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# Quantum Mechanics Simulation on Adsorption Behavior and Flotation Mechanism of Combined Sodium Oleic Acid and Oleamide onto Fluorapatite Surface in an Aqueous Environment

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## Abstract

In this study, the effects of various reagents-sodium carbonate and sodium hydroxide as pH regulators, calcium lignosulfonic acid as depressant, and combined sodium oleate and amide as collector on the flotation of apatite ore were investigated using flotation experiments, and adsorption mechanism of collector on apatite surface were evaluated using quantum mechanical simulations. The flotation experiments showed that the addition of 4 kg/t sodium carbonate and 1.5 kg/t sodium hydroxide as pH regulators, 3 kg/t calcium lignosulfonic acid as depressant and 60 g/t combined sodium oleic acid and oleamide (acid number of collector; 105 mgKOH/g) as collector exhibited excellent collecting ability for apatite. From low-grade apatite ore with P<sub>2</sub>O<sub>5</sub> 7.05%, a concentrate with P<sub>2</sub>O<sub>5</sub> 31.42% was obtained with 81.08% recovery in rougher flotation. Compared with the simulation results for the interaction energy between apatite {001} surface and collectors, and the relative concentration of collector on apatite {001} surface, adsorption strength has following order; combined sodium oleic acid and oleamide > sodium oleic acid > oleamide. From the simulation results on the equilibrium configuration of the collector with the fluorapatite {001} surface in the liquid environment, it was revealed that the two atoms (N and H) of the oleamide can form a strong bidentate conformation, and O atom in the C-O group and that in -C=O group of oleic acid anion can bond with the Ca atom on the surface {001} to form monodentate conformation.

## 1. Introduction

Now phosphate rock resources are now important mineral in industry and agriculture, such as the production of phosphate fertilizer, foodstuffs, drink, medicine, paints, dyes, match and ceramics, as well as non-renewable strategic mineral resources [1-4]. Fluorapatite is most commonly found as large, well-shaped crystals in igneous phosphate deposits [5].

Fluorapatite has been separated through various methods, and flotation has been the most widely used method for the beneficiation of phosphate ores, producing phosphate concentrates with 30% up P<sub>2</sub>O<sub>5</sub> [6, 7]. In the case of phosphate ores that contain significant amounts of carbonates, flotation becomes more difficult because of very similar

surface properties of phosphates and carbonates [9]. In the flotation of fluorapatite ores, the most widely used collectors in the world are long-chain sodium oleates obtained from vegetable species such as rice bran and soybean [6,8]. Fundamental studies were carried out to evaluate the selective flotation of calcite, apatite and quartz using collectors synthesized from flaxseed, nigella, and olive oils [9].

One approach to enhance the flotation performance of oleic acid is using a mixed collector. It was emphasized that the mixed collector of oleic acid, linoleic acid and linolenic acid improved the collector performance in phosphate flotation [7]. Severov et al. [10] reported

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that the use of a mixture of oxyethylenated cetyl ether with 2 oxyethylene groups and tall oil fatty acids considerably increased the apatite concentrate grade, keeping P<sub>2</sub>O<sub>5</sub> recovery at reasonably acceptable levels. Ding et al. [11] reported that a highest recovery of apatite could be obtained when a mixed collector was used with a molar ratio of oleamide to SDBS of 2:1 at pH=9 and the synergistic effects of mixed collector were mainly attributed to the decrease in the critical micelle concentration of oleamide in the presence of SDBS. Abdollahi et al. [34] reported that an apatite concentrate containing 23.2% P<sub>2</sub>O<sub>5</sub> with 90.5% recovery was achieved by rougher flotation experiments using a 600 g/t of mixed collector combined with tall oil fatty acid (TOFA) and oleic acid polyethylene glycol ester 6 mol (OAPEGE6) at a weight ratio of 70 to 30%, and an apatite concentrates with 32.9% P<sub>2</sub>O<sub>5</sub> and 59.1% recovery were obtained in the industrial scale. They explained that the synergistic effect of two collectors occurred by covering for each other's weakness in the adsorption reaction, which enhances the apatite surface hydrophobicity and improves the grade and recovery of P<sub>2</sub>O<sub>5</sub> in the concentrate [34]. However, since the composition and cost of the collectors, flotation process, and equipment characteristics used in each country are different, it is important to increase the grade and recovery of the apatite concentrate using an effective collector suitable for the conditions of the country.

Numerous studies have been conducted on the flotation mechanism for the adsorption of carboxylic acids onto mineral surfaces. At alkaline conditions, the sodium fatty acid released a negatively charged carboxylate ions. Then these ions reacted with Ca<sup>2+</sup> onto the apatite surface to form calcium carboxylate. This chemisorption method is generally considered to be the primary method of fatty acid adsorption onto the apatite surface at alkaline conditions [7,12,13]. Most of these studies were based on measurements such as zeta potential [14-16,33,34], FTIR spectroscopy [17,18,34], atomic force microscopy [18,19,27] and QCM-D, etc., but more computer simulations have recently been carried out to analyse flotation mechanism.

