THE AQUEOUS OXIDATION KINETICS OF COMPLEX POLYMETALLIC
SULPHIDE CONCENTRATES IN SULPHURIC ACID

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ABSTRACT

This paper describes bench scale studies on the aqueous oxidation
kinetics of complex polymetallic sulphide concentrates in sulphuric
acid. The multimetallic sulphides containing sphalerite, galena,
chalcopyrite and silver in a pyrite matrix were decomposed   at
120-150°C and oxygen pressures of 800-2000 KPa in dilute sulphuric
acid solutions for 15 to 120 minutes to yield 95% of the zinc in
the pregnant solution while about 85-90% of the lead and silver
remain in the residue together with most of the pyrite.   The
recovery of elemental sulphur was almost complete under optimized
experimental conditions. The selective leaching process appeared
to follow a diffusion control mechanism with an apparent low
activation energy of 55 kJ/mole. Metal extraction was affected
by variations in temperature, particle size, oxygen pressure ,
leachant concentration, time, and solid concentration in the
slurry.

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INTRODUCTION

Complex polymetallic sulphide ores, found in large quantities in Australia, Canada, Norway, and Spain, represent important sources of non-ferrous and precious metals [1,2]. Because of the peculiar mineralogical associations and the texture of the rock that comprises the ore, specific and difficult problems are presented during most stages of its overall benefication and extraction. It is sometimes possible to produce individual metal concentrates by flotation at low grade, and recovery and/or bulk concentrates, again of low grade, but at considerable higher recoveries.

An extensive computer literature search indicates that complex deposits, which are in finely disseminated form, seem to be less responsive to conventional processing techniques [1,3]. The dilemma posed by these ores is that the production of separate concentrates of acceptable grade involves a heavy loss of valuable minerals to the tailings, while the production of bulk concentrate with reasonable mill recovery involves a similar loss of values to smelter slags and residues. Also cost intensive fine grinding of these ores is essential to liberate the individual minerals: however under the conditions of very fine particle size, flotation kinetics and overall industrial flotation performance become extremely poor.

There is no technology available today to obtain significantly higher concentrate grade and recoveries from complex sulphide ores. A new metallurgical process, suitable for these finely disseminated (with considerable intergrowth) ores, and yielding high metal recoveries at moderate operating cost, must therefore be developed [4, 9, 10]. The metallurgical problems associated with complex sulphide ores may be tackled by adopting pyrometallurgical and/or hydrometallurgical methods. The former processes can be considered if the sale of sulphuric acid is economically feasible, but no single process will successfully treat these polymetallic concentrates. Hydrometallurgical processing appears to be the solution particularly in areas where the sale of the by-product acid is not possible and where it is becoming increasingly difficult to meet environmental standards [11, 12]. In this latter process, it would be possible to selectively dissolve sphalerite, galena, and chalcopyrite leaving pyrite virtually unattacked. Further, operating parameters could be selected such that, during the treatment, sulphide sulphur attached to the base metal sulphides could be converted into elemental sulphur. This would reduce waste disposal problems due to sulphate ions in aqueous effluents.

That enormous interest has been aroused in the treatment of complex sulphide ores is obvious from the number of conferences held on this topic and the numerous other research publications appearing to date [4-

21]. A variety of leachants have been suggested, e.g., $HCl + O_2$, H_2SO_4 + O_2, $FeCl_3$ solutions, $Fe_2(SO_4)_3$ solutions and $CuCl_2$ solutions. Out of the various processes proposed, only two processes viz Sherritt Gordon in Canada [14, 15, 18, 21] and Minemat Recherche in France [13], have received considerable attention. At Sherritt Gordon, the concentrate is leached in sulphuric acid and air under pressure at a high temperature for a fixed period. Zinc and copper are selectively dissolved whereas lead is converted into lead sulphate and lead jarosite [$Pb_{0.5}$ Fe: $(SO_4)_2(OH)_6$] and joins the residue along with the pyrite; any iron minerals that go into solution are reprecipitated. After filtration, the pregnant solution is purified and then electrolyzed to extract zinc metal; and the acid produced during electrolysis is recycled to the leaching step. Pyrite and elemental sulphur can be separated from the residue by flotation; however, the extraction of lead from the jarosite sets an acute problem since lead in this form is insoluble in the commonly used reagents.

