A Tof-SIMS analysis of the effect of lead nitrate on rare earth flotation

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ABSTRACT

The influence of lead nitrate on rare earth flotation in the presence of hydroxamates as collectors has been investigated by a combination of micro-flotation tests and time of flight secondary ion mass spectrometry (ToF-SIMS) surface chemical analysis. Micro-flotation tests identified a link between lead nitrate dose and an improved grade of REE minerals for concentrates. The testing also identified differences in the flotation behaviour of light rare earth (LREEs, La or Ce bearing minerals) and Y and Zr bearing minerals. TOF-SIMS analyses evaluated the variability in surface components on undifferentiated REE grains from the concentrates and tails samples in response to the varied lead nitrate dosing in micro-flotation tests. The surface analyses showed that both the REE grains and gangue phases reporting to the concentrate have higher relative surface proportions of both Pb and collectors as compared to those reporting to the tails. It is noted that the lead does not appear to be associated with an increase in collector adsorption, so the grade of REE can go up is not by selective adsorption of collectors. The significantly higher intensity of Pb species identified on the surface of the concentrate would suggest that lead addition can actually reverse the surface charge making it efficient for collectors to adsorb onto surfaces that they could not easily close to. It is also possible PbOH$^+$ potentially acting as a point activator.

1. Introduction

The Thor lake deposit is a world-class resource of rare earth (REE) metals and minerals in Canada. Concentration of REE from the host rocks is accomplished by flotation. In this deposit heavy rare earth elements (HREEs) are present in fergusonite ((Y, HREE)NbO$_4$) and zircon (ZrSiO$_4$), whereas the light rare earth elements (LREEs) are present in bastnaesite (Ce, La)CO$_3$F, synchysite Ca(Y, Ce)(CO$_3$)$_2$F, allanite (Ce, Ca, Y)$_2$(Al, Fe^{3+})$_3$(SiO$_4$)$_3$(OH) and monazite (Ce, La, Nd, Th)PO$_4$. Niobium and Tantalum are hosted in columbite (Mn, Fe^{2+})(Nb, Ta)$_2$O$_6$ as well as fergusonite (Paul et al., 2009; Cox et al., 2010).

Development work to optimize a REE mineral recovery process flowsheet is underway.

The original approach used to concentrate REE minerals has been flotation with alkyl phosphates and phosphoric acid ester as the collector. Open circuit and locked cycle flotation tests along with pilot plant testing on the Thor lake rare earth samples by using alkyl phosphates and phosphoric acid ester as the collector have been complete. It is reported that recoveries in the following

proportions are indicated: 90% of the zirconium oxide, 69% of the niobium oxide and 63% of the tantalum oxide to a flotation concentrate (Cox et al., 2010; Chehreh Chelgani et al., 2013).

Common collectors used for REE minerals (bastnaesite in particular) flotation include variations of organic phosphoric acids, fatty acids, hydroxamates and dicarboxylic acids (Jun et al., 2003). Fatty acids have traditionally been the collector of choice in REE minerals flotation due to their widespread availability and use in mineral flotation in general (Jordens et al., 2013). Early work comparing fatty acid and alkyl hydroxamate collectors as flotation reagents for the Mountain Pass ores by Pradip and Fuerstenau concluded that n-octanohydroxamate (OHA) was the more selective flotation reagent for bastnaesite (Fuerstenau and Pradip, 1984; Pradip and Fuerstenau, 1983, 1991). Subsequently there have been a number of investigations reporting successful flotation separation of rare earth minerals in general (bastnaesite in particular) using hydroxamate collectors (Pavez and Peres, 1994; Pavez et al., 1996; Assis et al., 1996; Lee et al., 2009; Cui et al., 2012; Pradip and Fuerstenau, 2013). The investigation of hydroxamate flotation of REE minerals has not been limited to n-octanohydroxamate. Xu et al. (2002); Ren et al. (1997) and Cheng et al. (2007) reported the use of naphthalenic hydroxamate collectors in rare earth flotation and now naphthalenic hydroxamates are the most commonly used collectors for rare earth minerals in China which accounts for

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97% of the world's cumulative rare earth production (Zhao et al., 2000; Liu et al., 2006; Cheng et al., 2007; Zhang and Edwards, 2012; Stefania and Marcello, 2013). In light of all the recent reactivity regarding REE recovery using hydroxamic acids as collectors, a testing program using a variety of these collectors was initiated to evaluate their performance on the Thor Lake ore and to possibly gain some insight as to attachment mechanisms in conjunction with the activator $Pb(NO_3)_2$.