Recently, computational simulations have proved to be a powerful tool for analyzing flotation mechanisms such as the adsorption of reagents on mineral surfaces at an atomic level, and have predicted with high accuracy the problems previously unexplained [17,18,23]. Liu et al. [20] have determined the optimal molecular structure

and calculate the relative energy, atomic charge values, the energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of collectors in aqueous media, in an attempt to predict the reactivity of these three different amine collectors with quartz mineral surfaces. Effect of pH on the adsorption of DDA on montmorillonite surface in aqueous solution was studied by Forcite plus module [17]. Adsorption configurations for oleate on most stable and most exposed surfaces of hematite, magnetite, and goethite were determined by carrying out Monte Carlo searches of the configurational space of the substrate-adsorbate system using COMPASS force field, followed by ab-initio calculations [21]. Zheng et al. [22] was quantitatively elucidated the distribution of NaOL on different crystal planes using COMPASS force field. Shen et al. calculated the relative concentration of water molecules near the kaolinite (001) surface to reveal the adsorption mechanism of the mixed collectors on the kaolinite (001) surface [23]. Wang et al. [24] calculated the density profiles of O and H atoms in water molecules on muscovite surface to study the adsorption configuration of the mixed surfactants (dodecylamine and sodium oleate) on muscovite surface. Yu et al. [18] found that the value of the Mulliken charge of mineralophilic group in oleic acid ion are more negative after associated with oleic acid molecule, which strengthens the bonding ability of it to the positive sites of mineral surface. Ghatee et al. [25] reported the results of classical molecular dynamics simulation of hexanoic acid adsorption on calcite (101 $\bar{4}$ ) surface plane using Pavese and AMBER force fields for calcite and hexanoic acid, respectively. DFT calculations indicated that hammer-like amidoxime surfactant reacted with nucleophilic reagent by the reactive site of -CH<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>C(NOH)N<sup>+</sup>H<sub>3</sub> group and more easily absorbed on the surface of phosphorite than 1-dodecylamine [26]. Marisa et al. [27] revealed that the better performance in quartz flotation from the combined use of monoamine and diamine can be explained by the energetic favoring when considering interactions between the collectors in neutral and protonated forms. Zhang et al. [33] reported that the Cl atom introduction allowed 2-chloro-9-octadecenoic acid collector to adopt a parallel adsorption configuration on the mineral surface.

As we all know, the development of the high-effective collector is the most important way for the improvement of direct flotation process. In our previous study, flotation behavior and mechanism of oleamide onto apatite surface has been carried

out by micro-flotation, zeta potential and XPS analysis [28]. Although oleamide have been employed as a collector in the flotation, the results of flotation of fluorapatite ore using combined sodium oleic acid and oleamide, a mixed collector, and its adsorption behavior on mineral surface have not yet been realized. The aim of this study was to investigate the flotation performance and mechanism of combined sodium oleic acid and oleamide onto the fluorapatite surface by flotation tests and quantum mechanics simulation in aqueous environment.

## 2. Experimental methods and materials

### 2.1. Materials

The raw ore sample was crushed into 100% pass 3 mm. The mineral components and chemical compositions of the raw ore are shown in Table 1 and Table 2. From Table 1, the valuable mineral in the raw ore is fluorapatite (13.2%) and the gangue minerals is dominated by calcite (68.3%). The overall grade of raw ore was 6.65% P<sub>2</sub>O<sub>5</sub>. The sizes of apatite grains in the ore were mainly 0.06 mm–0.3mm.

**Table 1. Mineral components of apatite raw ore**

Minerals	Fluor-apatite	Calcite	Magnetite	Quartz	Dolomite	Feldspar, etc.
Percentage (wt. %)	13.2	68.3	4.1	3.1	5.2	6.1

**Table 2. Chemical compositions of raw ore**

Composition	Percentage (wt. %)	Composition	Percentage (wt. %)
Ig. Loss	29.03	Na <sub>2</sub> O	0.99
P <sub>2</sub> O <sub>5</sub>	6.65	Al <sub>2</sub> O <sub>3</sub>	4.18
CaO	39.61	Fe <sub>2</sub> O <sub>3</sub>	6.49
K <sub>2</sub> O	1.80	MgO	3.12
SiO <sub>2</sub>	5.59	Sr	0.1
F	0.05	etc.	2.39

The sodium oleate was purchased from Tianjin Guangfu Fine Chemical Research Institute with purity of 99% and oleamide was synthesized according to the method described in our previous literature [28]. Chemical grade sodium carbonate and sodium hydroxide were used as pH regulators of slurry, and industrial grade calcium lignosulfonic acid was used as depressant for gangue minerals. The tap water (Ca<sup>2+</sup> 10.30 mg/L, Mg<sup>2+</sup> 2.56 mg/L, Na<sup>+</sup> 6.12 mg/L, CO<sub>3</sub><sup>2-</sup> 3.20 mg/L and SO<sub>4</sub><sup>2-</sup> 5.60 mg/L) was used for experiments.

### 2.2. Grinding and flotation

For each flotation experiment, 200 g apatite was ground to –0.074 mm at 60.3% in a rod mill at a concentration of 60% solids by mass. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and sodium hydroxide (NaOH) were added to the rod mill with the raw ore as pH modifier. The pH values of the slurry ranges from 8 to 12. The flotation tests were conducted in a flotation cell (model XFD, effective volume 0.75 L) at a concentration of 30% solids by mass. Calcium lignosulfonic acid was added as a depressant and, the collector was added and they were conditioned for 1 min respectively. The flotation was performed for 6 min, and the froth products(concentrate) was collected, filtered, dried under various flotation conditions. The pulp

temperature was maintained at 20±0.5 °C during the flotation tests. Each experiment was repeated three times with the mean value finally recorded.

