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A model system for the investigation of rare earth collector interaction

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ABSTRACT

A model system was used to investigate the interaction between carbonate mineral and octanohydroxamate collector. Bastnaesite (Ce) is the most important rare earth mineral that has been the dominant the rare earth source since 1960s. In this study, a synthetic cerium carbonate thin film on a calcite (most common gangue mineral occurring with rare earth minerals) substrate was formed for a surface interaction investigation. The cerium carbonate thin film system was characterized using Raman spectroscopy, atomic force microscopy and magnetic atomic force microscopy. An adsorption study between the model compound and hydroxamate was also conducted. The study established the utility of using atomic force microscopy and magnetic atomic force microscopy to investigate the mineral surface interaction. Weak adsorption on the thin film surface was observed after 5 h and 24 h of conditioning and the hydroxamate adsorption became evident after 72 h of conditioning. The adsorption studies for cerium carbonate and calcite also demonstrated that hydroxamate is selective to Ce over Ca.

1. Introduction

Froth flotation has been considered an effective processing approach for concentrating rare earths (REs) (Pradip and Fuerstenau, 1983; Fuerstenau and Pradip, 1984; Castor and Hedrick, 2006; Cui et al., 2012). Until now, bench-scale flotation studies have been normally undertaken to investigate the interaction of hydroxamates with rare earth minerals. Optimised site-specific flotation conditions were determined post flotation, by using extensive flotation testing regimes in which factors such as reagent type, concentration, depressant and other factors (temperature, pH etc.) were varied and tested. Limited fundamental research of the flotation reagent-surface interaction has been undertaken. To reduce the cost of the labour intensive optimisation testing programs and to develop a novel environmentally acceptable processing approach, it is imperative to understand the mechanism of the RE flotation. This involves the identification of the nature of the interaction between the flotation reagent and the target and/or gangue minerals. Due to the structural variations in the RE minerals and associated difficulties in fully characterizing natural samples, a model mineral compound was selected for these interaction studies.

Bastnaesite (Ce) is the most important RE mineral and has been the dominant RE source since 1960s (Jordens et al., 2013). Pradip et al. synthesized a cerium bastnaesite sample with the formula of $CeFCO_3$ (Pradip et al., 2013). The authors have obtained the final synthetic product in a powder form. In this study, we have synthesized a cerium carbonate thin film on a calcite substrate as a model sample resembling bastnaesite for interaction studies. The uniform thin film provided a platform that is suitable for surface interaction investigation. Calcite was chosen as the substrate due to the cleavage properties of the crystal structure that provides a natural flat surface. It is also one of the most common gangue minerals occurring with RE minerals.

The characterization of the cerium carbonate thin film is crucial prior to the interaction investigation. Atomic force microscopy (AFM) is a surface imaging technique that has been widely used in the material characterization area. However, to the authors' knowledge, the utilization of AFM for carbonate mineral surface characterization has not been reported. AFM utilises a sharp tip to scan the surface and a laser beam to maintain an appropriate force between the surface and the tip. It is well suited for samples with a flat surface and it is a non-destructive approach (Eaton and West, 2010). The surface images reveal the crystal sizes of the minerals. Appropriate grinding sizes of the ore contribute to the successful liberation of the mineral (Miettinen et al., 2010). The AFM and magnetic AFM images of the model compound can provide such guidance for an efficient grinding size during flotation. Detailed characterization of the model sample also provides the fundamental material for interaction investigation with the flotation reagent hydroxamate.

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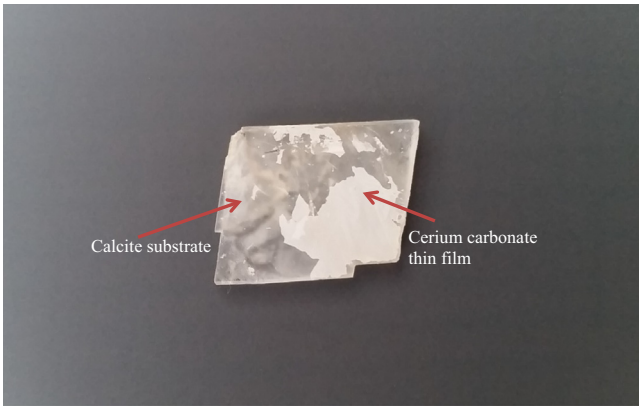

Fig. 1. Image for synthesized cerium carbonate on calcite.

