon any distinction between the Patera and Russell processes. The Kiss process always produces a low-grade precipitate containing a large excess of free sulphur and usually much gypsum also. Most of the free sulphur in the precipitate can be recovered by digesting with caustic soda,

TABLE XVI.—ANALYSES OF SULPHIDE PRECIPITATES.

	San F'cisco del Oro, 1887, Chihuahua, Russell Process.	San F'cisco del Oro, Chihuahua, Russell Process.	Sala, Sweden, 1892, Russell Process.	Sombrerete, Zacatecas (Mex.), 1895.	Marsac Mill, Park City, Utah.	Broken Hill Proprietary, N.S.W.
References, .	1.	2.	3.	4.	5.	6.
Silver, . .	19·00	21·60	9·00	34·0	34·78	21·0
Gold,. . .	0·04	0·01	...	...	...	0·002
Copper, . .	11·55	4·44	40·00	24·6	21·60	26·0
Lead, . .	30·64	21·60	9·00	7·2	0·50	6·5
Cadmium, . .	3·45	1·20	...	...	...	...
Zinc, . . .	4·30	13·86	...	8·6	...	...
Iron, . . .	0·72	2·68	6·00	0·8	0·75	...
Mercury, . .	...	...	0·04	...	...	...
Antimony, .	...	...	...	...	0·18	...
Alumina, . .	...	...	...	...	0·25	...
Lime, . .	3·88	3·62	...	0·9	..	...
Insoluble, . .	5·45	4·96	...	2·2	0·25	...
Sulphur, . .	14·90	19·37	...	18·3	20·74	...
SO_3, . . .	6·10	6·18	...	...	...	...
Soluble in water,	...	...	...	...	12·76	...
Ag ozs. per ton,	6207	7057	2940	11,100	11,360	6860
Au ozs. ,,	11·67	2·92	...	9 to 12	12·59	5·5

References.—1 and 2. Hofmann, *E. and M. J.* 3. Asbeck, *Proc. Inst. Civ. Eng.*, vol. cxvi., p. 469. 4. Hofmann, *private communication*, Nov., 1896. 5. R. B. Watson, *private communication*, Sept., 1896. 6. *Private notes*, Dec., 1896.

which dissolves it with the formation of sodium sulphide, which can be subsequently used as a precipitant. In most cases, however, it is simply roasted off and wasted.

Very base sulphides, such as those from the base-metal wash-water, and generally also those from the raw leaching of tailings by the Russell process, are best sold to the smelters, who treat them by melting down, with ordinary roasted lead matte and siliceous silver or gold ore as flux, producing a very rich lead bullion, and a rich copper matte which may be desilverised by the Ziervogel process or by any of those mentioned in Chapter XVII.

The ordinary sulphides, precipitated from the silver leaching of roasted ores by the Patera and Russell processes, contain usually between 6000 and 12,000 ozs. of silver per long ton (from 18 to 35 per cent.), and the composition of a few such is given in Table XVI., that of a Swedish precipitate from raw tailings being added for the sake of comparison.

These ordinary sulphides may be treated in several different ways:—

(1) By *roasting out* as much sulphur as possible, and then simply melting down in crucibles yielding a base bullion which is sold to refiners;

(2) By *scorification* on a bath of molten lead on a cupel, and subsequent cupellation of the lead;

(3) By *matting* and boiling out with sulphuric acid, subsequently precipitating the dissolved silver on copper plates; and

(4) By the *Dewey-Walter* sulphuric acid process.

(1) **The Roasting and Melting Process.**—The dried sulphides are ground and roasted at a low temperature in a reverberatory, the heat being raised only after nearly all the sulphur has been driven off. The roasting is always very incomplete, the resulting mass consisting largely of metallic silver-copper in lumps, and a mixture of half-fused copper sulphide and powdery oxide, the former predominating. The loss in dust and by volatilisation is always high.

The roasted mass is broken up and melted in graphite crucibles yielding low-grade bullion, and a large quantity of very high-grade copper matte, from which part of the silver can be precipitated by adding scrap-iron, at the expense, however, of debasing the silver bullion. Stetefeldt quotes[*] results of two such meltings at the Ontario Mill, in which, for 100 parts of silver bullion 875 fine the matte produced was, in one case, sixty-two parts, assaying 2720 ozs. silver per ton and 24 per cent. Cu, and, in the other case, seventy-six parts, assaying 3308 ozs. silver per ton and 27 per cent. Cu. More perfect roasting would have lessened the proportion of matte at the expense of producing a lower grade bullion and increasing the losses. This process is now practically abandoned, except in very small works.

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[*] *Trans. A.I.M.E.*, vol. xiii., p. 291.

(2) **The Scorification Process.**—This is by far the most widely used, as the sulphides produced at lixiviation mills can often be shipped to smelting and refining centres more advantageously than they can be handled on the spot. Where, however, there is a very large output of sulphides, it is more advantageous for the milling company to refine all its own sulphides than to sell them to outside smelters.

The process was in use at the *Bertrand* and other early lixiviation mills in the U.S., English cupel hearths being employed; the refining was in this case, however, not carried to completion, the bar silver produced being only 800 to 900 fine.[*]

At the *Sala* Works (Sweden) it is sometimes employed, though not very well suited to the very base cupriferous sulphides there produced.

At **Sombrerete** (Mexico) the sulphides produced, containing 31 per cent. Ag, are shipped to the smelting plant at San Luis Potosi belonging to the same corporation and treated by this process.

At **Promontorios** (Alamos, Sonora)[†] a circular German hearth, 6½ feet in diameter, is employed. The lead bath weighs 5 tons, and after it becomes well covered with litharge a charge of 150 to 200 lbs. precipitate is added with a ladle, and covered with three times its weight of litharge. As soon as the additions become pasty, blast is turned on, and the scum slagged and skimmed off, after which another addition is made with the blast turned off as before. The precipitate at these works averages 20 per cent. each of silver, copper, and lead, but sometimes the amount of copper is so great that soft lead has to be fed into the bath along with the precipitate to keep it in condition.

At the works of the **Broken Hill Proprietary Coy.**[‡] the dried and partially roasted lixiviation sulphides, containing on an average 21 per cent. Ag, 26 per cent. Cu, and 6 per cent. Pb, are "sweated" on a cupel, the lead used being that from the crust-liquating furnaces, which already contains about 120 ozs. Ag per ton. The cupel is first saturated with litharge, and is then three parts filled with lead of the kind named. When this reaches a red heat the first charge is added, consisting of about 60 lbs. of roasted sulphide, together with the same weight of "silver litharge" from the concentration cupels, containing about 90 ozs. Ag per ton. Each charge is completely melted down before adding another, so that successive charges are added at intervals of about an hour. After the third charge the cupel is quite full, and the slag is run off. Five more charges are then made at about one-hour intervals as before, and, lastly, the slag and

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[*] Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., 13.

lemes, *Proc. Inst. Civ. Eng.*, vol. cxxv., p. 121.

otes, 1896.

residual matte is run off by adding fresh lead at the back, so as to raise the level of the bath of metal. A little coal is then thrown on top to form a ring, from the inside of which clean bars can be dipped, and the whole of the lead ladled out into moulds. It usually assays about 2000 to 2500 ozs. silver and 1 oz. gold to the ton. From the slags the matte is picked out by hand. It usually amounts to about one-ninth of the total slag, assays 1300 ozs. per ton, and is returned to the cupel with the next lot of sulphides. The slag assays about 80 ozs. Ag, and is smelted in the refinery blast furnace together with other litharges and refinery products.

Wet Processes.—The losses by volatilisation and "dusting" in the dry process are considerable, and processes in which the precipitate can be treated by acid result much better as regards the actual recovery of precious metals. It usually happens that in mining districts sulphuric acid is very dear, and, therefore, acid solution processes as a rule have little or no chance of competing with the dry processes already described. When, however, there happens to be a good demand for copper sulphate, as, for example, in districts where silver amalgamation processes are in extensive use, or where the nature of the ore is such as to render the Russell process profitable, wet processes can be introduced with great advantage.

(3) **The Matting Sulphuric Acid Process.***—Stetefeldt refers to the chief difficulties in the way of roasting sulphides in a reverberatory which are:—(1) Melting of free sulphur with the formation of little balls. (2) Existence of separate individual particles of pure sulphides of silver and copper respectively. (3) Predominance of silver sulphide, which is reduced to metal instead of oxidising. (4) The copper oxide formed reacts upon adjacent particles of sulphides, reducing them to metal, which thereupon protects other particles of sulphide from further action. At the *Marsac* mill, therefore, this authority introduced a modification of the matting process invented by Hodges for refining base Comstock bullion, and already described in Chapter VIII. The matting of lixiviation sulphides is a much simpler operation, since no sulphur is required, the precipitate already containing an excess, and the melting down takes place very quickly. The process consisted of (*a*) matting, (*b*) roasting, (*c*) dissolving in dilute H_2SO_4, and simultaneously precipitating silver with copper plates, (*d*) crystallising out copper sulphate from the solution, (*e*) washing, pressing, and melting cement silver.

(*a*) **Matting.**—The cast-iron pot employed was covered by a sheet-iron hood with a working door in it, the fumes being all drawn through the Roessler converter to condense any vola-

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* Stetefeldt, *Trans. A. I. M. E.*, vol. xx., p. 37; xxi., p. 286; xxiv., p. 221.

tilised silver as well as the SO_2 formed. The sulphides fused at a low red heat, forming a very fluid matte which was poured out on cast-iron plates so as to get a brittle layer ¼ in. thick, easy to pulverise. The wear of the iron pot by corrosion on the inside was very slight owing to the greater affinity of sulphur for copper at such low temperatures. On each shift one man matted about 800 lbs. of sulphides, consuming 220 lbs. of coal.

The matte was crushed in a small ball mill of the Brückner-Sachsenberg type like those used at Mansfeld. At 28 revolutions 150 lbs. of matte per hour were pulverised to 40 mesh with a consumption of 1½ H.P.

(*b*) **Roasting.**—The furnace employed was a small muffle, heated from the top only, the construction of which was precisely similar to that used by Hodges.* At the end of the muffle were four iron pipes through which the fumes on their way to the Roessler converter were aspirated by means of a Körting ejector of hard lead. The charge of 600 lbs. took eight hours to roast at a low temperature, the draught being kept as low as possible. When finished a sample dropped into a beaker of water looked black while still showing the spangle reaction † owing to the presence of Cu_2O; the small black lumps should be apparently black throughout without a distinct red centre. All largish lumps and scales from tools, &c., were re-roasted. The roasting of 600 lbs. matte required 1000 lbs. of coal. The roasted matte was afterwards re-pulverised to pass through a 40 screen.

The *Roessler converter* is a lead-lined tank 4 feet diameter by 6 feet high, through the cover of which passes a 4-in. lead pipe connected with a large leaden ring with 1086 ⅛-in. holes in it standing 6 inches above the bottom. Between the inlet pipe and the furnaces is a Körting ejector which can be connected either with the roasting furnace or with the matting pot. Cement copper is charged into the tank together with a solution of bluestone; practically all the SO_2 and SO_3 in the furnace gases blown through the solution are condensed and converted into copper sulphate. It was formerly considered that in this appliance free sulphuric acid was formed, together with cuprous sulphate, which was then re-converted into cupric sulphate by the aid of free oxygen and of part of the free acid, the remainder acting upon the metallic copper present. Doubt is, however, cast upon this view by the experiments of Stetefeldt, ‡ and in all probability the action of SO_2 and O upon metallic copper is direct and simultaneous.

$$SO_2 + O_2 + Cu + H_2O = CuSO_4 + H_2O.$$

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* *Trans. A.I.M.E.*, vol. xiv., p. 741.

† *v.* Description of the Ziervogel process, chap. x.

‡ *Trans. A.I.M.E.*, vol. xxi.

Any silver contained in the fumes is condensed in the form of a reddish precipitate assaying from 470 to 900 ozs. of silver per ton, practically all as sulphide soluble in Russell's solution.

(*c*) **Solution of the Roasted Matte.**—This took place in two lead-lined tanks 3 feet 6 inches diameter by 5 feet 8 inches high, with conical bottoms closed by rubber plugs. A lead steam-pipe terminating in a perforated ring served to heat the solution. Each charge consisted of 300 lbs. of roasted matte together with 16 cubic feet of mother liquor from the crystallising vats, sufficient sulphuric acid being added to make up a total of 2 lbs. free H_2SO_4 present for each 1 lb. of copper in the matte. The solution was first put in and steam turned on, the matte being added gradually and boiled for two hours. Copper plates were suspended in the tanks in order to make sure of precipitating all the silver, but the wear of these was slight, as sufficient Cu_2O was present to decompose nearly all the silver as sulphate, while that converted into metal during roasting remained unaltered. The solutions were run into covered filter tanks with asbestos filters through which they were drawn by a Körting pump.

(*d*) **Crystallising the Bluestone.**—The lead-lined (6-lb. lead) crystallising vats still in use are 6 feet by 3 feet by 2 feet deep, and 48 strips of lead 20 inches by 3 inches are suspended in each to hasten the crystallisation and form small crystals. Upon these strips, and upon the lead lining of the tanks a thin coating of metallic copper was deposited arising from the spontaneous decomposition of cuprous sulphate (formed by direct solution of Cu_2O in acid) on cooling. The crystals produced were utilised in the mill for the preparation of extra solution.

The mother liquors after a time accumulated iron and other impurities, and were then precipitated by means of scrap iron; the washed cement copper contained a considerable amount of silver, derived from the liquors of the Roessler converter which were also passed through the scrap-iron tanks, and returned to the matting pot.

(*e*) **Washing, Pressing, and Melting Cement Silver.**—The accumulated silver from six charges of the dissolver is washed with one charge of hot water which is circulated by the Körting pump till it shows a gravity of 20° B., when it is turned into the crystallising tanks. Subsequent washings go first to a weak solution tank and then to the scrap-iron tank, washing being continued until the effluent hot water shows no blue colour on addition of ammonia.

The washed silver is dried, pressed in a hydraulic press into flat cakes 6 inches diameter, weighing 7 to 9 lbs., and melted down in crucibles in the ordinary melting furnace, yielding bars 950 fine.

The actual cost of refining by this process (at the Marsac refinery during 1892)—48·8 tons (of 2000 lbs.) of sulphides, averaging per ton, 11,449 ozs. silver, 11·77 ozs. gold, and 569·8 lbs. copper—was, according to Stetefeldt,* as follows:—

Labour, coal, acid, supplies, steam power, &c.,	$6,422.00	
Freight, insurance, commission, and mint charges,	10,173.00	
		$16,595.00
Less 107,650 lbs. bluestone produced at 5.6 cents,		6,027.00
Net cost,		$10,568.00

The net cost is equivalent to 10½ cents. per lb. of sulphides, or $18.70 (£3, 18s.) per 1000 ozs. of silver turned out. Leaving out of consideration the freight and other realisation charges, it will be seen that the total cost at the refinery was practically offset by the value of bluestone produced.

Comparing the precious metal contents of the material sent to the refinery with that of the products, there was a shortage of 5660 ozs. silver, or 1·01 per cent., and a surplusage of 2 ozs. gold, or 0·19 per cent. Stetefeldt considers that a large part of this loss took place in melting, and that it would be much reduced by substituting a reverberatory furnace for the crucibles.

The Dewey-Walter Process.†—This process, which has displaced that just described at the Marsac Mill, is based on the fact that finely-divided sulphides of silver and copper are converted into sulphates by boiling in strong sulphuric acid the silver sulphate remaining dissolved in the acid, while the copper sulphate is insoluble until the solution is diluted with water. The reaction which takes place in the case of Ag_2S is as follows:—

$$\begin{aligned} Ag_2S + 2H_2SO_4 &= Ag_2SO_4 + 2H_2O + SO_2 + S. \\ S + 2H_2SO_4 &= 2H_2O + 3SO_2. \end{aligned}$$

So that in all four molecules of H_2SO_4 are required for one of Ag_2S.

In practice the process consists of the following operations:—(*a*) Boiling the dried sulphides in an iron pot with strong H_2SO_4 (1·84 sp. gr.); (*b*) ladling into water in a dissolving tank, and washing the residue till nearly free from soluble silver; (*c*) precipitating the dissolved silver on copper plates; (*d*)

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* *Trans. A.I.M.E.*, vol. xxiv., p. 228.

† Dewey, *Colo. S.S.M.S.G.*, vol. ii., No. 1, p. 29; also *Trans. A.I.M.E.*, vol. xxvi., p. 242.

washing, drying, and melting the cement silver; (*e*) crystallising bluestone from the liquors; (*f*) treating the pot residues for gold.

(*a*) **Boiling in Acid.**—The pots used are 4 feet diameter, 3 feet deep, and 1 inch thick at the bottom, supported on a cast-iron plate, and they last on an average for about 24 charges. The charge is 975 lbs., to which at first 1000 lbs. of acid is added, as the action on the CuS is violent. When the boiling becomes quieter, more acid is added—100 lbs. at a time, up to the total of 3000 lbs.—stirring at intervals to break up the masses of anhydrous $CuSO_4$ which separate. Towards the end of the operation (which takes the greater part of 2 day shifts) the charge foams violently, and must be stirred over a low fire, after which it quiets down and the operation is over.

(*b*) **Dissolving.**—The dissolving tank, 4 feet by 8 feet by 2 feet deep, of 2-inch lumber, lined with 12-lb. lead, is provided with a lead steam pipe dipping down to near the bottom for heating the solution, and a lead-lined cover. Below it are two filter tanks, the filter being constructed of two layers of cocoa matting between perforated lead plates supported on ridged slats () of sheet lead. Upon the whole is beaten down a layer of clean quartz sand, 3 inches or 4 inches thick, which forms the actual filtering medium, and is most successful in keeping the solutions clear and free from residue. Every fortnight, or whenever the rate of filtration becomes too slow, water is run in below the false bottom and the sand first stirred up and then allowed to settle, while the muddy water is pumped off. Repeating this once or twice, the sand is perfectly cleaned, when it can be levelled off and beaten down again for renewed service.

The dissolving tank is at first filled with cold water, as the hot charge with excess of strong H_2SO_4 soon raises it to boiling. When the charge is in it is stirred, settled, and drawn through the filters; the first tankful of the solution, containing most of the copper being kept separate Subsequent washings of the thick white mud with weak acid yield silver sulphate liquors at about 20° B.

(*c*) **Precipitating.**—This is done in lead-lined (8-lb. lead) tanks, that for the first or copper solution being 8 feet by 5 feet by 3 feet, and that for the silver solutions being 9 feet by 7 feet by 3 feet. In each tank there is a leaden pipe for agitating with a jet of mixed air and steam, and copper plates are placed round the sides of the vat. The silver precipitates in about four or five hours, and after the liquor has been run through an asbestos cloth filter, the cement silver is shovelled out with a wooden shovel into the sweetening tanks.

(*d*) **Washing and Melting the Cement Silver.**—The process of washing, pressing, and drying the cement silver is conducted just as in the process already described. The cakes of pressed silver are then charged into a plumbago crucible holding about 2400 ozs., together with a little borax, more cakes being added as they melt down till the crucible has received its full charge. Nitre is then added, the molten metal is stirred with an iron rod and the slag removed with a skimmer. The additions of nitre and borax are repeated until the metal presents a bright, untarnished surface, when, after cleaning off the final slag, the metal is cast in warmed and greased cast-steel moulds, sugar being sprinkled on the liquid metal, and a cast-iron cover put over the mould to prevent sprouting on cooling. The chief impurity thus removed is iron, and about 1½ lbs. each of nitre and borax are used for each charge of 2400 ozs. The bar silver produced averages 999·4 fine, with no trace of gold.

(*e*) **Crystallising.**—The solution from the silver precipitation tanks goes back to the dissolving tank, until, from accumulation of copper sulphate, it reaches 20° or 25° B. It is then filtered, evaporated to 37° B., and crystallised in the same set of crystallisers used for the old process, giving a first crop of bluestone crystals with only 0·34 per cent. of iron. The mother liquor is evaporated to 42° B. and again crystallised, giving bluestone, which after once washing with cold water contains 0·69 per cent. Fe, and the liquor after again concentrating to 50° or 52° B. yields a small quantity of impure bluestone with 3·02 per cent. Fe. The strongly acid liquors, after standing to deposit as much iron as possible, are pumped up to the storage tanks and used in the pots. A scrap-iron "guard tank" is provided for all the final washings.

(*f*) **Residue.**—Five charges or 4875 lbs. of sulphides leave about 750 lbs. of (wet) residue, which is returned to the pot and boiled with its own weight of strong acid, after which it is washed, dried, and sent to the smelters. It consists chiefly of $PbSO_4$ with some AgCl and metallic silver, as well as earthy and siliceous matter from the filter. Of gold it carries from 123 to 141 ozs. per ton.

Results.—During 1894 the consumption of acid was 3·34 lbs. per lb. of sulphide or 0·68 lb. per oz. of silver; that of copper was 1 lb. for 2·27 lbs. of silver or 30·21 lbs. per 1000 ozs. silver, and the bluestone produced was 3·63 lbs. per lb. of copper sent to the refinery. One assayer and two labourers did all the ordinary work of the plant except shipment and clean up.

The silver contents of the sulphides were determined in triplicate on each lot by scorification assay, corrected by assay of slag and cupel. The net result of the clean-up for 1894 showed a direct return of 96·29 per cent. of the true assay-value of the sulphides as fine bullion, free from gold, and 4·07 per cent. as residues and cleanings on hand, so that there was a plus clean-up of 0·36 per cent. on the most careful corrected assays. This

Dewey justly claims* as a wonderful result, and summarises the advantages of the process as follows:—

(1) Highly satisfactory recovery of silver.

(2) Absence of roasting losses.

(3) Large proportion of silver recovered as "fine" bars.

(4) Small cost of operation, the bluestone recovered, returning a large proportion of the expense.

(5) Simplicity of the process (and inexpensiveness of the plant) render it suitable for installation at individual leaching works.

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* *Loc. cit.*

SECTION IV.—EXTRACTION OF SILVER BY SMELTING PROCESSES.

INTRODUCTORY.

It has been already seen from Part I. that silver may be extracted from all ores containing that metal by smelting them together with lead ores, when the reduced lead takes up most of the precious metal contents of the ore and thus serves as a vehicle for their concentration. There are, however, other materials which can be employed for the same purpose.

The smelting of silver ores, together with sufficient lead-bearing material to yield enough lead to carry away the whole of the silver, differs in no respect from the blast furnace smelting of lead ores properly so called; in fact, it may be said that in almost every blast furnace lead works the smelting of more or less dry silver ores forms part of the normal routine. The details of such silver-smelting on a lead basis have been fully described in Part I., Chapters VI. to XI. inclusive, which may be considered as common ground to the metallurgy of lead and of silver.

The collection of a portion of the silver in *matte* and *speiss* produced in lead furnaces has been already referred to, and it will be obvious that in the absence of a sufficient quantity of lead reliance may be placed on *matte* (or speiss) alone to effect a perfect collection of the precious metals. Speiss has been but seldom employed in practice, but the use of matte, common enough for at least a couple of centuries past, has of late undergone remarkable extension through the introduction of practical means for utilising the sulphur in an ore as a source of heat, in the modern system of so-called *pyritic smelting*.

Any kind of matte—except a pure iron matte—is found to be as efficacious in collecting the precious metals as lead itself, over which it possesses the advantage of non-volatility and the further advantage of permitting a higher degree of concentration without undue loss. In lead smelting, as has been already seen, the ore charge should yield at least 7 or 8 per cent. of that metal, equivalent to a concentration of twelve or fourteen parts of ore into one of product. In using matte as a vehicle it is in most cases quite easy to produce clean slags when smelting a charge which produces only 5 per cent. by weight, equivalent to a concentration of 20 into 1, while when necessary good results can be obtained in concentrating even 30 and 35 into 1. The drawbacks to the use of matte are two in number—viz., the greater expense for further treatment of the product of the ore furnace, and the greater difficulty of effecting a clean separation between the furnace products, owing to the closer approximation of their specific gravities.

Oxidised copper ores may under appropriate circumstances be used for the concentration and withdrawal of the precious metals[*] in the form of auriferous metallic copper. The metallic copper so produced, admits of as high a degree of concentration as other mattes, as much as 1 by 30 having been obtained without very great increase of the normal slag loss; moreover, the non-volatility of copper leads to a smaller loss of silver by volatilisation than is the case with lead furnaces. This use of metallic copper has, however, the drawback that the amount lost in slags, though not usually greater than in the case of lead, is yet far more valuable on account of the far higher price of the metal. Furthermore, such a copper concentration process can only be applied to the exceptional case in which dry non-sulphide ores of silver are to be smelted and where natural oxidised ores of copper are also available.

The treatment of silver ores by smelting without the use of lead may conveniently be described under the following heads:—(1) Matte smelting in reverberatories; (2) matte smelting with carbonaceous fuel in blast furnaces; and (3) "pyritic smelting," by which is meant, not the concentration of precious metals by means of iron pyrites described under that name by Percy,[†] but the utilisation of the heat of oxidation of iron and of sulphur as a means of fusing the whole charge.

The roasting of silver mattes differs in no wise from that of ordinary lead mattes already described in Part I., Chapter X., but their subsequent treatment may advantageously form the subject of a separate chapter. The special processes of extraction by means of metallic copper and of speiss are also referred to, the latter as a branch of matte smelting in Chapter XIV., the former in connection with the refining of argentiferous copper in Chapter XVII.

Matte Smelting.[‡]

By a "matte" the silver smelter understands any mixture of sulphides of the heavy metals which fuses at a smelting tempera-

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[*] *v.* the author's paper in *Proc. Inst. Civ. Eng.*, vol. cxii., pp. 154-159.

[†] *Metallurgy of Silver and Gold*, vol. i., p. 53.

[‡] A useful work, published under this title by Lang (New York, 1896), may be consulted with advantage.

ture and separates with a fair degree of completeness from the "slag," or fused mixture of silicates. The sulphur may be replaced to some extent by As or Sb, even in rare cases by Se or Te, and the heavy metals under appropriate conditions may be replaced by Ba, and partly even by Ca, while a great number of mattes contain dissolved magnetic oxide of iron, Fe_3O_4, and not a few metallic iron, copper, or lead, all of which separate out on cooling with greater or less perfection. Metallic silver and gold* may also, under suitable conditions, be dissolved by fused matte, and partially separate out on cooling, though probably this only happens in the absence of Se, Te, As, and Bi, all of which form definite fused compounds with the precious metals.

The general consensus of metallurgical opinion goes to show that a *pure iron matte*, FeS, is an extremely poor medium for collecting gold and silver, especially the former, though an iron matte, containing comparatively small quantities only of Cu, Bi, Te, and As, may be very efficacious when the accompanying slags are of bi- or sesqui-silicate type.† With slags of mono-silicate type, and with those still more basic, it seems impossible to successfully concentrate the precious metals without a considerable proportion of *copper* or *lead* in the matte. Very rich copper mattes, however, seem to collect silver less perfectly than those of moderate richness, say 10 to 30 per cent. Cu. *Lead matte* may be employed as a collector, instead of a purely iron or copper-iron matte, and probably with equal efficacy as regards separation from slag, &c., except in the presence of zinc, which is quite as harmful in the matting as in the lead smelting process. Lead matte, however, possesses the great disadvantage that, owing to the sublimation of PbS, the quantity of flue-dust produced is much increased, and that the volatilised PbS invariably carries with it a considerable proportion of silver.

