

Article

Surface Features of Fluorapatite and Dolomite in the Reverse Flotation Process Using Sulfuric Acid as a Depressor

Heng Zou¹, Qinbo Cao^{1,2,*}, Dianwen Liu^{1,2,*}, Xingcai Yu¹ and Hao Lai¹

- ¹ Faculty of Land Resources Engineering, Kunming University of Science and Technology, Kunming 650093, China; zh@kmust.edu.cn (H.Z.); kgyuxingcai@163.com (X.Y.); kjlaihao@163.com (H.L.)
- ² State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming 650093, China
- * Correspondence: cabdxx@163.com (Q.C.); ldwkust@126.com (D.L.); Tel.: +86-0871-65187068 (Q.C.); +86-0871-65915828 (D.L.)

Received: 29 November 2018; Accepted: 6 January 2019; Published: 11 January 2019



Abstract: The surface features of fluorapatite (FA, $Ca_5(PO_4)_3F$) and dolomite ($CaMg(CO_3)_2$) conditioned with sulfuric acid (H_2SO_4) were examined through flotation experiments, contact angle tests, time-of-flight secondary ion mass spectrometry (TOF-SIMS), and FTIR experiments. The flotation and contact angle results suggested that oleate insufficiently adsorbed onto the H_2SO_4 -treated FA surface such that the FA surface remained hydrophilic. However, using oleate as a collector, the recovery and hydrophobicity of H_2SO_4 -treated dolomite were satisfactory. TOF-SIMS and FTIR studies indicated that sulfate anion bound with Ca atoms on the FA surface, which hindered oleate adsorption onto the FA surface. Meanwhile, sulfate anion and oleate species appeared on the dolomite surface, thereby generating a hydrophobic dolomite and also a satisfactory recovery.

Keywords: flotation; fluorapatite; dolomite; sulfuric acid; depressor

1. Introduction

Dolomite $(CaMg(CO_3)_2)$ is a critical gangue mineral in most phosphate deposits in China [1]. The separation of dolomite from apatite determines the success of the phosphate flotation to some extent. Separating dolomite from apatite in an efficient and economically way is difficult for a collophane ore. Collophane is a type of unique phosphate ore containing cryptocrystalline apatite [2]. In a collophane ore, extra-fine minerals of apatite and dolomite may associate with each other to form aggregations [3,4]. The separation of extra-fine apatite from dolomite is considerably difficult.

Flotation is the main technique for upgrading collophane ore. In the direct flotation scheme, apatite is floated with fatty acid collectors in a basic solution [5]. Dolomite can also be floated with the collectors, because the traditional fatty acid collectors can adsorb not only on the apatite surface but also on the dolomite surface. Thus, depressors of dolomite, such as starch, are commonly needed [2]. Considerable selective collectors and efficient depressors have been developed for the flotation separation of apatite from dolomite or calcite [6,7]. These new reagents have great potential to be used in phosphate plants.

With regard to low-grade collophane ore, obtaining a satisfactory phosphate concentrate with a single direct flotation method is difficult because the dolomite content is relatively high in the ore, and thus cannot be completely depressed. Therefore, a reverse flotation strategy is used to separate dolomite from apatite in phosphate flotation plants [8]. Using such strategy, apatite is depressed with sulfuric or phosphoric acid (H_2SO_4/H_3PO_4), whereas dolomite can be floated with a fatty acid collector, such as oleate, in a weak acidic solution [9]. H_2SO_4 compared to H_3PO_4 is a more prevalent



depressor for apatite in industry due to its relatively lower price. This method has been widely used in the beneficiation of collophane ores in China.

Despite the successful industry practice to separate dolomite from apatite with the reverse flotation strategy, the depressing mechanism of H_2SO_4 has not yet been fully understood. The flotation of fluorapatite (FA, $Ca_5(PO_4)_3F$) with fatty acid collectors, such as oleate, is carried out in a basic solution. The adsorption of oleate onto the FA surface is governed by the chemisorption of oleate ion and surface/bulk precipitation of calcium dioleate salt on the surface [10,11]. SO_4^{2-} may react with Ca^{2+} on the FA surface to form $CaSO_4$ species due to the low solubility of $CaSO_4$ [8]. Thus, oleate cannot further adsorb on the Ca sites on the FA surface. However, no further direct evidence has been provided to validate this opinion in previous studies.

