

Received August 7, 2017; reviewed; accepted February 15, 2018

## The effect of polyacrylic acid on the surface properties of calcite and fluorite aiming at their selective flotation

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**Abstract:** In this study, the polyacrylic acid (PAA) was studied as a selective depressant for calcite in the selective flotation of fluorite and calcite, and the implications of this process for the separation of fluorite ore were studied using micro-flotation tests, and the results were analyzed with Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analyses. The flotation tests indicated that the preferential adsorption of PAA onto calcite rather than sodium oleate (NaOl) could selectively depress the flotation of calcite, allowing its separation from fluorite at pH 7. The zeta potential of calcite became more negative with the addition of PAA rather than with NaOl. However, the characteristic features of PAA adsorption were not observed for fluorite, suggesting that NaOl preferentially adsorbed on the surface of fluorite, or that PAA could be replaced by NaOl on the fluorite surface. FT-IR and XPS analysis were utilized to obtain a better understanding of the mechanism by which PAA was more strongly adsorbed on the calcite surface than NaOl. This was revealed to occur through chemical bonding between the carboxyl group of PAA and the hydroxyl groups of the Ca species on the calcite surface, modifying the structure of the adsorbed layer. A possible adsorption mechanism, along with a postulated adsorption mode for the surface interaction between PAA and calcite, is proposed.

**Keywords:** fluorite, calcite, selective flotation, polyacrylic acid

### 1. Introduction

Fluorite (CaF<sub>2</sub>) is an important nonrenewable mineral that is primarily used in the production of hydrofluoric acid and as a flux agent in steelmaking (Zhang and Song, 2003). Fluorite often coexists with calcite, and the two minerals must be separated by froth flotation (Aliaga et al., 2006; Song et al., 2006; Zawala et al., 2008).

Froth flotation has been regarded as one of the most effective physicochemical techniques for the separation and utilization of fluorite ores (Zhou et al., 2013; Gao et al., 2015). Fatty acids are the most commonly used anionic collectors for the flotation of the mineral fluorite, and thus, have been widely studied for fluorite flotation. Since the similar active Ca sites are present on the cleavage planes of many calcium-containing minerals, commonly used anionic collectors, such as sodium oleate, can strongly collect all these minerals, and exhibits little selectivity (Castro and Hoces, 1993; Sadowski, 1993; Castro et al., 1998; A. Lopez-Valdivieso A et al., 2000; Liu et al., 2016). Moreover, when sodium oleate is used as the collector, a large amount of water glass (WG), i.e., sodium silicate, must be added to depress calcite and fluorite to achieve selective separation (Castro et al., 1998; Shi et al., 2014; Bo et al., 2015). However, excessive WG in the pulp also reduces the floatability of fluorite (Kang et al., 2017). Therefore, satisfactory separation of fluorite and calcite is not always achieved in industry. In order to improve

this situation, the efficient flotation separation of fluorite from calcite minerals will require more selective depressants than have been previously reported.

Polyacrylic acid (PAA) is a commercial flocculant and scale inhibitor which is widely used in industry (Das and Somasundaran, 2004; Tang et al., 2008; Drzymala and Fuerstenau, 2014). Flocculation takes place when high-molecular weight polymers of PAA adsorbed on colloidal particles. PAA exhibits a "threshold effect" on  $\text{CaCO}_3$  inhibition, by which it can absorb the crystal phases growing on the nuclei and prevent vaterite from transforming into aragonite or calcite, resulting in distortion and retardation of the crystal growth. The combination of these two processes results in intensive absorption of PAA onto calcite. Until now, however, few reports have focused on the use of PAA as the depressant for fluorite flotation.

In this study, the flotation behavior of polyacrylic acid (PAA) at the  $\text{CaF}_2/\text{NaOI}$  and  $\text{CaCO}_3/\text{NaOI}$  interfaces and its effect on flotation performance were investigated. The aim of the present work was to reveal the effect of PAA on the interaction of fluorite with calcite. Micro-flotation tests, zeta-potential measurements, FT-IR, and XPS analysis were employed to shed light on the relationship between the flotation mechanism and the selective adsorption behavior of PAA.

## 2. Materials and methods

Pure fluorite and calcite samples were obtained from Hunan, China. X-ray powder diffraction (XRD) spectra (shown in Fig. 1) confirmed that the purities of the fluorite and calcite samples were greater than 98.41% and 97%, respectively. The fraction with a particle size of  $-74+37 \mu\text{m}$  was used for the flotation tests. The samples ground to  $-5 \mu\text{m}$  in an agate mortar were used for the infrared spectra and zeta potential measurements.

