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Interfacial properties of liquid sulfur in the pressure leaching of nickel concentrate

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ABSTRACT

The effects of sulfur dispersing agents in the oxygen pressure leaching of nickel concentrate at medium temperature were investigated by interfacial studies. Liquid sulfur–aqueous solution interfacial tensions and liquid sulfur–sulfide mineral contact angles were measured at 140 °C, 690 kPa overpressure by nitrogen. The effects of sulfur dispersing agents including lignosulfonate, Quebracho, o-phenylenediamine (OPD), and humic acid were evaluated by the calculation of the work of adhesion in the liquid sulfur–sulfide mineral–aqueous solution systems. It was found that the sulfide mineral surface is sulfophobic at pH from 4.1 to 4.5 due to the hydrolysis of nickel (II) ions to nickel hydroxide and the deposition of nickel hydroxide on the mineral surface. These findings apply to four different sulfide mineral systems, including pentlandite, nickeliferous pyrrhotite, pyrrhotite, and chalcopyrite. Lignosulfonate, Quebracho, and humic acid were found to significantly reduce the work of adhesion indicating they should be effective sulfur dispersing agents. OPD is ineffective in changing the work of adhesion of sulfur on the mineral sulfides indicating that it is not a good candidate for sulfur dispersion.

1. Introduction

In the 1970s Sherritt Gordon Mines Limited disclosed a rapid and complete zinc extraction method from zinc sulfide concentrates at 125–175 °C with the addition of sulfur dispersing agents (Kawulka et al., 1975). Lignosulfonate or Quebracho were used to prevent zinc sulfide particles from being coated by molten sulfur thus prevented the inhibition of the reaction. Based on the usage of sulfur dispersing agents, a two-stage pressure leaching process for zinc sulfide concentrates was invented (Veltman et al., 1977).

Alternative additives have been investigated for improving the zinc pressure leaching processes. OPD was found effective to increase the zinc extraction (De Nys and Terwinghe, 1990). Low rank coal was a cheap and effective additive with the potential to replace lignosulfonate and Quebracho (Collins and Kofluk, 1997; Barta et al., 1998).

Owusu (1989, 1993) studied the interfacial phenomena in the liquid sulfur–sphalerite–aqueous solution system in the absence or presence of sulfur dispersing agents, including lignosulfonate and OPD. The effective sulfur dispersing agents have an effect to decrease the work of adhesion in the system. The work of adhesion is a measure of the energy required to remove the sulfur from the sulfide mineral surface.

Hackl et al. (1995a) investigated the feasibility of using sulfur dispersing agents to solve sulfur wetting problem and to enhance copper extraction from the chalcopyrite mineral in the temperature range 125–155 °C. In Hackl's work, carried out at high acid concentration, most of the sulfur dispersing agents decomposed quickly. The best results were obtained with addition of 50 kg/t OPD continuously at 125 °C. Under these conditions, 80% copper was extracted into leach solution in 6 h. Chalcopyrite leached slowly even when molten sulfur was prevented from wetting the mineral surfaces. Hackl et al. (1995b) postulated that the reaction rate was ultimately controlled by a passivating mechanism unrelated to the elemental sulfur formation. It was suggested that chalcopyrite is passivated by a copper polysulfide layer formed during leaching. Dempsey and Dreisinger (2003) discovered that it was possible to combine the use of surfactants and fine grinding to overcome the sulfur wetting problem and the chalcopyrite passivation problem. This development has been named the Anglo American Corporation – University of British Columbia Copper Process (Dreisinger et al., 2002).

The Dynatec Copper process was developed to extract copper from copper concentrates (Burban and Collins, 1997; Collins and Kofluk, 1998; Barta et al., 1999; Collins et al., 2000). Low rank coal was added to the leaching solution instead of water-soluble sulfur dispersing agents. Dynatec advocated regrind and recycle of residue after elemental sulfur removal.

Dreisinger et al. (2003) investigated the effect of sulfur dispersing agent in the pressure oxidation of pyrite gold ores and concentrates. OPD was better than lignosulfonate to decrease the liquid–liquid interfacial tension and to increase the contact angle between molten sulfur and the pyrite mineral. The work of adhesion decreased greatly in the presence of OPD. The pyrite oxidation rate increased

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in the presence of OPD as measured by the oxygen consumptions in the oxygen pressure leaching experiments. OPD was fully degraded during the high temperature oxidation leaching processes since no residual OPD or degradation products of OPD were detected in the solution or leach residue.

Researchers at INCO worked on a pyrrhotite concentrate leach process and found that the addition of tall oil pitch to the leach solution allowed the operation to work smoothly at medium temperatures (Ryan, 1975; Jones et al., 1978). INCO proposed a method to treat nickel concentrates, which involved fine grinding, atmospheric acid chlorine leaching, and oxidative pressure leaching (Kerfoot et al., 2002). Copper and cobalt were recovered from solution by solvent extraction or precipitation and nickel was recovered by direct electrowinning. Brown and Papangelakis (2005) investigated the influence of lignosulfonate and chloride ion on the interfacial properties of liquid sulfur–pentlandite–aqueous solution system. Lignosulfonate significantly reduced the work of adhesion in this system and chloride ion enhanced the performance of lignosulfonate.

