EXTRACTION OF SILVER
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ORES OF SILVER.

"**Native" silver** occurs associated with ores of the metal; with gold, in electrum; with mercury, in amalgam (see p. 33).

Silver Sulphide (Ag_2S)--Argentite--occurs as a soft, malleable greyish-black substance, which is readily fusible. It contains 87 per cent. of silver. Deposits containing it in a state of purity occur in Norway, Hungary, Saxony, Bohemia, Mexico, and the United States. It is the principal ore of silver.

Horn Silver--Silver Chloride (AgC1)--is found in South America. The bromide and iodide also occur.

 Pyrargyrite.--Dark-red silver ore is a sulphantimonide of silver ($3Ag_2S.Sb_2S_3$) found in Mexico, South America, Transylvania, and elsewhere. **Proustite**–light-red silver ore--is a sulpharsenide ($3Ag_2S.As_2S_3$). **Stephanite** is another mineral of the same class.

Polybasite and **Argentiferous Fahl Ore** are compounds of copper, silver, arsenic, and antimony sulphides. The latter often contains other metals also.

Silver occurs in the ores of many other metals, probably as sulphide. Lead, zinc, and copper ores often contain it, and small quantities occur in iron pyrites and mispickel (arsenical iron pyrites). The production of silver from these sources is nearly one-half of the total extracted.

Extraction Processes. The high price of silver permits of poor ores being treated and the adoption of more costly methods. Hence chemical methods, preceded by careful mechanical preparation, are often followed.

The treatment of silver ores proper may be divided into--

>Amalgamation processes.
>Wet processes.
>Smelting with lead, or lead ores.
>Smelting With copper ores.

Amalgamation Processes include those in which the silver is obtained as an amalgam with mercury, from which it is recovered by distillation and volatilising the mercury. They may be divided into "floor," " barrel," and "pan" amalgamation processes. If not present as free silver or as chloride the first step of the process is to convert the metal into chloride.

Floor Amalgamation.--In the "patio" process, still followed in Mexico and South America, the ores are hand-picked, and then contain some 80 ozs. of silver per ton, as native silver, chloride, and sulphide. Base ores containing large amounts of foreign sulphides are unsuitable for treatment by this process. The ore is first reduced to a fine state of division by stamping or grinding.

The *quimbalete* consists of a large boulder lashed to the middle of a long pole, rocking on a flat stone, worked by men sitting astride the ends of the pole, and working see-saw fashion, the ores being thrown under the boulder.

The *trapiche* is a large stone wheel, 6 feet in diameter and 5 feet across; the axle on which it revolves is attached to a perpendicular shaft driven by a horizontal water-wheel on the top. The wheel travels round a stone track, and the ores are gradually crushed.

[1]The *arastra,* for fine grinding, is a circular trough paved with hard stone. In the centre is an upright post to which projecting arms are attached. Heavy stones are lashed to these, by thongs of raw hide, and they are dragged round by mules attached to the ends of the arms, which project over the edge of the trough. Water is added, and, if much free silver or gold is present, a little mercury, to amalgamate them. The ore is thus reduced to mud.

The *Chilian mill* for grinding ores is in principle like an ordinary mortar-mill,

The operations are conducted as follows :–(1) The mud is taken to the amalgamating floor, or patio--a paved court--and spread out in a layer 6 inches to a foot thick. Some 3 to 5 per cent. of salt is added and well trodden in by mules for several hours, after which the heap is allowed to rest.

(2) Next morning a quantity of roasted copper pyrites--*magistrall*[1] --is scattered over the heap, and some mercury. This, after mixing with shovels, is well trampled in; the turning over and trampling are repeated every other day for some days.

(3) Mercury to the extent of some 5 or 6 times the weight of silver present is sprinkled over the heap from canvas bags, and trampled in. If much antimony and arsenic, or other foreign sulphides are present, a hot solution of copper sulphate is added, together with copper precipitate (finely divided copper), and thoroughly incorporated.


[1] This contains both copper and iron sulphates and plays a material part in the reactions that occur

(4) After a further rest with repeated tramplings, a final addition of mercury is made to collect the amalgam, and after mixing, the stuff is conveyed to tanks where it is stirred up with water, and the heavy amalgam settles out. The earthy matters are carried away by the water current.

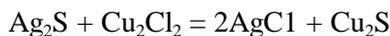The amalgam is treated in the ordinary manner (see later).

In this process a series of complicated reactions occurs. Copper chloride is formed by the reaction of the salt and copper sulphate.

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4$$
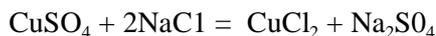
This attacks the metallic silver, thus:

$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2$$
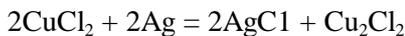
This cuprous chloride, which is soluble in the excess of salt employed, reacts on the sulphide of silver and converts it into chloride.
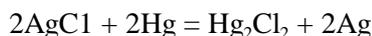
$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S$$

Some free sulphur is also ,separated, probably thus:

$$Ag_2S + 2CuCl_2 = Cu_2Cl_2 + 2AgCl + S$$

or

$$2Ag_2S + 4Cu_2Cl_2 + 6O = 2(CuCl_2.3CuO) + 4AgCl + 2S$$

The above reactions in some degree represent the chlorination, but the changes are very obscure. The silver chloride is decomposed by mercury, thus:

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag$$

the metal being dissolved by the excess of mercury. The operation occupies from 2 to 7 weeks.

Note.--The addition of copper precipitate is to ensure the reduction of the cupric salt to the cuprous state, or it will attack the mercury, forming calomel,[2] and will thus increase the consumption of mercury.

$$CuCl_2 + 2Hg = Hg_2Cl_2 + Cu_2Cl_2$$
$$2CuCl_2 + 2Cu = 2Cu_2Cl_2$$
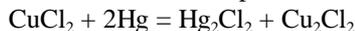
Formerly lime was added, to precipitate the copper, if in excess; but this hinders the chlorination by forming an inactive chloride.

Barrel Amalgamation was formerly practised at Freiberg. The chlorination of the metal is effected by roasting the ore with salt as described later. The roasted ore is next put into barrels capable of holding about a ton, supported horizontally on trunnions. Water is added to make it into a stiff paste (pulp), some 1¼ to 1¾[3] cwt. of sheet-iron scrap added, and the barrels revolved for several hours. The chloride is reduced by the iron, thus:

$$2AgCl + Fe = FeCl_2 + 2Ag$$

Mercury is then added to amalgamate the reduced silver, and the barrels again revolved some 16 hours. The contents of the barrels are then thinned by the addition of water, the amalgam collected together by slow revolution, and run off by a plug in the side. A little fresh mercury is added to collect any residual metal, and the barrels again revolved. This is run off as before. The residues are run into settlers and agitators--tanks with a current of water flowing through--by which the light matters are carried off and the amalgam (if any) sinks.

