Treatment of complex lead, copper and zinc sulfides

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FOR the adoption of conventional methods for the recovery of lead, copper and zinc from the complex sulfide ores, it is essential that these be beneficiated to a high grade concentrate. The minerals present in such complex ores are often found in such close inter-growth that it is either difficult to obtain a suitable grade of the concentrate by physical methods or the recovery of metals in the respective concentrates is poor. For example, the zinc that finds its way to a copper concentrate is always discarded in the slag as a waste, while copper in a lead concentrate leads to serious smelting problems. In such cases the cost of production by conventional smelting process becomes unfavourable and new approaches to process the ores become more attractive.

Hydrometallurgical methods based on leaching and precipitation rather than smelting will play an important role, in meeting the requirements for the treatment of such complex ores. Such processes can more easily be adapted to small scale operation than conventional smelting and refining. The purpose of this paper is to focus attention on the various approaches that have been made for the treatment of complex sulfide ores and to describe the laboratory scale experiments that have been carried out in a 6 cm. dia. fluo-solid roaster on bulk concentrate of copper, lead and zinc received from Sikkim Mining Corporation.

Methods of treating complex sulfide ores

The type of variations that are found in hydrometallurgical flowsheets for processing the complex sulphide ores depend on the nature of the gangue materials and the percentage composition of the various non-ferrous metals in the ore or in the bulk concentrate. The first major step in such methods aims at taking the non-ferrous values in solution and leaving behind major undesirable constituents in the leach residue.

The advent of fluo-solid roasters in the field of

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SYNOPSIS

A bulk float sulphide concentrate received from Sikkim Mining Corporation analysed Cu–14.45%, Pb–7.83%, Zn–6.65%, Fe–31.52%, S–29.92%, moisture 2.64% and insolubles 3.82%. The paper outlines the various possible approaches for the recovery of non-ferrous values from such concentrates. Thermo-dynamic calculations have been made to find the conditions necessary for sulfate roasting of Sikkim concentrate. Preliminary results obtained on roasting at different temperatures using a 6 cm dia. stainless steel reactor indicated that a maximum dissolution of 86.2% copper, 68.4% Zn with a minimum of 5.6% iron could be obtained at 900°K.

extraction metallurgy has assumed considerable importance especially in the roasting of mixed sulfides, as this provides for the selective conversion of non-ferrous values to soluble sulfates. In conventional hearth and kiln roasting it is difficult to obtain a satisfactory control over gas/solid reaction and the temperature variations are so large that it is not possible to attain a controlled reaction. In fluo-solid roasting, however, due to the vigorous mixing of materials inside the roaster, the temperature throughout the bed remains the same and the composition of the gases and calcine are uniform. The gas composition may generally be calculated fairly accurately from a knowledge of air and solid feed rates and accurate temperature control presents no problems. Under such conditions of operations thermodynamic data could be applied to the processes and the results of practical importance could be obtained. Kellogg[1] discussed the thermochemistry of sulfide roasting and with theoretical calculations, showed that with a fluo-solid roaster it is possible to control the calcine composition by controlling the temperature and air-solid ratio. He worked out various roasting conditions for an hypothetical copper concentrate which would give CuO, a mixture of CuO and basic sulphate, pure basic sulfate, a mixture of basic sulfate and normal sulfate and pure normal sulfates.
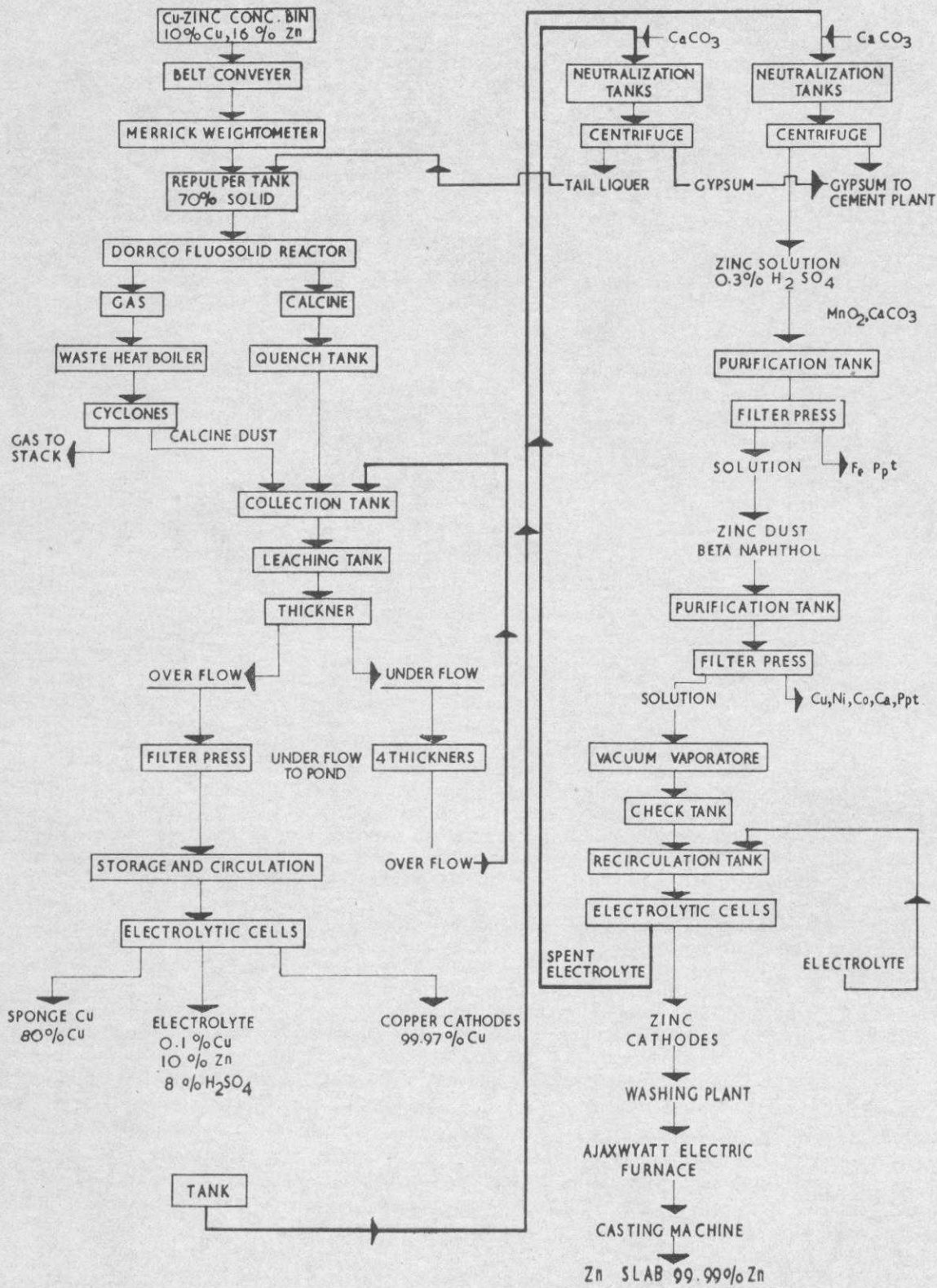
One recent approach for the treatment of the com-
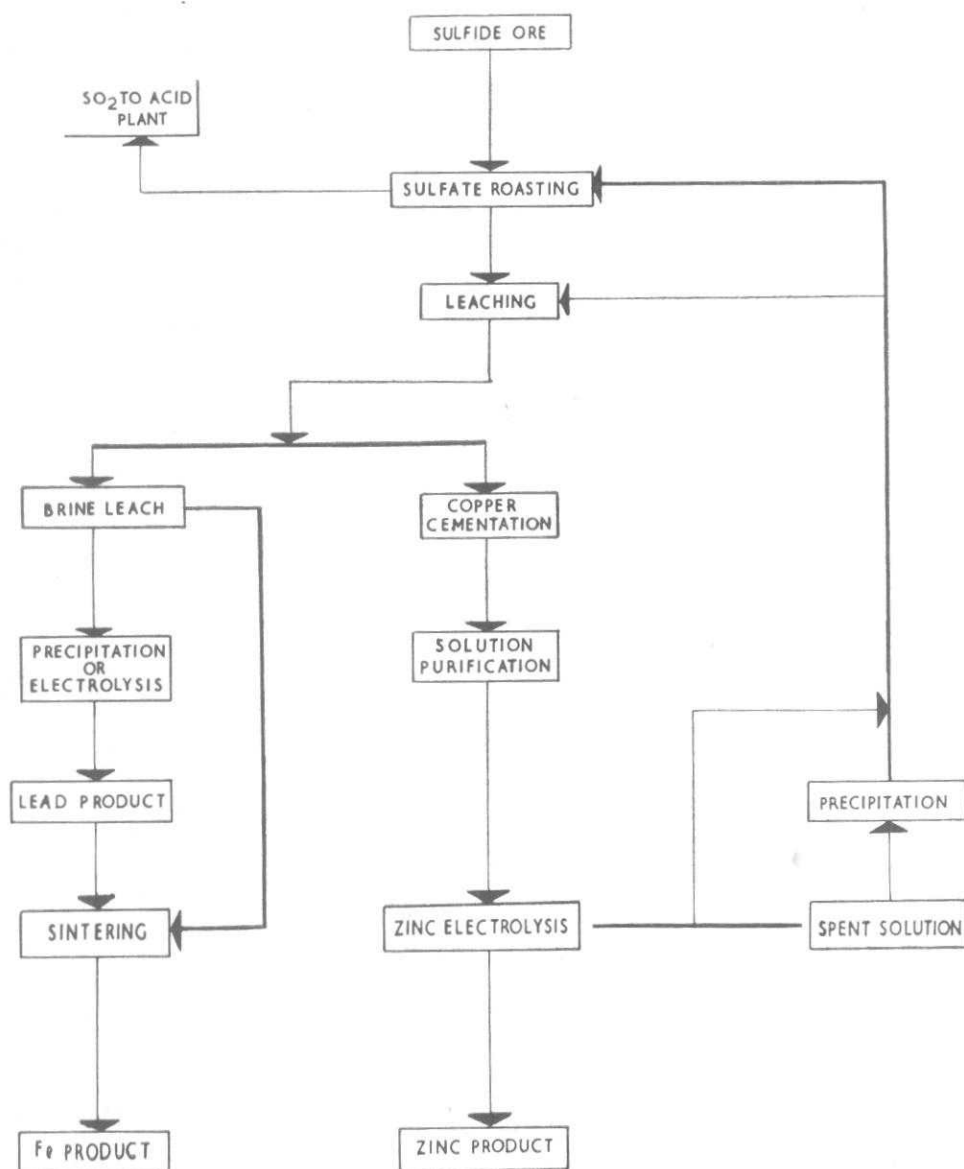
1 *Process flow sheet for treatment of complex sulphide ore as based on initial experimental investigation*

