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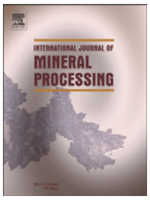

The effect of impurities and cleavage characteristics on talc hydrophobicity and polymer adsorption

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ABSTRACT

We have investigated three natural talc samples from different geographical locations (Rhode Island (USA), Delaware (USA), and Flinders Range (Australia)) to determine the effect of impurities and cleavage characteristics on hydrophobicity and polymer adsorption. Bulk (electron microprobe) and surface (X-ray photoelectron spectroscopy) composition measurements have indicated that the Rhode Island and Delaware talcs have the lowest level of Al atoms substituted within the talc structure (0.008%), and detectable at the cleaved basal plane surface (1.5 and 1.7%), and that the Flinders Range talc has the highest level of Al atoms (8.5% bulk; 8.2% surface). Contact angle measurements have highlighted the role of Al atom substitution and step-edge density (as revealed by AFM imaging) on the measured hydrophobicity of the cleaved surfaces, with the Flinders Range talc and the Rhode Island talc having significantly lower contact angles than the Delaware talc (65° and 83°, respectively, versus 90° for the Delaware). In addition, we have characterised the adsorption of two polysaccharide polymers on the three talc samples (CMC and Dextrin TY) using in situ tapping mode AFM. CMC adsorbs with the same morphology on all three talc samples, whereas Dextrin TY presents three different morphologies on the talc surfaces. The potential implications of the observed variation in adsorption behaviour on mineral flotation are discussed.

1. Introduction

As a pure mineral, talc is defined as a hydrated magnesium layered silicate (phylosilicate), with composition $Mg_3Si_4O_{10}(OH)_2$ (Harvey, 1988). Pure talc is a transparent mineral that appears white when finely ground. The crystal structure of talc consists of layers of magnesia octahedra, sandwiched between silica tetrahedra sheets. Off-white or discolored talc is indicative of elemental substitution within the talc crystal. This colour characteristic of talc classifies it as allochromatic, i.e. "other coloured" where the colour observed is due to trace impurities of composition (such as blue amazonite, yellow heliodor and rose quartz). Such minerals have a colour that is a variable and unpredictable property of the mineral, unlike idiochromatic ("self-coloured") minerals such as azurite, cinnabar, or malachite, whose colour comes from their mineralogically pure constituents.

In the case of talc, the impurities that cause the majority of variation in colour are aluminium and iron. Small amounts of Al^{3+} ions can substitute for Si^{4+} ions in the silica tetrahedral layer (Deer et al., 1992), and small to moderate amounts of Al^{3+}, Fe^{3+}, or Fe^{2+}, can substitute for magnesium in the octahedral layer (Ross, 1984). The impact of these substitutions on talc hydrophobicity is likely to be high. Al^{3+} substitutions in the silica tetrahedral layer should result in the presence of polar groups on talc basal planes, which would be expected to alter the talc hydrophobicity and the adsorption of molecules onto the basal plane surface (Burdukova et al., 2007). In addition, the substitution of these ions in the tetrahedral and octahedral layers of the mineral will alter the breakage of the bulk mineral. Mineralogically pure talc is a soft mineral that breaks to form plate-like particles with a dominance of the (001) crystal plane, with particle edges consisting of the (010) crystal plane. This reflects the weak van der Waals interactions between the tetrahedral–octahedral–tetrahedral sheets and the strong covalent interactions within the sheets. Ion substitution will alter the breakage of the mineral at the basal plane surface and within the sheets, resulting in different particle morphology and step-densities on the cleavage planes.

The impact of these variations in hydrophobicity and particle morphology has not been systematically addressed from the perspective of mineral processing and polymer adsorption. The adsorption of polymers onto talc, and the subsequent alteration of hydrophobicity and flotation outcomes, has been studied for many years (Beaussart et al., 2009b; Brossard et al., 2008; Du and Miller, 2007; Khraisheh et al., 2005; Leung et al., 2011; Ma and Pawlik, 2007; Mierczynska-Vasilev and Beattie, 2010; Mierczynska-Vasilev et al., 2008; Parolis et al., 2008; Rath et al., 1997; Steenberg and Harris, 1984). A number of these studies have been performed on mineralogically pure talc, and there remain questions as to whether such studies are relevant to actual flotation operations, where talc will contain varying levels of impurities, and will be of varying particle size and morphology due to the hardness of the talc material. Some studies exist into the role of particle size on polymer adsorption, where talc of different size distributions (and

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presumably different basal face to edge ratio) results in slightly different polymer adsorption characteristics (Rath et al., 1997; Steenberg and Harris, 1984) and flotation response. These studies have been motivated by the determination of varying properties of talc edge and basal plane surfaces (Nalaskowski et al., 2007; Yin et al., 2012). However, there has been very little work performed on measuring the varying hydrophobicity of talc due to varying impurity content, or on subsequent polymer adsorption. Forming the links between talc impurity content, hydrophobicity, and polymer adsorption would allow for tailored selection of polymer depressants for use in the processing of particular ore bodies.

The work presented here represents a first attempt to make these links. The data presented includes X-ray photoelectron spectroscopy (XPS), electron microprobe (EMP), AFM imaging, and sessile drop contact angle characterisation of three natural talcs (Rhode Island, Delaware, and Flinders Range) of different impurity content and cleavage characteristics. The effect of these differences in impurity content and hydrophobicity on polymer adsorption has been ascertained through an in situ AFM imaging investigation of the adsorption of two different polysaccharide-based polymers (regular maize dextrin, Dextrin TY, and carboxymethyl cellulose, CMC).