In the Krolinke[3] process, formerly in use at Benton, the roasting with salt is dispensed with. The chlorination of the silver is effected by an addition of cuprous chloride and salt. The cuprous chloride is prepared by boiling copper sulphate with salt and copper, or in other ways. The barrels may be arranged vertically or horizontally, and steam is blown in to heat the contents. Metallic copper is employed to reduce the silver, and the amalgamation with mercury takes pace, as before. The loss of mercury is greatly reduced, calomel not being formed. Aaron states that it can be brought as low as 2 lbs. per ton. Iron borings are sometimes used for the reduction. Base ores can be treated by this process, a yield of 8o to 95 per cent. being obtained.

In both these processes there is considerable loss of mercury by "flouring "--that is, the mercury is broken up into fine particles which will not coalesce to form a globule, and are carried off and lost. The addition of a little sodium amalgam is made to prevent this.

Kettle Amalgamation (Cazo Process).--The ores treated by this process are mainly chlorides, bromides, and iodides. The ore is ground to a pulp in the mill, or arastra, and transferred to kettles with bottoms made of copper. From 5 to 10
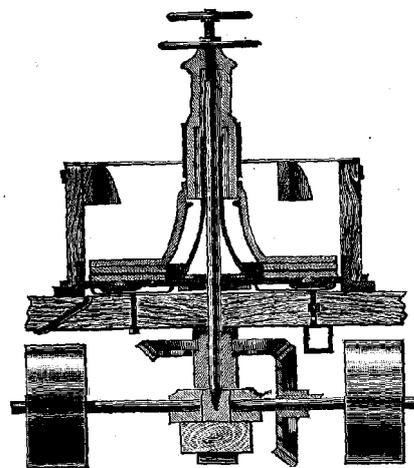

FIG. 137.—Amalgamating pan.

[2]The white insoluble mercurous chloride

3 *Iron*, Nos 93 and 94

per cent. of salt is added, and the mass heated with continual stirring. Mercury is added, and the heat is continued for some hours, till amalgamation is complete. ' The mass is then thinned with water, and the amalgam collected as before. The chloride, etc., is decomposed by the copper,

$$2AgCl + 2Cu = 2Ag + Cu_2Cl_2.$$
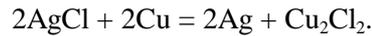
yielding silver and cuprous chloride. This, in the presence of salt, reacts to some extent on the sulphides, after the manner of the "patio" process, but sulphide ores generally retain enough silver to be subsequently treated on the "floor."

Pan Amalgamation.--The foregoing. methods have generally given way to treatment in pans, a great saving in time being effected

The pans employed in these processes vary somewhat in construction. One form is shown in Fig.137. It consists of a cast-iron pan some 5 feet in diameter, with a steam-jacketed bottom. Up the centre a hollow pillar rises, through which a shaft passes. To this the cast- iron muller is attached in a manner which permits of its being. raised or lowered to any desired height by means of the hand-wheels on top. The crushed ore is ground between the flat faces of the muller and the bottom of the pan, motion being communicated by the bevel-wheel gearing under the bench on which the pan rests. Steam is. admitted to keep the contents hot. A plug is provided for running off the pulp after amalgamation.

Instead of iron sides, wooden staves hooped with iron are employed, and copper bottoms and linings are sometimes employed.

Two methods of treating the ores are followed. In one they are treated direct, and in the other they undergo a previous roasting with salt to. chlorinate the silver..In the direct process the ore is broken in a "stone-breaker," or "ore-crusher" of the Blake type.. A (Fig. 138), passes to a stamp battery B, and is crushed "wet "--that is, with a supply of water, a 3o-mesh screen being employed. From the battery the crushed ore passes over the amalgamated copper plates C to catch any free gold present, and then to the tanks D, in which the mud settles.
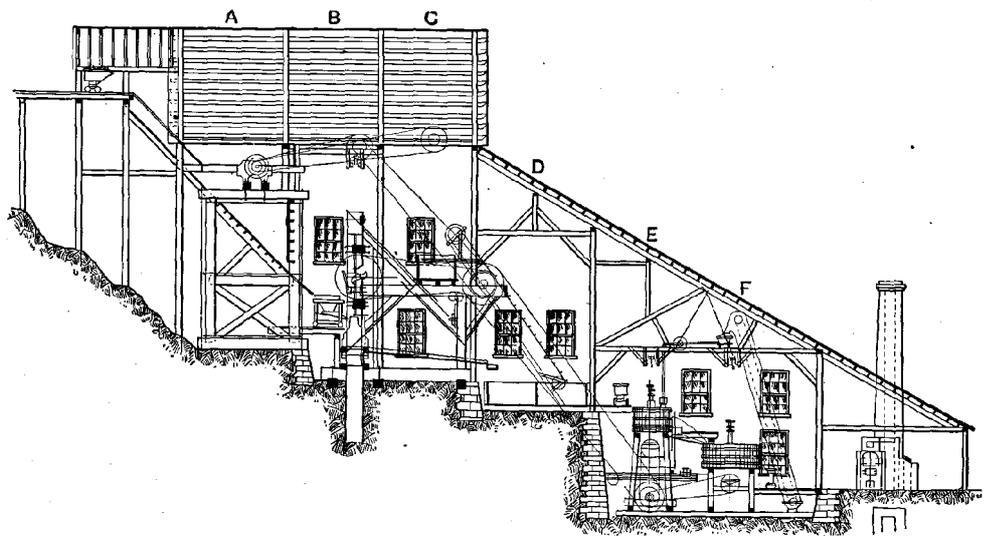

FIG. 138.--Wet-crushing sil

The mud (pulp) is charged into the pans E, water added to a pasty consistency, and the muller lowered and revolved at the rate of 8o to 100 revolutions per minute. Salt and copper sulphate are also added, and the temperature is maintained at about 90° C. This grinding is continued some 3 or 4 hours. The pulp will then pass through an 80-mesh sieve. About 10 or 15 per cent. of mercury is then added, and the muller, somewhat raised, is again revolved for 2 or 3 hours, to thoroughly incorporate the mercury. The pulp is then thinned by the addition of water, and run off by the plug into the settler F, which resembles the amalgamator save that the muller is replaced by a stirrer (Fig. 139) which makes some 10 revolutions per minute. Here the amalgam settles out. The mud is drawn off, by opening the holes in succession, into another settler--the agitator - and then passed on to "frue