 H_2SO_4 cannot prevent the flotation of dolomite with oleate as a collector. Interestingly, oleate can still adsorb onto the H_2SO_4 -treated dolomite surface. The possible occurrence of precipitation of CaSO₄ on the dolomite surface is uncertain due to the instability of dolomite in an acidic solution. Moreover, the pH of phosphate slurry with H_2SO_4 is much lower than that in the direct flotation of apatite. The pH of the solution is a vital factor in determining the adsorption state of oleate on a mineral surface [12]. However, the adsorption state of oleate on the H_2SO_4 -treated dolomite surface has yet to be reported in the literature.

Current knowledge regarding the effects of H_2SO_4 on the flotation of apatite and dolomite is lacking. The present study was aimed at investigating the adsorption behavior of oleate on the H_2SO_4 -treated fluorapatite (FA) and dolomite surfaces. Firstly, flotation and contact angle experiments were employed to assess the depressing capacity of H_2SO_4 for the flotation of FA/dolomite. Furthermore, the time-of-flight secondary ion mass spectrometry (TOF-SIMS) technique was used to reveal the distribution of SO_4^{2-} and collector on the minerals' surfaces. The oleate species on the dolomite surface were further determined with FTIR spectroscopy analysis.

2. Materials and Methods

2.1. Minerals and Reagents

The FA and dolomite pebbles (purities >98%) from the Geological Museum of Yunnan Province, China were used in this study. The analytical reagent (AR) grade reagents, including sodium oleate (NaOl) and concentrated H_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All experiments were conducted with deionized (DI) water at 23 °C.

2.2. Flotation Experiments

Flotation tests were conducted with an XFGC II flotation machine (Jilin Province Ore Exploration Machinery Factory, Changchun, China) and a 40 mL flotation cell. Two grams of pure mineral was used in each flotation experiment. The dolomite or FA sample was conditioned with H_2SO_4 solution for 3 min in the flotation cell, after which the desired amount of oleate was added into the flotation cell. The condition time for the collector was also 3 min. Air was used in the flotation tests at a flow rate of 20 mL/min, while the flotation time was controlled at 1 min. Each test was repeated three times.

2.3. Contact Angle Measurements

The contact angle experiments were performed with a GBX 3S instrument (GBS, Dublin, Ireland). The FA/dolomite pebble was well polished with 2000-, 4000-, and 6000-grit Al₂O₃ sand paper before each measurement. After the pebble had been treated with H₂SO₄ solution for 3 min and then with the collector for another 3 min, the crystal was air-dried for further measurement. A DI water droplet of approximately 2 mm was induced onto the crystal surface to generate the three-phase contact line. Each sample was measured three times, and the mean values were reported. The error of the measurements was less than $\pm 3^{\circ}$.

A TOF-SIM 5 (ION-TOF GmbH, Münster, Germany) was used in the tests. The surface images were analyzed with the spectrometry model using Bi_3^{++} primary ions (15 keV), and a 500 × 500 μ m² area on the mineral surface was measured. In the depth profiling tests, the Cs⁺ beam and non-interlaced model were used to determine the 3D distribution of secondary ions on the mineral surface. The sputter crater area was 300 × 300 μ m², and a 100 × 100 μ m² area was rastered over with a Bi_3^{++} beam with the spectrometry model. The well-polished FA and dolomite crystals were conditioned with the H₂SO₄ solution and/or the oleate solution for the TOF-SIMS study. The condition times were the same as those for the contact-angle measurements.

2.5. Attenuated Total Reflection (ATR)-FTIR Spectroscopy Experiments

An Avatar 300 (Thermo Electron Crop., Waltham, MA, USA) was used to record the FTIR spectra of the FA and dolomite samples. The FA and dolomite samples (1 g, -5μ m) were prepared by two different methods: (1) conditioned with 100 mL of H₂SO₄ solution (2 × 10⁻³ mol/L) for 3 min; (2) conditioned with 100 mL of H₂SO₄ solution (2 × 10⁻³ mol/L) for 3 min, and then with oleate for 40 min. In the second method, the desired amount of oleate was directly added into the H₂SO₄ solution to obtain a collector solution. After the conditioning with reagent solution, the suspension was filtered and then air-dried for the analysis. A ZnSe multiple internal reflection prism (Thermo Electron Crop., Waltham, MA, USA) was used to measure the ATR-FTIR spectra. The ZnSe prism was well cleaned with acetone, ethanol, and DI water before each measurement. The ATR-FTIR spectra were recorded at room temperature by co-addition of 300 interferograms at a resolution of 2 cm⁻¹.

