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MECHANISM OF CATALYTIC ACTION OF CUPRIC IONS IN FERRIC SALTS LEACHING OF MILLERITE

Based on experimental leaching results of millerite as well as changes in the composition and microstructure of solid residue surface after leaching with ferric salts acid solutions the mechanism of catalytic action of cupric ions has been proposed. The solid residues were examined using a scanning microscope (SEM), X-ray diffraction, electron microprobe and chemical analyses. It was found that cupric ions added to the ferric chloride solution oxidizes catalitically the sulphide ions on the surface of millerite to the elemental sulphur. During the ferric sulphate leaching of millerite a sulphurrich sulphide layer passivating the surface of the mineral was found, and addition of cupric ions has no influence on the leaching rate.

INTRODUCTION

It has been shown by several investigators that the addition of cupric ions to acidic oxidizing leach solution significantly accelerates the rate of dissolution of sphalerite (Dutrizac, MacDonald 1978; Crundwell 1987), chalcopyrite (Dutrizac 1978) and heazlewoodite (Mulak 1985; Mulak 1987, Mulak 1996).

Dutrizac and MacDonald (1978) studied the effect of $CuCl_2$ addition on dissolution rate of sphalerite disc in ferric chloride solution to which various amounts of $CuCl_2$ has been added. Although the rate increases steadily with copper concentration, the greatest influence was noted in going from 0 to 8 g/dcm^3 of $CuCl_2$. When copper was present in the solution, the surface of the disc became covered with a black film consisting of sphalerite and copper sulphides. Crundwell (1987) found that dissolution of sphalerite in ferric solutions with $CuSO_4$ addition resulted in diminished rate of the leaching.

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Mulak (1985, 1987, 1996) examined the addition of cupric ions on dissolution of heazlewoodite in nitric acid solutions. It was found that in the presence of cupric ions dissolution of Ni_3S_2 in dilute nitric acid solutions is controlled by surface mechanism. There is a suggestion that in moderate acidic oxidative conditions without cupric ions the hydrogen sulphide gas evolved in the first step produces some polysulphides which are more stable thermodynamically than the dissolved Ni_3S_2. Cupric ions eliminate the evolution of H_2S and oxodize it directly on the surface of dissolving sulphide by forming intermediate products which are oxidized faster in the leaching solution than hydrogen sulphide. A catalytic effect of cupric ions was also noticed during the bioleaching of metal sulphides (Ballaster et al. 1989; Ballaster et al. 1990).

The principal aim of presented work was to investigate the mechanism of millerite leaching in acid solutions of ferric chloride or ferric sulphate with cupric ions addition.

EXPERIMENTAL

Preparation of synthetic β-NiS, the equipment used, and this work procedure were described in our previous paper (Mulak 1983). Metal ions concentration in the solution was determined by atomic absorbtion spectroscopy method. Iron ions concentration in the ferric salts leaching was found by dichromate titration. The elemental sulphur content was measured by CS_2 extraction of washed and dried samples. In addition, the reaction residues at various levels of nickel extraction were examined by SEM, X-ray diffraction, electron microprobe and chemical analyses.

RESULTS AND DISCUSSION

FERRIC CHLORIDE LEACHING

Ferric chloride leaching of millerite was tested in 0.2M $FeCl_3$ – 1.0M HCl – 2.0 M NaCl solution at 95°C. After 5 hours leaching 21% of nickel was extracted. The addition of 0.2M cupric chloride to the leaching solution increases the nickel extraction from 21 to 51%. It was found that after the 1 hour leaching with cupric ions addition the fraction of nickel extracted vs. time obeys a linear law (Mulak, Wawrzak 1997). The constant dissolution rate seems to indicate that the reaction area remains constant during the leaching. Similar results have been obtained in catalytic action of cupric and ferric ions in nitric acid leaching of heazlewoodite (Mulak 1987).

Optical observation of the solid residues of millerite after the ferric chloride leaching with addition of cupric chloride shows that the characteristic colour of β-NiS (grey with metallic lustre) changes during the process to that of cupric sulphide, which is black. Due to the extreme thinness of the layer no measurable change in the cupric ions concentration can be detected.

Figure 1 shows some particles of solid residues after the reaction in the ferric chloride solution with the cupric ions addition at 95°C. Two types of elemental sulphur particles are visible in the leached regions: small, discrete granules of 0.5÷1 μm and much more globules of 5÷7 μm in diameter. Many such sulphur particles occur preferentially in certain chosen regions. This may indicate a selective dissolution in isolated active areas. The development of large, well formed, sulphur crystals during the process suggests that sulphur is deposited rather from species dissolved in the leaching solution and it is not formed directly by the immediate attack of millerite.
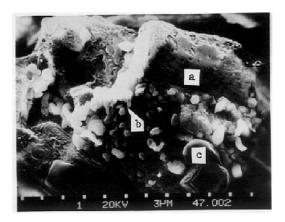

Fig. 1. SEM photograph of millerite leach residue after 5 hours leaching in 0.2M FeCl$_3$ - 0.2M CuCl$_2$ – 1.0M HCl – 2.0M NaCl solution at 95°C; (a) – leached millerite, (b) – small sulphur granules, (c) – large sulphur granules

We presume the following mechanism:

- step I: acid attack of millerite

$$NiS + 2H^+ = Ni^{2+} + H_2S(aq) \tag{a}$$

Hydrogen sulphide formed according to eq.(a) dissolves in the leaching solution at the millerite surface and then it is oxidized by cupric ions to the elemental sulphur.