FIG. 139.--Settler.

vanners," or otherwise treated, for the separation of the pyrites, etc. (concentrates), which often carry gold, while the light stuff is washed away.
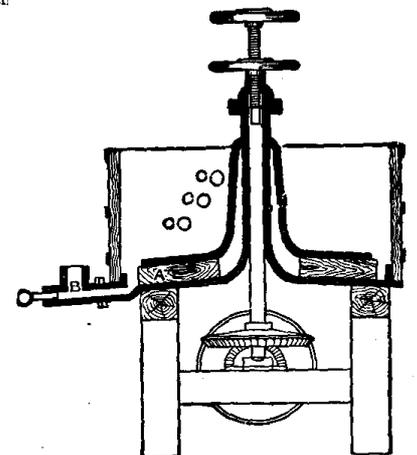
In amalgamation processes preceded by roasting the ores are crushed "dry." In "dry" crushing, the ore, after being broken, is dried, a rotary furnace being employed. The dried ore is stamped, and the crushed ore falling through the screens is conveyed away by means of Archimedean screws, travelling belts, or elevators. Fig. 140 shows a "dry" crushing mill. The powdered ore is next mixed with about 20 per cent. of salt, and roasted. Generally revolving furnaces of the Brückner type (Fig. 39) are employed. Stetefeldt calciners (Fig. 41), and multiple-bedded reverberatory furnaces

are also employed. This roasting occupies about 8 hours. The ore is then transferred to the amalgamators and treated as before. The yield by this treatment is much greater than in wet crushing, but the items of labour and fuel consumption are increased, while the output of a plant is seriously diminished.

FIG. 140.

The loss of mercury is about 2 pounds per ton of ore treated. It is customary to add a little sodium or zinc amalgam, to keep the mercury from *flouring,* the hydrogen evolved keeping the mercury bright and *lively,* and preventing the formation of a film on the small globules, which prevents them from coalescing. Potassium cyanide, in small quantities, is often used for the same purpose. In wet crushing, mercury is also introduced into the mortar-box to retain gold.

In the roasting of *dry-crushed* ores with salt, there is a liability to form gold chloride, which is soluble, and will be lost if not completely decomposed in the pans.

In " wet" crushing, the sulphide of silver in the ore seems to be partially decomposed by the iron of the pan during amalgamation, with the formation of sulphide of iron, assisted by the cuprous chloride, produced when salt and copper sulphate are added.

The *best grinding* is secured with a thin pulp, and the *best amalgamation* with thick pulp, which prevents the mercury from settling out. It is usual to add *residues* to thicken the pulp prior to adding mercury. It is soft enough if the mullet will turn in it.

Treatment of Amalgam.--The amalgam from the settlers and agitator is often transferred to a smaller "clean-up "pan, and stirred with water to free it from heavy particles.

It is then strained through canvas bags, or squeezed through wash-leather, or in cylinders, the ends of which are made of wood cut across the grain, by hydraulic pressure. The excess of mercury which is thus removed is used again. It contains silver, but this is recovered in the subsequent working. The pasty amalgam which remains is then "retorted" to expel the mercury. One form of retort is shown in Fig. 142. The amalgam is put into the crucible, which is of iron, the head adapted, and the mercury as it distils off is condensed by the water-cooled tube. The crucible is coated with limewash.

FIG. 141.—Amalgam safe, with strainer.

The porous mass obtained is subsequently melted down in crucibles, and cast into bars weighing about 1,000 ozs. The crude bullion contains bismuth, antimony, copper, zinc, arsenic, etc. It is subsequently refined. This is partially effected by exposing the surface to the air while molten, and permitting the impurities to oxidise, the scum of oxides being scraped off. It is afterwards refined by cupellation.

Wet processes.--The wet methods of extraction formerly practised depended on the solubility of chloride and sulphate of silver, the former in solutions of common salt and other chlorides and in thiosulphate of soda, and the latter in water more or less acidified. These processes have been almost entirely superseded by the simpler methods of extraction by cyanides of potassium and sodium. A brief resume of the older processes is given.

Sulphating roasting.--*Ziervogel Process.* This process or some modification of it was formerly largely followed for the treatment of copper and other mattes and for the preliminary treatment of bottoms or other argentiferous coppers, in addition to its application to certain ores containing silver. It depends on the conversion of the silver into sulphate by calcining under
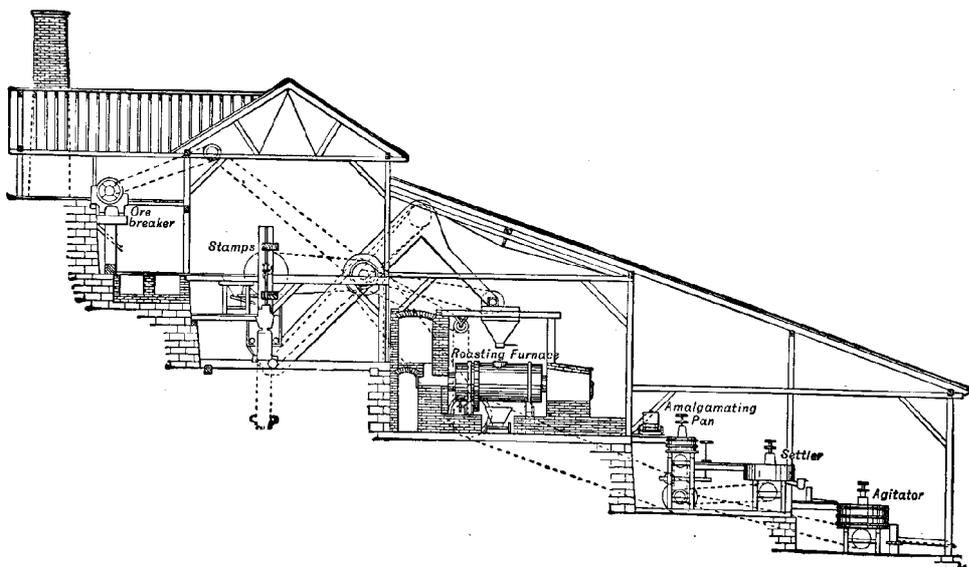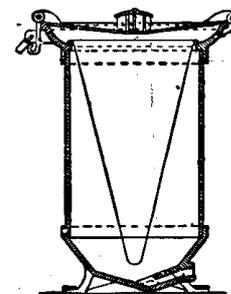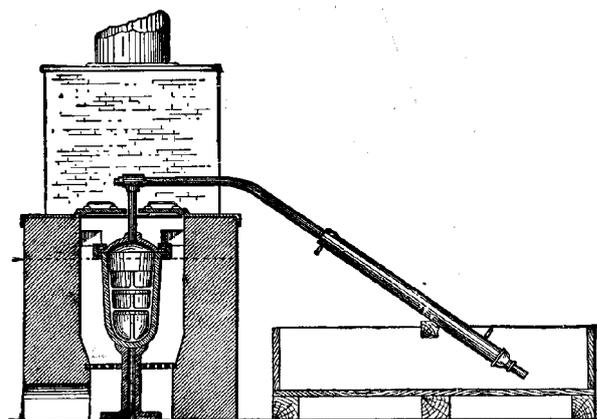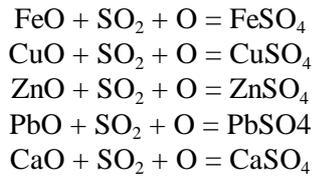

