Preprint 13-115

AN INVESTIGATION ON THE SURFACE CHEMISTRY OF SOME RARE EARTH MINERALS DURING FLOTATION BY TOF-SIMS (I-BENCH SCALE TESTS)

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ABSTRACT

The Thor lake deposit is a world class resource of rare earth (REE) metals and minerals in Canada. Development work to optimize a REE mineral recovery process flow sheet is underway, however, given the ore mineralogy; the developed reagent scheme is relatively complex. As part of a research project, micro flotation tests were conducted on a feed sample in order to examine factors affecting stream partitioning. SEM-EDX was performed to evaluate variability in grain composition between streams (concentrate and tails) and TOF-SIMS surface analysis was used to determine statistically significant differences in surface species particularly related to potential activation (or depression) of the examined mineral phases. SEM-EDX analysis reveal that the concentrate has a significantly higher proportion of REE bearing grains (carbonates and phosphates) relative to the tail (almost none were identified). Spectral fingerprinting by TOF-SIMS has allowed for the identification of all reagent species investigated. Reagent signal intensity discrimination on test stream mineral surfaces was observed by the TOF-SIMS analysis using reagents at plant concentration levels. TOF-SIMS analysis confirmed that REE bearing grains reporting to the concentrate are doing so in response to collector attachment whereas grains reporting to the tail are doing so in response to a lack of collector and/or in combination with the presence of the depressant. The surface analysis of gangue phases reveal a similar reagent discrimination; the signal intensity of collector species was significantly higher on the concentrate samples relative to the tails while depressant species were significantly enriched on the surface of the gangue phases in the tail samples. A detailed evaluation of the surface species representing the various reagents used in flotation scheme revealed a distinct competitive relationship between two of the reagents. The surface analysis identified that when used in concurrently, there appears to be a negative feedback resulting in a significant reduction in loading for several of the collectors on grains reporting to the concentrate. An evaluation of the effect of reagents on REE mineral in pilot plant is currently under way.

Key words: Rare earth minerals, Flotation, Surface chemistry, TOF-SIMS, SEM-EDX

INTRODUCTION

Starting in 1976, the Thor Lake Property (TLP) has been explored by a number of companies for Rare Earth Elements (REEs), Niobium and Tantalum. In the TLP deposit heavy rare earth elements (HREE) are present in fergusonite ((Y, HREE)NbO4) and zircon (ZrSiO4), whereas the light rare earth elements(LREE) 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. It is estimated that the property contains a REE mineral reserve of 12 million tonnes. The final products from processing will include a mixed rare earth oxide concentrate, a zirconium oxide concentrate, a niobium oxide concentrate, and a tantalum oxide concentrate(Paul et al., 2009; Cox et al., 2010).

Previous investigations indicated that separation of rare earth minerals from oxide and silicate gangue minerals has been successfully carried out by flotation (Abeidu, 1972; CHENG et al., 1993; Pavez et al., 1993, 1994; Cheng et al., 1993, 1995; Ren et al., 2000; Chen et al., 2005; Ren et al., 2009). Numerous open circuit and locked cycle flotation testsalong with pilot plant testing on the TLP samples indicates that at a d80 of -38 μm Total Rare Earth Oxide (TREO), ZrO2, Nb2O5 and Ta2O5 recoveries can be in the order of 80%. 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).

In flotation separation, surface chemistry is the principle determinant for selective separation of the various minerals. For that reason, understanding of the factors operating on the surface of REE minerals will potentially provide opportunities for modifying the flotation scenarios, promoting improved selectivity and discrimination of the value and non-added value minerals to selective streams. Measuring surface chemical variability between phases and stream products can be realized by time of flight secondary ion mass spectrometry (TOF-SIMS). The analytical technique is surface-sensitive, capable of sub monolayer analysis with parts-per-million (ppm) sensitivity (Chryssoulis et al., 1995; Nagaraj and Brinen, 1996, 1997, 2001; Smart et al., 2000; Piantadosi& Smart, 2002; Piantadosi et al., 2002; Hart et. al. 2006; Smart et. al., 2006).