3. Results and Discussion

3.1. Flotation Behavior

The influence of the H₂SO₄ dosage on the FA/dolomite flotation was examined using a laboratory mechanical flotation-machine. The flotation results only with oleate at natural pH (about 6.5) are also reported. In terms of FA, the recovery was about 30% with 1×10^{-4} mol/L of oleate at the natural pH (Figure 1), consistent with a previous report [12]. Moreover, the condition with H₂SO₄ led to an obviously reduction in FA recovery; the FA recoveries were <10% when the H₂SO₄ concentration was $\geq 1 \times 10^{-3}$ mol/L. A similar trend was found for FA with 2×10^{-4} mol/L of oleate, FA could not be efficiently collected by the collector when the H₂SO₄ concentration was $\geq 1 \times 10^{-3}$ mol/L.

In contrast, the treatment with H_2SO_4 slightly improved the flotation of dolomite. At each examined collector concentration (1 × 10⁻⁴ mol/L and 2 × 10⁻⁴ mol/L), the recovery of dolomite treated with 1 × 10⁻³ mol/L H_2SO_4 increased by 5–10% compared to that without H_2SO_4 treatment.

The carbonate ions on the dolomite surface are unstable in acidic solution and can be dissociated into H_2O and CO_2 . Thus, a considerable number of metal ions on the surface might be exposed to the solution, thereby providing substantial adsorption sites for the adsorption of oleate. Moreover, the dissolved metal ions may also favor the adsorption of collector to some extent [8]. In this regard, the treatment with H_2SO_4 could slightly enhance the dolomite flotation using oleate as a collector.

In addition, the separation of dolomite from FA was further investigated by the flotation tests using a 1:1 mixture of dolomite and FA. The concentration of oleate was 2×10^{-4} mol/L in such tests. The recovery of MgO was close to that of P₂O₅ in the absence of H₂SO₄, suggesting that oleate is not a selective collector for this flotation system (Table 1). While, the addition of H₂SO₄ into the slurry deteriorated the FA flotation. Moreover, the P₂O₅ recovery was <10% when the H₂SO₄ concentration reached 2×10^{-3} mol/L. It appears that more H₂SO₄ was required to depress FA in the flotation of FA-dolomite mixture, comparing with that in the single-mineral flotation of FA, while the MgO recoveries were over 69% regardless of the H₂SO₄ concentration. Such results demonstrate again that H₂SO₄ can be used as a specific depressor for FA.



Figure 1. Effect of H₂SO₄ concentration on the flotation of FA/dolomite with 1 means 1×10^{-4} mol/L and 2 means 2×10^{-4} mol/L of oleate.

Table 1. Effect of H_2SO_4 concentration on the flotation of FA–dolomite mixture with 2×10^{-4} mol/L of oleate.

H ₂ SO ₄ Concentration (mol/L)	$5 imes 10^{-4}$	1×10^{-3}	$2 imes 10^{-3}$
MgO	72.39%	69.45%	96.33%
P_2O_5	80.20%	37.61%	9.20%

3.2. Contact Angle Measurements

The difference in the hydrophobicity of minerals determines the separation efficiency of the flotation technique. The hydrophobicity of FA can be measured with the contact angle method [13]. In this work, this method was used to determine the hydrophobicity of FA/dolomite treated with H_2SO_4 and oleate.

Figure 2 shows that the contact angle of FA sharply decreased with an increase in H_2SO_4 concentration. When the FA was treated with 1×10^{-3} mol/L of H_2SO_4 , the contact angle was below 25° using 1×10^{-4} or 2×10^{-4} mol/L of oleate. These results imply that the usage of H_2SO_4 may prevent the adsorption of oleate species onto the FA surface, thereby allowing the FA surface to maintain a hydrophilic state in the slurry.