FIG. 142.—Retort.

favourable conditions. When a mixture of sulphides is calcined the chemical changes that take place depend mainly on (x) 'the basicity of the oxide formed, (2) the atmosphere of the furnace, (3) the temperature.

If the oxide of the metal resulting from the calcination be highly basic, the sulphur dioxide in the presence of free oxygen, and probably moisture, will be fixed as sulphate in proportion to the Basicity of the oxide and the stability of the sulphate when heated. Thus:

$$FeO + SO_2 + O = FeSO_4$$
$$CuO + SO_2 + O = CuSO_4$$
$$ZnO + SO_2 + O = ZnSO_4$$
$$PbO + SO_2 + O = PbSO4$$
$$CaO + SO_2 + O = CaSO_4$$

There is a *remote* possibility of the sulphate being formed directly. Sulphates which undergo decomposition to oxide when heated liberate sulphur trioxide, which may (1) be immediately dissociated, (2) serve as a powerful oxidising agent, or (3) unite at once with a base whose sulphate is stable at the temperature, thus increasing the proportion of sulphate of that metal produced. This may extend in extreme cases--a powerful base and little sulphur - to the fixation of the whole of the sulphur as sulphate.

Sulphur trioxide in the presence of moisture may behave like sulphuric acid and oxidise and combine with the oxide formed if the sulphate is stable at the temperatures.

Hence, in calcining a mixture of sulphides at a gradually increasing temperature, a series of progressive changes may take place, in addition to the main effects of eliminating sulphur and the formation of sulphates and oxides.

The sulphates of iron, copper, silver, zinc, lead, and calcium are decomposed by heat in the order named. When a mixture of the sulphides is calcined, part of the sulphide in each case (except silver) is converted into oxide and this partially into sulphate. As the temperature rises the decomposition which occurs increases the amount of those sulphates which are stable at that temperature. Thus in a mixture of iron and copper sulphides the decomposition of the iron sulphate tends to produce an increased amount of copper sulphate.

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$
$$CuO + SO_3 = CuSO_4$$
$$CuO + SO_2 + O = CuSO_4$$
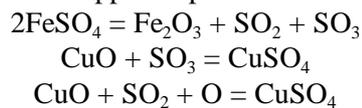
The ferric oxide (Fe_2O_3) formed acts as a catalyst and assists in the conversion of SO_2 into SO_3. This is also assisted by the brickwork of the furnace and siliceous matter in the ores. The presence of moisture is probably necessary. This applies generally.

Sulphide of silver does not form a basic oxide during calcination, but the sulphate is stable at higher temperatures than copper sulphate. When calcined the sulphide yields metallic silver. In a matte this would be in a very fine state of division and easily attacked by the sulphur trioxide from the decomposing sulphates of iron and copper.

$$2Ag + 2SO_3 + nH_2O = Ag_2SO_4 + SO_2 + nH_2O$$
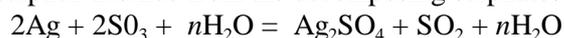
By controlling the temperature almost complete decomposition of the iron and copper sulphates may be secured, while the silver sulphate is unaffected.

The presence of zinc and lead oxides resulting from the sulphides present or the presence of lime would seriously affect the attack of the silver by forming sulphates which have no effect. This should also be noted in connection with the Percy-Patera and other similar processes, as the amount of these metals passing into solution is of importance, determining either the method of working or the purity of the silver sulphide precipitates obtained.

From' the above the function of iron sulphate sometimes added to oxide of copper for sulphating will be evident.
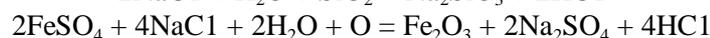
Chloridising roasting, as followed in the Augustin, Percy-' Patera, Russell, and other processes, has for its object the conversion of the silver into chloride.

Common salt is the usual source of the chlorine. The transference may be effected in various ways.

(1) By the action of free chlorine, generated thus--

$$(a) \ 2NaCl + O + SiO_2 = Na_2SiO_3 + Cl_2$$
$$(b) \qquad 2HC1 + O = H_2O + Cl_2$$

(2) Or by the action of hydrochloric acid gas, produced thus--

$$2NaC1 + H_2O + SiO_2 = Na_2SiO_3 + 2HC1$$
$$2FeSO_4 + 4NaC1 + 2H_2O + O = Fe_2O_3 + 2Na_2SO_4 + 4HC1$$

the moisture being present in the atmosphere of the furnace;

(3) By the action of chlorides of copper and iron produced by the reaction of sulphates on the salt added.

$$CuSO_4 + 2NaC1 = Na_2SO_4 + CuCl_2.$$
$$2CuCl_2 + 2Ag = 2AgC1 + Cu_2Cl_2$$
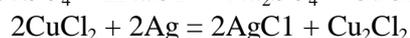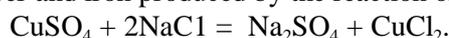
The Cyanide Process.[4]~--The application of the MacArthur-Forrest process of gold extraction by solutions of potassium cyanide has been adapted to the extraction of silver.

