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The interaction of xanthates and amines with pyroxene activated by copper and nickel ☆

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Abstract

In the flotation of platinum group minerals pyroxene is a major gangue mineral. This study shows using zeta potential and ToF-SIMS analyses that when pyroxene is exposed to copper, nickel and/or calcium ions in solution at alkaline pHs a surface reaction occurs between the hydroxy species, in the case of copper and nickel, or divalent calcium ions and the pyroxene surface which influences the floatability of the pyroxene. Following exposure to copper and nickel ions at pH 9 addition of SIBX resulted in the pyroxene floating readily. It is also shown, in the case of copper, that the activating effect of the adsorbed copper hydroxy species can be reduced by the addition of complexing amines prior to SIBX. Proposals are made to explain these observations.

Keywords: Flotation activators; Precious metal ores

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1. Introduction

Two gangue minerals which are commonly found associated with platinum group minerals are pyroxene and feldspar. Pyroxene is the most abundant mineral in the Merensky Reef, constituting about 60% of the reef by volume. In its most common form it has the general formula of $[(\mathrm{Mg, Fe, Ca})\,\mathrm{Si_2O_6}]$ consisting of single channels of linked tetrahedra. In a previous study by Phillips et al. (1993) it was found that pyroxene reports to the concentrate due to true flotation. Since it is assumed that sulphide collectors generally do not exhibit any affinity for siliceous minerals it is thus often inferred that the pyroxene surface can be activated by dissolved metal ions, such as copper and nickel ions, or their hydroxy forms. Being uncharged, pyroxene may be expected to behave in a manner similar to quartz. There are numerous reports of the activation of quartz by ions such as copper (James and Healy, 1972). Nagaraj and Brinen (1995) have studied copper ion adsorption on pyrite and pyroxene and reported that copper adsorbed onto both minerals but they did not study the ultimate effect on flotation. In the case of nickel, Mackenzie and O'Brien (1969) suggested that the adsorption of $\mathrm{NiOH^+}$ ions might involve hydrogen bonding between the OH groups of the metal complex and oxygen atoms of the quartz surface.

The present paper presents results of an investigation into the adsorption of copper and nickel ions onto pyroxene. The effect of adsorption of these ions on the flotation behaviour of pyroxene was also investigated as well as methods to remove the adsorbed metal species from the gangue surface. The effect of calcium ions present in the process water on the flotation of pyroxene was also investigated.

2. Experimental

The experimental procedures used were similar to those described previously (Malysiak et al., 2002).

☆ This is a slightly modified version of a paper that was presented at the centenary of Flotation Conference in Brisbane.

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2.1. Minerals

Natural pyroxene from the Merensky Reef in the Northern Province, South Africa, was crushed to 2 mm and selected by handpicking. Chemical analysis indicated that the pyroxene contained 13.2% Mg, 11.0% Fe, 3.7% Ca, 2.7% Al, and 25.1% Si. Copper activation was attained by dosing with copper sulphate. Nickel activation was attained by exposing samples to pentlandite which was synthesised at Anglo Platinum Research Centre (Malysiak et al., 2002). Calcium activation was attained by exposure to synthetic process water using different concentrations of calcium. All mineral samples were stored under argon in a freezer and freshly ground in an agate mortar just prior to each experiment. The products were screened to obtain size fractions of −25 μm for zeta potential determinations and +38—106 μm for microflotation tests.

2.2. Reagents

Purified sodium isobutyl xanthate (SIBX) was provided by SENMIN. Other chemicals were of analytical grade quality. Sodium carbonate (0.1 M) and hydrochloric acid (0.1 M) were used for pH adjustment. As already mentioned copper sulphate was used as activator. The amines used were ethylenediamine (EDA), diethylenetriamine (DETA), tetraethylenediamine (TETA) and ethylenediamine-tetraacetic acid (EDTA).