plex sulfide ores was reported by the research staff of the Extractive Metallurgy Division of the Batelle[2] Memorial Institute. The zinc in the sample was present as sphalerite, lead as galena and the iron as pyrite-pyrrhotite. The chemical analysis of the three samples was as follows :

Continuous laboratory scale fluidization tests were carried out by the authors at 1175°F to 1200°F. The percentage of copper, zinc and iron dissolved on leaching the calcine with water or sulpuric acid were as follows :

	Zinc	Cu	Pb	Iron (total)	Sulfur (total)
Sample 'A'	8·7	0·14	3·1	33·0	40
Sample 'B'	9·5	0·14	3·7	34·0	42·8
Sample 'C'	5·1	0·48	1·8	37·3	37·1

	Percentage dissolved in water	Percentage dissolved in 50 gm/l sulphuric acid
Copper	80	92
Zinc	92	92
Iron	2	3

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Cu-ZINC CONC. BIN          ┤← CaCO₃            ┤← CaCO₃
10% Cu, 16% Zn
      │                  NEUTRALIZATION      NEUTRALIZATION
  BELT CONVEYER              TANKS               TANKS
      │                       │                   │
 MERRICK WEIGHTOMETER     CENTRIFUGE          CENTRIFUGE
      │                    │                   │        │
  REPULPER TANK        TAIL LIQUER   GYPSUM   GYPSUM TO
  70% SOLID                                  CEMENT PLANT
      │                                           │
 DORRCO FLUOSOLID REACTOR              ZINC SOLUTION
      │            │                   0.3% H₂SO₄
    GAS        CALCINE                        │   MnO₂,CaCO₃
      │            │                   PURIFICATION TANK
WASTE HEAT BOILER  QUENCH TANK               │
      │            │                   FILTER PRESS
  CYCLONES                              │         │
   │      │                        SOLUTION    Fe Pₚt
GAS TO   CALCINE DUST                   │
STACK                              ZINC DUST
      │      │      │               BETA NAPHTHOL
   COLLECTION TANK                       │
         │                         PURIFICATION TANK
    LEACHING TANK                        │
         │                         FILTER PRESS
      THICKNER                      │         │
    │         │                 SOLUTION   Cu,Ni,Co,Ca,Ppt.
OVER FLOW   UNDER FLOW                  │
   │           │                  VACUUM VAPORATORE
FILTER   UNDER FLOW  4 THICKNERS        │
PRESS    TO POND                   CHECK TANK
   │                   │                │
STORAGE AND         OVER FLOW     RECIRCULATION TANK
CIRCULATION                            │
   │                               ELECTROLYTIC CELLS
ELECTROLYTIC CELLS                     │
  │      │      │              SPENT              ELECTROLYTE
SPONGE Cu ELECTROLYTE COPPER   ELECTROLYTE
80% Cu   0.1% Cu    CATHODES         │
         10% Zn     99.97% Cu     ZINC
         8% H₂SO₄                CATHODES
                                     │
    TANK                        WASHING PLANT
                                     │
                              AJAXWYATT ELECTRIC
                                  FURNACE
                                     │
                              CASTING MACHINE
                                     │
                              Zn SLAB 99.99% Zn
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2 *Hydrometallurgical plant flowsheet at Kosaka smelter of the Dowa Mining Co., Japan*

Since the concentration of copper in the leach solution was relatively low it could be recovered by cementation. The pregnant solution containing 100 gm per litre of zinc was electrolysed after purification. Spent electrolyte from the zinc cells is reported to contain, in an average, 40 gms of zinc per litre and 100 to 150 grams of sulfuric acid. The authors suggest a recycle of the spent electrolyte to the fluidised bed roaster where it could be utilised to prepare the feed slurry for roasting operation and the excess sulfuric acid could be eliminated as sulphur dioxide during the roasting operation.

The leach residue left after leaching the copper and zinc values, was treated with acidulated brine solution at a temperature of 70°F for 98% lead dissolution. Fig. 1 gives the process flowsheet of complex sulfide ore as based on their initial experimental investigation. 95% of lead could be recovered from the brine solution by electrolysis or by lime additions.

A different approach is made for the separation of copper and zinc in the hydro-metallurgical plant at Kosaka[3], Japan. The Kosaka ore is a microscopically fine mixture of copper, lead and zinc sulfides. The lead and the small amounts of the barite present can be separated by flotation. But any physical separation of copper and zinc was found difficult and the blast furnace operation for the recovery of copper resulted in discarding the whole of zinc in the slag.

To effect good recoveries of copper and zinc from their concentrate, Kosaka started treating the concentrate by hydrometallurgical methods during November, 1952. The concentrate analysed 8·7% copper, 15·4% zinc, 21·6% iron and 32·7% sulfur. Fluo-solid roasting followed by leaching of the calcine resulted in a dissolution of copper and zinc. The leach liquors contained 54 grams per litre copper, 100 g/l zinc and 2 g/l iron. Kosaka plant adopted electrolysis in stages for the separation of copper and zinc. The first stage produces cathode copper and the effluent liquor from this stage contains copper 15 to 17 g/l, sulphuric acid 65 g/l, and zinc 100 g/l. In the second stage sponge copper is produced from the effluent liquor and the spent liquor analyses copper 1·19 g/l, sulphuric acid 90 g/l and zinc 100 g/l. The solution is neutralised and iron precipitated by addition of pulverized limestone. The copper cadmium, nickel and cobalt are removed by the addition of zinc dust and Beta-napthol. The purified zinc containing liquor is electrolysed and the spent electrolyte is once again neutralised and sent to the leaching circuit. Fig. 2 gives the flowsheet of the Kosaka hydrometallurgical plant. Thus whatever sulphuric acid is generated in the electrolysis has to be neutralised by lime for subsequent recycling.