### 2.3. Computational simulation

All simulations were performed in Material Studio 8.0 software. The initial structure of fluorapatite model created from Materials Visualizer were optimized using the CASTEP module. The exchange correlation functional was the GGA-PBE. The plane-wave cut off energy of 630 eV was used throughout. The maximum displacement, maximum force, maximum energy change and maximum stress were 0.005 Å, 0.1eV/Å, 2.0×10<sup>-6</sup> eV/atom and 0.01 GPa, respectively. Pseudo atomic calculation was performed for O 2s22p4, F 2s22p5, P 3s23p3, Ca 3s23p64s2.

The geometry optimization of sodium oleic acid and oleamide was carried out, and the electron structural properties of the molecules were calculated by using DMOL3 module contained in MS software. The initial structure of these reagents imported from ChemBioOffice 2010 (Cambridge soft) was optimized using the DMOL3 module. The calculation was performed by using GGA/PBE as the exchange-correlation function, DND basis set (basis file of 4.5) and all electron core treatment. The water-reagent complexes were

created in Amorphous Cell modules. The construction of Amorphous cell contained five hundred water molecules and two oleate (three different condition).

Final complex model systems of the mineral-water-reagent for fluorapatite {001} surface were set in boxes of  $24.90 \text{ \AA} \times 25.57 \text{ \AA} \times 44.93 \text{ \AA}$  (total atoms:1774),  $25.73 \text{ \AA} \times 24.79 \text{ \AA} \times 45.00 \text{ \AA}$  (total atoms:1772) and  $24.66 \text{ \AA} \times 25.40 \text{ \AA} \times 45.74 \text{ \AA}$  (total atoms 1773), respectively. In this study, the molecular dynamics simulations using the Forcite modules were conducted in the order of a NVT, NPT and NVE methods at 298K with a time step 0.01-0.15 fs, and a total simulation time length of 0.5-5 ps.

### 3. Results and Discussion

#### 3.1 Flotation

Flotation tests for apatite ore were carried out to investigate the effect of reagent dosages on rougher flotation performance under different conditions. Figure 1 shows the variation tendency with different dosages of sodium carbonate on the flotation P<sub>2</sub>O<sub>5</sub> grade and recovery. The other reagents employed and their dosages are constant (sodium hydroxide: 1.25 kg/t, calcium lignosulfonic acid: 2 kg/t, combined sodium oleic acid and oleamide: 60 g/t, acid number of collector: 135 mgKOH/g). As the dosage of sodium carbonate increases, the recovery increases with increasing amount of froth mineralized in the flotation cell, but the P<sub>2</sub>O<sub>5</sub> grade decreases slightly when the dosage of sodium carbonate increases from 4 kg/t to 6 kg/t. Experiments showed that when the dosage of sodium carbonate was less than 2 kg/t, the mineralized froth in the flotation cell was poor and apatite was very difficult to float. The highest P<sub>2</sub>O<sub>5</sub> grade of 25.9% and recovery of 89.5% were obtained at 4 kg/t sodium carbonate, which showed higher flotation performance than ones at other dosages tested.

When the dosage was increased to 0.5 kg/t, sodium hydroxide produced a suitable concentrate grade and recovery (Figure 2). In this case, only sodium hydroxide was a variant, while the others were invariable except the addition of sodium carbonate (4 kg/t). The results showed that a low dosage of 0.5 kg/t sodium hydroxide was achieved the concentrate with 26.1% P<sub>2</sub>O<sub>5</sub> grade and 84.4% recovery. Especially for the dosage of 1.5 kg/t, the highest flotation recovery of 89.5% was achieved,

which was about 5.1% higher than the dosage of 0.5 kg/t.

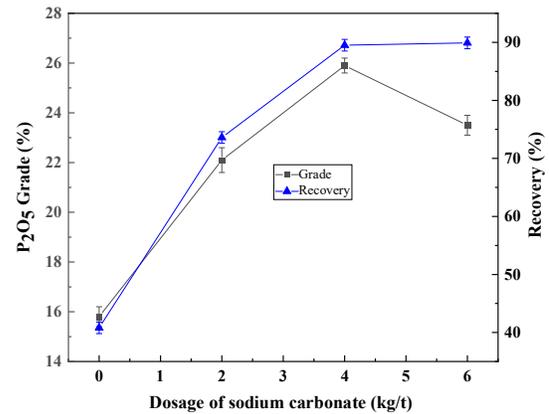
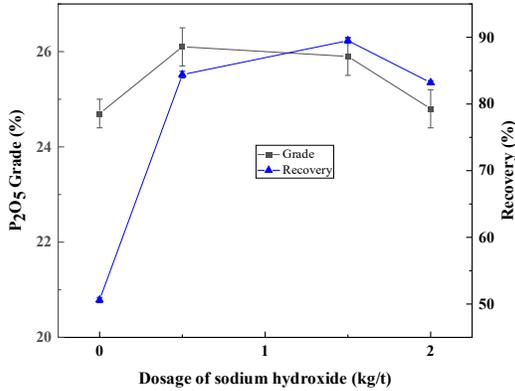


Figure 1. Fluorapatite grade and recovery as a function of dosage of sodium carbonate

Flotation results showed that the gangue minerals depressed and maintained comparatively high apatite floatability by up to the dosage of 2~3 kg/t. This finding suggested that the gangue minerals which was already depressed by calcium lignosulfonic acid and the fluorapatite were selectivity floated using combined sodium oleic acid and oleamide. The highest P<sub>2</sub>O<sub>5</sub> grade of the concentrate at a dosage 3 kg/t of calcium lignosulfonic acid was 27.13%, which recovered 82.35% of fluorapatite.

