

Article

Effect of Sodium Pyrophosphate on the Reverse Flotation of Dolomite from Apatite

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Abstract: In this study, the effect of sodium pyrophosphate (NaPP) on the separation of apatite from dolomite by flotation was systematically investigated. Flotation results revealed that NaPP could selectively depress the flotation of apatite, thus realizing the separation of apatite from dolomite. Further, the selective depression mechanism of NaPP was studied through zeta potential measurements, contact angle measurements, and X-ray photoelectron spectroscopy (XPS) analysis. The results demonstrated that the adsorption of sodium oleate (NaOL) onto apatite surface was depressed by the preferential interaction of NaPP with active Ca sites. For dolomite, while the presence of NaPP hindered the interaction of NaOL with active Ca sites, it appeared to enhance the reactivity with active Mg sites. Thus, the adsorption of NaOL onto dolomite surface was hardly influenced. In this way, the separation of apatite from dolomite was achieved.

Keywords: sodium pyrophosphate; flotation; depression; apatite; dolomite

1. Introduction

Phosphorous, as one of the most common elements on earth and essential elements in organisms, is widely used in the production of fertilizers, detergents, pharmaceuticals, fluxes, cement, and many other industrial processes [1–5]. Nevertheless, with the rapid development of China's economy, the production of phosphorous cannot meet the requirement of the country [6]. Hence, the efficient exploitation of phosphate ore resource becomes more and more important. Moreover, growing demands for phosphorous have motivated the development of new technologies to concentrate phosphates from low-grade ores [7].

China has the second largest reserve of phosphate ore. However, vast majority of these resources are complex low-grade ores [8,9]. In these ores, the main valuable mineral, apatite is usually associated with gangue minerals, such as dolomite. Reverse flotation can be applied for phosphate ores that have high dolomite content [9–12]. However, there are still considerable difficulties in separating apatite from dolomite by means of reverse flotation. Furthermore, for fine-grained dissemination and complex minerals composition, apatite is often intergrown with dolomite. On the other hand, as calcium-bearing minerals, apatite and dolomite have similar surface properties. Additionally, dissolved components from apatite and dolomite will hydrolyze, precipitate, and adsorb onto the minerals [13–15]. All of these factors determine the interfacial properties of the minerals and make it more difficult to separate apatite from dolomite.

For these reasons, to separate apatite from dolomite effectively, research has focused on developing selective flotation agent. As known, fatty acids are most widely used collectors in the flotation of apatite and dolomite, and the development of novel flotation collectors has been an area of research interest. Despite successful and economic recovery of apatite via reverse flotation, the selectivity of using fatty acids and their derivatives as collectors is still not satisfactory due to their similar surface reactivity of calcium-bearing minerals such as apatite and dolomite [10,16–18]. For effective

utilization of phosphate ore resource, it is important to selectively separate apatite from dolomite. Therefore, an effective depressant is essential for improving the floatability differences between apatite and dolomite.

Due to its extensive sources and low unit cost, H_2SO_4 has been widely used as a depressant in apatite flotation. However, large dosages of H_2SO_4 will lead to the corrosion of flotation equipment, and the production of acidic wastewater. In addition, the production of sediment (CaSO_4) could cause pipeline blocking, which cannot be appropriately resolved as yet [8,14,19]. Thus, the utilization of H_2SO_4 to separate apatite from dolomite remains a problem.

Sodium pyrophosphate, known as condensed phosphate, is formed by repeated condensation of tetrahedral $[\text{PO}_4]$ units. It is usually used as water softener, emulsifier, and chelating agent. For the presence of chelating group, the addition of sodium pyrophosphate may promote the formation of metal ion-pyrophosphate, preventing its reaction with collector [20]. It was demonstrated that sodium pyrophosphate could reduce the adverse effect of serpentine on the flotation of pentlandite by shifting the slime surface charge [21]. In addition, sodium pyrophosphate has also been used in scheelite flotation [22,23]. However, there are few reports on the utilization of sodium pyrophosphate as a depressant in apatite flotation.

In this paper, sodium pyrophosphate (NaPP) was introduced as a flotation depressant to selectively separate apatite from dolomite. Micro-flotation tests were performed to reveal the selective depression of apatite by NaPP. In addition, the underlying mechanism was investigated through zeta potential and contact angle measurements, and XPS analyses.

2. Experiments

2.1. Materials

The sample of apatite was obtained from Yunnan Phosphate Chemical Group Co., Ltd. located in Yunnan, China. The ore was dry-ground in a lab-scale ball mill and then sieved to get $-74 + 38 \mu\text{m}$ fraction for the flotation tests. In addition, a part of fine fraction ($-2 \mu\text{m}$) was also obtained for the zeta potential measurements. X-ray diffraction (XRD) analyses (Figure 1) revealed that the purity of apatite sample was considerably high with a bit of quartz.