Cyaniding for Silver.--The recovery from finely divided ore containing the silver as sulphide and chloride amounts to 80 to 95 per cent., but metallic silver is only acted on very slowly, and its malleability prevents its reduction to a fine state of division in milling.

In carrying out the process it is necessary to secure satisfactory concentration, to separate metallics as completely as possible, the earlier in the process the better, and to separate slimes and sands for separate treatment.

Note.--Slimes includes all material that will pass a 2oo-mesh sieve. Most of it will pass a 3oo-mesh

The stronger cyanide solutions employed make the greatest possible economic reduction in bulk necessary to reduce losses. Hand picking to remove rich material is followed by an elaborate crushing and concentrating campaign. Crushers, stamps, jigs, and Wilfley or other concentrating tables are used to remove the poorest portions of the ore. At every stage slimes are recovered by settling in Dorr thickeners or other devices as they are partly produced from the soft and rich material. All slimes pass to the special plant for separate treatment.

In cases where it is possible the ore is graded and the rich and poor portions concentrated separately, all the slimes being mixed. The preliminary concentration may separate 60 to 70 per cent. The metallics of the rich mineral are recovered from the rich material and from concentrates of both grades after prolonged fine grinding --*22* to 3o hours---in tube or other mills. When much silver is present --as at Cobalt--calcium hypochlorite and caustic soda are added as oxidising agents in the mill. The grinding flattens the silver and makes it flakey. It is separated in classifiers, and after roasting, fluxed, melted, and refined.

The pulp after removal of the metallics is settled, and washed free from chlorides prior to cyaniding. Elaborate plant of every description for crushing, concentrating, washing, and filtering is employed.
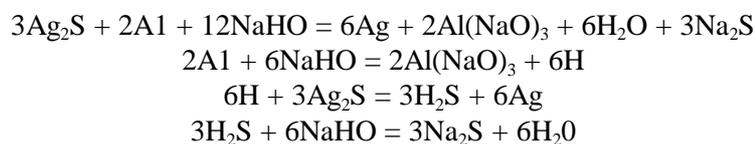
At Cobalt in Canada the final concentrate may be not more than 2 per cent. of the original ore treated. The slimes may total 6o per cent.

Treatment of Slimes.--They are allowed to settle and further dewatered by vacuum filtration till only 25 per cent. of water remains. The mud--pulp--is transferred to large tanks, 30 feet by 10 feet, capable of treating 80 to 85 tons, provided with agitating appliances for cyanide treatment. About 2 tons of solution per ton of slime is employed. This solution contains about 0.25 per cent. of cyanide, and the ore is agitated from 48 to 72 hours.

The liquor is drawn off at the end of the treatment, filtered, and clarified. Sodium sulphide is added to precipitate the silver and regenerate the cyanide, in tanks fitted with agitators similar to the treatment tanks. The sulphide is recovered by filtration through filter presses, the solution going back to storage tanks.

Treatment of *Sands--Concentrates.--After* removing metallicS the pulp is settled, washed free from chlorides, and dewatered by filtration. It is transferred to tanks and treated with 0.5 per cent. cyanide solution, the solution being precipitated after filtration with sodium sulphide as above and filter-pressed. The recovery may reach 95 per cent. of the silver present.

Treatment of Silver Sulphide Precipitates.--The sulphide collected in the' filter presses is thoroughly agitated in a tank with caustic soda solution. This mixture is pumped continuously through a revolving cylinder containing aluminium in massive form such as ingots, the silver sulphide is reduced by nascent hydrogen produced by the action of caustic soda on aluminium, sodium sulphide being formed. The reduction may occupy from 14 to 20 hours, and circulation is continued till tests show that reduction is complete.

$$3Ag_2S + 2Al + 12NaHO = 6Ag + 2Al(NaO)_3 + 6H_2O + 3Na_2S$$
$$2Al + 6NaHO = 2Al(NaO)_3 + 6H$$
$$6H + 3Ag_2S = 3H_2S + 6Ag$$
$$3H_2S + 6NaHO = 3Na_2S + 6H_2O$$

The silver pulp is filtered through a filter press and the solution of sulphide sent back for re-use.

After thorough washing to remove traces of soluble sulphide the precipitate, together with that removed as flake silver, is melted and refined.

The recovery of silver by cyaniding processes varies with (a) the form of occurrence; (5) fineness of milling; (c) strength of solutions; (d) efficiency of agitation and filtration. In some ores it reaches 95 per cent., but may fall as low as 80 per cent.

The elaborate concentration methods followed are necessary to reduce the cyanide consumption, which is high.

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[4]All processes for " wet" extraction of silver from silver ores have been largely replaced by cyanide extraction

Residues left in the filter after removing the cyanide solution may represent a very highly concentrated mineral product and be valuable as is the case in the Cobalt district in Canada, where they contain as much as 8 per cent. of nickel and 8 per cent. of cobalt.

Ziervogel Process.[5]

Roasting Copper Mattes.--They are first roasted to remove the greater part of the sulphur, and then ground very fine and carefully roasted at a low and gradually increasing temperature in a double- or triple-bedded reverberatory calcining furnace. The matte is first introduced on the bed farthest from the fire, and is moved forward towards the fireplace. When the iron and copper sulphates formed during the roasting are nearly decomposed--determined by boiling a sample with water and observing the colour--the material is raked out.

Argentiferous copper ores are generally run down for matte, which is thus treated.

The roasted material is then treated with water containing a little free sulphuric acid--*leached--in* wooden tanks capable of holding about 1000 gallons. From these the liquor is run into settling tanks, at a lower level, and thence into tanks containing copper, where the silver is precipitated. Two sets of precipitating tanks are usually empl0yed, the first containing heavy copper scrap or bars, and the latter precipitate and bean shot-copper.

$$Ag_2SO_4 + Cu = CuSO_4 + 2Ag$$
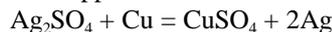
The copper is recovered by throwing it down with iron in similar tanks.

The residues contain the gold, a portion of the silver (owing to imperfect sulphating), copper,. and iron as oxides, lead as sulphate. If bismuth and antimony are present in the rnatte, more silver is retained, owing to the formation of insoluble compounds.

The residues are smelted for copper by the *"best* select" process. The bottoms obtained are treated by electrolysis, or in a manner subsequently described.

Augustin's Process.--This consists of roasting the material mixed with salt for the purpose of converting the silver into chloride, which is then dissolved out by brine and precipitated by copper.