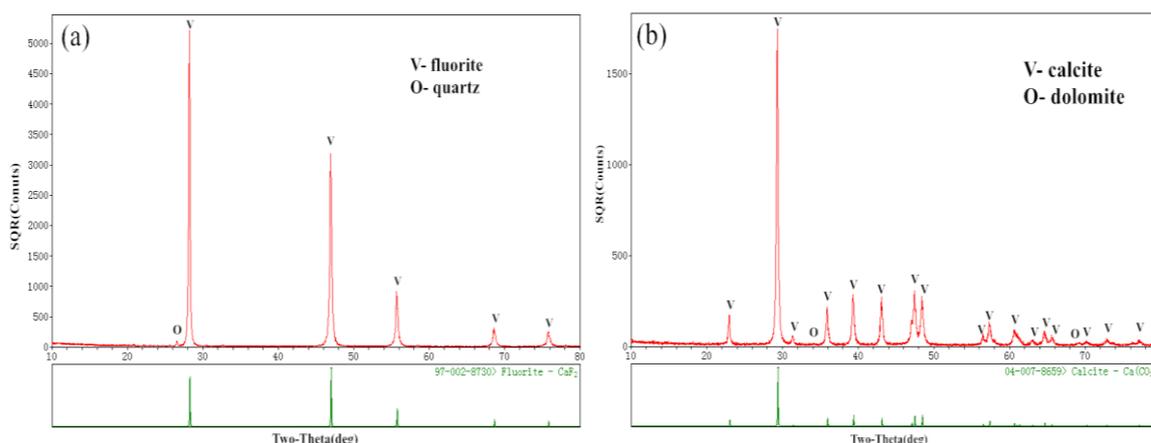


Fig. 1. XRD spectra of the fluorite (a) and calcite samples (b) used for the flotation tests

Chemically pure reagents, Polyacrylic acid ( $\text{C}_3\text{H}_4\text{O}_2$ , average molecular weight M.W.  $\sim 2000$ ) and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) were obtained from Aladdin Biological Technology Ltd., Shanghai, China. Sodium oleate ( $\text{NaOI}$ ,  $\text{C}_{18}\text{H}_{33}\text{O}_2\text{Na}$ ) was obtained from Baisaiqin Chemical Technology Co., Ltd., Shanghai, China. The pH was adjusted with NaOH or HCl stock solutions. Additionally, deionized water (DI,  $18 \text{ m}\Omega\text{-cm}$ ) was used for all experiments.

### 2.1 Micro-flotation experiments

Pure mineral flotation tests were carried out with an XFG-type flotation machine with a  $40 \text{ cm}^3$  Plexiglas cell, and the impeller speed was set to 1650 rpm. Pure mineral particles (2.0 g) were placed in the plexiglas cell that was filled with  $35 \text{ cm}^3$  of DI water. The pH of the suspension was adjusted by adding HCl or NaOH; after the conditioning for 2 min, the depressant was then added. After 3 min of conditioning with the depressant, the collector ( $\text{NaOI}$ ) was added, and the suspension was agitated for 3 min.

For individual mineral flotation, the float and sink products were collected, filtered, and dried. The flotation recovery was calculated based on the solid weight distribution between these two products.

The micro-flotation experiments were repeated three times, and the average value was reported as the final value.

## 2.2 Zeta potential measurements

Zeta potential measurements for the particles were conducted using a zeta potential analyzer (Zeta Plus, Bruker, Germany) at 20°C. A 0.02 g of solid was added into 40 cm<sup>3</sup> of 0.01 mol/dm<sup>3</sup> KCl (a background electrolyte) at a given pH and reagent concentration. After the suspension was left to settle down the coarse particles for 5 min, the supernatant was used for the zeta potential measurements. The average of three independent measurements was calculated with a typical variation of ±5 mV.

## 2.3 FT-IR spectral analysis

Fourier transform infrared (FT-IR) spectra of the samples as KBr pellets were recorded in the range 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> using a Bruker Alpha (Thermo, USA) FT-IR spectrometer at room temperature (25±1°C). The experimental procedure for powdered samples was as follows: 50 mg of a mineral sample was mixed with 30 cm<sup>3</sup> of distilled water in the absence or presence of 7.5 mg/dm<sup>3</sup> depressants at pH 7 and 25°C. After being stirred for 30 min, the sample was filtered, and a vacuum-drying method was used to obtain the solid for the subsequent analysis. The untreated mineral was used to record a reference infrared spectrum.

## 2.4 XPS analysis

The XPS spectra of fluorite, calcite, and Ca(OH)<sub>2</sub> before and after the addition of PAA were recorded using a K-Alpha 1063 (Thermo Scientific Co., USA) spectrometer with Al Ka as the sputtering source at 12 kV and 6 mA, with a pressure of 1·10<sup>-12</sup> Pa in the analytical chamber. A value of 284.7 eV was used as a C1s reference to calibrate the binding energy.

## 3. Results and discussion

### 3.1 Micro-flotation experiments

The flotation behavior of fluorite and calcite minerals in the absence of PAA is given in Fig. 2. As shown in Fig. 2a, the flotation recovery of fluorite and calcite increased sharply as the initial concentration of NaOl increased from 4 mg/dm<sup>3</sup> to 16 mg/dm<sup>3</sup>. Beyond this concentration, the floatability did not increase notably.

