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RECENT DEVELOPMENTS IN ACTIVATION
OF LEACHING OF METAL SULPHIDES

The activation of leaching processes of copper, zinc, and nickel sulphides in solutions of ferric sulphate, nitric acid as well as in sulphuric acid under oxygen pressure are presented. It was shown that fine grinding accelerates both the rate and the extent of leaching. This effect seems to be due to both the particle size and lattice distortions. An addition of silver, cupric, and ferric ions increases also the rate and extent of leaching due to reactions with H_2S evolved during the leaching. In these reactions intermediate products are formed which are oxidized faster than the H_2S gas. When molten elemental sulphur is formed during the leaching, surface active agents improve the process because they prevent agglomeration of sulphide with the sulphur.

1. INTRODUCTION

There are three main processes which can control the rate of a leaching reaction. First, the phase boundary reactions which usually involve adsorption or desorption step and may be of molecular or electrochemical nature. These reactions are unaffected by agitation, and the activation energy is usually above 40 kJ/mole, sometimes above 80 kJ/mole. The second main process is the diffusion of reactants through a hydrodynamic boundary layer situated within the liquid phase and is hydrodynamically controlled. The third process is the diffusion of reagents from solution through a layer of a solid product covering the reacting solid, or the diffusion of ions from the reacting solid through a layer of product to the solid-liquid interface at which reaction occurs (Peters, 1973).

The rate of diffusion depends on the properties of the solid. If it is porous, pore size is important, if the solid is non-porous, the solid-state diffusion must occur, and, in many cases, the diffusion coefficient will be sensitive to the degree of perfection of the lattice (Wadsworth, 1979).

The purpose of this paper is to survey the recent developments associated with activation techniques used in leaching of metal sulphides in ferric sulphate solutions as well as in sulphuric acid under oxygen pressure. The main attention is paid to the effect of fine grinding, addition of some metal ions, and modification of product layer with surface active agents.

2. EFFECT OF FINE GRINDING

Electrochemical study of the anodic dissolution of chalcopyrite shows that oxidation rate is limited by transport of ions through an unstable film of semiconductor metal deficient polysulphide (Parker et al. 1981; Biegler et al. 1985). This film achieves an equilibrium thickness, and aqueous oxidation of chalcopyrite can be greatly accelerated by fine grinding.

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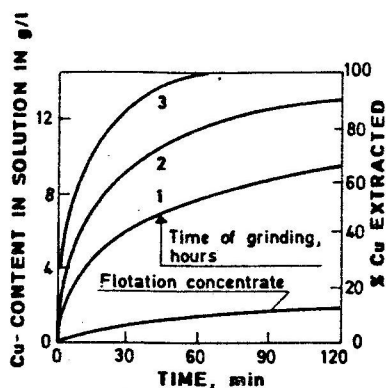Częstochowa, Poland

Fig. 1. Influence of the time of activation on the copper extraction from CuFeS$_2$ in acidic pressure leaching (Gerlach et al., 1976)
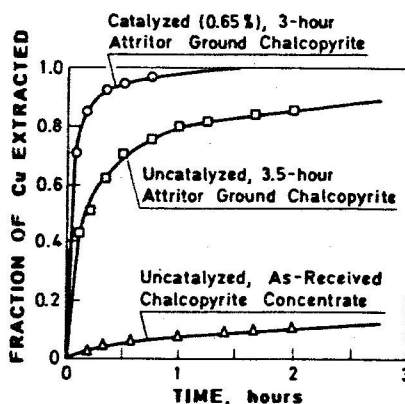
Fig. 2. The fraction of copper extracted as a function of time for different products in 1 M ferric sulphate leaching at 90°C (Miller et al., 1979)

Gerlach and co-workers (1973) found that the leaching conditions of CuFeS$_2$ can be made less drastic if the mineral was first subjected to a milling action in oscillating mill which is also called a vibration mill. Fig. 1 shows influence of the time of activation on the copper extraction from CuFeS$_2$. The authors suggested that such milling caused high distortion of crystal lattice and chalcopyrite takes up so much energy that complete and fast dissolution is possible in much less drastic conditions of the leaching.