The Time of Flight Secondary Ion Mass Spectrometer (TOF-SIMS) is unique in that, it measures the outermost atomic layers of any material. In this regard, the technique is particularly suited for the analyses of surface chemistry on materials from a variety of mineral processing applications. The TOF-SIMS technique utilizes an energetic primary ion beam to sputter (remove) and ionize small amounts of the sample surface including material adsorbed onto the sample surface. These generated secondary ion yields (SIY) are subsequently analyzed in a time-of-flight mass spectrometer that capable parallel detection of all mass species originating from the surface (Hart et al., 2006; Smart et al., 2006).

The purpose of this study is to investigate the surface chemical factors affecting the adsorption of surfactants (collectors) and depressants on the REE minerals from the TLP and evaluate their adsorption mechanisms during micro flotation tests. Scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDX) was used to get a general idea of the separation efficiency. The TOF-SIMS was used to explore the possible factors affecting reagent absorption on the minerals. The data will provide insight as to the surface chemical controls operating on the REE oxides and associated minerals. The investigations will potentially aide in modeling molecular interactions of surfactants and the REE mineral surface under specific conditions.

EXPERIMENTAL METHODOLOGY

Samples were obtained from the Thor Lake deposit. Several micro flotation tests were performed on samples in order to understand the reaction between reagents (collectors, and depressants) and rare

earth minerals during flotation.Prior to flotation the feed sample was prepared in order to remove magnetics and de-slime (Fig.1). For the micro-flotation test, 5g of the flotation feed was conditioned for 10 minutes at a pH of 6.5 (controlled by silica/Fe aerosol) to which the appropriate level of reagents listed in table 1 were added followed by several minutes of further conditioning. The mixture was then transferred to a 100-ml Siwek-type flotation cell (Siwek et al., 1981) and 0.05-ml MIBC as frother was added. Airflow rate was 0.76 ml/min and the flotation time was 5 min. The float and non-float products were collected and immediately frozen in order to preserve their surface chemical characteristics.
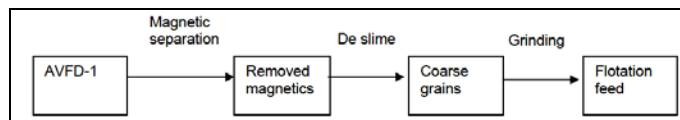

Figure 1. Sample preparation prior for flotation. Final flotation feed; P80 = 75 um.

The resulting samples were examined by SEM-EDX in order to get some idea of 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.

Table 1. Reagents and mass positions used for identification.

Flotation agent	Name	Components	Peak identifiers (mass, amu)
Conditioner (depressant)	Silica/Fe Aerosol	Sodium silicate	SiO, SiO_2, SiO_3
		Ferrous chloride, HCl	FeO
Depressant	MLC6 (R4)	Acumer 9400	102
		Alcomer 74A	119
		Alginic acis	283
Modifying agents (Depressant)	MX3	Oxalic acid, citric acid, lactic acid	195, 216
			265, 293
Collector	KBX36 (R5)	Phosphoric acid ester	S CNO, SO_3
		Alkylsulfate sodium	152, 154
		Xylere sulfonate	208, 210
		Alkyl succinamate	266, 268

Analytical techniques

The instruments used in this work are an ION-TOF, TOF SIMS IV secondary ion mass spectrometer, and Leo 440 Scanning Electron Microscope coupled with Energy Dispersive X ray Analysis (SEM-EDX).

TOF-SIMS allows for the analysis of the outermost atomic layers of a surface by mass spectrometry. An isotopically enriched 209Bi+ (Bismuth) primary ion beam is rastered across an area of interest on the sample surface. The raster size used was ~300 microns with an acquisition time of 100 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 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 concentration in the ppm range. The data were recorded with full mass spectra in 256x256 pixels using a hybrid focussed bunched mode 209Bi+3cluster ion beam. Sample charging was neutralized with an electron flood gun.

Along with the TOF-SIMS analyses the samples were examined using scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDX). Routine EDX analyses can detect all elements from carbon through to uranium, with a minimum detection limit of approximately 0.5 weight %. The samples were given a thin, carbon coating prior to the analysis in order to alleviate charging problems during the SEM examination. The brief examination was performed in order to evaluate the matrix composition of grains present in the samples. Selected areas from the flotation samples were examined (approximately 700 x 500 μm regions) and provide some

crude information regarding the separation efficiency. Individual grains were analysed for composition and x-ray intensity maps provide some information regarding the distribution of selected elements and hence grains of interest.

