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The role of citric acid in the flotation separation of rare earth from the silicates

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ABSTRACT

The Nechalacho project is the most advanced large heavy rare earth elements (HREE) project outside of China. Open circuit and locked cycle flotation tests along with pilot plant testing of rare earth elements (REE) concentration from the host rocks are accomplished with collectors of alkyl phosphates and the modifier of citric acid. In this study, the function of citric acid in the separation of rare metals against silicates is investigated by a combination of micro-flotation tests and time of flight secondary ion mass spectrometry (ToF-SIMS) surface chemical analysis. It was observed that there was little effect of citric acid on the REE recovery in the micro-flotation tests conditioned with de-ionized water (DIW). To evaluate the flotation response with excess secondary ions in the pulp, micro-flotation tests were performed to look at changes in recovery as a result of adding Al ions and the subsequent presence of citric acid. The results from three micro-flotation tests (DIW, DIW with the addition of 100 mg/L Al and DIW + 100 mg/L Al and 500 g/t citric acid) revealed that the addition of Al ions led to a decrease of REE grade, a lower REE minerals recovery and/or an unexpected promotion of silicates to the concentrate. Citric acid reduced the negative effect generated by the Al ions in the flotation, which was shown by an improvement in REE grade. ToF-SIMS surface analysis of undifferentiated grains from the tests with and without citric acid revealed that grains reporting to the concentrate are doing so in response to collector attachment in combination with having more secondary Al on their surface. Citric acid may partially form aqueous soluble metal–ligand complexes resulting in less Al ions on the grains surface, which were rejected to the tailings. Citric acid also may form chelation competing for adsorption on gangue minerals, resulting in a diminished effectiveness of the activation site.

1. Introduction

Previous investigations on the Nechalacho project indicated that the separation of rare earth minerals from oxide and silicate gangue minerals has been successfully carried out by flotation. The following flotation concentration recoveries have been reported: 90% of the zirconium oxide, 69% of the niobium oxide and 63% of the tantalum oxide (Cox et al., 2010). As part of the 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 tailings). The results showed that REE containing grains are tentatively identified as monazite, allenite and synchysite. Other minerals examined include zircon and pyrite, along with gangue aluminosilicate phases. The SEM/EDX evaluation indicated that the micro-flotation separation was very successful, as almost no REE grains were identified in the tailings samples (Chehreh Chelgani et al., 2013). However, the reagent scheme used in that micro-flotation was relatively complex and at plant concentration levels. Although reagent signal intensity discrimination on test stream mineral surfaces was observed by the TOF-SIMS analysis, the details of the differences in surface species, particularly related to potential activation (or depression) of the examined mineral phases, is still not clear.

One of the organic acids used in previous investigations was citric acid, which is a relatively common chelating agent employed in a variety of industries. It forms soluble, weakly bound complexes with metal ions, presumably by means of its carboxylate groups. Liu and Zhang (2000) found that citric acid could effectively remove Ca^{2+} from chalcopyrite surfaces to increase the selectivity of flotation separation between chalcopyrite and galena using

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dextrin. Liu and Liu (2004) reported that the role of citric acid in the depression of sulphide minerals seemed to be that of complexation of the copper ions, thus lowering their activity to catalyze the oxidation of thioglycollic acid. Gan et al. (2009) observed that the bitumen-quartz coagulation caused by hydrolysable multivalent metal cations (Fe^{3+}, Mg^{2+}, Ca^{2+}) was reduced or prevented by citric acid. It was summarised that activation of metal ions on flotation of gangue minerals can be reduced through formation of complexes with citric acid. If the mechanism is correct, theoretically EDTA should work for removing multivalent metal ions off gangue mineral surface, thereby reducing their potential for flotation and recovery. A reference reporting on the flotation of dolomite however showed that citric acid functions in a manner different from that of EDTA (Zheng and Smith, 1997). The carboxylate groups of citric acid can chemically adsorb onto the metal active points of the mineral surfaces (dolomite in this reference). It was indicated that citric acid could form chelation complexes with the Ca and Mg atoms on the mineral surface blocking activation sites for collector attachment. There is lots of interest to know how citric acid works as a modifier for flotation separation of rare earth against gangue minerals.