2.2.1. Synthetic water composition

Water, with a specific conductance of 0.7 μS cm^{-1} and a surface tension of 72.8 mN m^{-1} at 20 °C, produced by a MILLI-RO PLUS apparatus, was used during the study. This water was modified by the addition of various chemical salts to produce synthetic process water ($I = 3.5 \times 10^{-2}$). The synthetic water contained amounts of key ions similar to those typically found in circuit water, viz. Ca^{2+} 80 ppm, Mg^{2+} 80 ppm, Na^+ 135 ppm, Cl^- 270 ppm, SO_4^{2-} 250 ppm, NO_3^- 135 ppm, CO_3^{2-} 40 ppm, and a TDS value of 1030.

2.3. Zeta potential determinations

Zeta potential determinations were carried out on dilute dispersions of the individual minerals studied using a Malvern Zetasizer 4. During the experiments the interaction between sodium isobutyl xanthate (SIBX: 5×10^{-5} M), copper sulphate ($CuSO_4$: 5×10^{-5} M) and various amines (5×10^{-5} M) and the pyroxene surface was investigated. The instrument gives the electrophoretic mobility from which the zeta potential was calculated using the Smoluchowski equation, since $\kappa_a \ll 1$, κ_a being the ratio of particle radius to double layer thickness (Hunter, 1993). The zeta potential experiments were carried out in synthetic process water at various pH values at 25 °C. Conditioning of the mineral was carried out for 20 min. The E_h was allowed to vary naturally but was generally in the region of 100 mV.

2.4. Time of flight secondary ion mass spectrometry (ToF-SIMS)

Surface analysis of minerals was carried out using a PHI TRIFT II ToF-SIMS instrument operating in the static SIMS regime. A pulsed primary ion beam bombards the sample surface, causing the emission of atomic and molecular secondary ions. A small percentage of the secondary ions are charged and can therefore be extracted by an electric field into a mass spectrometer. The mass spectra are recorded by measuring the time difference between pulsing the primary ion gun and the arrival of secondary ions on a fast dual microchannelplate detector at the spectrometer, by means of a multi-stop time-to-digital converter. When mixtures were used they were conditioned in synthetic water in the presence of the desired reagents for 20 min. The samples were filtered and washed with water (conductivity 0.7 μmS cm^{-1}), adjusted to the desired pH, to remove any physically attached ions. All samples were dried in an argon atmosphere at ambient temperature. The 15 kV, 600 pA gallium beam was used throughout the investigation. About 30 grains for each mineral were imaged and analysed for Ca, Mg, Al, Si, Fe, Ni and Cu during positive ion analysis and O, OH, S and xanthate during negative ion analysis. The intensities obtained are normalised for the elements of interest and presented as a relative percent surface coverage.

2.5. Microflotation tests

A microflotation cell (volume 250 cm^3) was used to determine the flotation response/hydrophobicity of pyroxene and pentlandite–pyroxene mixtures. The cell consists of a conical tapered cylindrical tube with air introduced through a needle at the base of the cell (Wesseldijk et al., 1999). Mineral loaded bubbles rise through the cell and are deflected off the cone at the top of the cell, after which they burst, resulting in the minerals dropping into the concentrate launder. Each test was conducted at pH 9 using a 2 g sample of pure pyroxene. During the tests, various combinations of reagents were investigated. These were generally SIBX, [$CuSO_4$ + SIBX] and [$CuSO_4$ + AMINE + SIBX]. The sequence of reagent addition was as indicated by the sequence of reference in brackets. Conditioning periods for the reagents tested were 2 min for SIBX and 5 min for $CuSO_4$ and the amines.

3. Results and discussion

3.1. Surface analyses

3.1.1. ToF-SIMS analyses

ToF-SIMS analysis is a well-established technique for determining the occurrence of atomic/molecular species on the surface of mineral samples. It must be noted that ToF-SIMS results present relative and not absolute values. Table 1 shows the relative % abundances of copper on the