In contrast, the addition of H_2SO_4 into the slurry improved the contact angle of dolomite with 1×10^{-4} or 2×10^{-4} mol/L of oleate, which is in line with the above flotation results. For each oleate concentration, the contact angle reached the maximum value with 1×10^{-3} mol/L of H_2SO_4 . When the concentration of H_2SO_4 was above 1×10^{-3} mol/L, the contact angle of dolomite was lower than that with 1×10^{-3} mol/L of H_2SO_4 . The pH of dolomite slurry with 5×10^{-4} or 1×10^{-3} mol/L of H_2SO_4 was approximately 5.5 (Table 2). However, with 1.5×10^{-3} or 2×10^{-3} mol/L of H_2SO_4 , the pH of dolomite slurry was in the pH range of 4–5, and precipitation of oleate was observed in the solution. Therefore, oleate species cannot efficiently adsorb on the dolomite surface to produce a highly hydrophobic surface.

The gap in contact angles between FA and dolomite was approximately 83° when the FA and dolomite were treated by 1×10^{-3} mol/L of H₂SO₄ and 2×10^{-4} mol/L of oleate. Under these conditions, dolomite can be floated by oleate prior to FA. These results further demonstrate that H₂SO₄ can be used as a depressor for FA, in accordance with the reverse flotation phenomenon in phosphate plants.



Figure 2. Contact angles of dolomite and fluorapatite conditioned with sulfuric acid and 1 means 1×10^{-4} mol/L and 2 means 2×10^{-4} mol/L of oleate.

Table 2. The pH values of dolomite slurry with the addition of H_2SO_4 .

H ₂ SO ₄ Concentration (mol/L)	$5 imes 10^{-4}$	$1 imes 10^{-3}$	$1.5 imes 10^{-3}$	$2 imes 10^{-3}$
pН	5.7	5.4	4.4	4.6

3.3. TOF-SIMS Analysis

TOF-SIMS is a highly sensitive technique to determine the 2D/3D distributions of chemical fragments on a solid surface. A beam of primary ions, such as bismuth ions, is used to bombard the solid surface using the TOF-SIMS technique. Atoms or molecular fragments on the solid surface can overcome the surface binding energy to generate secondary ions/molecular fragments due to atomic collisions [14]. According to the mass spectroscopy of the secondary ions/molecular fragments, the distribution of these species on the solid surface can be remodeled [15]. This technique has been successfully used to investigate the surface characters of some minerals in their flotation system [16]. In this context, this method was used to determine the surface features of FA/dolomite conditioned with H_2SO_4 and oleate.

3.3.1. FA Surfaces

When the H₂SO₄-treated FA surface was bombarded with the Bi₃⁺⁺ primary ions, three types of secondary ion, namely, PO₃⁻, SO₄⁻, and CaO⁻, were emitted from the FA surface (Figure 3). Evidently, CaO⁻ and PO₃⁻ came from the original FA surface. The presence of SO₄⁻ was due to the adsorbed SO₄²⁻ ions on the FA surface. It is believed that SO₄²⁻ ions interacted with Ca²⁺ on the FA surface.



Figure 3. Cont.



Figure 3. Two-dimensional distributions of ions on the fluorapatite (FA) surface ($500 \times 500 \ \mu\text{m}^2$) treated with H₂SO₄ (1 × 10⁻³ mol/L): (**a**) overlap, (**b**) PO₃⁻, (**c**) SO₄⁻, and (**d**) CaO⁻.



Figure 4. Two-dimensional distributions of ions on the FA surface ($500 \times 500 \ \mu\text{m}^2$) treated with H₂SO₄ ($1 \times 10^{-3} \ \text{mol/L}$) and oleate ($2 \times 10^{-4} \ \text{mol/L}$): (**a**) overlap, (**b**) PO₃⁻, (**c**) SO₄⁻, and (**d**) CaO⁻.

On the FA surface treated with H_2SO_4 (1 × 10⁻³ mol/L) and oleate (2 × 10⁻⁴ mol/L), PO_3^- , SO_4^- , and CaO⁻ species were measured, and their distributions were found to be similar to those on the FA surface only conditioned with H_2SO_4 (Figure 4). Moreover, the molecular fragments related to oleate were not detected on the FA surface, thereby indicating that oleate did not occur on the FA surface treated with H_2SO_4 . Figure 5 further illustrates the 3D results of PO_3^- , SO_4^- , and CaO⁻ species on the FA surface conditioned with H_2SO_4 and oleate. It was found that PO_3^- and CaO⁻ were well distributed in the bulk phase of FA. In contrast, SO_4^- only presented on the top of the FA surface in an island-like structure.

According to the TOF-SIMS and flotation results of the FA samples, it is reasonable to expect that SO_4^{2-} ions reacted with Ca ions on the top of the FA surface to generate CaSO₄ species. Consequently, oleate cannot further adsorb onto the Ca sites on the H₂SO₄-treated FA surface; hence, a poor FA recovery was obtained.



