Proceedings of the International Conference on "Recent Advances in Metallurgical Processes"
Golden Jubilee Celebrations, Department of Metallurgy, Indian Institute of Science, Bangalore
Eds. D.H. Sastry, E.S. Dwarakadasa, G.N.K. Iyengar and S. Subramanian
New Age International Publishers, New Delhi (1997)

SIMULTANEOUS EXTRACTION OF ZINC AND MANGANESE DIOXIDE FROM ZINC SULPHIDE CONCENTRATE AND MANGANESE ORE

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Direct leaching studies of mixture of zinc sulphide concentrate (concentrate) of Himalayan origin and manganese ore (ore) in stoichiometric proportion according to the reaction :

$$ZnS + MnO_2 + 2H_2SO_4 = ZnSO_4 + MnSO_4 + S^o + 2H_2O$$

in dilute sulphuric acid (present in spent liquor from electro-winning cells) were carried out to test its amenability to a novel process developed at National Metallurgical Laboratory (NML). The liberated sulphur in the sludge was extracted in pure form. The effects of controlling parameters viz. acid-concentration, temperature and duration of leaching were investigated to optimize the leaching conditions. Extraction efficiencies of zinc and sulphur under best condition were ~82% each, while that of manganese was ~95%. The inextricable portion of zinc sulphide was investigated with the help of XRD analysis of the concentrate and the final residue. The leach solution purified by conventional hydro-metallurgical technique was fed to an electrolytic cell for simultaneous electro-winning of zinc and electrolytic manganese dioxide (EMD). The EMD was γ-variety as shown by TG/DTA and XRD analyses.

INTRODUCTION

Despite attempts by several workers [1-5], a comprehensive flow chart is yet to be developed. Zinc is produced conventionally by; oxidising roast, leach, purification of leach solution and electro-winning route. EMD similarly is produced by reducing roast, leach, purification of leach solution and electro-winning route. Pande et al [3], at NML, carried out detailed leaching studies coupled with the electro-winning of zinc and EMD and extraction of sulphur from sludge; and patented the process. The flow chart is shown in Fig. 1.

The novelties of the process are a single flow chart for production of zinc and EMD,elimination of roasting steps, recovery of elemental sulphur and freedom from emission of sulphur dioxide or other flue gas from roasting. and a very stable final residue towards ambient.

In the Ganesh Himal region of Nepal at a very high altitude zinc sulphide ore was explored by M/s Nepal Metal Co Ltd.. A detailed investigation of the amenability of the concentrate to this process was carried out at NML.

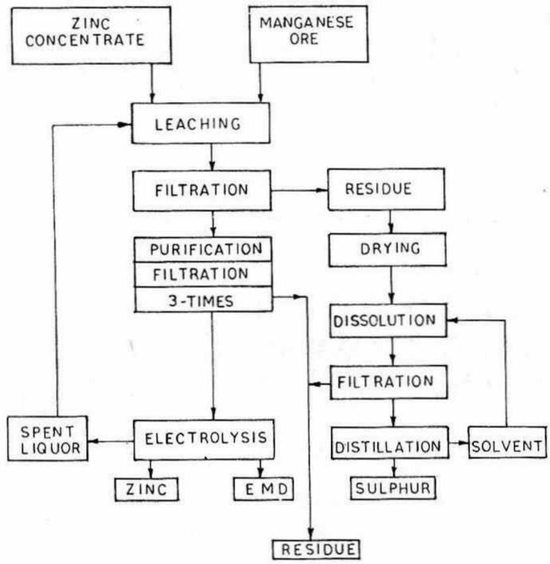

Fig. 1 Flowsheet for extraction of zinc, EMD and sulphur from zinc sulphide concentrate and manganese ore

SCOPE OF WORK

The amenability of the concentrate and ore mixture to the process depends primarily on successful leaching of its zinc and manganese content and recovery of liberated sulphur with reasonable leaching efficiencies and acceptable kinetics of the reaction

$$ZnS + MnO_2 + 2H_2SO_4 = ZnSO_4 + MnSO_4 + S^o + 2H_2O$$

followed by purification of the leached solution suitable for simultaneous electro-winning of zinc and EMD. The following investigations were carried out with a 6.0 kg. bulk of concentrate, namely efficiencies of leaching zinc and manganese and the kinetics of the reaction, recovery of elemental sulphur, purification of leach solution, characterisation of EMD and purity of zinc apart from exploration of the cause for the insoluble zinc content in the concentrate

EXPERIMENTAL

Materials and equipment:

Raw materials used were; concentrate, ore, sulphuric acid,calcium oxide, zinc dust and some chemicals for testing of impurities like iron, nickel. Table I shows the composition of the concentrate and the ore. The equipment required were; laboratory stirrer, beakers of various sizes, hot plate, filter pump (glass) plastic buckets, mercury in glass thermometer, pH indicator papers, distillation unit, balance and measuring cylinders.