A modification in the above approach was carried out by Surnikov and Yurenko[4] in Russia for the treatment of copper, lead and zinc intermediate products obtained from the Berezovka concentrations plant. The treated product analysed 24·8% zinc, 3·89% copper, 6·86% lead, 0·11% cadmium, 15·8% iron, 28·2% sulphur, 0·08% arsenic and 2·9% silica. The sample was roasted at 800°C in a laboratory fluidized bed roaster with 150–200% more air than that required
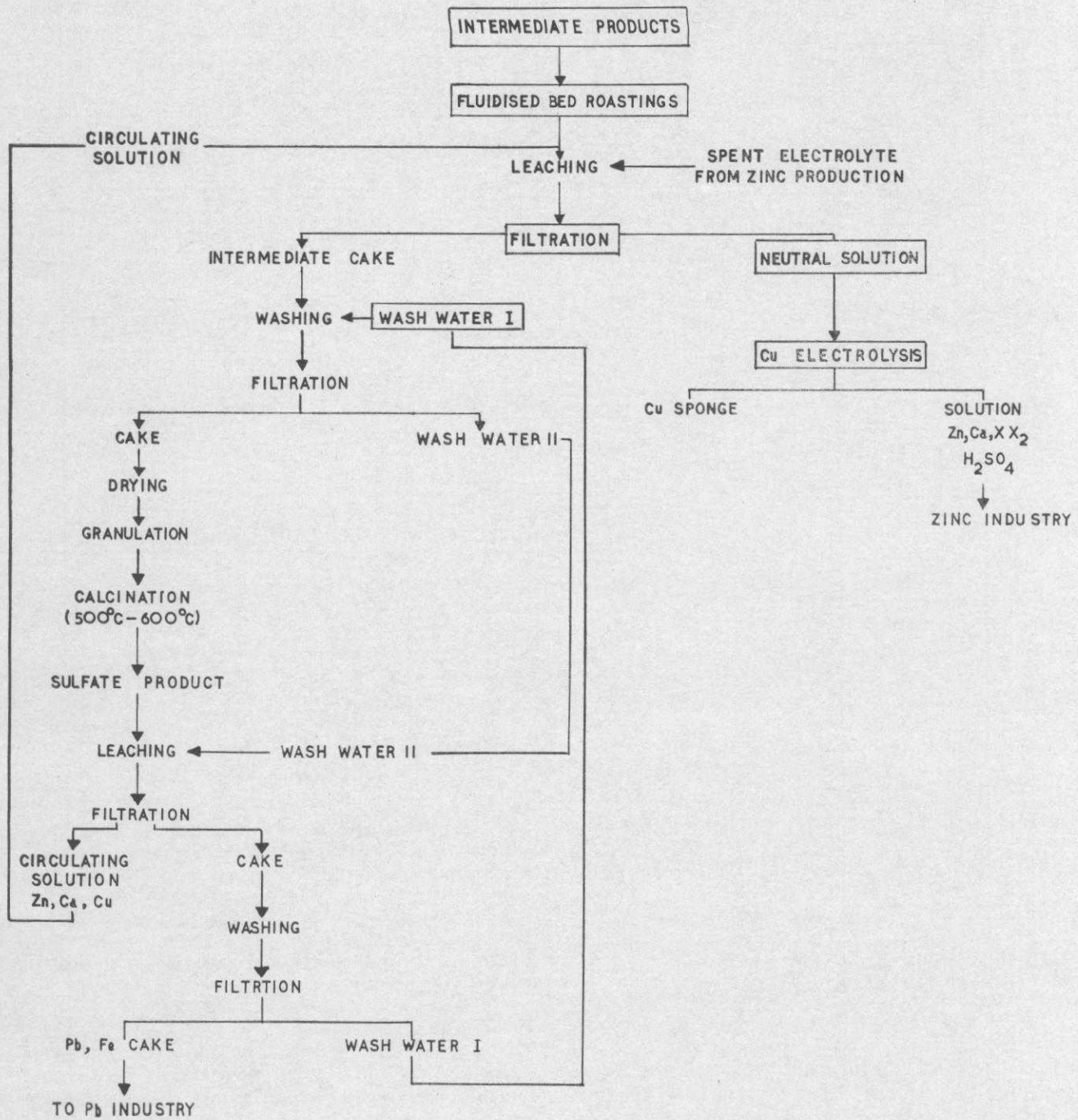
theoretically. The calcine was leached for 1 hr. with spent electrolyte containing 110·7 g/l sulphuric acid, 62·2 g/l zinc and 6·1 g/l manganese. Leaching was completed at various pH values from 1·6 to 4·1. The solution from the calcine leaching contained zinc 106–116 g/l, copper 8·3 to 9·4 g/l, cadmium 0·4 g/l and iron 0·08–0·2 g/l. The metal extraction in solution was 72% zinc, 50% copper and 8% cadmium. The insoluble residue left behind contained 11·5% zinc, 3% copper, ·017% cadmium, 28% iron and 12% lead. The residue was granulated with concentrated sulphuric acid and the granules obtained were calcined in a muffle furnace for 4 hours and leached with water. Extraction to solution in this step varied as 79·7–82·2% zinc, 82–83% copper and up to 90–90·3% cadmium. The mixed solution obtained from the leaching of calcine and sulfate product had the following composition : zinc 128 g/l, copper 10·3 g/l, cadmium ·48 g/l and iron ·3 g/l. Copper was precipitated in the form of a sponge by electrolysis. The flowsheet of the process as described by the authors is given in Fig. 3.

Mackiw,[5] Benz and Evans have suggested pressure leaching with acid for the complex sulfides of copper, lead and zinc, purely on theoretical basis. The discharge slurry was recommended to be treated with an excess of sulfide concentrate to precipitate copper as sulfide. After liquid/solid separation, iron is removed from the leach solution by pH adjustment and aeration and zinc is recovered by the conventional electrolysis. The leached residue is separated by flotation into sulfidic and oxidised fractions. Elemental sulfur is recovered from the sulfidic fraction by solvent extraction, hot filtration or steam distillation and the sulfides are re-leached, the solution purified and copper is recovered by either electrolysis or hydrogen reduction. Lead is recovered from the oxide residue by the amine leach process. Fig. 4 gives the suggested theoretical flow sheet. However actual tests carried out with bulk concentrates did not result in expected results. Autoclaving under these conditions dissolves most of the iron in solution, which has to be removed by subsequent treatment.
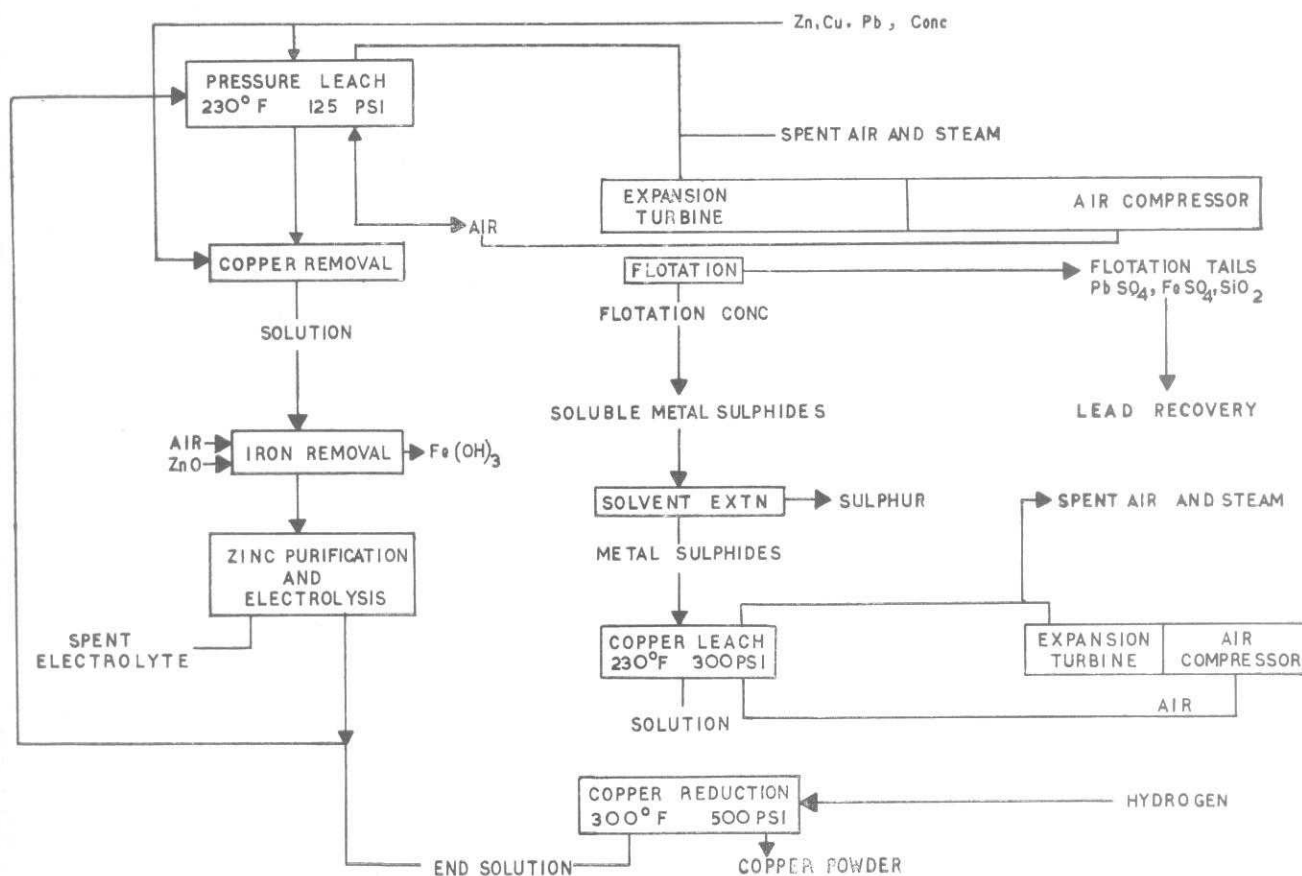
Solvent extraction