As regards apparatus, matte smelting is considered under the heads of matting in blast furnaces and in reverberatories respectively. As regards the reactions concerned in the process, however, blast furnace matting exhibits widely different phenomena, according to whether the necessary heat is generated by the combustion of coke or charcoal as in the lead blast furnace, or by the combustion of the sulphur and iron in raw ores. We have already seen that under very exceptional conditions sulphur in the lead blast furnace may be eliminated as SO_2, instead of combining with lead and iron to form matte, by the simple expedient of largely increasing the volume of air per square foot

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* *v.* as regards silver, Egleston, *S.M.Q.*, vol. xii., p. 201; and as regards gold, Pearce, *Trans. A.I.M.E.*, vol. xviii., p. 454, *et seq.*

† *v.* Spilsbury, *Trans. A.I.M.E.*, vol. xv., p. 767; also Austen, *ibidem*, vol. xvi., pp. 262, 268; and Pearce, *loc. cit.*; *v.* also Lang, *op. cit.*, p. 22, for comments on these references.

of hearth area—that is, by supplying the furnace through a number of large tuyeres with more air than can be consumed by the coke.

A great advantage which matte smelting possesses over smelting on a lead basis is the wider range of slag composition with which it is possible to obtain good results in the blast furnace as well as in the reverberatory. The tendency of lead to combine with silica and its great volatility confines the lead smelter within comparatively narrow limits of slag composition (*v.* Part I., Chap. VII.), for it is impossible to do good work with slags which are either too siliceous, too viscous, or which have too high a melting point. The matte smelter is free to make a slag of any convenient composition, so long as it can be made to separate completely from the matte; and as the question of volatilisation hardly comes in, it is usually advantageous and economical to make somewhat siliceous slags melting at a comparatively high temperature, their increased viscidity in a fluid state being more than compensated for by their lessened specific gravity, which enables the matte to separate out. In the ancient forms of furnace, and with slow smelting, such siliceous slags were accompanied by many disadvantages, "scaffolding," reduction of iron "bears" and "sows," local burning out of furnace linings, &c. In large modern water-jacketed furnaces and with fast driving such difficulties practically disappear, and quite siliceous slags (especially in pyritic smelting) are no more difficult to manipulate than those of more basic character, as will be seen hereafter.

Reactions in the Matting Processes.—In the case of matte smelting in blast furnaces with carbonaceous fuel, or what may be termed the German system, almost all substances present in the ore behave precisely as in ordinary blast furnace lead smelting described in Part I., Chapter VII. In reverberatory matte smelting and in pyritic smelting, however, some of them behave differently. The principal differences are brought out by Table XVII., borrowed, in the main, from that given by Lang.[*]

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[*] *Matte Smelting*, New York, 1896, pp. 85-89.

[redacted]

TABLE XVII.—COMPARISON OF VARIOUS SYSTEMS OF SMELTING.

	Lead Smelting and German System.	Reverberatory Matting.	Pyritic Smelting.
Lead, . . .	Almost completely recovered as metal and in matte.	Part enters matte. Larger part slagged.	Partly slagged, but chiefly volatilised.
Iron as Fe_2O_3,	Reduced to FeO and partly slagged. Partly reduced by carbon to metallic Fe, which either enters matte or forms "speiss" or "sows."	Reduced by sulphur to FeO, and then slagged. No reduction to metallic iron, or by carbon to FeO.	As in reverberatory matting.
Barytes, . .	Partly decomposed, forming silicate; partly reduced to BaS, which enters slag (and sometimes matte also). A part enters the slag unchanged.	Almost all is decomposed and slagged as silicate with volatilisation of SO_3.	With basic slags is chiefly driven into slag unaltered. With acid slags mostly decomposed and slagged as silicate.
Arsenic, . .	Reduced chiefly to speiss, but part also enters matte and bullion.	Partly volatilised; remainder forms speiss and matte.	Almost completely volatilised as As_2S_3, part, however, being oxidised to As_2O_3, with evolution of heat.
Sulphur, . . as Sulphides, Pyrites, Chalcopyrite, Pyrrhotite.	Sulphides may in part react direct upon metallic oxides, forming SO_2, but chiefly melt unaltered, and pyrites even absorbs Pb and Cu to form matte.	Part of sulphur volatilised from pyrites direct. That in other sulphides reacts in part upon metallic oxides, with evolution of SO_2, while the oxidised iron is slagged. The remainder of the sulphides simply melt down to matte.	With hot blast one atom of sulphur in pyrites is volatilised as such. With cold blast the S of pyrites, together with that of the other sulphides under all conditions, is burnt to SO_2. A portion of the sulphur may even be burnt to SO_3. A variable proportion of the sulphides remain unburnt as matte.
Sulphur, . . as Sulphates.	From $CaSO_4$ (also in part from $PbSO_4$. $ZnSO_4$, and other sulphates) SO_3 is expelled and volatilised as SO_2. The remainder being usually the larger part is reduced to sulphides of the heavy metals, forming matte.	Almost entirely expelled as SO_3 and SO_2, either by the action of heat alone or by reaction with SiO_2, forming silicates of the metals. No reduction to matte.	Entirely volatilised as SO_3, which, however, is partly dissociated into SO_2 and O.

CHAPTER XIV.

MATTE SMELTING IN BLAST FURNACES.

Reference has just been made to the fact that the reactions which take place in the matting process on the ordinary or German system do not materially differ in kind from those taking place in the ordinary lead blast furnace with reducing atmosphere. The system of concentrating poor sulphide ores of silver by partial roasting and smelting to matte is of great antiquity, and the chief point of difference between ancient and modern practice (besides the enormous difference in furnace capacity) is the fact that in the former, still extant in remote districts of Germany, Austria-Hungary, and Russia, it was considered necessary to have a matte-fall of from 30 to 50 per cent. of the weight of ore smelted, whereas in modern practice an average of from 5 to, at most, 8 per cent. is found amply sufficient.

The principles of matte smelting, as well as the reactions and manipulations, bear a general resemblance to those of lead smelting; the student may, therefore, refer to Part I., Chapters VII. to IX. before taking up the consideration of this and following chapter. Owing partly to lack of space, and partly in order to avoid repetitions, attention will be only devoted to those points in which matte smelting differs from the methods of smelting already described.

The Furnaces.—Almost any kind of furnace can be made to serve for the ordinary matting process, from the simple square brick or stone built stack of 2 feet square, blown by one tuyere at the back, up to the modern water-jacketed furnace of 3 feet wide by 8 to 12 feet long at the tuyeres. Generally speaking, the latter should be employed, and it is not considered necessary to describe them here because they in no wise differ from the furnaces employed in smelting copper ores, and are, therefore, better discussed in connection with the metallurgy of copper.*

Furnace Construction.—The only important respect in which these furnaces differ from those employed in lead smelting is in the construction and arrangement of the part below the tuyeres. Lead furnaces are almost always run with a crucible and automatic syphon tap for the lead; those smelting to matte may be either *sump* or *channel* furnaces. In the former case the crucible of the lead furnace is partly filled up, the slag runs continuously from the usual spout into a "settler" overflow pot or some kind of forehearth, in order to separate any shots of matte, while the bulk of the matte settles out quietly in the shallow interior

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* *v.* Peters, *Modern Copper Smelting*, 1895, pp. 250, *et seq.*

crucible, from which it is tapped at intervals into pots. In the latter system the furnace is provided with an air-cooled drop bottom, and the whole of the melted furnace products pass from the furnace into an exterior "forehearth," in which the separation of matte from slag is effected. The construction of these forehearths varies from that of a simple cast-iron or wrought-iron box on wheels to an elaborate fixed reverberatory with or without separate fireplace.*

Forehearths.—One very useful form of forehearth, composed of cast-iron plates, is shown in Figs. 66 and 67,† from which its construction will be evident. The front plate is provided with a straight matte spout near the bottom, and a skew slag spout at the top. Before use, if the matte is small in quantity and the slag somewhat siliceous as usually happens, the plates are lined with a mixture of clay and chopped straw; a firebrick lining, 4½ inches thick, may be employed when the slag is ferruginous and a large quantity of low grade matte is to be produced. A good wood fire is then made in the forehearth so as to heat it up as thoroughly as possible. Before tapping, the slag in the furnace is allowed to rise up to the tuyeres, and the slag spout of the forehearth stopped with clay so as to permit of its being filled up to the brim. The furnace is then tapped and the forehearth gradually fills, some thin faggot wood or charcoal being thrown upon the surface of the bath and an iron rod kept at work to

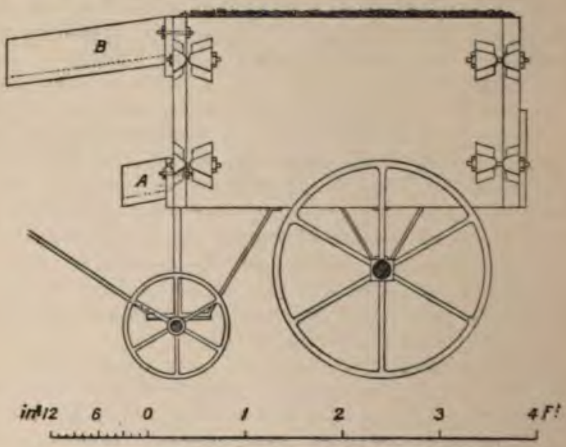

Fig. 66.—Forehearth.

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* The variety of shape and construction in forehearths is very considerable. Some of the leading forms are described and figured in Peters, *op. cit.*

† From Braden, *Trans. A.I.M.E.*, vol. xxv., p. 49.

prevent the formation of a crust. When the forehearth is brimming over the furnace is plugged, and a crust is allowed to form on the top; after a minute or two it will be sufficiently strong not to collapse when the molten slag beneath is tapped out to the level of the slag spout, and should then be covered with several inches of coke breeze to prevent further loss of heat by radiation.

This same form of forehearth may be employed when it is desired to run the slag from the furnaces continuously, trapping the blast, by providing an opening at the lower part of the back plate corresponding with a water-jacketed taphole on the furnace and bringing the two into close contact. This is now done at the matting furnaces of the *Arkansas Valley Smelting Works* (Leadville).

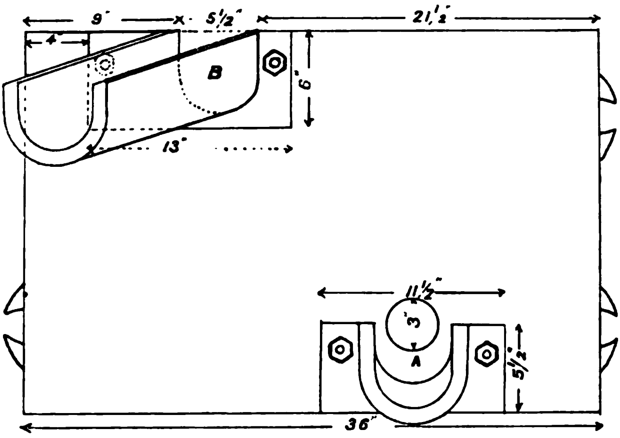

Fig. 67.—Forehearth. (Front plate with spouts attached.)

Sump Furnaces.—Even when a *sump* is retained for the matte a deep bottom is frequently used, as by its use the hot matte is prevented from cutting into the furnace bottom and enlarging the crucible, while should sows containing iron or other accretions be unfortunately formed (an event of very rare occurrence with large fast running furnaces) their removal is much facilitated.

Sump furnaces are best suited to the treatment of well-roasted mixtures, producing a matte-fall not over 10 or 15 per cent.; where the matte-fall is greater than this amount a channel furnace discharging the whole of its fused product into a suitable forehearth is more appropriate, since a large quantity of matte tends to cut out the bottom too much.

Fig. 68 represents in section a large modern sump furnace which, although originally designed for producing pig copper

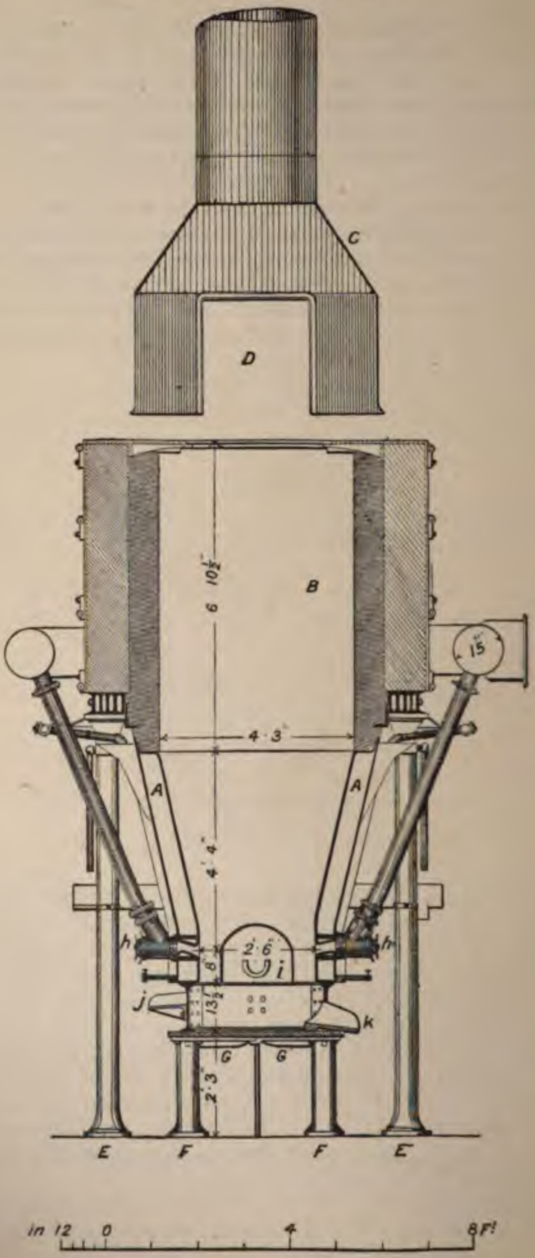

Fig. 68.—Sump Furnace.

from rich oxidised ores, is well suited to matte smelting of the ordinary kind where the matte-fall is not over 10 per cent. in amount or of a high percentage in copper. In this figure A A are the water-jackets; B is the furnace shaft, built of red brick strongly bound together and lined with firebrick; C is the sheet-iron hood which fits down upon the top of the furnace, containing in its lower part the charging doors, D, at each end, and in its upper part the downtake (not shown) for the furnace gases; E E are the pillars supporting the whole upper part of the stack; F F the short pillars supporting the heavy base-plate, upon which rests the crucible made of rolled wrought-iron girders, and these in turn support the water-jackets. The central portion of the base-plate is cut out, and the openings are closed by one or more pairs of drop doors, shown at G; *h h* are the tuyeres (in this case of the Devereux pattern), *i* is the slag spout, and *j* the matte spout, *k* being an emergency spout intended for use when the furnace is producing some copper-lead speiss or other product heavier than the matte; this spout may also be used for matte when the amount is only 5 per cent. or less.

The operations of blowing-in and blowing-out such a furnace and its manipulation differ but little from those necessary with lead furnaces. Generally speaking, matte furnaces are somewhat easier to handle on account of the absence of trouble connected with the crucible and lead-well. The regular work of such a furnace is almost precisely like that carried on in a furnace of similar character turning out matte from ordinary roasted copper ores, and any modern work on the metallurgy of copper may be consulted * for details.

Slag Composition.—The latitude allowed the metallurgist with regard to slag composition has been already referred to. The maximum variations in composition of slags actually made up to the present are about as follows :—

	SiO_2.	FeO.	Al_2O_3.	CaO.	MgO.	ZnO.	BaO.
Minimum, . .	20	2	2	2	0	0	0
Maximum, . .	57	70	18	40	8	20	42

These limits are obviously very much wider than the corresponding limits for successful lead smelting, because in matte smelting the non-volatility of the product renders it possible to employ difficultly fusible combinations so long as they are sufficiently thin in a fluid condition to admit of easy separation from slag.

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* Especially Peters, *Modern Copper Smelting*, 7th and subsequent editions.

Although, however, such great variations in slag composition are admissible under exceptional conditions, the student should never lose sight of the fact that under all ordinary conditions the best slags to make, because the most fusible, are the monosilicates of iron and lime. The most fusible of all is the silicate $2FeO,SiO_2$, but its great disadvantage is its high specific gravity, which causes it to separate with difficulty from the matte. A mixture of the monosilicates of iron and lime is, therefore, generally preferable when local conditions render it at all economical. Frequently, however, the ores are very basic with excess of iron, in which case it often pays better to make a monosilicate iron slag, even if somewhat foul from imperfect separation of matte, rather than bring in and smelt costly limestone as well as additional silica in order to produce a cleaner slag. Sometimes, on the other hand, the ores are siliceous and comparatively free from iron. In such cases even a bisilicate of lime slag may be the best possible, both economically and metallurgically, in spite of the higher consumption of fuel it entails.

Use of Hot Blast.—Another point to which sufficient attention has not hitherto been directed is the use of hot blast in connection with all slags of high melting point. The advantages of hot blast are frequently considered to be—(1) Greater total generation of heat inside the furnace, and therefore greater capacity; (2) greater concentration of the heat in front of the tuyeres; (3) less trouble from agglomeration of the charge higher up; and (4) more complete burning of coke to CO, and more perfect reducing action. Besides the above, another very great advantage is found in the fact that the cooling effect of the blast upon the pool of molten slag below the tuyeres is much less the higher its temperature. This cooling effect is unimportant with monosilicate iron slags, the melting point of which is much lower than the temperature actually attained before the tuyeres; but it assumes much greater importance with bisilicate, lime and alumina slags, the melting points of which are so much higher. Hence, with cold blast such slags are much more likely than the monosilicate slags to show signs of chilling and to give rise to furnace irregularities.

Wherever in matte smelting it becomes necessary to make slags of very acid type the use of a moderately hot blast should, therefore, be seriously considered, especially as with large modern furnaces with a high "hearth efficiency" the danger of forming "sows" is at a minimum, and almost entirely vanishes when an outside forehearth is employed.

Calculation of Charge.—The calculation of a charge for a matting furnace is conducted on the same lines as that for a lead furnace (see Part I., Chap. IX.), but it is a much less elaborate operation, and, owing to the wider variations of slag composition admissible, need not be carried out with anything like the same exactitude. Practically speaking, as a rule only *sulphur*, *iron* (copper and lead), *silica*, and the *earthy bases* (together) have to be taken into account, as under ordinary circumstances the small amounts of Pb, Cu, As, Sb, Bi, and other elements present will be amply sufficient to effect a good extraction of the precious metals in the matte, whatever the degree of concentration employed—and this holds true even when as many as 30 or 40 tons are run into one ton of product, provided the slag is sufficiently fusible. A good example of matting charge calculation is given by Peters.*

Fuel and Fluxes.—The *fluxes* employed will, as in lead smelting, vary according to the nature of the ore, although, owing to the wider limits of composition admissible, they play a much less prominent part in the problem. Either silica, iron ore, or limestone may be the flux indicated by the nature of the ores or by the local conditions prevailing. The two former can frequently be obtained carrying a greater or less proportion of valuable metal, either gold or silver. The employment of barren limestone is not nearly so often necessary in matting operations as in lead smelting, and should be avoided whenever a slag can be conveniently made containing up to, say, 45 per cent. SiO_2. Beyond this limit it will usually be advisable to add limestone, unless it be very expensive, and other basic material is not available; in which case even 50 per cent. of silica in the slag may be allowed with advantage in spite of the somewhat higher losses and more irregular, as well as slower, running.

As in lead smelting, coke is the *fuel* easiest to manage and most generally available. Under appropriate circumstances, however, charcoal may instead be exclusively employed, or coal may be substituted for part of the coke, as in lead smelting.† To Lang ‡ is due the substitution of wood for part of the coke charge of a matting furnace. At *Mineral* (Idaho) this metallurgist replaced half of a 100-lb. coke charge with 135 lbs. of dry firwood sawn into blocks a foot long. The wood used weighed 2340 lbs. per cord, and its efficiency compared with coke for equal weights was as 1 : 2½. The advantages of wood are that it helps to keep the charge open, and is, therefore, useful with fine charges and when an oxidising effect is desired. Its disadvantages are a large increase in the amount of flue-dust produced, and a decrease in smelting capacity. Lang thinks that some sulphur is volatilised in combination with carbon and hydrogen from the wood; it is certain, at all events, that the volatile constituents of the wood play an important part, for the charcoal formed by its carbonisation would be clearly insufficient to replace so large a proportion of coke.

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* *Modern Copper Smelting*, 7th edition, 1895, pp. 242, *et seq.*

† *v.* Part i., chap. vii.

‡ *Pyritic Smelting*, 1896, p. 47.

Blast Pressure.—The pressure of blast and rapidity of smelting, which, in the case of lead smelting, may vary only within comparatively narrow limits, are, in matte smelting, as variable as the construction of the furnace and the composition of the slags. Some data are given in Table XIX. to exemplify practice at different localities.

When the quantity of low-pressure blast forced into a furnace is greater than that required to burn all the coke to CO_2 a distinct oxidising effect is produced, and S is burned off as SO_2 instead of passing into the matte. In such cases, which are by far the commoner nowadays, we may say that there is some "pyritic effect," and the heat generated by the burning sulphur is usually sufficient to enable the proportion of coke to be reduced.

Similarly, when under such circumstances a mixture of roasted and unroasted copper sulphide ores is charged into the furnace, reaction may take place between the CuO and Cu_2S exactly as we have seen that it may take place in lead smelting between PbO and PbS under appropriate conditions. These cases, however, properly come under the head of copper smelting, and are not within the domain of silver matting.

Furnace Gases.—As might be expected, furnace gases from the pyritic process are very different in composition from those from the ordinary matting process conducted in a reducing atmosphere; in fact, analysis of the furnace gases is a very useful (though too often neglected) indication of the reactions proceeding inside the furnace.

TABLE XVIII.—COMPARISON OF FURNACE GASES.

Locality.	Matting, Mansfeld.		Pyritic Matting, Keswick, California.			Lead Smelting, Freiberg.	
Reference, .	1.		2.			3.	
CO_2, . . .	11·1	15·5	10·85	6·50	6·25	17·8	17·4
CO, . . .	20·6	12·8	3·27	0·00	0·00	5·2	4·3
CH_4, . . .	...	...	...	...	...	0·1	1·8
H, . . .	...	...	2·55	...	...	1·6	0·5
SO_2, . . .	...	...	9·01	10·00	19·30	...	...
O, . . .	...	...	0·00	4·02	2·59	...	...
N (by diff.), .	68·3	71·7	74·52	79·46	71·95	75·3	76·0
	100·0	100·0	100·00	99·98	100·09	100·0	100·0

References.—1. Egleston, *S.M.Q.*, vol. xii., p. 103. 2. Lang, *E. and M.J.*, Aug. 1, 1896. 3. Kerl, quoted by Hofmann, *Metallurgy of Lead*, p. 207.

The foregoing table gives analyses of the furnace gases at Mansfeld (reducing or ordinary matting) and of those at Keswick, California (pyritic smelting), a mean of the analyses by Schertel of gases from Freiberg lead smelting furnaces being added for comparison.

Examples of Matte Smelting.—Table XIX. gives comparative data from several matte-smelting plants in various parts of the world, and the practice at these same works may conveniently be described in somewhat greater detail.

At *Zalathna* (Transylvania)* pyritic concentrates carrying gold (partly in the metallic condition and partly as telluride) and silver (partly as telluride but chiefly as sulphide) are smelted after roasting together with small quantities of rich hand-picked telluride ores. The roasting furnace is a small Malétra shelf furnace with five or six superposed hearths, each holding 1 cwt. of concentrates; no fuel whatever is used, except occasionally to ignite a charge. In twenty-four hours each furnace roasts 16 cwts. of ore from 36 per cent. down to about 6 per cent. S. The roast-gases are all saved, and while the larger part is made direct into sulphuric acid another portion is conducted into chambers, where it reacts upon H_2S produced by dissolving the matte in H_2SO_4 and so precipitates free sulphur. The composition of the roasted ore is SiO_2 19·90, Fe 56·45, Mn 1·73, Cu and Zn traces, CaO 0·024, Al_2O_3 2·25, Ag 0·012 (3 ozs. 16 dwts. per ton), and Au 0·0044 (1 oz. 8 dwts. per ton).

The roasted concentrates are bricked with milk of lime and smelted in four small blast furnaces of sandstone, lined with fire-brick, the dimensions being 40 inches square inside and 15 feet from tuyeres to feed-floor. The furnaces are blown with three tuyeres at an average pressure of 3½ ozs. only, and are run as sump furnaces, slag running continuously, while matte is tapped every two or three hours. The charge is composed of about 50 per cent. of roasted concentrates, 17 per cent. of rich unroasted quartzose ores, with sometimes some sand to supply silica, and 33 per cent. of slag from the matte concentration furnace. Of the above charge, 10 or 11 tons per twenty-four hours are smelted in each furnace with a fuel consumption of 15 per cent. of charcoal. Each 100 tons of ore yields a sesquisilicate slag and about 33 tons of first iron matte, analyses of which appear in Tables XXI. and XXII. respectively.

The iron matte contains on an average about 15 per cent. of free metallic iron in shots of various sizes. This is, no doubt, due to the exceedingly powerful reducing action which goes on inside the furnace, and if the diameter of the tuyeres were enlarged, more wind supplied, and the height of the column of charge lowered, the furnace would give a lower matte fall and a more fusible slag, which, in turn, would lead to increased capacity.

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* *Private notes of a visit in 1888.*

Some fuller details are given in Table XIX.; the method of working up the matte is peculiar, and is described in Chapter XVII.

Gawrilow (*Altai*).*—At these works barytic ores averaging about 9 ozs. Ag, with but little silica and only very small quantities of metallic sulphides, are smelted together with about 25 per cent. of foul slag and 10 per cent. of desilverised ore matte in small blast furnaces with three tuyeres to an extraordinary matte, composed chiefly of barium sulphide and containing from 46 to 55 ozs. silver per ton. The slags are very siliceous, the composition corresponding almost with a trisilicate; they are exceedingly sticky, and the separation of matte is very incomplete, which, however, is of little importance seeing that the matte is comparatively poor, it is also unavoidable since the necessary fluxes for thinning the slag are not available. Analyses of slag and matte are given in Tables XXI. and XXII. respectively. The latter is treated by melting with lead as described in Chapter XVII.

Mansfeld (*Rhenish Prussia*).†—The works at *Mansfeld* which treat a cupriferous and bituminous schist with 3·25 per cent. copper and nearly 6 ozs. silver to the ton are usually described in connection with the metallurgy of copper, but they furnish a good illustration of the matting process.