This research is a systematic study aimed at elucidating the role of citric acid in flotation separation of rare earth minerals from silicates. Micro-flotation testing measured the effect of citric acid in the presence and absence of metal ions (Al^{3+}) in the pulp on the recovery of rare earth. Surface chemical analyses by ToF-SIMS were performed to reveal the relative difference in reagent(s) on grain surfaces from test stream products.

2. Experimental methodology

2.1. Minerals and reagents

A rare earth sample was obtained from Avalon Rare Metals Inc, which had been crushed to a size fraction of −2 mm when received. The micro-flotation feed was prepared in lab as follows: the as received sample was sieved, the coarse fraction (+200 mesh, >75 μm) was processed in a mild steel ball mill. The sieved fine fraction (−200 mesh, <75 μm) and the mill discharge sample (−200 mesh, <75 μm) were combined as stock. This sample was further ground to −400 mesh (<35 μm) for micro-flotation. Slimes were separated from the feed ore by settling in a 100 mL column and removing the upper 30 mL after 10 min. Chemical compositions of the REE in the non-deslimed flotation feed and the de-slimed flotation feed are shown in Table 1.

Collectors used in micro-flotation were also from Avalon Rare Metals Inc, which were Flotinor 1682 (F1682, Phosphoric acid ester) and Cytec 845 (A845, Alkyl succinamate); Other reagents $KAl(SO_4)_2\cdot H_2O$ and citric acid were of analytical grade and were acquired from Aldrich Chemical Company, Inc.

2.2. Micro-flotation

The micro-flotation cell used was modified from Siwek et al. (1981). The liquid volume was 100 mL and the charge sample size was 10 g. The cell was made of glass and was closed at the bottom by a glass frit of nominal pore size <5 μm. The impeller rotation speed was set at 2000 rpm and bubbles were generated by a controlled air flow at 0.76 mL/s at 30 psig. After 3 min of conditioning various modifying agents, collectors, and frothers were added in sequence and the pulp was conditioned for a further 3 min after each addition. The slurry was then transferred to the micro-flotation cell where separation was performed for 5 min. A flowsheet is shown in Fig. 1. For comparison between reagents, individual testing protocols were optimized to achieve a specific recovery by performing multiple tests. In all cases, the tests were performed in triplicate; the data shown in the graphs is that of the mean of the tests.

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

Rare metals (ppm)	La	Ce	Nb	Zr	Nd	Y	Ta
Non-deslimed sample	2200	4990	2910	23,700	2470	1830	356
Deslimed-sample	2430	5450	3430	29,100	2940	2100	372

The float (concentrate) and non-float products (tailings) were collected and immediately frozen in order to preserve their surface chemical characteristics. Aliquots of the float test products were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) 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 tailings.

2.3. ToF-SIMS surface analysis

To analyze the outer-most layer of samples, an ION-TOF, TOF SIMS IV™ secondary ion mass spectrometer was used. This technique allows for the analysis of the outermost 1–3 atomic layers of a surface by mass spectrometry. 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. This 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 in order to determine statistically significant differences in the surface species. Differences would then be evaluated with respect to the testing parameters, which 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. 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.

3. Results

3.1. Micro-flotation

Based on the chemical analysis of the minerals identified in the ore, the elements La, Ce and Nd are considered representative of

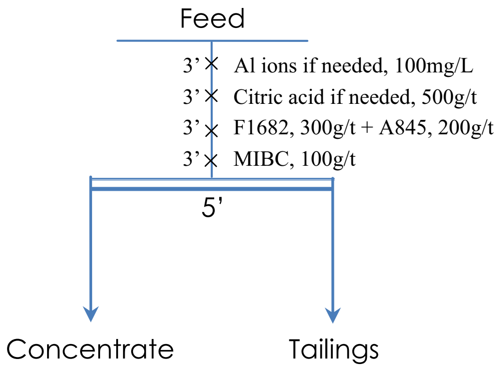

Fig. 1. Flotation flowsheet and testing parameters; using de-slimed feed sample.

light rare earth elements (LREE) whereas Nb and Y are considered more representative of the HREE. In addition, Zr was found in the same minerals as HREE, so it can also be considered representative of the HREE containing minerals. This convention will be used throughout this paper.