U.S.B.M has developed a process[6] recently for obtaining a clear separation of copper and zinc by means of solvent extraction and electrolysis. The leach liquor obtained after sulfatisation in a fluo-solid reactor is purified to remove iron and zinc is selectively recovered by solvent extraction with a Kerosene solution of calcium salt of di-2 ethyl hexyl phosphoric acid. Zinc is subsequently stripped from the loaded organic with sulfuric acid or spent zinc electrolyte and then recovered by conventional zinc electrolysis.

If the copper content of the zinc raffinate is high copper may be recovered directly by electro winning but for solution low in copper, the copper is extracted with another portion of the same solution used to extract zinc. From the loaded organic, sulfuric acid stripping yields the copper. Extraction of the metals is pH dependant and is based on the following reactions.

INTERMEDIATE PRODUCTS

FLUIDISED BED ROASTINGS

CIRCULATING SOLUTION

LEACHING ← SPENT ELECTROLYTE FROM ZINC PRODUCTION

FILTRATION

INTERMEDIATE CAKE

NEUTRAL SOLUTION

WASHING ← WASH WATER I

Cu ELECTROLYSIS

FILTRATION

Cu SPONGE

SOLUTION
Zn, Ca, X X$_2$
H$_2$SO$_4$

CAKE

WASH WATER II

DRYING

ZINC INDUSTRY

GRANULATION

CALCINATION
(500°C – 600°C)

SULFATE PRODUCT

LEACHING ← WASH WATER II

FILTRATION

CIRCULATING SOLUTION
Zn, Ca, Cu

CAKE

WASHING

FILTRTION

Pb, Fe CAKE

WASH WATER I

TO Pb INDUSTRY

3 *Flow sheet for treatment of intermediate products*

4 *Treatment of zinc, copper, lead, bulk concentrate*

1. $Ca(EHP)_2 + ZnSo_4 + 2H_2O \rightleftharpoons Zn(EHP)_2 + CaSo_4 \, 2H_2O$

2. $Ca(EHP)_2 + CuSo_4 + 2H_2O \rightleftharpoons Cu(EHP)_2 + CaSo_4 \, 2H_2O$

3. $Cu(EHP)_2 + ZnSo_4 \qquad \rightleftharpoons Zn(EHP)_2 + CuSo_4$

4. $Zn(EHP)_2 + H_2So_4 \qquad \rightleftharpoons 2\,HEHP + ZnSo_4$

5. $Cu(EHP)_2 + H_2So_4 \qquad \rightleftharpoons 2\,HEHP + CuSo_4$

It is claimed that the re-agent requirements are reported to be modest and include principally sulphuric acid and lime. The cost due to losses of organic extractant during solvent extraction of zinc and copper would amount to less than 0·5 cent per pound of metal.

Complex sulphide ore from Sikkim

The ore as mined analyses copper 0·67%, lead 1·45%, zinc 4·50%, iron 15·22%, sulphur 8·62%, silica 58·20%, alumina 6·70%. The chief sulfide minerals are chalcopyrite, galena, sphalerite and pyrrhotite whereas quartz and chlorite constitute the bulk of the gangue. The copper, lead and zinc minerals can be fairly freed from the siliceous gangue at about 48 mesh size. But fine grinding is necessary to liberate the sulfide minerals.

The bulk float sample received from Sikkim analysed copper 14·45%, lead 7·83%, zinc 6·65%, iron 31·52%, sulphur 29·92%, insolubles 3·82% and moisture 2·64%. Systematic investigations have been undertaken at NML on hydrometallurgical treatment so that this process can be adopted near the mining site.

Theoretical considerations

Important reactions that are taking place, when a sulfide concentrate is roasted, can be represented by the following equations :

$$MS + 3/2\, O_2 \rightleftharpoons MO + SO_2 \qquad \ldots (1)$$

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \qquad \ldots (2)$$

$$MO + SO_3 \rightleftharpoons MSO_4 \qquad \ldots (3)$$
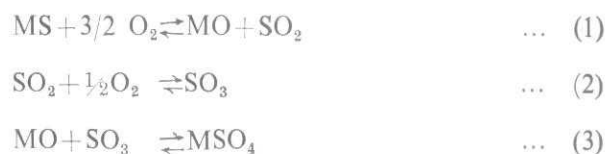
The reaction (1) is strongly exothermic and for all practical purposes during roasting, the equilibrium shifts to the right, with the formation of metallic
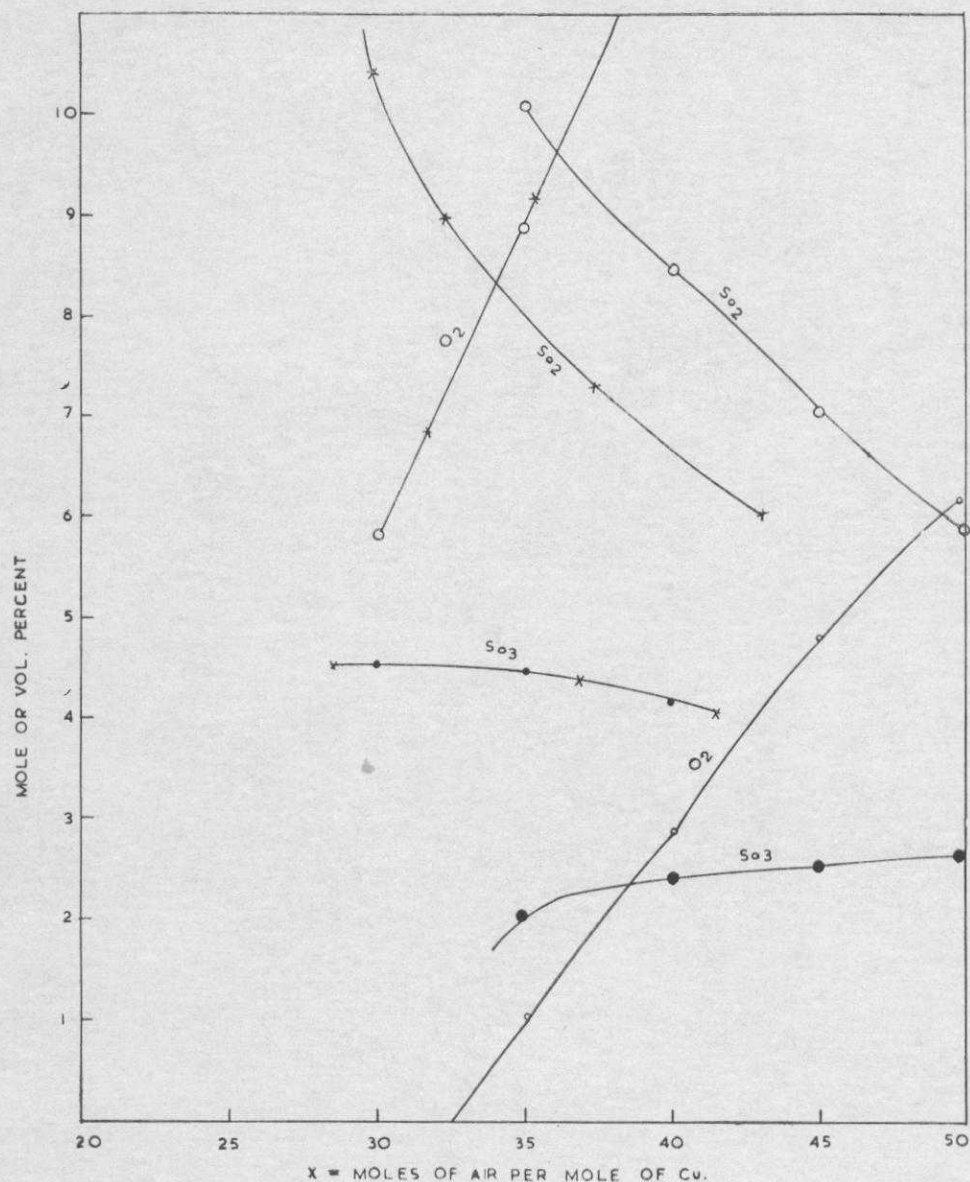
5 *Equilibrium gas composition for Sikkim concentrate roasting at 1000°K*
O = Normal air
X = Enriched air, oxygen 30%

