Technical Note

Refractory Behaviour of Two Sphalerite Concentrates to Dissolution in Ferric Sulphate Solutions

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ABSTRACT

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The dissolution of concentrates from the Rosh Pinah and Black Mountain deposits failed to exceed a conversion of 50% zinc to solution after 5 hours at 80°C with 0.5 M Fe(III) in an acidic ferric sulphate solution. The final conversion was proportional to the particle size, suggesting that the problem concerned a surface phenomenon. Removal of the sulphur product-layer did not result in any additional dissolution. X-ray diffraction analysis suggested the formation of an insoluble $PbSO_4$ or lead jarosite coating. These concentrates both have lead contents (about 2%) higher than those of concentrates (about 0.4%) studied previously which dissolve beyond 90%. Neither concentrate displayed passivation in ferric chloride solutions in which basic lead sulphates are soluble. Electron microprobe analysis was unable to detect a significant layer of material covering the leached particles.

INTRODUCTION

Oxidative dissolution is an important step in the hydrometallurgical extraction of metals from sulphide ores. Attention has been focussed on the development of processes for the leaching of sphalerite using oxidants such as ferric ion and oxygen in chloride solutions [1–13].

The kinetics of dissolution of sphalerite concentrates have been reported to follow the shrinking-particle mechanism, which for spherical geometry is given by:

$$k_r t = 1 - (1 - X)^{1/3} \tag{1}$$

where X is the conversion of zinc in the solid to zinc in solution, k_r is a constant, and t is the time elapsed. The leaching of sphalerite is slow relative to that of other sulphides, and the conversion usually exceeds 90%.

TABLE 1

Chemical compositions of the sphalerite concentrates (all values in %)

Element	Black Mountain	Rosh Pinah
Zn	49.8	56.7
Fe	9.72	4.35
Cu	0.37	0.25
Pb	3.46	1.46
Mn	1.26	0.29
Al	0.18	0.15
S^{2-}	28.6	30.1
S^0	2.1	0.7
Cd	0.138	0.121
BET area (m^2/g)	1.28	0.94

Kuzminkh and Yakoutova [14] leached two natural sphalerites with different mineralogical compositions and reported that the sphalerites leached at similar initial rates under equivalent conditions. However, for similar conditions, an excess of 80% conversion was achieved for the one, while only 33% was achieved for the other. They proposed that the difference in the mineralogical composition was the principal reason for the difference in the final extents of reaction.

The refractory behaviour of two sphalerite concentrates to dissolution in ferric sulphate solutions is reported in this note. Chemical and mineralogical techniques are used to investigate the formation of insoluble metal sulphate films on the surface of the particles.

EXPERIMENTAL

Two sphalerite concentrates were used in the present study. One of these was from the Rosh Pinah Deposit in Namibia, and the other was from the Black Mountain deposit in South Africa. Both concentrates were wet-screened and a sample in the size range $-53 + 44 \mu m$ was selected. This size fraction was washed with Na_2S to remove flotation reagents [5], and then washed in dilute sulphuric acid. The chemical compositions and surface areas are shown in Table 1. Mineralogical analyses were carried out on the sample as received and after they had been leached. The results are shown in Table 2. A microscopic examination of polished sections of the Black Mountain sample revealed a rim of fractured material.

The reactor consisted of a two litre cylindrical glass vessel with a flat stainless-steel impeller driven by a variable speed motor. A single stainless-steel baffle was installed. The temperature was maintained to within $0.5°C$ by a

TABLE 2

Mineralogical compositions of the concentrates (all values in %)

Constituents	Black Mountain		Rosh Pinah	
	As received	After leach	As received	After leach
Sphalerite — liberated	88.6	88.2	90.4	88.8
Sphalerite — locked to sulphides	8.2	9.4	1.6	2.2
Sphalerite — locked to gangue	0.6	0.2	0.2	0
Chalcopyrite	Trace	0.2	0.2	0.4
Galena	0.4	0	Trace	0.2
Pyrite + pyrrhotite	1.4	1.2	7.4	8.4
Gangue	0.8	0.8	0.2	0

contact thermometer connected to the heating element. A condenser was connected to one of the ports in the lid.

Samples of solution were taken during the reaction by use of a 15 mL syringe and filtered immediately under vacuum. The concentrations of the zinc and iron in solution were determined by atomic absorption spectrophotometry.

RESULTS

Figure 1 illustrates the extent of reaction for a typical run on Rosh Pinah and Black Mountain sphalerites. In contrast to the material previously studied [2], both these sphalerites display passivation, in that neither will dissolve completely. Previous investigation [3] has shown that unscreened flotation
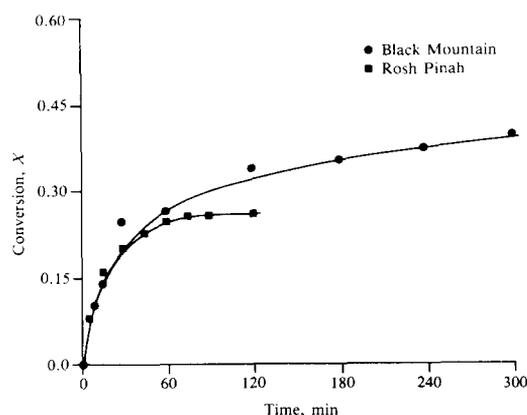

Fig. 1. Leaching of Black Mountain and Rosh Pinah sphalerites showing passivation behaviour in sulphate solutions. Conditions: $0.5\ M$ Fe(III), $0.1\ M$ H_2SO_4, and $78\,°C$.

concentrate from Black Mountain will not dissolve beyond a 50% conversion, and that the final extent of reaction is proportional to the surface area, indicating that a surface phenomenon is responsible for the passivation behaviour. Increasing the temperature of reaction from 50°C to 90°C increased the initial rate of reaction, but the final extent of reaction only increased from 24% conversion to 28% conversion for particles in the size range $-74 + 53 \mu m$ [3].