Micro-flotation tests conditioned in de-ionized water (DIW) were performed in the presence and absence of 500 g/t citric acid. Fig. 2 gives the flotation response of rare metals in the pair of tests. Except for the grade of Zr, which has a slight decrease after addition of citric acid in the pulp, there is little shift for the grade of other rare metals. It is indicated that without secondary ions in the pulp, citric acid as a modifier does not promote the concentration of REE minerals during flotation.

In an attempt to evaluate the flotation response with excess secondary ions, micro-flotation tests were performed to look at changes in recovery as a result of adding Al ions and the subsequent addition of citric acid. First, tests conditioned in DIW and DIW with the addition of 100 mg/L Al^{3+} were performed. The grade of REE in the presence and absence of Al ions is shown in Fig. 3. Al ions as a representative of secondary ions in the pulp at estimated plant level led to an obvious decrease in REE grade. Mass pull of the two flotation tests was almost identical, so the lower grade of REE the less REE recovery. It is also indicated that the addition of Al ions led to an unexpected promotion of silicates to the concentrate which is the main contaminant in the ore to the flotation concentrates.

Tests on the influence of Al^{3+} ions were further developed by adding citric acid as a modifier. Fig. 3 plotted the grade of REE in the blank and in the presence of citric acid. It is clear that the addition of citric acid reduces the negative effect generated by the Al ions in the flotation. This is shown by an improvement in REE grade, although not to the same grade as in the test with DIW. The mechanism of how citric acid affects flotation with the activation of Al^{3+} needs direct surface chemical characterisation. Streams (Concentrate and tailings) from micro-flotation tests were measured by ToF-SIMS.

3.2. ToF-SIMS

Four samples were analysed by ToF-SIMS, which were concentrates and tailings of blank micro-flotation test (DIW + 100 mg/L Al ions) and the products from the test in the presence of 500 g/t citric acid with 100 mg/L Al ions.

In order to identify collector F1682 and citric acid used in the micro-flotation, a sample of each was deposited on a silicon substrate and analysed by TOF-SIMS to generate spectral fingerprints. The dominant peak positions for each reagent examined were used to identify their presence and assess variations in loading between different grains in each of the four samples investigated. Reagent and activating or depressant specie loading can provide information regarding factors controlling mineral partitioning. Analysed grains were identified by the presence of any or all of the REE elements. Distinctions were not made between different mineral species. For each sample more than 36 grains were identified and analysed.

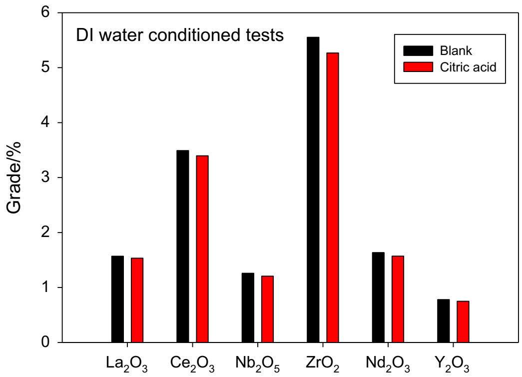

Fig. 2. Effect of citric acid on the grade of REE in the tests conditioned with DI water.

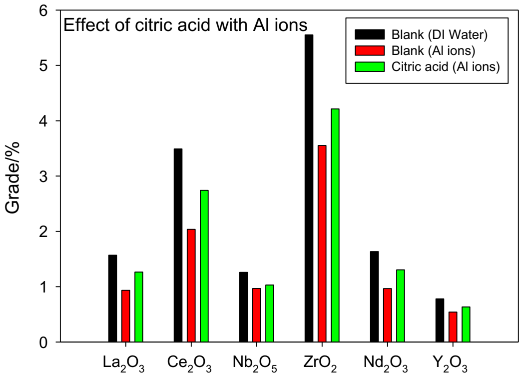

Fig. 3. Grade of the concentrates from the tests conditioned with DI water, in the presence of metal ions and with citric acids.

