

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



Liuyin Xia^{a,b,*}, Brian Hart^a, Brandon Loshusan^a

^a Surface Science Western, Research Park, University of Western Ontario, London, Ont. N6G0J3, Canada

^b Department of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:

Received 6 December 2013

Accepted 15 September 2014

Available online 3 October 2014

Keywords:

Rare earth
Lead nitrate
Hydroxamates
ToF-SIMS
Activation

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.

© 2014 Elsevier Ltd. All rights reserved.

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)NbO₄) and zircon (ZrSiO₄), whereas the light rare earth elements (LREEs) are present in bastnaesite (Ce, La)CO₃F, synchysite Ca(Y, Ce)(CO₃)₂F, allanite (Ce, Ca, Y)₂(Al, Fe³⁺)₃(SiO₄)₃(OH) and monazite (Ce, La, Nd, Th)PO₄. Niobium and Tantalum are hosted in columbite (Mn, Fe²⁺)(Nb, Ta)₂O₆ 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

* Corresponding author at: Surface Science Western, Research Park, University of Western Ontario, 999 Collip Cir, London, Ont. N6G 0J3, Canada. Tel.: +1 (519) 661 2173; fax: +1 (519) 661 3709.

E-mail address: lxia22@uwo.ca (L. Xia).

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 $\text{Pb}(\text{NO}_3)_2$.

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 $\text{Pb}(\text{II})$ with $\text{Zn}(\text{II})$, similar to Cu activation of sphalerite. This mechanism is proposed for pulps with a $\text{pH} < 7$ where the Pb substitutes for the Zn in the lattice and reacts with the xanthate to form Pb-X . However, Patrick 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 $\text{Pb}(\text{OH})^+$ 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.

Notwithstanding the fact that $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$ 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 $^\circ\text{C}$ to 55 $^\circ\text{C}$ 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 $^\circ\text{C}$.

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 $^{209}\text{Bi}^+$ (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 $^{209}\text{Bi}^{3+}$ 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

~0.3 pA; Pulse: 1 ns; Beam spot size: ~1 μm; Raster area: generally 300 × 300 μm (variable); Mass range: 1–850 amu; Mass resolution: 10,000 amu; Sample charging was neutralized with an electron flood gun.

Each sample was mounted on indium foil, introduced into the instrument, pumped down in the vacuum and analysed. From six regions on each sample, a minimum of six grains of each mineralogical type were examined. The analysis provides a comprehensive survey of the surface species on the mineral grains in the various samples. The analytical approach was to conduct comparative surface analyses of the conditioned test samples to determine statistically significant differences in the surface species. Differences will then be evaluated with respect to the testing parameters that may provide insight as to the role of the particular reagent under investigation. The intensity of selected species detected on the grain surfaces as positive or negative ions are plotted in vertical box plots and illustrate relative changes in surface specie abundance for the mineral grain examined in the sample. In the vertical box plots, the median is plotted as the solid line across the box whereas the mean is plotted as the dashed line. An illustration of a box plot showing the various components is given below (Fig. 1). All TOF-SIMS data presented (counts) are normalized by the total ion intensity (counts of the recorded total mass spectrum) for the region of interest.

2.4. SEM/EDX

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) was employed for analyses of the samples. Routine EDX analyses can detect all elements from carbon through to uranium, with a minimum detection limit of approximately 0.5 wt%. The samples were given a thin, carbon coating prior to the analysis in order to alleviate charging problems during the SEM examination. Selected areas from the flotation samples were examined (approximately 700 × 500 μm regions) and provide some crude information regarding the separation efficiency.

3. Results

3.1. Micro-flotation

Micro-flotation testing was performed with a 0 g/t, 500 g/t, 1000 g/t and 2000 g/t Pb(NO₃)₂ addition. Fig. 2 gives grade of rare earth in the presence and absence of lead nitrate with hydroxamates as collectors. The hydroxamate collectors LF-P81 (2900 g/t) and BHD (2900 g/t) were used in the flotation at pulp pH 9. For

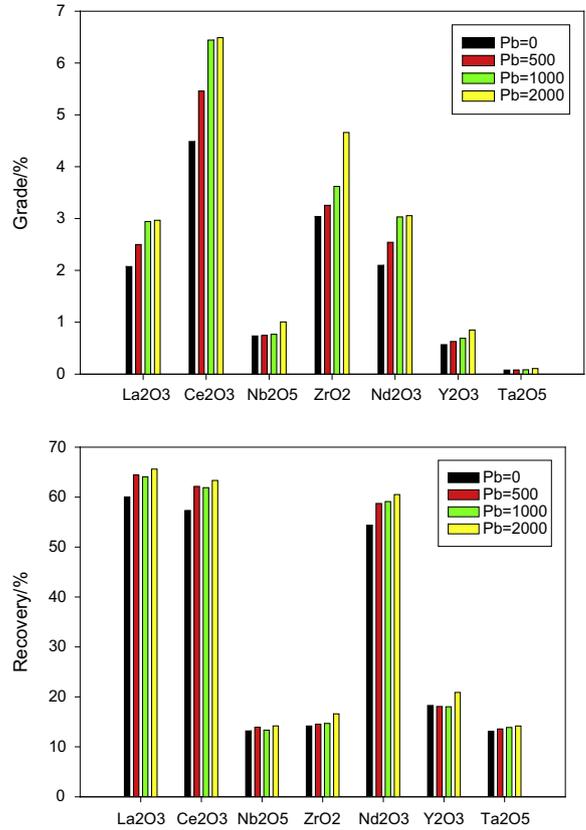


Fig. 2. Grade of concentrates and REEs recovery with different dose of Pb(NO₃)₂ when 2900 g/t LF-P81 and 2900 g/t BHD were used as collectors.

the remainder of the discussion the results from the test with LF-P81 at pH 9 are discussed unless otherwise indicated.

