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THE

METALLURGY OF SILVER.



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EDUCATION OF NEW SOUTH WALES.

SYDNEY:

THOMAS RICHARDS, GOVERNMENT PRINTER, PHILLIP-STREET.
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THE METALLURGY OF SILVER.



IN commencing this lecture it may be well to point out what is meant by the term Metallurgy. It has been defined as "the art of extracting metals from their ores," and the work of the metallurgist must be distinguished from that of the miner and ore dresser. It is the work of the miner to extract the ore from the earth, and he generally also dresses the ore; that is, separates it to a certain extent from the useless minerals associated with it. The dressed ore is then handed over to the metallurgist, who subjects it to various processes having for their object the final separation of the metal or metals in a tolerably pure state.

Of course a miner may be also a metallurgist, but this is not necessarily the case, and a man may be a skilful miner and yet know very little about metallurgy; and, on the other hand, a metallurgist may have no practical acquaintance with mines.

Before dealing with the various processes in use for obtaining the silver from its ore, I propose to say a few words about the properties of silver and the more important silver-bearing minerals. Silver is well known as a very white, rather soft metal, extremely malleable and ductile, and a very good conductor of heat and electricity. It has little affinity for oxygen, and is stable in the air. It combines with sulphur readily, however, and hence becomes rapidly coated with a black tarnish if exposed to sulphurous gases. Strong boiling sulphuric acid dissolves silver; but hydrochloric acid acts upon it very slowly, forming the insoluble chloride of silver. Nitric acid is the great solvent of silver, forming nitrate of silver. The nitrate is soluble in water, but readily precipitated by hydrochloric acid or a solution of a chloride (such as common salt). The chloride thus thrown down is dissolved by ammonia.

We may commence the subject of silver ores with *Native Silver*. The metal occurs native in many parts of the world, but mostly in small quantities. It often assumes curious forms, like wires twisted together, and may be recognized by its metallic appearance, and from possessing the properties of silver.

Argentite, Silver Glauce, or Sulphuret of Silver. This mineral is the sulphide of silver (Ag_2S), crystallizes in the cubic system, is very soft (2 to 2.5 in scale of hardness), so that it may be readily scratched with a knife, and sometimes even by the finger nail, and has a specific gravity of about 7. It is generally blackish to lead gray in colour, and when pure contains 87 per cent. of silver. It is perhaps the most common ore of silver, but seldom occurs in masses, being generally scattered through a large quantity of other materials.

Red Silver Ores or Ruby Silver. There are two species, called *Pyrrargyrite* and *Proustite*. *Pyrrargyrite* (dark red silver ore). This is a sulphide of silver and antimony, black to red in colour, with a high lustre, soft (2—2.5 in the scale), specific gravity between 5 and 6. *Proustite* (light red silver ore). This is a sulphide of silver and arsenic. Agrees with pyrrargyrite in most of its properties, but is usually of a lighter red.

Horn Silver or Kerargyrite. This is the chloride of silver (Ag. Cl.). It has a waxlike appearance, and may be readily cut and scratched by the finger nail; is generally of a pale gray colour, but may be white. When pure contains 75 per cent. of silver. It is not dissolved by nitric acid, but is by ammonia.

There are a number of other silver-bearing minerals, such as *Stephanite* (or brittle silver ore), *Freieslebenite*, *Polybasite*, &c., which it is not necessary to describe in detail. They are all sulphides of silver and other metals, and form valuable ores if in quantity; but practically it is comparatively rarely that one can identify a particular mineral in silver ores. There is one silver-bearing mineral, however, which must be alluded to. This is *Galena*, the sulphide of lead. All galenas contain a certain amount of silver, but the amount is often very small. How much silver a galena must contain to render it worth working as a silver ore will depend on where it occurs and other circumstances. There is no special character by which one can tell a rich argentiferous galena from a poor one.

It would be satisfactory if one could give some simple test by which to prove the presence of silver in an ore. Unfortunately this can hardly be done. If the ore is very rich, a bead of silver may be obtained by heating on charcoal before the blowpipe flame with a little carbonate of soda. Perhaps the best test is to treat the powdered mineral with nitric acid, when most ores are decomposed, the silver going into solution as nitrate, which may be thrown down by solution of common salt.