3.2.1. Al ions on the surface of the four samples

Without addition of Al^{3+} in the pulp, the Al species would reflect the mineralogy, aluminosilicates, so it should be reported higher in tailings than in the concentrate, as shown in our previous study (Chehreh Chelgani et al., 2013). In this work, ToF-SIMS surface chemical evaluation of undifferentiated grains revealed the addition of Al^{3+} resulting in a higher proportion of Al related species (Al in positive and Al_2O_3 in negative) on the surface of grains reporting to the concentrate relative to the tailings (Fig. 4). It is also noted that after citric acid addition, the intensity discrimination for Al species between the concentrate and tailings is significantly widened as a result of grains reporting to the tails having less Al on their surface.

3.2.2. K and Na ions on the surface of the four samples

K and Na reflect the gangue minerals feldspar, biotite and possibly dolomite, therefore a greater intensity was reported for the tailings relative to the concentrate as shown in Fig. 5.

3.2.3. Si and Si_xO_y ions on the surface of the four samples

Surface intensity data for Si and its related species (SiO_2, $HSiO_2$ and SiO_3 in negative) are shown in Fig. 6. The data illustrate a significant difference between the distribution of Si and SiO_2, $HSiO_2$, SiO_3. A significant decrease of species intensity on grains from the tailings with citric acid is identified for SiO_2, $HSiO_2$ and SiO_3 but not for Si. Si represents the silicates matrix and therefore for the same feed, surface intensity varies little between samples, and like K and Na ions distribution a greater intensity is reported for the tailings relative to the concentrate.

3.2.4. Collectors on the surface of the four samples

The collector used in the two micro-flotation tests, F1682, mainly contains phosphoric acid ester. The P_xO_y species could reflect the collector distribution information, along with the collector finger print peaks. The collector distribution results (Fig. 7) shows that the signal intensity of collector species is significantly higher on the concentrates relative to the tailings. An obvious increase in concentrate to tailings intensity discrimination was also noted; it is significantly higher on the concentrates and slightly lower on the tailings from the citric acid test relative to the blank test.

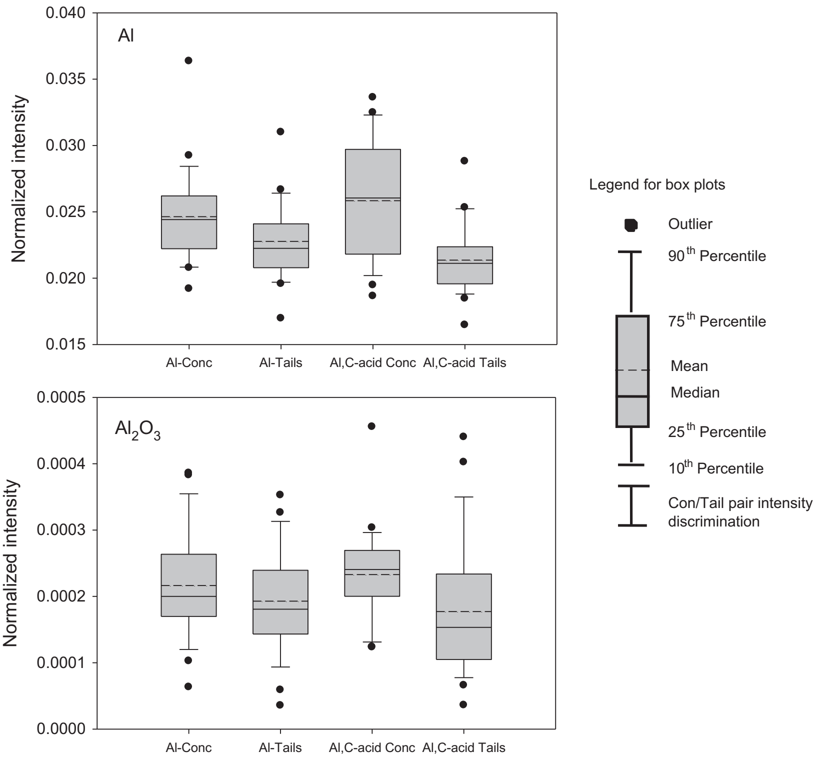

Fig. 4. Normalized intensity of Al and Al_2O_3 on grain surfaces from the blank test (no citric acid addition) and the test with 500 g/t citric acid addition.