In the treatment of copper bottoms, the two processes are often combined (at Freiberg, and some works in this country). The bottoms are granulated in water, and roasted to oxide, CuO, mixed with sulphur or sulphate of iron, and Ziervogelised.

The residues contain the gold and much silver, and are Augustinised. The gold passes into solution as chloride, and is, of course, precipitated by the copper. Great care is required in roasting, or the gold chloride will be decomposed by over-heating, the metal remaining in the residue.

Claudet's Process was in extensive. use for the recovery of silver from the cinders of iron pyrites used in vitriol manufacture, and is employed as an adjunct to the extraction of copper by Longmaid's process. In the chlorinating roasting for copper, the silver is also chlorinated, and in the lixiviation with water is dissolved out by the excess of salt added in roasting. The leachings, after cooling and settling in tanks--during which much lead sulphate and chloride separate out--are assayed for the amount of silver they contain. A soluble iodide is then added in sufficient quantity to precipitate it as insoluble silver iodide [6]

$$2AgCl + ZnI_2 = 2AgI + ZnCl_2$$
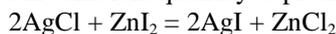
Care must be taken that the iodide is not in excess, or the following reaction will occur, cuprous iodide being precipitated--

$$2ZnI_2 + 2CuCl_2 = 2ZnCl_2 + CuCl^2 + I_2$$
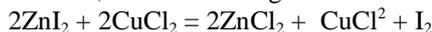
and iodine liberated. The iodide is well stirred in, and the precipitate allowed to settle.

After the withdrawal of the liquor, the mud is moistened with hydrochloric acid and treated with zinc, when the nascent hydrogen reduces the silver iodide and zinc iodide and metallic silver results.

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$H_2 + 2AgI = 2Ag + 2HI.$$
$$ZnCl_2 + 2HI = 2HC1 + ZnI_2$$
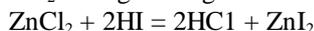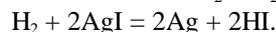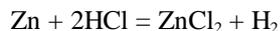
During the reduction the mass is kept warm by jets of steam.

The mud, or precipitate, after reduction, contains 6 to 12 per cent. of silver, a little gold, and a large percentage of lead and oxide of zinc, with sulphuric acid, lime, etc. The lead is reduced by the action of the zinc.

Percy-Patera Process.--The solution of the chloride produced in chlorinating roasting by thiosulphate of soda, "hyposulphite," and precipitation of the silver as sulphide by sodium or calcium sulphides, was first proposed by Dr.

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[5]Now obsolete. It should be remembered that the reduction in the value of silver has made many processes uneconomical

[6]In modern practice the precipitation with iodide has been superseded. The silver is precipitated by iron along with the copper, and is recovered in the electrolytic refining. In some cases the copper was precipitated in two stages, the first portion, containing the silver, being removed separately. Much less copper precipitate is now produced than formerly

Percy. Prior to the introduction of the cyanide process it was the most important "wet" process for the treatment of *silver ores.*

In the American silver mills, where this process was pursued, the dried and crushed ore was chlorinated by roasting with salt. After roasting--especially in White-Howell calciners--the ore was left for some hours in heaps, the chlorination proceeding after withdrawal from the furnace. It was then transferred to lixiviating vats, and leached with hot *water* to remove all soluble matters--zinc, manganese, copper, lead, and other chlorides--till the effluent liquor gave no precipitate with sodium sulphide. Some silver chloride also dissolves. The stronger liquors from the first leachings were run into tanks, and the silver they contained was precipitated by the careful addition of sodium sulphide.It is thrown down before the other metals present are completely precipitated. This precipitate contains about 4 to 6 per cent. of silver.

The ore was then leached with sodium thio-sulphate solution, of strength varying from ¼ to 1 per cent., according to the richness in silver. The solution was run by gutters under or alongside the tanks, into deep precipitation tanks holding about 1,000 gallons (5 feet diameter and 8 feet deep), sodium sulphide solution added, and silver sulphide precipitated thus--

$$(Ag_2S_2O_3.2Na_2S_2O_3) + Na_2S = Ag_2S + 3Na_2S_2O_3$$

The regenerated thiosulphate solution was available for use again.

Treatment of Sulphide Precipitates.--The sulphide precipitates are roasted in a furnace, and, if poor in silver, smelted with lead, which decomposes the sulphide and takes up the metal.

The lead is cupelled to extract the silver. If the sulphide is pure, after roasting, it is melted in crucibles with carbon.

In roasting, and in treatment by lead, there is great liability to loss by volatilisation and dusting. The flue dust from these furnaces assays up to 1200 ounces of silver per ton.

Formerly the silver precipitate was run down in crucibles with scrap iron, silver being liberated and iron sulphide formed. The regulus retained silver, and was re-treated. Calcium thiosulphate and calcium sulphide replaced the soda salts in the "Kiss" process.

Treatment of Base Ores. Ores containing much lead and zinc sulphides, antimony, arsenic, and bismuth, are unsuitable for treatment by the ordinary "hypo" process, the chlorinating and leaching being rendered difficult and incomplete in the presence of those bodies. Hence some of the silver remains in the mass as sulphide, and is not removed by hypo.

This difficulty is overcome in the Russell process, by following or, in some cases, preceding the ordinary thiosulphate leaching with a supplementary one by the double thiosulphate of soda and copper, formed by running the thiosulphate solution through a perforated box containing copper sulphate immersed in the leaching vat just above the ore. This method is rendered necessary by the ready decomposition of the double salt on exposure, and to prevent this the tanks are closed in. The double salt has the composition-

$$2Na_2S_2O_3, 3Cu_2S_2O_4$$

and the reaction is--
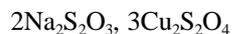
$$2Na_2S_2O_3,3Cu_2S_2O_3 + 3Ag_2S = 2Na_2S_2O_3,3Ag_2S_2O_3 + 3Cu_2S$$

The action of the *extra* solution is not rapid, and circulating pumps are employed to keep it in motion throughout the mass. Undecomposed sulphide of silver is thus dissolved out, and the silver in the residues is greatly reduced. The silver is precipitated by sodium sulphide as before.

The sulphide precipitates are, however, very impure, containing only 25 to 40 per cent. of silver. The excess of copper used in the *extra* solution is precipitated with the silver. Greater expense is entailed in refining in consequence. To obviate this, it has been proposed to treat the precipitate obtained from the *extra* solution with sodium nitrate and sulphuric acid, whereby the mixed sulphides are converted into soluble sulphates. The nitric acid fumes evolved are condensed, and the sulphur which separates used for making sodium sulphide.

