

Article

Selective Flotation of Calcite from Fluorite: A Novel Reagent Schedule

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Abstract: Fluorite is an important strategic mineral. In general, fluorite ores will contain a certain amount of calcite gangue mineral. Thus, they need to be separated from each other. For an economic separation, a reverse flotation process is used to float calcite gangue from fluorite. However, little information on the separation is available. In this study, a novel reagent schedule using citric acid (CA) as the depressant, sodium fluoride (NaF) as the regulator and sulfoleic acid (SOA) as the collector, was developed to separate calcite from fluorite. The results demonstrated a high selectivity for the flotation of calcite from fluorite using this new reagent schedule. The best selective separation for a single mineral and mixed binary minerals was obtained when 200 mg/L of NaF, 50 mg/L of CA, and 6 mg/L of SOA were used at pH 9. In addition, a batch flotation experiment was carried out using a run-of-mine feed material. Selective separation was achieved with 85.18% calcite removal while only 11.2% of fluorite was lost. An attempt was made to understand the effect of the new reagent schedule on the flotation of calcite. The results from both microflotation and bench scale flotation demonstrated a great potential for industrial application using this novel reagent schedule to upgrade fluorite ore.

Keywords: fluorite; calcite; flotation; citric acid; sodium fluoride; sulfoleic acid

1. Introduction

Fluorite (CaF_2), which is a major resource of fluorine, has been considered to be an important strategic mineral in recent years. Fluorite mineral are often associated with calcite (CaCO_3), and needs to be separated from each other by flotation. A fluorite-rich-ore usually contains 30% of fluorite and 10%–20% or less calcite. For an economic separation, a reverse flotation of calcite while depressing fluorite is generally considered according to the principle of “float less and depress more” [1]. However, little information was reported for this separation.

Fluorite and calcite have the same surface Ca^{2+} ions and hence have similar flotation response to commonly used fatty acid collectors [2,3]. Therefore, it is not practical to achieve their separation using a traditional flotation reagent. It is necessary to develop new reagents for efficient flotation of calcite from fluorite. However, there has been little information reported about reagents scheme in this system.

Previous work showed that citric acid (CA) does not have a significant depressive effect on the oleate flotation of calcite [4,5] but can moderately depress fluorite [6]. Furthermore, the depressive effect of CA is not affected by the hardness of water due to its strong chelating capacity with Ca^{2+} or Mg^{2+} [7]. Therefore, CA might be a depressant in the flotation of calcite from fluorite.

It was also reported that NaF depresses fluorapatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$), which also contains fluorine [8]. However, for collophanite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})$) with no fluorine, NaF can activate its flotation since

the chemisorption of fluoride at surface Ca sites can produce a fluoroapatite-type compound on its surface [9]. In this regard, it was expected that NaF can be used as a selective regulator to depress the fluorite and to activate the calcite flotation.

In this study, using depressant CA and regulator NaF, a novel reagent schedule for the flotation of calcite from fluorite was evaluated by flotation experiments using a single mineral sample flotation test. This new reagent schedule was further evaluated in the flotation experiments using the mixed binary mineral sample and run-of-mine ore sample. The mechanism of the selective separation was investigated through zeta potential measurement.

2. Materials and Methods

2.1. Pure Minerals and Reagents

Pure calcite and fluorite minerals were obtained from Xinyuan Mine, Chenzhou, Hunan, China. These minerals were ground in a porcelain ball mill with zirconia balls. The X-ray diffraction (XRD) spectrums (Figure 1) confirmed that the fluorite and calcite samples were over 99% and 99% pure, respectively. The $-74 + 37 \mu\text{m}$ milled samples were used for the flotation experiment. Samples further finely ground in a mortar and pestle to $-2 \mu\text{m}$ were used for zeta potential measurement.