In the Minemet process, the concentrate is leached in a solution of $CuCl_2$ (40 g/l Cu^{2+}) near the boiling point and at atmospheric pressure. The non-ferrous metal sulphides (ZnS, PbS, $CuFeS_2$) go into solution as chlorides, pyrite is unattacked, and elemental sulphur is generated. In order to keep CuCl, $PbCl_2$, and AgCl in solution, NaCl of the order of

250 g/l is added to the leachant. The solution is purified by precipitation FeOOH at pH 2.6 with air injection. Lead and silver are recovered by cementation with zinc and copper metals respectively. Thus the final solution will comprise of $ZnCl_2$, $CuCl$, $CuCl_2$, and $NaCl$. Zinc is then extracted by diethyl hexyl phosphoric acid and is stripped from the organic phase by H_2SO_4; the strip solution is electrolyzed in the conventional way. The leachant is regenerated by oxidation of acidified $CuCl$. In this process, no lead jarosite is generated, but there are a few other drawbacks such as a) the precipitation of iron as an extra step; b) the necessity of separating the complexed cuprous chloride from zinc chloride; c) indispensibility of adding a large quantity of sodium chloride to keep cuprous chloride in solution; and d) requirement of oxidizing cuprous chloride to cupric chloride for recycle. The process proposed by Mizoguchi and Habashi [12] is similar to the Sherritt Gordon Process [21] in which sulphuric acid is replaced by hydrochloric acid to minimize the presence of sulphate ions in solution. This restricts the formation of lead jarosite. The main drawback of this process is that the direct recovery of zinc from chloride medium is not as yet technically advanced.

In the present study, a series of tests were conducted to investigate the leaching behaviour of a natural complex polymetallic sulphide ore in sulphuric acid/oxygen leachant. The recovery of the individual metals was also attempted.

EXPERIMENTAL

1. <u>Raw Materials and Reagents</u>: 25 kg. of complex sulphide ore was subjected to crushing, grinding, classification, flotation, and drying to obtain bulk concentrates. From an ore containing 9.1% Zn, 4% Pb and 39 g/t Ag, the best bulk concentrate produced at a modest recovery assayed 19% Zn, 15% Pb and 101 g/t Ag. This flotation concentrates were 95% minus 75µm. Sodium lignin sulphonate was used as a surface active agent to ensure rapid and complete leaching. Dilute sulphuric acid was used as the leachant, and the residue was solubilized in the mixture of a sodium and calcium chloride solution.

2. <u>Equipment</u>: Leaching tests were conducted in a 600 ml titanium autoclave supplied by Parr Instrument Company, Moline, Illinois. X-ray diffraction and atomic absorption spectrometry were used for identification of phases in the residue, and for analysis of Pb, Zn, Ag, Cu and Fe in residues and the pregnant solution. The pH of the solution was measured with a Fisher pH-meter.

3. <u>Procedures</u>: Each test was carried out with 30 g of the concentrate to which 200 ml of leaching agent was added. The mixture was heated to the desired temperature and then pressurized by oxygen to the desired pressure. From this moment, the time of reaction was record-

ed. The oxygen pressure reported here is the difference between the total pressure before and after the oxygen introduction. At the end of each experiment, heating of the autoclave was shut off, the oxygen supply was stopped, and the reaction mixture was quenched to room temperature by introducing cold water in the cooling coils. The autoclave was emptied and its contents filtered using a vacuum filter. The solution and washings were adjusted to one litre and then analyzed for lead, zinc, copper, iron, and silver by atomic absorption spectrometry. Leach residues were dried for two hours at 90 C and then analyzed for lead, silver, elemental sulphur, and pyrite. Residues were also examined by X-ray diffraction. The clear filtrate was further purified precipitating iron and recovering metals such as copper and cadmium by cementation. The purified pregnant solution was concentrated and electrolyzed to obtain zinc.

In order to recover lead and silver, the leached residue was subjected to selective leaching at high temperature and pressure. The sodium chloride and calcium chloride mixture was used as leachant. Calcium chloride was added to control pH and sulphate build-up. Lead and silver went into the solution as $PbCl_2$ and $AgCl$. The calcium sulphate precipitate was filtered hot and the clear filtrate was then treated with sodium bicarbonate ($NaHCO_3$) to precipitate the lead as $PbCO_3$. This $PbCO_3$ was then calcined at 450C

to form lead oxide. The silver metal from the solution was recovered by cementation on lead powder.
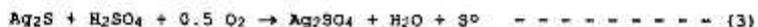
The influence of leachant concentration (0.5 - 2.00 N), temperature (120-150C), time of leaching (15 - 150 minutes), particle size 10-100μm, and oxygen pressure (800-2000 kPa) on the leaching efficiency of zinc were investigated. An experimental reproducibility of better than ±2% of the values reported has been achieved.

