Improvement of calcium mineral separation contrast using anionic reagents: electrokinetics properties and flotation

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Abstract. The flotation separation of salt type calcium minerals is problematic, due to the similarities in their same active Ca^{2+} related site for interaction with anionic collectors and similar physicochemical characteristics such as solubility, zero-point charge, surface speciation and Ca-site density. The work was performed to achieve effective and selective separation of the calcium-minerals using pure minerals samples: orange calcite with Mg impurities, optic calcite with impurities level and an apatite. The pure samples surface was examined using techniques sensitive near-surface like infrared spectroscopy (FTIR) and chemical composition was obtained by ICPMS. The isoelectric point (IEP) and point of zero charge (PZC) in electrolyte were recorded using electrophoresis method at different ionic strengths of the solution. Mechanisms of charge development at the mineral-water interface are discussed. The time of contact as important parameter for the charge equilibrium was deduced from kinetics study and fixed to 30 minutes. The difference in the values obtained between IEP and PZSE can be explained by the presence of a specific adsorption of cations and anions on the surface. The effect of pure anionic collectors such as oleic and linoleic acid were studied. At low pH, both collectors lead to a good recovery for the calcites. The flotation recovery of optic calcite at pH 9 with sodium oleate is higher than with sodium linoleate. At alkaline pH, apatite showed a better recovery with sodium linoleate.

1. Introduction

The separation of salt type minerals such as apatite and calcite from silicates has been successfully carried out by flotation methods. However, the flotation is difficult because of their similar surface properties and high surface reactivity with their conventional collectors such as fatty acid and alkyl sulphate [1] [2]. The surface chemistry of calcium minerals plays an essential role in the interaction between collectors with the mineral surface.

Fatty acids as collectors provides a successful recovery of phosphate via flotation. Indeed, oleic acid is the most common and traditionally used collector for Ca minerals. Additionally, the use of oleic acid may require high temperatures, resulting in high processing cost [3], [4]. Several researchers reported that sarcosine anion selectively adsorbs on the apatite but not on calcite neither dolomite [5]. Due to their high cost and complex synthesis, these collectors, despite they showed improved performance for phosphate flotation, have a limited use in industry. The most extensively used types

of anionic collectors are long-chain fatty acids and their salts, mainly oleic acid or its soap, sodium oleate.

Many studies, over the recent years, used the mixture of the reagents of different molecular carboxylic with non-ionic reagents i.e. aliphatic alcohols to enhance the selectivity in flotation separation of salt-type minerals [2], [6]. The critical micelle concentrations of the mixtures are higher than that of the surfactants alone) [7]. An important step forward in delineating the physical chemistry of flotation systems was bringing the concepts of the electrical double layer and electro kinetic potentials used in the interpretation of flotation phenomena [8].

The Point of Zero Charge (PZC) and isoelectric point (IEP) are two electrokinetics parameters describing the relation between solution pH and surface charge. Accordingly, the close correspondence between the IEP and the PZC of the solid suggests that they are governed by the same equilibrium which can be calculated from thermodynamic solubility data [9]. In addition, the PZC can be determined from the flotation response of the solid when treated with physically adsorbed anionic and cationic collectors. The zero-point of charge of calcite and apatite were investigated here by measuring the electrophoretic mobility solution equilibrium and flotation response of solution pH.

The study of electro kinetic behaviour of calcium minerals was expanded here to several calcite and apatite samples with different origin. This investigation aims at discovering if the trend of zeta *potential* changes would follow the same pattern despite the different origin, and to find the relationship between the zeta potential and the textural properties and the impurities presence in the sample of calcite and apatite. Additionally, we studied the improvement of calcium minerals separation contrast. The floatability of calcite and apatite using oleic and linoleic acid and their mixture with different ratio have been investigated by flotation tests.

2. Materials and methods

2.1. Samples
The calcium-bearing minerals used in this study were optic calcite, orange calcite, and apatite from Madagascar. The mineral samples were ground in agate mortar to achieve <5 μm size fraction for zeta potential measurement. The size fraction -106+38 μm for flotation tests was obtained with a tungsten annular grinder. Collectors used in this paper were 98% pure sodium oleate (Ol) and sodium linoleate (Li) purchased from Fluka-Sigma-Aldrich.