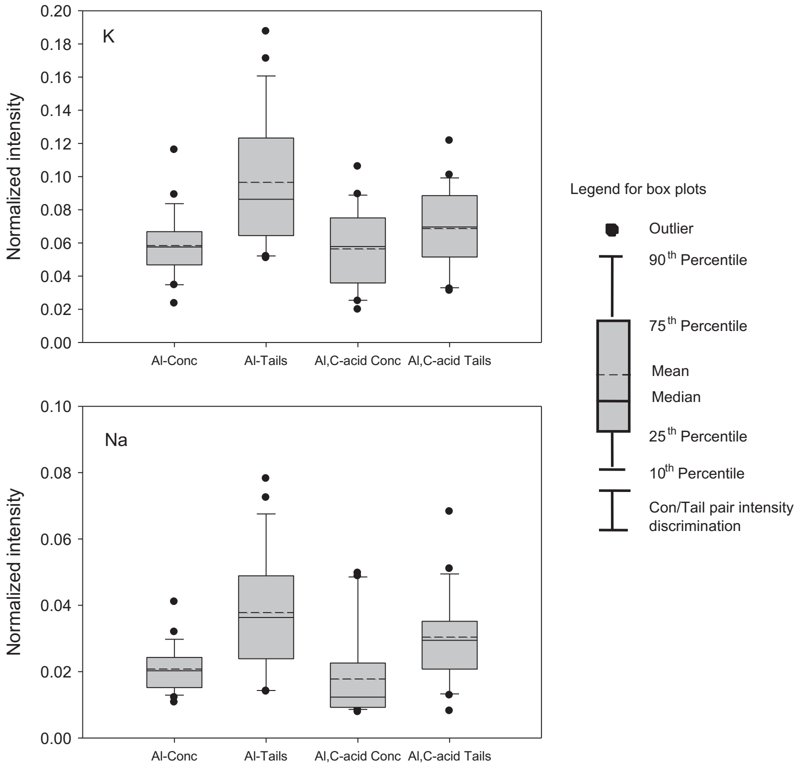

Fig. 5. Normalized intensity of K and Na on grain surfaces from the blank test (no citric acid addition) and the test with 500 g/t citric acid addition.

3.2.5. Citric acid on the surface of the four samples

Citric acid is adopted in the micro-flotation test as a modifier. The flotation test was performed at pH of 6.8–7.2. Two peaks from the negative spectrum of citric acid were identified by a fingerprint study; the results shown in Fig. 8 reveal that the intensities of the peaks indicative of citric acid are slightly higher on the grains from the tailings relative to the concentrates (Al, citric acid conc/tails).

