

Depressant function of high molecular weight polyacrylamide in the xanthate flotation of chalcopyrite and galena

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ABSTRACT

A high molecular weight polyacrylamide (PAM) was tested as a potential selective depressant in the differential flotation separation of galena and chalcopyrite using potassium ethyl xanthate (KEX) as a collector. In single mineral flotation, PAM depressed chalcopyrite while galena was floatable. Adsorption mechanism study indicated that PAM could adsorb on galena through hydrogen bonding, and on chalcopyrite through hydrogen bonding as well as ammonium-copper complexation. KEX could only break up the galena-PAM bonding. Therefore the combined use of PAM and KEX rendered the flotation of the two minerals selective.

In the flotation of mixtures of the two minerals, galena and chalcopyrite could be separated by PAM and KEX only after EDTA treatment of the mineral mixtures. Time of flight secondary ion mass spectrometric (ToF-SIMS) measurements indicated that when galena and chalcopyrite were present together in the suspension, PAM adsorbed on both galena and chalcopyrite. However, after prior treatment of the mineral mixtures by EDTA, PAM was found to mainly adsorb on chalcopyrite.

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1. Introduction

Sulfide ores are the major sources of base metals such as copper, lead, zinc, nickel, etc. In most cases, lead–copper–zinc–iron sulfide minerals tend to exist together in a deposit. In minerals industry, inorganic depressants such as sodium cyanide, potassium dichromate, sulfur dioxide, are routinely used in the flotation separation of these sulfide minerals from their ores. One obvious disadvantage of these inorganic depressants is that most of them are toxic and hazardous. In addition, they cannot truly depress the fine and ultrafine sulfide minerals due to the propensity of these particles to mechanically entrain into flotation concentrate owing to their low mass, although the inorganic depressants may render the fine and ultrafine particles completely hydrophilic.

Therefore, it has been argued that non-toxic high molecular weight polymeric depressants should be developed and used in differential sulfide flotation, not only to replace the toxic inorganic depressants but also to lower the entrainment of the fine and ultrafine mineral particles. This concept has been verified by the recent work of Liu et al. (2006) and Gong (2011) who showed that, in the flotation of oxides or sulfides, the use of high molecular weight selective polymeric flotation depressants could flocculate the fine and ultrafine iron oxide, hydroxyapatite, or quartz particles as well as render them hydrophilic (the so-called “dual functions”), thus lowering both the flotation and mechanical entrainment of these particles.

In the present study, polyacrylamide (PAM) with a high molecular weight was chosen as the dual function polymer depressant. PAM is a

widely used polymer flocculant in many industries including the minerals industry. Thus, our study focused on the selective depressive effect of PAM on Cu–Pb sulfide flotation, which to our knowledge has not been investigated before.

Polyacrylamide has a general chemical formula $-\text{CH}_2\text{CHCONH}_2-$ and is a water-soluble synthetic organic polymer (Fig. 1). PAM has been applied to minerals industry for decades, but mainly used as a flocculant (Moody, 1992). However, there are still several attempts in the laboratory to use PAM and its derivatives as depressants for mineral separation by flotation.

Moudgil (1983) showed that non-ionic PAM depressed coal flotation. The depressive effect was attributed to the adsorption of the hydrophilic polymer molecules on the coal particles which render the surface hydrophilic. Zhang et al. (2004) tested the depressant performance of a hydroxamic-PAM in the flotation of calcite, diasporite and pyrite. It was found that the hydroxamic-PAM strongly depressed pyrite. Adsorption mechanism study revealed that strong chemical interactions occurred between the hydroxamic-PAM and pyrite surface. Liu et al. (2007) studied the role of cationic PAM in the reverse flotation of diasporite bauxite. The reverse flotation separation of kaolinite and diasporite was achieved at pH 5.5–8.5 by using dodecylamine as a collector and the cationic PAM as a depressant. The cationic PAM adsorbed on diasporite by hydrogen bond and electrostatic forces, prevented the dodecylamine cationic species from adsorbing on the diasporite surface, and thus, depressed diasporite flotation. Boulton et al. (2001) used low molecular weight PAM polymers to separate copper-activated sphalerite from pyrite using isobutyl xanthate (IBX) as a collector. They grafted carboxyl, sulfonate, hydroxyl or thiourea functional groups to PAM to

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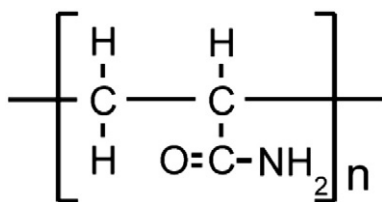


Fig. 1. Structure unit of PAM (Sojka and Lentz, 1994).

obtain PAMs with different characteristics. It was found that all the PAMs depressed pyrite with no or little depression of sphalerite. Among the modified PAMs, the hydroxyl PAM showed the strongest depression effect while the carboxyl PAM had the best selectivity. A recent study by using xanthation modified polyacrylamide (PAM-X) and PAM as depressants on galena and sphalerite flotation was carried out (Wang et al., 2012). In single mineral flotation with PAM-X as a depressant and potassium ethyl xanthate as a collector, it was found that galena was completely depressed while copper activated sphalerite was still floatable at pH 11. When using PAM as a depressant, however, copper-activated sphalerite was depressed while galena could be floated at pH 9–10.

The purpose of the experimental work carried out in the current study was to determine if PAM possesses unique selectivity in galena and chalcocopyrite single mineral flotation, and if it can be used to separate these two sulfide minerals by flotation. The adsorption mechanism of PAM on galena and chalcocopyrite is studied by several surface analysis techniques to understand the phenomenon observed in flotation tests.

