



Article Apatite–Calcite Flotation Separation Using Sodium N-Lauroylsarcosinate as a Selective Collector

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Abstract: Froth flotation is a commonly utilized beneficiation technique for effectively separating apatite from other gangue minerals, such as calcite. It is difficult to achieve good separation with fatty acid collectors due to their similar interactions with apatite and calcite. In this work, sodium N-lauroyl sarcosinate (SNLS) was used as the collector for the selective separation of calcite from apatite without a depressant. The experiments revealed that SNLS had a much better selectivity and a stronger affinity with calcite compared to apatite, with little effect on the flotation of apatite observed at a pH of 10. Fourier transform infrared (FTIR) analyses were conducted to explain the selective collector process of SNLS. The mechanism experiments demonstrate that SNLS can chemically bond to apatite and calcite minerals to produce Ca-NLS chelates. The active O atoms of the amide and carboxyl groups of SNLS accomplish this. Calcite has a greater Ca-reactivity than apatite, and as a result, the adsorption quantity on the calcite surface is greater than that on the apatite surface. FTIR analyses indicate that SNLS exhibits a greater affinity for the calcite surface than for apatite, a finding that is supported by first-principle density functional theory (DFT) calculations showing a higher adsorption energy of SNLS on the calcite surface. DFT calculations showed that SNLS forms stronger O-Ca bonds on the calcite surface and is less hindered by H₂O. This work shows that the surfactant sodium N-lauroylsarcosinate (SNLS) can be an ideal collector for the flotation of phosphate minerals.

Keywords: apatite; calcite; SNLS collector; flotation; selective adsorption

1. Introduction

Phosphate ore is widely used to produce phosphoric acid and is a raw material used as an essential substrate in manufacturing fertilizers [1]. The most valuable mineral in phosphate ore is apatite, which is associated with carbonate minerals such as calcite or dolomite. Significant efforts are being made to increase phosphate ore separation efficiency and increase apatite flotation recovery and grade. Progress has been made in thermodynamic analysis, environmental management of slurries, and the development of new reagents that can specifically differentiate between carbonates and phosphates. But many phosphate beneficiation methods still need efficient processes, high reagent consumption, and low phosphate recovery and grade. The calcareous phosphate ores are difficult to separate, especially using flotation. This is due to the similar physicochemical characteristics of the surfaces of the main constituents of calcareous phosphate ores. Some are frequently soluble, such as apatite, dolomite, and calcite [2,3].



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Copyright: © 2023 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 (https:// creativecommons.org/licenses/by/ 4.0/). The world's phosphate reserves were 49.7 billion tons in 2015, according to the United States Geological Survey (USGS), including 13 billion tons in China. Carbonate is the main associated gangue mineral in China's phosphate ores, primarily rich in sedimentary apatite. Morocco has the largest most enormous phosphate reserves, estimated at 50 billion tons. China is the only country producing a significant amount of phosphate ore used as agricultural fertilizer. It was estimated that the global consumption of P_2O_5 in phosphoric acid, fertilizers, and other products would increase worldwide, rising from 47 million tons in 2019 to 50 million tons in 2023 [4]. Although China has a large amount of phosphate ore reserves, most of them are of low quality. The mining process focuses on low-grade phosphate ores, which are processed by developing collectors and depressants with a high separation efficiency and are linked to minerals like silicates and carbonates to achieve a high ore concentration.

In recent years, some progress has been made in developing collectors and depressants for phosphate ore. The sodium salt of sulfonate oleic acid is a new anionic collector for the carbonate flotation of high-magnesium phosphate ore. It has good selectivity at pH 5.5-6 in the presence of sulfuric acid and sodium triphosphate as a depressant of phosphate ore [5]. Cashew gum is a new depressant of calcite and calcareous minerals, lowering the value of insoluble residues to 0.64% with a pH of 8.0 and improving carbonate recovery, which is effective and safe for the environment [6]. 2-phosphonobutane-1, 2, and 4-tricarboxylic acid (PBTCA) is a good calcite depressant, preventing sodium oleate adsorption on the calcite surface in an alkaline medium [7]. Sodium polyacrylate (PAAS) can inhibit calcite at pH ranges between 6.5 and 10.5, with sodium oleate (NaOL) acting as a collector [8]. Carboxymethyl chitosan was shown to adsorb on apatite surfaces through hydrogen bonding while adsorbing on calcite surfaces mainly through chemical chelating between Ca on the mineral surface and –COO, so it separated apatite from calcite well when sodium oleate (NaOL) was used as a collector and at pH 9 [9]. Pataua oil, as an anionic collector, has been used to separate apatite from quartz and calcite. It increased selectivity in neutral and alkaline media [10]. It was reported that benzohydroxamic acid exhibited a strong collecting capacity towards apatite over dolomite and had better selectivity than NaOL [11].