2.2. Characterization
The composition of the samples was determined by FTIR spectroscopy, X-ray diffraction and ICP-MS for trace elements and results are presented in Table 1.

Table 1. Chemicals analysis of Ca-minerals with ICP-MS.

				%					
	CaO	**P_2O_5**	**MgO**	**SiO_2**	**K_2O**	**Na_2O**	**Al_2O_3**	**LOI**	**Total**
Apatite Madagascar	53.45	37.73	-	3.89	-	0.05	-	0.61	95.76
Calcite optic China	55.44	-	0.27	0.06	-	-	-	43.54	99.31
Calcite orange Mexico	54.05	-	1.23	0.07	0.01	0.14	-	43.32	98.82

The influence of impurity ions on the surface charge and zeta potential values was also investigated. Apart from calcium carbonate as the principal component, other common minerals such as calcium sulfate, calcium phosphate, magnesium hydroxide and silica could influence the potential. Nucleation and crystallization of calcium carbonate in hard water seems evident and can be influenced by magnetic field [10], [11]. Despite, the corresponding mechanisms are still unknown, they can be grouped into four basic categories [12]: intra-atomic effects (e.g. changes in electron configuration),

contamination effects (due to magnetically-enhanced dissolution), inter-molecular/ionic effects and interfacial effects (e.g. distortion of the double layer). The major impurities were silica in the apatite sample and magnesium in the calcite orange sample with minor magnesium contents in all the other samples. The apatite sample also contain some quantities of cerium, thorium, lanthanum, neomidium and serium, in that order. Serium is also found in the calcite optic, and especially in the calcite orange. All these impurities may have some influence in the surface properties of these samples.

2.3. Zeta potential measurement
Analysis was conducted with a Zeta meter IV instrument from CAD. 30 mg of the minerals (particles size <5 μm) were first conditioned with 300 ml of KCL (10^{-2} and 10^{-3} M) for 30 min and 20 ml of the supernatant liquid were transferred into the measurement cell to measure the electrophoretic mobility of the particles as a function of pH. The pH of the solution was adjusted with small amounts of HCl and NaOH addition (1%). The zeta potential was calculated using the Smoluchowski equation.

2.4. Flotation tests
Flotation tests using pure minerals were performed in a MINIMET 180 mL cell using 3g of +38-106 μm size fraction samples for each test. The liquid-solid ratio was 1.7%. The pulp was aerated, and the froth product was collected for a total time of 5 min. After completion of the flotation test, the floated and sunk products were filtered, dried at 40 °C, weighed and analysed. The fatty acid collectors were also used as a mixture at sodium oleate: sodium linoléate mass ratios of 1:0, 2:1, 1:1, 1:2 and 0:1 but with the same total concentration of collectors.

3. Results and discussion

3.1. FTIR analysis
The two calcites have fundamental vibration absorption characteristics CO_3^2 groups around 1440 cm^{-1}, 876 cm^{-1} and 713 cm^{-1}. Other most intense bands at 2983 cm^{-1}, 2875 cm^{-1}, 2512 cm^{-1} and 1796 cm^{-1} correspond to harmonic vibrations and/or combinations of CO_3^{2-} groups (Fig. 1).
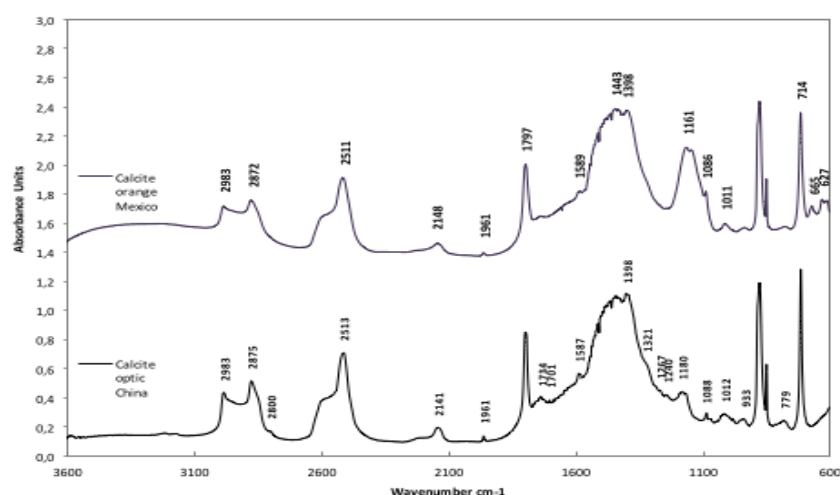