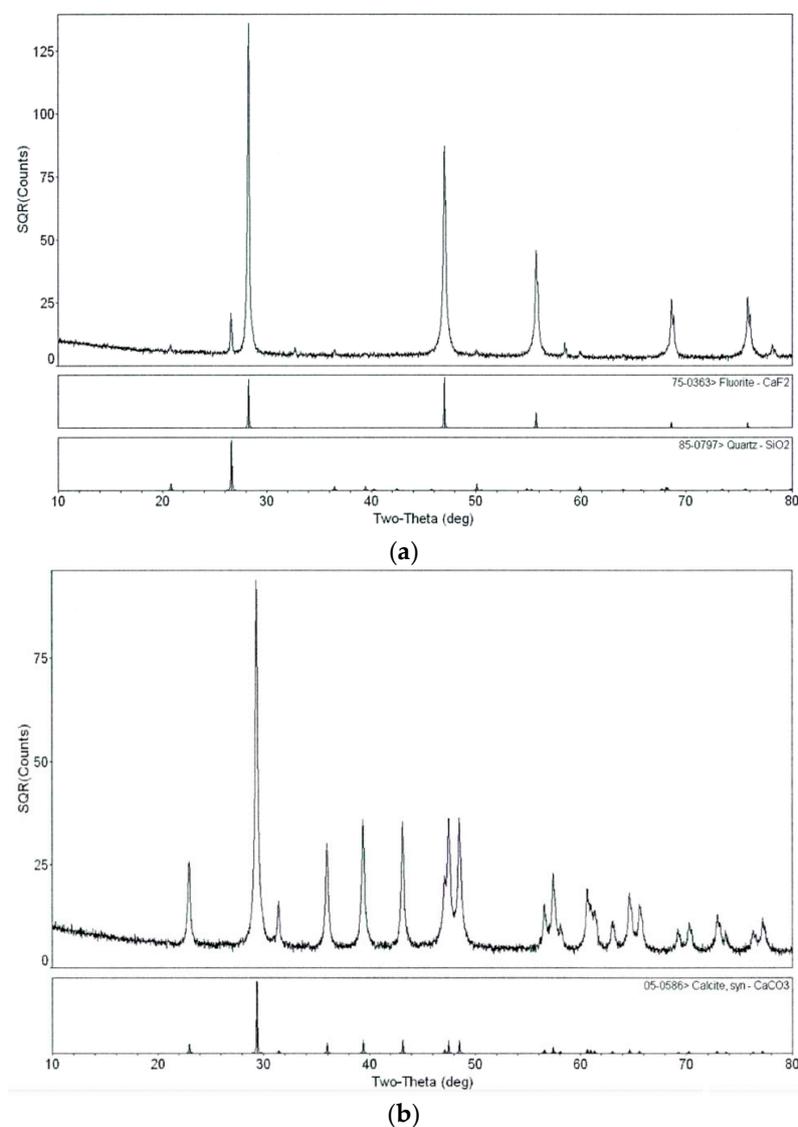


Figure 1. XRD spectrums of powder fluorite (a) and calcite (b) for flotation tests.

Industrial grade sulfoleic acid (SOA, $\text{CH}_3(\text{CH}_2)_8\text{CH}(\text{SO}_4\text{H})(\text{CH}_2)_7\text{COOH}$) was supplied by Zhuzhou Chemical Industry Research Institute, Zhuzhou, China. Analytically pure CA ($\text{C}_6\text{H}_8\text{O}_7$) was provided by Huihong Reagent Co., Ltd, Changsha, Hunan, China. Analytically pure NaF was purchased from Xilong Chemical Co., Ltd, Shantou, Guangdong, China. The pH was adjusted with sodium hydroxide (NaOH) or hydrochloric acid (HCl) stock solutions. Deionized (DI) water with a resistivity of over $18 \text{ M}\Omega \times \text{cm}$ was used throughout the experiments.