From Fig. 2, it is obvious that Pb(NO₃)₂ leads to a better flotation of rare earth. Comparing tests result between 1000 g/t of Pb(NO₃)₂ and 2000 g/t, the grade of La, Ce and Nd is almost identical, indicating that an addition of 1000 g/t of Pb(NO₃)₂ is sufficient for promoting the flotation of minerals containing La, Ce and Nb. For Nb and Zr, there is a very big (more than 10%) difference in grade using 2000 g/t indicating that this level of Pb(NO₃)₂ may be more appropriate for the recovery of zircon and columbite. The results with the addition of various doses of Pb(NO₃)₂ show that low doses (500 g/t or 1000 g/t) of lead nitrate could significantly improve the recovery of LREE. Only high doses of lead nitrate (up to 2000 g/t) result in a significant grade improvement of Zr and Nb.

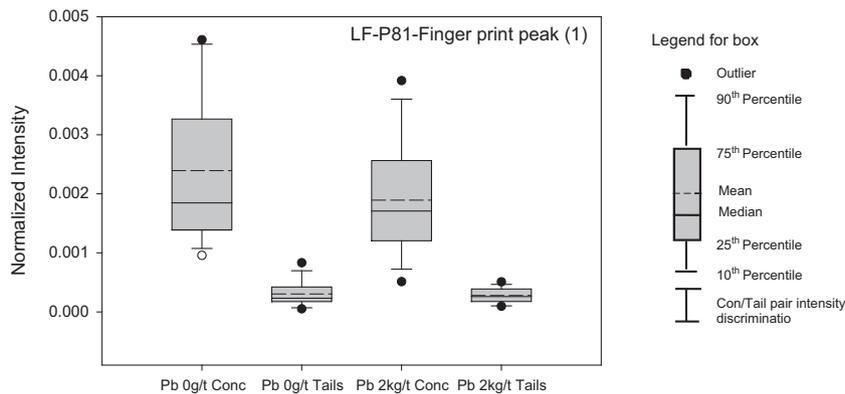


Fig. 1. An illustration of a box plot showing the various components.

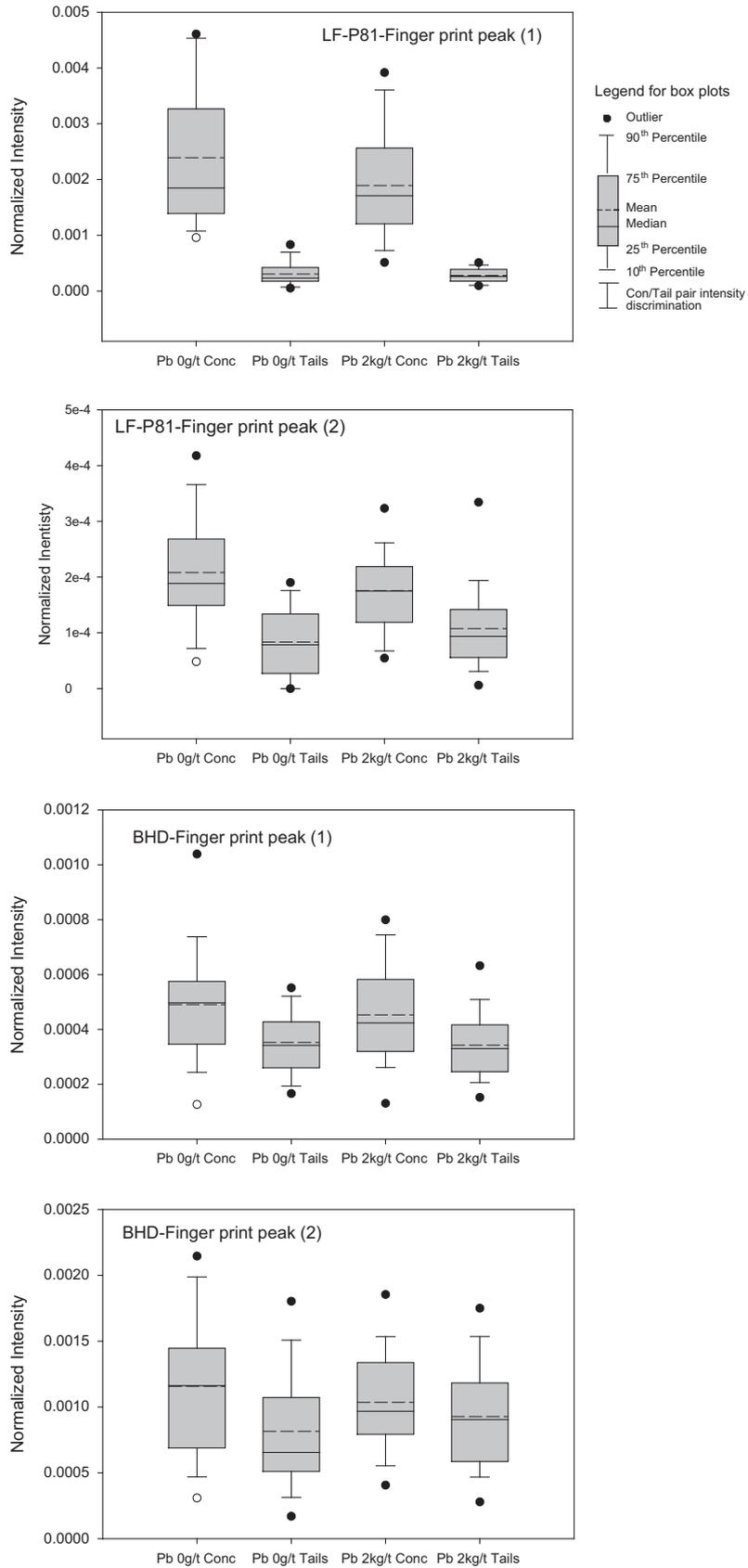


Fig. 3. Normalized intensity of mass positions indicative of the collectors LP-F81 and BHD on grain surfaces from the control test (no $Pb(NO_3)_2$ addition) and the test with 2000 g/t $Pb(NO_3)_2$ addition.