Figure 1. FTIR spectra of calcites samples.

The band at 713 cm^{-1} may correspond both to the presence of calcite and the aragonite. The vibration to 1084 cm^{-1} is, in turn, specific to aragonite. The massive cantered around 1440 cm^{-1} correspond to asymmetric stretching vibrations of CO_3^{2-}. The Mexico orange calcite presents additional bands at 1164, 1143 and 669 cm^{-1} which correspond to the presence of sulphate ions (SO_4^{2-}). vibration bands at 935 cm^{-1} and 849 cm^{-1} present in the orange calcite correspond to specific calcite bands. The orange calcite also shows a band at 775 cm^{-1} which corresponds to quartz.

3.2. *Zeta potential*

The studies show that the IEP of calcite varies with sample history and solution composition. Electrophoretic mobility measurements indicate that the potential-determining ions are not H^+ and OH^-, but rather Ca^{2+} and CO_3^{2-} (or HCO_3^- or $H_2CO_3^0$). This apparent conflict is resolved by a slight modification of the electrical double layer (EDL) model [13]. Thus, the sign and the value of zeta potential should impact the particle adhesion to a solid surface. First, for comparison purpose, in Figure 2 shows the change in zeta potential of calcite optic and orange, and apatite from Madagascar as a function of time in KCl 10^{-2} M for an initial pH of 9.0.
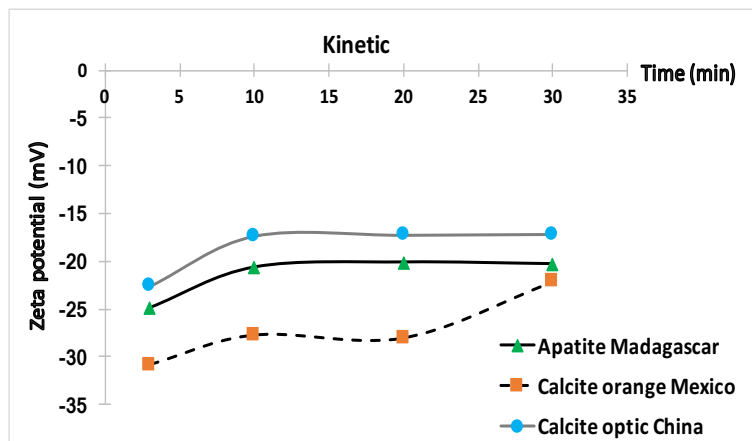

Figure 2. Variation of zeta potential of calcites and apatite with mixing in KCL 10^{-2} M at pH 9.