2.2. Flotation Experiment

An XFG flotation machine (Figure 2) (Exploring Machinery Plant, Changchun, China) with a 40 mL cell was used for flotation tests of single mineral and mixed binary minerals, while a 1.5 L cell was used for run-of-mine ore, at an impeller speed of 1700 rpm. The flotation pulp for single and mixed binary minerals was prepared by adding 2 g of mineral samples to 35 mL of DI water, while the pulp of run-of-mine ore was obtained by 500 g samples and 1000 mL DI water. The pulp was conditioned for 2 min, followed by 3 min of conditioning after the pH of the mineral suspension was adjusted to the desired value. A depressant was then added and the pulp conditioned for 3 min, followed by the addition of SOA and 3 min of conditioning. The stable value of pH was recorded before flotation. For single mineral flotation, the products were collected, dried, and weighed, and the recovery was calculated. For flotation tests of mixed minerals and run-of-mine ore, the concentrates and tails were assayed for W and Ca. At least 3 flotation tests were made for a confirmed experimental condition, and the average recovery and the standard deviation were calculated.



Figure 2. XFG flotation machine for a pure mineral flotation test.

2.3. Zeta Potential Measurement

Zeta potential measurements were conducted at 20°C using a Nano-ZS90 zeta potential analyzer (Malvern Instruments, Malvern, UK). A dilute mineral suspension was prepared by adding 0.02 g of mineral sample to 40 mL KCl (0.01 mol/L) solution. Then, the desired reagent(s) was added as the same order of flotation experiment, and the pH was adjusted and measured. The mineral suspension was magnetically stirred for 10 min. After standing for 5 min, the supernatant liquid of the mineral suspension was sucked out and used for zeta potential measurement. At least 3 measurements were made for every confirmed experimental condition, and the average zeta potential and the standard deviation were calculated.

3. Results and Discussions

3.1. Single Mineral Flotation Experiment Results

Previous reports showed that oleic acid (OA) has a stronger collecting power for fluorite than for calcite [10–12]. In this work, SOA was used to improve its collecting power for calcite. The flotation behavior of calcite and fluorite using SOA as the collector was evaluated by the single mineral flotation.

Figure 3a shows the effect of SOA dosage on flotation recoveries of calcite and fluorite. It can be seen that the recoveries of two minerals increase steadily with the increasing of SOA dosage at pH 9.0, and reach the maximum of 95.6% and 86.02%, respectively, when the SOA dosage is 6 mg/L. Figure 3b shows the effect of pH on flotation recoveries of calcite and fluorite. It can be seen that the recoveries for two minerals are virtually unchanged in the range of pH 8.0–11.5 at an SOA dosage of 6 mg/L. These results indicate that SOA has a slightly stronger collecting power for calcite than for fluorite, but using SOA collector alone cannot achieve the selective separation of calcite from fluorite. A selective depressant for fluorite is needed. An SOA dosage of 6 mg/L was preferred for all other flotation experiments.

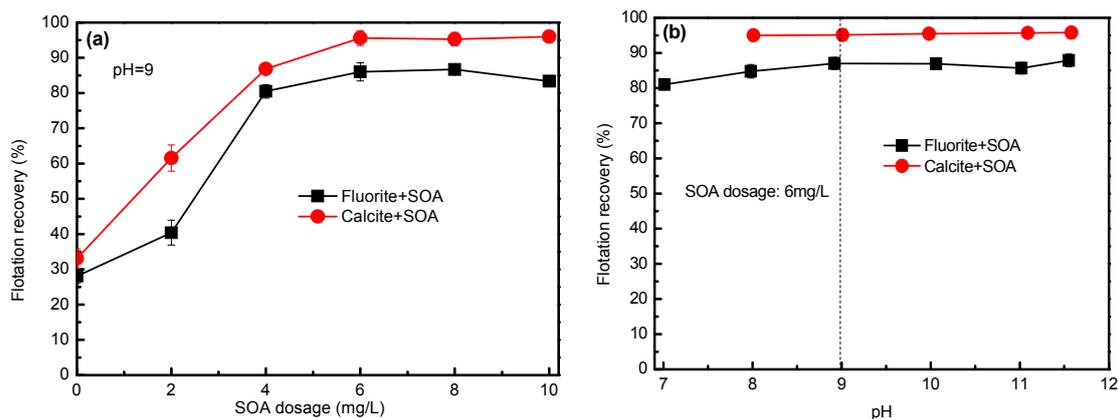


Figure 3. Effect of SOA dosage (a) and pH (b) on flotation recoveries of calcite and fluorite minerals using SOA as the collector.