Data Treatment

All raw spectra were processed using the IONTOF software. Peaks in the calibrated spectra were assigned to specific isotopes in accordance with their atomic mass unit (amu) and similarly peaks reflecting molecular species of the collector were assigned mass positions. The corrected ion intensity for each mass position, measured as the integrated area under each peak corrected for dead times can be related to abundance of the particular specie. In order to compare intensities between areas of different dimensions, corrected intensities were normalized to the total number of counts for the areas 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 provided samples in order to determine statistically significant differences in the surface composition of species particularly related to potential activation (or depression) of the examined mineral phases (there was no attempt to discriminate grain types during the analysis).

RESULTS

SEM-EDX

The SEM/EDX analysis of the concentrate and tail samples provides a rough evaluation of the flotation test performance. Large area analysis of the concentrate samples shows significantly higher concentrations of La, Ce and Nd relative to the tail samples where none of those elements were identified (Fig. 2-3). REE containing grains are tentatively identified (based on EDX data only) as monazite, allenite and synchysite. Other minerals examined include zircon, pyrite along with gangue alumino-silicate phases. Zircon was the only REE bearing mineral phase identified in the tail sample (Fig. 3). The simplified evaluation indicates that the flotation separation was very successful, as almost no REE grains were identified in the tail sample. The back scattered election (BSE) images suggest that many of the minerals of interest are not well liberated and that in a number of instances the REE phases occur disseminated throughout a silicate host (Fig.4).
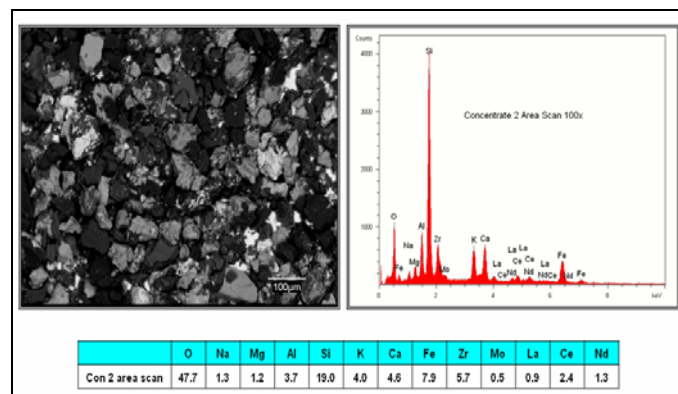

	O	Na	Mg	Al	Si	K	Ca	Fe	Zr	Mo	La	Ce	Nd
Con 2 area scan	47.7	1.3	1.2	3.7	19.0	4.0	4.6	7.9	5.7	0.5	0.9	2.4	1.3

Figure 2. Concentrate sample. Back scattered electron image (BSE), EDX spectra and semi-quantitative elemental analysis of the entire area in the image. In the BSE image grain brightness is a reflection of the grains average atomic number; brighter grains having elements with higher atomic numbers. The very bright grains in the in the above BSE image are identified as sulphides, zircons and rare earth element containing minerals. The remainder of the grains is primarily silicates of various compositions along with Fe oxides. Note REE peaks are clearly identified in the spectra with composition provided in the table.

