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Explaining surface interactions for common associated gangues of rare earth minerals in response to the oxalic acid

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ABSTRACT

In the flotation of rare earth minerals (REMs), oxalic acid is reportedly acting both as a depressant and pH modifier. Although results of testing have established the significance of oxalic acid in the flotation process, its specific role in either the recovery or selectivity of REMs over their common gangue minerals is not well understood. Pulp pH reduction trials with alternative acids have not shown the same effect on the REMs recovery or the depression of gangue phases. This work studies the effect of oxalic acid on the surface of common REMs gangue minerals (quartz and carbonates (dolomite and calcite)) in a series of conditioning tests. Gangue surface analyses by time of flight secondary ion mass spectroscopy (TOF-SIMS) indicate that oxalic acid inhibits the transfer of secondary ions generated during the conditioning process from one mineral to another. In this regard, the oxalate anion acts to fix ions in solution through chelation, limiting their participation in surface adsorption.

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1. Introduction

A major difficulty in the separation of rare earth minerals (REMs) by flotation is due to their similar surface characteristics with the two main contaminants: carbonates and silicates during the process [1–3]. Oxalic acid is one of the most widely used organic acids to depress the gangue minerals (carbonates and hematite) during flotation of ores that containing valuable oxide minerals (e.g., REMs, pyrochlore, zircon, etc.) [4–6].

Pervious investigations showed that the oxalic acid effectively eliminated the hydrophilic calcium film from the surface of pyrite during flotation, and hence increased the recovery [7]. Furthermore, it was reported that the addition of oxalic acid produced insoluble calcium oxalate dihydrate, decreased the production of $\text{Ca}(\text{OH})_2$ and prevented almost all production of CaCO_3 . The precipitation of Ca-oxalate decreased the concentration of Ca^{2+} in the solution, which in turn reduced the potential for a hydrophilic calcium film to be adsorbed on surface of other minerals. Consequently, the currently adsorbed hydrophilic film turned into an insoluble calcium salt which is then shelled off from the surface of pyrite [7].

In pyrochlore flotation (REMs usually are associated minerals with pyrochlore), oxalic acid is used to decrease pH (from 7 to

below 2), and has been shown to be a selective gangue (silicates and carbonates) depressant when using cationic collectors [8–10]. The oxalic acid reacts with Ca and Mg in solution to form oxalates and, where the process involves carbonate minerals, the consumption of acid can be very high. Electrokinetic measurements indicate that Ca^{2+} and Mg^{2+} cations strongly reduce the negative charge at the pyrochlore surface hindering cationic collector adsorption [11–14], hence a potential for improved recovery by limiting surface passivation. Other acids do not perform as efficiently as oxalic acid as indicated by lower pyrochlore recoveries (Table 1). Moreover, oxalic acid may be more environmentally acceptable relative to other reagents such as sodium hypochlorite, sulphur dioxide and sodium dithionite [7,11,15,16].

Taking all above mentioned phenomena, in the flotation of REMs, oxalic acid has been reported to act both as a depressant and pH modifier, and potentially has been effectively used in treating the surface chemistry of ores that contain quartz, dolomite, calcite, barite, or gangue minerals of a similar nature [4,17,18]. Surface chemistry can be the principal determinant for optimized separation of these minerals from the value minerals (i.e., REMs) by a selective depression, especially when the complexity of the processed ores increases, understanding surface interactions of various minerals during the conditioning is becoming extremely essential. Advanced surface analytical tools as exclusive method can correlate the surface properties of minerals to process

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Table 1
Pyrochlore recoveries with different pH modifiers [15].

Acids	H ₂ C ₂ O ₄	HCl	H ₃ PO ₄	HF
Recovery (%)	54.5	40.2	31.6	50.1

parameters in order to better understand interactions during separation by flotation [19,20].

Several investigations have indicated that time of flight secondary ion mass spectroscopy (TOF-SIMS) has the potential for determining the relative loading inorganic and organic surface modifiers, and mapping their distribution between phases and streams. TOF-SIMS consequently can be utilized as a diagnostic method for process optimization, and detect species with absorption rates in the 10⁻⁹–10⁻⁶ range [19,21–25]. In this investigation, the surface chemistry of common gangue minerals associated with REMs, was studied by using TOF-SIMS to evaluate a model quartz/carbonate system in response to the addition of oxalic acid. The model system was selected as both common gangue minerals in ores containing Nb, Ta and REE bearing minerals.

2. Experimental methods

2.1. Conditioning tests

For the mineralogical investigation, pure minerals and oxalic acid (OA) were prepared from the Niobec plant, west of Saint-Honore near Chicoutimi, Quebec. Minerals (calcite (C) and dolomite (D)) were grinded to +10–75 μm. Several different conditioning tests were performed with quartz and carbonate minerals by oxalic acid (1500 g/t). The tests were limited to two minerals and performed in de-ionized (DI) water (10 cm³) in order to minimize contributions from various other minerals in the pulp. The parameters of the conditioning tests are presented in Table 2. For all tests, the minerals plus DI water and oxalic acid were agitated for 10 min. Following conditioning, the test grains were removed, repeatedly rinsed with DI water, and then immediately transferred to the instrument for analysis. Pulp compositions were analyzed by ICP-OES for major element concentrations. Elements monitored include Na, Mg, A, Si, K, Ca and Fe.