The main difference between the material that dissolved beyond 90% conversion [2] and that from Black Mountain is the increased lead content of the latter (0.47% Pb for the previous concentrate [2] and 3.46% Pb for Black Mountain). The mechanism for passivation could be due to the formation of an insoluble coating of $PbSO_4$ or lead jarosite on the surface of the particle. The removal of the sulphur product-layer from the leached Black Mountain sphalerite was reported not to result in any additional dissolution [3].

The material from Rosh Pinah, which does not have as high a lead content as Black Mountain sphalerite, also displays passivation. Washing of the leached particles in CS_2 to remove the sulphur layer before they were returned to the leaching solution did not result in further dissolution.

Both the sphalerite concentrates studied by Kuzminkh and Yakoutova [14] had high lead contents (about 6.8% Pb). They reported that the concentrate that dissolved well was well liberated, while microscopic investigation of the concentrate that displayed passivation revealed that there was a close intergrowth of sphalerite with other sulphide minerals. This supports the hypothesis that the deposition of a basic lead sulphate coating is the reason for the passivation.

The effect of a chloride solution rather than a sulphate solution as the leaching solution is shown in Fig. 2, as a plot of $1-(1-X)^{1/3}$ against t (eqn. 1). This should be a straight line if the shrinking particle model is obeyed. The deviation from linear behaviour for sulphate solutions is a result of the passivation illustrated in Fig. 1. Figure 2 clearly illustrates that neither Black Mountain nor Rosh Pinah sphalerites passivate in chloride solutions.

X-ray diffraction showed minor peaks representing anglesite ($PbSO_4$) and jarosite $[K(Fe)_3(SO_4)_2(OH)_6]$ for the leached Black Mountain and Rosh Pinah sphalerites. Pb, Zn and trace amounts of Ag can be incorporated in the jarosite structure with the formula $Pb_{0.5}(Fe,Zn)_3(SO_4)_2(OH)_6$; Cu can be incorporated in a beaverite–plumbojarosite solid solution. These peaks were not observed for the leached material that displayed no passivation. Chemically precipitated jarosites are often insufficiently crystalline for reliable identification by X-ray diffraction, and a degree of uncertainty is present. However, the formation of anglesite and jarosite would not occur in chloride solutions, and their presence is consistent with the passivation observed.

Analysis of the particles using electron microprobe and scanning electron microscope with energy dispersive analyser (SEM–EDX) techniques did not reveal a layer of material covering the leached particles. The surface of the
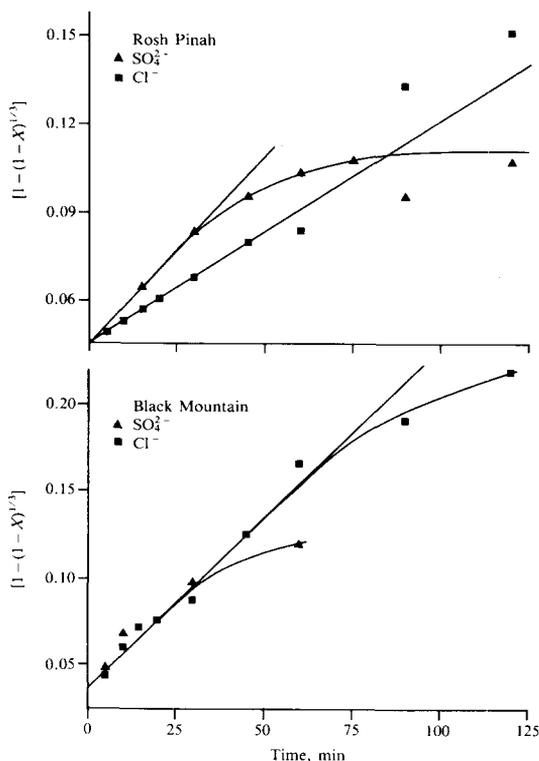
Fig. 2. Leaching of Black Mountain and Rosh Pinah sphalerites in sulphate and chloride solutions with 0.5 M Fe(III) at 78°C.

Black Mountain sphalerite was covered with numerous small ($<2\,\mu$m) $PbSO_4$ particles and sulphur product. The Rosh Pinah material was very similar to that of Black Mountain, except that it did not display as many $PbSO_4$ particles on the surface. Removal of $PbSO_4$ by washing the leached material in ammonium acetate before returning it to the leaching solution did not result in additional dissolution, indicating that the formation of lead jarosite is probably responsible for the refractory behaviour. However, extensive investigation of the particle surfaces using electron microprobe and SEM–EDX could not detect such a coating.

CONCLUSIONS

The formation of an insoluble surface film passivates the leaching of two high lead content (about 2% Pb) sphalerite concentrates in ferric sulphate solutions. Such passivation is not observed in ferric chloride solutions. This surface coating may consist of $PbSO_4$ or lead jarosite, both of which are insoluble in sulphate solutions.

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