Despite increasing performance for separating apatite and calcite, each of the current collectors and depressants has some limitations. This study presents a novel collector that is both environmentally friendly and shows a significant economic benefit with a low cost for selective flotation. Sodium N-lauroyl sarcosinate (SNLS) is a carboxyl and amide-based amino acid surfactant with strong reactivity [12]. SNLS could be selectively adsorbed on fluorite rather than on scheelite during flotation, and it was concluded that interactions cause SNLS (in the form of the negatively charged species NLS) to be more able to adsorb on positively charged fluorite than negatively charged scheelite. It also indicated that SNLS could be chemically adsorbed on both minerals to create Ca-NLS chelates through the active O atoms of the amide and carboxyl groups. The group worked with SNLS as a dolomite flotation collector in our previous study, showing high efficiency [13]. Its advantages include low cost, environmental friendliness, good biodegradability, and safe applications in biomedicine, electroplating, dyeing, and agriculture. Flotation tests of single minerals, binary mixed minerals, and actual ore evaluated the effect of SNLS on the flotation performance of apatite and calcite. Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT) calculations were used to reveal the adsorption mechanism of SNLS on the two minerals.

2. Materials and Methods

2.1. Materials

The Egyptian Mineral Resources Authority (EMRA) delivered pure apatite and calcite minerals. The samples were ground to a fineness of less than 0.100 mm in a porcelain mill. Desliming was used to remove fine fractions ($-0.075 \mu m$). The sodium N-lauryl sarcosinate (SNLS) used in this study had a purity of 95% and was supplied by Shanghai Macklin Biochemical Co., Ltd. located in Shanghai, China. The chemical structure of SNLS is shown

in Figure 1. Sodium hydroxide and hydrochloric acid from Sigma-Aldrich (Burlington, MA, USA) were used as pH modifiers.



Figure 1. Chemical structure of sodium N-lauroyl sarcosinate (SNLS).

2.2. Methods

2.2.1. Chemical Composition and X-ray Diffraction

The mineral samples were identified using X-ray diffraction (XRD) at 40 kV and 20 mA at a scanning speed of one theta per minute with a Ni filter and Cu-target (K α = 1.54 Å), X-ray diffraction (XRD) was used to detect the mineral phases on a Philips (Andover, MA, USA) type 1710 XRD unit, and the chemical analysis of the minerals was conducted using an X-ray fluorescence "Rigakusuper Mini 200". The sample was prepared as a pellet by mixing with Borex BM-0008 binder under a pressure of 15 tons/cm³.

2.2.2. Zeta Potential and FTIR Measurements

A laser Zeta Meter, "Malvern Instruments" Model Zeta Sizer Nano ZS, was employed to determine zeta potential. At room temperature, 0.05 g of the mineral is mixed with 50 mL of a 0.02 M (ionic strength) NaCl solution with or without a collector for 5 min at the desired pH. The solid samples were filtered, air-dried, and then subjected to FTIR for recording the spectra after interacting with the collector. A Spectrum 2000 Perkin Elmer spectrometer was employed. The spectrum was obtained over the wavenumber range between 4000 and 400 cm⁻¹. The mineral samples and flotation reagents were stirred in a beaker for 5 min, then filtered and washed in ultrapure water of the best pH.

2.2.3. Flotation Experiments

The flotation tests were conducted using single and mixed binary minerals in a column flotation machine at a rate of air of $0.65 \text{ cm}^3/\text{min}$ with a 100 mL column cell. The mineral suspension was made in a flotation column by adding 1 g of single or binary minerals (mixing apatite and calcite) at different pH values. The collector concentration was conditioned for 5 min. After collection, all products from single minerals, including both the sink and float fractions, were dried and weighed. All the flotation experiments were conducted at 20 °C. "Rigakusuper Mini 200" for X-ray fluorescence analysis of binary minerals was used to determine P_2O_5 and CaO. In the equation for the recovery and grade in binary mixed mineral flotation, artificial mixed mineral flotation studies used a mass ratio of 1:1 between calcite and apatite materials. To determine the amount of calcite recovered from the flotation experiments, the concentration and grade of calcite in the samples were compared. The variables W_1 and W_2 in Equation (1) represent the masses (g) of the concentrate and tailings, respectively. In Equation (2), γ_1 (%) and c (%) are the yield and calcite content of the concentrate in artificially mixed mineral flotation, respectively, while c_0 (%) is the calcite mass content in the artificially mixed mineral flotation.