Table I. Chemical composition of Concentrate and Ore

Material	Zn%	Pb%	S%	MnO_2%	Fe%	SiO_2 %	Al_2O_3%
Concentrate	55.97	0.51	32.55	---	6.5	0.20	trace
Ore	---	---	---	70.43	10.62	11.62	1.5

Leaching trials:

Concentrate and ore mixture having ZnS : MnO_2 in stoichiometric proportion was leached in hot dilute sulphuric acid in a 3.0 L beaker heated to ~100°C on a hot plate with vigorous stirring, for a maximum of 3 hours. The leached solution was cooled and filtered. The sludge was washed and rewashed to extract all the leached zinc and manganese. The total volume of the filtrate and the wash solution was measured and analyzed for zinc and manganese. The effects of parameters viz. temperature, acid-concentration, duration and particle size of the concentrate on leaching efficiencies of zinc and manganese were investigated.

Sulphur recovery:

The washed, dried and weighed residue was repulped thoroughly in pure carbon disulphide to dissolve all the liberated sulphur. The pregnant carbon disulphide solution was distilled to get solid sulphur as residue and pure carbon disulphide for reuse.

Purification of the leach solution:

The pH was adjusted between 4.0 to 5.0 and air was blown to precipitate out all dissolved iron as $Fe(OH)_3$ bulk precipitate till the solution tested negative for thiocyanate test. The filtered solution was then treated with barium sulphide solution maintaining the pH as before. This was continued till the solution tested negative with dimethyl glyoxime test for nickel. The solution after filtration was purified by zinc dust with stirring at ~80°C. The final pure solution was adjusted to pH 2.0 and stored for electro-winning zinc and EMD.

RESULTS

Leaching trials:

Effect of temperature on leaching efficiencies of manganese, zinc and liberation of sulphur at four temperatures between 343 K and 373 K was investigated. The conditions viz. acid concentration, duration of leaching and the ZnS: MnO_2 ratio were kept constant. The result is shown in fig. 2. The efficiencies improved steadily with temperature and were maximum;91% for manganese and 80% for zinc and sulphur at 373 K.

Effect of acid-concentration on leaching efficiencies of manganese, zinc and sulphur liberation was explored at 373 K keeping all other parameters constant as before, at varying the acid-concentration from 1.2 M to 2.2 M. At 1.8 M H_2SO_4 the maximum efficiency values were obtained as before. Beyond 1.8 M, H_2SO_4 no appreciable gain was observed.

The effect of particle size was studied with concentrate samples; having particles 92.4%, 97.8% and 100%; below 75μm; leached in 1.8 M H_2SO_4, at 100°C for 3 h. The result is shown in fig. 3. Sample with 100% below 75 μm gave the best result.

The figs. 4 and 5 show the Arrhenius plot for zinc and manganese from a series of experiments varying in leaching time with all other parameters constant. The activation energy for manganese was lower than that of zinc.

Sulphur recovery:

Efficiency of sulphur recover as already stated was equal to zinc recovery and the amount recovered was always stoichiometrically equivalent to the amount of zinc leached out as expected from the reaction .

Purification of the leach solution:

The purification was not problematic. Table II shows the concentration of impurities. This is comparable to a zinc plant cell feed solution.

Table II. Chemical composition of the purified leach solution

Elements	Zn g/l	Mn g/l	Fe ppm	Ni ppm	Pb ppm	As ppm	Co ppm	Cd ppm	Ag ppm
Assay	49.3	34.2	0.33	0.14	N F	0.14	N F	0.30	0.11

DISCUSSION

All the zinc in the concentrate could not be leached out. The lower leaching efficiency, 63%, of zinc and sulphur liberation of coarser concentrate particles (7.6% above 75 μm) compared to the higher value, 81% with no coarser particles (0% above 75 μm) indicated that the inextricable zinc was locked in some mineral phase other than sphalerite which is immune to the leaching media. Leaching with higher acid concentration showed no improvement. The d^o values corresponding to the highest intensity wave length in XRD pattern of the concentrate was for sphalerite (100%) followed by wurtzite/pyrite (80%) while, in case of the final residue the highest intensity(100%) wave length was that for wurtzite/pyrite and 34% for sphalerite. The findings point to the probable conjecture that a part of the zinc sulphide is present as wurtzite or pyrite. The d^o values correspond to both the wurtzite and pyrite phase.

The extraction of sulphur from the final residue via dissolution in CS_2 followed by distillation was quantitative. All the liberated sulphur could be recovered.