2. Materials and methods

2.1. Materials

Solutions were prepared using Analytical Reagent (AR)-grade chemicals and doubly de-ionized (DDI) water. $Ce(NO_3)_3{\cdot}6H_2O$ was purchased from Sigma-Aldrich. The n-octanohydroxamic acid was obtained by neutralising an alkaline (KOH) solution of potassium hydrogen n-octanohydroxamate (supplied by Axis House) with sulfuric acid. The precipitated hydroxamic acid was filtered, washed with DDI water and dried in air. The sample was then recrystallised from methanol and dried in air before use. Calcite was purchased from BK Minerals (Brisbane, Australia).

2.2. Vibrational spectroscopy

The Raman spectra were recorded on a Renishaw inVia spectrometer using a 632.8 nm excitation from a HeNe laser. The scattered light was detected with a Peltier-cooled CCD detector with spectral resolution ~2 cm^{-1}. All the spectra were collected on a Renishaw InVia Raman spectrometer that has a rotary encoded grating stage and an internal two stage Peltier cooled (−70 °C) CCD detector. Raman spectra were calibrated using the 520 cm^{-1} silicon band. Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed with the Wire 3.3 software (Renishaw, UK). The Raman mapping was performed on a computer controlled digital microscopy stage.

2.3. AFM and magnetic AFM

AFM and magnetic AFM measurements were performed using a NT-MDT Integra spectra system. The investigated areas of the sample were selected using an optical microscope (100 × objective) that coupled with live video camera output. All the measurements were carried out under ambient laboratory environment with semi-contact mode. The scanning probe was a Si cantilever (VIT_P series, from NT-MDT), with a thickness of 5 μm, which had a resonant frequency of 200–400 kHz and a force constant of 25–95 N/m. The AFM images were processed and analysed with Image Analysis (NT-MDT, 2007). Before scanning, an AFM reflection laser signal of near 10 was adopted while feedback gain was adjusted to 1 and the setpoint was set to half of the feedback value. Magnetic AFM was undertaken using the same setting as the AFM measurement except a CoCr coated tip (FMG01 provided by NT-MDT) was adopted. The tip was magnetized for a few minutes by placing a rare earth magnet closing to the tip with a distance of no more than 3 mm prior to the scans.

2.4. Synthesis of Ce carbonate on calcite and adsorption study with hydroxamate

The calcite mineral was cleaved into flat crystals. An inert substrate (a glass slide) was used as a reference deposition surface. The synthesized method reported by Unuma was extended to a reac-

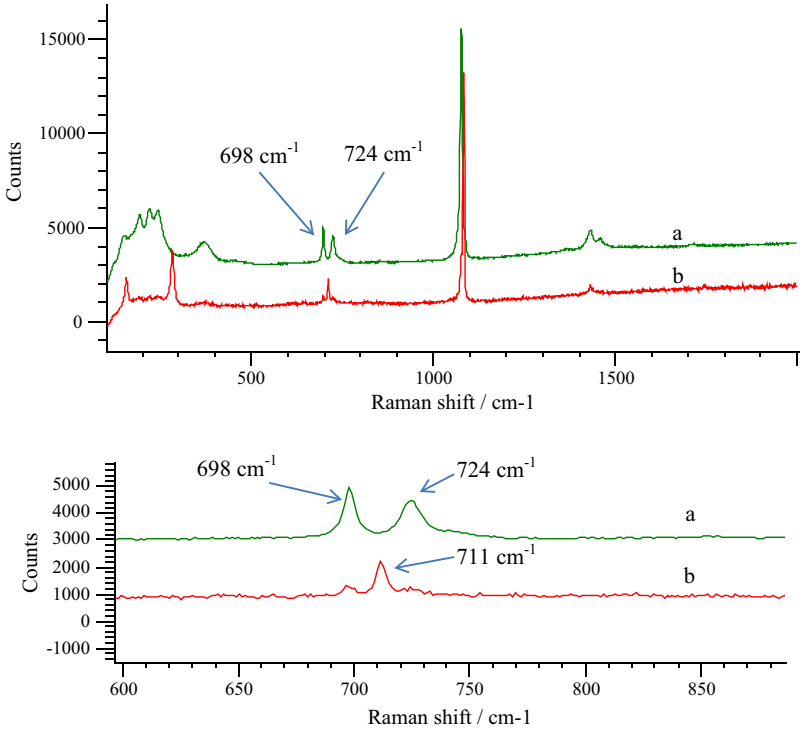

Fig. 2. Raman spectrum for (a) synthesized cerium carbonate thin film and (b) calcite in different ranges.

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