The schists are burnt in heaps to expel bitumen and combined water, but no sulphur seems to be eliminated in the burning. The height of the furnaces is about 25 feet above tuyere level, and they are built with closed throats after the pattern of iron blast furnaces, copper water tuyeres and cup-and-cone charging arrangements being employed, and a high-pressure blast furnished by blowing engines.

A very important feature of Mansfeld furnaces, which contributes largely to their great capacity in proportion to their size (the "*hearth-efficiency*" being 6·93 = tons per square foot of sectional area per twenty-four hours), is the use of hot blast. The heating apparatus is by no means the most perfect possible, being merely the old-fashioned pistol-pipe stoves formerly used in ironworks, which are heated by the combustible gases from the furnaces. The temperature of the blast varies according to the amount of gas available from 125° C. up to as high as 300° C. The whole of the furnace gases are, of course, collected, as they contain over 16 per cent. of CO, but only a portion is available for the hot blast stoves, the remainder being burnt under the boilers.

Some of the furnaces are worked as channel furnaces with

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* Jossa and Kurnakoff, *B. u. H. Zeitung*, 1886, Nos. 16-19; also quoted by Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 491.

† This description is mainly abstracted from Egleston's paper, *S.M.Q.*, vol. xii., pp. 85, *et seq.*

exterior forehearth, but, as the slags are very siliceous, and the matte small in amount, the larger furnaces run chiefly on the "sump" principle, which gives a better separation, at the cost, however, of forming "sows," owing to the powerful reducing action inside these high furnaces.* The operation is a simple melting down of the ore and separation of the heavy sulphide particles as matte by gravitation.

The average composition of slags and mattes produced during 1888 is given in Tables XXI. and XXII., but, exceptionally, slags have been made which carried as much as 57 per cent. silica and approximated to the composition

$$2(Al_2O_3 \,.\, 3SiO_2) + 3(FeO \,.\, SiO_2) + 6(2CaO \,.\, 3SiO_2),$$

or to that of a combination of silicate of iron, trisilicate of alumina, and sesquisilicate of lime.

The slag from the furnaces is received in very large cast-iron waggons, from which it is subsequently tapped in carefully levelled sand in large casting beds with sheet-iron partitions, and so moulded into paving and building blocks of any required size. About one-half the total slag is actually utilised as blocks, the remainder going to the slag-dumps and being subsequently used for roadmaking. These slags contain only 0·3 per cent. copper and are probably the poorest slags made as a regular thing in ore smelting anywhere. Most of the lead in the ore is volatilised, but a part is saved in the flue-dust, which contains 10 per cent. Pb and 2 per cent. Cu, and is smelted for lead in small furnaces with cold blast.

The subsequent treatment of the matte is by kiln roasting, which brings down the sulphur contents to 10 per cent., this is followed by smelting in reverberatory furnaces of the Swansea form to an argentiferous white metal suitable for the Ziervogel process.

Deadwood (*S. Dakota*).†—At the works of the Deadwood and Delaware Smelting Co. siliceous gold ores, averaging 78 per cent. SiO_2, 12 per cent. FeO, and a little Al_2O_3, CaO, and MgO, together with an average of 1 oz. Au and 2 ozs. Ag per ton, are smelted, together with a small percentage of pyrites containing 30 per cent. silica and a somewhat larger proportion of copper ore, to a gold-bearing matte containing about 10 per cent. Cu, 10 ozs. Au, and 20 ozs. Ag per ton. The only flux employed is a dolomitic limestone, the quantity of which used is about equal to that of the mixed ores, and the degree of concentration is about 20 tons of charge into 1 of matte. The slag produced

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* The perfection of the reduction is exemplified by the fact that on tapping the hearth empty, which is done once a week in order to clear out incipient "sows," liquid sulphur is sometimes found to separate out between the matte and the slag in the tap pit.

† For details of this extremely interesting practice the author is indebted to Dr. Franklin R. Carpenter, who originated the works and still manages them.

is exceedingly siliceous (52 per cent. SiO_2) and the matte fall, as already seen, quite small, yet this peculiarly composed charge, which would ordinarily be considered refractory, is smelted with a coke consumption of only 15 per cent. by weight of an inferior coke containing 25 per cent. ash.

The furnaces employed are 132 inches by 36 inches at tuyeres and 16 feet high to feed-floor. The daily capacity of such a furnace is about 215 tons of charge.

The matte is worked up by raw smelting with lead ores, as in the ordinary lead smelting practice; in doing so it is worthy of note that it takes up silver from the charge while giving up nearly all its gold to the lead bullion. The twice run and impoverished matte is then roasted and smelted, first to concentrated matte and then to black copper, which is sold to the copper refiners.

The gold obtained always exceeds the amount shown by assay, but the silver falls about 10 per cent. short, which is not surprising, the amount per ton of ore being so small.

Semi-Pyritic Smelting.—At many matting works a portion of the sulphur contents of the charge is burnt off and some heat generated with the double object of enriching the matte and of saving fuel. The following is an example of this practice.

Sunny Corner (*N.S. Wales*).*—The ore treated at these works is a complex low-grade mixture composed chiefly of massive pyrites with blende and quartzose gangue, having chalcopyrite and galena sprinkled through it in variable quantities, so as to bring up the average to about 1 per cent. copper and 5 or 6 per cent. lead. The smelting is conducted in old lead furnaces, the crucibles of which have been filled up and which are now run as sump furnaces, producing rich argentiferous matte for shipment.

At the time of the author's last visit in 1896 there were three furnaces of tuyere measurement, 36 inches by 84 inches, with circular ends. His notes are as follows:—The jackets are of cast iron, their height being 4 feet 6 inches—viz., 10 inches from the bottom to centre of tuyeres and 3 feet 8 inches from centre of tuyeres to top of jackets, above which to the feed-floor it is 11 feet. The furnaces are fed from the top through a short Pfordtt curtain about 6 feet by 2 feet, and the gases are drawn off into the usual dust-chamber connecting with a flue which runs up the side of the hill for 220 yards and terminates in a short brick stack.

The flue is excavated in the rock and lined with bricks, its dimensions being 6 feet wide at bottom and 7 feet high to the spring of the semi-circular arch; the draught is very great and most of the flue-dust escapes condensation. Each furnace in blast requires a blower (No. 6 Root or No. 5½ Baker) running

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* *Private notes*, 1896.

at about 135 revolutions, but all the blowers deliver into one blast reservoir and main.

The ten or twelve tuyeres in each furnace are 2¾ inches internal diameter, and are supplied with wind at only 9 ozs. pressure. With the object of burning off as much sulphur as possible from half-calcined ore, while at the same time volatilising zinc, the furnaces are run with a "hot-top," and the column of charge is only just above the top of the jackets. In this way the excess of sulphur, nearly all the lead, and a large proportion of the zinc are burnt off, but a great deal of heat is lost and, instead of effecting any substantial saving in fuel, the consumption is practically the same as if the smelting were conducted in the ordinary way, running with a cold-top and thoroughly roasted ore.

The average charge of each furnace is as follows:—Roasted sulphide ore, 8½ cwts.; raw ditto, 3 cwts.; siliceous gold-carrying gozzan, 1 cwt.; old slags, 2½ to 5 cwts.; limestone, none to ½ cwt.; returned first matte, none to 2 cwts. The fuel charge is 224 lbs. of coke from Wollongong, which contains 13 per cent. of ash, and costs about 42s. per ton delivered at the works in sacks.

Each furnace puts through, on an average, forty to forty-four of the above charges in the twenty-four hours, the heavier charge being equivalent to a total of 61,600 lbs. ore together with about 24,640 lbs. slags (at 5 cwts. per charge). The matte produced is tapped from the sump at intervals into ordinary slag pots, the cones from which, when cold, are broken up and simply returned to the furnace for re-smelting without any roasting, and in this way the twice run matte obtained is never so much as twice as rich as the first matte.

The slag, covered by a firebrick channel to retain the heat, runs continuously from the ordinary slag spout into a rectangular wrought-iron box on slag-pot wheels. This is furnished with a slag spout at the end opposite the furnace, and a matte spout low down on one side, and is lined with firebrick laid in clay 4½ inches thick. It has a hole in one end which is jammed up against the furnace so that the slag-spout channel of the latter enters flush with the lining of the "settler." In this way a great deal of the matte carried away in suspension by the thick sticky slag has an opportunity of settling out, and is tapped at intervals from the side. These settlers last on an average forty-eight hours before becoming chilled, and have been known to last a week if the slags are specially fusible.

No complete analyses of the ores have been made, but they will average roughly 6 per cent. lead, 1 per cent. copper, 10 ozs. silver, and 1½ to 2 dwts. gold per ton. The total value of the finished matte produced in copper, silver, and gold is equivalent to about 28s. 6d. on the ton of ore treated. Its average composition is as follows:—

		First or Once Run.	Second or Twice Run.
Copper, .	. per cent.,	16 to 20	28 to 34
Silver, .	ozs. per ton,	160 to 170	270 to 300
Gold, .	,, ,,	1 to 1½	2½ to 4

Analysis of a sample of slag produced in 1896[*] is given in Table XXI. The flue-dust produced, or rather collected, is small in quantity though richer in silver than the average ore charge, containing from 12 to 14 ozs. per ton. It is simply melted down and thrown back into the furnace.

Smelting at Sunny Corner is done very cheaply considering the high price of coke. Coal for boiler fuel costs 16s. per ton; inferior wood, 11s. per cord; and limestone for flux, 11s. 6d. per ton. The furnaces are worked on eight-hour shifts, the cost of labour per furnace during each shift being as follows:—One feeder (8s.) and part time (two-thirds) of a charge wheeler (7s.), both of whom are employed at the furnace top, while below are required one tapper (8s.), one pot runner (6s. 6d.), and the remaining (one-third) time of the labourer who wheels coke, &c., on the feed-floor. In addition to these costs for actual furnace attendance must be included the part cost per furnace of three labourers employed in sorting, &c., on the slag dump.

The total cost for labour in smelting is thus about 4s. per ton, for coke 6s. 8d per ton, for boiler fuel and sundries not over 2s. per ton—total, say, 12s. 6d. The roasting cost is only 1s. 9d. per ton.[†]

The Sunny Corner practice, described in Table XIX., is, in its main outlines, fairly well adapted to the ore, which, it should be understood, is the cheapest material available, and hence no great complication of methods is possible. There is, however, room for improvement, economically as well as metallurgically, in the following directions:—

(1) Reduction in the amount of coke used and increase of height in the column of charge, coupled with an increase in the diameter of the tuyeres so as to get a larger volume of air into the furnace, while reducing its pressure.

(2) Employment of much larger furnaces without boshes.

(3) Greater saving of flue-dust by cooling the furnace gases and checking the velocity of the current. Treating the accumulated flue-dust separately to recover lead and silver.

(4) Better facilities for settling and separating slag and matte.

(5) Running a lower-grade first matte and much increasing the degree of second concentration.

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[*] And for which the author is indebted to Mr. A. J. Bensusan, A.R.S.M.

[†] *v.* chap. vi., part i.

TABLE XIX.—Examples of Blast Furnace Matting.

	Zalathna, Transylvania.	Mansfeld, Rhenish Prussia.	Deadwood, S. Dakota.	Sunny Corner, N.S.W.	Hall Mines, British Columbia.
Reference, . . .	**1.**	**2.**	**3.**	**4.**	**5.**
Dimensions of furnace at tuyeres,	40" × 40"	5′ diam.	36" × 132"	36" × 90"	44" × 144"
Height tuyeres to feed-floor, .	15 ft.	25 ft.	16 ft.	11 ft.	12 ft. 6 ins.
No. and diameter of tuyeres, .	3 of 2½"	6 of 2½"	...	12 of 2¾"	16 of 3¾"
Total area of tuyeres, . sq. in.,	14·73	29·46	...	71·28	176·64
Sectional area at tuyeres, sq. ft.,	8·73	19·63	33	22·5	44
*Tuyere ratio, ...	about 1·34	1·50	...	3·17	4·01
Tonnage put through 24 hours, .	10 or 11	136	216	36-38	244·6
*Average hearth efficiency, . .	1·0	6·93	6·50	1·61	5·55
*Average tuyere efficiency, . .	0·75	4·62	...	0·508	1·39
Average blast pressure, . ozs.,	3½	32	...	9	...
Temperature of blast, ...	cold	...	cold	cold	cold
Height of column of charge, .	12 ft.	20 ft.	...	5 ft.	8 ft. 6 ins.
Rate of concentration tons into 1,	3	12·7	20	20	14·25
Composition of charge :—					
Raw sulphide ores, . . lbs.,	...	...	...	224	...
Roasted ,, ,, . . ,,	111	...	...	952	...
Quartzose gold ores, . . ,,	36	...	...	...	...
Gozzan and oxide ores, . ,,	...	...	...	112	...
Limestone, ... ,,	...	...	...	224†	...
Slag, ... ,,	73	...	...	338	...
Total net lbs., . .	220	2004	...	1850	4000
Nature of fuel employed, . .	charcoal	coke	coke	coke	coke
Percentage of fuel required, .	30	18·5	15	12·1	14½ to 16
Composition or ore charge :—					
Cu, ... per cent.,	...	...	...	...	4
S, ... ,,	...	...	...	...	3·2
Composition of matte :—					
Cu, ... per cent.,	0·74	...	...	...	49
Ag, . . . ozs. per ton,	12 ozs. 5 dwt.	...	...	...	...
Au, ... ,, ,,	4 ozs. 16 dwt.	...	...	...	...
Composition of slag :—					
SiO_2, ...	42	48	...	35	43
FeO and MnO, ...	50	5	...	29	21
Al_2O_3, ...	3·5	16	...	18	18
CaO, ...	3	24	...	6	15
Cu, ...	trace	0·24	...	0·41	0·345
Ag, . . . ozs. per ton,	trace	...	...	3 ozs. 14 dwt.	1·15 oz.

References.—1. *Private notes*, 1888. 2. Egleston, *S.M.Q.*, vol. xii., No. 2, p. 111. 3. *Private communication*, F. R. Carpenter, Oct. 28, 1896. 4. *Private notes*, 1896. 5. *E. and M. J.*, Dec. 11, 1897.

* Explanation of these terms is given in part i., chap. vii.

† Matte in this case—not limestone.

Speiss Smelting.—Besides *mattes* (sulphides), *speisses* (arsenides and antimonides) may be employed as vehicles for concentrating the precious metal contents of an ore into a valuable product which will bear transport and refining charges.

The use of speiss, however, must evidently be confined to such exceptional ores as are comparatively poor in sulphur, and either contain a fair proportion of arsenic or can be mixed with a sufficient quantity of arsenical ores, for, in the presence of much sulphur over the proportion required to form As_2S_2, almost all the arsenic would be volatilised.

Lang* considers speisses as being only genera of the great family of mattes, and logically this classification is quite accurate. The term "speiss," however, has such a very definite meaning and has been in general use among metallurgists for so many generations that it is not likely to be abandoned in favour of Lang's term "arsenide or antimonide matte." It should be remembered that we may have antimonide as well as arsenide speisses, only in the former case the electro-positive constituents are primarily Cu and Pb instead of Fe, Ni, and Co, which are the most characteristic heavy metals in the latter.

The speisses are so similar to the mattes in their melting points, in their behaviour when fluid and in other respects, that the methods and appliances used for matte smelting with sulphide ores can be used for speiss smelting with arsenical ores almost without alteration. Sump furnaces are more appropriate than those with continuous discharge, and, owing to the specific gravity of speisses being so much higher than that of mattes, (7·5 to 8·0 as against 5 to 6), comparatively little difficulty is experienced in getting a clean separation of slag. The great affinity, moreover, of both arsenic and antimony for silver ensures a fairly perfect concentration and the production of fairly clean slags.

Arsenical Speiss.—Although this material is so often formed incidentally in lead smelting, few particulars are obtainable as to its use as the principal or exclusive vehicle for collecting the precious metals.

Some years ago in Mexico the author had occasion to smelt on a small scale some low-grade gozzan ferruginous silver ores containing small quantities of arseniate of lead and carbonate of lead and copper, and averaging 12 ozs. silver per ton. The furnace products were first an impure arsenical copper-lead alloy with 265 ozs. silver and nearly 2 ozs. gold per ton, and, secondly, a copper-lead-arsenic speiss with 216 ozs. silver and 1⅓ ozs. gold per ton. The former, which was brittle and had a fibrous crystalline structure, was unfortunately not properly investigated, but the speiss which showed a brilliant laminated fracture, like that of spiegeleisen, was analysed more completely,

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* *Matte Smelting*, New York, 1896, p. 12.

its composition being given in Table XX., side by side with that of the Transvaal reverberatory speiss described in the next chapter.

The smelting was performed in a small circular water-jacket furnace, the fuel being very inferior coke with 20 per cent. ash, the consumption of which was 19 per cent. by weight of the charge. The degree of concentration was about 30 to 1, and the slags contained from 2 to 2½ ozs. silver per ton. Owing to the very low grade of the ore only 83·5 per cent. of its total contents became collected in the product, but had the ore been twice as rich in all probability the loss in slags would have been no greater, and the "percentage of extraction" would then have been something like 92 per cent. of the total contents of the ore. Even this extraction of 83·5 per cent., however, is much greater than could have been economically extracted by any other known process.

TABLE XX.—ANALYSES OF RICH SILVER SPEISSES.

	Torreon, Mexico.		Transvaal Speiss.
	Alloy.	Speiss.	
Copper,	56·7	37·1	52·5
Lead,	32·0	26·2	0·25
Iron,	...	10·4	3·6
Silver,	0·81	0·66	·59
Antimony,	trace	trace	38·0
Arsenic,	...	20·3	2·0
Sulphur,	...	3·1	2·06
	...	97·76	100·00
Ag, . per ton of 2240 lbs.,	265 ozs.	216 ozs.	...
Au, . ,, ,, ,,	1 oz. 18 dwt.	1 oz. 10 dwt.	...

References.—1 and 2. Author, *private notes*. 3. Bettel, *Chemical News*, June 26, 1891.

The activity of speiss, however, as a vehicle for collecting and extracting silver is very much less than that of matte, though gold is more perfectly concentrated in the former. This is an undoubted drawback to its employment, since the silver lost in slags will probably always be higher with speiss than with matte, although the slag loss would be comparatively a small matter if the other conditions were suitable. The peculiar adaptability of speiss smelting to arsenical gold ores is obvious, yet it does not seem to have found practical use hitherto. Seeing that auriferous mispickel ores and concentrates are particularly difficult to dead-roast for chlorination, it would appear that smelting might be more generally adopted for such material in Australia, for instance, than it is at present.

It should always be borne in mind that in remote regions with costly fuel and heavy transport charges it is usually the best policy to employ the cheapest and most direct process available, even at the cost of sacrificing a portion of the valuable metals, rather than to aim at perfect extraction by processes the cost of which, under the conditions named, is more than the value of the extra amount of precious metals recovered.

TABLE XXI.—SLAG ANALYSES FROM MATTE SMELTING OF SILVER ORES.

	Zalathna, Transylvania.	Gawrilow, Altai Mts., Siberia.	Mansfeld, Rhenish Prussia.	Schemnitz, Hungary.	Sunny Corner, N.S. Wales.
References, . .	1.	2.	3.	4.	5.
SiO_2, ...	41·60	45·50	47·31	53·72	34·75
FeO, ...	49·95	7·39	4·83	16·94	28·15
MnO, ...	0·82	...	0·65	2·41	1·12
Al_2O_3, ...	3·42	3·65	16·50	4·67	18·10
CaO, ...	2·66	2·02	20·55	7·94	5·65
MgO, ...	0·24	0·63	3·37	3·04	0·43
ZnO, ...	...	...	1·21	5·10	8·77
BaO, ...	...	41·86	...	...	...
K_2O, Na_2O, . . .	...	...	...	...	...
FeS, ...	...	...	...	...	...
S, ...	1·02	1·77	...	2·74	1·83
NiO, CoO, . . .	...	...	0·03	...	...
Pb, ...	...	...	0·20	1·84	0·33
Cu, ...	...	...	0·24	1·15	0·41
	...	...	...	...	99·54
Ag, . . per ton,	...	...	...	...	3 ozs. 14 dwts.
Au, . . ,,	...	...	...	...	traces

References.—1. *Private notes*, 1888. 2. Jossa and Kurnakoff, *B. u. H. Zeitung*, 1886, Nos. 16 to 19. 3. Egleston, *S.M.Q.*, vol. xii., p. 111, average of analyses given. 4. Crookes and Röhrig. 5. *Private analysis*, A. J. Bensusan.

Antimonial Speiss.—Bettel* describes the production of an antimony speiss from silver ores which, except that they contain antimony instead of arsenic, are almost free from lead, and are

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* *Chemical News*, June 26, 1891.

richer in both copper and silver, appear to be very similar to the Mexican ores smelted to speiss as above described.

In this case the smelting was done in reverberatories and will be found described in Chapter XVI.

Treatment of Argentiferous Speiss.—This material is always treated as a rich silver ore, being roasted and smelted together with lead ores, litharge, or refinery drosses. It is always better to roast speiss with pyritic ores rather than alone, since in this case the excess of sulphur in the pyrites combines with the arsenic to form volatile sulphides, and there is less tendency to the formation of arseniates.

TABLE XXII.—MATTE ANALYSES FROM BLAST FURNACE MATTING.

	Zalathna, Transylvania.	Gawrilow, Altai Mts., Siberia.	Mansfeld, Rhenish Prussia.	Schemnitz, Hungary.
References, . .	1.	2.	3.	4.
Fe, ...	67·10	20·38	23·60	46·89
Cu, ...	0·74	6·66	40·37	5·00
Pb, ...	2·23	0·21	0·82	2·45
Zn, ...	trace	2·73	5·03	6·30
Ag, ...	0·036	...	0·214	0·126
Au, ...	0·016	...	...	...
Mn, ...	...	...	0·78	...
Ni,Co, ...	...	...	0·59	...
Al, ...	...	0·47	...	...
Ba, ...	...	35·33	...	...
Ca, ...	0·04	0·89	...	...
Mg, ...	...	1·43	...	...
S, ...	29·30	25·70	25·94	36·97
Insol., ...	1·29	...	...	...
As, ...	...	...	0·10	trace
Ag, . . . per ton,	12 ozs. 5 dwts.	...	70 ozs.	...
Au, . . . ,,	4 ozs. 16 dwts.	...	...	...

References.—Same as for the corresponding numbers in the preceding table.

CHAPTER XV.

PYRITIC SMELTING.[*]

General Considerations and History.—Pyritic smelting may be described as the smelting of raw pyritic ores direct in the blast furnace without carbonaceous fuel, utilising as a source of heat the oxidation of part of the sulphur and iron contents of the ore itself. Pyrrhotite and chalcopyrite may serve instead of pyrites for this purpose, as also may ordinary iron mattes, which, indeed, but for their great fusibility would form an almost ideal material for the purpose. The natural or artificial sulphide present in the material smelted fulfils three functions, viz.—(*a*) that of a fuel, (*b*) that of a flux, (*c*) that of the collector of the precious metals together with copper, nickel, &c., as in ordinary matte smelting. Given cupriferous or argentiferous pyrites ores with too high a proportion of sulphur to form a valuable product by simple matting, as is the case with a large part of the high-grade Butte ores and with those at Mansfeld, it is obviously more advantageous to smelt them direct, utilising the sulphur as a source of heat, than to carefully drive off the greater proportion of that element by the slow, costly, and laborious process of roasting and then to smelt the residue with costly carbonaceous fuel. This fact was first practically realised by Hollway in 1878, and the experiments he carried out in the interest of the Rio Tinto Company in February, 1879, contained the germ of a practical success. Unfortunately, however, the capitalists interested had not the courage to give the process a thorough systematic trial under something like practical conditions; the experimental plant at Majdenpek in Servia was also comparatively unsuccessful, and so the process, as regards copper mattes, lapsed. In 1887, however, it was experimentally revived at Toston (Montana), and has, by the exertions of Sticht, Lang, and Austin, since become recognised as one of the standard processes of ore treatment.

It should be understood that up to the present it has not proved possible to do away altogether with the employment of carbonaceous fuel, for, even when a furnace runs for twenty-four hours without any fuel at all, the occurrence of slight irregularities usually renders it necessary to employ coke and slag charges, as in ordinary smelting, until normal conditions

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[*] For details *v.* Peters, *Copper Smelting*, 9th edition, 1895, pp. 372-395; Lang, *Matte Smelting*, N.Y., 1896; also an article in *E. and M. J.*, July 25 and Aug. 1, 1896, by the same author.

are restored. The regular use of a small proportion of coke as part of the ordinary charge is found to exert a mechanical effect, far above its mere thermal effect, in keeping the charge open, hence it is usual to employ from 1½ to 5 per cent. as a portion of the regular charge.

Besides sulphur and iron, the oxidation of arsenic (antimony, &c.), and even, in part, that of zinc, may be utilised as sources of heat. Arsenic in particular may be almost entirely expelled as As_2O_3 unless nickel or cobalt are present, when a portion may remain combined with those metals. Both As and Sb in the pyritic furnace have the disadvantage of carrying off silver in the fume, part of which is very difficult to recover. A portion of the zinc is also volatilised, and may carry away traces of silver with it. *Lead* is, however, a still less welcome constituent of ores to be treated by this process, for, although with basic slags it may be almost entirely volatilised, a notable proportion of silver invariably accompanies it. A part of both the lead and the silver so volatilised may be condensed by appropriate means,* and the recovered flue-dust treated separately as a lead ore, but such measures are very costly, and unless adopted the loss of silver in uncondensed fume becomes an important consideration. Except, therefore, where fuel is so dear as to render ordinary lead smelting methods impossible, silver ores containing much lead should be considered as unsuited to the pyritic process.

Variations in Pyritic Smelting.—Two main variations may be mentioned:—

(1) The *Austin system* of column charging, designed originally for the treatment of a mixture of clean pyritic ores, free from silica, with siliceous ores. The former are charged into the centre as fuel, the latter round the sides of the furnace. A highly heated blast and a large excess of pyrites are essential; a portion of sulphur distils off in the free state, the remainder being burnt to SO_2. The essential feature of this system, in addition to column charging, is the use of a large quantity of *hot* blast (800° to 1000° F.), which is forced in at high pressure through a large number of small tuyeres. These conditions bring about very rapid driving and consequently great capacity for a plant of small size, but the process is only applicable in cases where the pyrites ores to be used as fuel are in large lumps and comparatively free from silica, so that in order to form slag they have to take up that substance from the non-pyritous ores, which are charged separately. Another drawback of the very high pressure is found in the formation of large quantities of magnetic oxide of iron before the tuyeres. On account of these difficulties the process does not seem to be now used.

