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Adsorption of modified dextrins on molybdenite: AFM imaging, contact angle, and flotation studies

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ABSTRACT

The adsorption of three dextrins (a regular wheat dextrin, Dextrin TY, carboxymethyl (CM) Dextrin, and hydroxypropyl (HP) Dextrin) on molybdenite has been investigated using adsorption isotherms, tapping mode atomic force microscopy (TMAFM), contact angle measurements, and dynamic bubble-surface collisions. In addition, the effect of the polymers on the flotation recovery of molybdenite has been determined. The isotherms revealed the importance of molecular weight in determining the adsorbed amounts of the polymers on molybdenite at plateau coverage. TMAFM revealed the morphology of the three polymers, which consisted of randomly dispersed domains with a higher area fraction of surface coverage for the substituted dextrins. The contact angle of polymer-treated molybdenite indicated that polymer layer coverage and hydration influenced the mineral surface hydrophobicity. Bubble-surface collisions indicated that the polymers affected thin film rupture and dewetting rate differently, correlating with differences in the adsorbed layer morphology. Direct correlations were found between the surface coverage of the adsorbed layers, their impact on thin film rupture time, and their impact on flotation recovery, highlighting the paramount role of the polymer morphology in the bubble/particle attachment process and subsequent flotation.

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1. Introduction

In the mineral processing industry, the separation of the valuable minerals from unwanted minerals (termed gangue minerals) is commonly achieved through froth flotation. In froth flotation, gas bubbles are introduced into a mineral slurry generated by crushing and grinding the ore and mixing with water. The bubbles collect hydrophobic particles as they rise to the top of the flotation vessel forming a mineralised froth which can be collected, thus enabling a separation based on hydrophobicity contrast. Modification of mineral surface properties using adsorbed polymers becomes necessary when the inherent hydrophobicity of minerals cause unwanted attractive particle–bubble interactions [1–4]. The current understanding of the action of these polymers (termed depressants as they depress/reduce the recovery of minerals) is based on the enhancement of the wettability of the mineral phase onto which they adsorb. Therefore, until now, a great deal of research has focused on measurements of the induced changes in hydrophobicity and the decrease of flotation recovery of the unwanted minerals when increasing the amount of adsorbed polymer [5–9].

One of the major goals of our research has been to move beyond the simple correlation between adsorbed amount and flotation recovery, and to gain an understanding of the effect that polymers have on the surface properties of hydrophobic minerals, by studying the morphology of the adsorbed layer using *in situ* atomic force microscopy. We have shown that the morphology that polymers adopt on mineral surfaces is of fundamental importance and influences the effect of the polymers on mineral wettability [10,11], and on the dynamics of bubble/particle attachment [12]. These studies have been performed primarily with talc, a common, naturally hydrophobic waste mineral that causes problems in metal sulfide flotation. Molybdenite is another naturally hydrophobic mineral that displays natural floatability, and in contrast to talc is exceptionally valuable. However, it is still necessary to separate it from other metal sulfides in flotation to enable specific flotation concentrates/products to be generated. Therefore, a number of different methodologies have been developed to separate molybdenite from other sulfide minerals. In copper-bearing ores, a bulk concentrate of copper sulfides (e.g. chalcopyrite) and molybdenite is firstly produced, and molybdenite can subsequently either be floated or depressed in a second stage [13,14]. The most common plant practise involves depression of chalcopyrite from molybdenite using sodium cyanide, sodium hydrogen sulfide (NaSH) or Noke's reagent to generate a molybdenite concentrate. However, given the toxic nature of most of these chalcopyrite depressants, there have been

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significant efforts to determine the effect of non-toxic organic polymers on molybdenite flotation recovery [15–18], in an effort to find a benign reagent that will have a greater effect on chalcopyrite recovery than molybdenite.

A necessary first step in identifying an effective polymer for separating chalcopyrite and molybdenite is determining how polymers depress the minerals in question. By understanding the mechanism of depression for specific polymers on molybdenite, it then becomes feasible to selectively alter that chemistry to make them less likely to prevent bubble–particle attachment. In this paper, we present a study of polymer adsorption on molybdenite, combining the determination of the adsorbed polymer layers properties at equilibrium (in terms of adsorbed amount, morphology, contact angle, and bubble-surface collision studies), with the impact of the polymer on molybdenite flotation recovery. Three environmentally benign polysaccharide-based polymers were selected for the study, displaying a range of molecular weights and substitution chemistry. The effect of these structural modifications and characteristics on the adsorbed layer properties, and the subsequent effect on molybdenite flotation, is complex but the data allow one to link polymer chemistry and polymer layer properties with the effect of the polymers on bubble–particle attachment and flotation for this very valuable trace mineral.

