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The role of mineral surface chemistry in modified dextrin adsorption

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ABSTRACT

The adsorption of two modified dextrins (phenyl succinate dextrin – PS Dextrin; styrene oxide dextrin – SO Dextrin) on four different mineral surfaces has been studied using X-ray photoelectron spectroscopy (XPS), *in situ* atomic force microscopy (AFM) imaging, and captive bubble contact angle measurements. The four surfaces include highly orientated pyrolytic graphite (HOPG), freshly cleaved synthetic sphalerite (ZnS), and two surfaces produced through surface reactions of sphalerite: one oxidized in alkaline solution (pH 9, 1 h immersion); and one subjected to metal ion exchange between copper and zinc (i.e. copper activation: exposed to 1×10^{-3} M $CuSO_4$ solution for 1 h). XPS measurements indicate that the different sphalerite surfaces contain varying amounts of sulfur, zinc, oxygen, and copper, producing substrates for polymer adsorption with a range of possible binding sites. AFM imaging has shown that the two polymers adsorb to a similar extent on HOPG, and that the two polymers display very different propensities for adsorption on the three sphalerite surface types, with freshly cleaved sphalerite encouraging the least adsorption, and copper activated and oxidized sphalerite encouraging significantly more adsorption. Contact angle measurements of the four surfaces indicate that synthetic sphalerite has a low contact angle upon fracture, and that oxidation on the timescale of one hour substantially alters the hydrophobicity. HOPG and copper-activated sphalerite were the most hydrophobic, as expected due to the carbon and di/poly-sulfide rich surfaces of the two samples, respectively. SO Dextrin is seen to have a significant impact on the wettability of HOPG and the surface reacted sphalerite samples, highlighting the difficulty in selectively separating sphalerite from carbonaceous unwanted minerals in flotation. PS Dextrin has the least effect on the hydrophobicity of the reacted sphalerite surfaces, whilst still significantly increasing the wettability of graphite, and thus has more potential for use as a polymer depressant in this separation.

1. Introduction

Polymer–mineral interactions are critical in a range of areas of science and engineering. One of the most common applications that involve polymer–mineral interactions is when the state of aggregation of a mineral suspension needs to be altered. Polymers are used to adsorb onto minerals to result in either flocculation and settling [1], or dispersion and improved rheological properties [2,3]. Another area of importance for polymer–mineral interactions is in the modification of mineral surface hydrophobicity. Adsorbed polymers can reduce mineral hydrophobicity, encouraging wetting of the mineral by aqueous solution. This action of polymers has significant application in mineral processing [4,5]. The specific industrial process in which polymers are used in this fashion is mineral flotation [6], the dominant method through which base metal sulfide minerals are selectively separated from the surrounding worthless rock.

Mineral flotation is a three phase system involving a mineral suspension and rising air bubbles; hydrophobic mineral particles attach to the bubbles and rise to be collected in the froth formed at the surface of the suspension, whereas hydrophilic minerals remain in suspension. Polymers are used to make selected minerals more hydrophilic [7,8] and prevent their attachment to rising air bubbles [9,10]. Such prevention of flotation is termed polymer depression. Selectivity of adsorption and action of polymers in the mixed mineral suspension is critical in this process; polymers need to only affect the recovery of the mineral targeted for depression. In addition, mineral processing operations that employ flotation as a separation technique are often complex, with certain minerals being targeted for flotation or depression at various points in a multi-unit separation circuit [6]; a polymer might be used to target either a valuable or a worthless mineral phase, depending on the point of addition in a flotation circuit. As a result, polymer interactions with minerals that are viewed as valuable are just as important as those with minerals that are viewed as worthless.

A recent study from our research group attempted to address this issue in a study of carboxymethylcellulose (CMC) adsorption

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on chalcopyrite (the most important copper sulfide mineral) and talc (a problem hydrophobic worthless mineral) [11]. The polymer was seen to have an effect on both mineral surfaces in terms of their hydrophobicity and flotation recovery. Another problematic separation is that between sphalerite (zinc sulfide) and worthless minerals (commonly silica or pyrite) coated with carbonaceous material [12]. This separation is complicated by the fact that sphalerite can undergo a variety of surface reactions in solution (oxidation, metal ion substitution) that alter the mineral surface chemistry. Understanding the interaction of polymer depressants on carbon surfaces and reacted sphalerite surfaces is important if a successful separation of these minerals is to be achieved.

The issues of selectivity and the interaction of polymers with a range of minerals have resulted in the development and use of a number of polymer chemistries and modifications to polymer chemistries. Synthetic polymers (e.g. polyacrylamide-based polymers [13,14]) and natural polymers (e.g. dextrins, guar gums, carboxymethylcellulose [15–18]) are all in use in many flotation operations worldwide, as well as being the subject of many journal publications. In the area of carbonaceous mineral depression, starch has been tested as a graphite depressant [19]. Dextrins and particularly corn dextrin were found to be highly efficient for depressing carbonaceous materials in metal sulfide ores as early as 1939 [5]. In addition the adsorption of a dextrin polymer on graphite was more recently studied experimentally [20], and theoretically [21]. Recent research from our group has revealed an enhanced adsorption of dextrin on graphite as compared to minerals of similar hydrophobicity, namely talc and molybdenite, presumably due to a possible polymer/mineral structure matching [7]. This raises the possibility that an even better degree of adsorption and surface coverage (a key factor in reducing surface hydrophobicity and bubble-particle attachment [9]) might be achieved with an aromatic substitution on a dextrin polymer, as is seen with the enhanced adsorption of smaller aromatic compounds on graphite (e.g. naphthalene and quinine [22–24] and aromatic acids [25]).