(2) The ordinary system of *layer charging* worked out by Sticht, Lang, and others. In this system the various ores are

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* v. Part i., chap. xii.

spread in the furnace in layers exactly as in lead smelting or ordinary matting, the small proportion of fuel also being charged similarly. A small portion of the sulphur in the pyrites volatilises in the upper part of the shaft (carrying with it some arsenic if present), but by far the larger part of it is burned to SO_2. According to Lang, some SO_3 is also formed. The characteristics of this system are the employment of a large quantity of cold or moderately warm blast, supplied at a low pressure through numerous tuyeres of large area, and a low column of charge. These conditions are opposed to very fast driving of the furnace but favour oxidation, the air blown into the furnace being almost invariably in excess of that burnt, so that free oxygen is present in the escaping gases, as shown in the analyses already quoted.*

In the system now under consideration, the tonnage smelted in a furnace of given size is much less than under the Austin system, nor is it possible to greatly increase the rate of driving without decreasing the rate of concentration. A hotter blast does indeed give greater capacity without sacrificing the concentration, although at the expense of greater cost for fuel consumed outside the furnace. This disadvantage is, however, much diminished by the increased certainty attained in furnace manipulation, so that the tendency in future will undoubtedly be towards the use of hotter blast. The special advantages of a hot blast, particularly as regards the production of bisilicate and other comparatively infusible slags, have been considered in detail in the last chapter. A hot blast is also well nigh indispensable for smelting mixtures with 25 per cent. of sulphur and over. At present, however, admirable results are being obtained with a blast temperature not over 500° F. (260° C.), and although at this temperature it is difficult to get a concentration on ores rich in pyrites of more than 4 or 5 to 1, the concentration can be carried on in steps to any required degree by simply returning to the furnace the first matte produced. With a blast of this temperature Lang finds that it is most advantageous to produce monosilicate slags (chiefly of iron), and to treat an ore mixture containing from 10 to 15 per cent. of sulphur only.

Principles of Pyritic Smelting.—The principles underlying pyritic smelting have already been touched upon in considering the effect produced upon lead smelting by oxidising and reducing atmospheres respectively.† A large amount of blast at a low pressure must be used in order that the oxygen, instead of being forced into close contact with a mass of glowing sulphides and carbon in the centre of the furnace, and generating locally so much heat that the sulphides are melted faster than they can be burnt, may find room to escape upwards through the interstices of the charge, oxidising the latter during its passage.

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* Lang, *E. and M. J.*, Aug. 1, 1896.

† See part i., chap. vii., p. 121.

The low pressure of blast presupposes a long narrow furnace, so that the blast may penetrate freely to the centre, and the high ratio of ore surface exposed to sectional area possessed by a furnace of this shape is also specially favourable to oxidation, since a much larger proportion of the blast is able to exert its oxidising influence, instead of being completely burnt in the centre and rising inert through the column of charge.

The very conditions, however, which are favourable to oxidation also bring about an excessive cooling of the tuyere zone and a chilling effect upon the slag which renders it difficult to employ any but the most fusible varieties. It is just here that the advantage of hot blast is most felt, for by its aid sesqui- and bi-silicates can be made as fluid as the monosilicate of iron with cold blast.

Owing to the comparatively low temperature of the enlarged tuyere zone the tendency to form accretions through chilling of half-fused masses is enormously increased. These accretions have the effect of an artificial bosh, concentrating the heat into the centre, and so localising it that the sulphides are largely melted down unaltered, which gives a heavy increase in matte production, while the slag becomes much more acid and pasty, from the absence of a portion of the iron oxide which it formerly contained. As the aim of pyritic smelting is to concentrate the ore and produce as little matte and as much fluid slag as possible, it is essential to prevent any such restriction of the smelting zone by "barring off" all accretions as they begin to form. This can only be done by rendering all parts of the furnace easily accessible to barring from above, and hence pyritic furnaces are preferably run with "open tops."

The "hearth efficiency" of pyritic furnaces with blast of moderate temperature must always be low, for otherwise the oxidising effect is insufficient and too much matte is formed. Slow smelting with cold blast means moreover a comparatively cool hearth, and this may give rise to incomplete separation of slag and matte. In such cases it may sometimes be advisable to return the molten matte to the furnace as suggested by Lang,* which certainly has the advantage of heating up the bottom, though it increases the liability to loss by volatilisation and handling.

As, in order to get the oxidising effect of the blast, the charge must be freely penetrated by it, any large proportion of fines is particularly detrimental in the pyritic furnace; in fact, even a comparatively small proportion causes a decrease in furnace efficiency and largely increases the matte fall.

Another important feature in pyritic smelting is the large size of the charges, which should be from 150 to 200 lbs. per square foot at least. Theoretical reasoning and practical ex-

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* *Op. cit.*, p. 58.

perience alike teach that the more intimate the admixture of fuel and ore, the more powerful will be the reducing action in the furnace, and from this it follows that by employing very large charges, the different portions of which never become intimately mixed until they reach the actual zone of fusion, we shall encourage oxidation. Henrich[*] has pointed out that large charges (especially when their siliceous components are charged beneath those which are basic) result in a higher temperature at the smelting zone and in the hearth than small charges of well mixed ore and fluxes, on account of the formation of the final slag being a more gradual process. There is, therefore, a double advantage in the use of quite large charges.

Slags.—The slags made in pyritic smelting range from monosilicates to bisilicates, iron being in all cases the principal base. Austin has recommended the bisilicate of iron slag, $FeO,2SiO_2$, but Lang finds that with cold or only moderately warm blast the best slag to make, whenever the conditions permit, is the monosilicate. Its one disadvantage is its high specific gravity (nearly 4), which in the case of a matte consisting mainly of FeS (specific gravity only 5), renders a complete separation difficult, and to that extent increases the losses of precious metals in the slag. With a hot or moderately warm blast, and provided sufficient siliceous ores can be obtained, which is usually the case, it is, therefore, advisable to make a slag of at least sesquisilicate composition in order to decrease its specific gravity and so facilitate its separation from matte. When, however, only cold blast is available the greater viscosity resulting from the increased percentage of silica may compensate for its lower specific gravity.

When, however, the ores to be treated are already siliceous it will generally be found advisable to make even a bisilicate slag rather than to add barren fluxes, for the increased fluidity obtained by their use is rarely sufficient to offset their cost, especially when the greater bulk of slag produced is taken into account. An exception to this rule may be found in the case of quite siliceous ores where limestone is readily obtainable, when it may be advisable to aim at making a slag approximating in composition to that of type slag No. 7 of the lead smelter,[†] or even one a good deal more siliceous.

Alumina in pyritic smelting is usually objectionable, though not more so than in ordinary matting with coke fuel; it adds to the viscosity of most slags.

Zinc is almost as objectionable a constituent of a pyritic charge as of one for ordinary treatment, since although the metal becomes perfectly oxidised and does not enter the matte to any extent, yet the portion which enters the slag increases its specific

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[*] E. *and M. J.*, Dec. 20, 1890.

[†] See part i., chap. vii.

gravity and renders it pasty, while the portion volatilised carries away silver.

Fluxes.—These play a comparatively insignificant part in pyritic smelting owing to the fact that the variety of possible slags is so great, and to the further fact that the oxidation of the iron as sulphide always furnishes a certain proportion of the best of all possible fluxes—namely, ferrous oxide. Austin has indeed noted that with the high blast pressures he affects some of the iron is frequently burnt to Fe_2O_3, with the result that magnetic oxide of iron enters both slag and matte, rendering both more infusible, besides assimilating their specific gravities, and so affecting their separation. With a moderate pressure of blast, however, no difficulty of the kind is experienced, practically all of the iron oxidised entering the slag as FeO.

The best flux for an ore consisting chiefly of pyrites is quartz containing more or less silver, gold, or copper, but when this is unobtainable, vein quartz, sandstone, or quartzite, as rich as possible in silica, should be employed. Some writers have recommended the use of slate, diorite, or other silicate rock, but the neutralising efficiency of such silicates is less than that of pure silica, with the result that a much larger quantity has to be used. This is bad in two ways—(1) because the greater quantity lessens *pro tanto* the furnace capacity for ore, and (2) because the increased quantity of slag produced carries away a larger total amount of the precious metals. The introduction of alumina, moreover, is in general to be deprecated, although satisfactory results have been obtained in smelting very aluminous mixtures.

When somewhat siliceous ores are to be smelted by the pyritic or semi-pyritic method, and there is not sufficient iron present to form even a bisilicate, the addition of *limestone* is practically indispensable. *Gypsum* may, in pyritic (though not in ordinary) smelting, be substituted for limestone, its SO_3 being driven off, and *barytes* may be used in the same way, its base entering into combination with silica and forming very fluid slags. Barytic slags, however, although fluid, have a high specific gravity, and, therefore, do not separate well from ordinary iron mattes, requiring special precautions in the way of forehearths and resulting in the production of more or less foul slag.

Fuel.—The typical fuels in the pyritic process are *iron* and *sulphur*. The small quantity of carbonaceous fuel required (from 1½ to 5 or more per cent.) is practically always *coke*, though Lang has found that when using 5 per cent. of coke normally one-half may with advantage be replaced by *cord-wood*, as already described in connection with the ordinary matting process. In pyritic smelting this small proportion of wood has the special advantage of rendering the charge more easily permeable by the blast, and so counteracting the tendency of the pyrites to "pack" through decrepitation and agglomeration.

Plant.—The furnaces employed for pyritic smelting need differ but slightly from those used in matting on the ordinary system, except that the tuyere space should be larger and the tuyere connections adapted to the use of hot blast, while the absence of any large amount of "bosh" is indispensable. The tuyeres should be both large and numerous in order to give a large volume of blast, but the height of the furnace above the tuyeres need not be more than 10 feet, as the working column of charge is kept between 5 and 8 feet. The top of the furnace should be open in order to facilitate the constant barring down of incipient scaffolds, which is found necessary. The shape of the furnace should be a long narrow rectangle, owing to the low pressures of blast usually employed; the length may vary from 9 or 10 up to 15 feet, while the breadth should in no case exceed 36, and may be advantageously reduced to 33 inches. The furnace may be run either as a "spur-ofen," discharging the whole of its melted products into an exterior forehearth for separation, or as a "sumpf-ofen," the matte being retained in a pool inside the furnace and the blast trapped.

Heating the Blast.—When hot blast is used the stove is usually of the "hanging U" type, though in Colorado and also at Mount Lyell another type is used with horizontal pipes. The fuel may be any cheap kind, slack coal and petroleum refuse being those chiefly employed. The actual temperatures attained show great variations, a blast of only 300° F. being considerably more efficacious than cold blast, while temperatures up to 1000° and 1200° F. (600° C.) may be employed with advantage under special conditions.

At *Keswick* (Col.) Lang,* in carrying out a suggestion previously made by him, attempted to utilise the heat of the slag for the purpose of producing a hot blast, but the arrangement does not seem to have been very successful and has now been abandoned. The single-pot slag-trucks, holding about 1500 lbs. each, upon leaving the furnace, enter a brickwork arch, which is 90 feet long, 5 feet high at the open end next the dump and 17 feet high at the furnace end, which is provided with a door. The cold air entering at the dump end of the tunnel becomes gradually heated by radiation from the hot slag, and is drawn off at a temperature of near 500° F. from the upper portion of the arch near the furnace by a Sturtevant exhaust fan, which serves as blower. One of the weak points in this arrangement was the mechanical device for automatically moving on the whole line of slag-pots every time one freshly filled enters the tunnel, just the right distance for detaching a corresponding cooled pot at the other end. A higher temperature might probably be attained

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* *E. and M. J.*, July 25, 1896.

by a lower arch; possibly by the use of Hawdon's continuous pan slag-carrier or some other automatic conveyor in a closed brick tunnel of small size, a blast temperature of 800° to 1000° F. might be attained entirely from the waste heat of the slag, though the wear and tear on the apparatus would, no doubt, be considerable.

Furnace Construction.—The upper portion of the stack above the water-jackets may be built of brick, or a second tier of water-jackets may be employed, with a brick-lined plate-iron superstructure. Lang has employed vertical iron pipes rising through the brickwork from a very low water-jacket, in order to protect the bricks from "cutting," but Sticht's arrangement of a second tier of water-jackets will be usually preferable.

In any case an adequate installation of flues and settling chambers for the flue-dust is essential, for although the total volume of gases given off by a pyritic furnace is not much more than by any other kind of furnace putting through the same tonnage, yet the amount of dust blown through the low ore column is more considerable, and the liability to loss of silver through volatilisation of Pb, As, Sb, Zn, Bi, Se, and Te is much greater.

As regards tapping arrangements it has been already stated that sump furnaces should be preferred as losing less heat by radiation, and, therefore, tending to give a better separation of slag from matte, especially when the tap-hole for matte is kept 10 inches below that for slag. The slags will, however, always carry more or less matte-shots, and these should be settled out as far as possible in forehearths of any of the ordinary patterns,* reserving the shells for re-smelting. On very large furnaces any of the so-called matte separators, or "separator-taps," described in Part I., Chapter X., may be employed, but they are not so well adapted to the somewhat varying conditions of a purely pyritic furnace as to the steady march of a reducing matting furnace or of a lead smelting furnace with its accurately calculated charges and its uniformly fusible slag, the composition of which rarely changes more than 1 or 2 per cent. from day to day.

Mode of Working.—As already stated, heavy charges are preferable because more favourable to oxidation. In lead smelting light charges of only 15 to 30 lbs. per square foot are common, but in pyritic smelting the best results are given by charges of 150 to 220 lbs. per square foot, which give thick layers in the furnace. The charging should be in distinct layers, and the total height of the column above the tuyeres should be kept from 6 to 10 feet. Too low a column causes "fire-tops" with increased volatilisation losses, while too high a column is objec-

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* *v.* Peters, *Modern Copper Smelting*, 7th or 8th edition; also Braden, *Trans. A.I.M.E.*, vol. xxvi., pp. 44, *et seq.*

tionable in several ways. In the first place part of the sulphur in pyrites which is volatilised at a moderate heat may condense in the cool upper layers and agglutinate the charge to such an extent as to render it almost impervious to the passage of the blast. Then again all pyrites decrepitates more or less on heating, and the amount of decrepitation seems to depend chiefly upon the length of time it is exposed to heating influences. In a very high column, therefore, even lumps of pyrites of fist size would have time to decrepitate into fines and impede the blast long before they reached the actual fusion zone. A high column, moreover, would allow fire to creep up a considerable distance without being noticed, and this is most detrimental on account of the excess of FeS present which would be likely to fuse and agglomerate the charge above the smelting zone, forming scaffolds. The greatest difficulty, therefore, of the pyritic process (as it is, on the other hand, its most imperative and essential condition) is to keep the charge loose and porous throughout, and free from accretions of all kinds.

The "hearth efficiency" of pyritic furnaces with cold or only warm blast is, as has been already mentioned, usually less than that of furnaces of the same size running on coke fuel, as shown by the data given in Table XXIII., which, however, is hardly a fair comparison on account of the inadequacy of the blowing arrangements at some of the furnaces. With ample blowing power and a hot blast, it is probable that a higher tonnage would be shown by most of the furnaces.

Cost.—A few figures of cost are given in Table XXIII., from which it will be seen that the latter is always less than in ordinary smelting with coke fuel, to say nothing of the abolition of roasting, in itself no small saving. As a rough general average, it will be found that the cost of coke in the ordinary matting furnace is about 60 per cent. of the total cost of smelting per ton of charge including fluxes, whereas in pyritic smelting it rarely amounts to more than 20 or at most 25 per cent. of the total. The difference—viz., 35 or 40 per cent. of the total cost of smelting—would in itself be a sufficiently substantial economy, but if in addition we add the entire cost of the roasting operation with all its attendant losses in the shape of dusting and leaching, it will be seen that, with anything like suitable ores, the pyritic process effects something like a revolution and opens up fresh fields in the treatment of ores under conditions in which smelting processes have hitherto seemed to be out of the question.

Losses.—It must be admitted that the volatilisation loss of silver under ordinary conditions in pyritic smelting is somewhat greater than in lead- or plain matte-smelting. The difference, however, is not considerable, and the silver loss in slags appears to be about the same, while there is certainly no greater loss of gold. At *Leadville* (Colo.)[*] the total recovery in 1892 on commercial assays was 93 per cent. Ag and 95 per cent. Au.

At *Boulder* (Mont.)[†] the slags averaged only 8 dwts. to 18 dwts. per ton, the maximum being only 1½ ozs., while the recoveries were 89·2 per cent. of the silver and 102·5 per cent. of the gold on commercial assays, the high loss of silver being entirely in the flue-dust, which also contained much lead.

At *Toston* (Mont.)[‡] the recovery was 95·3 per cent. silver and 101·6 per cent. of gold. In neither of these cases was there any recovery of flue-dust; and Sticht is confident that with proper appliances for the collection of flue-dust, the loss of silver need not exceed 5 per cent., while the gold should show a small surplus as usual.

The experience of Lang[§] practically confirms the above figures. As regards copper, the same writer finds[||] that slags can be readily made carrying under 0·5 per cent. even when making a 30 per cent. or a 40 per cent. matte, so that the losses are no greater than with the ordinary matting furnace.

Bye-products of Pyritic Smelting.—A bye-product of pyritic smelting not yet utilised in practice, but which, under certain circumstances, may become very valuable, is the sulphurous acid in the gases, which, as shown by Lang,[¶] average something like 11 per cent. SO$_2$. Considering that the average percentage in gases from the pyrites kiln ordinarily employed for the manufacture of sulphuric acid is only 24 per cent., it is evident that the practical difficulties in the way are by no means insurmountable. Probably the manufacture of sulphuric acid from the gases of a pyritic furnace would have been undertaken long ago but for the fact that in the districts where pyritic smelting has hitherto found its most appropriate field, there is no demand or possible market for the acid.

Examples of Pyritic Smelting.—Table XXIII. shows comparative data of various pyritic plants in different parts of the world, but it may be well to give further details with reference to one or two typical plants.

At *Mount Lyell* (Tasmania)[**] four large water-jacketed furnaces, 40 inches by 168 inches at the tuyeres, are arranged with continuous discharge into external movable forehearths for separating matte and slag, and from these forehearths the matte is tapped direct into the converters for twice blowing up into argentiferous pig copper. The general arrangement of the plant is shown in Fig. 69.[††] Each furnace is built with a double tier

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[*] Sticht in Peters, *Modern Copper Smelting*, 7th edition, 1895, p. 429.

[†] *Ibid.*, p. 434.

[‡] *Ibid.*, p. 430.

[§] *Matte Smelting*, 1896, pp. 70 to 78.

[||] *Eng. and Min. Journ.*, Aug. 1, 1896.

[¶] *Ibidem.*

[**] *Private communication* from Mr. Robt. Sticht, Metallurgist in charge, Nov. 26, 1896. Additional furnaces have since been erected.

[††] From *Trans. Inst. Min. Met.*, vol. iv., p. 484.

of water-jackets slightly inclining outwards so as to give a space of 58 inches by 183 inches at the throat, and resting on bottom plates supported by screwjacks.

The side jackets are of $\frac{5}{16}$-in. steel, the end and tap jackets of cast iron. The lower tier of side jackets which contains the tuyeres is composed of six jackets—viz., two centre ones 42 inches long and four corner jackets 6 feet 9 inches long—while the upper tier is composed of eight jackets of the same material. There are two end jackets, one steel tymp jacket, and three tapping jackets. The total height of the two series of jackets is 6 feet 2 inches, or 5 feet above tuyere centres, the height from tuyere level to top of charge column being 11 feet 6 inches, and to feed-floor (which is 20 feet above tapping floor) 14 feet 6 inches. Above the jackets is the usual brick superstructure carried upon four columns, ending in a sheet-iron hood and chimney containing the feed-doors, with a damper on top, and a downtake for the fumes.

The matte and slag run together from the sump (protected by the steel tymp-jacket), into a large rectangular open cast-iron forehearth more or less of the design shown in Fig. 67, p. 259, except that, on account of the great matte-flow, it is cooled by water-circulating tubes round the sides, and that for the same reason, the matte has to be tapped through a small tapping-jacket. The slag flows continuously from the forehearth and is carried away by a strong jet of water. The outlet for matte and slag is in the centre of one long side of the furnace and not at the end.

The hot blast stoves (shown in Fig. 70) consist of a brick heating chamber with the ordinary hanging U-tubes, and fired with wood. The blast for each furnace is a No. 7 Roots blower with engine attached on the same bedplate, power being furnished by two Babcock & Wilcox boilers. The fumes and gases are carried uphill in a brick flue 250 feet long to the main chimney 244 feet above the slag-dump. The matte first produced is concentrated by running through a second time with the ordinary charge.

Further particulars as to the working of this plant (designed by Sticht) are given in Table XXIII.

At the *Bimetallic* smelter (Leadville, Colo.)* semi-pyritic smelting of a great variety of ores is carried on in two stages. The staple sulphide ore is a nearly pure pyrites with only 2 to 2½ per cent. Cu, 2 per cent. Pb, 4 per cent. Zn, 2 to 3 per cent. SiO_2 and 20 ozs. silver per ton, the rest being iron and sulphur; but over 60 per cent. of it is in a fine condition, which precludes the possibility of using it in the furnace as a flux for dry siliceous silver ores bought in the open market. The first operation, therefore, is to bring this ore into the condition of

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* *Private notes*, 1897.

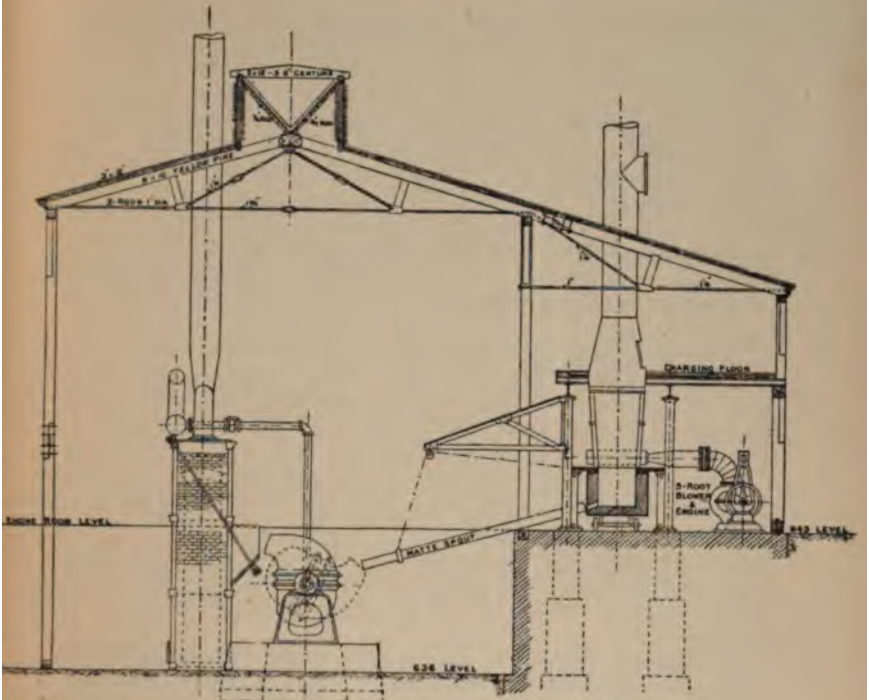

Fig. 69.—Furnace Plant used at Mount Lyell.

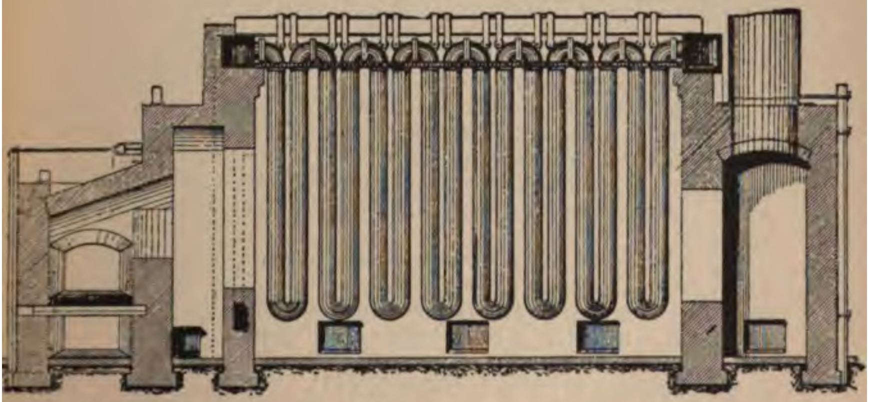

Fig. 70.—Hot Blast Stove (Mt. Lyell), **U**-pipe system (side view).

a low-grade matte, the ideal material for concentration on the pyritic system. In this first or concentration smelting only a low grade of concentration is aimed at, averaging 2 to 1, and the silica for slag forming is added in the form of siliceous slag from the second or silver smelting, the average charge being 2000 lbs. pyrites, 1200 lbs. siliceous slag, and 200 lbs. limestone. The very fine condition of the pyrites prevents much use being made of the sulphur as fuel, and the consumption of coke is from 7 to 12 per cent. of the weight of charge smelted. The first matte contains 4 per cent. copper and 40 ozs. silver per ton, the first slag, containing 35 to 38 per cent. silica, being clean enough to throw away after passing a huge forehearth and two successive catch-pots.

The second operation more nearly approaches a true pyritic smelting, for in it the low-grade matte already produced is employed at once as a vehicle, flux, and fuel for smelting dry siliceous silver ores upon which there is a high smelting charge. The rate of concentration is 6 to 1, the final matte containing 24 per cent. Cu and 240 to 360 ozs. Ag per ton, while the slag run is from 42 to 45 per cent. SiO_2—as siliceous, in fact, as possible; for since it is all saved for cleaning in the concentration smelting, there is no object in aiming at a specially close separation in this, which may be called the ore smelting. The slag accordingly carries 1½ to 2 per cent. copper and 3 to 5 ozs. silver per ton.

The furnace employed consists of a single battery or tier of cast-iron water-jackets resting on a heavy sectional cast-iron baseplate supported by ten screwjacks. The distance from baseplate to centre of tuyeres is 22 inches. Each long side of the furnace consists of nine sections, each containing two tuyeres 2½ inches diameter delivering blast at 10 to 14 ozs. pressure. Two No. 7 Roots blowers easily supply wind for three furnaces.

The matte and slag are delivered through an inclined settling-box of cast-iron plates lined with clay, which traps the blast into a large forehearth on wheels measuring 5 feet by 30 inches wide and 3 feet deep, formed of ⅞-inch cast-iron plates, flanged and strengthened with wrought-iron bands. The matte is tapped into pots through a tapping-block of solid cast iron 15 inches square and 3 inches thick, the centre portion of which, 5 inches square, and containing the 1-inch taphole, is renewed every thirty days.

The fumes from the furnace contain much lead, and are drawn off by fans and forced through spraying-towers, as described in Part I., Chapter XII. The product contains 25 to 40 per cent. lead, with silver a little higher than that in the charge; it is sold to the lead smelters. Other particulars with reference to these works are given in Table XXIII.