$$Recovery = \frac{W_1}{W_1 + W_2} \times 100\% \tag{1}$$

$$Recovery = \frac{\gamma_1 \times C}{c_0} \times 100\%$$
⁽²⁾

2.2.4. Computational Methods

First-principle calculations based on DFT calculations were performed using the CASTEP module [14] and GGA-PBE [15]. Ultrasoft pseudopotentials [16] were used to calculate the valence electrons and ionic core interaction. The plane wave cut-off energy was set to 450 eV, and the self-consistent field convergence accuracy was set to 2.0×10^{-6} eV/atom. The displacement between the two atoms was less than 2.0×10^{-3} Å. The convergence thresholds for the maximum energy change, force, and stress during the geometry optimization were set to 2×10^{-5} eV/atom, 0.05 eV/Å, and 0.1 GPa, respectively. The most common slab models of apatite (001) [17] and calcite (104) [18,19] were constructed by cleaving the optimized bulk crystals. The k-point was set to $2 \times 2 \times 1$ for the apatite slab and $1 \times 3 \times 1$ for the calcite slab, according to the Monkhorst–Pack method. The optimized slabs were then used to model SNLS adsorption. The adsorption energy of the SNLS on the mineral surface is calculated as

$$E_{ads} = E_{adsorbate/slab} - (E_{adsorbate} + E_{slab})$$
(3)

where E_{ads} is the adsorption energy, $E_{adsorbate}$ is the energy of SNLS, E_{slab} is the energy of the slab, and $E_{adsorbate/slab}$ is the energy of the slab after adsorbing SNLS. A more considerable negative value of E_{ads} indicates stronger adsorption of molecules on the surface.

3. Results and Discussion

3.1. Characterization of Apatite and Calcite Minerals

Table 1 shows the chemical analysis of the apatite mineral, which has a chemical formula of $[Ca_5 (PO_4)_3(OH, F, Cl)]$. The apatite mineral contained 56.97% CaO, 34.58% P₂O₅, 4.49% CO₂, and 3.89% fluoride, representing its theoretical composition and confirming its high purity as a pure phosphate mineral, while the calcite mineral $[CaCO_3]$ also contains 55.5% CaO and 43.9% CO₂, which indicates its high purity. The X-ray diffraction pattern of the calcite and apatite minerals has only their characteristic peaks without significant peaks of impurities (Figure 2), which confirms the higher purity of both minerals. The XRD pattern of the natural phosphate ore contains the characteristic peaks of apatite and calcite. It indicates that the apatite mineral is mainly associated with the calcite mineral. XRD and chemical analysis of the phosphate ore shows that it predominantly comprises apatite and calcite. The Nile Valley phosphate ore sample consisted of francolite minerals with accompanying impurities, especially calcite. As for natural ore, it is a sedimentary phosphate. The crude phosphate ore is mainly composed of apatite and calcite. It comprises 53.5% CaO, 21.1% P₂O₅, 19.5% CO₂, and 1.65% F.

Table 1. Chemical composition of calcite, apatite, binary mixed mineral samples, and natural phosphate ore.

	Weight %							
Item	Calcite	Apatite	Binary Mixed Mineral Sample	Natural Ore				
P ₂ O ₅	0.02	34.58	33.1	21.16				
CaO	55.5	56.97	43.5	53.5				
MgO	0.20	0.005	0.18	0.785				
Fe ₂ O ₃	0.014	0.001	0.012	1.45				
SiO ₂	0.195	0.003	0.22	1.27				
Al_2O_3	0.028	0.016	0. 035	0.4				
K ₂ O	0.016	0.012	0.015	0.15				
Na ₂ O	0.015	0.018	0.018	0.08				
CO ₂	43.9	4.498	20.5	19.5				
F	0.11	3.897	2.42	1.65				
Total	100	100	100	100				



Figure 2. X-ray diffraction patterns of the pure minerals and natural phosphate ore.