TOF-SIMS

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. The normalized intensity data are plotted in vertical box plots and illustrate relative changes in surface specie abundance for the mineral grain examined in the sample. Comparative analyses are discussed in relation to the reported median normalized intensity value for the individual data sets. 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.
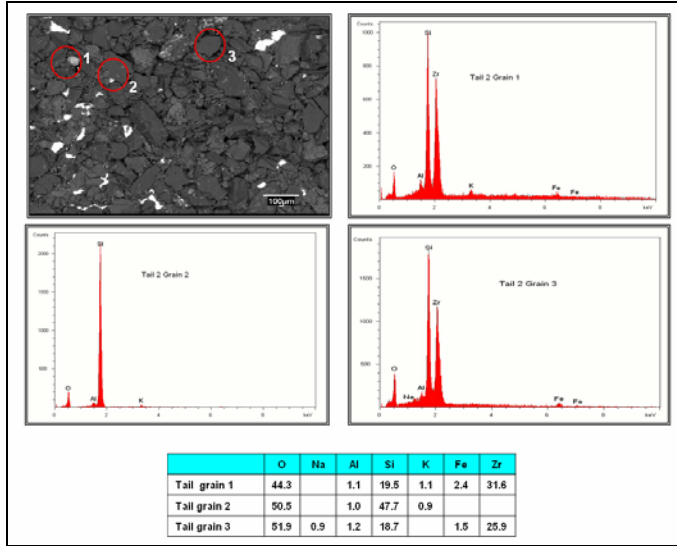
Figure 3. Tail sample, BSE image, EDX spectra and semi-quantitative elemental analysis of selected grains in the image. The numbers in the image correspond to the spectra and data in the table. All data in wt.%. In the BSE image grain brightness is a reflection of its average atomic number; brighter grains having elements with higher atomic numbers. The binary phase outlined in the red circle is an alumino-silicate with mixed zircon grains similar in composition to grain 3.
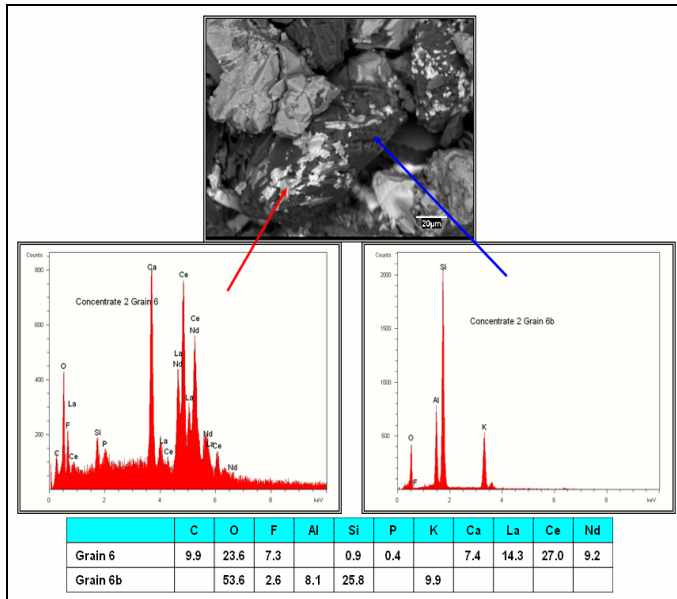

Figure 4. Concentrate sample. BSE image, EDX spectra and semi-quantitative elemental analysis of a multi-component grain. The grain is composed of a REE oxide (Synesite) and a potassium alumino-silicate. All data in wt. %. In the BSE image grain brightness is a reflection of its average atomic number; brighter grains having elements with higher atomic numbers.

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 given in table 1. The mass positions of these peaks were used to identify the presence of the reagents and asses variations in loading between different grains in each of the samples investigated.

These results of the grain surface analysis from the flotation test indicate that the normalized intensity of Ce, Nd, La and Zr is significantly higher on the grains analysed from the concentrate sample (Fig.5). Intensities of peaks representative of the collector KBX-36 (152, 154, 264 and 266 amu) are higher on the grains from the concentrate (Fig 6) while peaks representative of the depressant MLC-6 (mass positions 102 and 119) are higher on the grains from the tail sample (Fig 7). The intensity of the conditioner MX-3 (peaks at 195, 216, 265 and 293 amu) are also higher on the grains from the concentrate (Fig. 8). The normalized intensity of SiO_2 and Al_2O_3 are significantly higher on the grains analysed from the tail sample (Fig. 9).The normalized intensity of PO_3 and PO_4, S and SO_3 are significantly higher on the grains analysed from the concentrate sample (Fig10).
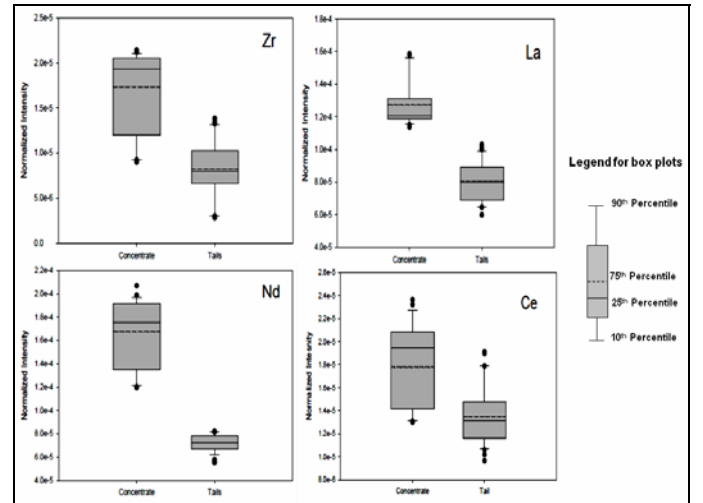

