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Spectroscopic investigation of the interaction of hydroxamate with bastnaesite (cerium) and rare earth oxides

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ABSTRACT

Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy have been undertaken to determine the nature of the interaction of n-octanohydroxamate with bastnaesite and rare earth oxides. Hydroxamate compounds of the rare earths, neodymium, erbium, dysprosium, gadolinium and holmium have been synthesised, and characterised by vibrational spectroscopy. Nd hydroxamate was also investigated by photoelectron spectroscopy, and its stoichiometry confirmed as Nd(hydroxamate)$_3$ by gravimetric analysis. Neodymium oxide, bastnaesite (cerium) crystals (Pakistan) and Mountain Pass ore samples were treated with hydroxamate. Interaction was observed at the surface of both the rare earth oxides and the minerals. The research reported has established the feasibility of applying vibrational and photoelectron spectroscopy to study the interaction of hydroxamate collectors with rare earth minerals.

1. Introduction

The major ore source for light rare earth oxides is bastnaesite, a fluorocarbonate, that contains a mix of rare earth elements and yttrium. Monazite and similar rare earth element (REE) phosphates are also important ores, and phosphosilicates form a significant ore source at Kvanefjeld. Other rare earth oxide (REO) source ores include sorosilicate, allanite, and fluorapatite. Heavy REO ores are less abundant, and the main source is xenotime.

The general approach used to concentrate bastnaesite minerals has been flotation with one of n-octanohydroxamate, an aromatic hydroxamate or a fatty acid collector, often in conjunction with other separation techniques (Pavez et al., 1996; Sawaji et al., 1992; Zheng and Lin, 1994). Pradip and Fuerstenau investigated the flotation of bastnaesite from Mountain Pass using both fatty acid and alkyl hydroxamate collectors (Fuerstenau and Pradip, 1984; Pradip and Fuerstenau, 1983, 1991). They concluded that n-octanohydroxamate (OHA) was a more selective flotation reagent than the fatty acid collector. The laboratory investigation of hydroxamate flotation of REO minerals generally has been limited to n-octanohydroxamate (Pradip, 1988; Pavez et al., 1996; Perereia and Peres, 1997) and naphthalenic hydroxamate collectors (Xu et al., 2002; Ren et al., 1997; Cheng et al., 2007). Xu et al. (2002) used 1-hydroxy-2-naphthylhydroxamic acid and obtained a 37% REO concentrate from an 11% feed with an 80% recovery. Ren et al. (1997) reported the use of a similar hydroxylated naphthalene hydroxamic acid (claiming superior collection properties) for the flotation of bastnaesite ore indicating there is scope for the development of more selective reagents.

Hydroxamates are the most commonly used flotation collectors for rare earth minerals and they have been extensively used to produce concentrates of these minerals in Chinese plants since the 1960s (Liu et al., 2006). These plants have produced around 2/3 of the world's cumulative rare earth production. Notwithstanding the fact that hydroxamate collectors are currently used productively for the concentration of some rare earth ores, there are yet to be developed rare earth ore-bodies that contain gangue minerals that might be expected to compete with the rare earth minerals for the hydroxamate collector. Accordingly, it is important to better understand the interaction of such collectors, not only with rare-earth host minerals, but also with the principal gangue minerals. An enhanced understanding requires direct surface and near-surface chemical characterisation, and the research reported here has been undertaken to assess the feasibility of applying X-ray photoelectron spectroscopy (XPS) and vibrational (Raman and infrared) spectroscopy for this purpose. Although XPS is an ex situ, UHV-based technique, it has been applied successfully to numerous other mineral/collector systems. However, rare earth oxide minerals present specific problems for XPS characterisation, including the typical presence of several rare earth elements in the one host oxide, the complex nature of the photoelectron spectrum from each rare earth, and the potential interference by X-ray excited Auger electrons from O and F as well as the rare earth elements themselves. For near-surface characterisation, Raman

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spectroscopy has the advantage of both in situ and ex situ applicability as well as high spatial resolution, but beam damage to a collector such as hydroxamate when adsorbed on an oxide mineral is a potential problem with both techniques that requires examination.

For this assessment, the interaction of n-octanohydroxamate collector with bastnaesite has been investigated by vibrational and photoelectron spectroscopic techniques supported by scanning electron microscopy. The interaction of hydroxamate with neodymium oxide and a model gangue material, an ore sample that would typically contain rare earth minerals, was also studied. The nature of the rare earth/collector bonding in any multilayer coverage has been deduced from a spectroscopic characterisation of several bulk rare earth n-octanohydroxamates that were synthesised for this purpose.

2. Materials and methods

2.1. Materials

Solutions were prepared using Analytical Reagent (AR)-grade chemicals and doubly de-ionized (DDI) water. Neodymium oxide (Nd_2O_3), dysprosium oxide (Dy_2O_3), gadolinium oxide (Gd_2O_3), holmium oxide (Ho_2O_3) and erbium oxide (Er_2O_3) were purchased from Sigma–Aldrich. The n-octanohydroxamic acid was obtained by neutralising an alkaline (KOH) solution of potassium hydrogen n-octanohydroxamate (trade name AM28, supplied by Axis House) with sulphuric 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. Bastnaesite crystals and bastnaesite ore, sourced from Pakistan and Mountain Pass in the USA, respectively, were purchased from BK Minerals (Brisbane, Australia).