3.2. Flotation of Single Minerals3.2.1. Effect of pH

During the mineral flotation tests, the effects of SNLS on apatite and calcite from single minerals were evaluated in the presence of different pH values (Figure 3). The results indicate that calcite and apatite may be separated through SNLS as a collector. Flotation recovery is much enhanced when flotation is carried out in the pH range of 8 to 10. At 0.05 mmol/L of SNLS at pH 10, calcite recovery increased to a maximum and decreased slightly. When the pH was increased to 7, the recovery of apatite improved gradually to 33.14% before declining.



Figure 3. Effects of pH on the floatability of single minerals in the presence of 0.05 mmol/L SNLS.

Figure 3 shows that a change in the pH value can significantly alter the maximum floatability between two minerals. In the presence of 0.05 mmol/L SNLS, the calcite

recovery increased with pH from 6 to 10, then decreased. The recovery of both minerals first increased and then decreased with increased pulp pH. When the pH increased from 6 to 10, the apatite flotation recovery increased from 25% to 33.15%. With a further increase in the pulp pH, the apatite recovery decreased to 13.0%. Under the same condition, calcite recovery significantly increased from 35.35% to 92.00% and then decreased gradually. A comparison of calcite and apatite recoveries at a pulp pH value of 10 revealed that the most significant difference in the floatability between the two minerals occurred at a pH of 10, with recoveries of 92.00% for calcite and 10.5% for apatite. Therefore, pH 10 was the best pH pulp value for calcite flotation. The maximum floatability difference (86%) was achieved at pH 10.

3.2.2. Effect of SNLS Concentration

Figure 4 shows that increasing the SNLS dose improved the recovery of calcite and apatite minerals at pH 10. The floatability of calcite reached its highest value when the SNLS concentration was 0.05 mmol/L, as measured by 92%. A further increase in concentration caused a negligible effect on the floatability improvement. The floatability of apatite under this condition has a poor value of 10.5%. Under the same collector concentration of pH 10, the floatability of calcite was always higher than that of apatite. The maximum difference in floatability of calcites between the two minerals was 86%, which indicates that the separation efficiency is better with SNLS concentrations of 0.05 mmol/L and pH 10.



Figure 4. Effects of SNLS concentration on the floatability of single minerals at pH 10.

3.3. Flotation of Binary Mixture

Effects of SNLS Concentration at Fixed pH

Figure 5 and Table 2 show the flotation results of binary mixed minerals (apatite/calcite = 1.0/1.0) using SNLS at pH 10. As the amount of SNLS increased, the recovery of calcite increased gradually. When the amount was 0.2 mmol/L, the recovery of calcite reached a maximum of 88%. When the SNLS dosage rose from 0.001 to 0.05 mmol/L, the recovery of apatite was less than 35%, while the recovery of calcite remained at a high value of 84%. When the SNLS dosage was raised from 0.001 to 0.2 mmol/L, the grade of apatite decreased from 13.0 to 7.4%, and the recovery of apatite decreased from 44.17 to 27.50%; the recovery of calcite rose from 73 to 88% while the grade increased from 25 to 31.5%. This result indicates that apatite and calcite could be separated using SNLS as a collector at pH 10. The recovery of apatite decreased with increasing SNLS concentration and significantly reduced when the concentration was over 0.05 mmol/L, while the recovery of calcite increased. The optimal dosage of SNLS was 0.05 mmol/L. Under these conditions,

calcite and apatite could be efficiently separated by flotation. It was observed that with this concentration, a degree of recovery of calcite was obtained at 84% with a grade of 29.8%. In comparison, a degree of recovery of apatite was obtained at 35% with a grade of 9.4%, and then after that, with increasing the dose, the separation improved gradually.



Figure 5. Effects of SNLS concentration at pH 10 on the recovery and grade of both calcite and apatite of the concentrate of the flotation of binary mixed minerals (apatite/calcite = 1.0/1.0).