Fig. 2b demonstrates that the flotation recovery of fluorite and calcite varied as a function of pH at a fixed NaOl concentration of 14 mg/dm<sup>3</sup>. The recovery of fluorite initially increased gradually with increasing pH, but then decreased at pH > 7. In contrast, the recovery of calcite increased with the increasing pH from pH 6 to 11. Notably, the difference in the recoveries of the two minerals was only about 5% at pH 7. Thus, conditions of 16 mg/dm<sup>3</sup> NaOl and pH 7 were used for all subsequent flotation tests.

From Figs. 2a and 2b, it can be noted that NaOl had a strong adsorption effect on both minerals in weakly alkaline solution, and led to a high recovery of fluorite and calcite in this basic region. Therefore, it is impossible to separate fluorite from calcite using NaOl as the collector without the addition of PAA.

The floatability values of fluorite and calcite using various PAA concentrations and pH values at a fixed NaOl collector concentration are shown in Fig. 3. Fig. 3a clearly indicates that the flotation recovery of calcite dramatically decreased as the PAA concentration increased up to approximately 7.5 mg/dm<sup>3</sup> PAA. At higher PAA concentrations, the recovery decreased very slightly. The difference between the flotation recoveries of calcite and fluorite slowly increased as the PAA concentration was increased from 0 to 40 mg/dm<sup>3</sup>. As expected, the decline was not large in the PAA range from 0 mg/dm<sup>3</sup> to 10 mg/dm<sup>3</sup>. Using a fixed NaOl concentration, the flotation recovery of calcite was less than 12% at a PAA concentration of 7.5 mg/dm<sup>3</sup>, while the flotation recovery of fluorite was greater than 70%. Thus, by adding an appropriate amount of PAA, calcite can be effectively depressed with little depression of fluorite. In other words, within a specific concentration range, PAA greatly hindered the interaction of the calcite surface with NaOl without significantly affecting the fluorite-NaOl interaction.

In addition, the effect of the pH of the pulp on the preferred depressant PAA (7.5 mg/dm<sup>3</sup>) was studied, and the results are presented in Fig. 3b. The flotation recovery of calcite was less than 12% throughout the entire range of pulp pH values studied, which illustrated that the inhibition of PAA on the calcite-NaOl interaction was not affected by pH. Excellent flotation performance was achieved for fluorite at pH 8, but compared to the results in the absence of PAA, the recovery of fluorite was slightly lower. These results demonstrate that separation of fluorite from calcite was effectively achieved at pH 8 using the depressant PAA.

From the above phenomenon, we assumed that a preferential adsorption site for PAA existed on the surface of calcite, and that the preference for the adsorption of PAA should be stronger on calcite than on fluorite. Therefore, the adsorption mechanism of PAA at the CaF<sub>2</sub>/NaOl and CaCO<sub>3</sub>/NaOl interfaces was further investigated.

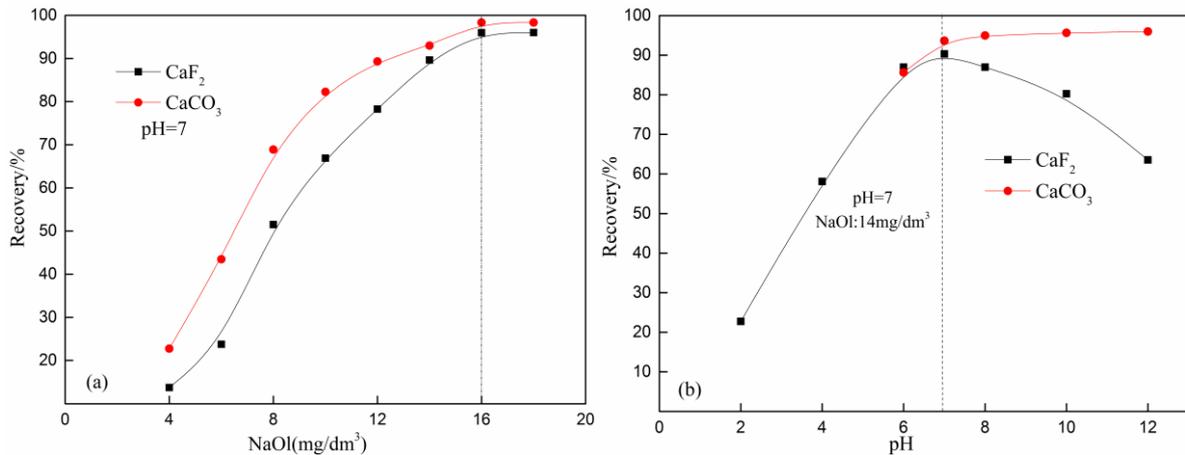


Fig. 2. Recovery of fluorite and calcite as a function of NaOl concentration (a) pH (b)