CA was used as a depressant for the flotation test. Figure 4a shows the effect of CA dosage on flotation recoveries of calcite and fluorite using the SOA collector. It is observed that the recovery of fluorite decreases more rapidly than that of calcite as the CA dosage increases. These results indicate that using a combination of CA + SOA can achieve the selective separation of calcite from fluorite at pH 9 and a CA dosage of over 50 mg/L. However, the calcite recovery is only about 62%. Figure 4b shows the effect of pH on flotation recoveries of calcite and fluorite using CA + SOA. It can be seen that the fluorite recovery increases from 11.32% to 48.53% with the pH increasing from 9 to 11, indicating that an increasing pH level can lower the depressing ability of CA for fluorite and has a detrimental effect on the separation performance. Therefore, a CA dosage of 50 mg/L and pH 9 were preferred in the following flotation tests.

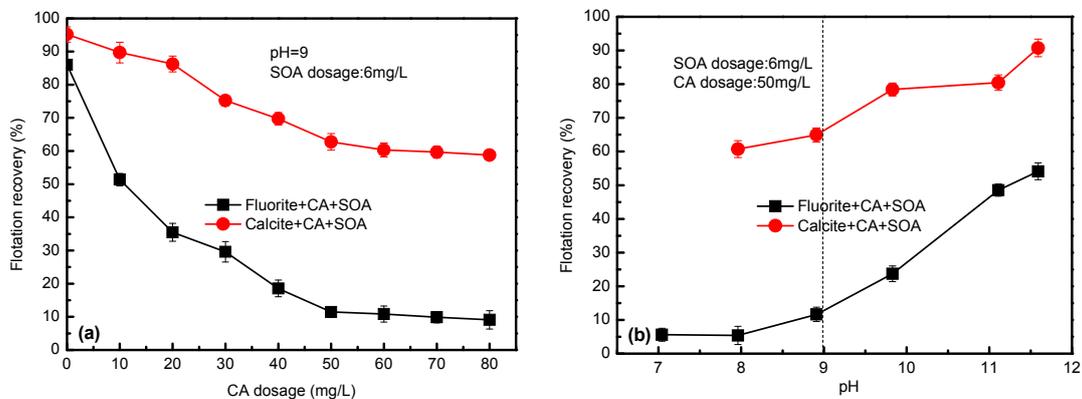


Figure 4. Effect of CA dosage (a) and pH (b) on flotation recoveries of calcite and fluorite minerals using SOA as the collector and CA as the depressant.

Regulator NaF was also used for a flotation test. Figure 5a shows the effect of NaF dosage on flotation recoveries of calcite and fluorite using the SOA collector. It was observed that as the NaF dosage increases, the calcite recovery approaches 100%, but the fluorite recovery decreases from 86% to 75%. The results suggest that NaF has a weak depressing effect on fluorite flotation and some activation effect on calcite flotation. Figure 5b shows the effect of pH on flotation recoveries of calcite and fluorite using NaF + SOA. It can be seen that while increasing pH level can reduce the depressing effect of NaF on fluorite flotation it has little influence on the activation effect on calcite flotation. Thus, pH 9 was used for the following flotation tests.