RESULTS AND DISCUSSION

The main objective of the leaching experiments was to evaluate the kinetics of leaching complex polymetallic sulphide concentrates by H_2SO_4 + O_2. The kinetics of dissolution are strongly dependent on factors such as temperature, particle size, oxygen pressure and leachant concentration. Results are presented in Figures 1 to 4 and Tables 1 to 3.
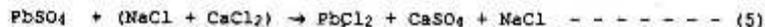
The chemistry of leaching complex sulphide concentrates by sulphuric acid plus oxygen can be represented by a scheme of equations. One of the most important features of these reactions is the production of elemental sulphur.

i) Preferential Dissolution of sphalerite and Chalcopyrite in dilute H_2SO_4

$$ZnS + H_2SO_4 + 0.5\ O_2 \rightarrow ZnSO_4 + H_2O + S^o \quad - - - - - - - - - \quad (1)$$

$$PbS + H_2SO_4 + 0.5\ O_2 \rightarrow PbSO_4 + H_2O + S^o \quad - - - - - - - - - \quad (2)$$

$$Ag_2S + H_2SO_4 + 0.5\ O_2 \rightarrow Ag_2SO_4 + H_2O + S^o \quad - - - - - - - - - \quad (3)$$

$$CuFeS_2 + H_2SO_4 + 1.5\ O_2 \rightarrow CuSO_4 + Fe\ OOH + 0.5\ H_2O + 2S^o \quad - - \quad (4)$$
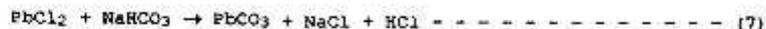
The zinc and copper go into solution while the lead and silver are transformed in their sulphates and retained in the residue together with pyrite and elemental sulphur.

ii) Selective Dissolution of Pb and Ag from Residues in NaCl and $CaCl_2$ Solution

$$PbSO_4 + (NaCl + CaCl_2) \rightarrow PbCl_2 + CaSO_4 + NaCl \quad - - - - - - - \quad (5)$$

$$Ag_2SO_4 + (NaCl + CaCl_2) \rightarrow 2AgCl + CaSO_4 + NaCl \quad - - - - - - - \quad (6)$$

iii) Precipitation of Lead as Carbonate

$$PbCl_2 + NaHCO_3 \rightarrow PbCO_3 + NaCl + HCl \quad - - - - - - - - - - - - - \quad (7)$$

iv) Calcination of $PbCO_3$ to PbO

$$PbCO_3 + 450\,C \rightarrow PbO + CO_2 \quad - - - - - - - - - - - - - - - - - \quad (8)$$

In leaching processes, the rate determining step is either chemical reaction at the surface of the solid or diffusion of reactant or product through a layer of residue or insoluble reaction product. If one approximates the ore particles as spheres, then using the 'shrinking core' model, when chemical processes alone are rate limiting[22], the relationship between the fraction conversion, $\propto$, and time, t, is:

$$[1 - (1 - \propto)^{1/3}] = k_c\, t \quad - - - - - - - - - - - - - \quad (9)$$

where k_c is the specific rate constant for chemical control. When the rate of diffusion (k_d) of the reactants through the product layer is rate limiting, then

$$[3/2 - \propto - 3/2\,(1 - \propto)^{2/3}] = k_d\, t - - - - - - - - - \quad (10)$$

By plotting these expressions, the values of k_c and k_d can be obtained from the slope of the resulting line. Figures 2 and 3 show the chemical and diffusion controlled models. The experimental data treated according to the kinetic model correlated well with diffusion control shown in Figure 3.

The rate of ZnS leaching was studied over the temperature range of 120-150C. Only above 120C was the mechanism of dissolution changed in favour of the faster kinetics. Increasing the temperature had a marked effect on zinc, copper and iron dissolution. Figure 1 shows the effect of temperature on leaching. The Arrhenius plot of lnk vs 1/T is shown in Figure 4. The activation energy obtained from the slope is 55 kJ/moles Zn, which appears rather high from the usual figures of 16 - 20 kJ/mole for a diffusion controlled process. However, Munoz, Miller and Wadsworth [19] have also reported high activation energies of 70 - 85 kJ/mole for pore diffusion controlled processes in the leaching of chalcopyrite by $Fe_2(SO_4)_3$. Therefore the relatively high activation energy, obtained in this work for pore diffusion control mechanism, is consistent with the findings of earlier researchers.

The recovery of zinc and elemental sulphur increases with increasing speed of agitation which also suggests the process is diffusion controlled. Acid leaching is a heterogenous dissolution process and hence agitation helps to keep the particles in suspension for efficient reaction, due to good liquid-solid contact throughout the leaching. Since higher pulp density necessitates more agitation, a pulp density of 0.15 has been maintained.

Figure 1 also shows that zinc recovery increases gradually with increasing time. After about 120 minutes at 150C and in 1N H_2SO_4, more

than 95% of the zinc has been dissolved. Also, with increasing reaction time, lead in solution, and the non-sulphide lead in the residue, decrease and more lead jarosite is formed.