- step II: intermediate products formation

$$2H_2S(aq) + 2Cu^{2+} = Cu_2S + S + 4H^+ \tag{b}$$

- step III: intermediate products oxidation

$$Cu_2S + 2Fe^{3+} = CuS + 2Fe^{2+} + Cu^{2+} \tag{c}$$

$$CuS + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} + S \tag{d}$$

It is worth mentioning that the elemental sulphur is formed in two stages: (b) and (d).

During the ferric chloride leaching in the case of absence of cupric ions hydrogen sulphide arising at the millerite surface is oxidized directly by ferric chloride:

$$2H_2S(aq) + 4FeCl_3 = 4FeCl_2 + 4HCl + 2S \tag{e}$$

Evidently, the leaching rate in the presence of cupric chloride in the leaching solution is markedly increased. The explanation of this fact seems to be apparent: chloride system consisting of three ions (Fe^{3+}, Cu^{2+}, Fe^{2+}) is more effective than this consisting of two ones (Fe^{3+}, Fe^{2+}). Ferric chloride quickly oxidizes the intermediate cuprous ions and maintains a high activity of cupric ions. This is the way in which the cupric ions act as catalyst in ferric chloride leaching.

FERRIC SULPHATE LEACHING

The leaching was tested in 0.2M $Fe_2(SO_4)_3$ – 1.0M H_2SO_4 solution at 95°C. It was found that after 30 min leaching only 2.5% of nickel dissolved . Unfortunately, an extension of the leaching time from 30 to 300 min increases the nickel extraction from 2.5 to 3.6% only. Similarly, any increasing the sulphuric acid concentration from 1 to 5M has no noticeable effect on the rate of the process. Varying the ferric sulphate concentration from 0.1 to 3 M has no influence on leaching rate of millerite too. Thus, the process is ineffective.
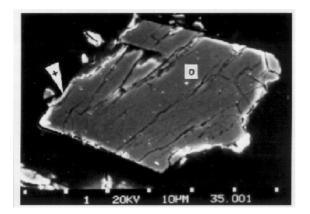

Fig. 2. SEM photograph of millerite particle cross-section after 5 hours leaching in 0.2M $Fe_2(SO_4)_3$ – 1.0M H_2SO_4 solution at 95°C; two different phases – grey and white – are denoted by o and +, respectively.

The residue from the leaching experiments after drying was washed with carbon disulphide. No elemental sulphur was detected. Figure 2 shows a SEM photograph of cross-section of solid residue after 5 hours leaching in 0.2M $Fe_2(SO_4)_3$ – 1.0M H_2SO_4 solution at 95°C. Two different phases are visible – a grey and a white one. The results of electron microprobe analysis of both the phases are shown in Figure 3a and 3b.

The grey part of the particle (marked by a circle in Figure 3a) is characterized by two distinct nickel and sulphur peaks of the same intensity. On the other hand, for the white part (indicated by a cross in Figure 3b) the sulphur peaks dominates indicating a sulphur-rich sulphide phase.
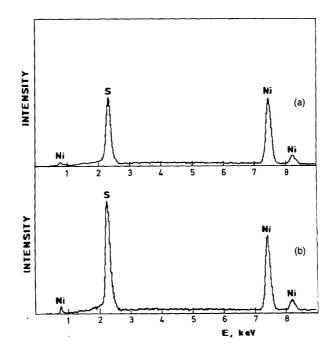
Fig. 3. Microprobe diagrams of the particle shown in Figure 2 for: grey phase (indicated by a circle), white phase (indicated by a cross)

The results of microprobe analyses suggest that the passivating layer is a sulphur-rich one. It is found as a result of modifications inside the solid phase that this layer occurs on the millerite surface during the leaching. The presence of the sulphur-rich sulphide layer passivating the surface of nickel sulphide was also demonstrated by Power (1981) during its anodic dissolution in acid solution within the potential range from 0 to 0.8V. The addition of cupric ions to the ferric sulphate solution has no influence on leaching rate of millerite.