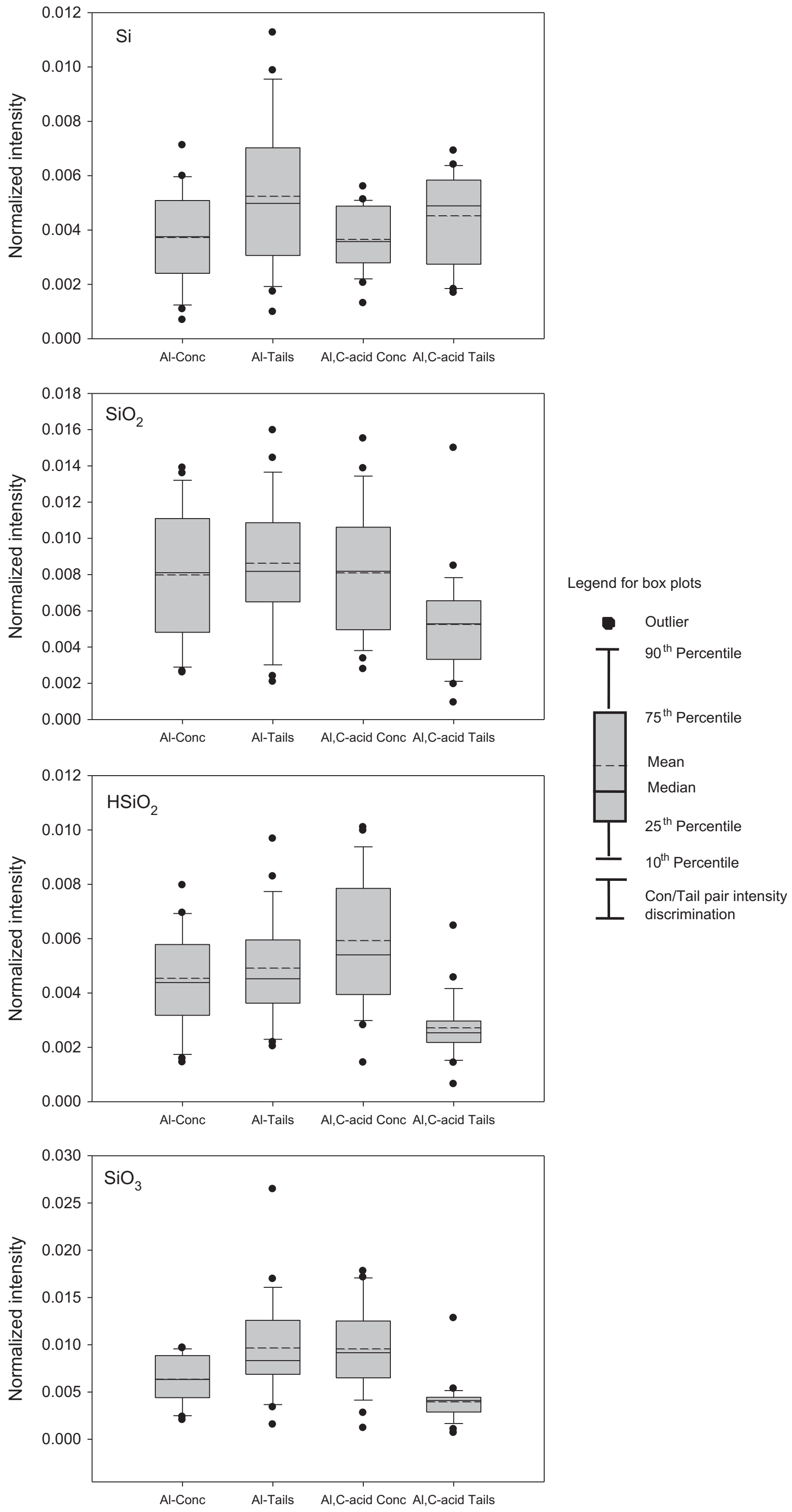

Fig. 6. Normalized intensity of Si species on grain surfaces from the blank test (no citric acid addition) and the test with 500 g/t citric acid addition.

4. Discussion

The normalized intensities of Al, Si, K and Na on the surface of grains analysed are associated with matrix composition. These should reflect the greater proportion of silicates or other gangue minerals reporting to the tailings relative to the flotation concentrates. In this work the Si, K and Na elements showed the same distribution as our previous study. However, with the addition of extra Al ions, the normalized intensity of Al and Al_2O_3 showed the reversed distribution, or a higher proportion of Al (Al_2O_3) on the surface of grains reporting to the concentrate relative to the tailings (Fig. 4). It is indicated that Al ions on the grains surface is not representative of the gangue mineral matrix. Moreover, grains reporting to the concentrate are doing so in response to a