Purification of the leach solution to the extent, required for electro-winning of zinc particularly at higher temperature (85°C), when the effect of impurities is intensified due to lowering of hydrogen overvoltage is difficult to attain. However the purified solution presented no problem during electro-winning trial. The EMD was analyzed and subjected to XRD analysis and TG/DT analysis. This was battery active γ- MnO_2.

CONCLUSIONS

Zinc and sulphur up to 80% and manganese up to 95% could be recovered, with leaching parameters: H_2SO_4 - 1.8M , concentrate : ore ratio - 1: 1.2, particle size of the concentrate - 100% below 75μm, time - 3 hours and temperature - 100°C. The particle size of the ore however could be as coarse as 251μm. Further investigation for leaching out the zinc locked in the wurtzite/pyrite phase should be carried out.

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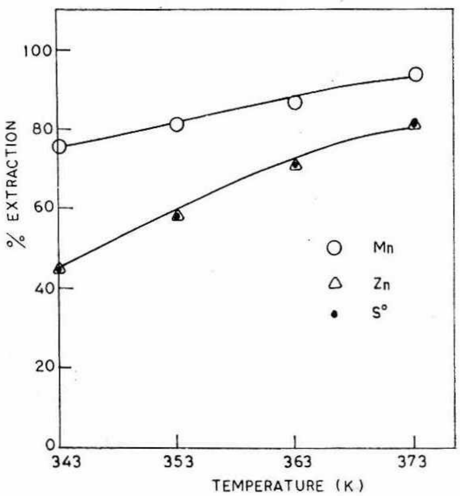

Fig. 2. Effect of temperature on the extraction efficiency of zinc, sulphur and manganese; (Particle size of concentrate 100% below 75 µm and ore -251µm ZnS : MnO_2 - 1 : 1.2, H_2SO_4 - 1.8 M and time - 3 hours.)

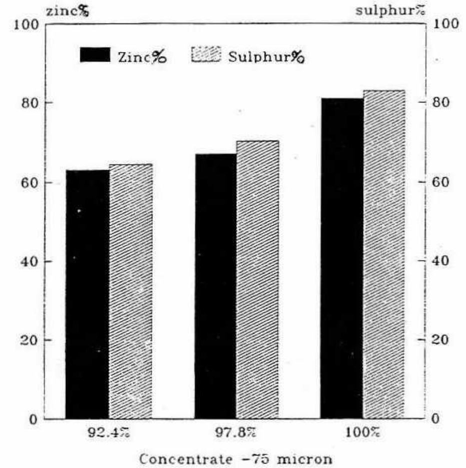

Fig. 4. Effect of particle size of concentrate on extraction efficiency of Zn, S and Mn (Particle size of ore - 251µm, ZnS : MnO_2 = 1 : 1.2, H_2SO_4 = 1.8 M, t = 3 h and temperature 373 K)

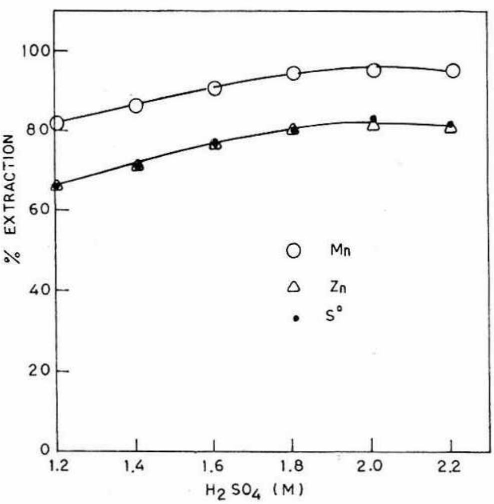

Fig. 3. Effect of acid concentration on the extraction efficiency of zinc, sulphur and manganese; (Particle size of concentrate 100% below 75 µm and ore -251µm, ZnS : MnO_2 - 1 : 1.2,temperature - 373 K and time - 3 hours.)

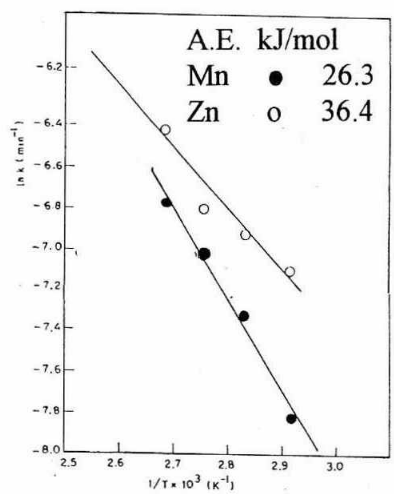

Fig. 5. Arrhenius plot for zinc and manganese recovery