Owing to the small percentage of silver in most ores it is rarely practicable to obtain the pure metal by processes of smelting, as practised for the extraction of copper, lead, and tin from their ores. Thus an ore containing 1 per cent. of silver would be regarded as rich, while an ore

containing 1 per cent. of copper, lead, or tin would not be worth smelting for those metals. The metallurgical processes for the extraction of silver are therefore more allied to those in use for treating gold ores than to those for extracting the baser metals; and, in almost all, the object in view is to dissolve the silver in some substance from which it may afterwards be separated by suitable means.

Regarded in this way, the various methods of treatment may be divided into three groups, viz. :—

- 1st. Those in which the silver is dissolved in mercury, or amalgamation processes.
- 2nd. Those in which it is dissolved in lead; and
- 3rd. Wet processes, in which some compound of silver is dissolved in a liquid such as water or brine.

In the course of an hour's popular lecture, it is out of the question to attempt to give anything like a complete account of the various and complicated processes which have been tried for the extraction of silver. The most one can hope to do is to describe in popular language a few methods which may be taken as typical, pointing out the principles underlying each.

Thus, under the first heading or amalgamation processes, I propose to describe briefly—(a) The Mexican Patio process; (b) the Washoe process of pan amalgamation, as practised on the ores of the Comstock lode; (c) the Freiberg process of amalgamating in barrels.

In the "Patio" process, the ore having been reduced to small pieces by stamping or otherwise, is ground in *arrastras*. These are shallow pits having a pole in the centre, to which four arms are pivoted; the arms have large angular masses of stone attached to them, and are dragged round by mules until the ore is reduced to a fine powder. It is then transferred to the *patios* or paved courtyards, where it is made into a large heap or *torta*, containing many tons of ore. Common salt is scattered over it, and gradually dissolves and mixes with the ore. A quantity of *magistral* is also added. Magistral varies in composition, but usually contains sulphate of copper, being formed by oxydation of copper pyrites. After addition of the salt and magistral, the pile of ore is trodden by mules and turned over by men with shovels. When the mixture is complete, mercury is squirted over the heap, and gradually amalgamates with the silver, samples being taken from the heap from time to time, and examined, to see if the amalgamation is going on satisfactorily, and more mercury added as required, lime being also added in some cases. When the process is found to be complete, the heap is removed to deep stone vats, where more mercury is added, and also water, which is kept running through the vats, while the mass is agitated by paddles driven by mules; the heavy amalgam then settles to the bottom, while the lighter earthy materials are carried away by the water. The fluid amalgam thus

obtained is then squeezed through canvas bags, by which the excess of mercury is strained off, and a semi-solid mass of amalgam remains. This is squeezed into pieces forming segments of circles, and taken to the *burning-house*, where the mercury is distilled off, and the silver remains as a spongy mass.

The object of the process is to cause the silver present in the ore to alloy or amalgamate with the mercury; but the chemical changes produced by the common salt and *magistral* are rather uncertain. The general effect appears to be, that any silver present as sulphide is converted into chloride of silver. This chloride is decomposed by the mercury, chloride of mercury (calomel) being formed and metallic silver liberated. The mercury thus changed to chloride is lost, but the silver is dissolved by the excess of mercury present.

Various modifications have been introduced in the Patio process of late years, and there are only a few parts of the world where it is still practised. It is a crude and wasteful process, but has the advantages of requiring little fuel, water, or mechanical appliances.

The Washoe process of amalgamation in pans. The ores of the Comstock lode were mostly sulphides of silver, with a little native silver, diffused in fine particles through a quartzose gangue. The rich were generally separated from the poor ores, as it was only the poor ores which were suited to pan amalgamation. The ore having been broken in a rock-breaker, is conveyed to the stamps, where it is subject to wet crushing and passes through a sieve, the sand going to settling tanks and the finer materials, or slimes, being collected separately. The sand is then transferred to the pans for grinding and amalgamation. A great many different forms of pan have been invented, such as the Wheeler pan, Peterson's pan, and others, some having flat bottoms, others conical or conoidal.