Figure 1 and Figure 2 shows that the ratio of CO<sub>3</sub><sup>2-</sup> ions and OH ions in the flotation slurry is very important. From Figure 4 and Figure 5, it can be seen that adjusting the dosage and acid number of combined sodium oleic acid and oleamide can easily change the selectivity and collecting ability of collector used in flotation, thus making it widely applicable for flotation of various non-sulfide minerals as well as apatite ores.

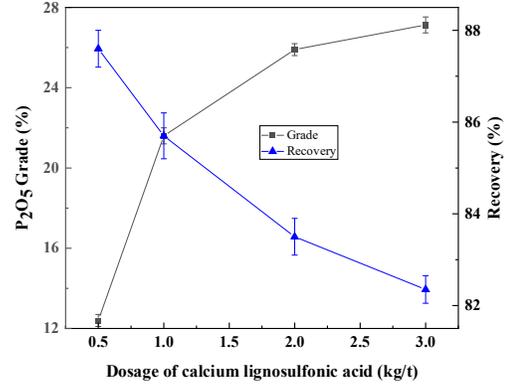
In our previous study [28], apatite flotation recoveries increased more at the pH 8-9 range, but in these experiments highest P<sub>2</sub>O<sub>5</sub> grade and recovery were obtained at the slurry pH of 10.7-10.9. In both cases, the difference in the pH of the flotation slurry is due to the different contents of various ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> etc. in the pulp. This is consistent with the explanation that the interactions of anionic collector with dissolved Ca<sup>2+</sup> ions can form an insoluble salt precipitating non-selectively on the mineral surface [6].



**Figure 2. Fluorapatite grade and recovery as a function of dosage of sodium hydroxide**

Figure 3 shows the variation tendency with different dosages of calcium lignosulfonic acid on the flotation P<sub>2</sub>O<sub>5</sub> grade and recovery. The other reagents employed and their dosages are constant (sodium carbonate: 4 kg/t, sodium hydroxide: 1.25 kg/t, combined sodium oleic acid and oleamide: 60 g/t, acid number of collector: 135 mgKOH/g). This indicates that the concentrate grade increases with the increase of dosages of calcium lignosulfonic acid from 0.5 kg/t to 3 kg/t and the highest P<sub>2</sub>O<sub>5</sub> grade (27.13%) was achieved when the dosage of depressant was 3 kg/t. Moreover, when the dosage of calcium lignosulfonic acid was 3 kg/t, the recovery of apatite was stable, but when the dosages of calcium lignosulfonic acid were more than 3 kg/t, apatite recoveries were very poor. This is because the addition of calcium lignosulfonic acid is too high to inhibit not only gangue but also apatite. The results show that calcium lignosulfonic acid as a depressant has considerably excellent inhibition performance for gangues in the apatite flotation.

The flotation results as a function of dosage of combined sodium oleic acid and oleamide is presented in Figure 4. The other reagents employed and their dosages are constant (sodium carbonate: 4 kg/t, sodium hydroxide: 1.25 kg/t, calcium lignosulfonic acid: 3 kg/t, acid number of collector: 135 mgKOH/g). When the dosage of combined sodium oleic acid and oleamide increased from 50 g/t to 70 g/t, the P<sub>2</sub>O<sub>5</sub> grade decreased slightly, but the flotation recovery increased greatly. These flotation results showed that the apatite maintained a comparatively high floatability by up to an additional 60-70 g/t of combined sodium oleic acid and oleamide, and that P<sub>2</sub>O<sub>5</sub> grade decreased at 80 g/t with addition of combined sodium oleic acid and oleamide. During the flotation experiments, it was observed that under the addition of combined

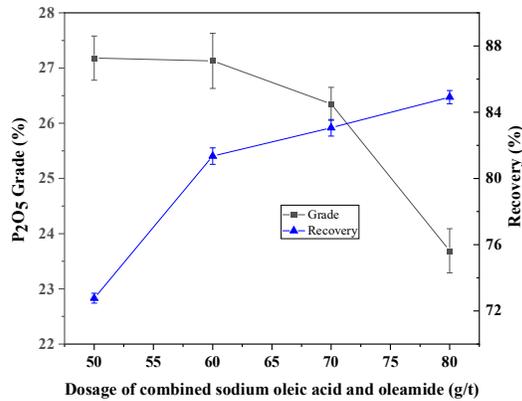


**Figure 3. Fluorapatite grade and recovery as a function of dosage of calcium lignosulfonic acid**

sodium oleic acid and amide is 60-70 g/t, the apatite mineral agglomerates better in the flotation cell and the concentrate grade is high through the weight of the froth recovered by the scraper. The flotation recovery of 81.35% and highest P<sub>2</sub>O<sub>5</sub> grade of 27.13% were obtained at the combined sodium oleic acid and oleamide addition of 60 g/t, which was considered to be better than the other flotation results.