However, Beckstead and co-workers (1976) reported that leaching rate of chalcopyrite was independent of lattice distortion but depended only on the specific surface area. They found that the leaching behaviour of annealed samples, in which the distortion was eliminated, was the same as that without annealing.

The study by Tkacova and Balaz (1988) connected with the influence of fine grinding on leaching rate of CuFeS$_2$ in ferric sulphate solutions showed that an increase in leaching rate seems to be due to both the particle size and lattice distortions of the material.

3. EFFECT OF ADDITION OF SOME METAL IONS

The accelerating effect of silver ion on the aqueous oxidation of chalcopyrite has been demonstrated by several investigators. Miller and Portillo (1979) summarised the results in solutions of sulphuric acid under oxygen pressure (Pawlek, 1976) and acid ferric sulphate (Snell and Sze, 1977).

Miller and Portillo (1979) showed that the leaching rate of attritor-ground chalcopyrite in ferric sulphate was greatly accelerated by addition of silver ions as catalyst to the leaching solution. Fig. 2 shows the fraction of copper extracted as a function of time for different products at 1 M Fe^{3+} and 90 °C. Uncatalyzed leaching of attritor-ground chalcopyrite (mean particle size 0.5 μm) to 80% reaction requires one hour retention time. On the other hand, in the presence of a silver catalyst, 80% reaction for a coarser attritor-ground concentrate can be achieved in 7 min. The authors suggest that the rate of leaching may be limited by the electrochemical reaction of Fe^{3+} at the surface of Ag$_2$S crystallites present in the film. The film is formed during the exchange reaction:
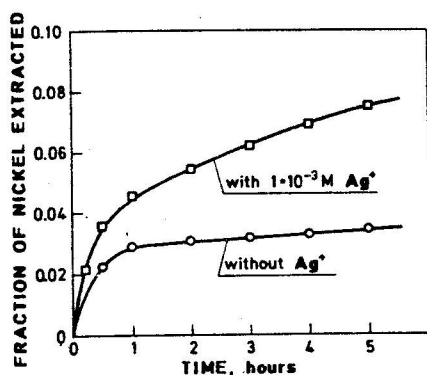
Fig. 3. Influence of silver ions on nickel extraction from millerite in 0.2 M ferric sulphate solution at 95 °C for fraction < 63 μm
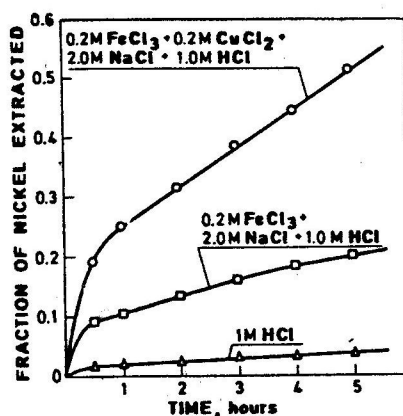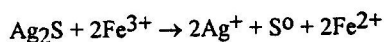
Fig. 4. Extraction of nickel from millerite with ferric solution at 95 °C for fraction < 63 μm

$$Ag_2S + 2Fe^{3+} \rightarrow 2Ag^+ + S^0 + 2Fe^{2+}$$

Elemental sulphur replaces the Ag_2S crystallites forming a porous non-protective layer and the Ag^+ generated acts as a transfer agent continually restoring the silver sulphide crystallites via the exchange reaction.

Catalytic action of silver ion was also found during the leaching of millerite in aqueous ferric sulphate solutions (Mulak, 1992). Fig. 3 shows the influence of silver ions on nickel extraction in 0.2 M $Fe_2(SO_4)_3$ with 1 M H_2SO_4 solution at 95 °C for fraction < 63 μm.

The dissolution rate of millerite in a chloride solution is about 4.5 times higher than that in sulphate media. Fig. 4 demonstrates that addition of 0.2 M $CuCl_2$ in ferric chloride leaching increases nickel extraction from 20.0% to 51.1%. This seems to be due to the cupric ion reacting with electrons more rapidly than ferric ion. Thus, the Fe^{3+}/Fe^{2+} system ensures reproduction of the Cu^{2+} ions by oxidizing Cu^+ ions by $FeCl_3$. In such a way, cupric ions act as catalyst in ferric chloride leaching (Parker et al. 1981).