At *Keswick* (California) a one-furnace plant for pyritic smelting low-grade ores was, not long ago, designed by Lang.* The plant is arranged upon one level, the motive power throughout being electricity, which, however, has to be generated from a central dynamo station using steam-power, as there is no water-power available. The generator is one of 40 kilowatts and the voltage used is 110, the installation serving also for lighting. Hydraulic lifts are used for raising the charges to the feed-floor, the pressure in the accumulator being 125 lbs. per square inch. Besides a rheostat in the field coils of the blower motor a number of different-sized pulleys are provided so as to vary the speed of the blower within any required limits. The arrangements for utilising the waste heat of the slag to warm the blast have been already described. The ores being poor in copper (only 2 per cent.) the matte first produced has to be concentrated twice by re-smelting with quartz ore and fine sulphides, so as finally to bring it up to 38 per cent. Cu.

The resulting matte is Bessemerised up to rough copper and refined electrolytically.

Pyritic Smelting to Speiss.—Hitherto nothing seems to have been attempted in this direction, but given suitable ores—*i.e.*, those containing a high proportion of mispickel—it would seem quite feasible to smelt them as pyrites ores are smelted, utilising the heat afforded by the combustion of arsenic as well as of sulphur and iron as the principal, if not the only, means of fusion. The greater specific gravity of speiss would seem to afford even greater facilities for obtaining clean slags, and therefore a high percentage of extraction. On the other hand, as already seen, the loss of combined silver in slags would be somewhat higher. Moreover (and this is really the weak point), the volatilisation loss of silver is undoubtedly much greater in the presence of a large quantity of volatile arsenic compounds—and still more is this the case with antimony compounds.

Gold, however, while even more perfectly concentrated in speiss than in matte, does not seem to be volatilised to any perceptible extent under the conditions prevailing inside a blast furnace, nor in the presence of arsenic or antimony. A speiss process, therefore, would seem to be eminently adapted to the concentration for shipment of gold-bearing mispickel ores or concentrates, which are always so difficult to dead roast for chlorination.

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* *E. and M. J.*, Aug., 1896.

TABLE XXIII.—Examples of Pyritic Smelting.

	Toston, Montana.	Kokomo, Colorado.	Boulder, Montana.	Bimetallic Smelter, Leadville, Colo.	Keswick, California.	Mount Lyell, Tasmania.
References, . .	1.	2.	3.	4.	5.	6.
No. of furnaces in blast, ...	...	...	..	3	1	4
Dimensions at tuyeres, ...	36″ × 78″	33″ × 140″	..	36″ × 163″	36″ × 180″	40″ × 168″
Height of tuyere-line to feed-floor, . .	...	...	...	10 ft.	7 ft. 6 ins.	14 ft. 6 ins.
Material of jackets, ...	...	...	...	cast iron	...	5/16″ steel
Number and diameter of tuyeres, . .	...	...	...	36 of 2½″	26 of 2″	32 of 3″
Total area of tuyeres, . . sq. ins.,	...	...	...	176·69	81·68	226·19
Sectional area at tuyeres, . . sq. ft.,	...	...	..	40·75	45	57·72
Tuyere ratio, ...	...	...	..	4·33	1·83	3·92
Tonnage put through per 24 hours, tons,	44·6	100	90½	200	132	240 to 260
Average hearth efficiency, ...	...	...	...	4·91	2·93	4·33
Average tuyere efficiency, ...	...	...	...	1·13	1·61	1·11
Average blast pressure, . . . ozs.,	...	...	12	12	5 to 5½	21
Average temperature of blast, . . .	...	...	...	cold	500° F.	400° to 450° F.
Height of column of charge, . . .	...	...	...	8 ft.	3½ to 4 ft.	11 ft. 6 ins.
Degree of concentration, . tons into 1,	6·6	...	about 8	about 5	about 4	about 5

Composition of charge :—			Per day;—			
Raw sulphide ores,	1000 lbs.	...	55 tons	2000 lbs.	2800 lbs.	...
Quartzose gold ores,		...		1000 lbs.	1000 lbs.	...
Gozzan and oxide ores,		...			1400 lbs	...
Limestone,	not given	...	15 tons	200 lbs.	none	very little
Slag,	280 lbs.	...	20½ tons	...	1400 lbs.	
Matte,	...	...	...	...	1400 lbs.	...
Total lbs.,	...	...	...	...	8000	6000
Percentage of fuel employed,	3 to 6	...	...	7 to 10	2·8 to 5	1·5 to 3
Number of charges in 24 hours,	...	...	...	...	65	90 to 100
Composition of ore charge :—						
Cu, . . . per cent.,	...	...	...	2 to 2¼	...	5·4
S, . . . ,,	...	...	...	over 25	...	over 30
Ag, . . . ozs. per ton,	10·53	...	...	20 to 25	...	2·5
Au, . . . ,, ,,	0·63	...	...	...	...	0·225
Composition of first matte :—						
Cu, . . . per cent.,	...	...	...	5	...	25
Ag, . . . ozs. per ton,	55·5	...	...	50	...	12·5
Au, . . . ,, ,,	2·7	...	...	...	...	1·25
Second or twice-run matte :—						
Cu, . . . per cent.,	..	...	14·2	24·0	...	52·0
Ag, . . . ozs. per ton,	...	...	82·4	240 to 300	...	25
Au, . . . ,, ,,	...	...	3·61	...	...	2·5
Composition of slag :—						
SiO_2,	41 to 48	...	...	40	30·43	...
FeO, MnO,	...	...	...	36	45·06	...
Al_2O_3,	...	...	...	4	10·72	...

TABLE XXIII.—(*Continued*).

	Toston, Montana.	Kokomo, Colorado.	Boulder, Montana.	Bimetallic Smelter, Leadville, Colo.	Keswick, California.	Mount Lyell, Tasmania.
Reference, ...	1.	2.	3.	4.	5.	6.
Composition of slag—*continued*:—						
CaO . MgO, ...	...	...	...	8	0·42	...
ZnO, ...	...	...	...	5	4·03	...
Cu, ...	...	...	...	...	0·58	0·5
Pb, ...	...	...	...	...	...	...
S, ...	...	...	...	...	2·6	...
Ag, ... ozs. per ton,	1	...	½ to 1½	...	...	0·12
Au, ... „ „	...	...	trace	...	...	0·05
Recovery of copper, ... per cent.,	...	...	95·7	...	...	...
Recovery of silver, ... „	95·3	85 to 90	86·19	...	...	...
Recovery of gold, ... „	101·6	100 to 103	105·63	...	...	...
Cost of smelting per ton of ore:—						
Labour, ...	£0 11 2	£0 5 3½	£0 7 2	...	£0 3 7½	..
Superintendence and assaying, . .	0 1 0	0 1 5½	0 3 2	...	0 1 6½	..
Coke (and furnace wood), . . .	0 2 10	0 1 0	0 3 2	£0 3 0	0 1 11¾	...
Limestone, ...	0 0 6½	0 1 10½	0 1 5½	...	...	...
Fuel for power, ...	0 3 4	0 0 11	0 0 6½	...	0 0 7¾	...
Fuel for heating blast, ...		0 0 5½	0 0 9½	...	...	...
Sundry supplies, oil and light, . . .	0 0 3½	0 0 7½	0 0 4½	...	0 0 6¼	...
Interest and depreciation, . . .	not known	not known	not known	...	0 0 11	...
Total, ...	£0 19 2	£0 11 7½	£0 16 8	...	£0 9 2¾	...
Cost of smelting per ton of charge, . .	£0 14 7	...	£0 10 3½	...	£0 5 11	...

References.—1, 2, and 3. From Peters, *Modern Copper Smelting*, 7th edition, 1895. 4. *Private notes*, 1897. 5. *Private communication*, R. Sticht, 1896. 6. Lang, *Eng. and Min. Journ.*, Aug. 1896.

CHAPTER XVI.

MATTE SMELTING IN REVERBERATORIES.

As in the case of blast furnace matting, reverberatory smelting of silver ores containing copper presents no special peculiarity to differentiate it from the similar smelting of copper ores. Practically speaking, therefore, silver matte smelting in reverberatories is a variation or offshoot from the ordinary English process of copper smelting.

Characteristics of Reverberatory Smelting.—The most important features in which reverberatory differs from blast furnace smelting are the following:—

(1) *Complete Separation of the Fuel from the Ore.*—The combustion chamber being entirely separated from the working portion of the furnace in which the ore is heated by flame only without direct contact with fuel, it is possible to raise or lower the temperature in the latter within certain limits almost at will. The ash of the fuel is not mixed with the ore and has not to be melted, therefore the slag produced is less in amount, and consists merely of the gangue of the ore itself, together with such material as may be taken up from the furnace lining by corrosion or abrasion.

(2) *Larger Consumption of Cheap Fuel.*—In the blast furnace the products of combustion passing up through the cold charge yield the greater part of their heat by direct contact, and, therefore, although the fuel employed is of an expensive kind (chiefly coke or charcoal) the "heat efficiency of the furnace—*i.e.*, the actual weight of charge smelted per ton of fuel consumed—is the highest possible.

In the smelting reverberatory the charge has to be heated for the most part by radiation from the flame and heated gases, and as the whole area of the furnace is practically at a nearly uniform temperature, the products of combustion must pass away at about this same temperature; consequently there is great waste of heat, and the "heat efficiency" of the whole appliance is very much lower than that of the blast furnace.

Against this drawback must be set the enormous advantage that the reverberatory does not require a high-class fuel, but will work nearly as well with almost any kind of small coal, slack, lignite, or even dry wood, providing the firebox and air supply are so arranged as to permit of the fuel burning with sufficient rapidity. As regards the waste of heat in escaping gases, this can be very greatly diminished by passing them round the conduits which bring to the grate its supply of air for supporting combustion, and by closing up the ashpits and fire-doors so that as little air as possible, other than that so heated, shall gain admittance to the interior of the furnace. One of the arrangements for doing this is mentioned below.

(3) *Intermittent instead of Continuous Working.*—In the blast furnace cold ore is being continuously charged at the top, while hot slag runs off at the bottom. Such continuous working has not as yet been found practicable in the reverberatory, and each charge has to be spread, warmed up, smelted, settled, and skimmed independently. Not only do the operations of spreading, warming up, and skimming cause great waste of time, but the first and last give rise to great loss of heat, since however rapidly they may be performed the furnace doors must remain open while the workmen are handling any part of the charge, and it is impossible to prevent cold air entering the furnace. The losses of time and of heat are greatly diminished by increasing the number of hoppers for charging and of doors for skimming.

(4) *Greater Range of Slag Composition.*—Here the reverberatory has a very decided advantage, for, owing to the greater length of time for settling out afforded to the matte-grains, it is by no means so essential that the slag shall be as perfectly fluid as that produced in the blast furnace. As far as removal from the furnace is concerned, quite pasty and viscous slags can be skimmed almost as readily as those which are more fusible, and, therefore, the only limiting factor as regards the composition of the slag is that it shall be sufficiently fluid to permit the shots of matte to settle out.

As a matter of practice it is found that with proper settling facilities outside the furnace for shots of matte brought out by the rabbles, reverberatory slags can be made cleaner than those of similar composition from the blast furnace, or, which comes to the same thing, equally clean slags can be made with a decidedly more siliceous charge. This saves flux and reduces the aggregate slag loss owing to the smaller weight of slag produced.

(5) *Adaptability to Fine Charges.*—It has been seen* that fine ore is a great trouble in ordinary low-blast furnaces, giving rise as it does to lessened capacity, irregular working, and increased losses in flue-dust and foul slags. In the reverberatory, however, fine ore is a positive advantage, since the individual particles more readily melt and flux each other; while, although the proportion of flue-dust produced is, of course, higher with fine ore, its absolute amount is so small, compared with the quantity produced in the blast furnace, that it becomes a comparatively insignificant matter.

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* See part i., chap. ix.

(6) *Differences in Reactions and Results.*—The atmosphere of the reverberatory furnace may be made, at will, oxidising or reducing, but may be regarded as normally neutral. The atmosphere of the blast furnace varies in different parts of its section and is, moreover, not so perfectly under control, though within certain limits it may be made oxidising. As a general rule, however, the blast furnace atmosphere is reducing, and it must always be so to a certain extent in the immediate neighbourhood of the burning fuel. In the blast furnace which smelts partially calcined ore with coke fuel practically all the sulphur present finds its way into the matte. In the reverberatory, however, oxides and sulphides mutually react upon each other, and sulphates (including barium sulphate) are split up in the neutral atmosphere, so that a large part of the sulphur present is driven off according to the following typical reactions, which are given as examples:—

$$\begin{aligned}
Cu_2S + 2Cu_2O &= 6Cu + SO_2. \\
2Cu + FeS + Fe_2O_3 &= Cu_2S + 3FeO. \\
FeS + 3Fe_2O_3 + 7SiO_2 &= 7(FeO,SiO_2) + SO_2. \\
CuSO_4 &= CuO + SO_3. \\
2BaSO_4 + SiO_2 &= 2BaO \, . \, SiO_2 + 2SO_3.
\end{aligned}$$

It is obvious, therefore, that with a charge of given composition much more sulphur will be expelled in a gaseous form when smelted in the reverberatory than in the blast furnace. The reverberatory, therefore, will produce from any given charge the richer matte, or, to put it in another way, will yield a matte of equal grade and permit of the same degree of concentration with a much less perfectly roasted charge. It is absolutely essential in a reverberatory charge to have some unroasted, or very imperfectly roasted, ore in order to supply sulphur not only for the matte but also as a reducing agent for the ferric oxide, which in a blast furnace has usually to be reduced by the agency of carbon or of carbonic oxide.

Reverberatory Smelting at Butte (Montana).—The most important centre of silver-copper reverberatory smelting in the world is undoubtedly that at *Butte* (Mont.). The ores which are smelted direct without concentration run from 11 to 30 ozs. silver, from 9 to 26 per cent. copper, and 7 to 28 per cent. insoluble residue; the concentrating ores contain 3 to 12 ozs. silver, 0·5 to 8 per cent. copper with 50 to 60 per cent. insoluble matter, the remainder in each case being chiefly iron and sulphur, together with, in some of the ores, lead, zinc, and manganese.

The concentrates are invariably roasted in one or other type of automatic furnace, and are then smelted together with small quantities of picked "smelting ore," also partly roasted or sometimes raw in part, in reverberatory furnaces of large size. The copper present in these ores being more valuable than the amount of silver contents, their smelting may be more properly considered as belonging to the metallurgy of copper than to that of silver.

Fig. 71 * shows a modern Butte reverberatory used at the Parrot works for smelting roasted silver-copper concentrates to matte. In this figure *a* is the firebox, *b* the hearth, and *c* the stack, *d d* are skimming side-doors, *e* the front door, and *f* the taphole. It will be noticed that the firebrick lining is in two distinct layers to facilitate replacement of the inner one when it becomes worn or corroded. Its "life" may be greatly lengthened by keeping a sort of ring or bank of siliceous ore piled against it all round the furnace. The stack must be of ample capacity without which it is impossible to secure the requisite rate of combustion in the firebox, but its height, for one furnace, need never exceed 65 feet. The inner lining of firebrick, separated by an air space from the main firebrick wall, is suppressed at 40 feet high, thus permitting the stack to have a somewhat larger sectional area at top than at bottom in spite of the latter. The

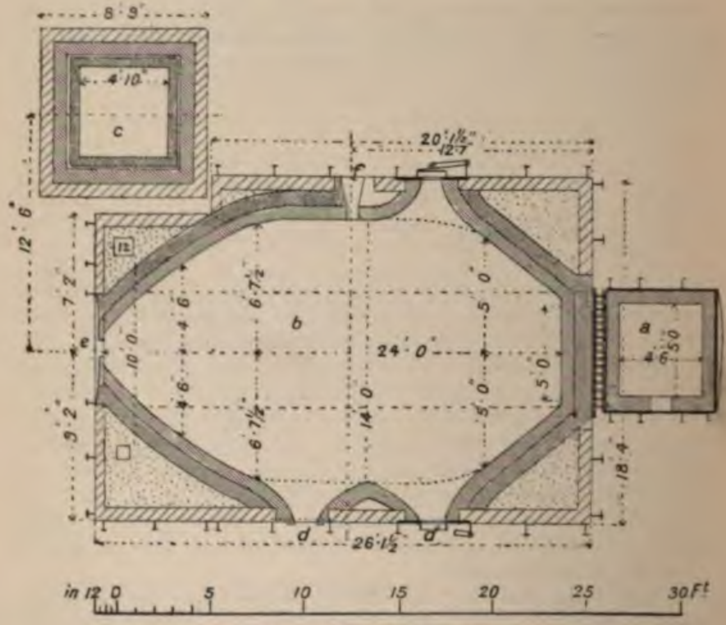

Fig. 71.—Butte Reverberatory Furnace.

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[*] From Peters, *Modern Copper Smelting*, 7th edition, p. 457.

sand bottom (of pure quartz sand softened and "tempered" by smelting sand-charges upon it) is from 2 to 3 feet thick, formed upon a brick bottom built in the form of an inverted arch.

A very good description of these modern furnaces and of the mode of operation is given in the latest editions of Dr. Peters' work, to which reference should be made for details. It may be sufficient to mention here that an oval furnace, the hearth of which is only 22 feet long by 12 or 14 feet wide, will smelt daily 48 or more short tons (of 2000 lbs.) of ore, the charge being composed of, say, 60 per cent. of hot calcined concentrates and 40 per cent. of siliceous crude ore, and the rate of concentration 3 or 3½ into 1.

Each charge, weighing 5 tons, is dropped from two or three hoppers into a bath of molten matte immediately after skimming the slag of the previous charge, and in this way not only does it spread almost automatically with very little help from the rabbles, but is prevented from sticking to the bottom and kept on top where it is directly exposed to the fierce heat of the flame. Under these conditions each 5-ton charge takes only two and a-half hours to work off.

The essential conditions which distinguish this modern method from the antiquated Welsh practice and render such large capacity possible are the following:—

1. Greatly enlarged hearth area, varying from 21 feet by 10 feet up to 24 feet by 14 feet 6 inches inside measurement.
2. Greatly enlarged sectional area of grate, flue, and chimney, also the use of all bituminous coal, and a thin layer of fuel on the bars instead of the "clinker grate," used for burning a mixture of anthracite and bituminous slack. All this has for its object the rapid combustion of fuel, 10 or 12 tons per day being burnt in a firebox of only 30 square feet sectional area.
3. Keeping a pool of molten matte, say 8 inches deep, always in the furnace so as to float up each new charge, spread it without any trouble, and prevent it from adhering to the bottom.
4. Rapidly skimming the slag through at least three doors at once, cutting off the chimney draught meanwhile* so as not to cool the furnace too much.
5. Previously heating the air by conducting it through suitable channels in the furnace brick work, or through cast-iron conduits heated by the furnace gases; allowing no cold air to pass through the fire.
6. Keeping the hearth as hot as possible by utilising the vault exclusively for heating the air for combustion, or, preferably, by abolishing it altogether.
7. Charging the roasted ore, while still red-hot, into the smelting furnace by means of two or three hoppers on its long axis.
8. Skimming as soon as the major portion of the charge has

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* By raising a sliding door covering an opening in the stack.

become fluid, without waiting for any sticky portion which may have accidentally adhered to the bottom.

Use of Heated Air under the Grate.—At *Anaconda*[*] a unique and very effective arrangement is in use for heating the air required for combustion up to a temperature of 600° to 700° F. (315° to 371° C.).

At one of the Anaconda plants a row of ten furnaces, each 21 feet by 13 feet inside hearth, with fireboxes 10 by 5, is fired with "run of mine" coal, largely slack, and provided with forced draught in a closed ashpit. The blast for all the furnaces is provided by eight fans, each 4 feet diameter, and driven at 2500 to 2800 revolutions per minute. The furnaces take 5-ton charges, six of which are, on the average, worked off per shift, making a daily capacity of 60 (short) tons per furnace. The coal used averages 14 tons for the 60 tons of charge, or 23·3 per cent. by weight, and the ashes are removed automatically from each firebox by a stream of water in a launder on an inclination of $\frac{3}{4}$ inch per foot.

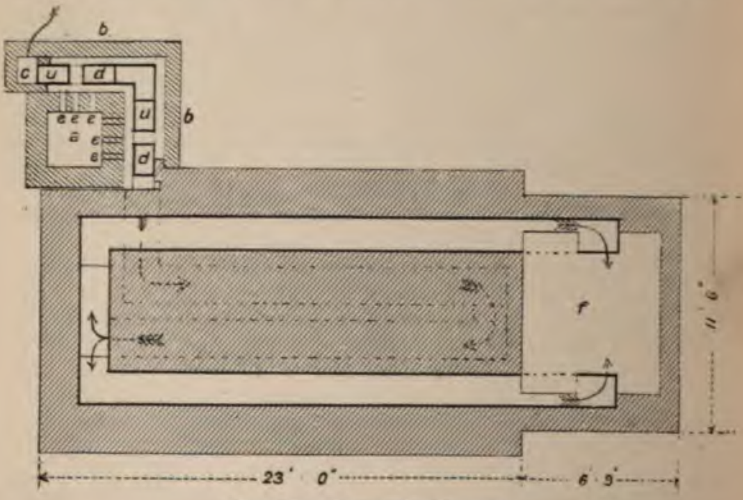

Fig. 72.—Anaconda Furnace.

The heating of the blast is commenced by running the 3-feet blast main through the whole length of the long underground flue, which serves forty roasting furnaces. It is completed by passing it through a system of rectangular cast-iron pipes under the hearth and heated by radiation from the flue. Fig. 72[†] shows in plan the arrangement of these pipes.

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te notes, 1897.

[†] Borrowed from Peters, *op. cit.*

Two sides of the main stack, *a*, are enclosed within outer walls, *b b*, for a height of about 20 feet from the ground, forming a space, *c*, which is heated by a number of radiation holes, *e e*, left in the stack wall itself. Through this enclosed hot-air chamber meanders in zig-zag fashion alternately up and down a rectangular cast-iron pipe, ***u***, 20 inches by 13 inches in section, containing the current of warm air from the main blast pipe, which thereupon becomes heated through the radiation holes, *e e*. The cast-iron pipe continues its course under the furnace hearth, as shown by the dotted lines and arrows, finally reaching the ashpit, *f*, at the temperature of 600° to 700° F.

There are several little peculi ties about these furnaces which tend to economy and eff y; among them may be mentioned the circular rolling d the steam jets in the ashpits tending to keep the cli nd spongy. The most important features not yet m the long three-necked hopper for the ore charge, g levers attached to the sliding doors, and the s for coal over the firebox.

Each furnace handling 30 r shift is attended by only two men per shift, o to the fire, while the other looks after chargi d both assist at skimming time. The great aces is partly due to the fact that the whole calcined ore" fresh from the roasting furna till red hot, as well as to the other peculiarities d.

Reverberatory Smelting at Argo.*— , Denver, managed by Dr. Richard Pearce, are s in the United States which smelt gold and silver e exclusively in reverberatory furnaces. Copper at merely a vehicle, and only sufficient cupriferous ore is emplo make sure of thoroughly collecting the precious metals, the rage charge smelted containing less than 2 per cent. Cu. The ores treated comprise—(1) Pyritic (auriferous) ores and concentrates from Gilpin County and elsewhere; (2) barytic silver ores from Aspen and Creede; (3) siliceous telluride and other gold ores from Cripple Creek; and (4) any and every kind of ore containing gold and silver, not too rich in lead.

Roasting.—The whole of the pyritic ores and concentrates are roasted (after crushing when necessary) in the Pearce turret furnace, described in Part I., Chapter VI. The capacity of each furnace is 15 tons of pyrites, containing 43 per cent. sulphur, roasted down to 5 or 6 per cent. sulphur in twenty-four hours, with a consumption of 2¾ tons or 17 per cent. by weight of coal. The cost of roasting is stated as follows:—Labour, 4·86d.; fuel, 16·00d.; power, steam, and oil, 3·88d.; repairs, 1·31d.; interest at 6 per cent., 2·76d.—total, 28·81d., or, say, 2s. 5d. per ton.

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* *Private notes.*

Smelting.—The red-hot calcined concentrates are mixed with about an equal proportion of the siliceous and other ores, cold and unroasted, and smelted in one of the modern reverberatories, which are absolutely the largest smelting reverberatories in the world. *Peters** gives figures showing the gradual increase in size of these furnaces from 1878 to 1894, and since then still larger furnaces have been built. Table XXIV. gives a few comparative data.

TABLE XXIV.—DEVELOPMENT OF ARGO REVERBERATORIES.

Particulars.	1878.	1882.	1887.	1891.	1893.	1894.	1896.
Area in sq. feet, stack, . .	7·56	7·56	9	9	12·25	16	?
,, ,, firebox, .	22·5	22·5	24·75	28·5	32·5	32·5	...
,, ,, hearth, .	105	139	198	265	402	481	810
Ratio, firebox (= 1) : hearth, .	4·67	6·18	8·00	9·30	12·37	14·80	?
,, ,, stack, .	·336	·336	·364	·315	·376	·491	...
Tons coal burned per 24 hrs.,	5	7	9	10	13	13·5	17
Percentage of area lost in corners, ...	28	24·5	26	23	16	14	?
Tons smelted per 24 hours, cold, ...	12	17	24	28	35	...	...
Tons smelted per 24 hours, hot, ...	...	...	...	...	43	50	72
Tons smelted per ton of coal, .	2·4	2·43	2·67	2·8	3·3	3·7	4·2
Percentage of fuel used, .	42	41	37·5	36	30	27	24
Pounds smelted per sq. ft. of hearth, ...	229	245	242	211	213	208	177

Up to 1893 the whole of the ore charge was smelted cold, but in that year the calcined portion was charged direct from the roasting furnaces, with the result that the weight of charge smelted per twenty-four hours with a given consumption of coal was increased by 23 per cent., while the capacity of the furnace per square foot of hearth area remained at the same figure, in spite of the more thorough utilisation of the heat of combination realised by the larger furnace.

The charge for the largest 45 by 18 feet furnace (called the "Cambria") is 12 tons, which is dropped into the hearth from four hoppers simultaneously so as to assist it in spreading quickly over the whole surface of the molten bath of matte. The hoppers are situated over the centre line of the hearth, and are connected with the cast-iron pipes passing through the arch by means of wrought-iron funnel tubes, which are temporarily raised during the process of charging. These hoppers are filled by means of overhead tram lines running over the calcining furnaces to the

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* *Op. cit.*, 7th edition, pp. 445, 446.

ore bins, so that there is no handling of hot ore, the trucks filled under the vaults of the turret roasters being raised by a lift and run direct into the hoppers of the smelting reverberatories. Each charge of 12 tons takes four hours to work off.

Disposal of Slag.—When ready the slag is skimmed from four doors at once into a system of clay-lined cast-iron launders running round it, and provided with settling pots in front of each skimming door, and at the corner of the furnace, in order to catch shots of matte. The stream of molten slag is conveyed outside the building by means of a continuation of this launder at the very low inclination of only $\frac{1}{2}$ inch per foot (the section across the track being counterbalanced so as to be raised out of the way when not wanted), and there cast in pigs in sand beds. This is found quite satisfactory at Argo because the Railway Companies are glad to get the slag for use as ballast, and pay a price for it loaded into trucks which considerably more than covers the cost of casting and loading by hand.