The flotation results as a function of acid number of collector are shown in Figure 5. The other reagents employed and their dosages are constant (sodium carbonate: 4 kg/t, sodium hydroxide: 1.25 kg/t, calcium lignosulfonic acid: 3 kg/t, sodium oleic acid/oleamide: 60 g/t). In these experiments, the pH values of the pulp were adjusted from 10.7 to 10.9. The result indicates that P<sub>2</sub>O<sub>5</sub> grade decreases with increasing acid number of collector from 105 mgKOH/g to 135 mgKOH/g, and the highest P<sub>2</sub>O<sub>5</sub> grade (31.42%) was obtained when the acid number of collector was 105 mgKOH/g. When the acid number of the collector was in the range of 105-110 mgKOH/g, the recoveries were above 80% and there was no significant variation. Therefore, setting the acid number of the collector in the range 105-110, it can be seen that the P<sub>2</sub>O<sub>5</sub> grade can be more than 30% and the recovery can be more than 80%.

When the combined sodium oleic acid and oleamide were employed, it showed excellent collecting ability compared with sodium oleic acid or oleamide on fluorapatite surface. This suggests that the correct adjustment of the acid number as well as combined sodium oleic acid and amide dosage can enhance the P<sub>2</sub>O<sub>5</sub> grade and recovery of the flotation concentrate, and that combined sodium oleic acid and oleamide may have excellent collecting ability onto the fluorapatite surface.

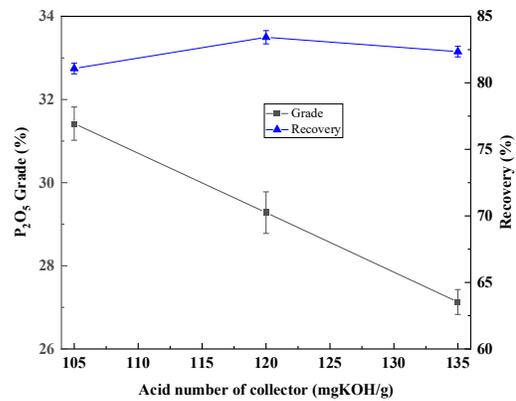


**Figure 4. Fluorapatite grade and recovery as a function of dosage of combined sodium oleic acid and oleamide**

Experiments to find the optimum operating parameters for flotation of Jordanian phosphate showed that the grade and recovery of the concentrate changed irregularly with increasing collector dosage [29]. The results of single factorial experiments [30] on sodium carbonate dosage showed that with low or high sodium carbonate dosage, the P<sub>2</sub>O<sub>5</sub> grade and recovery of concentrate decreased, which was similar to our experimental results (Figure 1 and Figure 2). They demonstrated that OL- and (Ol)22- were the most effective components for colophonite flotation, and when pH was too high, OH- in the pulp would compete with the collector anions for the mineral surface and expel the adsorbed (RCOO)2H- and RCOO- ions from the surface of the colophonite, causing rapid decrease in the grade and recovery of the colophonite concentrate [30]. The variation of factors such as sodium carbonate, sodium hydroxide, calcium lignosulfonic acid, combined sodium oleic acid and oleamide and acid number of collector, which affect the P<sub>2</sub>O<sub>5</sub> grade and recovery of the concentrate were determined by a single-factor experiment, but the level of these factors cannot be considered to be the optimal value.

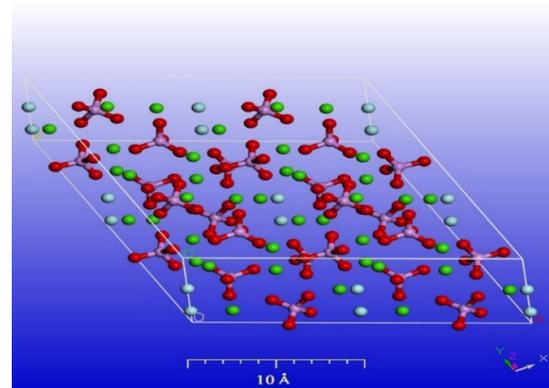
### 3.2. Computational simulation

The fluorapatite is hexagonal with space group P6<sub>3</sub>/m and parameters  $a=9.3973 \text{ \AA}$ ,  $b=9.3973 \text{ \AA}$ ,  $c=6.8782 \text{ \AA}$ ,  $\alpha=90^\circ$ ,  $\beta=90^\circ$  and  $\gamma=120^\circ$  with one formula unit of fluorapatite per unit cell. These parameters are in good agreement with the previous studies [31]. The fluorapatite {001} surface is the most commonly exposed surface for minerals grinding. The geometry optimization of fluorapatite {001} surface structure is shown in



**Figure 5. The effect of acid number of collector on rougher flotation**

Figure 6, where little green is Ca, light blue is F and red is O, while purple is P. The fluorapatite unit cell has two distinct Ca sites: Ca1 and Ca2. In the four adjacent unit cells  $2 \times 2 \times 1$ , four Ca1 form "columnar" parallel to the c-axis. Fluorine ions located on 1/4 sites, lying on the edge along c-axis of unit cell. Fluorine ions are situated in the center of hexagonal prism formed by six Ca1 of {001} surface from both above and below, respectively. While fluorine ions also located in the center of small triangle, vertex of which are Ca2, perpendicular to the c-axis. These triangles formed by the Ca2 are rotated by  $180^\circ$  each other.