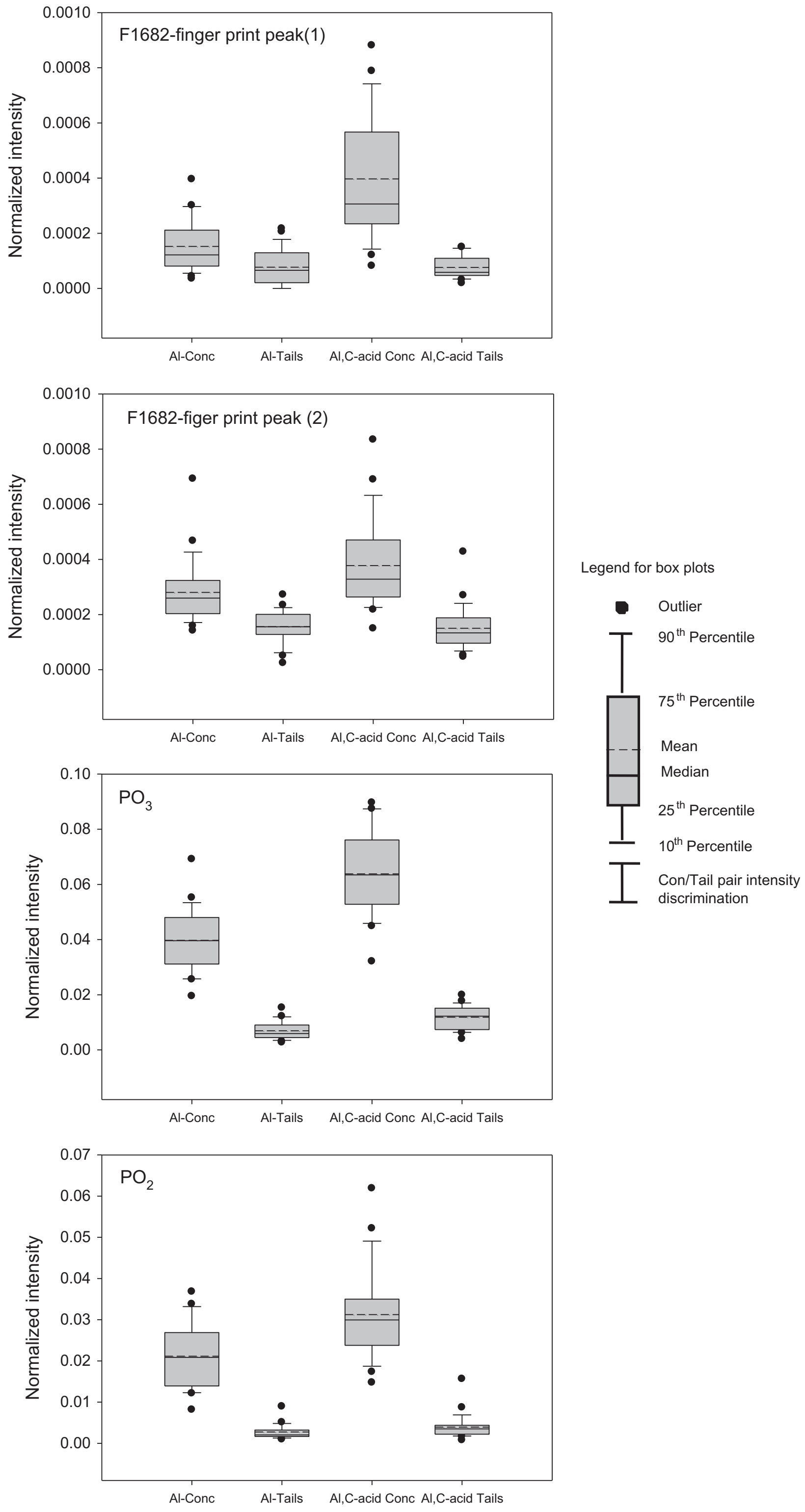

Fig. 7. Normalized intensity of mass positions indicative of the collectors on grain surfaces from the blank test (no citric acid addition) and the test with 500 g/t citric acid addition.

high loading of collector in combination with having more secondary Al on their surface. Subsequently, after the addition of citric acid there is a slight decrease of Al species intensity on the grains from tailings in comparison to the blank tests (Al tails *Vs* Al C-acid Tails). This is attributed to the citric acid on the mineral surfaces having some impact on flotation stream partitioning resulting in the removal of Al ions on the surface of tailings. It is suspected that citric acid as a chelating agent forms soluble, weakly bound complexes with Al ions, which potentially remove the Al ions to aqueous phase.

Species identified as representative of collector F1682 and the peaks of P_xO_y reveal the same distribution as the Al species.