Table 2. Flotation of binary mixed minerals of different ratios, using 0.05 m

Feed				Concentrate				
No.	Weig	;ht, %	Apatita %	Calcite, %	Weigl	ht, %	Recovery %	Crada %
	Apatite	Calcite	Apatite, 70		Float	Sink	Recovery, 70	Glade, /0
1	1	1	16.5	22	62	38	83.1	29.5
2	1.5	0.5	24.7	11	32	68	90.5	31.1

Figure 6 and Table 2 show the flotation results of binary mixed minerals (apatite/calcite = 1.5/0.5) using SNLS at pH 10. The recovery of calcite increased from 76 to 90.5%, while the calcite grade increased from 26.0 to 31.1% when the SNLS concentration was increased from 0.01 to 0.05 mmol/L. The recovery of apatite significantly declines from 18.0 to 9.8%, while the grade of apatite reduces from 14 to 7.5%. This result demonstrates that calcite and apatite can separate at a pH of 10 due to the collector SNLS preference for calcite over apatite. A concentrate of 32.3% P₂O₅ from 24.79% was produced from synthetic mixed binary minerals using 0.05 mmol/L of SNLS at pH 10.

3.4. Flotation of the Natural Phosphate Ore

Table 3 shows the flotation results of a real phosphate ore sourced from Nile Valley. The phosphate ore is composed of the apatite mineral with associated gangue minerals, mainly calcite. Under optimal flotation conditions at pH 10 with 0.05 mmol/L SNLS, the new collector SNLS has a high selectivity for calcite from apatite. It showed that the grades of calcite and apatite obtained in the floating concentrate were 41.2% and 5.7%, respectively. And the concentration of apatite in the sink product is 30.5%, while that of calcite is 3.5% as shown in Figure 7. The increase in SNLS dosage would improve the grade of the calcite from 30 to 41.2% while decreasing the grade of the apatite from 15.5 to 5.6%. On the other hand, the P_2O_5 % increases from 21.1 to about 30.5%. Figure 7 indicates that the novel collector SNLS exhibits high selectivity for calcite over apatite at a concentration of 0.05 mmol/L SNLS and a pH of 10.



Figure 6. Effects of SNLS dose at pH 10 on the recovery and grade of both calcite and apatite of the concentrate of the flotation of binary mixed minerals (apatite/calcite = 1.5/0.5).

Tab	le 3.	F	lotation	results	of	the	Nile	Val	ley	pho	spl	hate	ore.
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CNU C Commenter L	Concentrate					
SNLS Concentrate, mmol/L	Weight, %	Recovery, %	G Calcite, %	Grade Calcite, % Apatite, %		
0.001	26	40.5	30	15.8		
0.01	31	54.02	34	12.9		
0.03	35	65.5	36.5	10.6		
0.05	39	80	41.2	5.6		
Total	100	100	19.5	21.1		



Figure 7. Flowchart for flotation of Nile Valley phosphate ore.

3.5. Zeta Potential Measurements of Treated Minerals

The results of the zeta potential experiments on the apatite and calcite were evaluated as a function of pH to understand the adsorption behavior of SNLS further. Figure 8 shows the zeta potential results. Apatite has a positive zeta potential in the pH range of 3–6.8, but it has a negative potential above pH 6.5. The point of zero charges of apatite has changed almost from 6.8 to 6.5, as has the weak interaction between SNLS and the apatite surface and a little positive shift in the zeta potential of apatite in the pH range of 3–11. Figure 9 shows that surface calcite is positively charged at pH 3–10.2 and negatively charged above pH 10. The zeta potential indicates that negatively charged SNLS species were adsorbed on the calcite surface, accounting for the floatability of calcite treated with SNLS. In addition, the zero-point charges change from 10.2 to 9.1, indicating a significantly strong interaction

between SNLS and the calcite mineral surface. The adsorption of SNLS causes the calcium surface to be even more negatively charged in the pH range of 6–10. The results show that the zeta potential of apatite varies by approximately 3 mV when 0.05 mmol/L of SNLS is used at a pH of 10, while the zeta potential of calcite changes by roughly 9.2 mV. According to the results of flotation experiments at a dose of 0.05 mmol/L and pH 10, A zeta potential analysis revealed that SNLS bonds more strongly to the surface of calcite than apatite [20,21].



Figure 8. The zeta potential of apatite mineral at different pH values.



Figure 9. The zeta potential of calcite mineral at different pH values.

3.6. FTIR Measurements of Treated Minerals

Figures 10 and 11 illustrate the FTIR spectra of the calcite and apatite minerals. The functional group of SNLS involved in the adsorption should be determined. Therefore, the FTIR spectra of the calcite and apatite before and after the SNLS treatment are obtained to further understand the selective adsorption mechanism of SNLS on both minerals. The FTIR spectra of SNLS include two peaks at 2922 and 2848 cm⁻¹ for the stretching vibrations of the –CH₂ and –CH₃ groups, respectively. The peaks at 1608 and 1396 cm⁻¹

correspond to the carbonyl groups stretching the vibration of the carboxyl (–COO) group. Another characteristic peak of SNLS appears at 1633 cm⁻¹, attributed to the amide carbonyl stretching vibration in –CON [22,23].