The zeta potential of the minerals at pH 9.0 is negative with the zeta potential of calcite orange being larger than that of the apatite from Madagascar. The zeta potential appears to decrease in magnitude in the first 10 minutes of conditioning. Figure 3 shows that the pH of the solution containing calcite and apatite increases in the first 30 min of conditioning before plateauing at longer times. Somasundaran and Agar [14] reported a similar increase in pH with conditioning time of calcite until an equilibrium pH value was reached when the initial pH values were acidic or neutral, while pH was found to decrease to a similar equilibrium pH value when the initial pH values were basic. This equilibrium pH value at 8.2 was associated to the point of zero charge of calcite. For calcite at low pH values, carbonate in solution or at the surface consumes proton ($CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-$) resulting in a pH increase while at high pH values calcium in solution or at the surface consumes hydroxyl ions ($Ca^{2+} + OH^- \Leftrightarrow CaOH^-$) resulting in a pH decrease. In all the suspensions, the pH increased on the time scale. The only conclusion that at present might be drawn is that the measured zeta potentials are still not equilibrium ones and they are not determined by the pH of the bulk phase. Thus, they are determined rather by concentrations of Ca^{2+} and CO_3^{2-} in the solution and especially by the latter ones. Moreover, pH 8.2 is the experimental isoelectric point of calcite [14]. At pH values, lower than the IEP, the solution will become more alkaline by addition of calcite. At high pH values, the reverse is true, and the pH of solution will decrease.
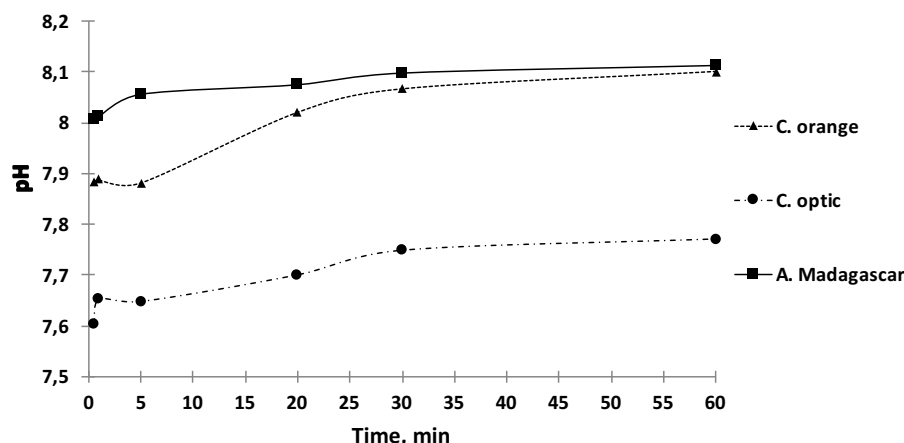
Figure 3 Changes of pH versus time for calcites and apatite in 10^{-2} M KCl.

The ionic impurities affect the zeta potential of freshly precipitated $CaCO_3$ in comparison with that of pure carbonate. The presence of Fe^{2+} keeps the potential positive during 2 h [15], while SO_4^{2-} causes it negative. The effect of Mg^{2+} on the zeta potential is less clear, thought it can form isomorphic replacement. It is possible to suggest the similar behaviour of Mg^{2+} as for Fe^{2+} because of close ionic radius to Ca^{2+}. Thus, the effect of Mg^{2+} and SO_4^{2-} ions released in solution from the impurities on the zeta potential of calcium carbonate probably results from their specific adsorption on the hydrolysed surface, comparing respective zeta potential and pH changes.