At the *Parrot* works (Butte) the slag is granulated by means of a stream of water from a 6-inch pipe under a 12 feet head, and so carried away, while at *Great Falls* the same method is used for removing the slag from the great gas-fired tilting reverberatories there employed. Where water is scarce the slag may be skimmed into large slag pots, and hauled by mules to a tip as usual.

Disposal of Matte.—The matte at *Argo* is small in amount, the usual rate of concentration being 15 or 16 into 1. It is usually allowed to accumulate for six days, and then tapped out into sand beds, as in the usual Welsh practice, the sand which adheres to the pigs not being objectionable at these works on account of the very small quantity of matte. Most works, however, tap into a bed of cast-iron or steel moulds; this gives much cleaner matte and a smaller quantity to be re-handled, besides being much more convenient when the furnace has to be tapped once a day or oftener.

Composition of Matte and Slag.—Both matte and slag produced at *Argo* vary considerably in composition. The ore charge is, however, usually so compounded as to contain about 3 per cent. of copper, the resulting matte when concentrated 16 to 1 running to about 45 per cent. copper, 400 ozs. silver, and 15 ozs. of gold per ton. The slag carries $\frac{2}{10}$ or $\frac{3}{10}$ of copper, $1\frac{1}{2}$ ozs. silver, and under 1 dwt. gold per ton. The following table shows the composition of the average slag and matte produced at Argo some time ago, the average composition of the ore charge at a later date being added for comparison. The latter, however, does not correspond with the slag analysis, as will be noticed; this is because the material now treated is much more siliceous and barytic than formerly. Column 4 shows the approximate composition of the slag which would be produced from the ore charge in column 1; column 5 that of a slag exceptionally rich in zinc sometimes produced.

TABLE XXV.—Argo Analyses.

	Ore charge.*	Matte.	Slags.		
References,	1.	2.	3.	4.	5.
SiO_2,	33·90	0·65	41·77	45·2	36·52
$BaSO_4$,	15·50	...	...	...	...
BaO,	...	...	6·89	13·6	...
FeO(MnO),	...	...	32·25	16·0	35·14
Fe,	10·80	17·67	...	...	...
Al_2O_3,	5·60	...	6·91	7·5	1·29
CaO,	4·80	...	3·27	6·0	3·57
MgO,	2·80	...	1·26	3·7	...
ZnO,	6·10	...	5·80	7·6	20·08
Zn,	...	2·73	...	...	...
CuO,	...	...	0·23	...	...
Cu,	2·50	47·30	...	...	...
PbO,	...	...	0·75	...	1·50
Pb,	1·00	8·07	...	...	...
Ag,	0·093	1·38	...	...	...
Au,	0·0059	0·088	...	...	...
S,	5·1	21·58	...	...	...
SO_3,	...	...	...	...	...
O,	6·4	...	...	...	...
CO_2,	6·7	...	...	...	...
	...	99·468	99·13	99·6	98·10
Ag, ozs. per ton,	31	450	$\frac{3}{4}$	...	...
Au, ,, ,,	1·91	28·75	tr.	...	...

References.—1. Peters, *Modern Copper Smelting*, 7th edition, 1895, p. 446. 2 and 3. H. Pearce, *Private communication*, Oct. 20, 1896. 4. *E. and M. J.*, Sept. 12, 1896. 5. Calculated.

The composition of the slags, the analyses of which are given in Table XXIV., is as follows:—

Zinc Slag, Column 5.—This is almost exactly a sesquisilicate, its formula working out as

$$3[4RO \cdot 3SiO_2] + CaO \cdot SiO_2.$$

R being in this case $\frac{2}{3}$ Fe and $\frac{1}{3}$ Zn.

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* According to the author's information the average ore charge still con-
ns more roasted pyrites than would be indicated by analysis 1, so that
lag actually produced is intermediate in composition between those
in columns 3 and 4.

Slag in Column 3.—This, which may perhaps be considered as the normal Argo slag, is rather more than a sesquisilicate, its oxygen ratio being as 1 : 1·6, and its formula

$$16[4RO\,.\,3SiO_2] + 7[Al_2O_3\,.\,3SiO_2].$$

Where R is $\frac{44}{65}$ Fe, $\frac{7}{65}$ Zn, $\frac{5}{65}$ Ba, and $\frac{9}{65}$ Ca.

Slag in Column 4.—This is nearly a bisilicate, its oxygen ratio working out as 1 : 1·83, or as 5 : 9, and its formula

$$4[4RO\,.\,3SiO_2] + 17[R'O\,.\,SiO_2] + 4[Al_2O_3\,.\,3SiO_2].$$

R in the first term being $\frac{5}{17}$ Zn, $\frac{12}{17}$ Fe, and R′ in the second term $\frac{5}{17}$ Ba, $\frac{12}{17}$ Ca.

Cost of Smelting.—The fuel consumption has been already given. The labour employed on the large furnaces at Argo per twelve-hour shift is one fireman per furnace, one skimmer per two furnaces, and one slagman and labourer for two furnaces. The nett cost for labour, not allowing for transport of ore and fuel, for repairing furnace or for handling slag is under 30 cents per ton, which is no more than it would be with blast furnaces.

Comparison between Reverberatories and Blast Furnaces.—The introductory remarks on the principles of reverberatory smelting will have already drawn attention to the chief reasons which should be taken into consideration in determining the type of furnace best suited to any particular set of conditions. With a large, well-arranged, modern plant, the cost of labour is pretty nearly equal in each case, and there is comparatively little difference in the results, as the smaller bulk and higher grade of the matte turned out by the reverberatory is an offset to the poorer slag usually produced in the blast furnace.

The comparative *cost* of reverberatory- compared with blast-furnace treatment practically resolves itself into a question of transport. In districts hundreds or thousands of miles away from a coalfield, and especially if at some distance from rail or water transport, it will usually be more economical to adopt the blast furnace with its small percentage consumption of highly concentrated fuel of somewhat high initial cost, whereas in colliery districts where small coal can be obtained at a very cheap rate the reverberatory possesses obvious advantages.

As a rule, the more *siliceous slags* can be produced with less irregularity of working and more certainty in the reverberatory. On the other hand, however, the water-jacketed blast furnace requires scarcely any firebrick or other refractory material for repairs, while the reverberatory demands a steady supply of clay and of crushed quartz for fettling, besides a considerable number of firebricks for repairs. In certain inaccessible districts this greater simplicity of the blast furnace and its comparative independence of refractory material becomes a decisive factor of the highest importance. Any great scarcity of water for cooling at once turns the scale in favour of the reverberatory again.

Another most important difference between the two types of furnace which would often determine the choice of the blast furnace for inaccessible and out of the way localities is the character of the labour required. With a water-jacket plant, even if comprising, say, two furnaces of a daily capacity of 100 tons or more each, only one man on each shift need be a really skilled smelter, the rest being merely labourers. For a reverberatory plant of the same capacity, however, to work with anything like economy and regularity, freedom from accidents and a reasonable cost for repairs, almost every man about the furnaces, including certainly firemen as well as skimmers, should be comparatively skilled men. An unskilled fireman may easily burn 50 per cent. more coal to no purpose, while the least want of care in maintaining the ring of fettling round the side walls or in firing on an unprotected bottom may result in ruining a furnace in a single shift; none, therefore, but the most experienced and trustworthy men obtainable should be employed on reverberatory smelting furnaces. It is this adaptability of the water-jacketed blast furnace to handling by unskilled and ignorant workmen which constitutes one of its greatest advantages, especially in out of the way places.

Speiss Smelting in Reverberatories.—The use of speiss, instead of matte, as a vehicle for concentrating the precious metals in blast furnace work has been referred to in Chapter XIV. The only case known to the author in which the reverberatory has been employed for smelting to speiss is that which will now be briefly described:—*

Speiss Smelting in the Transvaal.—Near *Pretoria* (S.A.R.) an ore, consisting chiefly of hydrous oxides of iron containing antimony (as antimoniate?), about 4 per cent. copper as carbonate, and averaging 35 to 40 ozs. silver per ton, was smelted direct in reverberatories to an antimonial speiss, a siliceous ferruginous and dolomitic limestone being used as flux in the proportion of 13½ cwts. per ton of ore.

The reverberatories were built with a system of firebrick channels between hearth and vault through which hot air was delivered under the grate as well as through the bridge and roof of the furnace. The coal was of poor quality, containing 18 to a possible 40 per cent. of ash. Closed ashpits and a steam blast under the grate were, therefore, adopted in order to cool the grate bars and prevent clinkering above.

The steam blast for two furnaces was furnished by an 8 H.P. locomotive boiler consuming 800 lbs. coal per shift at 56s. per ton. The steam was delivered at 20 lbs. pressure through two jets $\frac{5}{16}$ in. diameter to each furnace, and produced, instead of the ordinary clinker, a friable ash, while, even with the worst

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* Abridged from an article by Bettel in *E. and M. J.*, July 18, 1891.

coal, the clinker, instead of being slaggy, was always rotten and friable.

The usual rate of concentration with 35 ozs. ore was 16·4 tons ore (or 27·5 tons of charge) into 1 of product. With ore of this grade the recovery of silver averaged about 80 per cent.; with ore of 40 ozs. as much as 91 per cent. entered the matte, 7½ per cent. going into the slag and the remainder volatilising.

The following analyses give the composition respectively of the siliceous flux (the presence in which of anthracitic carbon may be noted as peculiar) and of the slag produced :—

Flux.	
Insoluble,	37·40
Al_2O_3,	2·94
MnO,	tr.
$FeCO_3$,	9·57
$MgCO_3$,	8·92
$CaCO_3$,	30·40
Water and volatile,	5·77
Carbon (anthracitic) by difference,	5·00
	100·00

Slag.	
SiO_2,	27·05
FeO,	53·30
Fe_2O_3,	2·55
Al_2O_3,	4·50
MnO,	3·00
P_2O_5 and As_2O_3,	0·265
Sb_2O_3 and Bi_2O_3,	0·230
CaO,	5·32
MgO,	2·80
PbO,	0·45
Cu_2O,	0·45
Ag,	0·005
S,	0·05
	99·97

The matte was subsequently "blown up" on another reverberatory hearth furnished with a hot blast, to a crude argentiferous copper which was granulated, the slag from this operation containing 15 ozs. Ag, as well as 12 per cent. of the copper and 10 per cent. of the antimony in the speiss going back to the ore furnaces. Analyses of the speiss and of the shot copper are as follows :—

	Speiss.	*Shot Copper.*
Copper,	52·50	93·55
Iron,	3·60	...
Lead,	0·25	...
Silver,	1·59	3·26
Antimony,	38·00	1·31
Arsenic,	2·00	0·60
Sulphur,	2·06	1·28
Oxygen and loss,	...	
	100·00	100·00
Silver, per ton of 2240 lbs.,	520 ozs.	1065 ozs.

CHAPTER XVII.

TREATMENT OF ARGENTIFEROUS MATTES.

The treatment of argentiferous mattes obtained direct from the ore furnace, either by lead smelting, ordinary matting, or pyritic methods, must be preceded by a process of concentration in order to eliminate some of the lead and iron, while producing a matte richer both in copper and in silver, and therefore easier to desilverise by most of the methods at present in vogue.

The concentration process may occasionally take the form of a treatment by acid (as at Zalathna), but with ordinary mattes not too rich in copper it almost invariably consists of roasting to eliminate sulphur, followed by smelting with siliceous ores to slag away iron and reduce lead.

Matte Concentration for Mattes of 30 per cent. and under—*Roasting.*—The roasting and subsequent smelting of ordinary lead mattes has been dealt with in Part I., Chapter X., to which reference should be made for details.

It will be borne in mind that by roasting lead mattes and re-smelting with siliceous ores containing lead only a portion of the silver contents of the matte passes into the lead bullion, another portion remaining obstinately combined with the copper in a "second," "concentrated," or "twice-run" matte which is much richer in copper than the first or ore matte, but still always contains 8 to 12 per cent. or more lead, together with a variable amount of silver which may be either more or less than that in the original ore matte according to the richness of the additions to the concentration charge.

The roasting of mattes produced in other than lead furnaces presents no peculiarity whatever, and as regards their concentration the only difference to be noted is the absence of lead bullion among the products and the consequent concentration of silver in the resulting matte to a higher degree than is the case with lead mattes.

In furnaces the atmosphere of which is largely oxidising, and which, therefore, utilise to a greater or less extent the sulphur and iron contents of the charge as fuel, the first matte is frequently concentrated to a considerable extent by simply returning to the furnace. This is done at *Sunny Corner*, also at *Mount Lyell*, *Keswick*, and other pyritic plants. When, however, the "reducing matting" process is employed, the matte must be more or less completely roasted before any part of the iron it contains can be eliminated by slagging, and before any concentration can, therefore, take place.

When the matte is to be treated by a "pyritic" process, either alone or together with ore, it is, of course, charged in a lump form, and the form of blast furnace employed is that used for the pyritic smelting of ores. When, however, the matte has to be roasted before concentration, the latter operation can be conducted in blast furnaces only under the following conditions:—(1) Kilns or stalls must be used for the roasting operation, so that a large part of the product is still in lump form; or (2) the roasted matte must be "bricked" before smelting and a considerable proportion of rich ore in lump form used with it.

Where reverberatories or mechanical furnaces have been used for roasting and where it is expensive or inconvenient to form the fine roasted matte into coherent bricks before smelting, a reverberatory furnace may be with great advantage used for the smelting process, as is now done at Mansfeld and at several English works. The reverberatories used for this purpose at Argo have been described in the last chapter.

Direct Process.—At the *Burry Port* Smelting Works (S. Wales) James* has found it possible to apply his "*direct*" process to the concentration of argentiferous mattes, and even of those rich in lead, as well as to the copper mattes for which it was invented. In this process a portion of the matte is roasted, and then added to a second unroasted portion and melted down in a reverberatory furnace, sufficient siliceous ore being added to combine with the lead. The classical reaction, $Cu_2S + 2CuO = 4Cu + SO_2$, then takes place, and a very rich white or pimple metal or a rough copper may be produced at will by varying the proportions of raw and roasted matte.

One of the most important advantages of the direct process lies in the fact that the reaction between sulphide and oxide takes place so much more rapidly than in any other method for the elimination of sulphur (*i.e.*, Swansea "roasting" or bessemerisation) that the loss of silver and copper by the combined agencies of "boiling" and true volatilisation usually so considerable at this stage is practically nil. James indeed claims that there is no volatilisation of silver during the ordinary calcination of argentiferous mattes rich in lead, but most metallurgists will probably require more complete proofs than those brought forward before allowing that there is no volatilisation loss during the dead roasting of an ordinary leadworks matte. It is, however, certain that even in presence of PbS the volatilisation of silver is quite small up to the point at which Ag_2S begins to be decomposed, and therefore the total loss in both stages of the "direct" process has thus far proved to be a negligible quantity.

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* *Trans. Inst. Min. Met.*, vol. v., p. 37.

Blast Furnace Concentration.—If it is preferred to use blast furnaces for concentration, the matte must be more or less perfectly bricked and can then be smelted, together with an equal proportion of coarse material (rich ore and slag), in any form of blast furnace employed for reducing matting, but it is necessary to employ a light blast and to provide ample flue and chamber space to settle out the rather large amount of fine matte-dust which will inevitably be blown over. A very considerable expansion of the walls of the furnace towards the feed-floor is advantageous in all such cases in order to diminish, as far as possible, the velocity of the effluent gases. By the adoption of suitable settlers or forehearths it is possible to produce, together with copper mattes of almost any tenor in silver, slags sufficiently poor to be thrown away. Unless, however, a considerable addition of siliceous ore is made, the slags produced will be more basic than monosilicate, and hence they sometimes form very desirable additions to the charge in the original ore smelting, especially when the ores are deficient in iron.

Treatment of Mattes with upwards of 40 per cent. Copper.—When the concentrated matte contains upwards of 40 per cent. copper, its further treatment may be undertaken in two different ways according to the respective values of its copper and its precious metal contents, to the presence or absence of lead and other volatile metals, and to various local conditions.

When large quantities of concentrated matte are produced, containing 40 to 50 per cent. copper and not more than 1 or 1½ ozs. Ag for each percentage of copper present, while virtually free from lead, antimony, &c., it is advisable to treat it as a copper matte pure and simple, converting it into rough or blister copper either by the process of *bessemerisation* (Manhes process) where labour and fuel are dear, or, where both are cheap, by the Swansea so-called "*roasting process.*" The silver contents of the resulting rough copper are afterwards extracted, usually by electrolysis, though one of the other methods described in the next chapter may be adopted where suitable.

Bessemerisation of Copper Mattes.—This subject properly belongs to the metallurgy of copper, and works on that subject should be consulted for details.[*] It will be sufficient to mention here that mattes of 40 to 50 per cent., first melted in cupolas and then run into the converters in charges of from 2500 to 20,000 lbs., are blown with a blast which varies in pressure from 5½ to 16 lbs. per square inch, according to the interior form of the converter and the height of the column of molten material.

The blowing is conducted in two stages. In the first stage

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[*] *v.* Peters, *Metallurgy of Copper*, 7th edition, pp. 528-575; also *Min. Ind. N.Y.*, vol. i., pp. 151-162; vol. iii., pp. 223-231; and Hixon, *Notes on Lead and Copper Smelting*.

the matte of whatever grade (over 50 per cent. being preferred) has its iron completely oxidised, and becomes concentrated to "white" or "pimple" metal with 75 to 80 per cent. copper. The converter is turned down and the slag skimmed off, after which the converter is turned up again, a little cold matte added, and the second stage of sulphur oxidation commences.

The final result is a blister copper of 98 to 99 per cent. Cu, which carries practically all the gold and almost all the silver of the original matte. Considerable quantities of both silver and copper are volatilised and carried away as fine dust, at least 3 per cent. of the latter and 5 per cent. of the former with mattes of moderate richness. With a good arrangement of flues and dust chambers, the actual *loss* of copper may be reduced to from 1 to 1½ per cent., and that of silver to 2 to 2½ per cent., provided the matte is practically free from volatile metals. The flue-dust caught is usually small in amount but it is always very rich.

As a rule, however, the provision of settling chambers is wholly inadequate, and the losses are in reality much higher, though seldom ascertained exactly owing partly to the difficulty of making accurate "clean-ups" without stopping the regular work, and partly to the loose system of bookkeeping frequently adopted. In working up a lot of about 450 tons of matte containing 52·5 per cent. Cu, 72·8 ozs. Ag, and 6 dwts. Au per ton, which was kept separate and cleaned up closely on account of containing 2·2 per cent. of bismuth, the loss of copper was found to be 2·9 per cent. and that of silver 5·6 per cent.*

In presence of considerable quantities of volatile metals the loss is almost incredible, thus a second matte from lead smelting works, containing 40 per cent. copper and from 10 to 15 per cent. lead, when concentrated to blister copper in this way, will lose as much as 33 to 50 per cent. of its silver contents as oxide† —part of which might, no doubt, be recovered by filtering the effluent gases were the quantity of these not so great as to render them inconvenient to handle. It is evident, therefore, that the bessemerising process is only suitable to the treatment of argentiferous mattes when they are practically free from lead and other volatile metals.

Details of the Bessemerising Process.—At the works of the *Anaconda*‡ Company (near Butte, Mont.), now, as regards amount, the second producer of silver in the world, the whole of the valuable metals in the ore are concentrated into a matte which contains on an average 56½ per cent. copper, 71 ozs. silver, and 4 dwts. gold per ton.

This matte is blown up in a row of eleven Bessemer converters, each measuring 10 feet high and 6 feet in outside diameter, worked by hydraulic power, the charge with a new lining being

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* *Mineral Industry*, vol. iii., p. 230.

† Peters, *op. cit.*, p. 569.

‡ *Private notes*, 1897.

7000 lbs. increasing to 17,000 lbs. as the lining wears away. The blast pressure is 13 lbs. per square inch, delivered from six tuyeres. Each blow usually lasts in all 1½ to 2 hours, of which the blowing-up to white metal, or "slagging," stage takes forty to forty-five minutes, and the blowing to blister, or "making copper," forty-five to fifty-five minutes, twenty to thirty minutes being taken up by running in the molten charge, skimming off the slag and pouring. Three converters usually form a set or battery, and each set works off about thirty-two blows in the twenty-four hours, the average daily production being thus about 60 to 70 tons of blister copper, containing 98·1 per cent. Cu, 123 ozs. Ag, and 7 dwts. Au per ton.

Each set of three converter stands is provided with seven converter bodies, or shells, of which three are in use at any given time, while two are drying, one is being re-lined, and the seventh is cooling off. The lining usually lasts for nine blows, after which it is so corroded as to endanger the burning of the shell, and must be partially repaired, though a complete new lining is only required for each shell about once in seven weeks on an average. The lining is composed of quartz as pure as possible, crushed to pass a ⅝ trommel, and then mixed, coarse and fine together, with any available clay as plastic as possible but not necessarily at all refractory, the proportions being from two to four shovelfuls of clay to each wheelbarrow of crushed quartz. The mixture is made in an ordinary mortar mill, using as little water as possible. For the bottom the mixture is about six parts of quartz to one of clay tamped as dry as possible; for the mouth, re-crushed old lining is chiefly used mixed with one-sixth more clay, wetted, and made up into balls. The drying is usually done by means of a wood fire and a light blast, but in a very large plant a blast of hot air is more convenient.

The corrosion of the lining is necessarily great, for the whole of the iron which is oxidised requires silica in order to form slag. Many attempts have been made to diminish this corrosion by blowing in sand together with the blast or by throwing sand or finely-ground siliceous ore on its surface. Such added silica, however, rises at once to the surface of the bath, and there becomes aggregated into almost infusible lumps which float about in the slag and destroy its fluidity without effecting much saving of the lining. When magnesite bricks were tried as lining the difficulty of supplying silica became even more pronounced, while other troubles were experienced, including "scaling" of the bricks themselves and overheating of the converter shells owing to the comparatively high heat-conductivity of magnesia. Practically, therefore, it is better to put up with a normal corrosion of lining than to attempt to reduce it by any of the methods commonly employed in other kinds of smelting operations.

After running in the molten matte from the re-melting cupola (Parrot and Anaconda) or from the ladle (Great Falls), the blast must be turned on full before the converter is turned up in order to prevent clogging of the tuyeres. A high pressure of blast (over 11 lbs. per sq. in.) is with ordinary shaped converters much more easily managed and requires less clearing of the tuyeres, though it gives rise to greater losses by projection and volatilisation.

As the iron becomes slagged, the flame, at first dense and accompanied by white smoke clouds composed of oxides of the volatile metals, shortens, and turns, first green and then pale blue, showing that practically all the iron has been slagged off. The converter is then turned down, the blast turned nearly off, and the slag skimmed into slags-pots, after which any scraps, chips, and floor sweepings are thrown in, together with a few lumps of cold matte (Parrot) or a few shovelsful of siliceous ore (Anaconda).* The blast is turned on, the converter turned up again, and the second stage of blowing continued until the flame turns from blue through rose to brownish-red, and until the small globules projected by the blast, instead of glowing and attaching themselves to the hood wall, appear to cool instantaneously and rebound sharply.

The copper is poured either into cast-iron moulds or, as at *Anaconda*, into copper moulds with cast-iron bottoms, made on the works, casting being done by tilting the converter gradually over a row of moulds on a truck, which is run back under the converter as the moulds are filled. It may also, as at *Great Falls*, be poured into ladles and cast direct into anode plates. A very ingenious gas-fired cylindrical tilting furnace together with a small hydraulic ladle-crane are used at *Anaconda* for taking the molten copper from the ladle, keeping it at the right temperature and casting the anode plates continuously.

Converter Slags, &c.—The converter slags are naturally always rich enough for re-smelting. At *Anaconda* they vary from 0·7 up to 5·3 per cent. Cu, averaging about 2 per cent. copper and 1½ ozs. silver per ton. They are taken up to the feed-floor in the original slag-pots and re-smelted in the ore furnace while still red hot, forming a useful flux, since they contain about 36 per cent. SiO_2, with over 50 per cent. FeO and hardly any CaO or Al_2O_3.

At *Great Falls* the converter slag, skimmed into a ladle, is conveyed by an electric crane to the large ore-tilting reverber-

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* It is a remarkable fact that the noses which commence to form on the tuyeres as soon as the iron is nearly all oxidised are melted off in a few moments by either of these additions. It is not easy to see the *modus operandi* of either, but the fact remains that either a couple of cwt. of cold matte or 75 to 100 lbs. of siliceous ore will rapidly melt off noses which otherwise would soon choke up the blast altogether and lead to freezing-up of the charge.

atories already referred to, and is poured upon the charge there just before skimming, by which means its copper contents are reduced so low that it can be poured off and discarded, together with the ore slag proper. The flue-dust is bricked and returned to the ore furnaces.

Cost of Bessemerisation.—The exact cost at each individual works is jealously guarded, but according to Peters [*] the average cost at Butte (Montana), the principal centre of the process, per ton of 2240 lbs., is as follows:—Labour, 12s. 10d.; power, 7s.; remelting cupola, 6s. 6½d.; supplies, 5s. 1½d.; repairs, &c., 5s. 10d.—total, 37s. 4d., in which estimate nothing is allowed either for interest or depreciation, the latter of which is a considerable item.

Where water power is available for producing the blast and the matte is taken from the ore blast furnaces direct to the converters without re-smelting, the total cost does not exceed 28s. per ton of 2240 lbs.

Concentration by Roasting and Smelting.—Where labour and fuel are both cheap it may be just as economical to convert matte into blister by this process as by bessemerisation, while the expenditure for plant is less and the loss of silver almost nil instead of being very considerable (for instance, 2½ to 3 per cent. as a minimum).

Since, however, the cost of silver extraction from blister copper is higher than from white metal or other rich matte, it is usually advantageous to stop the simultaneous concentration of silver and copper at the white metal stage, or even lower in the case of impure mattes containing much lead; to extract the silver by the Ziervogel or by one of the special processes subsequently to be described, and then to extract the copper from the residue either by reducing it to metal (Mansfeld) or by converting it into sulphate (Freiberg).

At *Mansfeld* [†] the ore matte (with 40 per cent. Cu and 70 ozs. Ag per ton) is roasted in kilns from 25 per cent. sulphur down to about 10 per cent., and, together with 5 to 7 per cent. of unroasted matte and slags from a previous operation, is smelted in a small Swansea reverberatory blister furnace to white metal and a small quantity of copper bottoms. During 1889, 41,400 tons of roasted matte yielded 51 per cent. by weight of concentrated matte with 75 per cent. Cu and 144 ozs. Ag per ton, and ¾ per cent. by weight of bottoms with 96 per cent. Cu and 306 ozs. Ag per ton. Each charge consists of 2 to 2¾ tons of roasted matte together with 1 to 2 cwt. of quartz sand. It is charged, spread, and fired hard for three to three and a-half hours before the first rabbling. Firing and rabbling is repeated till it rises off the bottom, when, after a final heating, the furnace is tapped out, by means of a movable spout, over a few shallow

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[*] *Op. cit.*, p. 569.