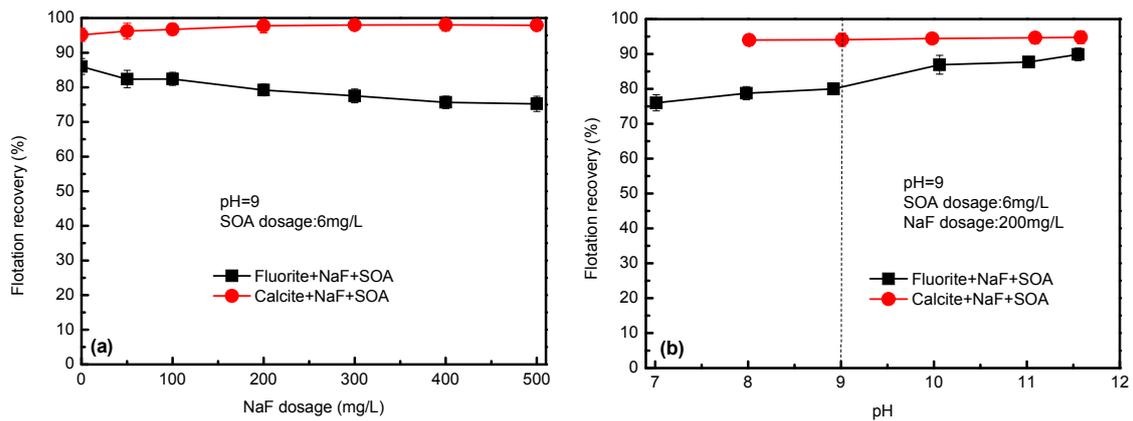


Figure 5. Effect of NaF dosage (a) and pH (b) on flotation recoveries of calcite and fluorite minerals using SOA as the collector and NaF as the depressant.

Using the combination of CA + SOA can strongly depress the fluorite flotation and reduce the calcite flotation moderately. However, using the combination of NaF + SOA can partly activate calcite flotation and depress fluorite flotation. Therefore, using a depressant CA, regulator NaF and collector SOA, the flotation behavior of calcite and fluorite was investigated at pH 9. Figure 6 shows the effect of NaF dosage and order of addition of NaF and CA on flotation recoveries of calcite and fluorite. It can be seen that calcite recovery stays over 88% while that of fluorite is only 1.8% when the NaF dosage is above 200 mg/L. It is interesting to notice that the addition order of NaF and CA has little effect on the separation performance. Thus, the novel reagent combination of CA (50 mg/L) + NaF (200 mg/L) + SOA (6 mg/L) at pH 9 can be a desirable reagent schedule for the flotation separation of calcite from fluorite.

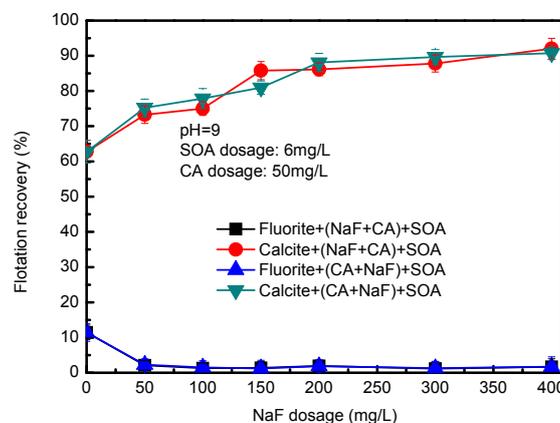


Figure 6. Effect of NaF dosage and order of addition of NaF and CA on flotation recoveries of calcite and fluorite minerals using SOA as the collector and NaF + CA as the depressant. (NaF + CA denotes the adding order of NaF and then CA; CA + NaF denotes the adding order of CA and then NaF).

It should be noted that the reagent schedule of “CA (50 mg/L) + NaF (200 mg/L) + SOA (6 mg/L) at pH 9” was developed by one-factor-at-a-time (OFAT) methodology. Orthogonal array design (OAD) is to incorporate the advantages of simplex method and factorial design [13]. This method arranges different factors for effective optimization of experimental conditions. To evaluate the interactions among those four factors and effects on the flotation recoveries of fluorite and calcite, a design of experiment based on OAD was used, L25(5⁶) [14], (where for four factors, five levels for each factor, the total number of factors and responses is six. The total experiment is 25 runs). The detailed design of experiment and results of orthogonal experiment were presented in Tables S1–S3 in the Supplementary Material. The results showed that the reagent schedule developed by OFAT methodology was adequate.