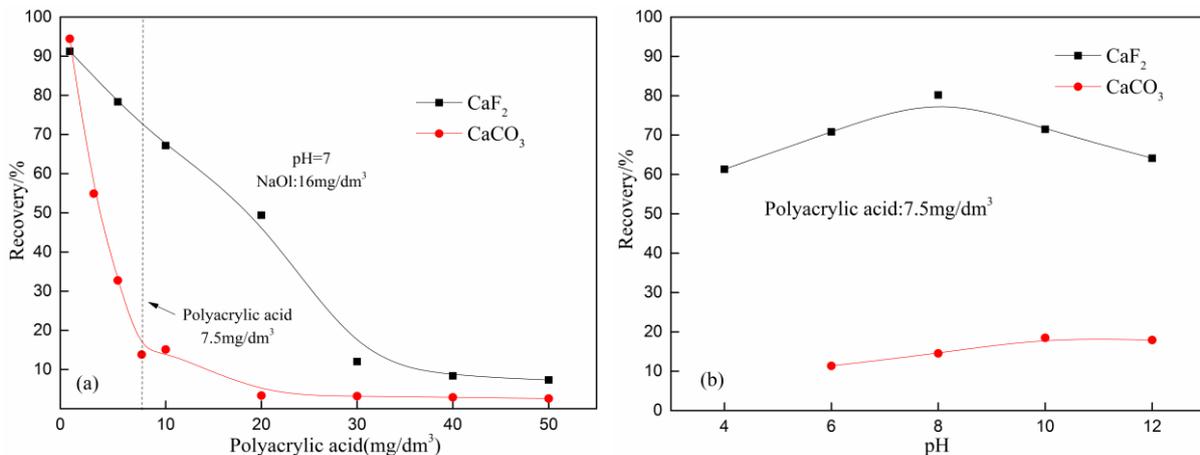


Fig. 3. Recovery of fluorite and calcite as a function of polyacrylic acid concentration (a) pH (b)

### 3.2 Zeta potential measurements

The zeta potential is normally obtained during the flotation field to study the electro-kinetic changes that occur on the mineral surfaces due to conditioning in an aqueous system with flotation reagents. Figs. 4a and 4b show the zeta potential of fluorite and calcite as a function of pH with and without PAA treatment and in the absence or presence of NaOl. The isoelectric point (IEP) of the fluorite untreated with any reagent occurred at approximately pH 7.5 (Miller et al., 2004; Shoeleh Assemi et al., 2006), and that of untreated calcite was pH 9.4. These values were consistent with previous reports (Hu and Xu, 2003; Yuan et al., 2008).

The zeta potential of fluorite underwent a pronounced shift towards more negative zeta potentials in the presence of NaOl, indicating that the oleate anions were adsorbed onto fluorite through electrostatic forces and chemical adsorption of calcium dioleate. The fluorite particles reached a

maximum floatability at neutral pH, and poor floatability was observed at pH 8-10, which was in agreement with the previous flotation tests. Additionally, when PAA was added, the zeta potentials became highly negative, and the IEP value was lower than that of untreated fluorite, indicating that coating occurred. In the presence of NaOl, the decrease in the zeta potential at pH < 4 was larger for PAA-treated fluorite than for untreated fluorite, demonstrating that NaOl and PAA were both adsorbed on the surface of fluorite at the same time. However, the opposite behavior was observed at pH > 4. This finding indicated that NaOl either caused desorption of PAA from the fluorite surface or replaced PAA in this pH range.

Fig. 4b shows the zeta potential of calcite treated with PAA and untreated calcite as a function of pH in the absence or presence of NaOl. The zeta potential of calcite became markedly more negative in the presence of reagents, similar to the trend that was observed in fluorite, indicating that the reagents were adsorbed onto the surface of the minerals. The negative shifts in the zeta potential values of calcite in the presence of PAA were larger than those obtained when only NaOl was added, indicating that the adsorption capacity of PAA on the calcite surfaces was stronger. Furthermore, the largest decrease in the zeta potential occurred after treatment with PAA in the presence of NaOl. This finding deviated from other flotation study results. This difference could be attributed to the formation of a PAA/CaCO<sub>3</sub> surface, which was subsequently covered by an additional layer of excess NaOl. This implied that the adsorption of PAA on the calcite surface was not affected by NaOl, and that the depressant mechanism was related to the adsorption mode.