Our previous study (Björling and Mulak, 1976) showed that dissolution rate of millerite even in 3.0 M HNO_3 at temperature below 50°C is very low because H_2S gas is evolved and a formation of passive layer of NiS_2 occurs. Fig. 5 shows the effect of 1.10^{-3} M addition of catalytic ions on dissolution rate of millerite (fraction <63 μm) in 2.0 M HNO_3 solution at 50° C. The greatest catalytic effect is observed for Ag^+ ions, whereas cupric ions increase the dissolution rate only slightly.

An addition of silver, cupric, and ferric ions increases dissolution rate due to reaction of these ions with H_2S and intermediate products are formed which are oxidized faster by nitric acid than hydrogen sulphide (Mulak, 1987a; 1987b). Examination of the experimental data permits postulation of the following reaction mechanism in the presence of silver ions:

step I: acidic attack of NiS

$$NiS + 2H^+ = Ni^{2+} + H_2S$$
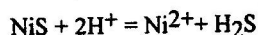
step II: production of intermediate product
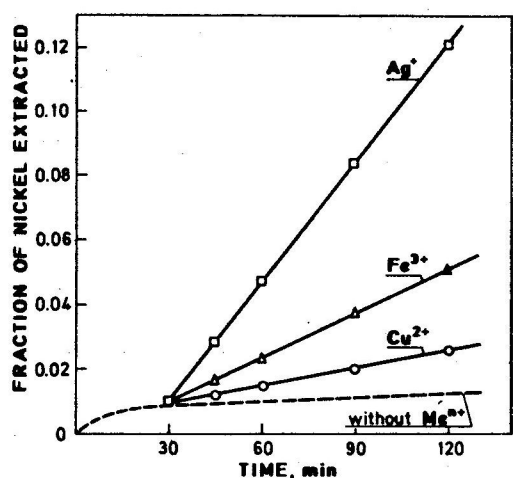
Fig. 5. Effect of silver, cupric and ferric ions on dissolution rate of millerite in 2.0 M HNO$_3$ at 50 $^{\circ}$C

$$2Ag^+ + H_2S = Ag_2S + 2H^+$$
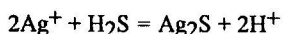
step III: oxidation of intermediate product

$$3Ag_2S + 2NO^-_3 + 8H^+ = 6Ag^+ + 3S^0 + 2NO + 4H_2O$$
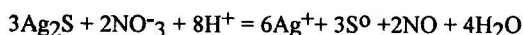
Electron microscopy examination of the solid residue after leaching shows a large difference between the forms of elemental sulphur produced in catalyzed and uncatalyzed reactions.

Fig. 6a shows the particle of solid residue after leaching, in 2.0 M HNO$_3$ at 70 $^{\circ}$C in presence the of 1.10^{-3} Ag$^+$ for the fraction of nickel extracted α being equal to about 0.5. The elemental sulphur occurs in the form of big crystallites. After leaching in the same conditions without the presence of silver ions, elemental sulphur is formed on the surface of millerite in the form of small particles (Fig. 6b).
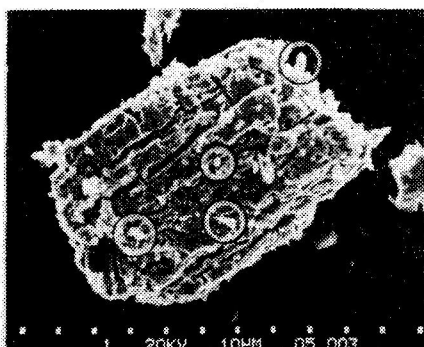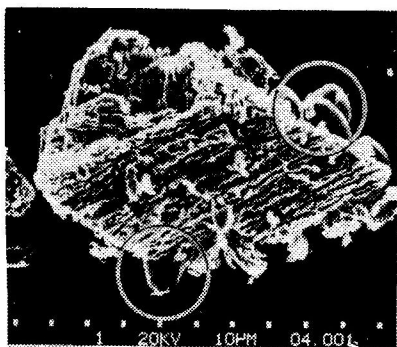