The silver from the sulphate in the solution is then precipitated by copper, and the copper subsequently by iron.

In dealing with ores containing much galena, the lead sulphate and chloride formed in roasting dissolve in the thiosulphate. The lead is removed by the addition of sodium carbonate before precipitating the silver.

In zinc ores treated by this process, the zinc sulphate formed is dissolved out in the preliminary leaching with water.

In these processes, any gold contained in the ore was extracted to a large extent, and precipitated with the silver as sulphide. During the leaching it is attacked by the thiosulphate, and thus dissolved out.

The wooden tanks employed in these lixiviation processes are either round or square, well coated on the inside with tar. They are provided with a perforated false bottom covered with canvas, on which a layer of filtering material, about a foot thick, is laid. This material consists of gravel and silver sand, in layers, or of sawdust, according to circumstances. Over the top of the filter is another canvas covering.

The leaching liquor is frequently poured on the top of the ore, but sometimes is introduced by a pipe below the false bottom, and allowed to percolate upwards until the mass is soaked, to avoid air being trapped and secure uniform wetting and percolation,after which it is poured on top as usual. Below the false bottom is an opening in the side of the tank, by which the liquors are run off and carried by gutters into the settling and precipitation tanks. These, for convenience, should, if possible, be placed at a lower level. Steam-jet injectors are employed to elevate the liquors if necessary

Silver from Lead.--Patties's process for the concentration of the small amount of silver occurring in lead has been noted (in anther part of the book) and the melting with lead of the roasted sulphide precipitates obtained in the Von Pater,

earlier. Silver ores,. if pure sulphides, are sometimes added to a bath of lead in a reverberatory furnace, much in the same manner as the poor Von Patera precipitates

. The silver compounds are decomposed by the lead, and the silver passes into and alloys with the excess. Silver ores and precipitates are also smelted with lead ores or litharge in water-jacketed furnaces. A highly argentiferous lead is also obtained by the treatment of the 'zinc crusts removed in Parkes' process for desilverising lead *[in another part of the book]*.

Cupellation of Rich Lead. The lead is separated from the silver and gold by exposing the surface of the molten metal at a red heat to the action of a blast of air. The lead combines with oxygen, forming litharge (PbO), which melts, and is blown off the topi thus exposing fresh surfaces to the action of the air. Copper and other base metals present are also oxidised, and the oxides dissolved in the melted lead oxide are carried away by it (see p.

FIG. 144.

238). The silver and gold, which are unoxidisable, are left behind. Some little is, however, carried away in the oxide, particularly when the alloy becomes very rich. Bismuth remains until the last. In the English copulation furnace, this oxidation is conducted on a bone-ash cupel, and some of the litbarge is absorbed by the porous material. The bed of the German copulation furnace is made of marl brasque--a mixture of marl, or clay and lime, with wood ashes.

The English cupel or test is made by ramming bone-ash, moistened with a solution of pearl-ash, into an iron frame, with mallets. Cement and other porous basic materials have largely replaced bone-ash. The frame, A, is elliptical in shape, 4 to 5 feet long and 2 feet 6 inches to 3 feet wide, made of 5-inch flat iron, from ½ to ¾ inch thick. Five iron ribs, 3 to 4 inches wide and ½ inch thick, cross the bottom (a, Fig. 144). The bone-ash is rammed in in layers, and a cavity, E, scooped out with a trowel, leaving the sides about 2 inches thick round the top and 3 at the bottom, and the bottom itself about 1½ inches thick. At one end, some 5 inches of bone-ash are left, and an opening, F, is made clean through

the bottom, leaving a 2-inch dam, B. The litharge is thus prevented from coming into contact with the ironwork and corroding it. The cupel holds about 5 cwts. of lead.

This cupel forms the hearth of the copulation furnace (Fig. 145). G is the fireplace, C the hearth, and B the stack. A tuyère, N, having a downward direction; enters at the back, and over the door is a hood H, to carry away the fumes of litharge PbO. P is a pot in which the lead is melted. Coal is used as fuel.

The cupel, carefully dried

FIG. 145.

for some days, is placed on a truck, run under the furnace, and lifted into its place, in which it fits loosely. It is secured by wedges, crossbars, or by projecting eyes, and the edge of the iron ring covered with bone-ash. After carefully heating to redness, lead is introduced from the lead-pot, or in pigs, through a 'channel at the back. The blast is supplied by a fan, or occasionally by a steam jet. The litharge which forms is removed by making a little gutter in the bridge in front, through which it flows into conical iron moulds on wheels, placed beneath to receive it. The furnace is maintained at a cherry-red heat. As the lead is removed by oxidation, fresh additions are made to keep up the level in the cupel.