3.2. Mixed Binary Mineral Flotation Experiment Results

A flotation test on mixed binary minerals of calcite (0.33 g) and fluorite (1.67 g) was carried out to evaluate the separation performance of the novel reagent schedule, the results are presented in Table 1. Table 1 shows that in the calcite concentrate, the calcite recovery was 88.1% while that of fluorite was only 6.5%. These results indicate that, using the novel reagent schedule, a high separation efficiency between calcite and fluorite can be achieved with a fluorite concentrate having low calcite contaminations. The novel reagent scheme can be used to remove the calcite from a binary mineral mixture of calcite and fluorite.

Table 1. The results of mixed binary minerals (a) and run-of-mine fluorite ore (b) flotation tests using the reagent schedule of CA + NaF + SOA at pH 9.

	Weight (g)		Grade (%)				Recovery (%)			
	(a)	(b)	(a)		(b)		(a)		(b)	
			Fluorite	Calcite	Fluorite	Calcite	Fluorite	Calcite	Fluorite	Calcite
Concentrate	0.4 (0.02)	121.6 (2.3)	27.07 (1.7)	72.93 (2.1)	18.59 (1.1)	66.67 (1.3)	6.5 (0.2)	88.1 (1.5)	11.2 (0.9)	85.2 (1.9)
Tailings	1.6 (0.08)	373.4 (3.4)	97.57 (2.3)	2.43 (0.12)	48.01 (1.5)	3.78 (0.4)	93.5 (2.1)	11.9 (0.8)	88.8 (2.0)	14.8 (0.7)
Total	2.0	495 (2.8)	66.7	33.3	40.78 (1.4)	19.23 (0.6)	100.00	100.00	100.00	100.00

Note: the number in parentheses shows the standard deviation.

3.3. Run-of-Mine Ore Batch Flotation Test Results

Batch flotation practice on a run-of-mine fluorite ore was carried out. A feed ore contains 39.97% fluorite and 17.87% calcite, with the other main components being 36.69% micaceous minerals and 3.35% limonite. The grinding fineness was 93% –74 μm. The reagent schedule was as follows: pH 9, CA 3000 g/t, NaF 8000 g/t and SOA 150 g/t. The flotation results are presented in Table 1. It can be seen that, in calcite concentrate, the calcite recovery is up to 85.2% while fluorite has a very low recovery of 11.2%. A tailing with 48.01% of fluorite and 3.78% of calcite was produced and further processed to obtain a high grade fluorite concentrate. Those results indicate that using this novel reagent scheme can selectively remove calcite from a fluorite–calcite ore.

3.4. Zeta Potential Measurement Results

The mechanism of the selective separation was investigated through zeta potential measurement. Zeta potentials of calcite and fluorite minerals in the absence and presence of flotation reagents were measured, and the results are shown in Figure 7. It can be observed that in the absence of any reagent, isoelectric points (IEPs) of pH 9.1 and pH 10.6 were obtained for fluorite and calcite, respectively, which are in agreement with previous reports [15–20]. Figure 7 also shows that, at pH 9, the addition of SOA causes a greater decrease, by 35 mV, for calcite zeta potential compared with 20 mV for fluorite. Those results indicate that at pH 9 anionic SOA can interact more strongly on the positively charged calcite surface than on the fluorite surface, which agrees well with the flotation results (Figure 3).

Figure 7a shows that at pH 9, the addition of CA or CA + SOA causes a similar change to the fluorite zeta potential, indicating that SOA cannot favorably adsorb on “fluorite + CA” surface

(i.e., fluorite surface with pre-adsorbed CA). Figure 7b shows that SOA addition shifts the zeta potential of “calcite + CA” surface to a more negative value by 6 mV, indicating that SOA can adsorb on the “calcite + CA” surface. The difference of SOA adsorption on “fluorite + CA” and “calcite + CA” surfaces can explain relatively high calcite recovery and a low fluorite recovery using CA + SOA reagent schedule (Figure 4).

