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THE PROFITABLE TREATMENT OF SILICEOUS LOW-GRADE COPPER ORES.

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The question of the economic treatment of these ores is of the highest importance, and will require to be seriously undertaken at some future time. The writer, in discussing this question, does not propose to touch on the fire concentration or smelting methods. The majority of these deposits are situated in positions that would not admit of the importation of fluxes and fuels to effect a smelting operation at a commercial profit.

No doubt in many typical cases of self-fluxing ores, or with such fluxes and fuels adjacent to the copper ore deposits, the method of matte smelting and converting the product to copper could not be surpassed, either as regards continuous action in operation or the cost of same.

Unfortunately, the notable successes in that line do not account for the ultimate metallurgical destiny of the isolated deposits of the above classes of ores.

If we take chalcopyrite ore, distributed in small particles through a siliceous matrix, it will be sufficiently representative of the isolated deposits scattered through Australia and Tasmania. It will be clearly seen that there is a wide field for discussion regarding their profitable treatment. For some years past the writer has occupied a considerable portion of his time in an investigation and study of this class of ore from the other States and the West Coast of Tasmania. In consequence, the fact has been fully borne home to him that, in regarding these occurrences individually, and as a possible source of profit to their owners, the lines of investigation must be carried out in some other direction than fire concentration. The writer therefore commenced his lengthy series of investigations with the experimental concentration of low-grade copper sulphide ores by water.

Experimental Concentration by Water.

The aim in this test was to obtain a degree of concentration, both in bulk, by weight of material, and increase in copper contents of the concentrates, that would about return the costs of the operation, leaving any profit that might be possible to be recovered from the tailings. It appeared that if operation costs could be thus returned, a deferred profit might be acceptable. The test which most closely resembles this result will now be described. The ore-sample used was 100 lbs. of a typical low-grade ore, as described hereunder. It was carefully weighed after grinding and crushing on a castiron board, and passed through a sieve of 40 holes to the linear inch. The ore was then carefully concentrated in small lots in a riffle dish by an expert manipulator. The three products, investigated in rotation, are as follows :—First, the crude ore; second, the concentrates; third, the tailings.

The following is the writer's analysis of the crude ore :—

Copper. Per cent.	Iron. Per cent.	Silica. Per cent.	Alumina. Per cent.	Sulphur, alkali, &c., undetermined. Per cent.
3 ·9	9 ·55	50 ·15	16 ·85	19 ·51

The concentrates, after being dried at 100° C., were found to contain by weight 7 ·277 per cent. of the original ore-sample tested of 100 lbs., and a separation into the tailings of 92 ·723 per cent.

The writer's analysis of these concentrates was as follows :—

Copper. Per cent.	Iron. Per cent.	Silica. Per cent.	Alumina. Per cent.	Undetermined Per cent.
11 ·12	28 ·40	14 ·40	4 ·60	41 ·48

The tailings, after being dried at 100° C., were then assayed for copper, and found to contain 3 ·37 per cent., as the tailings contained by weight 92 ·723 per cent. of the original ore-sample this calculated out to a separation into the tailings of 3 ·13 per cent. of the copper contents of the crude ore, and a recovery in the concentrates of 0 ·81 per cent. of the copper contents of the crude ore.

The concentrates should then contain by calculation $0 \cdot 81 \div 7 \cdot 277 \times 100 = 11 \cdot 13$ per cent. of copper, proving the assay to be concordant to 0 ·01 per cent.

The small percentage of copper recovery in the concentrates is accounted for by the sliming of the ore.

The results of the writer's tests clearly show that, in the case of low-grade chalcopyrite ore, the grinding of the material to the necessary degree of fineness, to prepare it for lixiviation, pulverises the chalcopyrite contained in the rock to so minutely divided powder that each microscopic particle has a gravity unequal to settling in the bulk of water in contact with it; and, in consequence, it floats away on the surface of the water. The tailings from this experiment were then subjected to a lixiviation test, as follows :—A 5 per cent. solution of sulphuric acid by volume was adopted on the basis of one ton of solution to one ton of tailings, and as temperature plays an important part in the time of extraction, the vat was kept as nearly as possible at a temperature of 70° F., to agree with a climate that would be favourable to a method of this description.

The following table shows the time of extraction of the copper from the tailings under these conditions :—

No. of Assay.	Tailings.	Copper Per cent.	Extraction Per cent.
1	At start	3 ·37	Nil.
2	After 12 weeks	0 ·50	2 ·87

The conclusions at which the writer arrives is that the wet concentration of the sulphide ores of copper should not be attempted unless it is intended to make a profitable recovery from the prepared and residual tailings.