Figure 5. Three-dimensional distributions of ions on the FA surface treated with H_2SO_4 (1 × 10⁻³ mol/L) and oleate (2 × 10⁻⁴ mol/L): (a) SO_4^- , (b) PO_3^- , and (c) CaO^- .

3.3.2. Dolomite Surfaces

With regard to the dolomite surface treated with 1×10^{-3} mol/L of H₂SO₄, the secondary ions, including CO₃⁻, CaO⁻, and MgO⁻, from the original dolomite surface were measured by the TOF-SIMS method (Figure 6). The SO₄⁻ was also present on the H₂SO₄-treated dolomite surface. These results revealed that SO₄²⁻ can also adsorb on the dolomite surface. However, the amount of SO₄⁻ on the dolomite surface was less than that of CO₃⁻.



Figure 6. Two-dimensional distributions of ions on the dolomite surface ($500 \times 500 \ \mu\text{m}^2$) treated with H₂SO₄ (1 × 10⁻³ mol/L): (**a**) overlap, (**b**) SO₄⁻, (**c**) CO₃⁻, (**d**) CaO⁻, and (**e**) MgO⁻.

When the H_2SO_4 -treated dolomite was further conditioned with oleate, SO_4^- ions were still found on the mineral surface along with CaO⁻, MgO⁻, and CO₃⁻ ions (Figure 7). Furthermore, a new molecular fragment (i.e., $C_2H_3O_2^-$) was measured on the dolomite surface. Evidently, the bombardment of the Bi₃⁺⁺ beam to the oleate species broke the oleate molecule, thereby resulting in the generation of $C_2H_3O_2^-$. Moreover, the amount of $C_2H_3O_2^-$ was evident on the dolomite surface, suggesting that oleate species and SO_4^{2-} can simultaneously adsorb on the dolomite surface. In other words, the presence of SO_4^{2-} on the dolomite surface did not prevent further adsorption of oleate. The 3D distribution results of these secondary ions/molecular fragments are summarized in Figure 8. Notably, SO_4^- and $C_2H_3O_2^-$ islands were located on the top of the H₂SO₄-treated dolomite surface, while other ions were found throughout the entire measured region.



Figure 7. Two-dimensional distributions of ions on the dolomite surface $(500 \times 500 \ \mu\text{m}^2)$ treated with H₂SO₄ (1 × 10⁻³ mol/L) and oleate (2 × 10⁻⁴ mol/L): (**a**) overlap, (**b**) SO₄⁻, (**c**) CO₃⁻, (**d**) CaO⁻, (**e**) MgO⁻, and (**f**) C₂H₃O₂⁻.



Figure 8. Three-dimensional distributions of ions on the FA surface treated with H_2SO_4 (1 × 10⁻³ mol/L) and oleate (2 × 10⁻⁴ mol/L): (a) SO_4^- , (b) CO_3^- , (c) CaO^- , (d) MgO^- , and (e) $C_2H_3O_2^-$.

 Ca^{2+} and Mg^{2+} ions exist on the dolomite surface. Similar to that on the FA surface, SO_4^{2-} could also bind with Ca^{2+} on the dolomite surface forming surface $CaSO_4$ species. Mg^{2+} on the dolomite surface cannot react with SO_4^{2-} due to the high solubility of $MgSO_4$. Thus, Mg sites on the surface

were valuable for the adsorption of oleate. As previously mentioned, Ca^{2+} and Mg^{2+} on the deeper layer of mineral surface may have been exposed to the solution due to the dissociation of CO_3^{2-} on the dolomite surface, which could also provide adsorption sites for oleate. In both events, oleate species can occur on the H₂SO₄-treated dolomite surface to generate a hydrophobic mineral surface.

Moreover, it seems that the measured density of SO_4^- on the dolomite surface was lower than that on the FA surface. The dissolution of the dolomite surface in the H_2SO_4 solution may release Ca^{2+} ions into the solution. In the bulk solution, Ca^{2+} ions could bond to SO_4^{2-} to preferentially form a bulk precipitation of $CaSO_4$. As a result, a portion of SO_4^{2-} ions in the solution was consumed, resulting in a relatively low adsorption density on the dolomite surface.