Indeed, the sites on the surface of the calcite may be likened to two types of primary hydration sites/protonation: $\equiv CaOH^0$ and $\equiv CO_3H^0$ products by the reactions of protonation and hydration of the surface sites of calcite in aqueous medium, control the calcite surface reactivity [16]. Other point can be determined by potentiometric titrations, it is the point without salt effect (PZSE). According to the theory, all charges curves obtained for different ionic strengths intersect at a point corresponding to PZSE which is considered as PZC. Indeed, the point of zero charge, the number of positive groups is equal to negative groups; therefore, the surface is generally neutral. However, a change in ionic strength or an electrolyte concentration change must leave the invariant surface charge for this pH. It is different for the other pH since in this case the surface charge will end up strongly screened by the ions against the electrolyte and therefore the surface charge is measured will change. Indeed, when the solution pH is more basic than the PZSE, negative ions and complexes will predominate at the interface and the surface will be negatively charged. In a similar way, when a solution pH is more acidic than the PZSE, positive species will predominate and the surface will be positively charged. The PZSE obtained from the potential measurements may differ from the IEP if any specific adsorption of ion occurs (Figure 4).
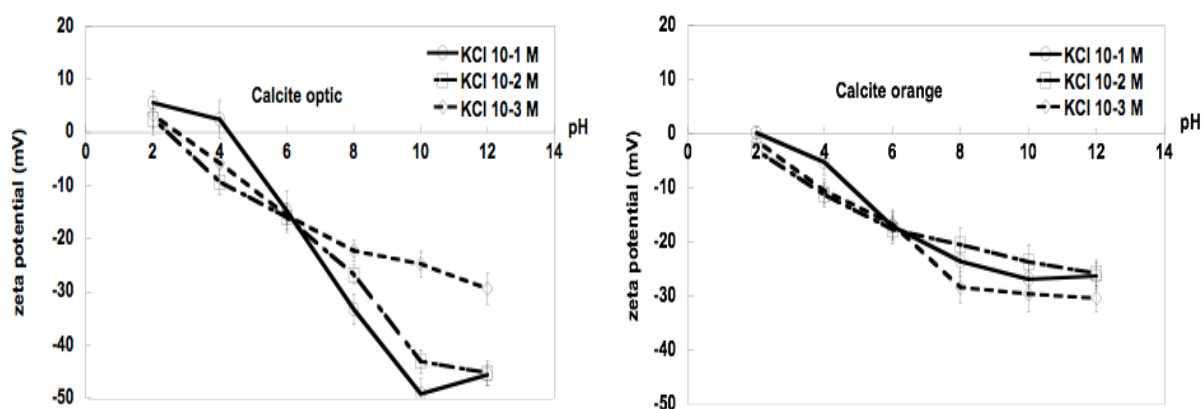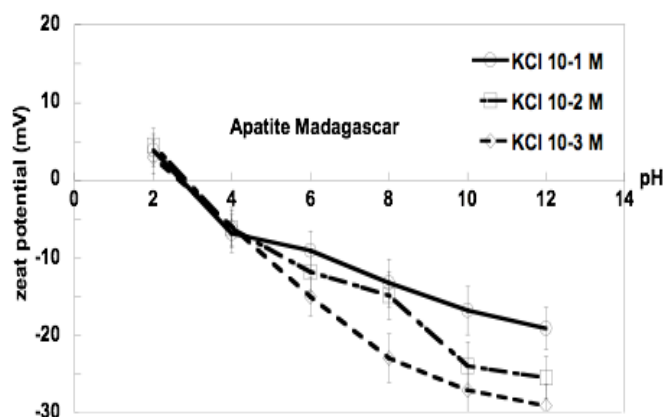
Figure 4. Zeta potential dependence of calcites and apatite on the pH. Supporting electrolyte is 10^{-1}, 10^{-2} and 10^{-3} M KCl.

Thus, this difference can be observed if equilibrium has not yet been attained. Therefore, Ca^{2+} and HCO_3^- are the principal potential determining ions, then a PZSE higher than the IEP (as observed here for calcite and apatite) could be explained, because the calcium ion, being bivalent, would be specifically adsorbed.

3.3. *Flotation tests*

Flotation recovery was studied in the pH range of 5-11 for all minerals at a collector concentration of 10^{-5} M and results are presented in Figure . With increasing pH, calcite recovery decreases while apatite recovery increases when using oleate as the collector. The high mineral recovery obtained is the result of collector adsorption on the mineral surface because recovery of these minerals in the absence of collector is low (<10%) and attributed to entrainment.