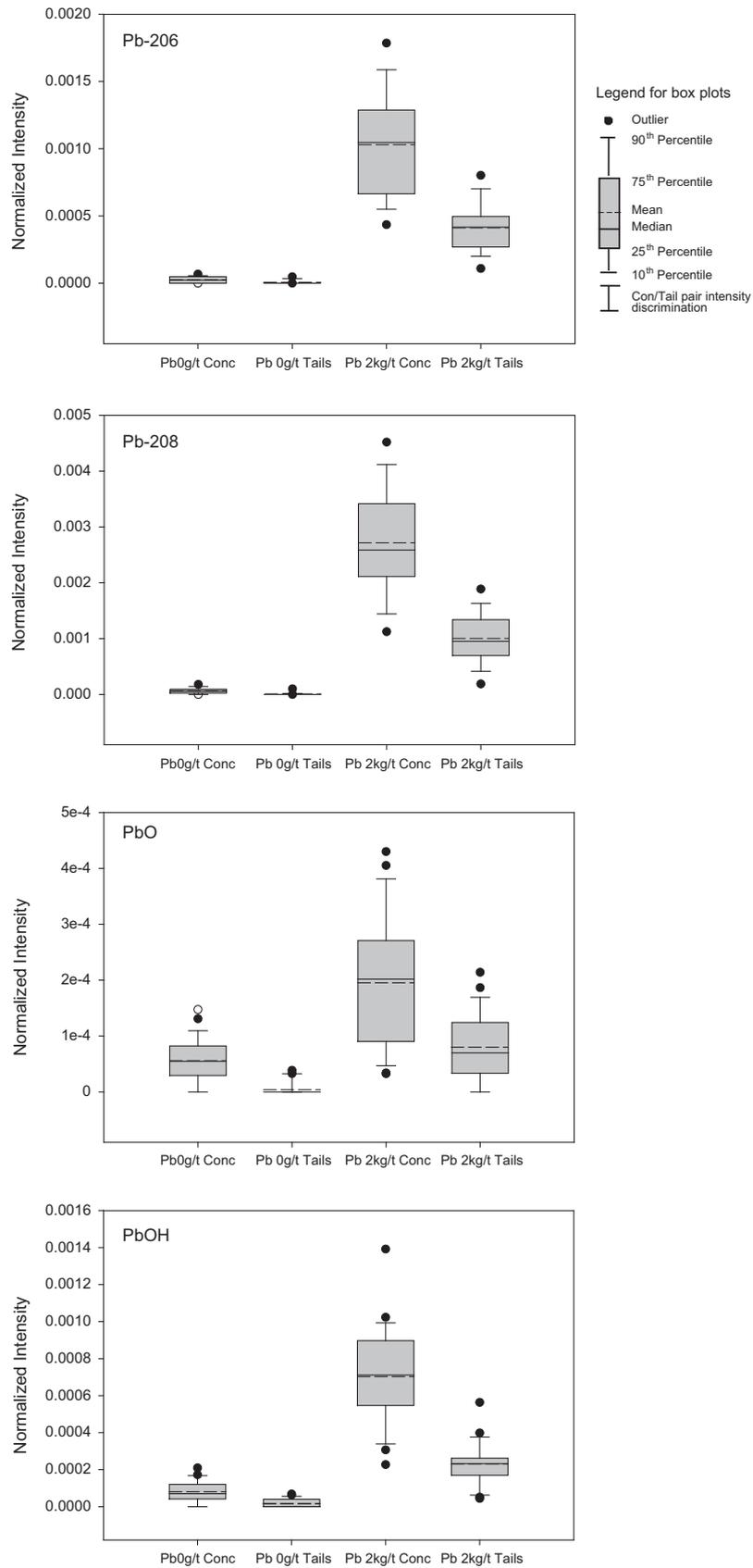


Fig. 4. Normalized intensity of Pb, PbO and PbOH on grain surfaces from the control test (no $\text{Pb}(\text{NO}_3)_2$ addition) and the test with 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition.

3.2. ToF-SIMS

A surface chemical evaluation of the micro-flotation testing products by ToF-SIMS was performed in order to potentially identify factors promoting stream partitioning in relation to the addition of $\text{Pb}(\text{NO}_3)_2$. Four samples were analysed by ToF-SIMS: flotation concentrate and tails of the test in the absence of lead nitrate (0 g/t of lead nitrate) and test products in presence of 2000 g/t lead nitrate.

All ToF-SIMS data presented (counts) are normalized by the total ion intensity (counts of the recorded total mass spectrum) for the region of interest. It should be noted that the TOF-SIMS analysis reported here is for undifferentiated grains. The data therefore will be partially biased towards surface characteristics representative of gangue grains relative to REE bearing grains as there is a greater proportion of those grains in the samples analysed.

Prior to the analysis of the samples the various reagents used in the flotation scheme were deposited on a silicon substrate and analysed by TOF-SIMS in order to generate spectral fingerprints for each reagent. The dominant peak positions (molecular fragments) for the reagents examined are used to identify the presence of the reagents and assess variations in loading between different grains in each of the samples investigated.

Normalized intensities for mass positions identified as representative of the collectors LF-P81 and BHD are given in Fig. 3. Higher normalized intensities for both collectors are reported on the surface of the grains reporting to the concentrate. There does not appear to be any significant difference in the relative intensity of the collector on grains between the concentrate/tails pairs from the control test (no $\text{Pb}(\text{NO}_3)_2$ addition) and the test with 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition. Normalized intensities for Pb and various other Pb species are given in Fig. 4. The data show that the intensities for

Pb, PbO and PbOH are very low in the control test and there is no discrimination in loading between the concentrate and tail grains. The normalized intensities for Pb, PbO and PbOH are significantly higher on grains from the test with 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition. There is a significant difference in the relative intensity of Pb, PbO and PbOH on grains between the concentrate/tail pairs with $\text{Pb}(\text{NO}_3)_2$ addition. Normalized intensities for NO_3 and Ce are given in Fig. 5. For the control test, the grains from the concentrate show a slightly higher normalized intensity of NO_3 than grains from the tails. For the 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition test, the grains from the concentrate show a significantly higher normalized intensity than grains from the tails. The intensity of NO_3 on grains from the tails in this test is very similar to that for the tails in the control. For both the control test and the 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition test, there is discrimination of Ce intensity between the concentrate and tails samples; the intensity on grains from the concentrate samples is higher. Overall, the Ce intensity between the two tests shows that there is no significant difference nor is there a difference in con/tail discrimination intensity between the tests.

