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Physicochemical aspects of allanite flotation

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Abstract: This paper investigated the physicochemical properties of allanite, a RE-silicate, by measuring zeta potential in the absence and presence of three different flotation collectors (benzohydroxamic acid, sodium oleate and dodecylamine). This data was then verified by microflotation experiments and with bubble-particle attachment pictures. The investigated properties of allanite were compared to those of quartz, a common gangue mineral in many RE deposits. The results of this work indicated that only dodecylamine was able to achieve a selective separation of allanite and quartz. This was accomplished by lowering the dodecylamine dosage so that only quartz was recovered by microflotation.

Keywords: allanite; flotation; surface chemistry; zeta potential; bubble-particle attachment; rare earths

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Rare earth elements (REE) consist of the lanthanide group of elements along with yttrium and are often differentiated based on their atomic weight between “light” (LREE) and “heavy” (HREE) where LREE refers to La-Eu and HREE refers to Gd-Yb[1]. REE are found in over 250 different minerals worldwide, however the bulk of the world’s rare earth (RE) supply originates from only a select few minerals including bastnäsite, monazite, xenotime and the ion-adsorbed clays from southern China[2]. The REE are used in many different applications including high-strength permanent magnets and phosphors for electronic displays[3]. Since 2010 the Chinese government has imposed quotas on the export of REE as domestic Chinese demand for these elements has increased substantially[4]. As China is currently responsible for 97% of the world’s REE production this quota system has resulted in increased recycling efforts as well as the development of many new RE mining projects including the Thor Lake Project in the Northwest Territories of Canada[5].

Allanite is a rare earth silicate of the epidote mineral group with the chemical formula $Ca[REE]Al_2Fe^{2+}Si_3O_{12}(OH)$[6]. Epidotes belong to the sorosilicate structural division, indicating that the $[SiO_4]$ tetrahedral units in this mineral are found in groups of two tetrahedral units linked by a common oxygen atom[7]. This type of tetrahedral linkage leads to a preferred cleavage direction parallel to the linked tetrahedral units[7]. Allanite can contain significant amounts of REE (up to 51% RE oxide) and is found frequently worldwide as an accessory phase in igneous, metamorphic, metasomatic and sedimentary rocks[8]. In the case of the Thor Lake deposit allanite is one of the valuable RE minerals, representing 12.3% of all ore minerals in the deposit[9]. The Thor Lake deposit also contains quartz as the primary gangue mineral.

Rare earth minerals are beneficiated using a combination of many mineral processing techniques; the most important of these techniques is froth flotation. For an overview of the beneficiation of RE minerals, reviews by Jordens et al. (2013)[10] and Zhang and Edwards (2012)[2] should be consulted.

The flotation of RE minerals is typically accomplished with a fatty acid or hydroxamate collector system[11]. The majority of RE flotation research has focused on the two largest rare earth industrial complexes (Mountain Pass, USA and Bayan Obo, China) where the primary RE mineral is bastnäsite[11]. Fatty acids, in particular sodium oleate, have been used as a non-selective collector for bastnäsite, however, flotation under these conditions requires large doses of depressant and often elevated temperatures[12,13]. In response to the issues associated with the use of sodium oleate, hydroxamic acids have been investigated for both the Mountain Pass and Bayan Obo deposits[14–16]. Flotation using hydroxamic acid is now the primary beneficiation technique used for the Bayan Obo deposit[2]. The mechanism of RE mineral flotation using fatty acids and hydroxamic acids has been described as chemical adsorption (chemisorption) of these collectors to the mineral surface[17–19]. The evidence for this is that zeta potential investigations of these two collector types with bastnäsite have shown adsorption of these anionic collectors (both fatty acids and hydroxamates

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are anionic in aqueous environments) at a pH range where the bastnäsite surface is negatively charged[17,18]. This adsorption is not electrostatically favourable therefore it must occur due to some type of chemical attraction. No such investigations exist in literature for surface collector adsorption or the flotation response of allanite.