Taking a typical flat-bottomed pan, it may be described as practically a large round tub, generally of cast iron, with the sides sometimes lined with wood. It has a hollow pillar at the centre surrounding an upright shaft; the shaft is connected with gearing below the pan, and drives the muller or upper grinding surface. The bottom of the pan is usually covered by a false bottom, forming the lower grinding surface. The muller is a circular plate of iron, usually shod with iron pieces. The pans vary a good deal in size and the charge they take. Some are charged with 600 lbs. of ore, others with as much as 5,000 lbs.; but 1,200 to 1,500 lbs. would be an average charge. The pan being charged the muller is set in motion and gradually lowered, the sand being reduced to a pulp with water. After a time, some mercury is added, and usually some *chemicals*. These chemicals are generally common salt and sulphate of copper; but all sorts of materials have been tried, such as tobacco juice and decoction of sage brush. The amount of chemicals also varies greatly, sometimes merely a handful, sometimes 3 or

4 lbs. to a charge. The contents of the pan are kept at a moderate heat by steam, which is either introduced directly into the pan or into a separate chamber in communication with it.

The amalgamation being complete, the whole mass is washed into the settlers or separators. These are round tubs like the pans, but generally of larger diameter, having revolving arms extending from the centre, the object being not to grind the materials but to keep them agitated, so that the amalgam may settle to the bottom while the earthy materials may flow out of the top of the pan, and after a time, plugs are removed from the side of the settlers and allow the water to drain off. The amalgam is then washed, strained, and the solid amalgam retorted, that is, the mercury distilled off, leaving the silver. The residues carried away by the water from the separators form the *tailings*, and may contain enough silver to be worth further treatment for its extraction. The chemical reactions which go on in the pan have been a good deal debated. It was generally held that the chemicals had a considerable effect; but, from the very small quantities used in some cases, they can hardly have much effect, while it has been found that when they are omitted altogether the yield is little if at all reduced; so that it would appear that the iron of the pan itself is the most active agent in bringing the silver into a condition in which it can be dissolved by the mercury.

It has been mentioned that the richer ores of the Comstock lode were not found to be suited for treatment in pans, and these were mostly calcined with salt and amalgamated in barrels by what is known as the "Freiberg" process, from the part of Germany where it was formerly largely used, although now the amalgamation processes have been largely superseded in Germany by the various wet processes.

In treating ores by the Freiberg process they are crushed dry and calcined with common salt. Many forms of calciner have been tried, but it is often an ordinary reverberatory furnace, on the bed of which the ore mixed with salt is exposed to a moderate heat, which must be carefully regulated. The result of the calcination is first to convert the sulphide of silver to sulphate, and this is acted on by the salt and chloride of silver formed. The calcined ore is ground and introduced into strong barrels, which can be caused to revolve by gearing. A quantity of water is added, and some scrap or bar iron, the barrel closed and set revolving. After a time it is stopped and mercury run in, the barrel again closed, and caused to revolve rather more rapidly than before. When the amalgamation is complete, the amalgam is run off, washed, strained, and retorted as usual.

The action of the scrap iron is to reduce the chloride of silver to the metallic state, and it then combines with the mercury, so that no chloride of mercury should be formed if the process is properly conducted.

Methods of extracting Silver by concentration with Lead.

There are many silver ores, such as argentiferous galenas, which are not suited for treatment by amalgamation, and these may often be conveniently treated by dissolving the silver in a quantity of lead, while almost all ores may be treated in this way if the conditions are favourable. Tolerably pure argentiferous galenas are of course smelted by the usual process for smelting lead ores, either in reverberatory or blast furnaces, while where the lead is not present in sufficient quantity, it may be added to the charge either as metallic lead or in the form of galena or other lead compounds which are reduced in the furnace. In some cases, however, especially if the ore contains pyrites, it may be advisable to have a preliminary roasting and smelting for the production of a regulus or malt which can be afterwards smelted with lead.

Formerly, the process of "liquation" was practised in Germany, but is now almost superseded. In this process the copper ores, containing a small quantity of silver, were smelted in the usual way to the stage of "black copper" or "fine metal," and this was then smelted with a quantity of lead. An alloy of lead and copper was thus obtained, and this having been cast into cakes, was arranged in a sort of rack surrounded with charcoal powder, and having a channel below for the lead to flow off. A fire was then made, and the temperature raised above the melting point of lead but below that of copper, when the bulk of the lead liquates or sweats out, leaving a mass of copper with some lead, but very little silver, which is mostly contained in the lead which flows away.