Normalized intensities for Si and Si–O species are given in Fig. 6. For both the control test and the 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition test there is no discrimination for Si between the concentrate and tails samples; the intensity for Si is the same on the grains from all tests. For the control test, there is little discrimination for Si–O or H–Si–O species between the concentrate and tails samples. For the 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition test, the grains from the concentrate show a significantly higher normalized intensity for Si–O species than grains from the tails. Normalized intensities for Na, K, Al and Al–O species are given in Fig. 7. For both the control test and the 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition test, the normalized intensity of Na, K, Al and Al–O species is higher on the grain surface from the tails relative to the concentrates.

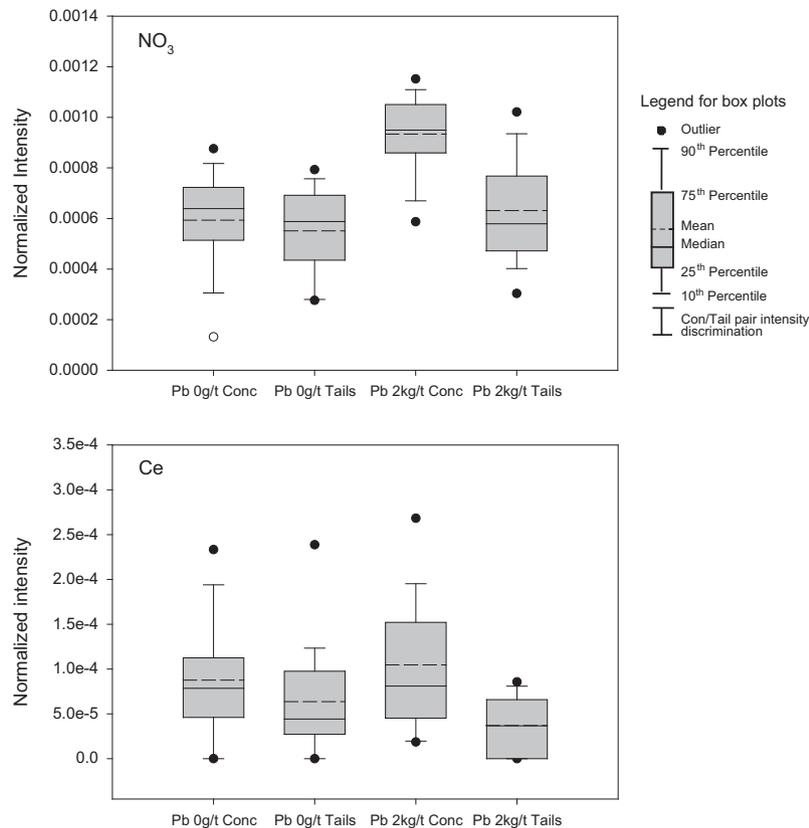


Fig. 5. Normalized intensity of NO_3 and Ce on grain surfaces from the control test (no $\text{Pb}(\text{NO}_3)_2$ addition) and the test with 2000 g/t $\text{Pb}(\text{NO}_3)_2$ addition.