In this work, to investigate whether the inclusion of aromatic functionality on dextrin polymers would result in enhanced adsorption on graphite over that on other minerals, two dextrins containing aromatic rings, phenyl succinate (PS) Dextrin and styrene oxide (SO) Dextrin have been studied in their adsorption on graphite using *in situ* AFM imaging and captive bubble contact angle measurements. In addition, these two polymers have been studied in their adsorption on sphalerite in various surface states: freshly cleaved, exposed to alkaline solution, and exposed to Cu ions in solution. Although resistant to oxidation in aqueous solution, sphalerite in alkaline media does oxidize to some extent [26]. In the presence of copper (generally encountered in the suspension due to dissolution of other sulfide minerals such as chalcopyrite, or purposely added as copper sulfate), the sphalerite surface reacts by adsorbing the copper ions from the solution and releasing Zn^{2+} in stoichiometric amounts [27–29]. The sphalerite surface is also rendered hydrophobic through formation of surface sulfur species such as di- or poly-sulfides [30], and implanted with copper ions that increase the adsorption of molecules, like xanthate [31–33], which are used to enhance the flotation recovery of sphalerite. The combination of two polymers and four different mineral surface types has provided us with the opportunity to correlate variable surface chemistries with polymer adsorption characteristics and hydrophobicity reduction, as well as providing insights into the potential effectiveness of these polymers for the separation of carbonaceous minerals and sphalerite.

2. Experimental

2.1. Materials and sample preparation

Two dextrin-based polymers were used in this work: a phenyl succinate substituted dextrin, referred to as PS Dextrin and a styrene oxide substituted dextrin, SO Dextrin, whose structures are depicted in Fig. 1. The polymers, supplied by Penford Australia, were used to prepare stock solutions of 2000 mg L^{-1}. The appropriate mass of solid polymer was dissolved in background electrolyte solution and stirred overnight to ensure complete hydration. The average molecular weights of the polymers, M_w, were determined using size exclusion chromatography (SEC), giving values of 9630 and 12,100 g mol^{-1} for PS Dextrin and SO Dextrin, respectively [10]. A Malvern Zetasizer Nano was used to determine the hydrodynamic diameter and Zeta potential of the two polymers: PS Dextrin – 8 ± 2 nm and −13 mV; SO Dextrin – 8 ± 1 nm and −5 mV (measured at 1×10^{-2} M KCL, pH 9).

The first substrate of this study is graphite, used as freshly cleaved mineral surface for AFM imaging and contact angle measurements. Graphite flat mineral samples were obtained by cleaving the top layer of a highly ordered pyrolytic graphite (HOPG) sample, purchased from SPI, Holgate Scientific (grade 1).

The second mineral substrate used was sphalerite. Synthetic sphalerite, sourced from the Bayville Chemical Company, New York, was used in this work to ensure a consistent low concentration of Fe impurities in the sample. X-ray microprobe analysis has confirmed that the sample was free from impurities [34]. Each square crystal sample, as received from the provider, was cut into 4 rectangular rods of approximately $1 \times 0.5 \times 0.5$ cm in length, width and depth, with a fine slow diamond saw. Freshly cleaved surfaces used for AFM and contact angle experiments were

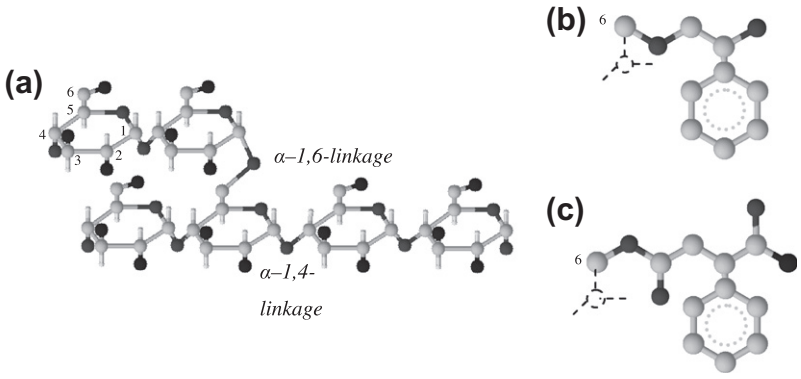

Fig. 1. (a) General structure for Dextrin-based polymers. Additional functional groups of SO Dextrin (b) and PS Dextrin (c), located at position C6 of the glucopyranose ring. Grey indicates carbon, black indicates oxygen (when in ring) or hydroxyl (when pendant), white indicates hydrogen.