In the development of hydroxamate reagent strategies, naphthalenic hydroxamate (LF-P81) and benzyl hydroxamate (BHD) were adopted for Thor lake samples. Internal research conducted by Avalon Rare Metals Inc. has indicated a positive effect of lead nitrate addition when floating with hydroxamate collectors, but the flotation behaviour of each rare earth bearing mineral is not clear. Furthermore, its particular role as an activator of these phases or any other REE phase is not clearly understood. Based on a literature review, lead nitrate works as an activator in the flotation of pyrite and sphalerite, with an activation process often described by at least two somewhat conflicting mechanisms. Finkelstein (1997) suggested that lead activation of sphalerite occurred through the exchange of Pb(II) with Zn(II), similar to Cu activation of sphalerite. This mechanism is proposed for pulps with a pH < 7 where the Pb substitutes for the Zn in the lattice and reacts with the xanthate to form Pb–X. However, Pattrick et al. (1998) suggested that, due primarily to its atomic radius, Pb diffusion through the sphalerite lattice will be quite difficult, and propose rather that $Pb(OH)^+$ adsorbs onto the surface of sphalerite where it can interact with collectors. McNeil and Mohr (1993) attributed the activation of pyrite to lead surface complexes such as hydroxides or carbonates and indicated that the formation of new lead-sulphide species is not required for collector attachment. Trahar et al. (1997) also showed that the adsorbed lead hydroxides do not necessarily convert to PbS to promote the flotation of lead activated sphalerite in the presence of xanthate. They believe that the interaction between xanthate and the adsorbed lead complexes occurs at the surface and result in the formation of lead-xanthate species.

Not withstanding the fact that $Pb(NO_3)_2$ is currently a proven reagent for improved flotation recovery of rare earth minerals in conjunction with hydroxamates as collectors, it is indeed important to understand the interaction of collectors and activators with the rare-earth host minerals along with the principal gangue phases. An enhanced understanding requires direct surface chemical characterisation linked to flotation recovery data. The research reported here applies ToF-SIMS analyses to the flotation stream products generated from micro-flotation tests.

2. Experimental methodology

2.1. Minerals and reagents

The rare earth feed sample was obtained from the Thor Lake deposit owned and operated by Avalon Rare Metals Inc. The micro-flotation feed was prepared in lab as follows: as received sample (−2 mm) was sieved, the coarse fraction (+200 mesh, >75 μm) was processed in a mild steel ball mill. The sieved as

received fine fraction (−200 mesh, <75 μm) and the mill discharge sample (−200 mesh, <75 μm) were combined as stock. This sample was further cut to −400 mesh (<35 μm) for micro-flotation. Chemical composition of the rare earth feed is shown in Table 1.

Collectors (provided by Avalon Rare Metals Inc.) used in micro-flotation include benzyl hydroxamate (BHD) and naphthalenic hydroxamate (LF-P81); Other reagents Na_2SiO_3, NaOH and $Pb(NO_3)_2$ were of analytical grade and were acquired from Aldrich Chemical Company, Inc.

2.2. Micro-flotation

The micro-flotation cell is modified from the design by Siwek et al. (1981). The liquid volume was 100 ml and sample size was 10 g for rare earth flotation. The cell was made of glass to facilitate cleaning and was closed at the bottom by a glass frit of nominal pore size of −5 μm. A controlled flow of air was used as flotation gas at 0.76 ml/s and 30 psig. The pulp conditioning temperature was controlled between 45 °C to 55 °C and the impeller rotation speed was set at 2000 rpm. After 3 min conditioning, the pulp pH was adjusted by NaOH solution to 8.5–9.0. If the tests required lead nitrate, it was added during the 3 min conditioning stage. Na_2SiO_3 (1000 g/t), collectors (2900 g/t of LF-P81 and 2900 g/t of BHD) and frothers (as required) were added and the pulp was conditioned for additional 3 min after each addition. The slurry was then transferred to the micro-flotation cell and processed for 5 min at a controlled temperature of 45–55 °C.

The float and non-float products (concentrate and tails) were collected and immediately frozen by liquid nitrogen in order to preserve their surface chemical characteristics. The resulting samples were analysed for composition by ICPMS and SEM/EDX in order to get the separation efficiency. A separate sample was analysed by the TOF-SIMS to identify the loading characteristics of selected reagents on the surfaces of mineral grains reporting to the concentrate and tails.

2.3. ToF-SIMS surface analysis

The instrument used in this work is an ION-TOF, TOF SIMS IV™ secondary ion mass spectrometer. This technique allows for the analysis of the outermost 1–3 atomic layers of a surface by mass spectrometry. An isotopically enriched $^{209}Bi^+$ (bismuth) primary ion beam is rastered across an area of interest on the sample surface. The raster size used was ∼300 μm with an acquisition time of 125 scans. The bombardment of the surface with the bismuth primary ion beam induces the emission of positively and negatively charged secondary ions from the sample surface. These secondary ions are extracted from the sample surface and mass analysed using a time-of-flight secondary ion mass spectrometer. A plot of secondary ion intensity *versus* mass results in a traditional first order mass spectrum, with a resolution of 10,000 above 200 atomic mass units (amu). TOF-SIMS can detect species with concentrations in the ppm–ppb range. The data were recorded with full mass spectra in 256×256 pixels using a hybrid focused bunched mode $^{209}Bi^{3+}$ ion beam and the following beam conditions for mass and spatial resolution: Ion source: 25 kV Bi^{3+}; Current:

Table 1
Chemical composition of the rare earth in the feed samples.

Rare earth	La	Ce	Nb	Zr	Nd	Y	Ta	Dy	Er	Pr
ppm	2200	4990	2910	23,700	2470	1830	356	482	211	612

Rare earth	Sm	Rb	Hf	Gd	Yb	Th	Tb	Sn	Ho	Eu
ppm	574	366	584	542	183	95.4	92.5	54	86.6	71.1