Figure 5. Box plots showing the normalized intensity for Nd, Ce, La and Zr on grains from micro-flotation test concentrate and tails samples.
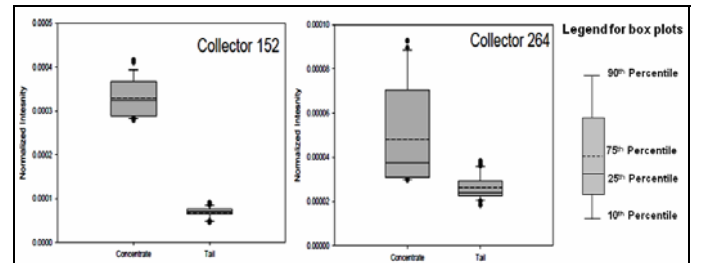

Figure 6. Box plots showing the normalized intensity collector peaks 152 and 264 on grains from micro-flotation test concentrate and tails samples.

DISCUSSION

In this investigation, the grains were not differentiated with respect to matrix composition. The normalized surface intensity of the REE elements Ce, Nd and La along with Zr reflects the greater proportion of REE bearing mineral phases and zircon reporting to the concentrate relative to the tails. With sulphide flotation some degree of element transfer between phases is commonly observed in surface chemical analyses. The best example of this is the transfer of Cu from bornite, chalcocite or chalcopyrite to sphalerite (Chandra and Gerson, 2009). For this test, given the relative low solubilises of the REE containing

minerals in the samples, it is unlikely that any significant transfer of REE elements between phases would be observed and therefore the mass intensities observed on the surface of grains are most likely related to the mineral composition. This agrees well with the SEM-EDX evaluation of the concentrate and tail samples which showed a significantly greater proportion of REE mineral phases in the concentrate sample while the grains in the tail are predominantly silicates.
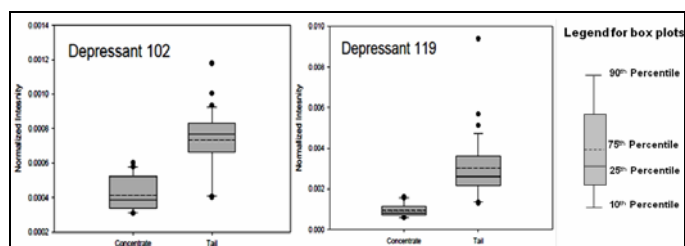

Figure 7. Box plots showing the normalized intensity for depressant (MLC-6) peaks 102 and 119 on grains from micro-flotation test concentrate and tails samples.
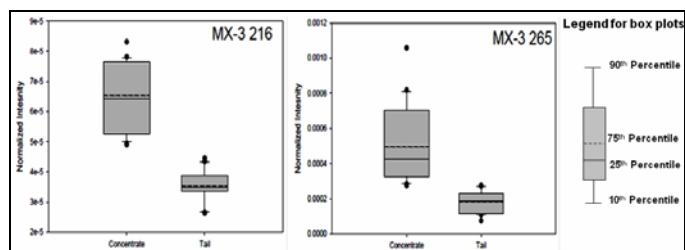

Figure 8. Box plots showing the normalized intensity for conditioner peaks 216 and 265 on grains from micro-flotation test concentrate and tails samples.
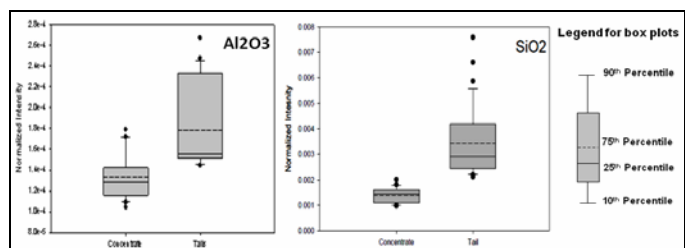