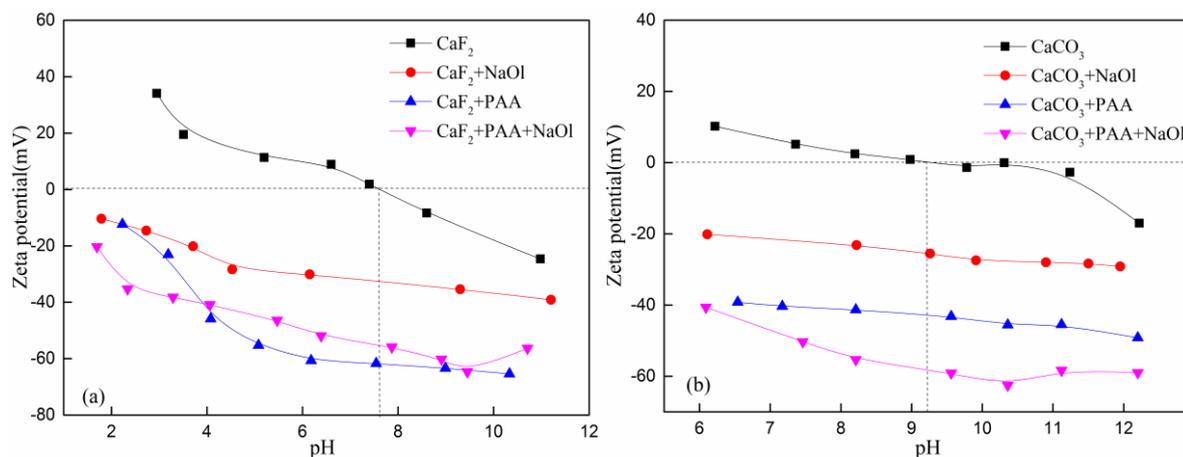


Fig. 4. Effect of the addition of different reagents on the zeta potentials of the minerals fluorite (a) calcite (b) (polyacrylic acid concentration=7.5 mg/dm<sup>3</sup>)

### 3.3 FT-IR results

The FT-IR spectra of fluorite and calcite before and after interaction with polyacrylic acid are shown in Fig. 5. In the fluorite and calcite spectra, the peaks at 2357 cm<sup>-1</sup> and 2360 cm<sup>-1</sup> were attributed to carbon dioxide impurities (exclusions). The results in Fig. 5a indicated that the characteristic C=O peaks and C-O stretching bands of the -COOH groups of PAA appeared approximately in the regions of 1618 cm<sup>-1</sup> and 1108 cm<sup>-1</sup>, and the -OH bending bands emerged at approximately 1275 cm<sup>-1</sup> (Zeng et al., 2015; Anirudhan et al., 2016). After PAA treatment, peaks appeared at 1618 and 1108 cm<sup>-1</sup> on the fluorite surfaces. The new peaks were not shifted from their positions in the PAA spectra, except for a small change in the -OH bending bands ( Billingham et al., 1997; Alexander et al., 2015). Therefore, PAA was demonstrated to adsorb physically onto the surface of fluorite without chemical interaction.

The spectra of calcite with or without PAA treatment are shown in Fig. 5b. After the treatment with PAA, the calcite surface exhibited new adsorption bands corresponding to the C=O and -OH units of the -COOH groups at 1627 cm<sup>-1</sup> and 1319 cm<sup>-1</sup>, which illustrated that PAA may undergo chemical adsorption on the surface of calcite. The C=O stretching vibration at approximately 1618 cm<sup>-1</sup> shifted 9 cm<sup>-1</sup> to a higher energy of approximately 1627 cm<sup>-1</sup>. This may correspond to the vibration of a Ca(OH)+PAA surface complex. However, the -OH bending vibrations at around 1275 cm<sup>-1</sup> shifted 44 cm<sup>-1</sup> to a higher energy of approximately 1319 cm<sup>-1</sup>, which might be attributed to the formation of a hydrogen

bond by the weakening a covalent bond between O and H. In other words, electrostatic adsorption of PAA occurred on the calcite surface. These results indicate that PAA might undergo both chemisorption and electrostatic adsorption onto calcite surfaces at the same time, while no chemical interaction between PAA and fluorite was observed.