2. Experimental

2.1. Materials

Three polysaccharide-based polymers were used as received from the supplier, Penford Australia. A regular wheat dextrin, Dextrin TY as well as two dextrins containing substitutions at position C6, carboxylmethyl (CM) Dextrin, and hydroxypropyl (HP) Dextrin, depicted in Fig. 1, were chosen. The modified polymers have a degree of substitution less than 10% (i.e., D.S. <0.3). The molecular weight averages, determined by size exclusion chromatography (SEC) [19] are 5000, 34,000 and 64,000 g mol^{-1} for Dextrin TY, CM and HP Dextrins, respectively. To prepare stock solutions for HP Dextrin and Dextrin TY of 2000 mg L^{-1}, the appropriate mass of solid sample polymer was dissolved in background electrolyte solution and the entire hydration of the dextrin molecules was ensured by letting the solution stir overnight. A different procedure was used to prepare CM Dextrin. A few drops of Milli-Q water were added to the appropriate mass of polymer powder and mixed, followed by addition of a small amount 2% KOH solution until a solid gel was formed. Once gelled, the background solution was slowly added until the desired concentration was obtained. All polymer solutions were optically clear.

Molybdenite particles used for adsorption isotherms and flotation were purchased from Fluka (purum powder). The Brunauer–Emmett–Tellet (BET) surface area was measured at 3.1 m^2 g^{-1}. Using a Malvern Instrument Mastersizer, the apparent particle size distribution of the particulate sample was distributed between 0.4 and 30.2 μm with the following distribution parameters: D_{10} of 3.0 μm, D_{50} of 7.4 μm and D_{90} of 15.5 μm. AFM images and contact angle measurements were taken on rock mineral samples from the Northern Territory, provided by the Mineralogy Department of the South Australia Museum. The crystal structure of molybdenite is depicted in Fig. 1. Freshly cleaved surfaces were obtained by peeling the top layer of the mineral sample using a sharp blade to reveal a freshly cleaved flat basal plane. As determined in our previous paper [10], no impurities were detected by X-ray photoelectron spectroscopy (XPS), neither on molybdenite rock sample nor powder.

High-purity Milli-Q water was supplied by an Elga UHQ water system, with a conductivity less than 1×10^{-6} S cm^{-1} and a surface tension of 72.8 mN m^{-1} at 20 °C. Analytical grade HCl and KOH solutions were carefully added in small quantity to adjust solution pH. All experiments were conducted in 10^{-2} M KCl background electrolyte at pH 9, unless otherwise stated.

2.2. Adsorption isotherms

Adsorption studies were performed using the batch depletion method. A 3.5 wt.% mineral suspension was prepared and separated in individual vials, to which solutions of different polymer concentrations were added. The resulting suspensions were then tumbled during 2 h to ensure adsorption equilibrium was reached. After centrifugation, the polymer concentration of the supernatant was determined via a complexation reaction between the polysaccharide, phenol and sulphuric acid analysed by UV–vis spectroscopy [20]. Assuming that all polymer depleted from solution is adsorbed onto the solid surface, the polymer adsorbed amount was calculated for different equilibrium concentrations.

When a polymer adsorbs at the solid–liquid interface often the Langmuir expression can be used to fit the observed high affinity isotherm [21], allowing determination of the adsorption equilibrium constant (K) and the Langmuir affinity constant (b). The Langmuir equation is given by:

$$\theta = \frac{\Gamma_{ads}}{\Gamma_{ads}^{m}} = \frac{KC_{eq}}{55.5 + KC_{eq}} = \frac{bC_{eq}}{1 + bC_{eq}} \tag{1}$$

where Γ_{ads} is the adsorbed amount (mol m^{-2}), Γ_{ads}^{m} is the plateau adsorbed amount (mol m^{-2}), C_{eq} is the polymer equilibrium solution concentration (mol L^{-1}), K is the adsorption equilibrium constant and b is the Langmuir affinity constant (L mol^{-1}). Polymer adsorption does not satisfy the majority of assumptions of the Langmuir model (reversibility of the adsorption, equal size of the solvent and solute molecules, etc.), therefore thermodynamic constants have not been calculated. However, determination of the maximum adsorbed amount and the affinity constant for the polymers on molybdenite is worthwhile for comparison between different polymers adsorbing on the same mineral surface.

2.3. Tapping mode atomic force microscopy (TMAFM) imaging

A Multimode Nanoscope III (Digital Instruments, Santa Barbara, California) operated in tapping mode was used to obtain *in situ* AFM images. Tapping mode cantilevers (V-shaped cantilever configuration, Digital Instruments, Santa Barbara) with a typical spring constant of 0.2 N/m^{-1} and a resonant frequency between 5 and 10 Hz and a tapping-mode fluid cell were used after being cleaned in ethanol and dried with nitrogen prior to imaging. The freshly cleaved mineral basal plane was adhered to a holder and placed in the AFM liquid cell where the polymer solution of appropriate concentration (or background electrolyte for imaging of the bare sample) was gently introduced using a syringe. Images were acquired after 30 min of exposure to polymer solutions to ensure adsorption equilibrium was reached. To avoid complications due to possible desorption, images were taken in polymer solution rather than in background electrolyte. No modification of the image quality was observed for similar images taken in both media. AFM images were acquired at 5 × 5 μm and subjected to the second-ordered flattening before parameters were determined. Nanoscope software was used to assess the root-mean-squared (RMS) roughness and average height of the polymer domains was determined with WSxM v3.0 [22]. Distinction between the areas of the image corresponding to polymer domains and bare mineral was established using phase image and roughness analysis. The area fraction of polymer coverage was determined using ImageJ

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