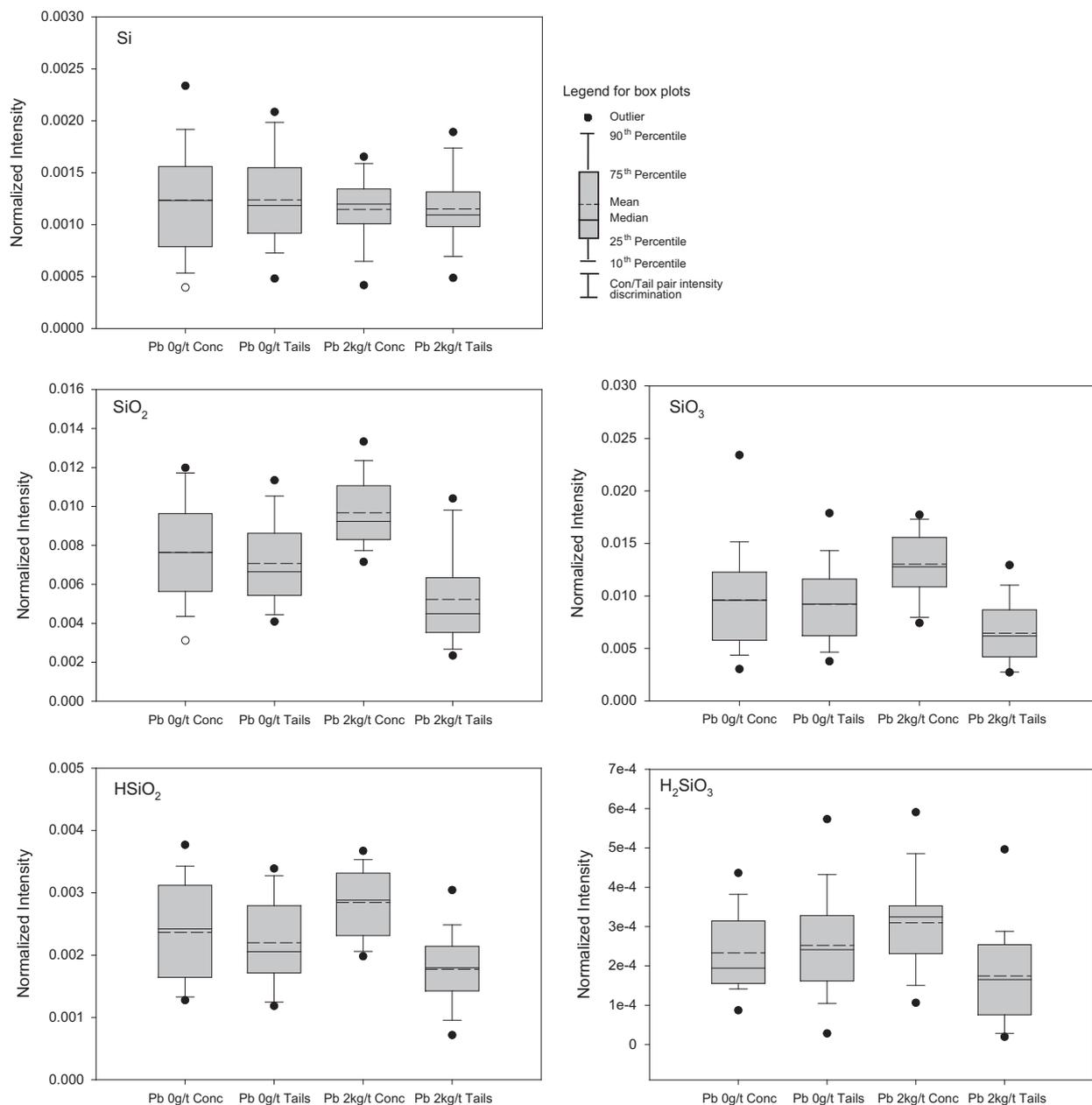


Fig. 6. Normalized intensity of Si, Si–O and H–Si–O species on grain surfaces from the control test (no Pb(NO₃)₂ addition) and the test with 2000 g/t Pb(NO₃)₂ addition.

3.3. SEM/EDX

The SEM/EDX analysis of the concentrate and tail samples provides a rough evaluation of the flotation test performance. Fig. 8 shows the back scattered electron images along with semi-quantitative elemental analyses of micro-flotation concentrate and tails samples from control test. Large area analysis of the concentrate samples shows significantly higher concentrations of La, Ce and Nd relative to the tails where none of those elements were identified.

4. Discussion

In the literature there is little information related to the role of Pb(NO₃)₂ in the promotion of selectivity or enhanced hydroxamate attachment to various REE minerals. There are a number of papers discussing the role of Pb(NO₃)₂, however mostly in the sulphide

context (Trahar et al., 1997; Finkelstein, 1997; Pecina et al., 2006). The limited references using Pb(NO₃)₂ in non sulphide systems includes work by Chen and Ye (1999) and by Fan and Rowson (2000). It was reported that the zeta potential of wolframite (Fe, Mn(WO₄)) and ilmenite increases in the presence of lead nitrate. In the tests of wolframite, with 1×10^{-4} mol/L lead nitrate, the zeta potential moved up 15 mv. Their testing also showed that an increase in zeta potential rose in accordance to the dose of lead nitrate. Possibly, the dissociation product (PbOH⁺) adsorbing through electrostatic attraction to the mineral surface results in an increased zeta potential rendering the surface less negative and thereby more apt to attract anionic collectors.

From the surface chemical analyses performed in this work, grains are reporting to the concentrate in response to collector loading. The intensity of Na, K and Al reflects components of the dominant gangue minerals (silicates; Fig. 7) and based on their distribution on con/tail pair grains (higher on grains from the tails, Fig. 8) along with the recovery data (Fig. 2) there is some degree