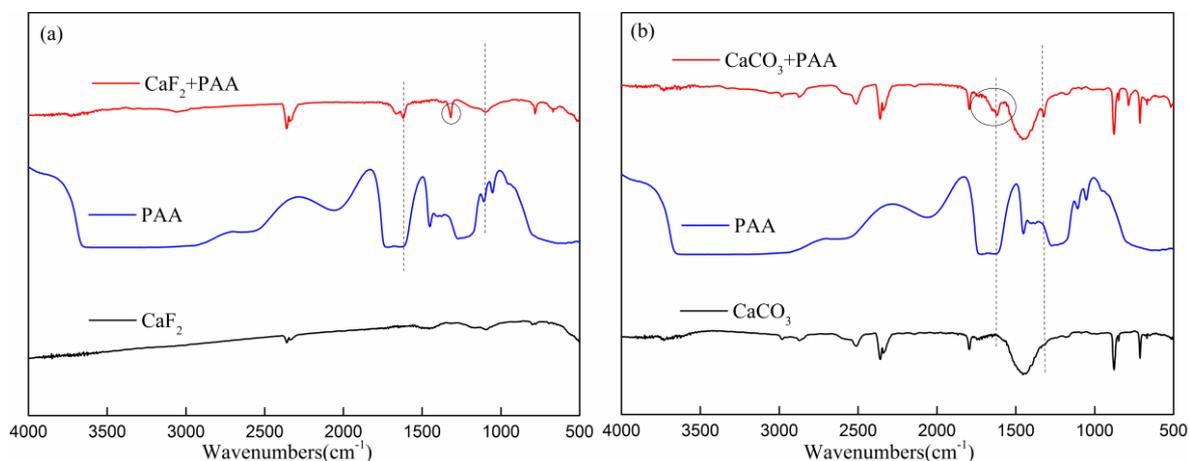


Fig. 5. FT-IR spectra of fluorite (a) and calcite (b) before and after interaction with polyacrylic acid

### 3.4 XPS results

XPS analysis was then carried out to further examine the interaction of PAA with the mineral surface, and in particular, whether the chemisorption site of PAA on calcite in calcite solution could be  $\text{Ca}(\text{OH})^+$ . Figs. 6, 7, 8, and 9 show the XPS spectra of fluorite, calcite, and calcium hydroxide samples before and after reaction with PAA. As expected, C, Ca, F, and O were the major constituents, and no evidence of contamination or impurities of other elements could be found.

The C1s spectra of  $\text{Ca}(\text{OH})_2+\text{PAA}$  and of fluorite before and after PAA treatment are shown in Fig. 6a. The C1s peaks at 284.84 and 286.69 eV were related to adventitious carbon, because carbonaceous contamination existed on all the mineral surfaces exposed to pulp solutions or the atmosphere. Thus, qualitative analysis was difficult. Analogously, as shown in Fig. 6b, except for the reference peak at 284.74 eV, the remaining peaks at 286.34 and 289.69 eV were attributed to the corresponding C1s peaks mentioned above, providing evidence of the adsorption of PAA on the fluorite and calcite surfaces.

Combined with the results of the previous experiments, the emphasis during further investigation was the differences among the calcium ion species, especially the products distributed at the surface of the minerals. Fig. 7a presents the Ca2p spectra of the  $\text{Ca}(\text{OH})_2+\text{PAA}$  complexes and of fluorite before and after PAA treatment. The spectrum of fluorite without PAA treatment was well fitted by two spin-orbital splitting peaks, with binding energies of 348.04 eV for the Ca2p<sub>3/2</sub> level and 351.54 for the Ca2p<sub>1/2</sub> level (Bahadur et al., 1996). The calcium peaks of the  $\text{CaF}_2+\text{PAA}$  spectra were shifted to higher binding energies of 351.64 and 348.14 eV. However, the difference in binding energy was only 0.1 eV, which indicated that PAA had a weak effect on the chemical characteristics of the Ca atoms of fluorite. These results were consistent with the F1s spectrum findings (Fig. 8). In other words, the electron density of the Ca atoms did not change significantly after the adsorption of PAA. In agreement with the FT-IR results, PAA was adsorbed on the fluorite surface though electrostatic interactions.

Fig. 7b presents the Ca2p spectra of the  $\text{Ca}(\text{OH})_2+\text{PAA}$  complexes, and of calcite before and after PAA treatment. The calcite without PAA was well fitted by two spin-orbital splitting peaks, with binding energies of 347.04 eV for the Ca2p<sub>3/2</sub> level and 350.59 for the Ca2p<sub>1/2</sub> level (Chada et al., 2005). After PAA treatment, both the Ca2p<sub>3/2</sub> and Ca2p<sub>1/2</sub> peaks shifted to higher binding energies of approximately 347.34 and 350.89 eV, respectively. This suggests that as PAA is adsorbed on the calcite surface, it becomes strongly attached to the surface, possibly through  $\text{COO}^-$ . However, the resulting binding energy was different from that of the  $\text{Ca}(\text{OH})_2+\text{PAA}$  complexes, which indicated that the surface chemistry reaction was complex.

Further analysis of the O1s peak was also very instructive in assigning the new calcium spectral features. Fig. 9 shows that the O1s spectra could be fitted using one component related to the C-O/C=O

group in calcite at 531.24 eV (Dalby et al., 2007). The sharp increase of the -COOH peak at 531.54 eV after PAA adsorption suggests that the molecules might have been bound to the surface through this functional group. This binding energy was very similar to that of the  $\text{Ca}(\text{OH})_2$ +PAA complexes. Moreover, a new peak corresponding to water (O-H) from the chemical reaction of the molecules appeared on the surface at 533.14 eV. This upward shift may be explained as electron transfer occurring between the calcium ions and the PAA molecule, thus providing further evidence for a possible chemical reaction between PAA and calcite during the adsorption process (Cizaire et al., 2004).