CONCLUSIONS

Based on experimental leaching results of millerite as well as changes in composition and microstructure of surface of solid residue after leaching with ferric salts acid solutions the mechanism of catalytic action of cupric ions has been proposed. The solid residues were examined using a scanning microscope (SEM), X-ray diffraction, electron microprobe and chemical analyses. It was found that cupric ions added to the ferric chloride solution eliminate the evolution of hydrogen sulphide oxidizing it directly on the surface of dissolving millerite by forming intermediate products which are oxidized faster by ferric ions than hydrogen sulphide. Leaching of millerite in ferric sulphate solution produces a sulphur–rich sulphide layer passivating the millerite surface and the addition of cupric ions has no influence on the leaching

rate. The main requirement for metal ion to exhibit the catalytic activity appears to be the formation of such intermediate products, which are oxidized by the leaching solution in consequence of which the catalytic ion is reproduced.

REFERENCES

DUTRIZAC, J.E. and MACDONALD, R.J.C.: *The dissolution of sphalerite in ferric chloride solutions*, Metal. Trans., 9B, 543-551, 1978

CRUNDWELL, P.K.: *Kinetics and mechanism of the oxidative dissolution of a zinc sulphide concentrate in ferric sulphate solutions*, Hydrometallurgy, 19, 227-242, 1987

DUTRIZAC, J.E.: *The kinetics of dissolution of chalcopyrite in ferric ion media*, Metal. Trans., 9B, 431-438, 1978

MULAK, W.: *Kinetics of dissolution of synthetic heazlewoodite (Ni$_3$S$_2$) in nitric acid solutions*, Hydrometallurgy, 14, 67-87, 1985

MULAK, W.: *The catalytic action of cupric and ferric ions in nitric acid leaching of Ni$_3$S$_2$*, Hydrometallurgy, 17, 201-214, 1987

MULAK, W.: *Metal ions catalysis in acidic leaching of metal sulphides*. In: Changing Scopes in Mineral Processing, M. Kemal, V. Arslan, A. Akar, M. Canbazoǧlu (eds), A.A. Balkema, Rotterdam, 1996, pp.495-498

BALLASTER, A., BLÁZGUEZ, M.L., GONZÁLES, F.: *Kinetic study of bioleaching of mineral sulphides: sphalerite and complex sulphide*, Erzmetall, 42, 62-65, 1989

BALLASTER, A., GONZÁLES, F., BLÁZGUEZ, M.L., MIER, J.L.: *The influence of various ions in the bioleaching of metal sulphides*, Hydrometallurgy, 23, 221-235, 1990

MULAK, W.: *Kinetics of dissolution of synthetic millerite (β-NiS) in acidic potassium dichromate*, Hydrometallurgy, 11, 79-89, 1983

MULAK, W. and WAWRZAK, D.: *Leaching behaviour of millerite (β–NiS) in moderate oxidizing and reducing media*. In: Proceedings of the XX Intern. Miner. Proc., Achen 1997, H. Hoberg and H. von Blottnitz (eds), GDMB, Clausthal–Zellerfeld 1997, Vol. 4, pp. 189-198

POWER, G.P.: *The electrochemistry of the nickel sulphides*. I. NiS, Austr. J. Chem., 34, 2287-2296, 1981

Mulak W., Chojnacka M, Wawrzak D., Mechanizm katalitycznego działania jonów miedzi w procesie ługowania millerytu, Fizykochemiczne Problemy Mineralurgii, 35, 2001, 67-72, (w jęz. ang.)

W oparciu o wyniki ługowania milerytu jak również nowe dane eksperymentalne dotyczące zmiany składu i mikrostruktury powierzchni faz stałych po ługowaniu w roztworach soli żelaza (III) zaproponowano mechanizm katalitycznego wpływu jonów miedzi (II) na proces ługowania. Fazy stałe po ługowaniu badano mikroskopem skaningowym, mikrosondą rentgenowską, jak również poddano analizie rentgenowskiej i chemicznej. Ługowanie prowadzono w czasie 5 godz. w roztworach zawierających 0.2M FeCl$_3$ – 1.0M HCl – 2.0 M NaCl w temperaturze 95°C. Stwierdzono, że dodatek 0.2 M CuCl$_2$ w powyższych warunkach ługowania zwiększa wyługowanie niklu z 21 do 51%. Zaproponowano mechanizm katalitycznego wpływu jonów miedzi (II) na proces ługowania. Zgodnie z tym mechanizmem jony miedzi (II) biorą bezpośredni udział w utlenieniu wydzielanego siarkowodoru z utworzeniem produktów pośrednich ulegających szybciej utlenianiu przez jony żelaza (III) niż siarkowodór. Wykazano, że podczas ługowania milerytu roztworami siarczanu żelaza (III) następuje tworzenie się pasywnej warstewki polisiarczku niklu na powierzchni milerytu. Dodatek jonów miedzi (II) do roztworu siarczanu żelaza (III) nie wpływa na szybkość ługowania milerytu. Warunkiem koniecznym, aby jony miedzi (II) spełniały rolę katalizatora w procesie ługowania jest powstawanie takich produktów pośrednich z jonami siarczkowymi, z których roztwór ługujący szybko odtwarza jony miedzi (II).