In the case of some American ores which were mainly galena (sulphide of lead) and sulphide of antimony, they were first roasted, then melted in reverberatory furnaces and repeatedly skimmed, the skimmings being suitable for the manufacture of type metal; and finally, a rich lead was obtained, which was cupelled.

In order to finally separate the silver from the lead, cupellation is always resorted to; but if the lead is poor,—that is, not containing enough silver to be worth cupelling at once,—it is treated by one of the processes for enriching it, or concentrating most of the silver in a part of the lead. There are many of these processes, but that known as the Pattinson process, from its inventor, has been most largely used. When lead containing a small quantity of silver is melted, and then allowed to cool slowly, it is found that the lead which solidifies first is very poor in silver, while the part which remains longest liquid is much richer. Advantage is taken of this in the Pattinson process. A number of large iron basins or pots are arranged in a series, and having a separate fire-place under each. In commencing the process, we may suppose one of the pots near the centre of the series to be

charged with, say, 10 tons of lead, containing 10 ozs. silver per ton. The lead is melted, and then allowed to cool, while, as it cools, the metal is stirred by the workman with an iron rod to prevent it clinging to the sides. As soon as it begins to solidify, a perforated ladle is introduced; and the crystals which form scooped out, allowed to drain, and passed to the next pot to the right. This goes on until about two-thirds of the lead has been thus removed, which will contain about 5 ozs. silver to the ton, while about one-third of the charge remains liquid as enriched lead containing 20 ozs. silver to the ton. This is removed to the next pot to the left. By repeating the process on the enriched lead, a still richer product containing 40 ozs. to the ton is obtained, and again passed to the left, while the poorer part containing 10 ozs. to the ton, goes back into the pot with which we started. This goes on, several pots being treated at one time, the poor lead being always passed in one direction and the enriched lead in the other, until at one end of the series we may get a lead containing 150 ozs. silver to the ton, which may be cupelled; while at the other is a very poor one, containing perhaps only $\frac{1}{2}$ -oz. of silver to the ton, which is not worth further treatment, but may be sent into the market as pure lead. The Pattinson process may be modified in various ways, as to the number and size of the pots, &c. I can only allude to one other process for enriching lead. In Parkes' process, advantage is taken of the fact, that when lead and zinc are melted together, and subsequently cooled slowly, the zinc separates as a crust on top of the lead, carrying most of the silver with it, while the residue consists of lead with some zinc, but very little silver.

Cupellation. This beautiful process has been known and practised from very early times, although, of course, the ancients were ignorant of the chemical actions involved. These may be briefly summarised by saying, that when melted lead is exposed to a current of air it combines with the oxygen of the air to form oxide of lead or litharge, while any copper, antimony, or other base metals which may be present, are oxydised at the same time. At a high temperature the oxide melts, and either flows away or is absorbed by the bed on which the metal rests; while the silver, not being acted on by the air, accumulates in the residue, until at last, all the base metals being removed, the pure silver alone remains.

On the large scale, the process is carried on in a sort of reverberatory furnace, in which the bed, called a test or cupel, is formed of some absorbent substance, such as bone ash or marl, and there is an arrangement for directing a jet of air on the melted metal. There are two modifications, known respectively as the German and English methods of cupellation, but the differences between them are rather in detail than in principle. Thus, in the English method, the test is usually moveable and formed in a frame, the roof of the furnace being fixed. In the German method, the hearth is somewhat different in shape, and fixed, while the cover of the furnace is moveable.

In both, the lead is placed on the test or hearth and melted down, the blast is turned on, and the lead is gradually oxydised, the molten litharge flowing away or being absorbed by the test. Fresh lead may be added from time to time, and when the remaining lead is very rich, the process may be interrupted, and the last stage of refining be performed on a fresh cupel. When very impure lead is cupelled, the first litharge formed may contain a good deal of the oxides of copper, iron, zinc, &c., and this, forming the "abzug" and "abstrich" of the Germans, is kept separate from the purer litharge formed later. As the process approaches completion, the silver is only covered by a thin film of litharge, and this finally disappears, and the cake of pure silver brightens as it is called. The silver must be cooled carefully, as a good deal of oxygen is absorbed or occluded by molten silver, and this is given off in jets as it cools, producing spitting, which may cause a loss of silver. The whole of the silver contained in the lead should be obtained by cupellation if properly conducted, and so accurate is the process, that it is almost universally used in the assay of silver ores.