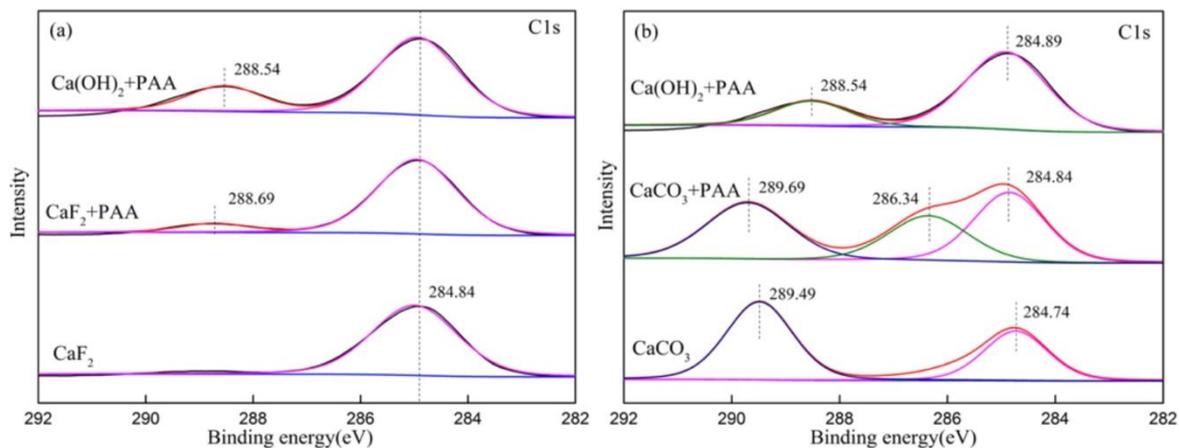


Fig. 6. C1s XPS spectra of fluorite (a) calcite (b)