It might be possible by a lengthy lock-up of capital to obtain a slow profit in the way described in the foregoing test, but it does not recommend itself as having and particular merit.

In the large pyritic deposits in Spain, a country whose climate is eminently suited to it, large profits are made by natural lixiviation, when the persistent formation of sulphates can be relied on.

The writer regards the concentration tests by water as merely a useful basis from which to start in following up the inquiry.

PART II.—*Chemical Methods.*

The next stage in the investigation was a careful examination of the various chemical methods that have been employed or proposed in various countries for the treatment of this class of ore. The writer started with the old and well-known method of the chloridising roast. The principle involved in this process is the conversion of the copper sulphides to cupric chlorides by roasting the crushed ores with an admixture of salt. Very nicely drawn conditions require to be observed in order to obtain a high extraction of the copper. The roasting operation requires to be carried out in a muffle furnace provided with water-condensers, to recover the cupric chloride that is largely volatilised. The cost of this operation is therefore much higher than a roast carried out in an open hearth reverberatory calciner, where the heat generated by the fuel used is applied directly to the ore.

The other conditions necessary to successful operation were, according to the writer's tests, as follows :—First, the sulphur should not exceed 1½ times the quantity of copper present; second, from 5 to 6 per cent. of copper is the outside limit that the ore should contain; third, the temperature of the furnace should not exceed dull redness. Over a number of trials on ores containing various copper contents, it was found that a proportion of anything less than four units of salt to one unit of copper gave most unsatisfactory extractions.

With all the conditions carefully observed and attended to, an extraction of 70 per cent. of the copper present could be relied upon. The writer's conclusions, however, are that the high charges of a muffle roast, coupled with the cost and importation of the necessary quantities of salt, would not admit of profitable treatment.

The Hunt-Douglas Method.

The principles laid down in this method were the next in order of the investigation programme. The crushed and roasted ores are treated by a solvent solution, whereby the copper is taken into solution as its chloride; and it is precipitated from the solution by the injection of sulphurous acid gas. The solution is regenerated by addition of salt. This process gives excellent results where the conditions are favourable to its operation. The necessary adjunct of a cheaply-mined pyritic body would strictly limit the economic value of its application. It can therefore be passed over in the present consideration of the various methods. Various other methods of minor importance were then tried, and, with one exception, they did not offer sufficient encouragement to follow up. The exception referred to is the method of roasting the crushed ores with ferrous sulphate. It is carried out very cheaply in some countries, in the following manner :—The crushed ores are made into stiff paste bricks with cementation liquors, and then burnt in kilns, thus converting the low-grade sulphides into sulphates, which are soluble in water. After arriving at this stage, it appeared essential that a satisfactory financial solution was of equal importance with a successful hydro-metallurgical one, and, in addition, a continuous and sustained action that would compare with that obtained by a smelting operation. If these opposing factors could be reconciled, it appeared evident that a satisfactory solution of this problem could be arrived at. The field of investigation was now narrowed down to definite lines of inquiry, and the final outcome was that the writer has demonstrated that the following method will fulfil all of the above conditions. All ore was selected for treatment typical of the low-grade siliceous ores surrounding the Mount Lyell field, and from the Mount Lyell Comstock Mine.

The following is a complete analysis of it by the writer :—

	Per cent.
Silica	48 ·0
Copper	4 ·56
Iron	13 ·29
Sulphur	12 ·60
Alumina	12 ·90
Zinc	1 ·17
Manganese	1 ·26
Lead	1 ·40
Magnesia	3 ·40
Oxygen, and loss	1 ·42
	100 ·00

It will be seen from the conditions that these ores contain considerable sulphur contents, and, moreover, that by a judicious selection of a small proportion of the ores as they leave the mine, the sulphur contents of that small portion can be considerably increased. This is the main factor on which the writer proceeded to work out this method for their profitable treatment, and he now proposes to follow the ores in their progress from the mine to their final conversion to a marketable product. The following is a detailed description of the method :—

Operations at the Mine.

When the ore is extracted from its place *in situ* by any of the usual systems, the aim should be to roughly and cheaply throw out the richer sulphides, to the extent of from 1-8th to 1-10th of the bulk of the ore treated. In the generality of cases an enriched sulphide zone has been deposited on the footwalls of these ore-bodies. If they are not greatly enriched in copper, owing to the increased amount of iron sulphide present, these narrow zones are notably increased in sulphur contents. When this is the case, the taking out of this portion separately would save the small additional cost of the rough selection. This smaller proportion is reserved for separate treatment, and the main bulk of the ore then goes forward to the regular plant.

Preparation of the Ore (main bulk).