Wet Processes.

There is only time to give a very brief account of some of the wet processes which have been or are in use for the extraction of silver.

Augustin's Method. In this, one of the oldest of the wet processes, the ore is roasted with common salt, as in that for the Freiberg process of amalgamation and for the same object, namely, to convert the silver present into chloride. Sometimes the roasting is done in two stages, the ore being first roasted alone and some of the arsenic and sulphur expelled; afterwards ground, mixed with salt, 5 to 15 per cent., and roasted again, the heat being carefully regulated, any sulphide of silver present being converted into sulphate, and this decomposed by the salt,—chloride of silver resulting. The roasted ore is withdrawn, and carefully washed or lixiviated with a strong solution of common salt, for, although a solution of salt precipitates silver from a solution of the nitrate, yet the chloride of silver thus formed may be dissolved in a large quantity of strong brine. The brine containing the silver in solution is then passed over copper, which takes the place of the silver in solution, the latter metal separating in the metallic state. The precipitated silver is collected and fused in crucibles.

Ziervogel Process. This process has superseded that of Augustin in some works, and is said to give the best results when carefully conducted. The ore is first subjected to a very careful roasting. During this, the copper and iron present are first converted into sulphates, and the silver is also changed to sulphate. By raising the temperature, the sulphates of copper and iron are broken up, oxides of those metals being formed which are insoluble in water. If the roasting were kept on too long, the sulphate of silver would be also broken up and metallic silver left; but by stopping the

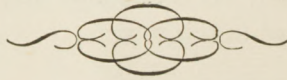
roasting at the right time, the silver, with a little copper, alone remain as sulphate, which may be dissolved in water. For this purpose, the roasted ore is removed to tanks or tubs, where it is lixiviated with hot water very carefully, and the solution passed over copper, when the silver separates as cement silver, as usual. The process is often applied to ores which have undergone a preliminary smelting for the formation of a regulus or matt. Although the process is a very good one for some ores, it is not suited for others, especially for those containing lead, antimony, or arsenic, since much of the silver is likely to be lost in these cases. It also requires considerable skill and experience in those who superintend the roasting. For these reasons, a combination of the Ziervogel and Augustin processes has been used in some works.

Von Patera's Method. This process, which does not seem to have been much used, is similar in the first stage to Augustin's, that is, the roasting with common salt. A solution of hyposulphite (thiosulphate) of soda is used to extract the chloride of silver, which is more readily soluble in this solution than in brine. From the solution the silver is thrown down, as sulphide, by a solution of sulphide of sodium. The sulphide of silver may be reduced by heating, and afterwards fusing with iron in crucibles.

In the Claudet process, small quantities of silver chloride contained in the liquors resulting from treating cupriferous pyrites in the wet way, are precipitated by a soluble iodide. The iodide of silver is decomposed by metallic zinc, iodide of zinc being formed, which can be used to precipitate a further quantity of silver. It is said that very small quantities of silver may be profitably extracted in this way.

From this brief review of some of the metallurgical processes used in the treatment of silver ores, one can hardly fail to be struck with their great variety, as well as the skill and ingenuity shown in devising and carrying out some of them. But if the question be asked, which are the best? no definite reply can be given, since so much depends on the circumstances of each particular case, such as the character of the ores and of the minerals associated with them, whether they must be treated at the mines or may be carried to a distance, what materials are available for the construction of plant, or as re-agents to be used in the process chosen; what labour is available, and whether it would be necessary to specially train the workmen; whether it is desirable to extract other metals besides silver from the ores, and similar considerations. The skill of the scientific metallurgist is in fact shown by his selecting the most suitable process for treating the ores with which he has to deal, and then in carrying out the process in the best and most economical way, introducing any modifications which may be necessary, since the ores of two localities are scarcely ever exactly alike.

The subject of the metallurgy of silver is already of considerable importance in New South Wales, and is likely to become more so, since the silver produced in the Colony is considerable in quantity now, and will probably increase largely as new deposits of ore are discovered and those already known are more extensively worked. No allusion has been made to the methods at present adopted in treating those ores, as the object of this lecture is merely to give a popular account of the methods adopted for treating silver ores in various parts of the world, especially in those countries where they have been successfully worked for a long time, but all will join in cordially wishing prosperity to the silver industries of New South Wales.



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