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 $Ca(OH)_2$ 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 be 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

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

Acids	$H_2C_2O_4$	HCl	H_3PO_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 cm^3) 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

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
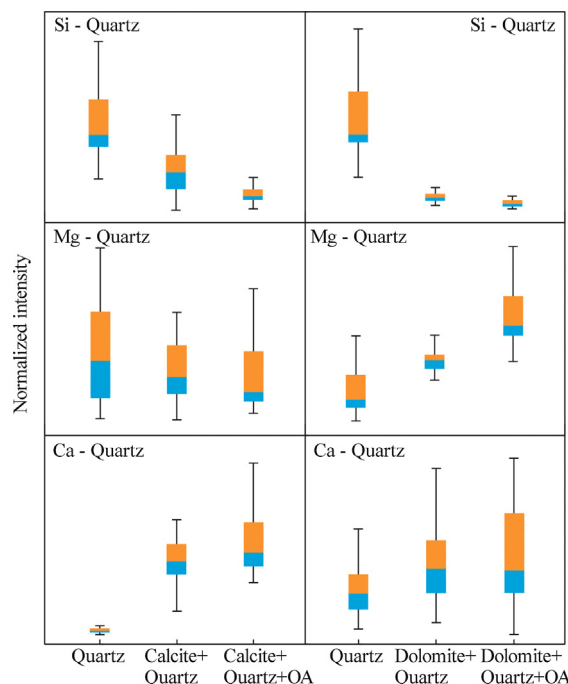
Table 2
Various conditioning tests.

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

Fig. 1. Box plot showing the normalized intensity of Si, Ca and Mg detected by TOF-SIMS on the surface of quartz grains.
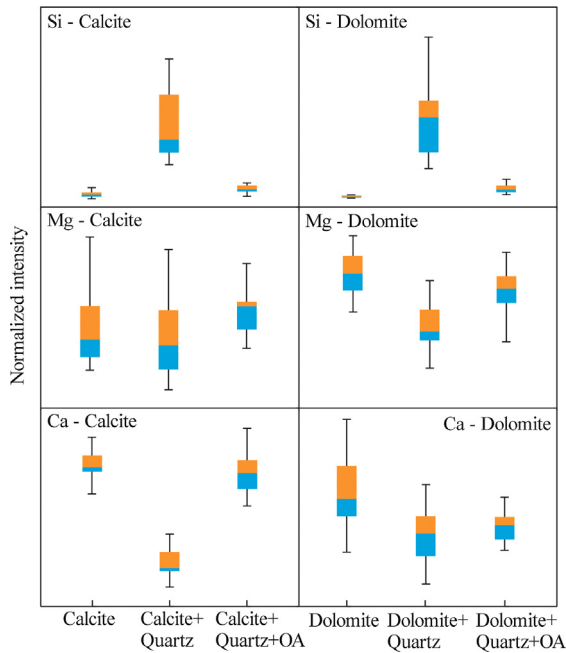
Fig. 2. Box plot showing the normalized intensity of Si, Ca and Mg detected by TOF-SIMS on the surface of carbonates grains.

of matrix Mg, Ca and/or surface Mg/CaO$_x$ species. Dolomite and calcite grain surfaces from the Q + D and Q + C tests show a very significant increase in Si relative to the control test, D and C only (Fig. 2). Upon addition of oxalic acid, however, the Ca (on the calcite) and Mg (on the dolomite) intensity recovers to levels indicative of the pristine carbonate minerals (i.e. that of the C and D only test) while the Si intensity drops to the D & C only test level (Fig. 2). The data suggest that the decrease in Ca and Mg intensity appears to be related to surface Si adsorption and that the concentration of oxalic acid in the tests was sufficient to fix Si and limit transferring to the surface of the dolomite and calcite grains. The decrease in surface Si on dolomite and calcite in the Q + D + OA and Q + C + OA test supports the contention that dissolved Si from quartz is maintained in solution, possibly as an oxalate, thereby inhibiting further precipitation on dolomite and calcite surfaces.

The observed surface chemical relationships are supported by the solution chemistry from the different tests (Fig. 3). The solution data for the Q alone conditioning test show that both the Ca and Mg content are very low while Si is high. Upon addition of carbonates during the conditioning, the proportion of Mg and Ca increases dramatically while that of Si decreases. The decrease in solution Si reflects the surface adsorption of Si on to carbonate grains while the introduction of both Ca and Mg to the system results in their adsorption on the surface of quartz, both of which were identified
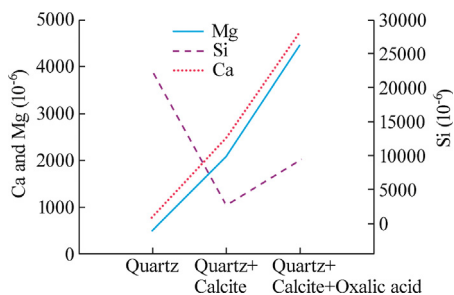
in the surface analyses of quartz and carbonates. With the addition of oxalic acid to the tests, solution Si content increases, while the surface content of Si on both calcite and dolomite decreases to near pristine levels reflecting the chelation of Si during conditioning inhibiting transfer. The continued increase in both Ca and Mg to solution, as a result of a decrease in pH with the addition of oxalic acid, results in the continued build-up of Mg and to a lesser degree Ca on the surface of the quartz. There is some questions as to the nature of the surface Mg and Ca in these tests with oxalic addition.

4. Conclusion

The surface analyses of the carbonate mineral grains from the tests show that there is significant transfer and surface adsorption of species in response to the dissolution of the minerals. The data also suggest that, with the addition of oxalic acid, several species are inhibited from surface attachment. The decrease in surface adsorption or transfer is likely related to the chelating ability of the oxalic acid. The data indicate a number of scenarios for the oxalate ions in the quartz-carbonate mineral system: (1) Oxalate ions do not inhibit the transfer and adsorption Mg and Ca ions from the carbonate minerals to the surface of quartz in the tests; they may however limit the proportion transferred through chelation. (2) Oxalate ions appear to chelate dissolved Si ions effectively not allowing them to precipitate on the surface of the carbonate mineral surfaces. (3) The measured transfer of surface ions between carbonate minerals and quartz both without and with the addition of oxalic acid is very similar. (4) The generation of Ca/Mg ions in solution and transfer to quartz surfaces appears to be difficult to control. (5) The data suggest that the reduction in pH as a result of oxalic acid addition may result in an increased rate of carbonate mineral dissolution and transfer to silicates, and decrease in silicate surface dissolution limiting transfer Si ions to carbonate surfaces. (6) The implication here is that the transfer of Ca and Mg from carbonate minerals may be more prevalent at low pH. The function of keeping ions in solution can have several effects towards improved selectivity or mass recovery. The oxalic acid partially acts to keep dissolved species in solution, therefore limiting their transfer and potential participation in inadvertent activation, as in the case of Si on the carbonate minerals. The bench tests to date suggest that the oxalic acid is least effective in limiting transfer and adsorption for Ca and Mg particularly to the surface of quartz. This is likely related to the significant reduction in pH (7.7–3.8 and 7.2–4.4) and the increased dissolution of carbonates, which are significantly less stable than silicates in the ore, but may also be related to the surface precipitation of Ca and Mg oxalate species. The end result may be that passivation of the silicate grains by a secondary oxalate precipitate inhibits collector attachment, limiting flotation.

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Fig. 3. Solution chemistry of the pulp associated with the conditioning tests.

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