Fig. 6. SEM photographs of millerite leach residue in 2.0 M HNO$_3$ at 70 $^{\circ}$C,
a) with $1 \cdot 10^{-3}$ M Ag$^+$ addition, for α = 0.56, b) without silver ions addition, for α = 0.53

4. EFFECT OF PRODUCT LAYER MODIFICATION WITH SURFACE ACTIVE AGENTS

Forward and Veltman's study (1961) on acidic leaching of ZnS under oxygen pressure shows that zinc extraction increases with temperature up to about 115 °C and then decreases. At 110 °C and lower temperatures the extraction rate is quite slow but a very high extraction (>95%) can be obtained after prolonged leaching. Above 113 °C the leaching rate increases rapidly but levels off at about 70% extraction. Even prolonged leaching at 150 °C does not reliably permit extraction of zinc in excess of 75%. This behaviour was traced to the presence of molten sulphur (mp. = 119 °C) which wets the zinc sulphide surface and thereby causes the ore particles to agglomerate. When Pb concentrates are used instead of Zn concentrates an insoluble $PbSO_4$ product layer is formed. It was found that molten sulphur did not have any adverse effect on PbS decomposition. Apparently, molten sulphur did not wet the $PbSO_4$ surface.

It has been discovered by researchers at the Sherritt Gordon Mines Ltd. (Veltman and Bolton, 1980) that additives such as tannin compounds, lignin sulphonates at dosages as small as 500-1500 g/ton of concentrate can result in dramatic improvements in the leaching rates of ZnS concentrates. Owusu et al. (1992) has recently shown that lignin sulphonate lowers the interfacial tension of liquid sulphur in acidic zinc sulphate solution from about 54 to about 28-30 mN/m.

The first commercial plant using a direct zinc sulphide pressure leach process commenced operations in 1981. Zinc extraction in excess of 98% and elemental sulphur recovery higher than 95% have been reported (Parker et al., 1982)

It is likely that surface active agents may also be used in other leaching processes where rate-limiting reaction products are formed.

5. SUMMARY AND CONCLUSIONS

Once an insoluble film of product layer is formed during the leaching, the diffusion through such a layer generally becomes rate-controlling. The rate of reaction diminishes in proportion to the thickness of the insoluble layer. An intensification of leaching may be accomplished by the following: fine grinding, addition of some metal ions to the leaching solution, modification of product layer with surface active agents. Fine grinding accelerates both the rate and the extent of leaching. This effect seems to be due to both the particle size and lattice distortions. An addition of silver, cupric and ferric ions increases also the rate and extent of leaching due to reactions with H_2S evolved during the leaching. In these reactions intermediate products are formed which are oxidized faster than the H_2S gas. When molten elemental sulphur is formed during the leaching, surface active agents improve the process because they prevent agglomeration of sulphide with the sulphur.

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Przedstawiono sposoby aktywacji procesów ługowania siarczków miedzi, cynku i niklu w roztworach siarczanu żelazowego, kwasu azotowego oraz siarkowego pod ciśnieniem tlenu. Wykazano, że drobnoziarniste mielenie minerału powoduje przyśpieszenie szybkości oraz zwiększenie wydajności procesu ługowania. Efekt ten jest spowodowany zarówno zwiększeniem powierzchni ziaren, jak również dystorsją sieci w ziarnach ługowanego siarczku. Dodatek jonów srebra, miedzi i żelaza zwiększa szybkość ługowania poprzez tworzenie produktów pośrednich z wydzielanym H_2S. Produkty te utleniane są szybciej niż gazowy siarkowodór. Jeżeli podczas procesu ługowania pojawia się stopiona siarka elementarna, to dodatek substancji powierzchniowo czynnych zwiększa wydajność procesu przez zapobieganie aglomeracji siarki z ługowanym siarczkiem.