In the equilibrium stability diagram of oleic acid, neutral oleic acid is the more stable species at pH values below 8 in both the aqueous and liquid form while at higher pH values negatively charged oleate species as monomer or dimer are dominant. As the concentration of calcium dissolved from calcite increases with decreasing pH values, this should result in more calcium-oleate complex formation ($Ca(OL)_{2.s}$) at the solution-mineral interface followed by its precipitation on the mineral surface, which should therefore increase calcite flotation as pH decreases. Figure 5 shows that the trend in apatite recovery with pH is the same in the presence of oleate or linoleate. It is postulated that the presence of two double bonds and more precisely the stronger chain-chain interaction in the linoleate dimer than in the oleate dimer, increases the interaction with calcium ions in solution (lower solubility of the calcium-(linoleate)$_2$ complex).
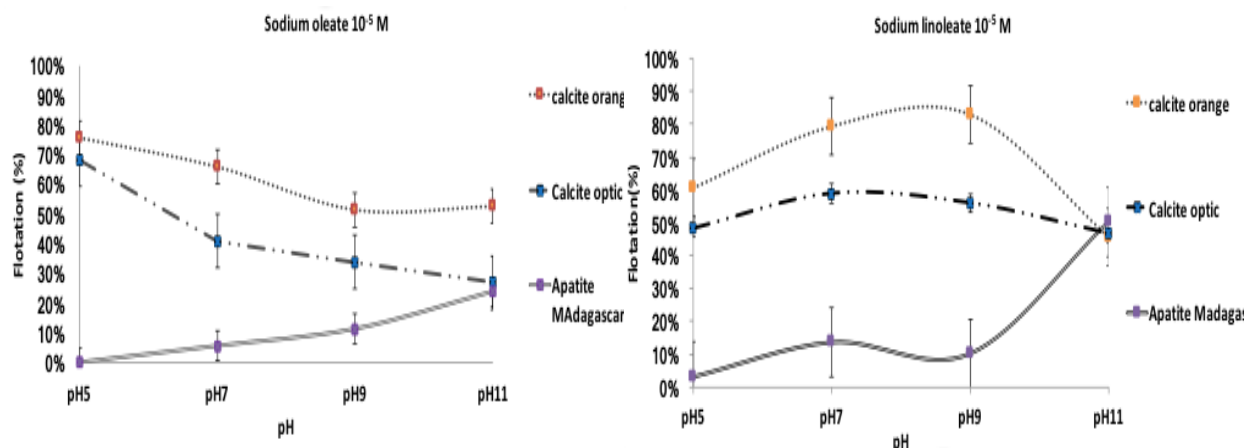
Figure 5. Flotation recovery as a function of pH, in the presence of 10^{-5}M sodium oleate (top) or linoleate (bottom).

This mechanism is also supported by the fact that the dimer, $(linoleate)_2H^-$, is more stable at an intermediate pH value where calcite recovery is at its maximum value (Figure), there are obviously considerable differences in flotation efficiency between them. At low pH, both the collectors lead to a good recovery for the calcites, while with optic calcite and orange calcite the use of sodium oleate shows a better flotation recovery than with linoleate. At higher pH, the trend is reversed showing better recovery with sodium linoleate. The decrease of flotation with calcite below pH 9.0 is due to its dissolution. At pH values below 8 oleate exists in solution mainly in the form of neutral oleic acid molecules and precipitated oleic acid.

However, at pH 9, flotation of calcite is lower which may be due to saturation of the surface, which can cause a decrease in adsorption strength of the collectors. But according to [16], at pH above 8.2, the $CaCO_3^-$ group mainly composes the surface of calcite; and the collector cannot fix and calcite floats less. Thus, at this pH, the use of sodium linoleate alone is more efficient than the oleate alone.

The only differences between surface properties of calcite and apatite are at the level of dissolution of the mineral content, and the proportion of species and group located on their surface. The Ca^{2+} site density on the surface of these minerals is almost identical. The most common chemical species on the surface of these two minerals are Ca^{2+} and HCO_3^-. Then, Ca^{2+} is more important in proportion to pH 8 on the surface of the calcite and HCO_3^-, on the surface of the apatite. According to the species distribution diagram of oleic acid [19], we can note that the concentrations of oleic ion monomer and dimer remain almost constant above the precipitation pH and decrease sharply below it

4. Conclusion

Following of electrokinetics studies the calcites and apatites separation were discussed in this paper by using anionic collectors. The close correspondence between the IEP and the PZSE determined for calcite and apatite shows different values. The zeta potential experiments implied that chemical adsorption was achieved in the surface of calcium minerals. The surface charge of calcite and apatite became more negative after adsorption of sodium oleate and sodium linoleate. The maximum flotation recovery of calcite and apatite was obtained at low and high pH, respectively. The results are consistent with the oleic and linoleic acid hydrolyses to form ions ($RCOO^-$) at high pH and molecules ($RCOOH$) at acid and neutral pH which defines the differential behaviour of two calcium minerals.