oxide and SO_2. Normally the heat evolved in this reaction is enough to sustain the necessary thermal requirements of the roaster. The higher the temperature, the faster is the reaction and the conditions that are available in a fluo-solid roaster, such as thorough mixing of the gas phase with the solids proves an added advantage.

Reaction (2) is of far more importance for sulfate roasting since the partial pressure of SO_3, in the furnace atmosphere whether higher or lower than the equilibrium partial pressure decides the presence or absence of sulphates in the calcine. In an oxidising atmosphere, and at lower temperatures, more of SO_3 is formed. At higher temperatures, SO_2 is more stable and over 700°C especially in presence of metallic oxides, the reaction

rate is higher and more of SO_3 would decompose to give SO_2. Nevertheless some amount of SO_3 will always be present and the roaster gases contain nearly equilibrium proportions of SO_2 and SO_3. The change of equilibrium constant with temperature for the reaction is given by the empirical formula represented by Wagner[7]

$$-\mathrm{Log}\ K = 8 \cdot 8557 - \frac{5665 \cdot 5}{T} - 1 \cdot 21572\ \log_{10}T \quad \ldots \quad (4)$$

the values obtained for K for different temperatures have been utilised in the calculations.

The formation of metallic sulphates depends on the equilibrium constants for the reactions of the type

$$MO\ (s) + So_3\ (g) \rightleftharpoons MSO_4\ (s) \qquad \ldots\ (3)$$

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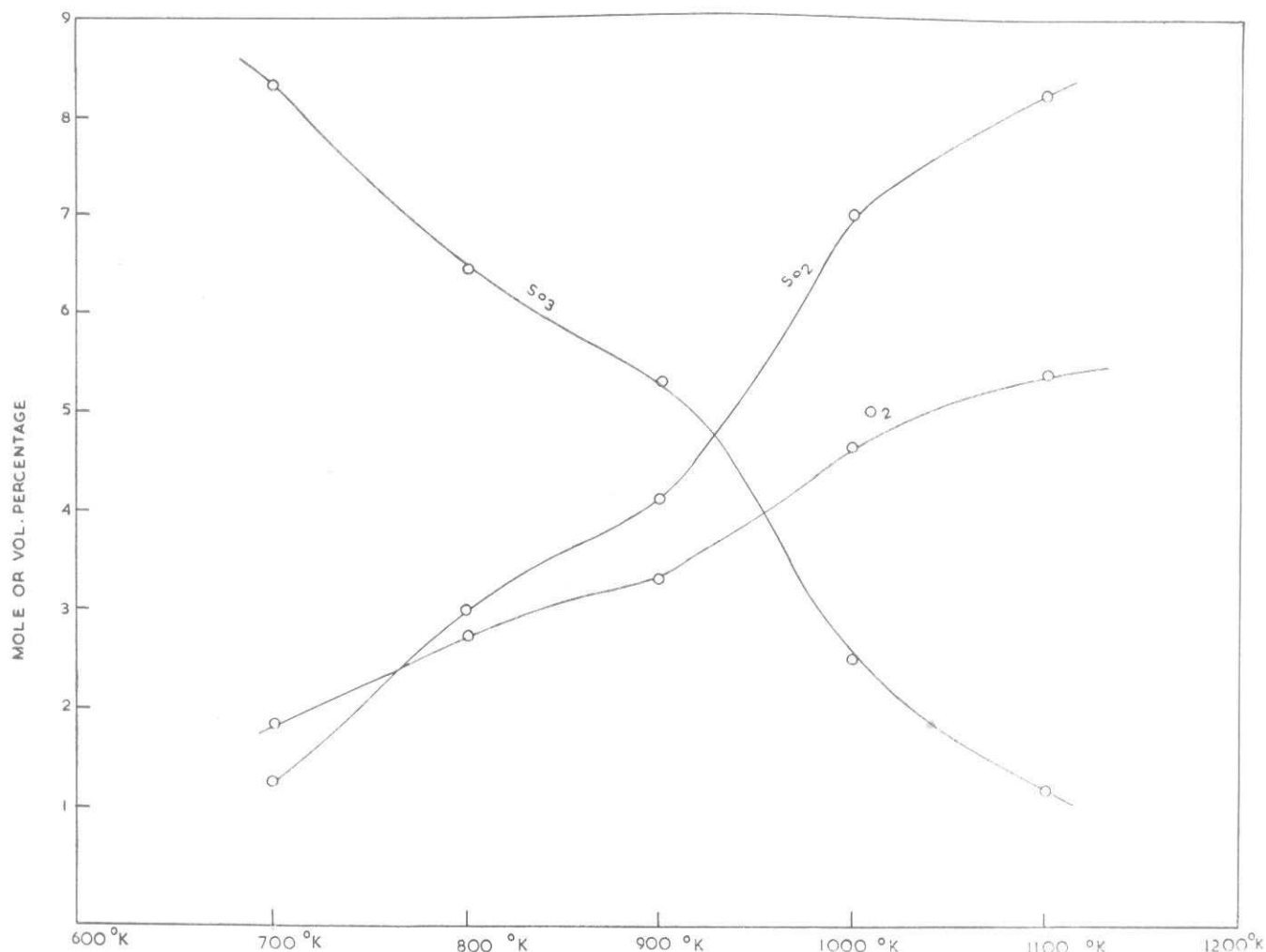
6 *Equilibrium gas compositions on roasting of Sikkim bulk ore concentrate at 1 atm pressure 45 mole of air per mole of Cu*

$$K_p = \frac{<MSO_4>}{<MO>p(SO_3)}$$

Since the MO and MSO_4 are solids, their activities can be taken as unity and thus the values of K_p depends on the partial pressures of SO_3. If the SO_3 partial pressure in the furnace atmosphere is more than the equilibrium pressures of SO_3 for the reaction (3), then more of the oxides formed in the reactor according to the reaction (1) would react to form the sulfates according to reaction (3).