2. Experimental

2.1. Materials and sample preparation

Two different polysaccharide-based polymers were used. These polymers are: Dextrin TY (regular maize dextrin; supplied by Penford Australia), and CMC (carboxymethyl cellulose; purchased from Aldrich). The general chemical structure of these polymers is presented in Fig. 1. The CMC used has a D.S. of 0.7. The weight average molecular weights (M_w) of the polymers were calculated using size exclusion chromatography, and are as follows: 5000 and 229000 g mol^{-1} for Dextrin TY and CMC, respectively. Dextrin TY and CMC stock solutions of 2000 mg L^{-1} were prepared by weighing the appropriate mass of solid polymer in 10^{-2} M KCl Milli-Q water, then stirring overnight to ensure complete hydration.

High-purity Milli-Q water was supplied by an Elga UHQ water system and had conductivity less than 1×10^{-6} S cm^{-1} and surface tension of 72.8 mN m^{-1} 25 °C. The solution pH was adjusted with small additions of analytical grade HCl and KOH solutions. All aqueous solutions were at pH 9 with a 10^{-2} M KCl background concentration.

The talc samples used for atomic force microscopy imaging experiments were three different rock minerals from Providence, Rhode Island (USA); Delaware (USA); and Mount Fitton, Flinders Ranges (Australia) provided by the Mineralogy Department of the South Australian Museum (see Fig. 3). Freshly cleaved Rhode Island and Delaware talc samples for imaging experiments were prepared by carefully adhering a small piece of sticking tape on a flat section of the mineral and gently peeling the tape to reveal a freshly cleaved mineral basal plane. The Flinders Range talc sample was prepared by fracture/breakage of the mineral using pliers.

2.2. X-ray photoelectron spectroscopy

The surface chemical composition of freshly cleaved or fractured/broken talc surfaces was determined by X-ray photoelectron spectroscopy (XPS). This analysis was conducted using a Kratos Axis Ultra fitted with a delay-line detector, a monochromated Al K_α source (1486.6 eV) operating at 10 kV and 13 mA, utilising a spot size of 300 × 700 μm. The samples were analysed at a pressure of 2×10^{-9} Torr at room temperature. All surfaces were examined in survey mode over the binding energy range from 0 to 1400 eV in order to identify all species. Freshly cleaved mineral surfaces samples were deposited on conducting copper tape and mounted on a stainless steel bar prior to sample loading to the instrument.

2.3. Electron microprobe (EMP)

The elemental concentration analysis was conducted on a Cameca SX51 Electron Microprobe, using a 15 kV primary beam voltage of 20 nA beam current. The spot was defocused to a 10 μm spot to prevent diffusion of elements caused by localized beam heating. For the electron microprobe analysis the talc samples surfaces were immobilised in resin (GY Resin 791, hardener HY951). The resin-encased sample was cut and ground to prepare an exposed talc surface, which was subsequently polished by rubbing with 600 grit silicon carbide grinding powder on a flat glass plate, to flatten the surface. The exposed, flat talc surface was then successively polished using a Kent polishing machine, with decreasing size of diamond polishing paste (7, 3, then 1 μm).

2.4. AFM imaging

Surface imaging through tapping mode atomic force microscopy was performed with a Nanoscope III (Digital Instruments, Santa Barbara, California). To facilitate comparison between images, all height images have been filtered in the same manner. The filtering options used are flatten (second order flattening process). Imaging in solution (in situ) was performed using a fluid cell and narrow, thin silicon nitride Si_3N_4 cantilevers (V-shape cantilever configuration) with a typical spring constant of 0.2 N/m and a resonant frequency around 9 Hz. A piezoelectric tube scanner E with the 10 × 10 μm scan size in the XY direction and a 2.5 μm vertical range was used. The cantilever and tip were cleaned by immersion in ethanol, rinsing with copious

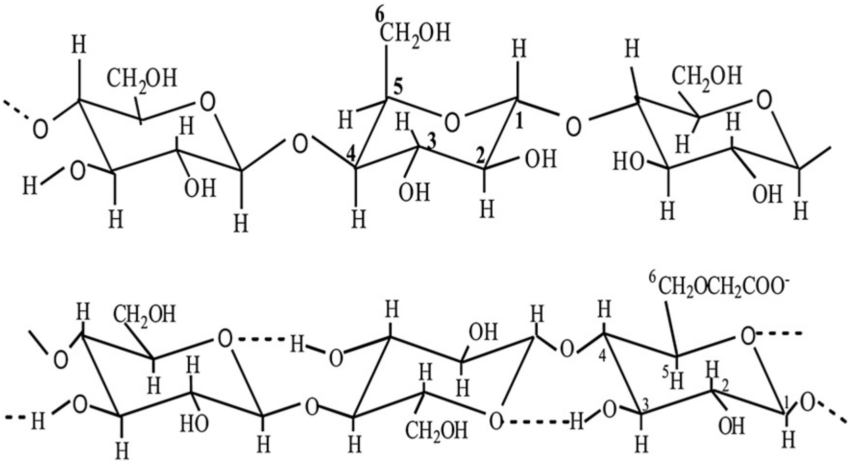

Fig. 1. Top: general chemical structure for dextrin. Bottom: general chemical structure for carboxymethyl cellulose (CMC) (both structures adapted from Coultate, 1996).