When a sample of relatively coarse ore was leached, zinc and copper were slow to report to solution. The effect of decreasing particle size, however, was very marked and indicated that rapid dissolution of zinc was possible (Table 1). Examination of leaching behaviour with respect to particle size reveals an insensitivity on the part of lead and a large dependency on the part of zinc. This behaviour corroborates mineralogical analysis. Zinc passed rapidly into solution when finely ground ore was reacted.

Leaching in the absence of oxygen is slower than when oxygen is present (Table 2). Also in the absence of oxygen, lead recovery decreases with increasing temperature. X-ray diffraction analysis of the residue showed that at 150 C practically all of the ZnS dissolved while the PbS did not. On the contrary, when leaching was conducted in the presence of oxygen, the recovery of zinc, silver and elemental sulphur increases rapidly with increased oxygen pressure up to 1000 kPa then slowly at higher oxygen pressure (1500 kPa). As indicated by X-ray diffraction, at 1500 kPa oxygen pressure precipitation of mainly lead jarosite was achieved, but at 1000 kPa oxygen pressure mainly $PbSO_4$ was precipitated.

From the results presented in Table 3, it appears that zinc recovery is profoundly influenced by the concentration of leachant up to 2N H_2SO_4, beyond which there is no significant improvement. Elemental sulphur recovery is also markedly influenced by the higher concentration of leachant. Higher concentration of H_2SO_4 leachant seem to be detrimental to the dissolution of lead.

PROPOSED TREATMENT METHOD

The experimental results of the present investigation suggest the viability of a process similar to the Sherritt Gordon Process in which H_2SO_4 + O_2 is used as leachant. The benefits would be increased by reaction rates and improved lead recovery since formation of lead jarosite is minimized due to judicious selection of parameters. A flowsheet for the proposed treatment method is given in Figure 5. The detailed results on the processing of leached residue to recover lead and silver are being communicated separately. Although the proposed hydrometallurgical extraction route for the processing of sulphide concentrates seems promising, large scale trials are necessary to evaluate process economics.

CONCLUSIONS

The present study on the aqueous oxidation kinetics of complex polymetallic sulphide concentrate in sulphuric acid clearly demonstrates the following:

1. Complex polymetallic sulphides containing sphalerite, galena, chalcopyrite and silver in a pyrite matrix can be decomposed at 150 C and oxygen pressure of 1000 kPa in 1N H_2SO_4 for 60 minutes to yield 95% of the zinc in the pregnant solution.

2. Eighty-five to 90% of the lead and silver remain in the residue together with most pyrite and elemental sulphur.

3. Leaching is markedly faster in the presence of oxygen.

4. Aqueous oxidation with dilute H_2SO_4 is diffusion controlled through a boundary layer; the process is strongly dependent on temperature and agitation; and the activation energy is 55 kJ/mole.

5. Optimum conditions for 85% recovery of lead from the leached residue are temperature of 60 C, NaCl concentration of 260 g/litre, and time of 60 minutes.

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TABLE-1

EFFECT OF PARTICLE SIZE OF THE CONCENTRATE ON THE RECOVERY

Concentrate	30 g
Solution	200 ml
Concentration of Leachant	1N H_2SO_4
Temperature	120°C
Time	60 minutes
Agitation	1000 rpm
Oxygen Pressure	1000 kPa

Particle Size	Percentage Metal Recovery		
μm	Zinc	Lead	Copper
10	92	79	65
50	86	78	62
75	80	76	60
100	55	76	48

TABLE-2

ETTECT OF OXYGEN PRESSURE ON THE RECOVERY (%)

Concentrate	30g
Solution	200 ml
Temperature	120°C
Time	60 minutes
Concentration of Leachant	1N H_2SO_4
Particle Size	(~75)μm

| Oxygen Pressure | Percentage Metal Recovery | | | |
kPa	Zinc	Silver	Lead	Sulphur, S⁰
800	74	29	78	40
1000	80	38	76	68
1500	90	36	58	69
2000	91	35	47	71

TABLE-3

EFFECT OF SULPHURIC ACID CONCENTRATION ON THE RATE OF RECOVERY OF VARIOUS METALS

Concentrate	30g
Solution	200 ml
Temperature	120°C
Time	60 minutes
Oxygen Pressure	1000 kPa
Particle Size	(-75)µm