3.4. FTIR Study

As stated in the Introduction section, the adsorption state of oleate species on a calcium-bearing mineral surface highly depends on the oleate concentration. In this section, the ATR-FTIR method was used to determine the oleate species on the dolomite surface at selected oleate concentrations. The ATR-FTIR spectra of FA samples were also measured for comparison.



Figure 9. FTIR spectra of (a) FA samples $(1\text{--}FA; 2\text{--}FA \text{ with } 1 \times 10^{-3} \text{ mol/L of } H_2SO_4; 3\text{--}FA \text{ with } 1 \times 10^{-3} \text{ mol/L of } H_2SO_4 \text{ and } 2 \times 10^{-4} \text{ mol/L of oleate}); and (b) dolomite samples (1---dolomite and 2---dolomite with <math>1 \times 10^{-3} \text{ mol/L of } H_2SO_4)$.

Figure 9 summarizes the ATR-FTIR spectra of FA samples. In the spectrum of natural FA, the intense band at 1019 cm⁻¹ can be assigned to the asymmetrical stretching vibration PO_4^{3-} group [17]. This band was also observed in the spectrum of FA treated with H_2SO_4 (1 × 10⁻³ mol/L). Unexpectedly, the characteristic peaks of SO_4^{2-} were not found for FA treated with H_2SO_4 . The results

show that FTIR is less sensitive in detecting the CaSO₄ species on FA surface compared with the TOF-SIMS technique. In terms of FA treated with H_2SO_4 (1 × 10⁻³ mol/L) and oleate (2 × 10⁻⁴ mol/L), the spectrum was similar to that of the natural FA. The characteristic peaks of the CH₂ and CH₃ vibrations did not occur in the spectrum. It appears that oleate cannot adsorb onto the FA surface conditioned with H_2SO_4 , which is in accordance with the abovementioned TOF-SIMS results.

In the ATR-FTIR spectrum of the natural dolomite (Figure 9), the band at 1417 cm⁻¹ was due to the asymmetric stretching of CO₃ in dolomite. The peaks at 876 cm⁻¹ and 729 cm⁻¹ were attributed to the vibrations of CO₃ of dolomite [18]. The peak at approximately 729 cm⁻¹ was commonly used to distinguish dolomite from calcite [18,19]. Similar to the FTIR results of the FA sample, the spectrum of dolomite treated with H₂SO₄ was almost the same as that of natural dolomite. It is expected that the concentration of CaSO₄ on dolomite surface was particularly limited to measurement by the ATR-FTIR method.



Figure 10. FTIR spectra (**a**) 3300–2500 cm⁻¹; (**b**) 2000–1000 cm⁻¹ of dolomite with 1×10^{-3} mol/L of H₂SO₄ and oleate at different concentrations (1—1 × 10⁻⁴ mol/L, 2—2 × 10⁻⁴ mol/L, 3—2.5 × 10⁻⁴ mol/L and 4—3 × 10⁻⁴ mol/L).

In terms of dolomite treated with H_2SO_4 (1 × 10⁻³ mol/L) and further with oleate (1–3 × 10⁻⁴ mol/L), two new adsorption bands at 2850 cm⁻¹ (symmetry stretching of CH₂) and 2920 cm⁻¹ (asymmetry stretching of CH₂) were observed in the spectrum (Figure 10) [20,21]. Furthermore, the intensities of these new bands became stronger with an increase in oleate concentration, which indicates that oleate species were adsorbed on the H₂SO₄-treated dolomite surface.

The characteristic peaks of oleate species are in the range of 1800 cm⁻¹ to 1300 cm⁻¹ [10]. In the case of dolomite conditioned with 1×10^{-4} mol/L of oleate, the adsorption of oleate could not generate any new peaks in this wave number range. It seems that the adsorbed amount of oleate on the dolomtie surface was limited with 1×10^{-4} mol/L of the oleate, which cannot generate an IR signal in the spectrum from 1800 cm⁻¹ to 1300 cm⁻¹.