2. Experimental

2.1. Materials and reagents

Natural galena, pyrite, sphalerite and chalcocopyrite minerals were purchased from Ward's Scientific Establishments, Ontario, Canada. The lumps of each mineral were separately crushed (Retsch jaw crusher, USA) and hand-picked to obtain high purity samples, and then further crushed and pulverized with a Pulverisette 2 mechanized agate mortar/pestle grinder (Fritsch, Germany). The $-75 + 38 \mu\text{m}$ size fractions were screened out for use in the flotation test. The $-38 \mu\text{m}$ size fractions were utilized for surface analysis. In order to minimize oxidation, all mineral samples were sealed in plastic bottles and stored in a freezer at -10°C .

X-ray diffraction measurements of the mineral samples showed that there were minor amounts of quartz in chalcocopyrite and no impurities in galena, pyrite and sphalerite. Chemical analysis of the samples showed that the chalcocopyrite bulk sample contained 29.26% Cu, representing a purity of 84.5% chalcocopyrite, and that galena bulk sample contained 84.00% Pb, indicating a purity of 97.0% galena. The sphalerite bulk sample assayed 63.00% zinc, representing a purity of 98.3% sphalerite, and the pyrite bulk sample assayed 43.3% Fe, indicating a purity of 93.1% pyrite.

The non-ionic PAM used in this work was of analytical grade with high purity (99.999%) and a molecular weight of 5,000,000–6,000,000 purchased from ACROS Canada Inc. Hydrochloric acid and sodium hydroxide (Fisher Scientific Canada) were used to adjust pH. Potassium ethyl xanthate (KEX) was obtained from Prospec Chemicals Ltd, Canada, and used as a collector in the flotation tests. It was purified by washing with ethyl ether anhydrous and acetone (Fisher Scientific Canada) following the protocol of Foster (1928) before use. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fisher Scientific Canada) was used as the source of Cu^{2+} ion in the solution to activate sphalerite. Distilled water was used throughout the tests.

2.2. Froth flotation

The froth flotation tests were conducted in a small-scale flotation tube. The bottom of this tube was a sintered glass frit with a pore size

of $1.6 \mu\text{m}$ on which a magnetic stirring bar was used to agitate the flotation pulp. The top of the flotation tube was a collection bulb modeled after Siwek et al. (1981). The throat that connects the flotation tube and the collection bulb was narrow that only one gas bubble could pass through it at one time when no frother was used, thus minimizing mechanical entrainment.

In single mineral flotation test, 1.5 g single mineral sample with particle sizes of $-75 + 38 \mu\text{m}$ was first washed by 0.1% HCl and then by distilled water. The washed sample was mixed with 150 mL distilled water in a 250 mL beaker. The pH of the suspension was adjusted to appropriate values by NaOH or HCl. This was followed by the addition of stock PAM solution (with a concentration of 1 g/L) and stock potassium ethyl xanthate solution (1.2 g/L), with 3 min stirring after adding each reagent, respectively. The conditioned slurry was transferred to the flotation tube and floated for 5 min using high purity nitrogen gas. In sphalerite flotation, 10^{-4} M CuSO_4 solution was used as an activator prior to the addition of the polymer depressant. The mineral recovery was calculated from the dry weights of the flotation concentrates and tails.

In mineral mixture flotation, 1 g each of galena and chalcocopyrite were mixed as flotation feed sample, and the procedure was the same as above. In mineral mixture flotation, EDTA was used in selected tests. When it was used, the stock EDTA solution (with a concentration of 1 g/L) was added before the addition of PAM solution. After flotation, both the froth product and tailings were collected, dried, weighed, and assayed for Cu and Pb contents. This was done by dissolving the dried samples with aqua regia and analyzing the solutions using a Varian SpectraAA-220FS (Varian, USA) atomic absorption spectrometer (AAS).

2.3. Contact angle measurements

The contact angle measurements were conducted using a Krüss drop shape analysis system (DSA 10-MK2, Germany). The sessile drop method was utilized to determine the contact angle of water on the surface of a 10 mm diameter pressed pellet of powdered mineral samples. The samples ($-38 \mu\text{m}$) were prepared by following the same procedure in single mineral flotation. The pellet was prepared from ~ 0.3 g of the fine mineral under a pressure of 5000 psi (340 atm) (ICL International Crystal Laboratories, USA) for 3 min. A drop of distilled water was placed on the surface of the pressed pellet and a set of microscopic images of the drop and the pellet were taken immediately. Then one image with the best stable view was chosen to determine the contact angle by fitting a tangent to the shape of the sessile drop on the microscopic image.

2.4. X-Ray element mapping measurements

X-ray element mapping measurements were conducted using a Hitachi S-2700 Scanning Electron Microscope (SEM) equipped with a PGT (Princeton Gamma-Tech) IMIX digital imaging system and a PGT PRISM IG (Intrinsic Germanium) detector for Energy Dispersive X-Ray Analysis (EDX). The Backscattered Electron Detector is a GW Electronics System 47 four quadrant solid state backscattered electron detector. The standard operating conditions for X-ray element mapping were at 20 kV accelerating voltage, 17 mm working distance, and a beam current of between 1 and 1.5 nA. The $-75 + 38 \mu\text{m}$ mineral particles were used for the measurements and the samples were prepared following the same procedures as in mineral mixture flotation.

2.5. ToF-SIMS measurements

Time of flight secondary ion mass spectrometric (ToF-SIMS) measurements were conducted using a ToF-SIMS IV-100 spectrometer (ION-TOF GmbH), using 25 keV Bi⁺ primary ions. The area of each sample for spectra acquisition was $146.5 \mu\text{m} \times 146.5 \mu\text{m}$. The positive ion spectra, as a function of mass, were calibrated using the H^+ , CH_3^+

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