Research on the nature of molecular interactions in the liquid sulfur–nickel sulfide mineral–nickel sulfate aqueous system is required to advance the study and commercial design of processes operating at 150 °C. Few studies have been performed on the behavior of sulfur dispersing agents in the direct oxygen pressure leaching of nickel concentrates at medium temperatures. The main objective of this investigation was to study the influence of acidity and addition of sulfur dispersing agents on the interfacial properties in the liquid sulfur–sulfide mineral–aqueous solution system. This includes the understanding of the influence of acidity on the interfacial tension, contact angle, and the work of adhesion; to understand the influence of four different kinds of sulfur dispersing agents, including lignosulfonate, Quebracho, OPD, and humic acid on the interfacial properties in three different systems.

2. Experimental

2.1. Minerals

The massive mineral specimens used in the measurement of contact angles were: (1) Pyrrhotite, from Essex County, NY; (2) Pyrrhotite (nickeliferous), from XSTRATA Nickel, Ont.; (3) Pentlandite from Vale INCO - Voisey's Bay mine; (4) Pentlandite in pyrrhotite, from Sudbury, Ont.; (5) Chalcopyrite, from Messina, Transvaal Republic of South Africa.

The mineral samples were cut into small cubes using a diamond saw. Samples with obvious color and grain differences were discarded. The cubes were polished as smooth as possible by sequentially grinding on successively finer grit grinding wheels and finishing with a 1 μm alumina/water suspension polish. The polished face was washed with a stream of water to remove loosely attached alumina particles, followed by cleaning in an ultrasonic bath. The sample was washed with a stream of water once again and finally rinsed with deionized water.

2.2. Materials

Nickel sulfate and ferrous sulfate solutions were prepared with reagent grade chemicals and deionized water. The chemicals used in interfacial experiments were: sulfur powder, 99.999%, from Alfa Aesar; nickel (II) sulfate hexahydrate, 99%, from Sigma Aldrich; Sulfuric acid, 95.0–98.0%, from Fisher; iron (II) sulfate heptahydrate, from Fisher.

Four kinds of water-soluble sulfur dispersing agents were investigated in the interfacial studies. BorrePAL U is sodium based softwood lignosulfonate with MW 45000–75000. Orfom® grade 2 Tannin was obtained from Chevron Phillips Chemical Company LP which contained 85–95% sulfited Quebracho and 5–15% water. OPD has the chemical formula $C_6H_4(NH_2)_2$ which belongs to the aromatic amine family. Humic acid–potassium salt, the modified lignite, was obtained from Borregaard Lignotech, USA. All the sulfur dispersing agents were used without pretreatment.

2.3. Apparatus and experimental procedures

The pendant drop method is suitable for the liquid–liquid interfacial tension measurement under controlled environment at conditions such as high pressure and high temperature (Cheng et al., 1990). The contact angle between liquid sulfur and sulfide mineral was measured by sessile drop method. Interfacial experiments were performed using the high temperature high pressure apparatus used by Owusu. The primary procedures of the measurement have been provided in literature (Owusu, 1993).

2.4. Interfacial tension and contact angle

Fig. 1 illustrates the profile of a pendant drop. The method of the selected plane is a procedure to determine interfacial tension from pendant drop images. The interfacial tension was calculated from Eq. (1)

$$\gamma = \frac{\Delta\rho g d_e^2}{H} \tag{1}$$

where $\Delta\rho$ is the density difference between the liquid sulfur and aqueous solution; g is acceleration due to gravity; d_e is equatorial diameter of the drop; H is a function of drop shape; $S = d_s/d_e$. Tables of values of H as a function of S are available in the literature (Ambwani and Fort Jr., 1979). The results of repeated experiments were within ±2%.

The contact angle with relation to interfacial tension can be represented by Young's equation, Eq. (2). (Adamson and Gast, 1997; Chattoraj and Birdi, 1984)

$$\gamma_{MA} - \gamma_{MS} = \gamma_{SA}\cos\theta \tag{2}$$

where γ_{MA} is the mineral–aqueous solution interfacial tension, mN/m; γ_{MS} is the mineral–liquid sulfur interfacial tension, mN/m; γ_{SA} is

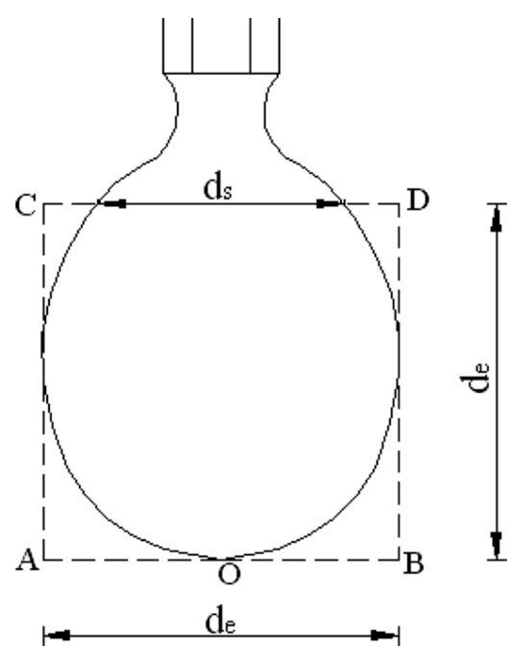

Fig. 1. Profile of a pendant drop.