A doublet at 1570 cm⁻¹ and 1538 cm⁻¹ was found for dolomite with 2×10^{-4} mol/L of oleate (Figure 10). Furthermore, the peak at 1570 cm⁻¹ shifted to a higher wave number side with an increase in oleate concentration. In contrast, the position of the peak at 1538 cm⁻¹ barely changed in the examined oleate concentration range. Lu et al. assigned the doublet at 1574 cm⁻¹ and 1538 cm⁻¹ to the asymmetric vibration of carboxylate of Ca(OI)₂ on the FA surface [10]. The vibration of carboxylate stretching of Mg(OI)₂ also occurs at approximately 1572 cm⁻¹ [22]. It is possible that Mg(OI)₂ and Ca(OI)₂ can exist on the H₂SO₄-treated dolomite surface. It seems that SO₄²⁻ cannot bind with all the Ca²⁺ on the dolomite surface. Again, this may be caused by the dissociation of CO₃²⁻ on the dolomite surface; a considerable number of Ca²⁺ ions can exist on the top of dolomite surface, and thus SO₄²⁻ ions cannot interact with all the Ca²⁺ ions on the surface. Therefore, oleate can still adsorb onto some Ca sites on the dolomite surface to form precipitation of Ca(OI)₂. On the other hand, it is also possible that the bulk precipitation of Ca(OI)₂ could adsorb onto the dolomite surface phycially.

Although it was difficult measure the CaSO₄ species on the FA/dolomite surface with the ATR-FTIR method, the oleate species on the dolomite surface can be determined using this method. In addition, the above contact angle tests suggest that the contact angle of H₂SO₄-treated dolomite was approximately 110° with 2×10^{-4} mol/L of oleate. At this oleate concentration, Mg(OI)₂ and/or Ca(OI)₂ was measured on the mineral surface. Thus, it is concluded that the precipitation of Mg(OI)₂ and/or Ca(OI)₂ on the dolomite surface plays an important role in generating a hydrophobic surface.

4. Conclusions

 SO_4^{2-} ions can interact with Ca^{2+} ions on the FA surface to produce $CaSO_4$ species, which prevents the adsorption of oleate on the Ca sites on the FA surface to generate a hydrophobic surface. Hence, a poor FA recovery is obtained.

As expected, CaSO₄ species can also form on the H_2SO_4 -treated dolomite surface. Mg²⁺ ions on the dolomite surface cannot be involved in the interaction with SO₄²⁻ ions. We hypothesize that a considerable number of metal atoms on the dolomite surface might be exposed to the solution considering the dissociation of CO₃²⁻ on the dolomite surface in the solution of H₂SO₄, and thus SO₄²⁻ ions cannot bind with all of the Ca²⁺ ions on the dolomite surface. As a result, oleate species still adsorb on some Ca and Mg sites on the dolomite surface. In addition, the precipitation of Mg(OI)₂ and/or Ca(OI)₂ on the H₂SO₄-treated dolomite surface accounts for the hydrophobicity of dolomite surface using 2 × 10⁻⁴ mol/L of oleate. In this regard, the H₂SO₄-treated dolomite still could be collected by oleate at this concentration.

Author Contributions: Q.C. and D.L. conceived and designed the experiments; H.Z. performed the experiments; X.Y. and H.L. analyzed the data; D.L. contributed reagents/materials/analysis tools; H.Z. wrote the paper.

Funding: This research was funded by the Analysis and Testing Foundation of Kunming University of Science and Technology (China).

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

References

- 1. Prasad, M.; Majumder, A.K.; Rao, T.C. Reverse flotation of sedimentary calcareous/dolomitic rock phosphate ore—An overview. *Min. Metall. Explor.* **2000**, *17*, 49–55. [CrossRef]
- 2. Zheng, X.; Smith, R.W. Dolomite depressants in the flotation of apatite and collophane from dolomite. *Miner. Eng.* **1997**, *10*, 537–545. [CrossRef]