Concentration of H_2SO_4, N	Percentage Metal Recovery			
	Zinc	Copper	Lead	Sulphur, S^o
0.5	60	40	83	52
1.0	80	60	76	68
1.5	83	62	72	70
2.0	89	68	70	76
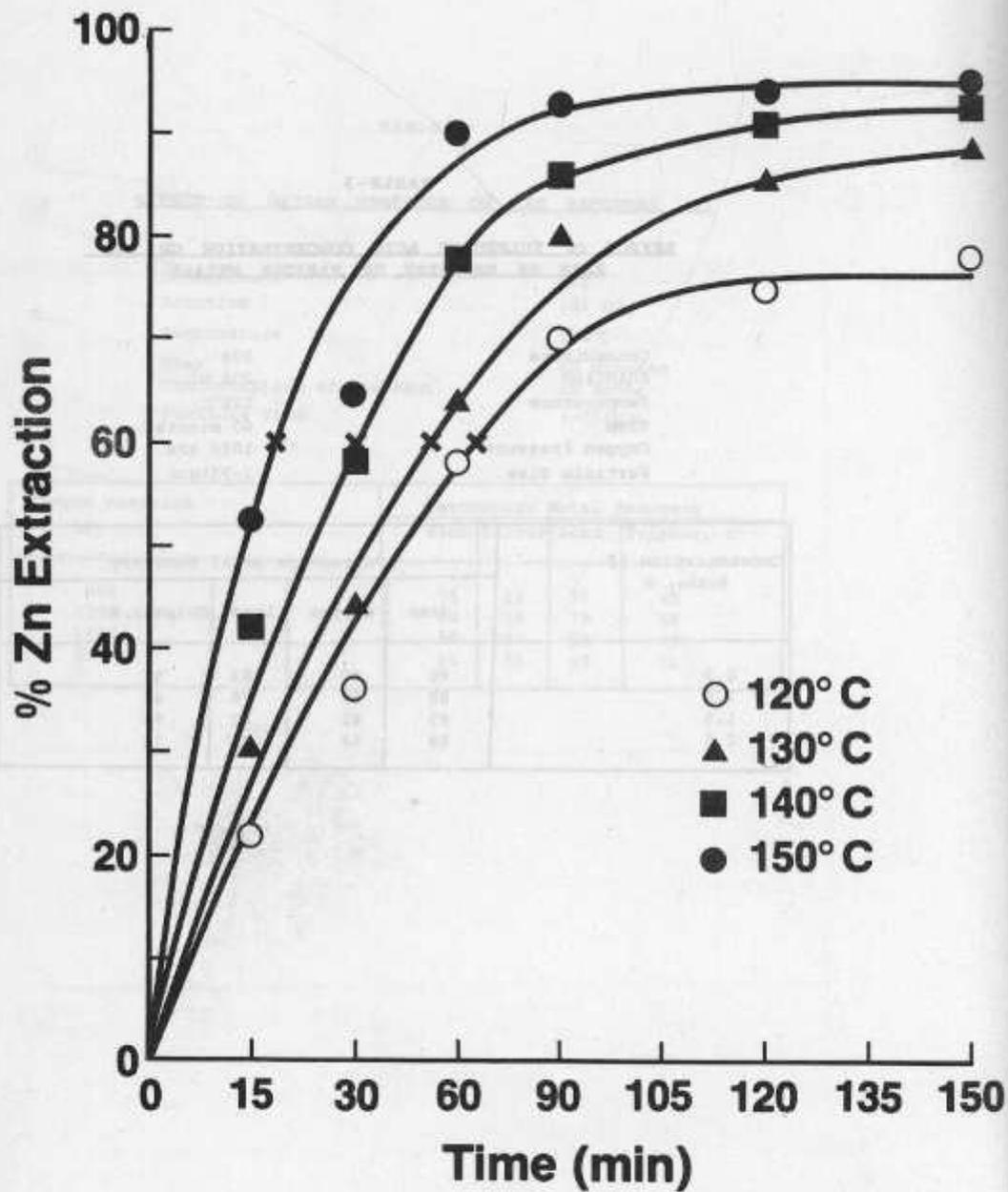