Figure 10. FTIR spectra of SNLS, calcite mineral, and treated calcite with SNLS.



Figure 11. FTIR spectra of SNLS, apatite mineral, and treated apatite with SNLS.

The FTIR spectra of the treated calcite indicate the adsorption of SNLS onto the calcite surfaces. It was demonstrated by solid absorption bands between 3436 and 2521 cm⁻¹ and other peaks at 1811, 1429, 877, and 713 cm⁻¹. Also, the FTIR spectra of carbonate include bands assigned to the in-plane bending (v4) mode of CO_3^{2-} in the carbonate structure [24]. The FTIR spectra of calcite showed absorption bands at 713 and 2521 cm^{-1,} indicating the presence of calcite (Figure 11). The peaks at 877, 1429, and 1811 cm⁻¹ are related to CO_3^{2-} ions. The stretching vibrations of adsorbed water molecules were responsible for the band at 3436 cm⁻¹ [25]. The spectrum of the treated calcite mineral with SNLS showed a new peak at 1603 cm^{-1,} related to the carbonyl group stretching vibration of the carboxyl (–COO) group, which shifted from its original value at 1608 cm⁻¹. Another peak of SNLS appeared at 1637 cm⁻¹, which shifted from its original value of 1633 cm⁻¹. It was attributed to the amide carbonyl stretching in –CON after the SNLS peaks at 2922 and

2848 cm⁻¹ for the stretching vibrations of $-CH_2$ and $-CH_3$ groups of SNLS changed to 2942 and 2836 cm⁻¹ after interaction with the calcite [26]. The peak at 1396 cm⁻¹ of the carbonyl group stretching vibration of the carboxyl (-COO) group shifted inside the calcite band located at 1429 cm⁻¹. This reveals the strong SNLS adsorption on the surface of the calcite. The chemical adsorption of the two active O atoms of SNLS on the calcite was strong. These O atoms could form a Ca-SNLS complex because of the higher Ca reactivity on the calcite mineral surface.

As shown in Figure 10, apatite has various bands in its spectrum. The strong band observed around 1046 cm⁻¹ is attributed to the asymmetric stretching vibration of PO_4^{3-} apatite anions. The P-O mode is assigned to the peaks at 792 and 606 cm⁻¹, and the v2 phosphate mode produces a 469 cm⁻¹ band. Other bands at 875, 1425, and 1646 cm⁻¹ are related to CO_3^{2-} ions. The stretching vibrations of adsorbed water molecules were responsible for the IR peaks at 2915 and 3436 cm⁻¹.

The spectra of the treated apatite show new bands at 2922 and 2848 cm⁻¹, which are associated with the $-CH_2$ and $-CH_3$ groups in SNLS, as well as two additional bands at 1631 and 1609 cm⁻¹, attributed to the -CON and -COO groups in SNLS. These findings suggest that SNLS is chemically adsorbed on the apatite surface. However, compared to the band shifts observed for the -CON and -COO groups in the calcite FTIR spectra, the changes in the apatite spectra are slight. Specifically, the -CON band shifts from 1633 to 1631 cm⁻¹, and the -COO band shifts from 1608 to 1609 cm⁻¹. This result indicates that SNLS exhibits weaker chemical adsorption on the apatite surface compared to the calcite surface [27].