Thermodynamic calculations for equilibrium roaster gas compositions

Knowing the analysis of the concentrate, being investigated it is possible to theoretically study the effect of (1) the varying proportions of air to concentrate in the feed (2) the enrichment of air with oxygen and (3) the temperature of roasting on the roaster gas composition and thus arrive at the conditions for selective sulfati-
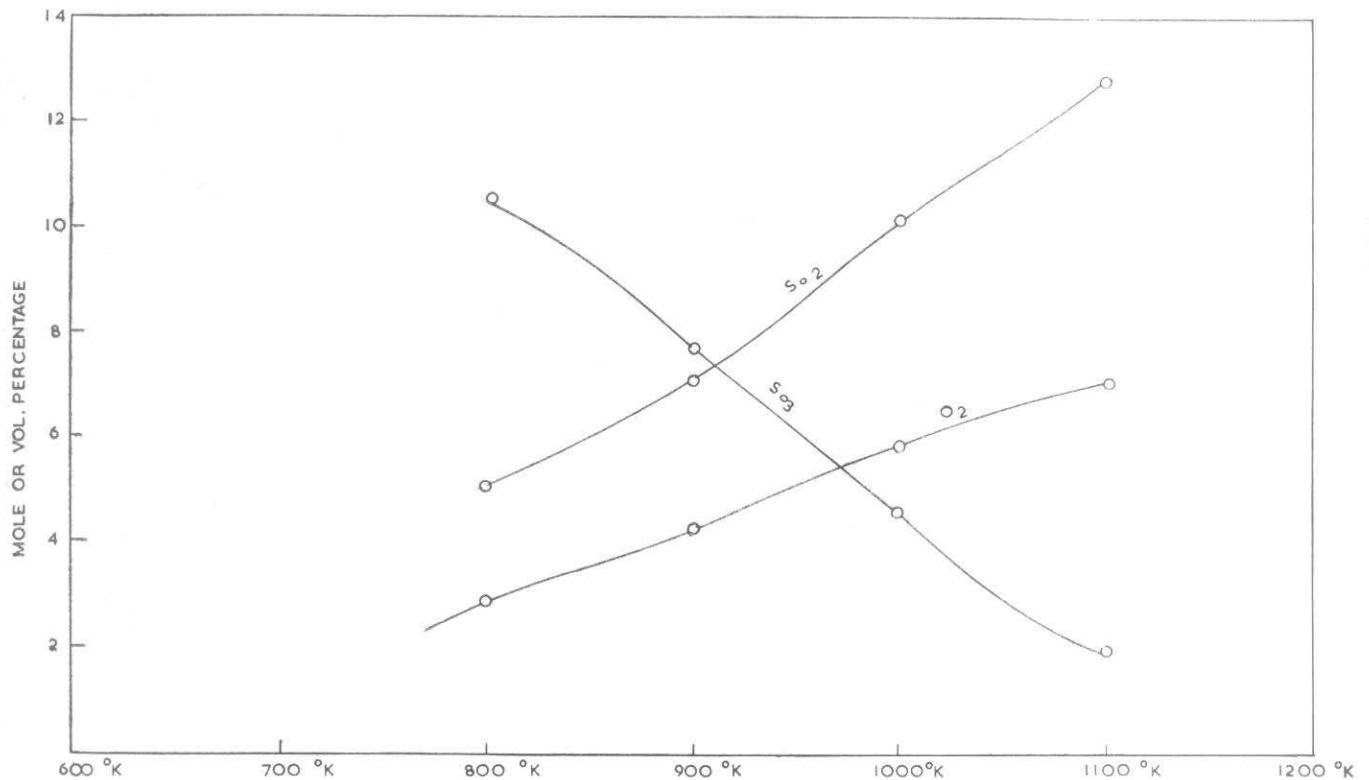
cation. Table I gives the analysis of the Sikkim concentrate in mole percentages and the last column expresses the various elements present as mole per mole of copper.

TABLE I Analysis of Sikkim concentrate

	Wt %	Mole %	Mole/Mole Cu.
Copper as sulfide	14·45	0·2274	1·00
Lead as sulfide	7·83	0·0378	0·1662
Sulphur as sulfide	29·92	0·9335	4·1050
Zinc as sulfide	6·65	0·1017	0·4470
Iron as sulfide	31·52	0·055	2·4430
Moisture	2·64	0·1466	0·6446

TABLE II Decomposition pressure of various sulphates

TEMPERATURE IN °K	$\tfrac{1}{3}Fe_2(SO_4)_3 = \tfrac{1}{3}Fe_2O_3 + SO_3$	$CuO \cdot CuSO_4 = 2CuO + SO_3$	$2CuSO_4 = CuO \cdot CuSO_4 + SO_3$	$3ZnSO_4 = ZnO \cdot 2ZnSO_4 + SO_3$	$\tfrac{1}{2}(ZnO \cdot 2ZnSO_4) = \tfrac{3}{2}(ZnO) + SO_3$	$2PbSO_4 = PbSO_4 \cdot PbO + SO_3$	$3(PbSO_4 \cdot PbO) = 2(PbSO_4 \cdot 2PbO) + SO_3$	$\tfrac{5}{3}(PbSO_4 \cdot PbO) = \tfrac{2}{3}(2PbSO_4 \cdot 4PbO) + SO_3$	$\tfrac{5}{2}(PbSO_4 \cdot 2PbO) = \tfrac{3}{2}(2PbSO_4 \cdot 4PbO) + SO_3$	$PbSO_4 \cdot 4PbO = 5PbO + SO_3$
700 °K	—	—	7.464×10^{-7}	—	—	—	—	—	—	—
800 °K	1.1197×10^{-3}	1.259×10^{-3}	6.653×10^{-5}	—	—	2.553×10^{-10}	—	—	1.8322×10^{-13}	7.9620×10^{-14}
900 °K	2.891×10^{-2}	4.169×10^{-4}	2.173×10^{-3}	6.8×10^{-4}	3.547×10^{-5}	2.924×10^{-8}	3.499×10^{-10}	3.112×10^{-10}	—	10.33×10^{-11}
1000 °K	3.631×10^{-1}	6.776×10^{-3}	3.491×10^{-2}	1.37×10^{-2}	7.288×10^{-4}	1.242×10^{-6}	3.243×10^{-8}	1.143×10^{-8}	—	7.94×10^{-10}
1100 °K	2.831	6.592×10^{-2}	3.357×10^{-1}	8.738×10^{-2}	8.513×10^{-3}	2.582×10^{-6}	1.276×10^{-6}	2.109×10^{-7}	—	1.706×10^{-8}

7 *Equilibrium gas compositions on roasting of Sikkim bulk ore concentrate at 1 atm with oxygen enriched air, 30% oxygen, 30 moles of air per mole Cu content. Assumption no sulfate formed.*

Theoretical requirement of oxygen to convert all the elements into oxide from a quantity of ore containing 1 mole of Cu can be calculated.

1 mole of copper would require $\frac{1}{2}$ mole of oxygen to form CuO.

1 Cu + 0.5 O_2	=	CuO	
0.1662 Pb + 0.0831 O_2	=	0.1662 PbO	
0.4470 Zn + 0.2235 O_2	=	0.4470 ZnO	
2.4430 Fe + 0.75 × 2.4443 O_2	=	1.2215 Fe_2O_3	
4.1050 S + 4.105 O_2	=	4.1050 SO_2	
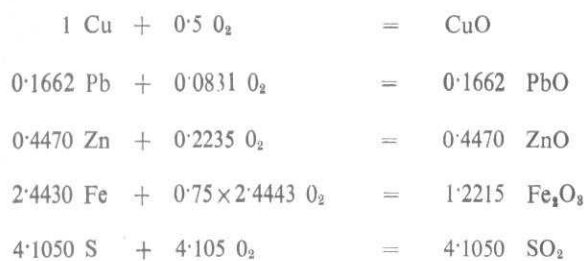
Thus the total stoichiometric requirement of oxygen is 6.7436 moles which could be obtained roughly from 32.5 moles of air.

(1) Effect of proportion of air to concentrate in the feed.

From the stoichiometry of the various reactions shown above, it is possible to arrive at a material balance for the various gases in the roaster, once the proportion of air to concentrate feed is known : Thus for a feed ratio of 50 moles of air per mole of copper we have

Moles of O_2 available in 50 moles air :

50 × ·207	=	10.35 moles
Moles of O_2 reacted	=	6.7436 ,,
Moles of free O_2	=	3.6064 ,,
Moles of SO_2 formed	=	4.105 ,,
Moles of N_2 in air	=	39.650 ,,
No. of moles of moisture from concentrate }	=	0.6646 ,,
Total no. of moles after reaction	=	48.006 ,,

Now taking into consideration the equilibrium :

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3 \qquad \qquad \dots (2)$$

If X be the moles of SO_3 formed, then X moles of SO_2 would have reacted with $\dfrac{X}{2}$ moles of oxygen.