FIGURE 1   EFFECT OF TEMPERATURE ON THE RECOVERY OF ZINC
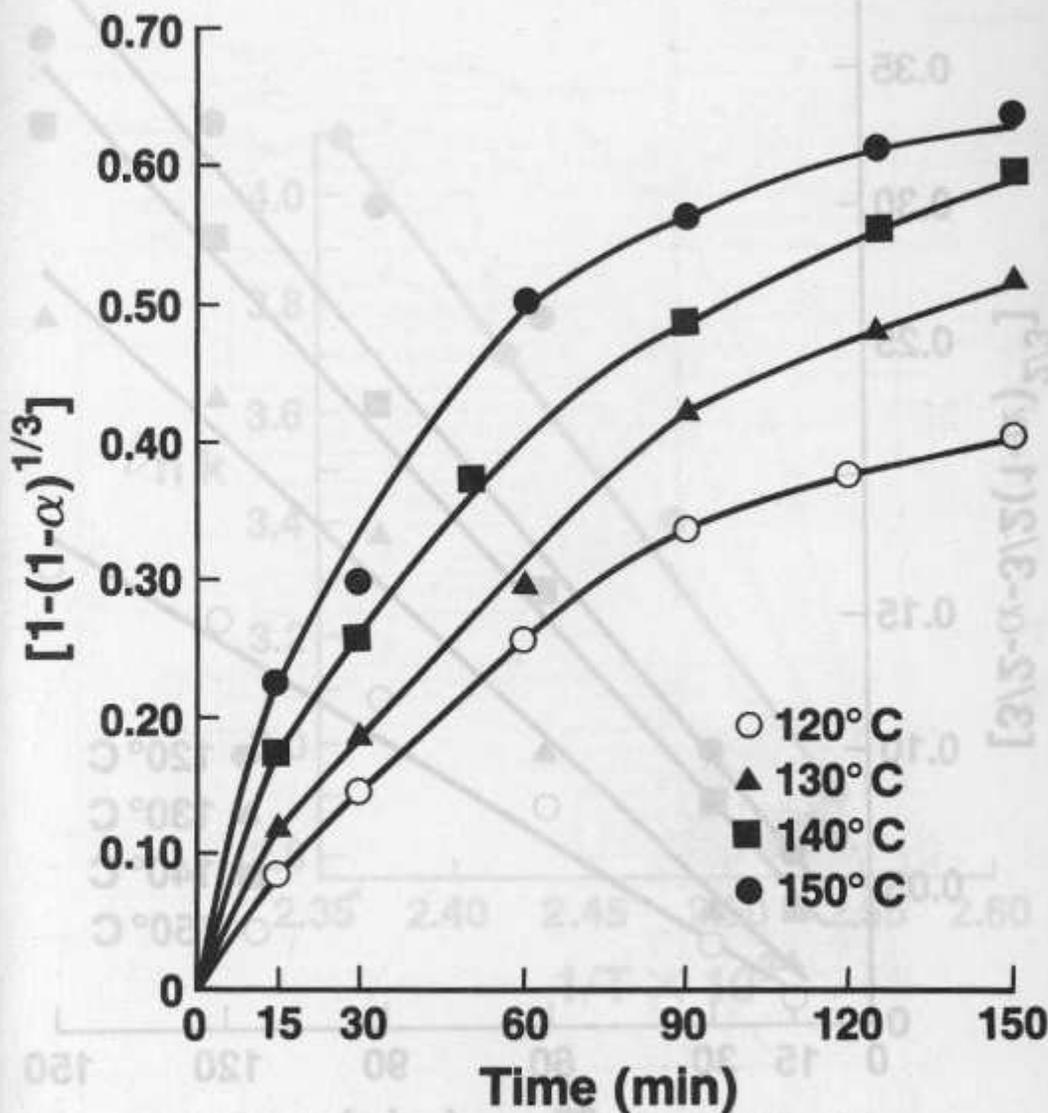
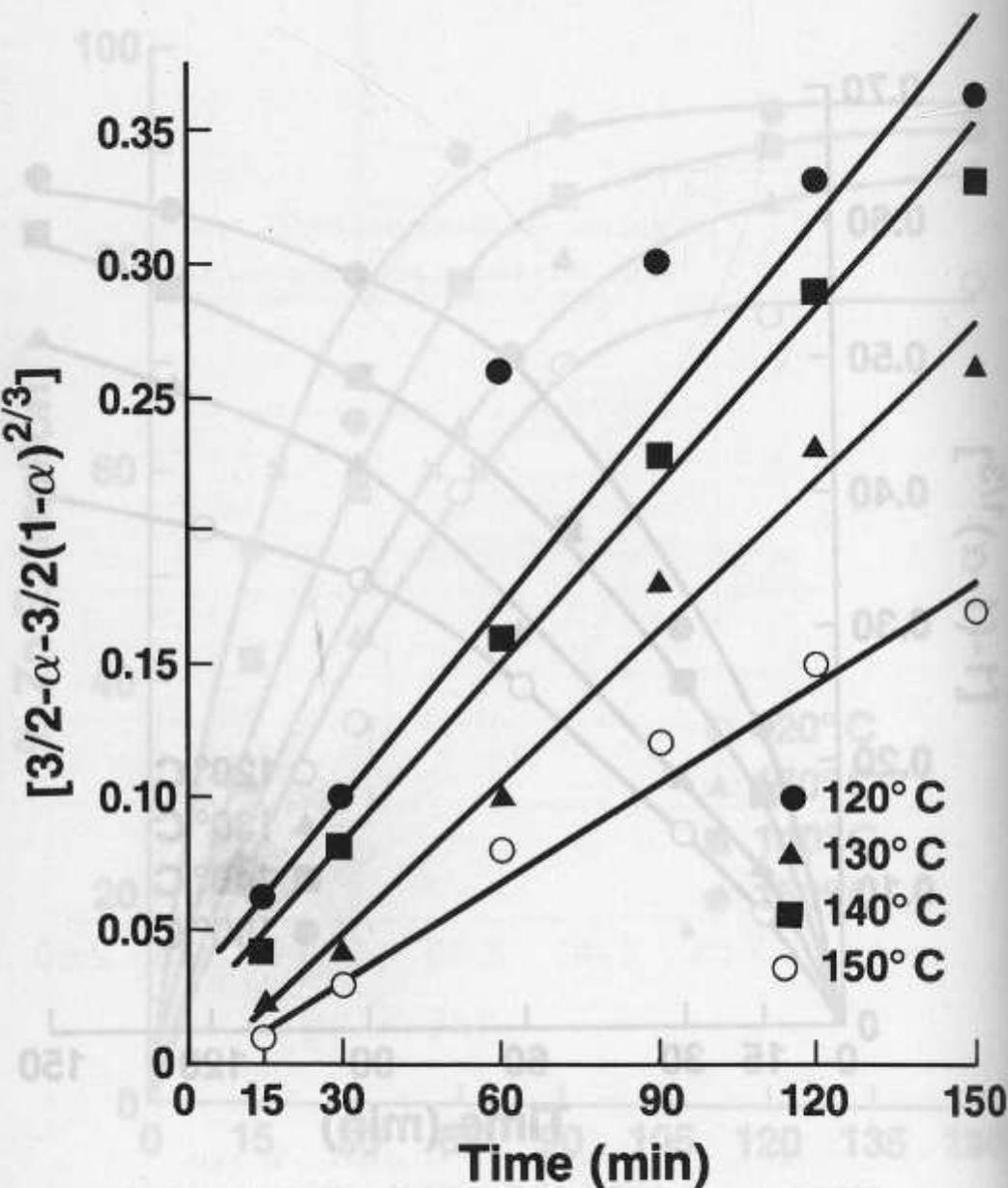FIGURE 2 PLOT OF $[1-(1-\alpha)^{1/3}]$ AGAINST t FOR THE EXTRACTION OF ZINC