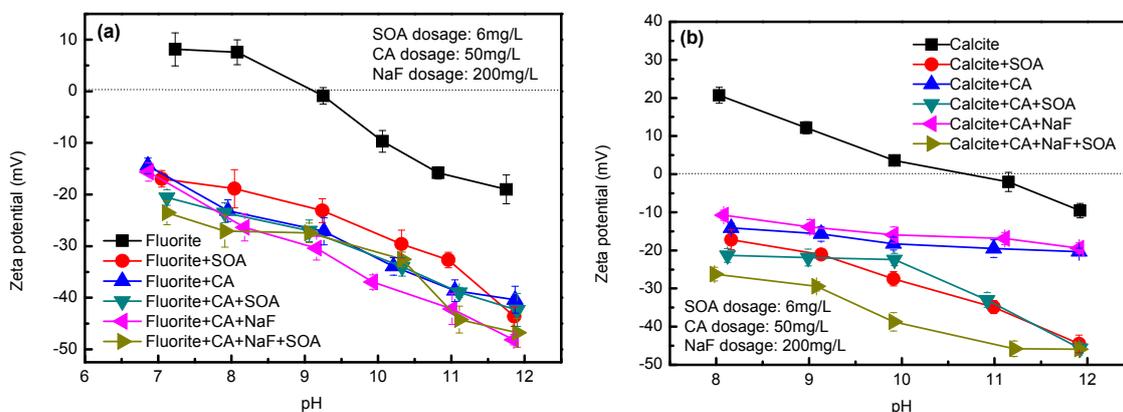


Figure 7. Zeta potentials of fluorite (a) and calcite (b) in the absence and presence of different reagents.

It is also seen that, at pH 9, the addition of CA + NaF reverses the zeta potentials of fluorite and calcite from positive to negative almost to the same degree. The adding of SOA causes a slight increase for the zeta potential of the “fluorite + CA + NaF” surface (Figure 7a), indicating that SOA cannot readily adsorb on the “fluorite + CA + NaF” surface. For calcite, SOA addition shifts the zeta potential of the “calcite + CA + NaF” surface to a more negative value by 16 mV (Figure 7b), suggesting that SOA can further favorably adsorb on the “calcite + CA + NaF” surface. The difference of SOA adsorption on “fluorite + CA + NaF” and “calcite + CA + NaF” surfaces can explain a high calcite recovery and absolute depressed flotation of fluorite using a “CA + NaF + SOA” reagent schedule (Figure 6).

It is interesting to notice that the decrease by 16 mV from the zeta potential of the “calcite + CA + NaF” surface to that of “calcite + CA + NaF + SOA”, is much higher than the decline by 6 mV from the zeta potential of “calcite + CA” surface to that of “calcite + CA + SOA”. These results indicated that NaF plays an important role in the enhanced adsorption of SOA on the “calcite + CA” surface, which agrees well with the higher calcite recovery using “CA + NaF + SOA” (Figure 6) than using “CA + SOA” (Figure 4).

4. Conclusions

A novel reagent schedule of depressant CA, regulator NaF and collector SOA was developed in this work. It demonstrates a high selectivity for the flotation removal of calcite from fluorite–calcite ore. The addition order of NaF and CA has little impact on the adsorption of SOA on calcite and fluorite surfaces. Flotation tests on a single mineral and mixed binary minerals showed that the reagent schedule of CA 50 mg/L, NaF 200 mg/L and SOA 6 mg/L at pH 9 could achieve selective flotation of calcite from fluorite. Batch flotation tests on a run-of-mine fluorite–calcite ore indicated that, using this reagent schedule, the calcite removal rate could reach above 85% while fluorite has a loss rate of below 11%. The novel reagent schedule of “CA + NaF + SOA” exhibits great potential for industrial application in the flotation of fluorite–calcite ore.

Supplementary Materials: The following are available online at www.mdpi.com/2075-163X/6/4/114/s1, Table S1: Attribution of factors to the levels in $L_{25}(5^6)$ OAD experiments; Table S2: $L_{25}(5^6)$ OAD matrix with the experimental results; Table S3: Results of range analysis.

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Author Contributions: Zhiyong Gao and Wei Sun conceived and designed the experiments; Yiyang Zhu and Yuesheng Gao performed the experiments; Zhiyong Gao and Yuehua Hu analyzed the data; Zhiyong Gao wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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