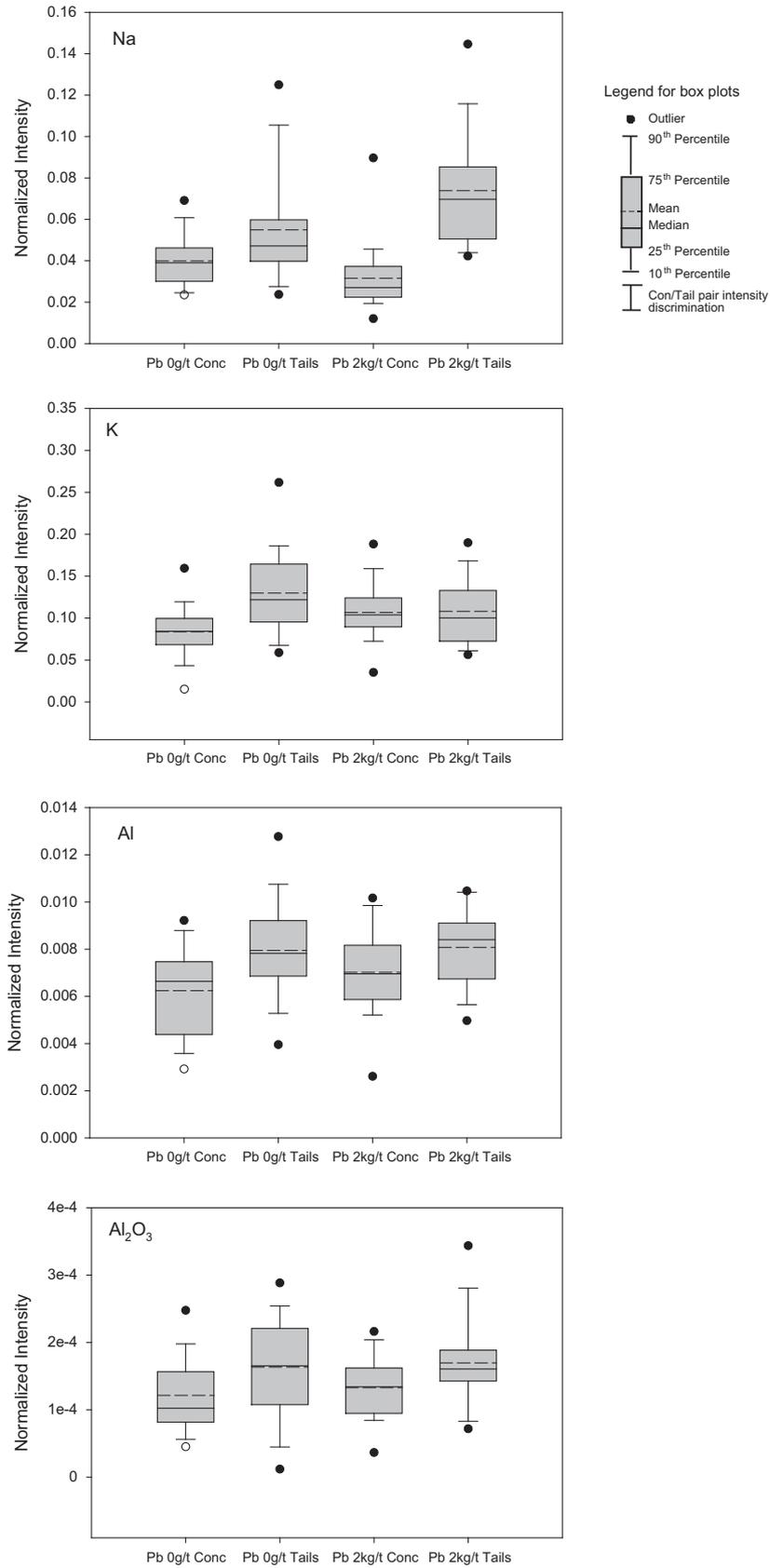


Fig. 7. Normalized intensity of Na, K, Al and Al–O species on grain surfaces from the control test (no Pb(NO₃)₂ addition) and the test with 2000 g/t Pb(NO₃)₂ addition.

of selectivity exhibited by the hydroxamate collectors. The data also shows that there is no real difference in collector loading between tests nor is there any difference in the amount of discrim-

ination between the con/tail pairs from both tests. The implication here is that the addition of Pb(NO₃)₂ does not affect collector loading i.e. it does not appear to increase the proportion of collector on

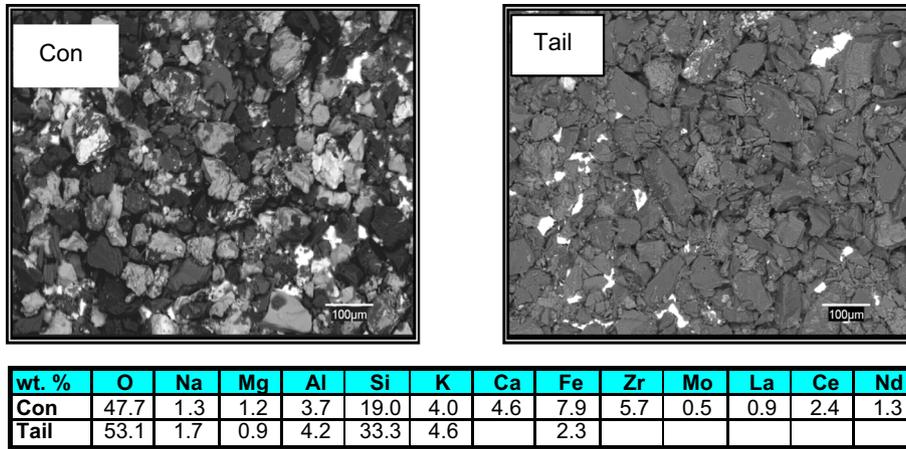


Fig. 8. Back scattered electron images along with semi-quantitative elemental analyses of microflotation concentrate and tails samples from control test. All data are reported in weight percent and are from the area in the images.

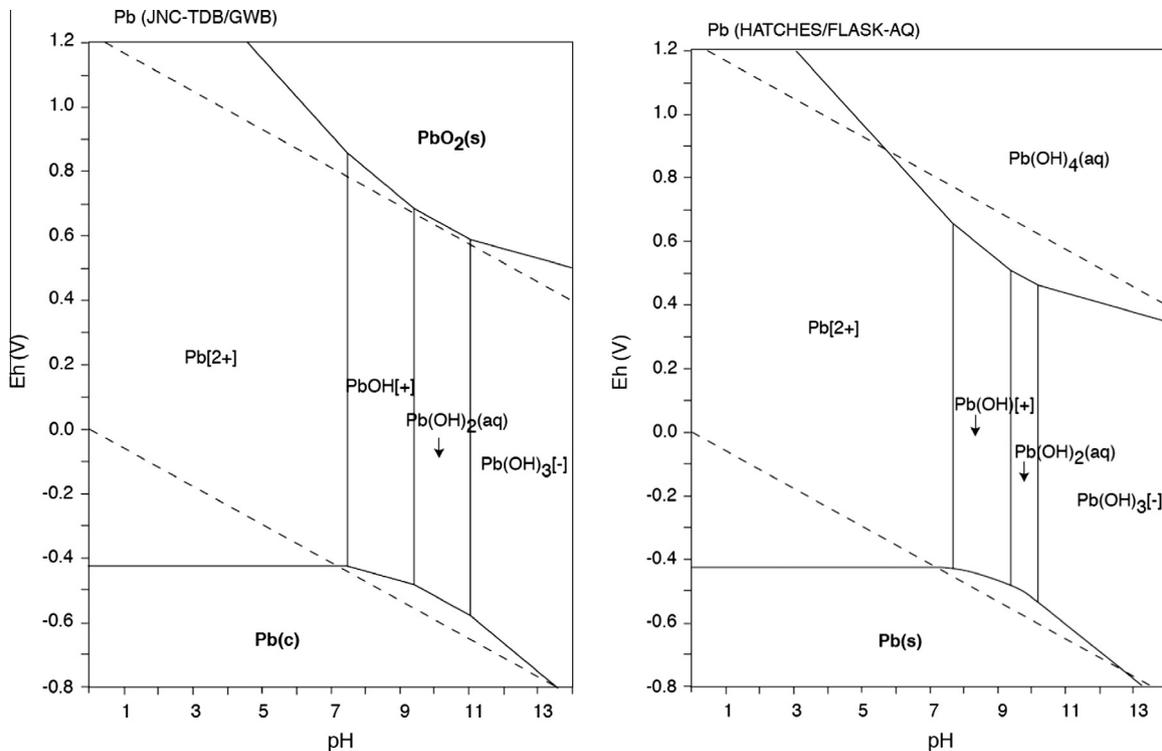


Fig. 9. Eh-pH stability diagrams for the Pb-O system. Stability fields are drawn at 25 °C, (Atlas of Eh-pH diagrams, 2005).