5. References

[1]   S. K. Mishra 1982 Electrokinetic properties and flotation behaviour of apatite and calcite in the presence of sodium oleate and sodium metasilicate *Int. J. Miner. Process.* **9** 59–73.

[2]   I. V. Filippova, L. O. Filippov, A. Duverger, and V. V. Severov 2014 Synergetic effect of a mixture of anionic and non-ionic reagents: Ca mineral contrast separation by flotation at neutral pH *Miner. Eng.* **66–68** 135–44.

[3]   H. Sis and S. Chander 2003 Reagents used in the flotation of phosphate ores: a critical review," *Miner. Eng.* **16** 577–85.

[4]   G. Ying-yong, G. Shun-peng, X. Zeng, and Y. Yu 2008 Double reverse flotation process of collophanite and regulating froth action *Trans. Nonferrous Met. Soc. China* **18** 449–53

[5]   J. Gordeijev and P. Hirva 1999 Theoretical studies on the interaction of oleoyl sarcosine with the surface of apatite *Surf. Sci.* **440** 321–26.

[6]   L. Filippov, A. Duverger, I. Filippova, H. Kasaini, and J. Thiry 2012 Selective flotation of silicates and Ca-bearing minerals: The role of non-ionic reagent on cationic flotation *Miner. Eng.* **36–38** 314–23.

[7]   K. H. Rao, J. M. Cases, P. De Donato, and K. S. E. Forssberg 1991 Mechanism of oleate interaction on salt-type minerals *J. Colloid Interface Sci.* **145** 314–29.

[8]   A.Gaudin, D. Fuerstenau 1955 Quartz flotation with anionic collectors *Trans AIME* **202** 66–72.

[9]   G. Parks and P. de Bruyn 1962 The zero point of charge of oxides *Phys Chem* **66** 967–73.

[10] E. Chibowski and L. Hołysz 1995 Changes in zeta potential of TiO2 and CaCO3 suspensions treated with a radiofrequency electric field as measured with a Zeta Plus instrument. *Colloids Surf. Physicochem. Eng. Asp.* **105** 211–20.

[11] K. Higashitani, H. Iseri, K. Okuhara, A. Kage, and S. Hatade 1995 Magnetic Effects on Zeta Potential and Diffusivity of Nonmagnetic Colloidal Particles *J Colloid Interface Sci* **172** 383–88.

[12] J. S. Baker and S. J. Judd 1996 Magnetic amelioration of scale formation *Water Res.* **30** 247–60.

[13] S. L. S. Stipp 1999 Toward a conceptual model of the calcite surface: hydration, hydrolysis, and surface potential *Geochim. Cosmochim. Acta* **63** 3121–31.

[14] P. Somasundaran and G. E. Agar 1967 The zero point of charge of calcite *J. Colloid Interface Sci.* **24** 433–40.

[15] E. Chibowski, L. Hotysz, and A. Szcześ 2003 Time dependent changes in zeta potential of freshly precipitated calcium carbonate *Colloids Surf. Physicochem. Eng. Asp.* **222** 41–54.

[16] O. S. Pokrovsky, J. Mielczarski, O. Barres, and J. Schott 2000 Surface Speciation Models of Calcite and Dolomite/Aqueous Solution Interfaces and Their Spectroscopic Evaluation *Langmuir* **16** 2677-88.

[17] D. Fuerstenau 1956 Streaming Potential Studies on Quartz in Solutions of Aminium Acetates in Relation to the Formation of Hemi- micelles at the Quartz-Solution Interface **60** 981–85.

[18] D. W. Fuerstenau and Pradip 2005 Zeta potentials in the flotation of oxide and silicate minerals," *Adv. Colloid Interface Sci.* **114–115** 9–26.

[19] P. Somasundaran, K. P. Ananthapadmanabhan, and I. B. Ivanov 1984 Dimerization of oleate in aqueous solutions *J. Colloid Interface Sci.* **99** 128–35.