

METALLURGY OF COMPLEX Pb,
Cu AND ZINC SULFIDES (*)

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For the winning of Pb, Cu and zinc from sulfides ores by conventional methods, it is essential that these be beneficiated to high grade concentrates. The ore minerals in polymetallic and complex deposits are often found to be in close mutual penetration with each other and to the non-metallic gangue. In many cases where the attempts have been made to concentrate these ores, it is either difficult to obtain a suitable grade of the concentrate by conventional flotation methods or the recovery of metals into the respective concentrate is poor. Zinc that finds its way to a copper concentrate is always discarded in the slag as a waste, while copper in a Pb concentrate leads to serious smelting problems. In such cases the cost of production by a smelting process becomes unfavourable and new approaches to process these ores become more attractive. Hydrometallurgical processes, based on leaching and precipitation alone, or in combination with conventional extractive metallurgical methods will play an important role in meeting the requirements of such complex ores. Such processes can more easily be adopted to small scale operation than conventional smelting and refining.

Polymetallic copper, lead and zinc sulfides occurring in Sikkim analyse Cu 0.67%, Pb 1.48%, Zn 4.50%, Fe 15.22% S-8.68 and SiO₂ 58.20, Chalcopyrite, Galena, Sphalerite and pyrrhotite are the chief sulfide minerals, whereas Quartz and chlorite constituted the bulk of the gangue. The copper, lead and zinc minerals are fairly free from the silicious gangue at about 48 mesh size. But fine grinding is found to be necessary to liberate the sulfide minerals. A bulk float received from Sikkim Mining Corporation analysed Cu=14.45%, Pb=7.83%, Zn=6.65%, Fe=31.52% S 29.92% and

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insolubles 3.82% and it is estimated that daily production of the bulk float will amount to 10 tons. A small plant based on hydrometallurgical treatment near the mining site would be a right answer for the recovery of metals.

Methods of treating complex sulfides:

The type of variations that are found in hydro-metallurgical flowsheets for the processing of complex sulfides ores depend on the nature of the gangue materials and the percentage composition of the various non-ferrous metals present in the ore or in obtained bulk concentrates. The first major step in such methods aims at taking the non-ferrous metallic values in solution and leaving behind major iron in the leach residue. The next steps are solution purification, separation of the non-ferrous metals from each other by cementation, precipitation, solvent extraction or by electrolysis. Fluosolid roasting a fairly new comer to the field of Extraction metallurgy helps in the selective conversion of non-ferrous values in the ore to sulfates which are soluble in dilute acids or water and thus permit a good separation of iron which exists in the roaster calcine as an insoluble ferric oxide. Due to the vigorous mixing of materials inside a fluo solid roaster, the temperature through-out the bed remains the same and can be easily controlled. By fixing the proportion of air to solid feed in the roaster, calcine or gas compositions can be controlled and thus a selectivity in the sulfation can be achieved.

One such recent approach for the development of a bench scale process for the treatment/complex sulfides is of carried out by the research staff of the Extraction Metallurgy Division of the Battelle Memorial Institute, Ohio. The ore in question analysed 8.7% zinc .14% Cu and 3.1% Pb 33% Fe and 40% total sulfur. A small percentage of Cu occurring with substantial amounts of zinc and Pb is a characteristic of the ore. After selective sulfation in a fluidized bed resulted in the solubility of 92% Cu and zinc in dilute sulfuric acid (50 grams per litre) leaving behind Pb and iron in the residue. As the concentration of Cu in the leach solution was relatively low in this case, copper could be recovered economically by cementation, and the pregnant liquor with zinc could be purified and Zn won by electrolysis.

However where the copper occurs in substantial amounts, as in the case of Kosoka Plant in Japan the bulk concentrate which analyse 8.5% Cu and 14.7% zinc a method based on the cementation for Cu recovery from leach liquors containing Cu and Zinc would prove uneconomical and the

copper recovery step had to be modified. The Kosaka plant adopted a method based purely on electrolysis for the separation of Cu and zinc. Cu electrolysis from the leach solutions analysing 54 gm. per litres Cu, 100 gm. per litres zinc and 2 grams per litres iron is done in stages. The first stage produces cathode copper bringing down the copper content of the solution to low values and in the second stage sponge copper is produced. The spent liquor from this stage contains 1.1 gram/litre of Cu, 90 gm/litre H_2SO_4 and 100 gm/litre H_2SO_4 . The solution is to be neutralised and iron precipitated by addition of lime before solution purification can be effected for electrolysis of zinc. However in both the above cases the spent liquor containing average about 40 gm/litre zinc and 100 to 110 gm/litre H_2SO_4 had to be recycled in the first case, to the stage of preparing a feed for the roaster and in the second case, to the leaching circuit after H_2SO_4 acid neutralisation by lime.

Pressure leaching for the treatment of complex sulfides had been recommended by M/s Machiw, Benz and Evans purely on a theoretical basis and possible methods of separation of Cu and zinc indicated. However Autoclaving under these conditions would take most of the Fe in solution which would have to be removed by subsequent treatment.

SOLVENT EXTRACTION:

U.S.B.M. has developed a process recently for obtaining a clean separation of copper and zinc by solvent extraction and electrolysis. The leach liquor obtained by sulfate roasting and leaching is purified to remove iron, and zinc is selectively recovered by solvent extraction with a kerosene solution of calcium salt - 2 ethylexyle phosphoric acid and subsequently stripped from the loaded organic with sulfuric acid or spent electrolyte by conventional zinc electrolysis. If the copper content of the zinc raffinate is high copper may be recovered directly by electrowinning.

TREATMENT OF SIKKIM CONCENTRATE:

Thermodynamic calculations have been made for the equilibrium composition of the roaster gas for sulfate roasting of Sikkim concentrate in the Fluo-solid roaster. For a ratio of 45 moles of air per mole of Cu in the feed in a roaster it is seen that the Ferric sulfate would start decomposing at a temperature of $900^\circ K$ whereas the other sulfates would remain stable. The effect of

oxygen enrichment of the air has also been considered. Preliminary experiments were carried out in a 6 cm. stainless steel fluo-solid reactor at different temperatures ranging from 750°K to 925°K with 45 moles of air per mole of Cu in the feed. The roasted product obtained in all the experiments was leached with 2.5% sulfuric acid for dissolving copper and zinc. The results reveal that a maximum dissolution of 86.2% Cu, 68.4% zinc with a minimum of 5-6% Fe could be obtained by roasting at 900°K.

The results obtained indicate the feasibility of recovering Cu, Zn, Pb present in Sikkim concentrate by the following steps:-

- 1) Fluidised bed roasting of Sikkim concentrate.
- 2) Weak acid leaching for the dissolution of Cu and Zn.
- 3) Recovery of copper by electrolysis or by solvent extraction.
- 4) Recovery of zinc by electrolysis.
- 5) Recovery of the Pb from the leach residue by brine leaching and precipitation as basic hydroxide using lime.

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