grains reporting to the concentrates. For both LF-P81 and BHD there is no difference in loading rates between the tests and furthermore, there is no improvement in collector loading discrimination between concentrate and tails grains from the 2000 g/t Pb(NO₃)₂ addition test. The value of Pb(NO₃)₂ then does not appear to be associated with an increase in collector adsorption.

The surface chemical data for Pb on the other hand show a strong intensity discrimination on con/tail pair grains from the test with 2000 g/t Pb(NO₃)₂ addition. The intensity data indicates that there is significantly more Pb on the surface of the grains reporting to the concentrate than the tails. This greater proportion of Pb (and species) on grain surfaces from the concentrate would indicate that Pb(NO₃)₂ is indeed participating in the discrimination process.

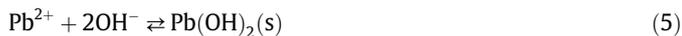
Based on a literature review, it appears that lead nitrate can enhance flotation in a couple of ways: (i) it can act as an activator, a point of attachment as in the flotation of pyrite and sphalerite, or

(ii) by surface adsorption, similar to cation attachment, shift the IEP of the mineral surface upward resulting in an increase zeta potential from a dominantly negative to a more positive surface, like ilmenite and wolframite. Therefore, in order to accommodate flotation in these conditions, the hydroxamate may become fixed to the mineral surface via the following two mechanisms: (1) Via an electrostatic attraction (physi-sorption) of the hydroxamate to the mineral surface. (2) By forming a chemical bond with a positively charged site on the mineral surface (chemisorption). Hydroxamates are believed to be the highly selective chelating collectors due to their specificity towards metal complexes as opposed to K, Na, Al, and Si.

In regards to a change in zeta potential, we will use the example of monazite and zircon. Work performed by Marek Kosmulski (2009) and Cheng (2000) reported that both minerals have a very wide range of the point of zero charge (PZC). However in the pH

range of 8.5–9.0 that of the micro-flotation tests, the surface of both monazite and zircon are negatively charged. Gangue minerals are also negatively charged as their PZC is no higher than 5.0. Furthermore at pH above 8 the hydroxamate collectors tested here are anionic. Therefore in this pH range both the targeted minerals and the collectors are negatively charged. There is evidence that the positively charged PbOH^+ can be adsorbed on the negatively charged mineral surface resulting in driving the IEP upward potentially producing a more positive zeta potential. In a micro-flotation system containing monazite, other REE phases, zircon and a variety of other oxides and silicates which are all negatively charged the addition of lead nitrate could potentially increase their zeta potential, resulting in a more favourable environment for anionic collector attachment. While zeta potential measurements were not made on these samples, the significantly higher intensity of Pb species identified on the surface of the concentrate grains would certainly support this conclusion.

It is also possible that PbOH^+ potentially acting as a point activator. In the micro-flotation with 2000 g/t of lead nitrate, the pulp solution system contains the following possible species:



At a pH range of 8.5–9.0, $\text{Pb}(\text{OH})^+$ is the dominant lead specie in the pulp solution as shown in Fig. 9. An adsorption model can be envisioned to account for the observed Pb enrichment on the surface of REE minerals. PbOH^+ adsorbs onto the mineral surface the H disassociates and the hydroxamate chemisorbs (chelates) to the mineral surface via the Pb.

5. Conclusions

Based on the above results and discussion, it is concluded that:

- (1) When Thor Lake rare earth ore was processed with naphthalenic hydroxamate and benzyl hydroxamate as collectors, in the presence of lead nitrate, there is an obvious improvement in grade of REEs reporting to concentrates.
- (2) Micro-flotation tests as a function of the dose of lead nitrate indicate that there is an improvement in recovery of light rare earth (LREEs, La or Ce bearing ore) at low addition rates and Y and Zr bearing ores at higher rates of addition. With 1000 g/t lead nitrate, the grade of La and Ce in micro-flotation concentrate increases in the order of around 40%.
- (3) TOF-SIMS investigation confirmed that both REE bearing grains and gangue phases reporting to the concentrate are doing so in response to collector attachment and high Pb surface loading whereas grains reporting to the tail are in response to a lack of collector in combination with the absence of Pb.
- (4) ToF-SIMS analyses indicates that for both hydroxamate collectors there is no difference in loading rates between the tests in the presence or absence of lead nitrate. Furthermore there is no improvement in collector loading discrimination between concentrate and tails grains from the $\text{Pb}(\text{NO}_3)_2$ addition. The implication here is that the addition of $\text{Pb}(\text{NO}_3)_2$ does not affect collector loading.

Acknowledgement

This work was completed with funding provided by Avalon Rare Metals Inc. The authors would like to thank the company for allowing us to publish this information. The help of National Nature Science Foundation of China Grant No. 51004114 is gratefully acknowledged for providing some lab samples of hydroxamates for this work.