When solid particles are put into an aqueous suspension they will develop a charge on the surface. This surface charge can originate via multiple routes and will result in a layer of oppositely charged counter ions closely bound to the mineral particle surface as well as a second diffuse layer of counter ions[20]. Together these layers are called the diffuse double layer and result in a decreasing electrochemical potential as a function of distance from the particle surface[21]. When one of either the particle or the surrounding fluid is put in motion a shear plane may be defined between the bulk fluid, and the particle (along with the counter ions that move with it)[20]. The zeta potential of a particle suspension is defined as the potential measured at this plane of shear[20]. An excellent introduction into the concepts of zeta potential and surface charge may be found in Riley (2005)[20].

Zeta potential measurements can be, and are, used in mineral processing as a technique to understand the surface characteristics of mineral particles for froth flotation. By analysing the changes in the zeta potential of a mineral as a function of pH it is possible to define an isoelectric point (IEP) as the pH at which the zeta potential is zero. In the case of collector adsorption the zeta potential of the mineral in the presence of collector should be different from the zeta potential of the pure mineral. Work by Kosmulski[22–26] and Parks[27] provides IEP data for many common minerals and work by Fuerstenau and Pradip (2005)[28] presents a good overview of how zeta potential data of oxide/silicate minerals may be related to flotation.

For the purposes of small-scale (microflotation) flotation research several different experimental setups have been used, including modifications of a Hallimond tube and the Partridge-Smith design[29–33]. Common benefits of small-scale flotation experiments in all of these cases are low reagent and mineral requirements, easily manipulated flotation parameters and repeatability. The chief advantage of the Partridge-Smith design is that the volume of both the flotation cell and required mineral mass are very low. These features make the Partridge-Smith design especially suited to single mineral flotation experiments.

In cases where insufficient material is available for an adequate microflotation investigation, the interactions of very small amounts (~0.1 g per test) of mineral particles with a single bubble may be used as an indicator of expected flotation performance. These bubble-particle interactions may be analysed by comparing images of bubble-particle attachment under different conditions[34–36].

In this paper the flotation behaviour of allanite was compared with that of quartz, a common gangue mineral. Three different collectors (a hydroxamic acid, a fatty acid and an amine) were investigated using zeta potential measurements, microflotation tests and bubble-particle attachment photos.

1 Experimental

1.1 Raw materials

The allanite and quartz minerals used in this work were purchased from Gregory, Bottley and Lloyd (UK) and Daubois (Canada) respectively. Sodium oleate, dodecylamine and methyl isobutyl carbinol (MIBC) were purchased from Sigma-Aldrich, benzohydroxamic acid was purchased from Alfa Aesar and F150 was obtained from Flottec. All reagents were used as supplied.

Sodium hydroxide and hydrochloric acid (Fisher Scientific) were used for pH modification in all work diluted to 0.1–1 mol/L. Stock solutions of benzohydroxamic acid and sodium oleate were prepared by dissolving the respective solids in aqueous solution whereas dodecylamine was dissolved in acetic acid at a 4:1 molar ratio of acetic acid:dodecylamine before being diluted with deionised water.

The quartz was ground in a rod mill and then screened (wet and dry) to obtain a –106+38 μm fraction for flotation testing and bubble-particle attachment photos.

1.2 Allanite purification

The allanite obtained for this work was analysed using the quantitative evaluation of materials by scanning electron microscopy (QEMSCAN) technique to determine the mineralogical composition. All QEMSCAN analyses were carried out by SGS Minerals Services (Lakefield, Canada). With knowledge of the mineralogy of the allanite sample, the sample was pulverized to a top size of 106 μm and then wet screened to remove all particles less than 25 μm. The resultant –106+25 μm fraction was then put through a Frantz Isodynamic Separator to remove unwanted ferromagnetic and diamagnetic minerals. The resultant purified allanite was then wet screened at 38 μm to produce a –106+38 μm fraction for flotation tests and bubble-particle attachment photos. Measurements of chemical composition were also conducted on the allanite sample as-received using inductively coupled plasma mass spectrometry (ICP-MS). Results for the ICP-MS measurements were also supplied by SGS Minerals Services (Lakefield, Canada).

After these separation steps, X-ray diffraction (XRD) was employed to verify the concentration of allanite. The XRD analysis in this work was performed using a Bruker