**Figure 6. The optimized structures of fluorapatite {001} crystals**

The optimized geometry structures of sodium oleic acid and oleamide are shown in our previous report [32]. As reported in the literature [16,18], sodium oleic acid mainly exists as oleic acid anion in slurry. Besides, the active component of the oleamide is a non-ionic polar molecule or, in rare cases, an anion species in the flotation slurry of pH above 9 [32]. Therefore, the structures of sodium oleic acid and oleamide are used to simulate. In

final complex model systems, we consider the adsorption behavior between the fluorapatite {001} surface and water-reagent complexes. Figure 7 shows the equilibrium configuration of sodium oleic acid, oleamide and combined sodium oleic acid and oleamide onto the fluorapatite {001} surface. The interaction energy between mineral surface and the collectors could be quantified using Eq. (1):

$$\Delta E = E_{\text{total}} - (E_{\text{surface}} + E_{\text{reagent}}) \quad (1)$$

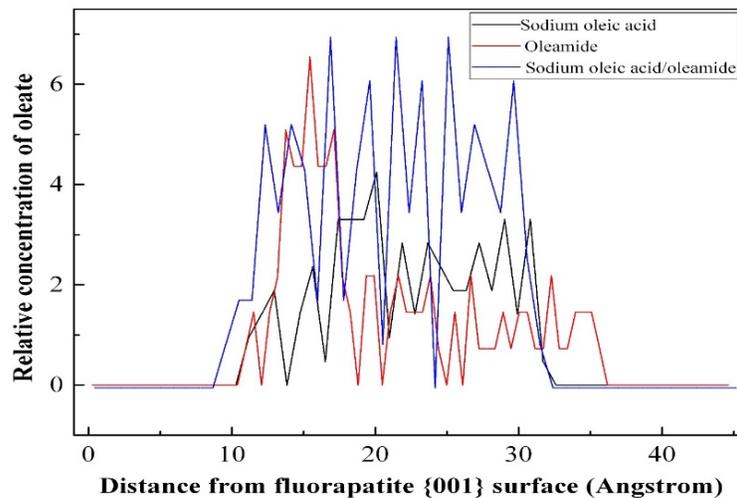
where  $E_{\text{total}}$ ,  $E_{\text{surface}}$ , and  $E_{\text{reagent}}$  are the total energy of the simulated fluorapatite surface-reagent, fluorapatite surface and reagent, respectively [20,23]. The value of the interaction energy ( $\Delta E$ ) is negative, which indicates that the interaction between the mineral surface and reagent is stronger, and the reagent will be more easily adsorbed onto the mineral surface [23].

**Table 3. Interaction energy between fluorapatite surface and reagent**

System	$E_{\text{total}}$ (Hartree)	$E_{\text{surface}}$ (Hartree)	$E_{\text{reagent}}$ (Hartree)	$\Delta E$ (Hartree)	$\Delta E$ (kJ/mol)
sodium oleic acid	-53 499.062 41	-51 480.982 81	-2 017.726 36	-0.353 24	-927.431 6
oleamide	-53 317.248 95	-51 480.982 81	-1 835.953 77	-0.312 37	-820.127 4
Combined sodium oleic acid and oleamide	-54 335.146 99	-51 480.982 81	-2 853.772 81	-0.391 37	-1027.541 9

From Table 3, in the three systems, after the interaction of the water-reagent model with the fluorapatite {001} surface, the total energy decreases resulting negative  $\Delta E$ . Adsorption strength have the following order: combined sodium oleic acid and oleamide > sodium oleic acid > oleamide. The lowest negative  $\Delta E$  was found in the fluorapatite-combined sodium oleic acid and oleamide system, which indicated the strongest interaction of combined sodium oleic acid anion and oleamide molecular on the surface

of fluorapatite {001} in the aqueous state. Meanwhile, the interaction energy of other two systems were different, which revealed that fluorapatite {001} surface can be interacted with sodium oleic acid anion or oleamide molecular. But the interaction of fluorapatite {001} surface with sodium oleic acid is stronger than that with oleamide. Thus, the combined sodium oleic acid and oleamide could be predicted to have a higher collecting ability on fluorapatite than sodium oleic acid or oleamide.