2.2. Surface analysis

To analyze the outer-most 1–3 monolayers of samples, an ION-TOF, TOF-SIMS IV™ was used [26]. The spectra are obtained by bombarding the surface of the particles with a pulsed primary ion beam to desorb and ionize species from grain surfaces. The rate of damage to these uppermost atomic layers is minimized by using extremely low primary ion fluxes [27]. The products of this process

Table 2
Various conditioning tests.

Test	Condition	pH
Quartz only (Q)	Quartz (0.5 g) + deionized water (DIW) (10 cm ³)	7.2
Dolomite only (D)	Dolomite (0.5 g) + DIW (10 cm ³)	7.5
Calcite only (C)	Calcite (0.5 g) + DIW (10 cm ³)	7.4
Quartz + dolomite (Q + D)	Quartz (0.5 g) + dolomite (0.5 g) + DIW (10 cm ³)	7.9
Quartz + calcite (Q + C)	Quartz (0.5 g) + calcite (0.5 g) + DIW (10 cm ³)	7.7
Quartz + dolomite + oxalic acid (Q + D + OA)	Quartz (0.5 g) + dolomite (0.5 g) + DIW (10 cm ³) + oxalic acid (1500 g/t)	3.8
Quartz + calcite + oxalic acid (Q + C + OA)	Quartz (0.5 g) + calcite (0.5 g) + DIW (10 cm ³) + oxalic acid (1500 g/t)	4.4

would be sputtered neutrals as well as positive and negatively charged ions. In this study, for TOF-SIMS analyses, after introducing samples into the instrument, six different locations of each sample (generally 300 μm × 300 μm) were selected and the surface properties of minimum six grains of each mineral type were examined. A detailed of standard TOF-SIMS procedure to analyses surface properties of particles from flotation conditions is outlined by Chehreh Chelgani et al. [9,13,26,27].

3. Results and discussion

Comparative analyses for surface chemical data are discussed in relation to the reported median normalized intensity value for the individual data sets. The median in all figures is defined by the solid line in the box. The decrease in Si intensity on the surface of quartz grains from the test of quartz plus dolomite/calcite implies surface coverage by second phase which is blocking the matrix Si species (Fig. 1). Quartz grain surfaces from the quartz plus dolomite and calcite tests show a significant increase in Mg for the Q + D test along with an increase in Ca for the Q + C test relative to the control test, Q only (Fig. 1).

The data reveal that the decrease in Si intensity on quartz grains is related to surface Mg and/or Ca adsorption. Upon the addition of oxalic acid for both tests, the Si specie intensity does not recover to pristine quartz levels (i.e., that of the Q only test) (Fig. 1). The data suggest that, coincidence with the drop in pH (from ~7.2 Q to ~4 Q + C + OA), dolomite/calcite dissolution may be accelerated resulting in the increase of Mg and Ca ions to the solution for transfer. It is also possible that there is insufficient oxalate ion in the solution for Mg or Ca fixation suggesting that there may be potential requirement for a greater proportion of oxalate ions for chelation. However, the addition of acid could promote an increase in the rate of carbonate dissolution resulting in an increase in the production of Mg and Ca to the solution.

For the surface of dolomite and calcite grains, the decrease in Mg intensity on grains from the Q + D and Q + C tests (Fig. 2) implies surface coverage by second phase results in the blocking

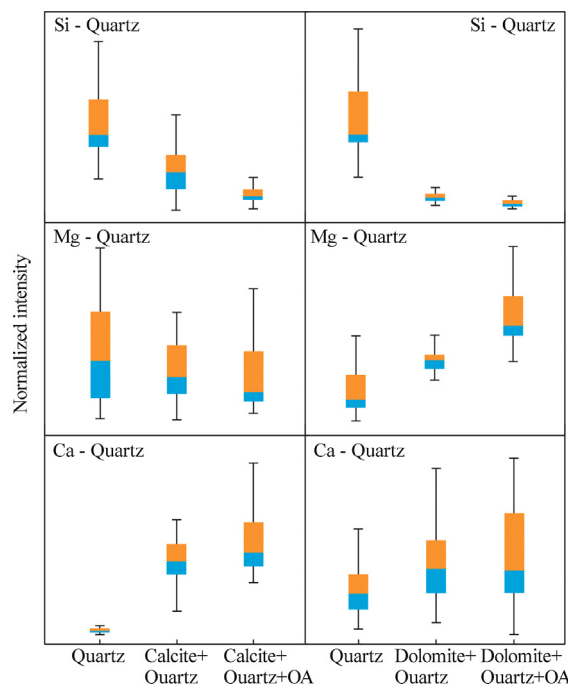


Fig. 1. Box plot showing the normalized intensity of Si, Ca and Mg detected by TOF-SIMS on the surface of quartz grains.

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