Now the number of moles of various gases would be :

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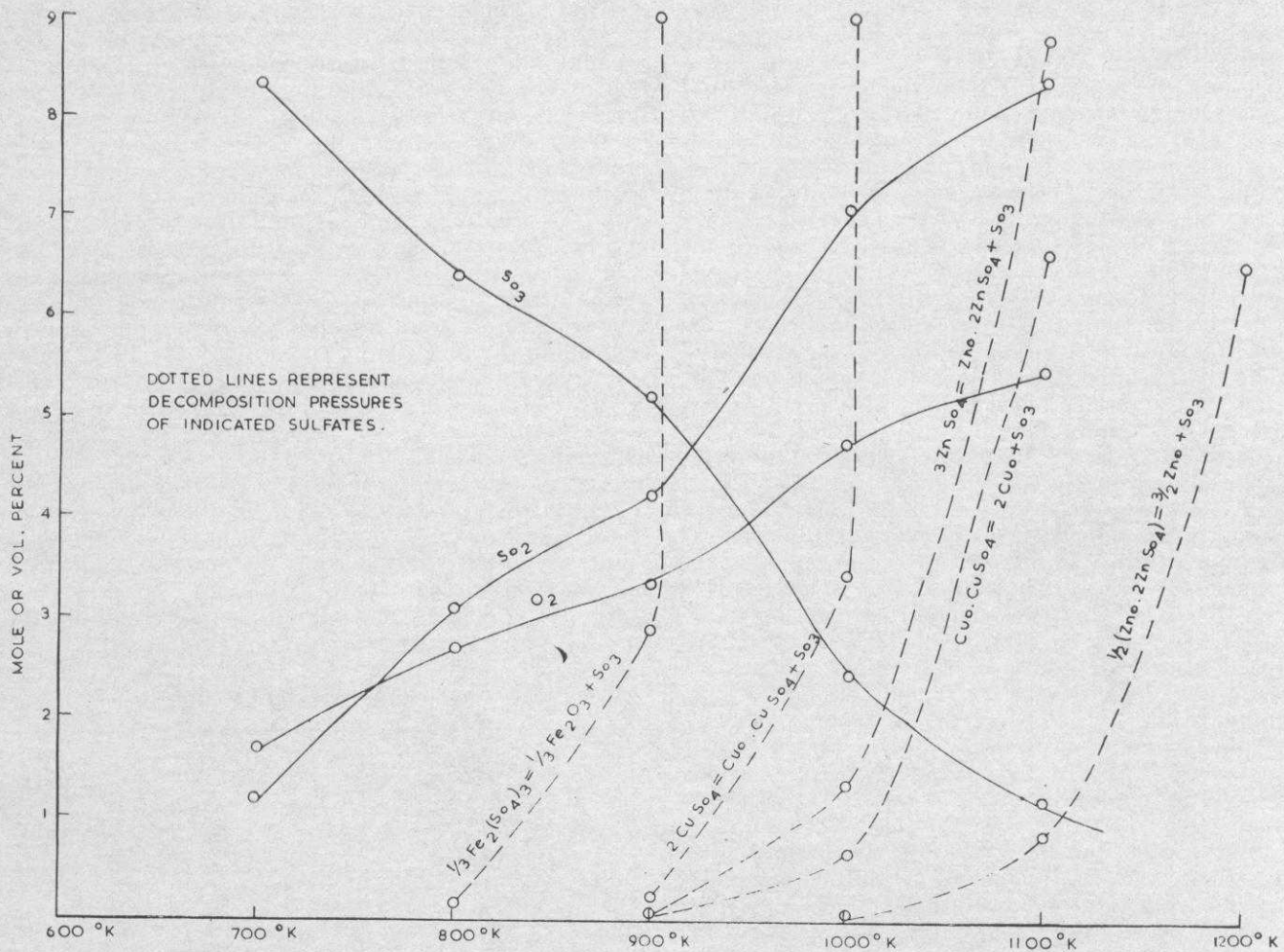
8 *Equilibrium gas compositions on roasting of Sikkim bulk ore concentrate at 1 atm pressure, 45 moles of air per mole Cu*

O_2 = (3·6064 — X/2) moles

SO_2 = (4·105 — X) „

SO_3 = X moles

Total = $\left(48·0006 - \dfrac{X}{2}\right)$ moles

Hence the partial pressures of the various gases would be :

$$pO_2 = \frac{(3·6064 - X/2)}{(48·006 - X/2)}$$

$$pSO_2 = \frac{(4·105 - X)}{(48·006 - X/2)}$$

$$pSO_3 = \frac{X}{(48·006 - X/2)}$$

The equilibrium constant is given by :

$$K = \frac{\dfrac{X}{(48·006 - X/2)}}{\left[\left(\dfrac{4·105 - X}{48·006 - X/2}\right)\left(\dfrac{3·6064 - X/2}{48·006 - X/2}\right)\right]^{\frac{1}{2}}} \quad (5)$$

The value of K for any particular temperature can be obtained from the Wagner's empirical formula :

$$- \log K = 8·8557 - \frac{5665·5}{T} - 1·21572 \log_{10} T \quad … \quad (4)$$

Substituting this value of K in equation (5) we can get the value of X for any particular temperature, then the values of partial pressure of gases or their molar percentage in the roaster gases can be arrived at. The values thus obtained, for quantities of air varying bet-

ween 35 and 50 moles per mole of copper in the feed have been plotted in Fig. 5 for a roasting temperature of 1000°K. Molar percentage of SO_2 falls from about 10 per cent to 5·8 per cent by changing the feed ratio of air to concentrate from 35 to 50. The changes in SO_3 percentage is not much affected, because of the increased amount of oxygen available, more of SO_2 is converted into SO_3 thus compensating for any solution effect on SO_3 percentages due to the increased volume. In the same plot are recorded calculated values for the equilibrium mole percentages of various gases, using enriched air containing 30% oxygen. The advantage of oxygen enrichment is that a higher SO_2 content in the roaster gas can be achieved with a smaller volume of air and particularly where the sulfide content is low, the use of oxygen enrichment may also result in the autogenous roasting of the ore.

Figure 6 indicates the calculated values for the equilibrium gas compositions, on roasting between 600°K and 1 200°K Sikkim concentrates at 1 atm. with a ratio of 45 moles of air/mole of copper whilst the theoretical equilibrium gas composition obtained on using 30 moles of oxygen enriched air/mole of copper is indicated in Fig. 7. It is seen from these figures that SO_3 content is higher at lower temperatures, while SO_2 content are higher at higher temperatures. The values indicated in these figures are however, valid only at higher temperatures. Since the temperature is lowered, a stage would be reached when the solid oxides present in the calcine would start absorbing SO_3 forming the various sulfates. The temperatures at which such reactions start can be determined by plotting the variation of the decomposition pressures of the various sulfates, with temperatures in the above figures. Table II gives the decomposition pressures of the various possible sulfates. The values were calculated from the log K values for the various reactions as given by Kellogg.[7]

The decomposition pressures for the two zinc sulfates normal as well as basic two copper sulfates and the ferric sulfate have been plotted by dotted lines as a function of temperature in Fig. 8 and the points of inter-section of these lines with that representing roaster gas SO_3 composition, represents the temperature up to which the various sulfates indicated are stable in the roaster atmosphere. The decomposition pressures for the various sulfates of lead are much less than the other sulfates and these have not been plotted. It is observed from Fig. 8 that at 910°K, the ferric sulfate starts decomposing to form ferric oxides, while all other sulfates at this temperature are quite stable. The normal sulfate of copper decomposes into its basic sulfate at 1 000°K and the basic sulfate into cupric oxide at 1 028°K. Normal sulfate of zinc starts decomposing at 1010°K to its basic sulfate and the latter is stable up to 1110°K when the ZnO starts forming. Thus between 900°K and 1000°K the decomposition of ferric sulfate takes place, while the copper, zinc and lead sulfates remain stable.

Results of the preliminary experiments

The bench scale fluidised bed roasting experiments on

the Sikkim bulk float concentrate, were carried out in a 6 cm dia. and 100 cm height stainless steel reactor. The detailed experimental set up is shown in Fig. 6. The flow rate of air for fluidization was measured with the help of rotameter. A pressure indicator was introduced between the rotameter and the compressed air line, so that back pressure developed during roasting can be observed. The material was fed along with the fluidising air and the rate of feed of the material was the same as to that of roasted product collected in the cyclones. The reactor was externally heated before the start of the experiment and the reaction temperature was thereafter controlled manually by controlling the flow of the combustion gas.