FIGURE 3   PLOT OF $[3/2-\alpha-3/2(1-\alpha)^{2/3}]$ AGAINST t
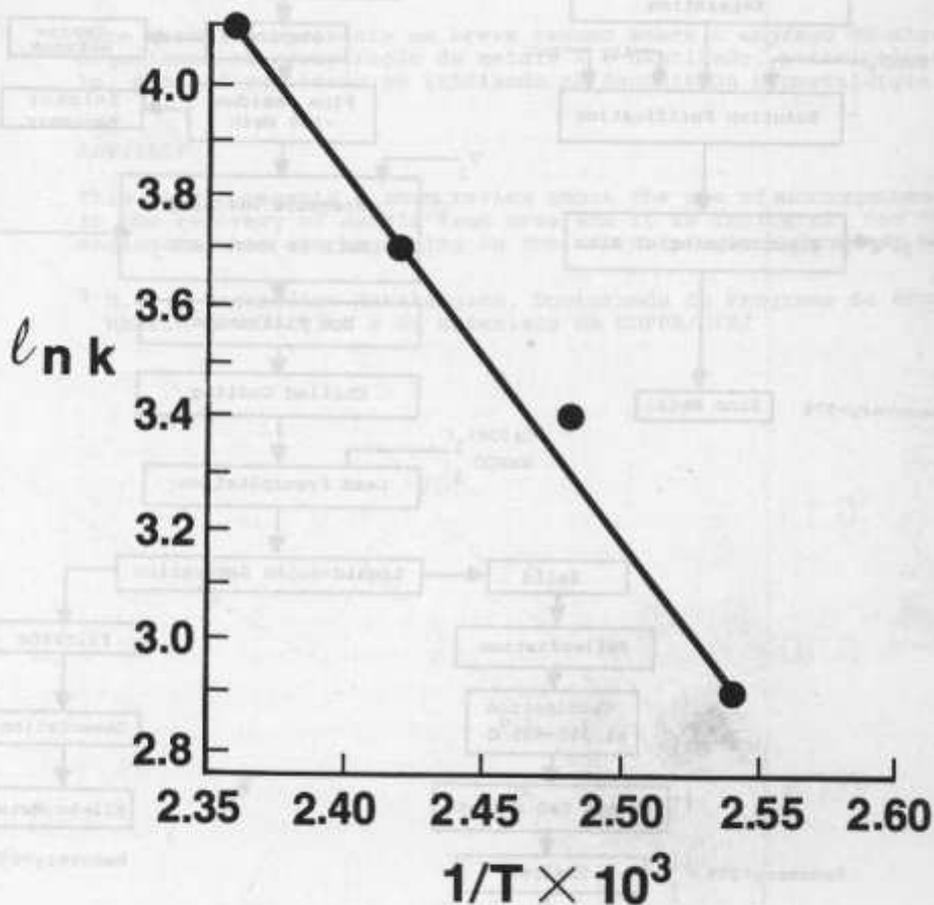FOR THE EXTRACTION OF ZINC