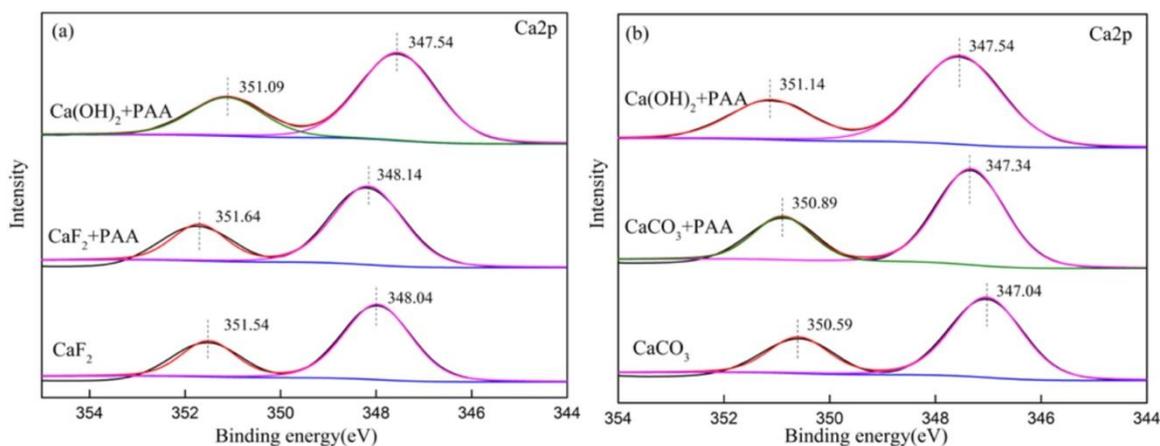


Fig. 7. Ca2p XPS spectra of fluorite (a) and calcite (b) samples

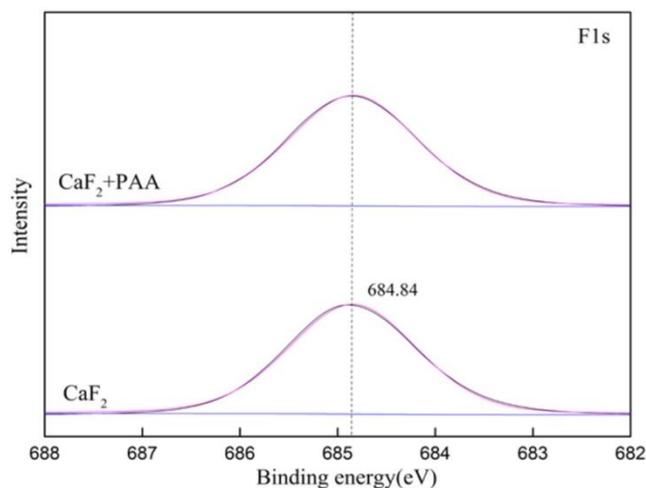


Fig. 8. F1s XPS spectra of fluorite

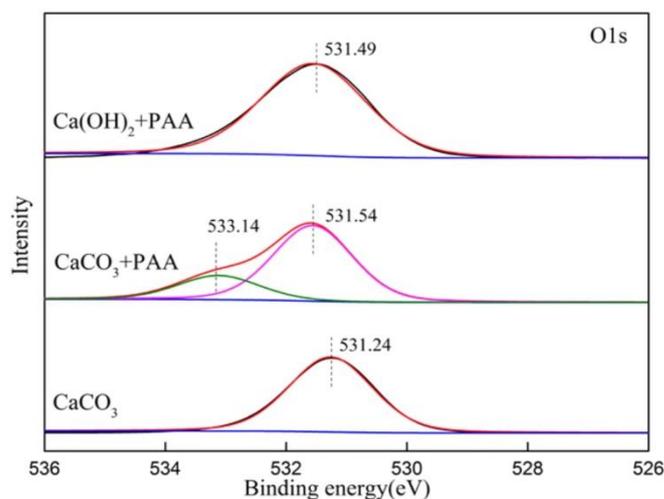


Fig. 9. O1s XPS spectra of calcite

### 3.5 Adsorption model

The results showed that PAA adsorbed on the fluorite surface through electrostatic interactions. Compared with NaOl, the  $K_{sp}$  for  $\text{Ca(OH)}_2$  was  $10^{-16}$  in the solution system (Free, 1996), which was more stable than Ca-PAA (soluble). Therefore, the formation of  $\text{Ca(OH)}_2$  occurred prior to the formation of Ca-PAA. Here again, our findings indicated that the adsorption of NaOl on the fluorite surface was stronger than that of PAA, which follows the general rules of solution chemistry (Huang et al., 1991).

Additionally, among other similar reports, the authors of a few recent theoretical studies (Li et al., 2016; Al Mahrouqi et al., 2017) predicted that under favorable hydroxylation conditions, the calcite surface was converted to a fully hydroxylated Ca-terminated or O-terminated surface. These studies suggested that the type of hydroxyl coordination was related to the surface activity of the metal cations. Furthermore, the FT-IR analysis indicated that the -OH group of PAA persisted, and that the -COOH groups shifted after chemisorption onto calcite. The XPS results further supported this proposal, as the organic C-O/C=O groups were found to remain on the surface after PAA adsorption. Moreover, a new peak corresponding to bound water (O-H) from the chemical reaction of the molecules in the inner layer appeared. The significant shift of the O1s binding energy suggested a specific interaction in the Stern layer. Based on the above findings, the adsorption models were postulated for the surface interactions between PAA and calcite (Fig. 10). The results provided evidence of the adsorption of PAA on the calcite surface with a higher affinity than NaOl.

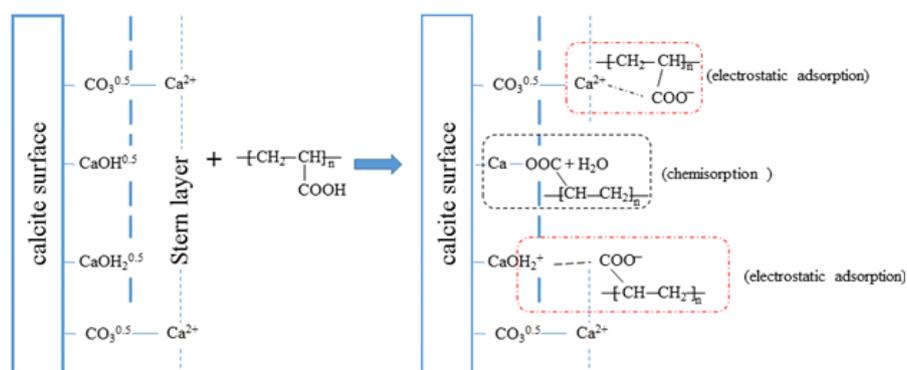


Fig. 10. Proposed models for the adsorption of PAA on calcite surface

## 4. Conclusions

The effective separation of fluorite and calcite was achieved via the addition of an appropriate amount of PAA ( $7.5 \text{ mg/dm}^3$ ) at  $\text{pH}=8$  in the presence of the collector NaOl.

Adsorption of PAA onto the surface of fluorite occurred via electrostatic interactions without chemical interaction. Thus, with the addition of NaOH, PAA could be replaced by NaOH on the fluorite surface.

Adsorption of PAA onto calcite surfaces occurred through both electrostatic interactions and chemical adsorption. The main chemical interaction of PAA was the bonding of its carboxyl group with the hydroxyl groups of the Ca species on the calcite surface, modifying the structure of the adsorbed layer. The adsorption of PAA on the calcite surface had a higher affinity than that of NaOH, thereby decreasing the floatability of calcite.

### Acknowledgements

The authors would like to acknowledge the financial support provided by the National 111 Project (No. B14034), the National Science and Technology Support Project of China (No. 2015BAB14B02), and Supported by Innovation Driven Plan of Central South University (No. 2015CX005).

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