The ore is first reduced to such a degree of fineness as the operator may find necessary, in order to expose the small sulphide particles to the oxidising flame of the calciner. The machinery employed for this purpose can be adopted by any particular operator to suit himself.

Calcination of the Ore.

This operation is of great importance, and a consideration of the chemistry of calcination is essential. When the ore is subjected to an oxidising roast in its pulverised state, it undergoes two important changes, viz., a chemical and a physical one. The chemical change is, firstly, the oxidising of the first atom of sulphur, which is feebly combined, with the generation of sulphurous acid gas; and, secondly, the combustion of the second atom with the generation of both sulphurous and sulphuric acid gases; and, finally, as the temperature is raised, the formation of oxides and sulphates of copper.

Although these reactions are well-known, it is not generally known that the physical change imparted to the finely-ground ore is of equal importance where a leaching operation is contemplated. The fine rock particles are granulated, and are made amenable to free percolation, and perfect leaching. This fact has now become so well recognised in America that the slimes from a previous operation, and which require a further wet treatment, now undergo a preliminary roast, when they are found in good physical condition for percolation and leaching. The stage to which the calcination of the ore is carried is the first important consideration, and, provided that the last of the sulphides as such are converted, it is a matter of no moment what proportion the residual oxides and sulphates bear to one another, and the charges can be drawn at that stage. It can be noted that the over-roasting of the charge has no prejudicial effect on subsequent operations, except slightly adding to the cost. Automatic reverberatory calciners, when used on a large proposition, are the most economical; but the hand-rabbled type on small and isolated mines are less costly.

Forced Leaching of the Ore.

The calcined ore is then transferred to the wooden leaching-vats (fitted with filter bottoms), and discharged gradually and hot from the calciner into the sulphurous and sulphuric acid solution in the leaching vats, derived from the ore that has been separately treated. The best mixing proportion is 200 gallons of solution to one ton of ore. The ore is well covered, and the temperature raised considerably by the hot ore. The discharge-pipe from the muffle furnace (described under the separate treatment) is then started, and the temperature is further raised by that means. The copper sulphates in the charge being easily soluble, the writer has provided for the attack on the oxides only. These are then attacked very rapidly by the sulphurous and sulphuric acid solution ,and the reaction completed in a very short time.

1st. $CuO + H_2SO_3 = CuSO_3 + H_2O$

2nd. $CuO + H_2SO_4 = CuSO_4 + H_2O$.

The hot oxygen of the blast also tends to oxidise the surplus, H_2SO_3 to H_2SO_4, which is an advantage.

Precipitation of the Copper.

The strong copper solution is then run through the filter-taps into the precipitating vats on to bars of pigiron, and the precipitation effected hot. About 1-12th of the copper contents will be retained by the dampness of the charge in soluble form. This can be recovered with one wash water.

Separate Treatment of the Selected Portion of the Ore.

This portion, being higher in sulphur contents than the main portion of the ore-body, is used for making the sulphurous and sulphuric acid waters necessary for leaching the whole of the ore. By a convenient muffle arrangement of a small type, the furnace gases are injected into the ore-extraction vats, thus generating the sulphurous and sulphuric acids in the solution. This is further increased by arranging a hot-air coil in the fire-chamber and passing the hot-air also through the muffle. As pyrites does not give up the whole of its sulphur in a closed muffle, this obviates that difficulty, and reduces cost.

Treatment Cost per ton of Crude Ore.

These costs have been carefully considered, and are on the conservative side :—

	Cost per ton.	
	s.	d.
Crushing schistose ores	5	0
Reverberatory roast	3	6
Labour on leaching-vats	0	6
Hot air	0	6
Sulphurous and sulphuric acid waters ...	2	6
Pigiron	1	0
Total	13	0

Against this a reduction of 4*s*. can be safely made on the copper values from the muffle roast, making the treatment charges against the ore 9*s*. per ton.

With the mining charges added, it will leave a range of profit on a fairly low grade ore. The precipitated copper would be the final product, and it would range in assay value from 70 to 80 per cent. of copper. There is a ready Australian market for this high-grade product, which only requires a common melting operation to convert it to copper.

Conclusion.

After a long investigation of this subject, the writer has arrived at the conclusion that this process will fulfil the conditions necessary for the successful treatment of these ores. The action is rapid, continuous, and complete. Various further economies in the costs of running can be made, notably in the regeneration of the solutions, &c.

A plant in full running order, capable of treating 100 tons of ore per diem, could be installed for about £2500; and for every 100 tons additional, an increase of 25 per cent. on that amount.

An advantage of this process is that it is not based on finely-drawn chemical equations, as most chemical processes are; and a few days' experience on an ore would show the best working conditions to each individual operator.