In working on Patties lead containing from 500 to 700 ozs. to the ton, the operation is conducted in two stages. In the initial stage a lead containing 8 per cent.---4,000 to 5,000 ozs. per ton is produced. The litharge produced in this stage is poor enough in silver to be sent into the market. It is sold for glass-making, etc. The enriched lead is then generally removed, being run into pigs by boring a hole through the bottom of the cupel. More poor lead is then treated in the same cupel after stopping the hole.
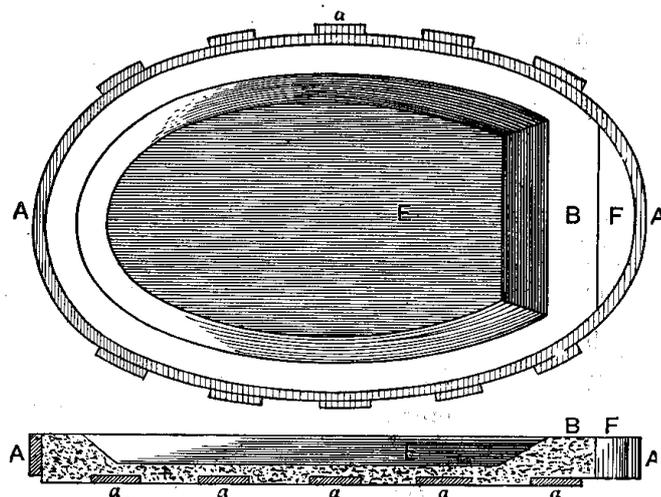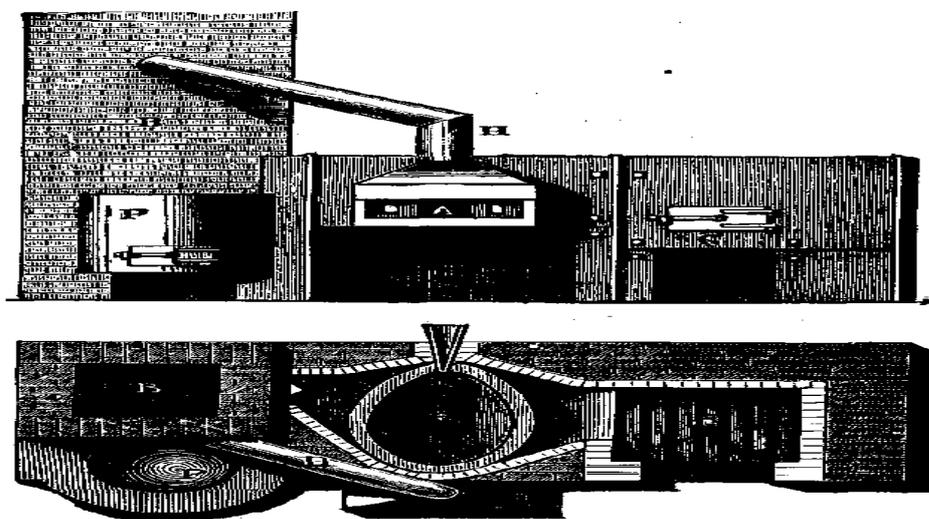
The rich lead is then similarly treated on a new test, the litharge being saved separately. It is reduced as described (earlier in the book), and yields lead containing some 4o ozs. of silver per ton. As the copulation approaches completion the surface of the metal becomes iridescent (rainbow tinted) and strikingly beautiful. As the last film of oxide clears off, the metal flashes out brightly, presenting a clear, brilliant, bluish-white appearance, Ithe surface reflecting the roof of the furnace, This is known as the "brightening" or "coruscation." The cooling of the silver must be effected slowly to prevent loss by "spitting." This, as already indicated, is prevented by a small amount of impurity, and its occurrence is an index of the purity of the metal. Many curious and fantastic forms result by the throwing up of the surface, partly caused by the escape of oxygen and partly by contraction of the mass expelling the fluid interior. Instead of solidifying in the cupel the silver may be run into moulds by making a hole through the test.

Oil-fired furnaces are also used.

In an ordinary furnace from 4 to 5 cwts. of lead are oxidised per hour, some 1½ cwt. of coal being required.

The silver is generally about 995 to 998 fine. The cupels are broken up and the parts saturated with litharge smelted with fluor-spar in a blast furnace to recover the lead.

Refining.--The refining of impure silver is effected either by copulation, or, if very impure, such as is sometimes obtained by amalgamation methods, by melting it and exposing it to the air or under oxidising fluxes in crucibles. Copper iron, etc., may thus be largely removed as dross. The purified metal is then refined on bone-ash cupels.

Separation of Silver from Copper.--Formerly a method of separating silver from argentiferous copper by means of lead was largely practised. The copper, melted with about four times its weight of lead, was cast into flat cakes I8 inches in diameter and 3 inches thick. These were then carefully heated and the lead allowed to liquate out, carrying the silver with it. The residues were subjected to a second liquation at a higher temperature. The argentiferous lead was afterwards cupelled.

Treatment of Slimes from Electro-refining Copper After roasting for 1½ to 8 hours at $700°$ F. to oxidise copper and other base metals the mud is boiled for several hours with from 15 to 2o per cent. sulphuric acid till silver shows on test in the solution. Sufficient *raw* slimes are added to precipitate any silver dissolved and the liquor syphoned off.

The residue is thoroughly washed finally on an Oliver filter. (If on testing selenium or tellurium is found in the liquor it is boiled with copper foil to precipitate it before sending it back to the tank room.)

The treated slime contains less than 2 per cent. of copper and is furnace refined.

Refining silver slimes containing selenium and tellurium.-The treated slimes containing. less than 2 per cent. copper and *25* to 50 per cent. moisture are melted in a magnesite lined reverberatory furnace, some 8 to 10 tons of wet slimes being introduced during 30 hours. During melting lead and much antimony oxidise, and combining with silica produce a glassy slag, which is skimmed off when completely melted. Air pipes are introduced and the charge thoroughly rabbled for some 6 hours. The remainder of the antimony, the arsenic and some selenium and tellurium are thus removed. Sodium carbonate is added to the charge in considerable amounts and soda nitrate to oxidise selenium, tellurium and copper and remove them with other base metals as a water soluble slag. This is continued till the impurities are eliminated and bullion of 99'5 per cent. purity is obtained. It may contain 98 per cent. silver and 1.5 per cent. gold. This is ladled out and cast into anodes, 6½ by 9 by ½ inches, for electrolytic parting by the Moebius process.

The dust produced in melting is recovered in dust catchers, scrubbing towers and Cottrell electric precipitators carrying current at 50,000 volts.

After drying, roasting to remove any selenium and arsenic, the residue of lead and antimony oxides is sent to the lead refinery.

The glassy slag produced in melting down is also sent to the lead works. Selenium and tellurium are recovered from the highly caustic solution of selenite and tellurite of soda obtained by leaching the alkaline slag.

Silver Refining Copper Slimes[7].- At Copper Cliff, Ontario, the typical slimes contain 24 per cent. copper, 20 per cent. nickel, 15 per cent. selenium, and 3.5 per cent. tellurium with silver, gold, also lead and arsenic. Copper and nickel are removed by treating with concentrated sulphuric acid by a sulphatising roast in an oil-fired reverberatory furnace with a cast-iron hearth. Just enough acid to combine with the copper and nickel is used. The temperature is carefully watched and the charge continually rabbled. The roasted slimes are leached in lead-lined tanks with 10 per cent. sulphuric acid followed by water. The liquor is raised nearly to boiling-point and agitated for an hour by steam fan. After settling, the slimes pass to a 40-inch suspended centrifugal with a rubber-covered steel basket, are washed with hot water, and transferred to the furnace room for treatment in the Doré furnace.

Any silver, selenium, and tellurium removed in leaching is precipitated by cement copper. The liquor is returned for re-use and the slime produced given the same treatment as raw slimes.

The treatment of the slime in the doré furnace, and subsequently, follows the usual lines (see above)

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[7]Bernard, Copper Metallurgy. American Inst. of Min. and Met. Engineers, 1934