- 3. Liu, X.; Luo, H.; Cheng, R.; Li, C.; Zhang, J. Effect of citric acid and flotation performance of combined depressant on collophanite ore. *Miner. Eng.* **2017**, *109*, 162–168. [CrossRef]
- 4. Ge, Y.Y.; Gan, S.P.; Zeng, X.B.; Yu, Y.F. Double reverse flotation process of collophanite and regulating froth action. *Trans. Nonferr. Met. Soc. China* **2008**, *18*, 449–453. [CrossRef]
- Sis, H.; Chander, S. Reagents used in the flotation of phosphate ores: A critical review. *Miner. Eng.* 2003, 16, 577–585. [CrossRef]
- 6. Karlkvist, T.; Patra, A.; Rao, K.H.; Bordes, R.; Holmberg, K. Flotation selectivity of novel alkyl dicarboxylate reagents for apatite–calcite separation. *J. Colloid Interface Sci.* **2015**, *445*, 40–47. [CrossRef]
- 7. Yu, J.; Ge, Y.; Guo, X.; Guo, W. The depression effect and mechanism of NSFC on dolomite in the flotation of phosphate ore. *Sep. Purif. Technol.* **2016**, *161*, 88–95. [CrossRef]
- 8. Liu, X.; Li, C.; Luo, H.; Cheng, R.; Liu, F. Selective reverse flotation of apatite from dolomite in collophanite ore using saponified gutter oil fatty acid as a collector. *Int. J. Min. Process.* **2017**, *165*. [CrossRef]
- Mohammadkhani, M.; Noaparast, M.; Shafaei, S.Z.; Amini, A.; Amini, E.; Abdollahi, H. Double reverse flotation of a very low grade sedimentary phosphate rock, rich in carbonate and silicate. *Int. J. Min. Process.* 2011, 100, 157–165. [CrossRef]
- 10. Lu, Y.; Drelich, J.; Miller, J.D. Oleate adsorption at an apatite surface studied by ex-situ FTIR internal reflection spectroscopy. *J. Colloid Interface Sci.* **1998**, 202, 462–476. [CrossRef]
- 11. Rao, K.H.; Antti, B.M.; Forssberg, E. Mechanism of oleate interaction on salt-type minerals, Part II. Adsorption and electrokinetic studies of apatite in the presence of sodium oleate and sodium metasilicate. *Int. J. Min. Process.* **1990**, *28*, 59–79. [CrossRef]
- 12. DR, V.; DS, R.; SD, D. Electrokinetic properties of hydroxyapatite under flotation conditions. J. Colloid Interface Sci. 2010, 343, 239–245. [CrossRef]
- 13. Sis, H.; Chander, S. Adsorption and contact angle of single and binary mixtures of surfactants on apatite. *Miner. Eng.* **2003**, *16*, 839–848. [CrossRef]
- 14. Sodhi, R.N.S. Time-of-flight secondary ion mass spectrometry (TOF-SIMS):—Versatility in chemical and imaging surface analysis. *Analyst* **2004**, *129*, 483–487. [CrossRef] [PubMed]
- 15. Benninghoven, A. Chemical analysis of inorganic and organic surfaces and thin films by static time-of-flight secondary ion sass spectrometry (TOF-SIMS). *Angew. Chem. Int. Ed.* **2010**, *33*, 1023–1043. [CrossRef]
- 16. Chehreh Chelgani, S.; Hart, B. TOF-SIMS studies of surface chemistry of minerals subjected to flotation separation—A review. *Miner. Eng.* **2014**, *57*, 1–11. [CrossRef]
- Albano, M.P.; Garrido, L.B. Processing of concentrated aqueous fluorapatite suspensions by slip casting. *J. Mater. Sci.* 2011, 46, 5117–5128. [CrossRef]
- Müller, C.M.; Pejcic, B.; Esteban, L.; Piane, C.D.; Raven, M.; Mizaikoff, B. Infrared Attenuated Total Reflectance Spectroscopy: An Innovative Strategy for Analyzing Mineral Components in Energy Relevant Systems. *Sci. Rep.* 2014, *4*, 6764. [CrossRef]
- 19. Gunasekaran, S.; Anbalagan, G.; Pandi, S. Raman and infrared spectra of carbonates of calcite structure. *J. Raman Spectrosc.* **2010**, *37*, 892–899. [CrossRef]
- 20. Huang, Z.; Cheng, C.; Li, L.; Guo, Z.; He, G.; Yu, X.; Liu, R.; Han, H.; Deng, L.; Fu, W. Morpholine-based gemini surfactant: Synthesis and its application for reverse froth flotation of carnallite ore in potassium fertilizer production. *J. Agric. Food Chem.* **2018**, *66*, 13126–13132. [CrossRef]
- 21. Liu, C.; Feng, Q.; Zhang, G.; Ma, W.; Meng, Q.; Chen, Y. Effects of lead ions on the flotation of hemimorphite using sodium oleate. *Miner. Eng.* **2016**, *89*, 163–167. [CrossRef]
- 22. Wensel, R.W.; Penaloza, M.; Cross, W.M.; Winter, R.M.; Kellar, J.J. Adsorption behavior of oleate on Mg(OH)₂ as revealed by FT-IR spectroscopy. *Langmuir* **1995**, *11*, 4593–4595. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).