**Figure 7. Relative concentration of oleate on the distance from fluorapatite {001} surface.**

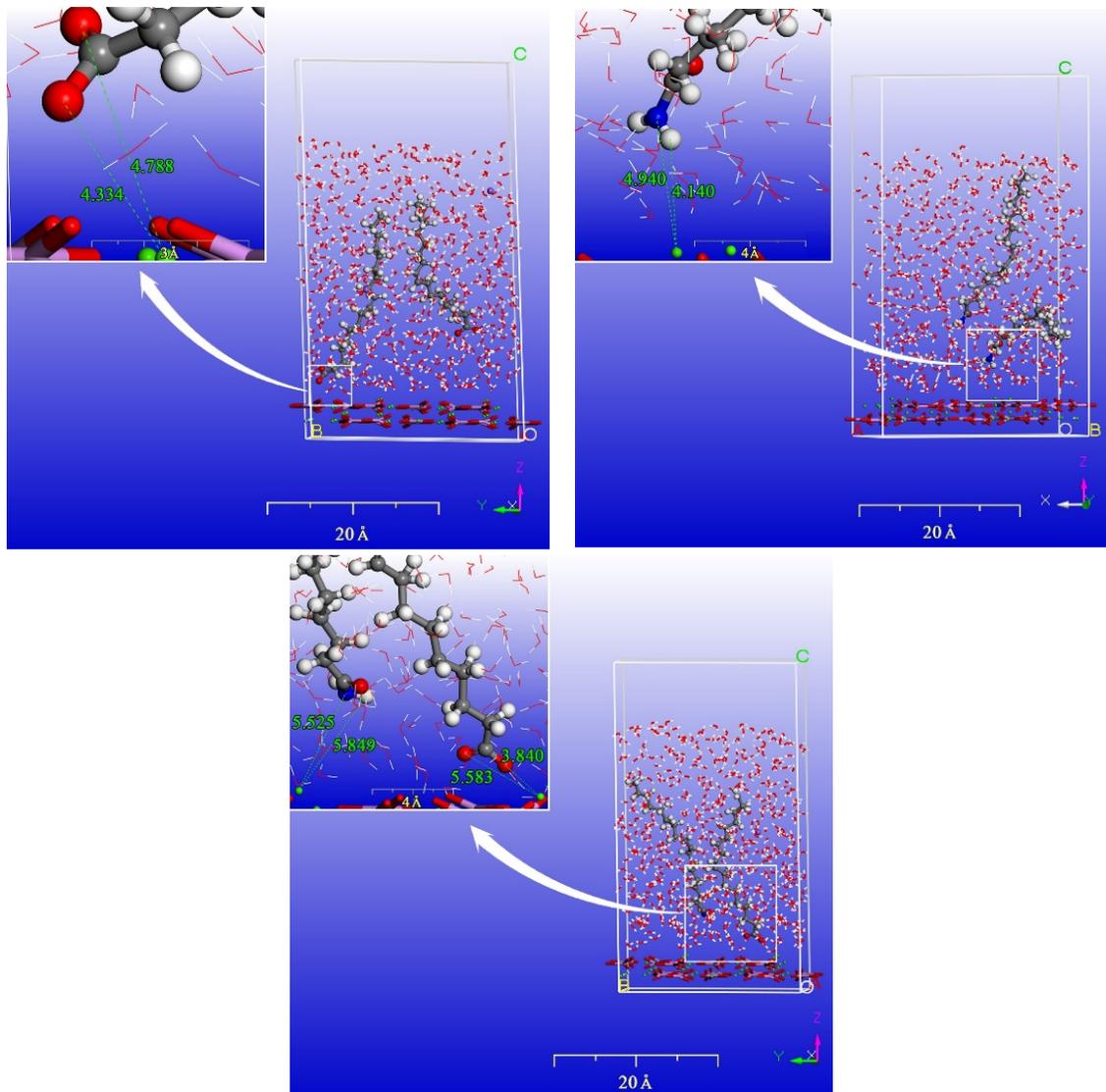
Figure 7 present the relative concentration of oleate (carboxyl groups and amide groups) along the z-direction and z-axis was normal to the fluorapatite {001} surface. The concentration distribution of carboxyl groups in combined sodium oleic acid and oleamide system were close to the fluorapatite {001} surface. Specially, in this

system carboxyl groups and amide groups were distributed in the distance range 9-33 Å and concentrated around the distance 17-33 Å from the fluorapatite {001} surface. Moreover, as shown in the simulation results, the concentration distribution of oleate in combined sodium oleic acid and oleamide system were more densely

distributed than the ones in the sodium oleic acid system and oleamide system. Therefore, the simulation results suggested that adsorption density of oleate groups by combined sodium oleic acid and oleamide onto fluorapatite surface were higher compared to the ones by sodium oleic acid system or oleamide system.

As we all know, the adsorption status of ions or molecules with mineral surface was determined by minimum distance between the special atom of a polar head group of reagent and the metal sites at the mineral surface. The equilibrium configuration of sodium oleic acid, oleamide, and combined sodium oleic acid and oleamide on fluorapatite {001} surface in an aqueous environment are shown in Figure 8, where color representation is as

follows: ash color, C; white, H; blue, N; purple, Na; and red, O). As shown in Figure 8(a), the distance between the O atom of C-O group and outmost Ca atoms onto the fluorapatite {001} surface is 4.334 Å, which is shorter than that of  $-C=O$  group (4.788 Å). This implies that the two O atoms in C-O group and  $-C=O$  group of oleic acid anion can bond with surface Ca atom to form a weak bidentate conformation. The distance between the N atom of  $-C(=O)-NH$  group and the Ca atom of the fluorapatite {001} surface is 4.940 Å which is longer than that of H atom and the Ca atom onto surface (4.140 Å). This suggests that the N atom in  $-C(=O)-NH$  group of oleamide can bond with surface Ca atom to form a monodentate conformation (Figure 8(b)).