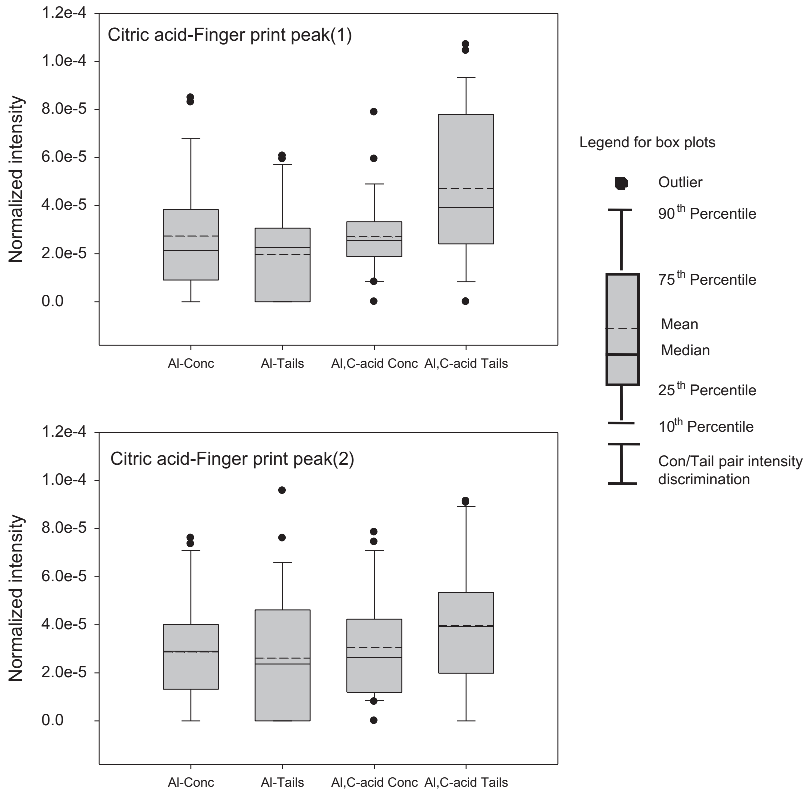

Fig. 8. Normalized intensity of mass positions indicative of citric acid on grain surfaces from the blank test (no citric acid addition) and the test with 500 g/t citric acid addition.

Comparing the tests with and without citric acid, normalized intensity of collector species is significantly higher on the concentrates and slightly lower on the tailings from the test with the addition of citric acid relative to the blank test. The implication here is the presence of the collector on these phases is related to the loading of Al ions on the grain surface. Grains for surface analysis were not differentiated with respect to matrix composition, so that both REE bearing grains and gangue phases reporting to the tailings are in response to less collector attachment and reduced Al surface loading due to the presence of citric acid.

Species of SiO_2, $HSiO_2$ and SiO_3 shows a significant difference between the distributions of Si. It is very clear that the intensity of SiO_2, $HSiO_2$ and SiO_3 on the surface of the grains in the tailings with citric acid is significantly diminished. The large discrimination of concentrates to tailings shown in Fig. 6 suggests that the SiO_2, $HSiO_2$ and SiO_3 on the surface are possibly acting as or representing a site for collector adsorption that played some role in stream partitioning. However after citric acid addition, these sites are inhibited. The data about citric acid loading on the grains surface reflects that citric acid may form surface chelation and potentially acts as a depressant, decreasing the number of active sites for collector adsorption. As a result, the diminished effectiveness of the activation site partitioned the grain to the tailings.

5. Conclusion

In this micro-flotation investigation, it is confirmed that the reduction of REE recovery caused by Al^{3+} cations was reduced or prevented by citric acid. Direct surface chemical characterisation of grains from the streams identified that both REE bearing grains and gangue phases reporting to the tailings are in response to less collector attachment and reduced Al surface loading due to addition of citric acid. It is suggest that citric acid partially forms aqueous soluble metal–ligand complexes resulting in the removal of Al ions from minerals surface. It is also possible form surface chelation inhibiting the active sites, competed for adsorption on gangue minerals depressing the flotation of the silicates.

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