FIGURE 4   TEMPERATURE DEPENDENCE OF RATE
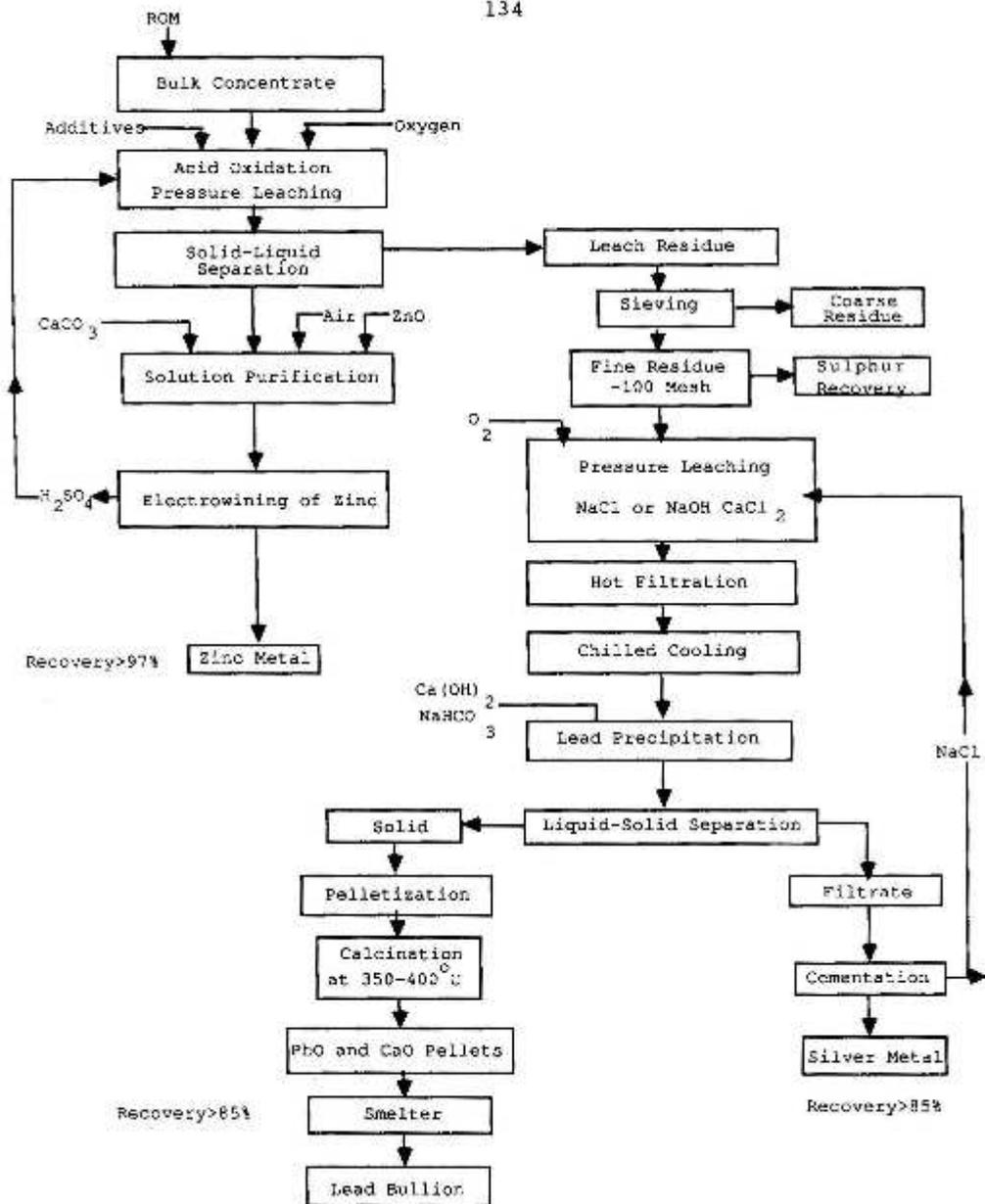CONSTANT AS lnk AGAINST $\frac{1}{T} \times 10^3$

FIGURE 5   FLOWSHEET OF THE PROPOSED HYDROMETALLURGICAL
PROCESSING OF COMPLEX POLYMETALLIC SULPHIDE
CONCENTRATES