A series of continuous fluidization experiments were carried out using calculated amount of air to make a ratio of 50 moles of air per mole of copper at temperatures ranging from 750°K–923°K. The rate of feeding of the concentrate was uniform during the run.

The roasted product obtained in all the experiments was leached in 2·5% sulphuric acid (V/V) at 60°C. The slurry was filtered and the leached liquor was analysed for copper, iron and zinc. The percentage dissolution at different temperatures is shown in Table III.

TABLE III Percentage dissolution at different temperatures

Exp. no.	Temp.	%SO₄ sulphur in the roasted product	% Cu in solution	% Zn in solution	% Fe in solution
1.	750°K	7·23	46·7	41·8	27·2%
2.	800°K	8·76	55·7	51·8	25·8%
3.	850°K	10·18	77·4	61·1	21·2%
4.	875°K	11·32	88·5	70·5	10·2%
5.	900°K	—	86·2%	68·4	5·6%
6.	925°K	—	74·18%	62·4%	4·2%

It is observed from Table III that the percentage of copper and zinc dissolved increases from 46·7 and 41·8 at 748°K to 88·5 and 70·5 at 873°K respectively and thereafter decreases. The iron dissolved during leaching however decreases continuously from 750°K to 925°K.

For complete conversion of lead, copper and zinc to their respective normal sulphates, the calcine should theoretically contain 12·88% sulphur. The sulphate sulphur in the calcine increases from 7·23 at 723°K to 11·32% at 873°K for the same retention time, indicating better sulphate conversion at higher temperature. It is felt that still better recoveries can be obtained at about 900°K on increasing the retention period and further work is in progress.

From the results so far obtained it is felt that

1. STAINLESS FLUIDISED BED REACTOR
2. BRICK LINING
3. CONTINUOUS FEEDING ARRANGEMENT
4. BROOKS ROTAMETER TYPE 110
5. PRESSURE INDICATOR
6. THERMOCOUPLE INSERTION TUBE
7. THERMOCOUPLE INSERTION TUBE
8. TEMPERATURE INDICATOR
9. CALCINE RECEIVER
10. CALCINE RECEIVER
11. CYCLONE
12. CYCLONE
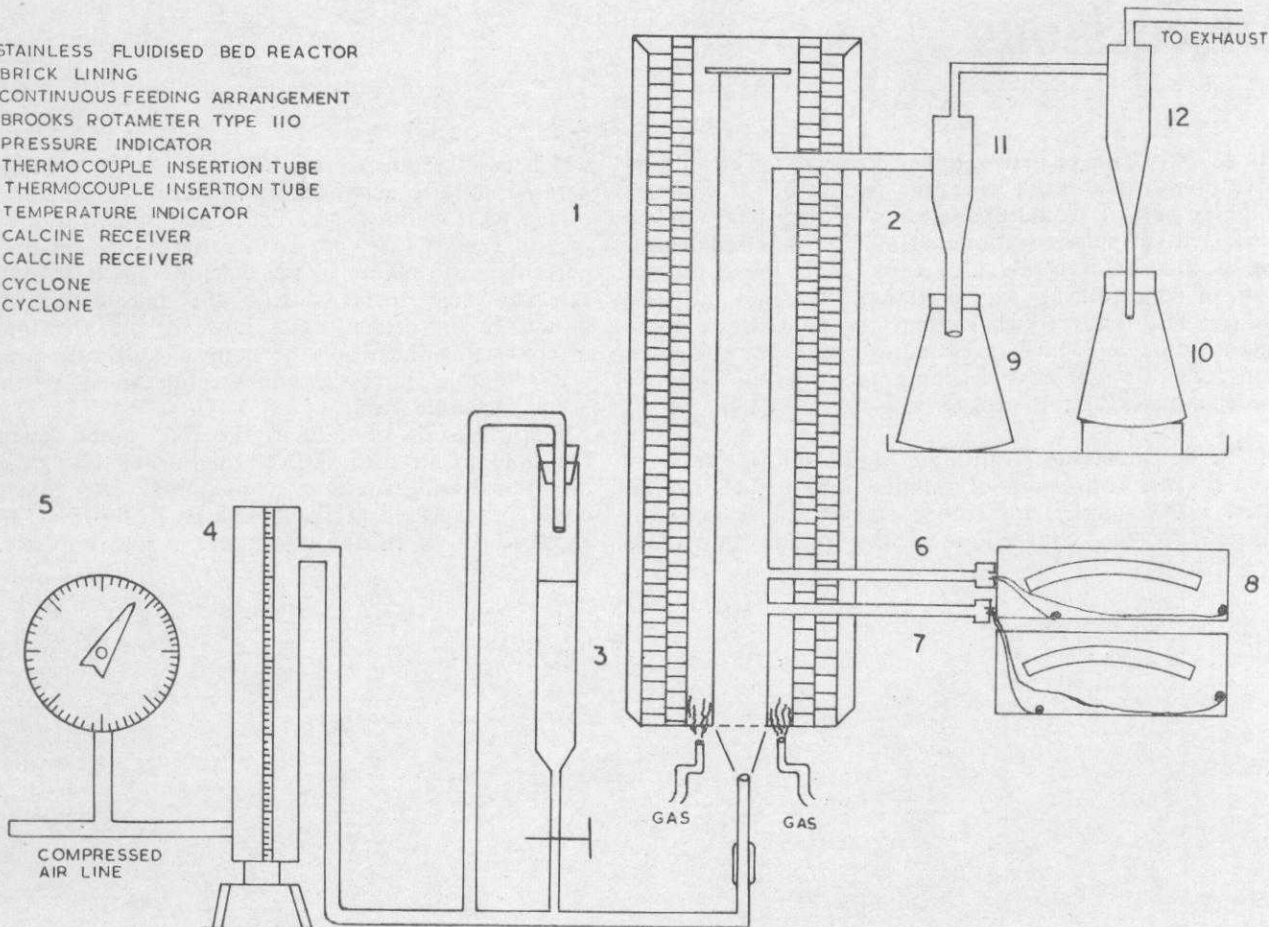
9 Bench scale fluidised bed reactor

copper, zinc and lead present in Sikkim concentrate can be recovered as follows:

1. Fluidised bed roasting of sulphide ore.
2. Weak acid leaching for the dissolution of copper and zinc and to separate lead as lead sulphate.
3. Recovery of copper by electrolysis or solvent extraction.
4. Recovery of zinc by electrolysis.
5. Recovery of lead by flotation or by chemical methods.

Further work on arriving at optimum condition for roasting in presence of alkali salt which will lessen ferrite formation and at the same time promote the sulfatisation property of copper and zinc are planned using a Dorco 6-inch fluo-solid roaster recently installed at this Laboratory.

It is also proposed to have extensive studies on the recovery of copper and zinc from the leach liquor by electrolysis and solvent extraction. The lead leaching with acidulated sodiumchloride is in progress and lead can easily be precipitated as basic hydroxide by lime addition.

Acknowledgement

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Discussions

Mr **L. N. Misra** (Khetri Copper Project) : The authors have done useful work on the metallurgy of complex sulphide ores. I would like to know if they have studied the extent of sulphatisation during the fluidised roasting as this factor would ultimately affect the consumption of acid during the leaching. It would also be interesting to know to what extent the flue gases contain sulphur-dioxide which eventually could be converted into acid for the acid leaching in order to improve the economics of the process.

Mr **S. R. Srinivasan** (Author) : Fluo-solid roasters are used for the conversion of sulfides into oxides or sulfates. For example, zinc sulfide concentrate is normally roasted for the conversion of the sulfide into oxide which is subsequently leached with sulfuric acid. Regenerated sulfuric acid during electrolysis of zinc is recycled to leaching stage. The conditions for the roasting, in such a case, are so chosen as to have a small percentage of sulfate in the calcine, so as to compensate any acid losses during the purification of leach liquor. In the present case, however, we are interested in converting the whole of copper and zinc values to water soluble sulfates, while keeping most of the iron as an insoluble oxide.

Sulfur-dioxide content in the flue gases depends on the solid to air feed ratio to the roaster. Using ordinary air for sulfating roasting, a maximum of 3 to 4% SO_2 could be expected in the flue gases. If, however, oxygen-enriched air is utilised this figure would improve.