3.7. Adsorption of SNLS on Apatite and Calcite Surfaces

Figure 12 and Table 4 show the adsorption structure, adsorption energy value, bond length, and Mulliken overlap population of SNLS or H_2O on the apatite (001) and calcite (104), respectively. Figure 12a,b show that the adsorption of SNLS occurs via its carboxyl O atoms and Ca atoms on the surfaces of the apatite and calcite through the O-Ca bond. The bond length and the Mulliken overlap population of the formed bonds can be seen in Table 4. In Table 4, the O atoms of SNLS bonded with Ca atoms with bond lengths of 2.413 and 2.437 Å when SNLS adsorbs on the apatite (001), respectively, which are longer than those when SNLS adsorbs on calcite (104) (2.394 and 2.387 Å). This result shows that the adsorption of SNLS on calcite (104) is more stable than on apatite (001). The Mulliken overlap population is from 0 to 1 and is used to describe the covalency and strength of a bond. The larger the Mulliken overlap population value, the more covalent the bond is and the stronger it is. The Mulliken overlap population values of O-Ca of SNLS on the calcite (104) are more significant than those on apatite (001), which indicates that the O atoms of SNLS can form O-Ca bonds with calcite (104) more easily. The adsorption energy allows a more direct comparison of the adsorption strength. As can be seen in Table 4, the adsorption energy of SNLS on the calcite (104) is -229.302 kJ/mol, which is more negative than that on the apatite (001) (-111.473 kJ/mol), suggesting that SNLS has stronger adsorption on the calcite surface. In addition, Figure 12c,d show that H₂O forms O-Ca bonds on both the apatite and calcite surfaces; in contrast to the calcite, the H₂O on the surface of the apatite also forms a hydrogen bond with the PO_4^{3-} , which indicates that the H_2O starts stronger adsorption on the apatite surface. As can be seen in Table 4, the adsorption energy of H_2O on the calcite (104) is (-53.785 kJ/mol), which is weaker than that on the apatite (001) (-145.147 kJ/mol), suggesting that H₂O has stronger adsorption on the apatite surface. The Mulliken overlap population values of O-Ca of H_2O on the apatite (001) are more significant than those on the calcite (104), and the bond length of H_2O on the apatite (001) is shorter. Therefore, SNLS adsorbs strongly on calcite surfaces and weakly on apatite surfaces, and H₂O adsorbs strongly on apatite surfaces and weakly on calcite surfaces. The H₂O on the apatite surface prevents the adsorption of SNLS, leaving less SNLS able to be adsorbed on the apatite surface. Ultimately, SNLS adsorption on calcite and apatite surfaces appears to differ, enabling the separation of the two.

(a)





(b)

Figure 12. Optimized adsorption models of SNLS on apatite (001) (a) and calcite (104) (b) and H₂O on apatite (001) (c) and calcite (104) (d).

Table 4. Adsorption energy, bond length, and Mulliken overlap population between SNLS, apatite (001), and calcite (104).

Reagent	Mineral Surface	Adsorption Energy (kJ/mol)	Bond	Bond Length (Å)	Mulliken Overlap Population
SNLS	Apatite (001)	-111 473	O1–Ca1	2.413	0.11
	11punite (001)	111.170	O2–Ca2	2.437	0.09
	$C_{\text{algita}}(104)$	220 202	O3–Ca3	2.394	0.12
	Calcile (104)	-229.302	O4–Ca4	2.387	0.14
H ₂ O	Apatite (001)	-145.147	O–Ca	2.355	0.14
	Calcite (104)	-53.785	O–Ca	2.459	0.08

4. Conclusions

In this study, sodium N-lauroylsarcosinate (SNLS) was applied as a selective collector for calcite flotation in the apatite–calcite system. The effects of collector dosage and pulp pH on the floatability of apatite and calcite in the SNLS system were systematically studied. The best optimum conditions for the interaction between the flotation reagent and minerals were discovered for the flotation separation of apatite and calcite. In the SNLS flotation system, apatite and calcite were effectively separated when the pulp pH was 10 and the SNLS dosage was 0.05 mmol/L. The underlying adsorption mechanism of SNLS on both minerals is investigated through FTIR and DFT calculations. FT-IR investigations revealed that SNLS could be chemically adsorbed on calcite and apatite minerals. SNLS can be chemically adsorbed on both minerals to form Ca-SNLS chelates through the active O atoms of the amide and carboxyl groups. SNLS on calcite had more obvious band shifts

than on apatite, which indicated SNLS had stronger adsorption on the calcite surface. First-principle computations show that the adsorption of SNLS in place of water on the calcite surface is energetically more effective, with an increase in the exothermicity of -229.302 kJ/mol, as compared to -111.473 kJ/mol on the apatite surface. The difference in the adsorption energies of SNLS on the apatite and calcite surfaces is attributed to the difference in the reactivities and densities of Ca²⁺ ions on the two mineral surfaces. DFT calculations showed that SNLS forms more decisive O–Ca bonds on the calcite surface, while SNLS is weakly adsorbed on the apatite surfaces and is hindered by H₂O. These results showed that calcite and phosphate ore could be separated using SNLS, which is both inexpensive and environmentally friendly.

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