[†] Egleston, *S. M. Q.*, vol. xii., p. 199.

pots to catch the bottoms, the matte running on and solidifying quickly in a thin sheet on cast-iron plates—an arrangement employed to prevent separation of metallic silver on slow cooling. As soon as the slag appears the stream is turned into a series of settling pots. On an average each charge takes six hours to work off, the quantity treated by each furnace averaging from 8 to 9 tons per day with a fuel consumption of 9 per cent. coal. Each ton of matte yields about 10½ cwts. of slag with 9½ per cent. copper as shots and combined.

The concentrated matte is then roasted and desilverised by the *Ziervogel* process,* the residues containing 8 to 13 ozs. silver being re-roasted and submitted to the process a second time, which brings down their silver contents to 5 or 6 ozs. per ton.

At *Freiberg* the ore matte containing 24 to 30 per cent. Cu, 5 to 8 per cent. Pb, and 25 to 50 ozs. Ag per ton is concentrated by similar methods up to 69 to 74 per cent. Cu, 3 to 7 per cent. Pb, and 75 to 190 ozs. Ag per ton, its subsequent treatment being by the Freiberg sulphuric acid process.

Extraction of Silver from Mattes.—The treatment of concentrated argentiferous copper mattes, when it is desired to extract the silver direct without first producing blister copper, may be carried out in various ways, as follows :—

Methods suitable only to Rich White Metals fairly free from Impurities.

(1) *The Ziervogel process.*
(2) *The Freiberg sulphuric acid process.*

Methods applicable to Impure Mattes Rich in Lead.

(*a*) (*Dry processes.*)
  (3) *Stirring with lead in a molten condition, or "sweating" on a lead bath.*
(*b*) (*Wet processes.*)
  (4) *The Zalathna acid process* (*for iron mattes only*).
  (5) *The Hunt-Douglas process.*

1. **The Ziervogel process** itself has been already described in Chapter X., to which reference should be made for details.

Treatment of Residues from the Ziervogel Process.—At *Mansfeld*† the final residues, after being twice submitted to the process, contain 75 per cent. Cu (as CuO), 5 or 6 ozs. Ag per ton, and practically no traces of gold. They are dried, mixed with about 9 per cent. of fine coal and then smelted direct to refined copper in a refining furnace of more or less English pattern, without any intermediate production of blister. The total charge is 10 tons, of which, however, only 8 tons are added at first, the remainder following after five hours. Melting down takes nine to ten hours, and drawing the slag one hour more. Oxidation

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* See chap. x.

† Egleston, *S.M.Q.*, vol. xii., p. 208.

of the residual sulphur, iron, and zinc takes five to six hours, and the various "polings" three or three and a-half hours, while ladling the "tough pitch" copper takes from two to two and a-half hours. In all, allowing for charging and fettling the furnace, one ore charge can be worked off per twenty-four hours. The resulting refined copper contains 99½ per cent. Cu and 0·25 per cent. Ni with traces of Fe, Pb, and Ag.

At the *Argo Works** the matte treated by the Ziervogel process is very much richer in silver than at Mansfeld, containing, indeed, on an average, 700 ozs. as already stated. The residues, besides containing about 45 ozs. Ag per ton, contain over 60 per cent. Cu (as CuO) and about 10 ozs. of gold per ton. They are re-smelted, together with rich siliceous and pyritous gold-bearing ores low in silver, and yield a "residue metal" which contains 65 per cent. copper, about 90 ozs. silver, and 10 to 15 ozs. gold per ton, the slag being clean enough to throw away.

The separation of gold from this matte is effected by the old Welsh "bottoms" or "best-selecting" process, the pigs of matte being piled on the hearth of a reverberatory furnace and gradually roasted down so as to obtain a certain proportion of the copper (in practice about one-fifteenth) in the metallic condition. The charge of matte is 12 tons, and the roasting period takes about seven hours, almost all of which is taken up in oxidising the iron of the matte, very little copper being oxidised. At the end of this period the air openings are closed and the heat raised so as to thoroughly liquefy the charge, a reaction then taking place between copper oxide and unaltered sulphide by which metallic copper is formed and falls to the bottom of the charge, carrying with it practically all the gold together with Pb, Bi, As, and other foreign metals. The "bottoms" thus obtained average 60 per cent. Cu, over 30 per cent. Pb, and from 100 to 200 ozs. Au and 300 ozs. Ag per ton. They are treated by a "secret process" further referred to below.

The "finished matte" which remains above the bottoms in the foregoing process contains 77 per cent. Cu, 90 to 100 ozs. Ag, and from 2 to 4 dwts. Au per ton; it is again treated by the Ziervogel process, but in a separate set of furnaces, to avoid mixture with the ordinary gold-bearing matte. The residue from the second Ziervogel treatment contains less than 11 ozs. Ag per ton, and impurities, such as lead, arsenic, &c., having been removed in the copper bottoms, consists of practically pure CuO. It is not treated further at the works, but finds a ready market with the petroleum refiners, portions not thus used being shipped east to bluestone works or reduced with slack coal to refined copper, according to the condition of the market for bluestone.

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* *Private notes*; see also Pearce, *Trans. A.I.M.E.*, vol. xviii., pp. 460, et

Extraction of Gold from the Bottoms.—The treatment of the copper bottoms at Argo is conducted by a "secret process," which, however, probably consists first in melting and *granulation*, followed by *scorification*, either with pyrites (Gilpin County concentrates) by which means most of the copper is "matted" leaving the precious metals in a greatly enriched "bottom," or else by slow oxidation to form oxide of copper, which is then slagged away by successive additions of litharge, leaving nothing but a rich gold-silver alloy. In all probability the process as worked at Argo comprises both operations, the bulk of the copper being scorified away with pyrites, while the rich alloy is then oxidised, and scorification finished with the aid of litharge and powdered quartz to form a lead slag, which carries away the last remains of copper and other base metals, leaving the gold and silver on the hearth.

The slags and matte produced during scorification with pyrites would be simply returned to the "pimple-metal" furnace and re-worked with the regular charge. The litharge slag produced is glassy and red like copper-refining slag, and is sold to the lead smelters for its lead, silver, and copper contents.

The following analyses of the copper bottoms and of the slag produced by their scorification with litharge are by Trippel.[*]

Copper Bottoms.	
Cu,	92·56
Ag,	1·01
Au,	2·93
Bi,	1·14
Sb,	0·57
As,	0·12
Fe, Pb, Zn, &c.,	1·67
	100·00
Ag per ton,	330 ozs.
Au per ton,	1045 ozs.

Litharge Slag.	
SiO_2,	14·48
PbO,	60·91
Cu_2O,	11·53
FeO,	6·08
Al_2O_3,	4·97
MgO,	0·14
CaO,	trace
Sb_2O_3,	trace
Ag,	undet.
	98·11

The "bottoms" now produced at Argo are much richer in lead and poorer in gold than would be indicated by the above analysis.

2. **The Freiberg Sulphuric Acid Process.**[†]—This process depends upon the formation of copper sulphate by dissolving the sweet-roasted matte in sulphuric acid. Iron would interfere with the crystallisation besides using up acid to no purpose, therefore it is an essential condition of the process that the matte shall be concentrated to a 70 to 72 per cent. white metal. Further concentration (*e.g.*, to pimple metal) is, however, not advantageous, owing to the formation of metallic copper, and a

[*] *E. and M. J.*, June 23, 1888.

[†] Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 624.

small percentage of lead does not interfere with the subsequent process.

The white metal, concentrated by several roastings and smeltings, as already described, contains 70 or 74 per cent. Cu, 3 to 7 per cent. Pb, 0·3 to 0·4 per cent. Ag, 0·2 per cent. Fe, 0·3 per cent. Co and Ni, 0·5 to 1 per cent. Sb and As, and 14 to 19 per cent. S. It is dead roasted in small reverberatory furnaces, the charge of 1 ton remaining in the furnace for sixteen hours; it is afterwards passed through a sieve to separate any imperfectly roasted portions, which are re-crushed and returned.

Solution takes place in cylinders of hard lead, provided with stopcocks at the bottom and measuring about 4 feet 6 inches in diameter by 4 feet high. Into each of these is charged 4 cwts of chamber acid (50° B.), together with an equal quantity of water, and steam is then introduced to heat the mixture. When boiling, the calculated quantity of roasted and sifted white metal (now almost entirely reduced to oxide) is introduced in quantities of 100 to 150 kilos. at a time and well stirred with a wooden paddle. More water or mother-liquor from the crystallisation tanks is added from time to time to keep the copper sulphate in solution. When the acid is nearly all neutralised (which takes five hours) the mixture is allowed to stand for one hour to settle out the silver slime, and the supernatant liquor then syphoned off with a leaden syphon into crystallising vessels. The first crystals enclose some silver precipitate and are re-dissolved, run through a filter of granulated copper in another hard lead cylinder to separate any silver in solution, and re-crystallised on leaden strips as usual. Any bluestone containing as much as 0·35 per cent. Fe is re-dissolved and re-crystallised.

The mother-liquors are used over and over again till they become too rich in iron, when the still remaining copper is precipitated with scrap-iron.

The silver slime contains from 1 to 2 per cent. Ag, 5 to 11 per cent. Cu, and about 40 per cent. Pb. It is purified by washing with steam and dilute sulphuric acid, filtered and dried, and then smelted with silver ores to rich work-lead.

Matte for the Freiberg process must be more free from iron than for the Ziervogel process, in which 10 per cent. Fe is no disadvantage, but it may contain relatively considerable quantities of Pb, As, Sb, &c., none of which interfere to any extent when present to the amount of a few per cent., though they would be fatal to clean work in the Ziervogel process. Where sulphuric acid can be obtained cheaply and there is a good market for the copper sulphate, the process is, therefore, sometimes more suitable than the Ziervogel, especially as the per-c xtraction of silver is much higher.

3. **Melting and Stirring with Lead.**—This very old process is still in use in a few Continental localities.

At *Gawrilow* (Altai)[*] the barytic matte described in Chapter XV., containing 6 per cent. Cu and 45 to 55 ozs. Ag per ton,[†] is melted down in a small hearth of brasque by means of coal fuel and a blast. When completely melted the slag is skimmed off and the surface of the bath covered with sticks of charcoal, upon which small bars of lead are placed. The lead gradually melts and drops through the matte bath, absorbing in its progress the greater part of its silver contents. When the lead has all melted down, a green pole is thrust to the bottom of the bath and held there for three minutes, the vigorous evolution of gases ensuring a thorough mixing. The bath is then allowed to stand a few minutes, and the lead tapped out from the bottom. The process is repeated three successive times with similar additions of lead, by which the silver contents of the matte are reduced to from 8 to 12 ozs. per ton. Only the first tap of lead which contains about 115 ozs. Ag per ton is cupelled, the subsequent additions being used over again for the next charge of matte. The loss of silver by volatilisation and dusting is said to be 6 per cent. of the total present in the matte, the loss of lead being sixteen times that of the silver.

At *Kongsberg* (Norway)[‡] a similar process was formerly in use for concentrated matte, but the lead was added direct to the tap-pit of the concentrating blast furnace after skimming off the slags. Six cwts. of lead were used for each ton of matte, and thoroughly stirred in with an iron paddle. Although the lead was by this means enriched to 5 per cent. silver the matte was very incompletely desilverised, still containing 240 to 300 ozs. per ton. Its further desilverisation was carried out by smelting with litharge and other refinery products. In spite of the imperfection of the direct desilverisation with lead it was found advantageous under the conditions formerly prevailing at Kongsberg, since in the small rude blast furnaces then employed the loss of silver in slags and by volatilisation was very high, and directly in proportion to the richness of the material treated.

It is worth noting that the proportion of silver which can be extracted from matte by means of lead is greater the higher the temperature and *vice versâ*. When too cold the matte will even re-absorb a portion of silver from rich lead. On the other hand, a high temperature means high volatilisation loss.

The Crooke Process.[§]—This is based upon the process already described, with the important difference that it is carried on in

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Schnabel, *op. cit.*, p. 494.

Analysis of this matte will be found in Table xxii., p. 275.

[‡] *v.* Percy, *Metallurgy of Silver and Gold*, p. 510.

[§] Hofmann, *Met. of Lead*, p. 267; Douglas, *Journ. Soc. Arts*, Aug. 30, 1895.

larger furnaces, that the matte is not melted but remains in a granular condition, and that the subsequent treatment of the desilverised residue is carried out on more modern lines.

The process was until recently in use at the works of the *Pueblo Smelting and Refining Co.* (Pueblo, Colo.). The matte was coarsely crushed and spread over a bath of metallic lead kept at a red heat; after a short time nearly all the gold and about three-fourths of the silver present were found to have been sweated out and absorbed by the lead bath. The matte absorbs some lead and the lead some copper; the amount of the latter, however, can be kept low by introducing bars of iron, which are fastened across the furnace at the bottom of the lead bath.

Four reverberatory furnaces similar to softening furnaces, and holding 25 tons each, were employed in this process, arranged in terrace form so that the lead from one can be tapped into the next below. The matte was introduced first into the lowest furnace containing the richest lead, on the surface of which it was stirred about for three-quarters of an hour, after which it was skimmed off and passed successively over each of the others, so that its silver contents were nearly extracted by the time it reached the uppermost bath of nearly pure lead. Each charge of matte weighed 3000 lbs., and took about six hours passing through the series of four furnaces; the total quantity treated per day was about 25 tons, allowing for time lost in charging, transferring, and discharging the lead.

The enriched lead tapped from the lowest furnace contained from 2 to 3 per cent. copper with a little arsenic and antimony. It was softened and desilverised as usual.

In this process the matte, which often carries under 1 oz. Ag per ton, is desilverised by four distinct operations in as many separate furnaces.

(*a*) The granular lead-bearing matte is roasted in a reverberatory calciner to oxidise the iron and reduce its sulphur contents down to about 13 per cent.

(*b*) It is then oxidised with thorough rabbling in another reverberatory, having a tuyere on each side of the bridge, the temperature being kept below the melting point of copper. The oxide formed by the blast reacts on residual sulphide, reducing copper to the metallic condition as "moss copper," while some lead, arsenic, and antimony are volatilised, part, however, remaining as oxide.

(*c*) The charge is transferred to a blister furnace and there melted down, the first slags, containing lead, arsenic, and antimony, being drawn separately and used for antimony metal smelting, while those formed subsequently contain much copper and go back to the matte concentrating furnace.

ister copper, containing 99 per cent. of metal, tapped into moulds from the preceding furnace, is re-melted, refined, and poled in the usual way.

4. **The Zalathna Acid Process** (**for iron mattes only**).—At *Zalathna* (Transylvania)* an iron matte containing about 12 ozs. silver and 4½ to 5 ozs. gold per ton† is ground in a Ball mill and then treated in lead-lined vats with chamber sulphuric acid, the charge for each vat being 8 cwts. of matte and 31 cwts. of acid. The mixture is stirred by rotary paddles, and solution requires thirty-six hours. The sulphuric acid is obtained from the roasting of the pyritic ores in shelf furnaces preparatory to their fusion, 1·3 tons of chamber acid being obtained from each ton of ore, nearly all of which is used in the works. The H_2S given off from the vats is conducted to towers, where it is mixed with SO_2 from the pyrites burners, and free sulphur is precipitated (Schaffner and Helbig process). The fine precipitated sulphur is melted by steam under pressure and cast in moulds, the quantity recovered being about 4½ cwts. per ton of matte treated in the works. The sulphur being very pure is converted into carbon bisulphide, CS_2, for more advantageous sale.

The sulphate liquors are crystallised, and the green vitriol sold, its weight equalling that of the matte dissolved.

The insoluble residue is about 10 per cent. by weight of the matte treated, or 3·33 per cent. of the weight of the original ore. It contains Fe 19 per cent., Pb 16 per cent., Cu 7·4 per cent., Ag 0·36 per cent., Au 0·15 per cent., and S 22·2 per cent. It is not washed in any way, but with the adhering ferrous sulphate liquor is allowed to dry in the air for four or five days, and smelted together with rich roasted pyritic and lead ores, giving a rich lead bullion and a copper matte. The latter is sold to copper smelters; the former is cupelled in a German hearth yielding doré bullion 334 fine in gold and 664 in silver, which is parted in the Mint at Kremnitz.

This process is only economically practicable when a supply of cheap sulphuric acid is available and when there is a market for green vitriol. In the vast majority of cases it is much more advantageous to concentrate the matte by roasting and smelting in the usual way, working up the concentrated matte by such of the processes already described as may be best suited to the composition of the matte and to the local conditions.

5. **The Hunt-Douglas Process.**‡—This process was until very recently in use at the Argentine works of the Con. Kan. City S. and R. Co. for treating direct the twice-run lead furnace matte containing 25 to 30 per cent. Cu, not over 15 per cent. Pb, and not over 300 ozs. Ag per ton. The operations are as follows :—

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* Farbaky, *Berg- und Hüttenmannische Zeitung*, 1894, p. 177.

† For composition of this matte *v.* chap. xv., p. 275.

‡ *v.* Hofmann, *op. cit.*, p. 269; *Mineral Industry*, vol. ii., 1893, p. 295; Douglas, *Journ. Soc. Arts*, No. 2232, Aug. 30, 1895.

(*a*) The finely pulverised matte is roasted slowly at a low temperature so as to produce as much copper sulphate as possible without forming silver sulphate, the roasted matte still containing 8 to 10 per cent. sulphur, mostly as sulphate. It is then leached out with dilute sulphuric acid (10 per cent. H_2SO_4); the residues, containing all the lead, iron, silver, and gold of the original matte together with a portion of the copper, being returned to the blast furnace.

(*b*) The copper sulphate liquors, after filtering, are run into chloridising vats, where they are treated with calcium chloride solution from a previous operation in quantity more than sufficient to form Cu_2Cl_2 with the whole of the copper present. Calcium sulphate is formed by the double decomposition, and is allowed to settle out, dried, and burned for plaster of Paris—

$$CuSO_4 + CaCl_2 = CuCl_2 + CaSO_4.$$

(*c*) The cupric chloride liquors, now containing 6 to 8 per cent. of copper pass to "reducers" or closed wooden vats, through which sulphurous acid gas is pumped by a bronze force-pump. The gas is generated by burning pyrites in a Douglas "central flue" cylinder calciner with carefully regulated supply of air, and washed in a coke tower before being pumped through the vat. Three hours passage of strong gas is sufficient to reduce the copper contents of the solution to about 1½ per cent., a heavy precipitate of Cu_2Cl_2 settling out. It is impossible, however, to get anything like complete precipitation, because cuprous chloride is slightly soluble in sulphuric acid and still more so in hydrochloric acid, both of which are set free by the reaction as shown by the equation :—

$$2CuCl_2 + SO_2 + 2H_2O = Cu_2Cl_2 + 2HCl + H_2SO_4.$$

The acid molten liquor is freed from SO_2 by blowing hot air through it, after which it is used again together with more sulphuric acid as the solvent for a fresh charge of matte, by which any iron present and oxidised by the air current is again reduced. Zinc, nickel, and other metals, as well as iron, gradually accumulate in the solution, which has to be purified at intervals by concentration and crystallisation.

(*d*) The precipitated cuprous chloride is reduced by milk of lime in so-called "converters" to cuprous oxide, regenerating calcium chloride for use in the "chloridisers." The cuprous oxide is pumped into filter-presses and there washed, the cakes being dried and smelted direct in a refining furnace to ingots of high quality.

CHAPTER XVIII.

SILVER-COPPER SMELTING AND REFINING.

REFERENCE has been already made (Introductory to Section IV.) to the fact that some ores of the precious metals may be concentrated by smelting processes, using instead of the familiar *lead bullion* or *matte*, *speiss* or *metallic copper* as vehicles for concentration.

Silver-Copper Smelting—*Limitation of the Method.*—The use of metallic copper is confined to ores comparatively free from sulphur, arsenic, and lead, since the first would give rise to the production of matte, the second to that of speiss, while the third would yield alloys of copper and lead, which are subject to very heavy deductions at the refining works.

It is but rarely that silver ores practically free from lead and from sulphides of the heavy metals are found in the neighbourhood of ferruginous oxidised ores of copper. Such cases do occur, however, particularly in parts of Mexico and S. America, and in these cases smelting to argentiferous black copper is at once indicated as the cheapest and most direct method of bringing the metallic constituents of the ores into a portable and marketable form. Unfortunately, however, the scope of the process is still further limited by the scarcity of fuel in many of the very localities where it would otherwise be the ideal process of ore treatment.

*Plant Employed.**—The plant is identical with that employed in Arizona for smelting the non-argentiferous carbonate of copper ores, once so common in various parts of that territory, to pig-copper. The furnaces are completely water-jacketed, the jackets being usually of wrought iron or mild steel, though sometimes the inner skin is of thick sheet copper. They always have an interior "sump" for the separation of the fused products, because the comparatively high fusing point of metallic copper and its low specific heat cause it to chill much too rapidly to admit of the employment of exterior forehearths.

Some suitable form of "settler" or overflow pot is, however, provided for the collection of small globules of matte or metal carried over by the slag stream, and the addition in this settler of thin sheet scrap-iron (as first practised by the author) affords an opportunity of saving some of the combined copper and silver in the slag.

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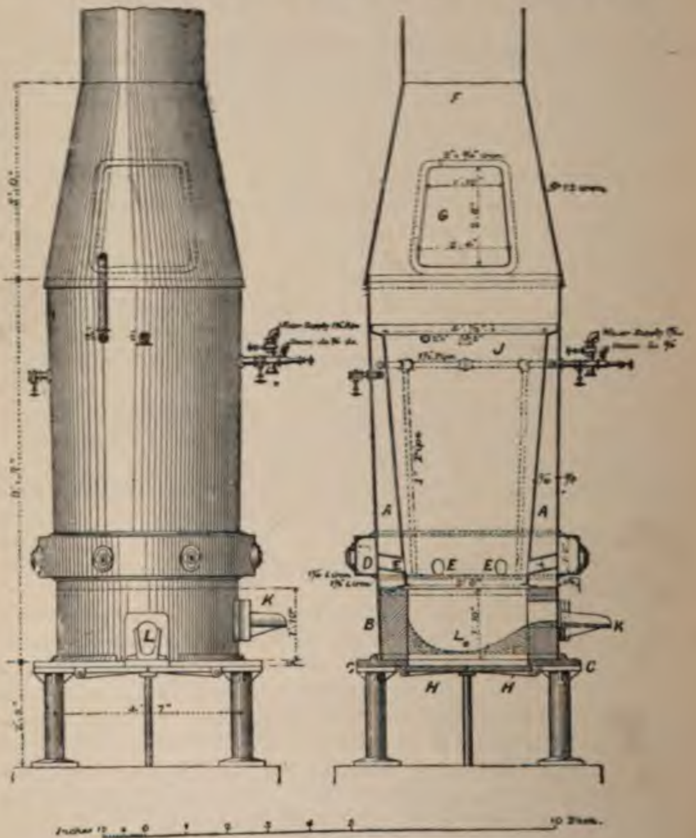
* *v.* the author's paper in *Proc. Inst. Civ. Eng.*, vol. cxii., p. 148.

It is usual to support the whole of the furnace upon cast-iron base-plates resting on short corner columns, the bottom of the interior crucible being formed of one or more pairs of drop-doors with a thin brick or brasque lining.

Figs. 73 and 74* show in section and elevation the small 36-inch circular water-jacketed pig-copper furnace. A is the jacket of



Figs. 73 and 74.—Pig-copper Furnace.

mild steel plate and B its downward continuation, a mere boiler plate brick-lined shell resting on the base-plate, C. At D is shown the windbox forming a circle round the furnace and giving access to the six tuyeres, E, opposite each of which is a mica- or glass-covered peep hole. F is the sheet-iron hood,

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* *Proc. Inst. Civ. Eng.*, vol. cxii., plate ii.

G the charging hole, H H the drop doors, and J the water-circulating pipes in the jackets; K is the slag spout, and at L is the copper taphole provided with its spout.

Another form of furnace, much to be preferred for working on a large scale, is that already described and shown in Fig. 68.*

Mode of Working.—Small charges must be employed in order to secure powerful reduction; as a rule, charges of not more than 40 to 50 lbs. per square foot are best. With small furnaces it is of great importance that the charge should not contain any large proportion of fines or of lumps larger than a man's fist. It is also important to keep the bottom hot by walling up the open space between the foundation columns, preventing the circulation of air and so diminishing the loss of heat by radiation.

The degree of concentration, which is in practice convenient in this method, varies according to the richness of the ores from about 10 to 20 of ore into 1 of product. The higher of these ratios is about the extreme practical limit, for the quantity of product is then so small that it chills readily and gives a good deal of trouble in keeping the bottom hot. Taking, for example, the small 36-inch round furnace, even with a coarse fusible charge it will rarely be possible to put through more than 40 tons per day; and with charges containing, on an average, 25 per cent. of fines, 25 to 30 tons is about the limit. At 30 tons per day, and with a concentration of 20 tons into 1, the total weight of product would be only 30 cwts. per day, or about 1½ cwts. per hour, which is barely enough to keep the bottom in reasonably good condition.

The copper is tapped about every hour into cast-iron (or cast-steel) moulds on wheels, a potful or two of slag being allowed to follow the copper through the same taphole in order to assist in keeping the bottom hot. With the same object in view the pigs of copper are sometimes returned to the furnace in order to keep a considerable quantity always in the crucible, but this practice has the drawback of exposing the precious metal contained in the ore to a double loss by volatilisation if not by slagging. As a rule, it is best to tap the furnace for pig-copper regularly every hour, and only return scraps detached in cleaning-up and from the settlers and mis-shapen pigs. In any case, to keep the tapping breast and bottom of a black-copper furnace in proper condition requires much more care and attention on the part of the furnace foreman than in the case of matte, the specific heat of which is so much higher.

Slags, &c.—As regards slag composition almost any proportion of silica may be run, varying from 25 up to over 50 per cent. With the higher proportions, however, the loss of copper is much increased, owing to the formation of silicates from which

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* Chap. xiv.

the metal, in the absence of sulphur to combine with it, cannot be reduced with any reasonable consumption of fuel.

As a matter of practical convenience sesquisilicate slags with about 40 per cent. SiO_2 give about the best results. The general formula of such slags may be written :—

$$x(2FeO . SiO_2) + y(CaO . SiO_2) + z(Al_2O_3 . 3SiO_2)$$

where the ratio $\frac{x}{y}$ may vary between $\frac{1}{3}$ and $\frac{3}{2}$ and $\frac{z}{x + y}$ may be from $\frac{1}{20}$ or less up to $\frac{1}{6}$.

When the ores are very siliceous a bisilicate may be run ; thus the slag run by the author on one occasion for thirty-one days continuously when flux ores were scarce (Column 3, Table XXIII.) possessed the following composition :—

$$8(FeO . SiO_2) + 4(CaO . SiO_2) + Al_2O_3 . 3SiO_2,$$

and ran fairly well, though very sticky and containing more combined copper than usual.