Figure 9. Box plots showing the normalized intensity for SiO2 and Al2O3 on grains from micro-flotation test concentrate and tail samples.
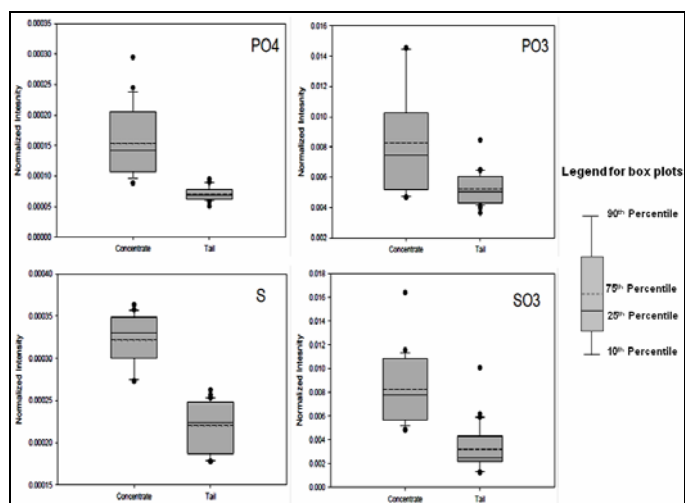

Figure 10. Box plots showing the normalized intensity PO3, PO4, S and SO3 on grains from micro-flotation test concentrate and tails samples.

From the surface analysis, species identified as representative of the collectors indicate that phases reporting to the concentrate do so in response to collector adsorption. This is irrespective of grain composition, it would appear that both the REE phases and some of the gangue phases report to the concentrate in response to collector loading. The presence of the collector on these phases is also supported by the higher intensities of sulphur and phosphate species reflective of the sulphonate and the phosphoric acid ester collectors found in the KBX36 reagent mix.

Surface analyses indicate that the grains reporting to the tail show lower collector loadings while containing a greater proportion of depressant (MLC-6) on their surfaces. The higher proportion of Si and Al species on grains from the tails may be related to their matrix composition. The SEM/EDX evaluation reported a greater proportion of grains in the tails are silicates. An alternative explanation to the Si enrichment on the grains from the tails may be related to the addition of the modifier Na-silicate which due to surface attachment may also be performing as a depressant.

There is a curious enrichment of the MX-3 species on the surface of the grains from the concentrate.It may be related to differences in surface reactions between by the components in MX-3 with the phosphates and carbonates (identified in greater proportion in the concentrate) relative to the silicates. One possible explanation may be related to their ability to complex with various positive surface ions. For the silicates, interaction with the organic acids involves surface modification by a chelating effect. The soluble chelated specie is subsequently removed from the mineral surface, consistent with the surface chemical data, which in turn blocks or controls the action of metal ions causing depression in part, by not allowing collector attachment. On the surface of REE bearing carbonates or phosphates, the action of exposed ions may significantly more difficult to control. The interaction of organic acids with positively charged exposed surface ions, for example Ca, La, Ce, may result in the formation of a complex rather than a chelate. While still soluble, the data suggests that there does not appear to be significant removal of surface ions, nor is the activity of the surface species significantly reduced by the metal ion-acid complex. Given the distribution of the collector species, viz. much higher intensities on grains in the concentrate, the presence of MX-3 does not appear to interfere with the flotation process.

CONCLUSION

Based on the micro-flotation tests:

SEM-EDX analysis of concentrate and tails sample grains from the micro-flotation test reveal that the concentrate has a significantly higher proportion of REE bearing grains (carbonates and phosphates) relative to the tail (where almost none were identified). SEM-EDX analyses also indicate that many of the minerals of interest are not well liberated and that, in a number of instances, the REE phases occur disseminated throughout a silicate host. Surface analyses of concentrate and tails sample grains from micro-flotation tests with the TOF-SIMS reveals that grains reporting to the concentrate are doing so in response to collector attachment. The grains reporting to the tail are responding to a lack of collector and/or in combination with the presence of the depressant. Factors controlling the discrimination of the collectors may be related to the presence of surface exposed REE along with the action of the modifying agent MX-3. Along with the presence of the depressant in the grains from the tails, there is also some suggestion that their discrimination to the tails may be facilitated by the addition of the Na-silicate.

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