**Figure 8.** Equilibrium configuration on the fluorapatite {001} surface under different condition (a); sodium oleic acid (b); oleamide (c); combined sodium oleic acid and oleamide

It is worthwhile mentioning that the distances of O-Ca bond and N-Ca bond in the combined sodium oleic acid and oleamide system are changed for the other two cases where the distance between the O atom of C-O group and the surface Ca atom is changed to 3.840 Å, and the distance between the N atom of -C(=O)-NH group and the surface Ca atom is changed to 5.525 Å. However, it can be hypothesized that the Ca atom onto the surface and two atoms (N and H) of oleamide can form a strong bidentate conformation because the distances between the surface Ca atom and two atoms (N and H) of the -C(=O)-NH group in the oleamide molecule are almost the same. The O atom in C-O group of oleic acid anion can bond with surface Ca atom to form monodentate conformation (Figure 8(c)). Therefore, it can be observed that the combined sodium oleic acid and oleamide system showed a stronger adsorption ability on fluorapatite surface than that of the sodium oleic acid system or oleamide system. The simulation result is consistent with the flotation experiment.

In the next paper, we will report on optimizing the operating parameters and rational adjustment of the slurry pH to achieve an ideal P2O5 grade and recovery in industrial practice.

#### 4. Conclusions

In this study, mixture of sodium oleic acid and oleamide was adopted as a combined collector in the flotation of apatite ore. Based on the results from flotation tests and quantum mechanics simulation, the following conclusions could be arrived: (1) throughout the flotation experiments, it can be seen that the concentrate with 31.42% P2O5 grade and 81.08% recovery was obtained by one-stage direct flotation; (2) the computational simulations for the interaction energy between apatite {001} surface and collectors indicate that combined collector has a stronger collecting ability than others; (3) the relative concentration distributions of oleate in combined sodium oleic acid and oleamide system were more densely and widely distributed than the ones in the sodium oleic acid system or oleamide system; (4) the computational simulations for the relative concentration of oleate on the distance from fluorapatite {001} surface showed how the collector was distributed on the surface and what conformations they formed.

#### Data Availability

The data used to support the findings of this work are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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## شبیه‌سازی مکانیک کوانتومی بر رفتار جذب و مکانیسم شناورسازی ترکیب سدیم اولئیک اسید و اولئامید بر روی سطح فلورآپاتیت در یک محیط آبی

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### چکیده:

در این مطالعه، تأثیر واکنشگرهای مختلف - کربنات سدیم و هیدروکسید سدیم به عنوان تنظیم‌کننده‌های pH، اسید لیگنوسولفونیک کلسیم به عنوان بازدارنده، و ترکیب اولئات سدیم و آمید به عنوان کلکتور - بر فلوتاسیون سنگ معدن آپاتیت با استفاده از آزمایش‌های فلوتاسیون بررسی شد و مکانیسم جذب کلکتور بر روی سطح آپاتیت با استفاده از شبیه‌سازی‌های مکانیک کوانتومی ارزیابی شد. آزمایش‌های فلوتاسیون نشان داد که افزودن ۴ کیلوگرم بر تن کربنات سدیم و ۱.۵ کیلوگرم بر تن هیدروکسید سدیم به عنوان تنظیم‌کننده‌های pH، ۳ کیلوگرم بر تن اسید لیگنوسولفونیک کلسیم به عنوان بازدارنده و ۶۰ گرم بر تن اسید اولئیک سدیم و اولامید (عدد اسیدی کلکتور؛ ۱۰۵ میلی‌گرم پتاسیم بر گرم) به عنوان کلکتور، توانایی جمع‌آوری عالی آپاتیت را نشان می‌دهد. از سنگ معدن آپاتیت کم‌عیار با ۷.۰۵٪ P<sub>2</sub>O<sub>5</sub>، کنسانتره‌ای با ۳۱.۴۲٪ P<sub>2</sub>O<sub>5</sub> با بازیابی ۸۱.۰۸٪ در فلوتاسیون رافر به دست آمد. در مقایسه با نتایج شبیه‌سازی برای انرژی برهمکنش بین سطح آپاتیت {۰۰۱} و کلکتورها، و غلظت نسبی کلکتور روی سطح آپاتیت {۰۰۱}، قدرت جذب به ترتیب زیر است: ترکیب سدیم اولئیک اسید و اولئامید < سدیم اولئیک اسید < اولئامید. از نتایج شبیه‌سازی روی پیکربندی تعادلی کلکتور با سطح فلورآپاتیت {۰۰۱} در محیط مایع، مشخص شد که دو اتم (H و N) اولئامید می‌توانند یک ترکیب دو دندان‌ای قوی تشکیل دهند، و اتم O در گروه C-O و در گروه C=O آنیون اسید اولئیک می‌تواند با اتم Ca روی سطح {۰۰۱} پیوند برقرار کند و ترکیب تک دندان‌ای تشکیل دهد.

**کلمات کلیدی:** فلوتاسیون فلورآپاتیت، سدیم اولئیک اسید، اولئامید، عدد اسیدی، مکانیک کوانتومی.