Aluminate slags may also be run as described by Henrich.*

Costs, Losses, &c.—The percentage rate of extraction in this process is at least as great as by any other process on poor ores. Thus, in the case described in Table XXIII., 91·7 per cent. of the silver was actually extracted from a mixture of ores containing only 7½ ozs., and 91·3 per cent. of another mixture containing 13·3 ozs., the rate of concentration being about 18 to 1. During another month's run on low grade copper ores alone, with a degree of concentration of 35 to 1, the extraction of silver was 88 per cent. of the total.

The loss of copper in slags, though certainly no greater than that of lead in lead smelting with siliceous ores, is of more importance owing to the greater intrinsic value of the former metal ; on the other hand, there is practically no loss by volatilisation. The absolute loss of copper—viz., 1½ to 1¾ per cent. —is much greater than the loss of that metal in matte smelting, and, owing to the absence of all reducing effect of sulphur, by far the larger part of the copper lost in slags exists in a combined state as silicate.

The cost of smelting on a copper basis is not materially greater than on a matte basis. As with every other kind of smelting, the cost will depend chiefly upon local circumstances, the prices of coke and of fluxes, and upon the capacity of the furnace plant, small furnaces being much more expensive to run than those of larger size. Some figures of cost under different circumstances are given in Table XXVII.

One of the disadvantages of the silver-copper smelting process is the way in which small quantities of impurities in the ores become concentrated in the product. This is shown by the

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* *E. and M. J.*, Dec. 27, 1890.

following partial analyses from Torreon, A being the product of the run detailed in column 1 (Table XXIII.), while B and C correspond respectively with columns 2 and 3 of the same Table, and D is an analysis of black copper from Oker added for the sake of comparison.

TABLE XXVI.—Analyses of Argentiferous Coppers.

	A	B	C	D
Copper, ...	95·7	86·68	96·5	92·636
Iron, ...	0·33	0·35	0·38	0·157
Lead, ...	undet.	3·06	...	0·337
Bismuth, ...		0·64	...	0·464
Zinc, ...		0·27	...	...
Nickel and Cobalt, . .		trace	...	0·245
Silver, ...	0·36	0·73	0·30	0·405
Antimony, ...	trace	trace	...	2·950
Arsenic, ...	1·12	3·29	...	2·154
Sulphur, ...	0·25	1·75	0·31	...
Insoluble, Oxygen, &c., .	undet.	undet.	...	...
	97·76	96·77	97·49	99·348

References.—A, B, and C. *Author.* D. *Min. Ind.*, vol. iv., 1895, p. 14.

The impurity of the resulting product, as soon as any very large quantity of silver ores containing considerable traces of lead and arsenic is smelted, is shown in analysis B; this is one of the principal drawbacks to the process, since impure copper of that description is subject to heavy refinery deductions.

TABLE XXVII.—Silver-copper Smelting at Torreon, Mexico.

	Normal Work.		Siliceous Slag.
Proportion of silver ores (siliceous), .	Small.	Considerable.	None.
Dimensions of furnace at tuyeres, .	36-in. diameter circular.		
Height tuyere line to feed-floor, .	7 ft. 6 ins.		
Material of jackets, ...	wrought-iron.		
No. and diameter of tuyeres, . .	six of 3 ins. diameter.		
Total area of tuyeres, . sq. ins.,	42·42		
Sectional area at tuyeres, . sq. ft.,	7·07		
Tuyere ratio, ...	0·600		
Tonnage put through, 24 hours, .	40·5	28·0	40·4
Average hearth efficiency, . . .	5·73	3·96	5·71
Average tuyere efficiency, . . .	0·955	0·66	0·951
Average blast pressure, . . .	8 ozs.	10 ozs.	11 ozs.
Concentration, tons into 1, . .	17·8	17·9	35

TABLE XXVII.—*Continued.*

	Normal Work.		Siliceous Slag.
Composition of charge:—			
1st class copper ore (siliceous),	100 lbs.	55 lbs.	...
2nd class copper ore (ferruginous),	350 ,,	100 ,,	415 lbs.
Silver ores (siliceous),	25 ,,	80 ,,	...
Limestone flux,	...	30 ,,	...
Foul slag,	50 ,,	25 ,,	25 ,,
Total charge,	525 lbs.	290 lbs.	440 lbs.
Weight of coke to above charge, lbs.,	90	55	70
Percentage of fuel employed,	17·1	19	15·9
No. of above charges in 24 hours,	173	215	206
Ore smelted, tons per 24 hours,	36·7	22·6	38·4
Composition of ore charge:—			
Cu, per cent.,	6·77	5·83	5·06
Ag, per ton of 2240 lbs.,	7·5 ozs.	13·3 ozs.	3·25 ozs.
Product per 24 hours:—			
Argentiferous black copper, lbs.,	4611	2814	2196
Argentiferous white metal, ,,	206	342	573
Composition of copper:—			
Cu, per cent.,	95·7	86·7	96·5
Ag, per ton of 2240 lbs.,	118 ozs.	239 ozs.	99·7 ozs.
Au, ,, ,,	11 dwts.	17 dwts.	13 dwts.
Composition of white metal:—			
Cu, per cent.,	77	76	76
Ag, per ton of 2240 lbs.,	56 ozs.	186 ozs.	42·5 ozs.
Composition of slag:—			
SiO_2,	39·41	40·80	50·05
FeO,	36·14	28·50	29·75
Al_2O_3,	4·26	5·10	5·25
CaO,	17·24	20·95	11·00
MgO,	0·21	0·36	0·70
Cu_2O,	1·88	1·64	2·08
S, Pb, Zn, Alkalies,	0·86	2·65	0·80
Total,	100·00	100·00	100·00
Silver per ton of slag,	15 dwts.	1 oz 7 dwts.	10 dwts.
Recovery of copper, per cent.,	82·3	81·2	60·5
Recovery of silver, ,,	91·7	91·3	88
Cost of smelting per ton of charge,	£1 0 8½	£1 6 9	...
Cost of smelting per ton of ore:—			
Labour, including getting flux,	£0 5 7½	£0 10 4	
Superintendence and assaying,	0 2 8¾	0 5 5½	Same
Supplies, oil, light, tools, and repairs,	0 1 2½	0 2 3	as
Boiler fuel, coal, and wood,	0 1 6½	0 2 5	column 1.
Coke at £3, 7s. per ton, delivered,	0 11 4¾	0 12 8½	
er ton of 2240 lbs.,	£1 2 6	£1 13 2	...

Treatment of Argentiferous Copper.—There are two methods of treating argentiferous copper, in both of which the copper is, in the first instance, separated as a solution of copper sulphate, while the silver remains with gold and other undissolved metals as a slime or mud. The *Oker solution method* is cheap and simple, yielding its product in the usually readily saleable form of bluestone, and requires no specially skilled superintendence, but it can only be carried out where a supply of cheap sulphuric acid is available.

The *electrolytic method* now in such general use requires a large and expensive plant and much skilled superintendence, besides cheap fuel or other source of power, but it has the great advantage of turning out nearly the whole of the copper present as "conductivity" metal, fetching the highest price in the market.

The Oker Sulphuric Acid Process.[*]—The argentiferous black copper, containing 92 to 95 per cent. Cu,[†] produced at Oker by smelting roasted copper matte in small reverberatory furnaces, is first purified from Fe, Ni, Co, and S by an oxidising smelting in small reverberatories with sand bottoms holding about 3½ tons, the process lasting about twelve hours. Besides a slag which is returned to the ore-smelting furnaces, the product is a fair blister copper of about 98 per cent. Cu, which is tapped direct into water in order to granulate it. The granulations are then placed in lead-lined vessels and alternately treated with hot dilute sulphuric acid and exposed to the air, by which means the copper oxidises, and is dissolved together with traces of Fe, Ni, and Co, leaving Pb, Ag, and other metals undissolved in the residue. The reaction which takes place may be written—

$$2Cu + 2O + 2H_2SO_4 = 2CuSO_4 + 2H_2O.$$

The plant is simple. A lead-lined solution storage tank contains chamber sulphuric acid, which is diluted with mother liquor to about 30° B., and kept at a temperature of about 70° C. by means of a steam-coil of leaden pipe. Below the storage tank is a row of lead-lined dissolving tubs about 5 feet 3 inches high and 2 feet 9 inches diameter, provided with slats, upon which rest large irregular-shaped pieces of copper forming a rough filter bottom. Upon these pieces of copper about a ton of granulations is charged, forming a layer about 3 feet 6 inches deep.

The process is carried on as follows:—The granulated copper in one of the vats having been moistened with hot acid by means of a leaden syphon with stop-cock, oxidation at once sets in and the surface of the copper is converted into sulphate, the silver remaining on the surface of each granule as a grey slime. The copper being exposed to the influence of air during a-half to

[*] See Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 619.

[†] See analysis D in Table xxvi.

three-quarters of an hour uses up all the acid moistening its surface, when the stream of acid is again turned on for five minutes to dissolve the copper sulphate formed, while at the same time washing off the silver slime. These operations alternate continuously, and as the granulations dissolve away more are added at the top of the tub so as to keep the layer always of about the same thickness.

The opening at the bottom of the tub is 8 inches square, and discharges the solution into a series of serpentine lead-lined troughs with an inclined draining platform between. In these troughs the solution cools and, having deposited most of its dissolved copper sulphate together with the argentiferous slime, thence passes into a sump, from which it is again raised to the storage tank where more sulphuric acid is added to fit it for use over again. The length of the depositing trough for six dissolving tubs at Oker is about 350 feet.

As the crystals of bluestone collect in this trough they are shovelled out and thrown upon the inclined platform to drain. Those deposited at the top end is the richest in silver slime, while the deposit at the lower end contains much arseniate and antimoniate of lead as well as gypsum. The separation of these slimes from the bluestone is carried out in thick leaden boiling pans, 11 feet 6 inches long by 10 feet 6 inches wide by 21 inches deep, supported on cast-iron girders and heated by means of flues underneath. Mother liquors diluted with water down to 18° or 19° B. are used for the solution, and they are heated to about 70° C., sufficient crude crystals only being added to bring up the specific gravity to 28° B., with the object of obtaining fine large crystals on cooling. Dissolving takes about one hour and settling out the silver slime from six to eight hours more, after which the solution is run through a filter composed of finely-granulated copper in order to precipitate any silver sulphate and retain any slime carried over. The clear solution is then allowed to crystallise in lead-lined wooden boxes about 6 feet by 5 feet 6 inches by 3 feet 8 inches deep, each of which holds the charge of a boiling pan. The crystals deposit upon the sides of the box and upon the leaden strips hung from the top during about eight or twelve days, while the mother liquor is used over again till it contains too much iron for that purpose, when the remaining copper is precipitated on scrap iron.

The silver mud is washed on a filter and dried; it contains from 12 to 15 per cent. silver. It is smelted together with zinc-crusts from the Parkes process, silver slime from the electrolytic copper works, and litharge, to a rich work-lead for cupellation.

Each 100 kilos. of granulated copper produces 380 kilos. of bluestone, and requires 160 kilos. of chamber sulphuric acid at 50° B.

At *Altenau* the same process is in use. During 1888, 209 tons of granulated copper were dissolved in 488 tons of sulphuric acid (50° B.), producing 862 tons of bluestone and 85·5 tons of silver slime, the consumption of coal for heating, pumping solutions, and drying being 763 tons.

Where the price of copper sulphate is high, owing to local demand; and where sulphuric acid can be had cheaply, this process offers many advantages, and can even compete successfully with the electrolytic process for small establishments. But owing to the recent improvements made in the electrolytic process, there are few localities in which it is not preferable, even for works of only moderate size, and it is much more suitable for the treatment of blister copper of good quality (99 per cent. and over), produced by the bessemerising (Manhes) or so-called "converter" process.

Electrolytic Copper Refining.—The electrolytic refining process is now a very important part of the metallurgy of copper, and is described at length in works on that subject.* The impure rough or blister copper is cast in the form of plates ¾ to 1 inch thick and weighing 200 to 250 lbs., which are arranged as anodes, either in "series" or, as is now more common, in "multiple arc" in lead-lined tanks, copper sulphate solution acidified with sulphuric acid being the electrolyte which is circulated through the tanks, and thin sheets of electrolytic copper the cathodes. The copper deposited on the cathodes is removed from time to time, melted, slightly oxidised, brought to pitch by "poling," and cast into ingots.

The currents used are about 3 to 10 amperes per square foot of cathode surface, and the best result attained in practice is about 95 or 96 per cent. of the theoretical efficiency, so that a current of about 8·15 amperes per square foot of cathode deposits ½ lb. of copper per square foot per twenty-four hours. This rate of deposition, however, is only possible with fairly pure anodes, the presence of bismuth, antimony, and arsenic in any quantity requiring a slower rate of current, say only 3 amperes per square foot, in order to produce a good conductivity copper, and consuming much more energy. Thus, with anodes of 99 per cent. Cu, 1 H.P. hour will produce 2·4 lbs. of copper, whereas with 95 per cent. Cu only one-half the quantity of electrolytic copper results from the consumption of the same amount of energy.

The voltage will depend upon the number of tanks and the way in which they are arranged, but it is usually reckoned that each tank containing, say, sixty plates requires an E.M.F. of about 12 volts between the terminals.

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* Reference should be made to Peters, *Modern Copper Smelting*, 7th edition, 1895, pp. 576-606; also to the monographs in *Mineral Industry*, vol. i., p. 163; vol. ii., p. 273; vol. iii., p. 185; vol. v., p. 227.

Metals Present in the Copper.—Impurities in the copper pass either into solution or into the slime which falls to the bottom of the tanks. *Silver* and *gold* are both found almost completely in the slime and in the metallic condition, the deposited copper from even 100-oz. anodes containing under 1 oz. per ton. *Lead* also enters the slime partly as sulphate, partly as arseniate. *Bismuth* and *antimony* are both converted into basic oxysulphates, *tin* into a stannate of arsenic or antimony, while *arsenic*, which also passes into the slime, is found partly as an acid combined with lead, and partly as a base combined with tin.

Neither bismuth, antimony, nor arsenic, however, is completely eliminated from anode copper by electrolysis, for they accumulate in the solution and impair the purity of the deposited metal. Thus, according to Keller,* in the case of comparatively pure copper with only small percentages of these elements the following proportions were found in the residues:—

	No. 1.		No. 2.	
	Percentage in Original Anodes.	Percentage of Total found in Residues.	Percentage in Original Anodes.	Percentage of Total found in Residues.
Bismuth, . .	·0320	78·22	·0035	60·71
Antimony, . .	·0651	61·14	·0510	29·90
Arsenic, . .	·0586	22·90	·0180	37·84

Both bismuth and antimony can be partly eliminated from the electrolyte, and therefore from the subsequently deposited copper, by oxidising in the storage tank with jets of air, while the elimination of arsenic is assisted by melting a small quantity of tin with the anode during casting.† *Iron* in the anodes all passes into the solution, from which it must be removed at intervals, either by crystallisation of bluestone and running the mother liquor over scrap iron; by precipitating the whole of the copper by passing the current from lead anodes; or, as at *Anaconda*, by blowing air through it and filtering between each circulation. This has the advantage of removing practically the whole of the objectionable metals as well as iron, or at least of preventing their accumulation.

Anaconda Refinery.‡—The new refinery at Anaconda, with a present capacity of about 120 tons and a maximum of about 200 tons per day, consists of six "systems," each of two hundred

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* *Journ. Amer. Chem. Soc.*, 1897, vol. xix., No. 10.

† Lead would probably serve the same purpose.

‡ *E. and M. J.*, Sept. 19, 1896.

lead-lined tanks 2·50 metres long, 1·50 metres wide, and 1·00 metre deep, arranged in rows of ten, each row forming a unit with separate supply of electrolyte, while each "system" has its own separate current generator of the Westinghouse type furnishing 270 kilowatts and absorbing about 462 H.P. The conductors are solid bars of copper along the sides of the tanks, and iron bars stretching across these serve as supports for the anodes as well as to transmit current, the anodes and cathodes being suspended from them by means of copper hooks. Electric overhead cranes lift the full charge of cathodes from each tank at once and load it on small trucks, the trains of trucks being drawn away by an electric locomotive, while the remnants of the anodes are removed in the same way. Fresh charges of anodes and of cathode plates are handled in the same way by electric power, so saving much costly labour, which at 12s. 6d. per day must be economised wherever possible. The blister copper treated averages 98 per cent. conductivity, 1¼ per cent. elongation, and 64,000 to 65,000 lbs. per square inch tensile strength. The treatment of the silver slimes will be described subsequently.

In a new plant lately erected, which is not yet in full work, Thofehrn appears to have successfully solved the problem so long attacked with only partial success by Elmore and others—viz., that of the production of bars for wire or plates for rolling direct from the cathode without the expensive and unsatisfactory preliminary melting. The cathode is a cylinder 8 feet long by 3 feet diameter, and the dense finely fibrous grain of the deposited copper is produced by forcing a multitude of jets of clean electrolyte under pressure against the surface of the revolving cylinder, the density of the current being 10 to 20 amperes per square foot. When any required thickness of ½ to 1 inch has been deposited upon the cylinder, this is made to expand by means of hydraulic jacks so as to stretch the covering, which is then slid off, slit up, rolled out flat, and either rolled down into sheets or slit up into bars for wire by means of a circular saw. The bars produced in this way have a conductivity of 100 per cent., elongation 2 per cent., and tensile strength 75,000 lbs. per square inch. The total cost of refining to bars for wire by this process is claimed to be £3, 14s. 8d. per ton of 2240 lbs.

Cost of Electrolytic Refining.—The cost of refining under exceptionally favourable circumstances may fall to £2, 10s. per ton,* but will average something like £4, 2s.†—these figures both referring to the American ton of 2000 lbs. Peters gives ‡ two estimates, from which it appears that in a large plant turning

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* Thofehrn, *Mineral Industry*, vol. ii., p. 283.

† Ulke, *op. cit.*, vol. iii., p. 199.

‡ *Modern Copper Smelting*, 7th edition, p. 581.

out 30,000 lbs. of cathode copper daily the average cost, working in multiple arc, will be about £3, 3s., and in series about £3, 10s. per ton of 2000 lbs. (say, £3, 10s. and £4 respectively per English ton). At *Anaconda* the cost is said to be only £2, 18s. 4d. per short ton, or £3, 9s. 6d. per ton of 2240 lbs., of which £1, 5s. 8d. is for fuel. Limitations of space forbid further discussion of the subject, for which the student is referred to the special literature bearing upon it.

Treatment of Argentiferous Slimes.—Slimes from the electrolytic process vary greatly in composition according to that of the blister or rough copper submitted to the process. The proportion of silver is usually from 40 to 55 per cent., gold from 0·2 to 1·3 per cent., and copper 10 to 20 per cent., the remainder being scraps of metallic copper, copper oxide, and sulphide, sulphates of lead, bismuth and tin, free sulphur, basic arseniates and antimoniates of iron and lead, and other compounds of arsenic, antimony, selenium, and tellurium, besides occasionally traces of platinum and other rare metals. The following analyses show the composition of slimes from Butte, Montana, No. 1 being from reverberatory blister, and No. 2 blister produced by the converter process:—*

	No. 1.	No. 2.
Silver, . . .	53·894	55·150
Gold, . . .	0·2959	0·198
Copper, . . .	11·010	13·820
Lead, . . .	0·910	2·070
Bismuth, . . .	3·930	0·340
Antimony, . .	6·250	2·440
Arsenic, . . .	2·107	1·090
Selenium, . .	0·394	0·718
Tellurium, . .	1·174	0·892
Iron, . . .	...	0·800
SO_4, . . .	5·268	10·680
Combined water, .	2·365	2·604

The slimes are usually placed on a 16-mesh screen and washed through with some of the electrolyte in order to separate the larger fragments of undissolved metallic copper which remain upon the screen and are returned for melting to the anode furnace, while the muddy solution is settled in tanks to be afterwards again washed with water and drained out in a tank with filter bottom.

Besides smelting with litharge to rich work-lead and copper matte (and speiss), a process which is now nearly obsolete, four principal methods for treating these slimes may be described:—

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* Ed. Keller, *Journ. Amer. Chem. Soc.*, vol. xix., 1897, No. 10.

(1) Direct treatment with concentrated sulphuric acid; (2) the Cabell-Whitehead process; (3) Thofehrn's new process; and (4) direct treatment with sulphuric acid and air.

(1) *Direct Treatment with Concentrated Sulphuric Acid.*—This process is like the Dewey-Walter process for treating lixiviation sulphides, already described in Chapter XIII. The presence, however, of a large quantity of free metallic copper in the mud gives rise to a great production of SO_2 which is practically lost, so that the method is expensive and is now practically obsolete.

(2) *The Cabell-Whitehead Process.*[*]—In this process, used at the Baltimore S. and R. Company's Works, dilute sulphuric acid and silver sulphate are boiled with the slime, by which means the metallic copper present is dissolved, precipitating an equivalent proportion of silver. The residue after thorough washing is melted and cast into bars.

(3) *Thofehrn's New Process.*[†]—This process is particularly suited to the treatment of very base slimes containing 25 per cent. Cu or upwards and only 1 to 6 per cent. Ag. The slimes are melted to get rid of lead, arsenic, and everything but copper and silver in a small reverberatory with hearth of magnesia brick, producing a complex slag and a rich pimple metal with 80 per cent. copper and 15 per cent. silver, which is cast direct into plates and electrolysed in special vats, using, however, the same current and electrolyte as in the ordinary process. The copper produced is of fair though not of high quality, and the resulting very rich slimes can be treated with concentrated sulphuric acid.

(4) *The Direct Sulphuric Acid-and-Air Process.*[‡]—This process is in use at the Anaconda Works. At these works over 4,000,000 ozs. silver and 18,000 ozs. gold are turned out annually.[§] The silver mud is first screened through a fine sieve to take out as much of the scrap metallic copper as possible. It is then put into a lead-lined boiling tank, together with an equal weight of dilute H_2SO_4 (1 : 3), and a mixture of steam and air is forced through by means of a Körting injector, by which treatment the residual copper is completely dissolved out. When the parting plant is at work no addition of sulphuric acid is required, for the fumes from the parting kettle, containing H_2SO_4 and SO_2, are blown through the tank of slimes, to which in this case ordinary electrolyte is added instead of dilute acid. The reactions which take place are those of the Rössler converter,[‖] and generate sufficient heat to be independent of any extraneous source beyond the steam.

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[*] *Mineral Industry*, vol. ii., p. 281.

[†] *Ibid.*

[‡] Peters, *op. cit.*, p. 603; also *E. and M. J.*, Sept. 19, 1896.

[§] Only one company produces a larger amount, viz., the Broken Hill Proprietary Coy. of New South Wales.

[‖] See chap. xiii.

When the copper is all dissolved the silver slimes are run through a filter, washed, dried, mixed with 20 per cent. of soda-ash and smelted to auriferous silver bullion 980 fine in a small reverberatory furnace.

Although this process is the best hitherto invented, the losses in the smelting to bullion of a rich material containing much lead, arsenic, and antimony must necessarily be large. Barnett accordingly proposes* after dissolving all the copper to add sufficient acid to dissolve 75 per cent. of the silver, leach out and precipitate on metallic copper, and sweeten, wash, dry, and melt the cement silver as usual. The remaining slimes now contain only one-fourth of their original silver contents, and, therefore, in smelting to auriferous silver bullion, are exposed to only one-fourth of the percentage losses, while the bullion to be parted is only one-fourth as bulky and four times richer in gold, so that both the cost of parting and the loss of gold are much less than when the whole of the bullion has to be parted.

The most recent *Anaconda* practice is as follows:—From the first boiling tank the silver mud is run on to a filter, where it is washed with hot water, and thence into a second boiling tank, where arsenic and antimony as well as the remaining copper are largely removed. After re-washing on a second filter it is dried in cast-iron pans, mixed with a little soda, and melted down with wood fuel as rapidly as possible in charges of 2 tons at a time on the reverberatory hearth, from which it is tapped into a train of moulds in front of the furnace. The ingots are then parted with sulphuric acid as usual, and the product turned out as 1200 ozs. ingots, 999 fine.

Parting of Doré (or Auriferous Silver) Bullion.—This subject may be with more propriety considered as belonging to the metallurgy of gold, and will accordingly be found described in works on that subject.† The student may be also referred to a very able recent article on parting plants by Ulke.‡

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* Peters, *op. cit.*, p. 695.

† *v.*, for example, Rose, *Metallurgy of Gold* in this series, pp. 349-377.

‡ *Mineral Industry*, vol. iv., 1895, p. 343.

ERRATA.

Page 22, line 26, *for* "Guanaceir" *read* "Guanacevi."

„ 41, line 16, same substitution.

„ 41, heading of last par., *for* "Gold amalgam" *read* "Copper amalgam."

„ 72, in the first member of 1st equation, *for* "Cu_2Cl" *read* "Cu_2Cl_2."

„ 87, line 24, *for* "Fig. 28 shows the *Boss Combination* pan" *read* "Fig. 29 shows the *Combination* pan."

„ 87, line 34, *for* "stots" *read* "slots."

„ 88, description of figs., *for* "Figs. 28 and 29, Boss Combination Pans" *read* "Fig. 28, Boss pan (left hand), Fig. 29, Combination pan (right hand)."

„ 94, description of Fig. 33, *for* "Filter" *read* "Amalgam Strainer-safe."

„ 105, heading, column 10, *for* "Black Line" *read* "Black Pine."

„ 127, line 4, *for* "Labour, 113 shifts" *read* "0·113 shift."

„ 156, description of Fig. 53, *for* "Oxland-Hocking Calciner" *read* "Howell-White furnace."

„ 172, line 8, *for* "thiosulphite" *read* "thiosulphate."

„ 176, description, Fig. 56, *for* "Precipitation tanks" *read* "Tanks for Augustin process."

„ 192, line 18, *for* "practical" *read* "practised."

„ 194, line 19, *for* "feet" *read* "foot."

„ 200, line 26, *for* "$CuCl_4$" *read* "$CuCl_2$."

„ 214, line 20, *for* "stowes" *read* "staves."

Page 219, description, Fig. 65, *for* "Filter Press" *read* "Press-tank."

„ 267, lines 13 and 14, *for* "Silicate of iron, trisilicate of alumina, and sesquisilicate of lime" *read* "bisilicates of iron and alumina with trisilicate of lime."

„ 272, line 9, *for* "As_2S_2" *read* "As_2S_3."

„ 280, line 15, *for* "$FeO, 2SiO_2$" *read* "$FeO . SiO_2$."

„ 285, line 40, *for* "twice blowing up" *read* "blowing up in two stages."

„ 298, description of Fig. 72, *for* "Anaconda furnace" *read* "Plan of hot-air flues of Anaconda furnace."

„ 299, line 33, *for* "less than 2 per cent." *read* "not over 3 per cent."

„ 302, Table XXV., the reference to Columns 4 and 5 should be exchanged.

„ 305, 1st line below analyses, *for* "matte" *read* "speiss."

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⁂ *For INDEX, see next page.*

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