2.2. Synthesis of the REE compounds with hydroxamate and interaction of hydroxamate with surfaces

REE hydroxamates were prepared after the method used by Feng and Fernando (1961) for preparing 4-hydroxybenzothiazole complexes with rare earths. REOs were dissolved in approximately 30 mL of 70% nitric acid with heating as required. The n-octanohydroxamic acid was dissolved in ethanol and then added to the rare earth nitrate solution at a ratio of 3:1. The reaction solvent consisted of 50/50 water and ethanol. Ammonia (25%) was added dropwise until the first permanent precipitate was observed, then 3–4 drops more of ammonia solution were added. The pH was measured at this point. All the hydroxamate rare earth metal complexes (Nd, Er, Dy, Gd, and Ho) were synthesised in a similar manner.

The stoichiometry of the Nd hydroxamate was confirmed as being close to Nd(hydroxamate)$_3$ by gravimetric analysis. In that procedure, a known mass of the compound that had been vacuum dried for 48 h was heated for 2 h in a muffle furnace at 1000 °C, and the mass loss determined. The stoichiometry of the compound was calculated as Nd(hydroxamate)$_{3.16}$ on the assumption that Nd_2O_3 remained after the heat treatment.

Nd_2O_3 was chosen as the model compound to identify the interaction between REOs and hydroxamate. A range of exposure times (4, 24, 48 and 52 h) for Nd_2O_3 in 0.5 mmol dm^{-3} potassium hydrogen n-octanohydroxamate at pH 9.6 and 13 were conducted in 1:1 ethanol: water (V/V). The solid was collected by filtering, then washed three times with water, and dried under vacuum before further investigation.

The exposed surfaces of a fractured bastnaesite crystal and a ground ore sample were investigated for short exposure to the hydroxamate reagent. Potassium hydrogen *n*-octanohydroxamate in saturated aqueous (10 min) and 0.5 mmol dm^{-3} in 1:1 ethanol: water (40 min) solution at pH 9.6 were investigated. The bastnaesite ore was prepared using a diamond wafering saw lubricated with water and ground prior to use using silicon carbide paper to 400 grade to produce a surface for microRaman investigation. The bastnaesite ore sample was mounted on the Raman microscope stage, and a suitable region of the surface located. A layer of the potassium hydrogen n-octanohydroxamate solution was then contacted with the surface. Following the conditioning, the surface was washed three times with DDI water and dried in situ retaining the position of the sample on the Raman microscope stage.

2.3. Scanning electron microscopy (SEM)

The bastnaesite ore sample from Mountain Pass was prepared by grinding and polished to 1 μm using a diamond lap. The mounted sample was etched for 20 s in 1 mol dm^{-3} HCl before washing, drying and coating with gold. Micrographs were collected using a JEOL JSM 6510LV with a 10–12 mm working distance, a spot size of 0.2 μm and a beam energy of 15 kV with secondary or back scattered electron detection.

2.4. 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}. Raman spectra were calibrated using the 520 cm^{-1} silicon band. Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed with GRAMS32 software (Galactic Industries, Salem, NH, USA). Fourier transform infrared (FT-IR) spectra were undertaken on a Thermo Nicolet Nexus FT-IR spectrometer equipped with EverGlo IR source optics which provides a stabilised signal and 0.5 cm^{-1} resolution. The spectrometer had a DTGS detector with KBr window and Ge on KBr beamsplitter. FT-IR spectra were acquired in the range of 4000–500 cm^{-1}.

2.5. X-ray photoelectron spectroscopy

For mineral and ore specimens, most X-ray photoelectron spectra were collected from a surface of a single slice or crystal of area ranging from 1 to 8 mm^2 rather than particles of floatable size. The surface of a slice was abraded until relatively smooth to the unaided eye before conditioning in a saturated aqueous $KH(OHA)_2$ solution at its unadjusted pH (~9.5), rinsing with water, and subsequent characterisation by XPS at ambient temperature. Crushed mineral particles can provide information that is more representative of the bulk than an abraded surface, and in the few cases such specimens were characterised, the fine particles were pressed into a freshly exposed surface of indium. Specimens of microcrystalline compounds such as Nd hydroxamate were also prepared by pressing the powder into indium.

XPS data were obtained on an ESCALAB 250Xi spectrometer using monochromatised Al Kα X-rays focused to a spot size of 0.5 mm and an electron analyser pass energy of 20 eV for narrow range scans. Included in the binding energies employed for calibration were 83.96 eV for Au $4f_{7/2}$ of metallic gold and 932.6 eV for Cu $2p_{3/2}$ of Cu metal. The pressure in the analysis chamber was better than 5×10^{-9} mbar during spectral acquisition. Because of the poor electrical conductivity of the minerals and compounds investigated, photoelectron spectra had to be obtained while the specimen was under the influence of a low energy electron beam (4 V, 175 μA) from a charge-neutralisation flood gun. The observed