References

- Assis, S.M., Montenegro, L.C.M., Peres, A.E.C., 1996. Utilisation of hydroxamates in minerals froth flotation. *Miner. Eng.* 9 (1), 103–114.
- Atlas of Eh-pH diagrams, 2005. National Institute of Advanced Industrial Science and Technology. Naoto TAKENO. Intercomparison of thermodynamic databases. Geological Survey of Japan Open File Report No. 419, p. 187.
- Chehreh Chelgani, S., Hart, B., Xia, L., 2013. A TOF-SIMS surface chemical analytical study of rare earth element minerals from micro-flotation tests products. *Miner. Eng.* 45, 32–40.
- Chen, W., Ye, Z., 1999. Study on wolframite flotation activated by lead nitrate. *J. Guangdong Non-ferr. Met.* 9 (1), 13–17.
- Cheng, J., Hou, Y., Che, L., 2007. Flotation separation on rare earth minerals and gangues. *J. Rare Earth* 25, 62–66.
- Cheng, T.W., 2000. The point of zero charge of monazite and xenotime. *Miner. Eng.* 13 (1), 105–109.
- Cox, J.J., Moreton, Ch., Goode, J.R., Hains, D.H., 2010. Technical Report on the Thor Lake Project. Northwest Territories, Canada, pp. 1–350.
- Cui, J., Hope, G.A., Buckley, A.N., 2012. Spectroscopic investigation of the interaction of hydroxamate with bastnaesite (cerium) and rare earth oxides. *Miner. Eng.* 36–38, 91–99.
- Fan, X., Rowson, N.A., 2000. The effect of $\text{Pb}(\text{NO}_3)_2$ on ilmenite flotation. *Miner. Eng.* 13 (2), 205–215.
- Finkelstein, N.P., 1997. The activation of sulphide minerals for flotation: a review. *Int. J. Miner. Process.* 52, 81–120.
- Fuerstenau, D.W., Pradip, 1984. Mineral flotation with hydroxamate collectors. In: Jones, M.J., Oblatt, R. (Eds.), *Reagents in the Minerals Industry*. Inst of Mining & Metallurgy Publication, pp. 161–168.
- Jordens, A., Cheng, Y.P., Waters, K.E., 2013. A review of the beneficiation of rare earth element bearing minerals. *Miner. Eng.* 41, 97–114.
- Jun, R., Wenmei, W., Jiakel, L., Gaoyun, Z., Fangqiong, T., 2003. Progress of flotation reagents of rare earth minerals in China. *J. Rare Earths* 21 (1), 1–8.
- Kosmulski, M., 2009. PH-dependent surface charging and points of zero charge. IV. Update and new approach. *J. Colloid Interface Sci.* 337, 439–448.
- Lee, K., Archibald, D., McLean, J., Reuter, M.A., 2009. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Miner. Eng.* 22 (4), 395–401.
- Liu, W., Wang, B., Dai, S., Ma, A., Wei, D., 2006. Current application and development prospect of hydroxamic acid in flotation. *Non-ferr. Min. Metall.* 22, 25–27.
- McNeil, M.B., Mohr, D.W., 1993. Formation of copper-iron sulfide minerals during corrosion of artifacts and possible implications for pseudogilding. *Geoarchaeology* 8, 23–33.
- Patrick, R.A.D., Charnock, J.M., England, K.E.R., Wright, K., 1998. Lead sorption on the surface of ZnS with relevance to flotation: a fluorescence REFLEXAFS study. *Miner. Eng.* 11 (11), 1025–1033.
- Paul, J., Stubens, T.C., Arseneau, G., Maunula, T., 2009. Avalon Rare Metals Inc. Thor Lake – Lake Zone Mineral Resource Update, pp. 1–193.
- Pavez, O., Peres, A.E.C., 1994. Technical note bench scale flotation of a Brazilian monazite ore. *Miner. Eng.* 7 (12), 1561–1564.
- Pavez, O. et al., 1996. Adsorption of oleate and octyl-hydroxamate on rare-earth minerals. *Miner. Eng.* 9 (3), 357–366.
- Pecina, E.T., Uribe, A., Nava, F., Finch, J.A., 2006. The role of copper and lead in the activation of pyrite in xanthate and non-xanthate systems. *Miner. Eng.* 19, 172–179.
- Pradip, Fuerstenau, D.W., 1983. The adsorption of hydroxamate collectors on semi-soluble minerals, Part I: adsorption on barite, Calcite and Bastnaesite. *Colloids Surf.* 8, 103–119.
- Pradip, Fuerstenau, D.W., 1991. The role of inorganic and organic reagents in the flotation separation of rare-earth ores. *Int. J. Miner. Process.* 32 (1–2), 1–22.
- Pradip, Fuerstenau, D.W., 2013. Design and development of novel flotation reagents for the beneficiation of Mountain Pass rare-earth ore. *Miner. Metall. Process.* 30 (1), 1–9.
- Ren, J., Lu, S., Song, S., Niu, J., 1997. A new collector for rare earth mineral flotation. *Miner. Eng.* 10, 1395–1404.
- Siwiek, B., Zembala, M., Pomianowski, A., 1981. A method for determination of fine particle floatability. *Int. J. Miner. Process.* 8, 85.
- Stefania, M., Marcello, R., 2013. Rare earth elements as critical raw materials: focus on international markets and future strategies. *Resour. Policy* 38 (1), 36–43.
- Trahar, W.J., Senior, G.D., Heyes, G.W., Creed, M.D., 1997. The activation of sphalerite by lead – a flotation perspective. *Int. J. Miner. Process.* 49, 121–148.
- Xu, J., Xu, X., Wang, J., 2002. Synthesis of 1-hydroxy-2-naphthyl hydroxamic acid and application to collecting rare earth minerals. *Nonferr. Met.* 54, 72–73.

Zhang, J., Edwards, C., 2012. A review of rare earth mineral processing technology. In: 44th Annual Meeting of the Canadian Mineral Processors. CIM, Ottawa, pp. 79–102.

Zhao, C., Chen, H., Yue, X., 2000. Application of LF-8 and LF-6 collectors in rare earth beneficiation. *Chinese Rare Earths* 21 (3), 100.