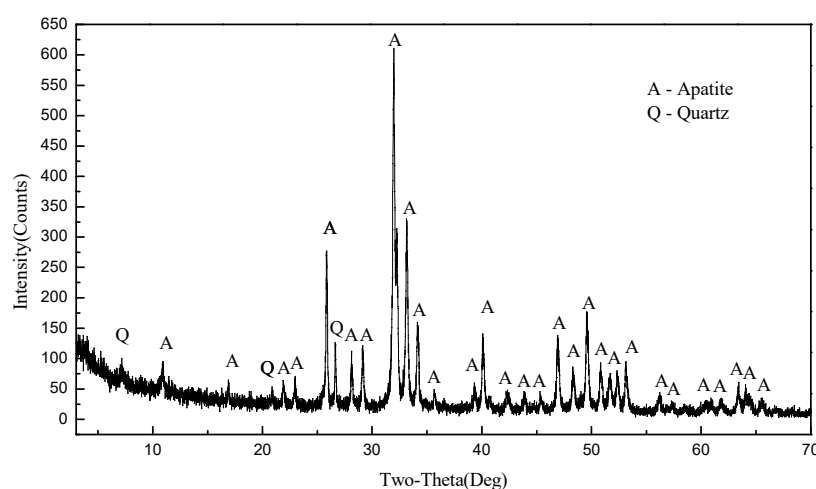


Figure 1. X-ray diffraction (XRD) pattern of the apatite sample.

The sample of dolomite was obtained from Changsha Ore Powder Factory located in Hunan, China. The ore was dry-ground in a lab-scale ball mill and then sieved to get to get $-74 + 38 \mu\text{m}$ fraction for the flotation tests. In addition, a part of fine fraction ($-2 \mu\text{m}$) was also obtained for the

zeta potential measurements. X-ray diffraction (XRD) analyses (Figure 2) revealed that the purity of dolomite sample was very high.

Sodium pyrophosphate (NaPP) used as the depressant in this study was bought from Tianjin Yongda Chemical Reagent Development Center. Sodium oleate (NaOL) bought from Tianjin Kermil Chemical Reagents Development Centre was used as a collector. HCl and NaOH obtained from Aladdin Reagent Co. Ltd. (Shanghai, China) were used to adjust the pH value. All the reagents used in this study were of analytical grade. Deionized water was used for all the tests.

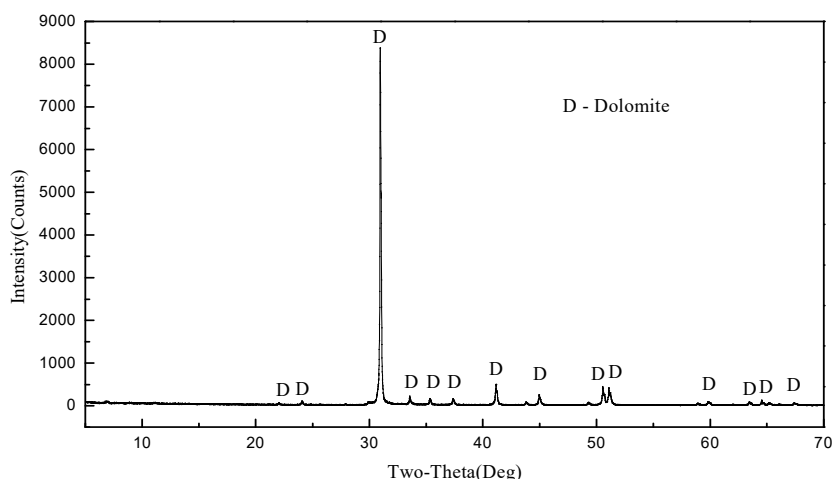


Figure 2. XRD pattern of the dolomite sample.

2.2. Micro-Flotation Experiments

Micro-flotation experiments were carried out in an XFG flotation machine (Exploring machinery Plant, Changchun, China) equipped with a 40-mL cell at 2000 rpm agitation speed. For single mineral tests, 2.0 g of pure mineral was placed in the flotation cell with 35 mL deionized water and then conditioned for 1 min. NaPP and NaOL were successively added and stirred for 3 min, respectively. The flotation process lasted 3 min for each test. Following this, the flotation recoveries were calculated based on the weights of concentrates and tailings.

For artificial mixed minerals flotation experiments, the mass ratio of apatite and dolomite mineral was 1:1 for binary mixture. The flotation process was the same as single mineral tests. After the flotation process, the concentrates and tailings were assayed for P and Ca. The recovery of apatite was calculated based on P_2O_5 contents of concentrates and tailings.

2.3. Zeta Potential Measurements

Zeta potential measurements were carried out using a Zeta Plus Zeta Potential Meter (Bruker, Karlsruhe, Germany). KNO_3 was used to maintain the ionic strength at 10^{-3} mol/L. Small amounts of sample below $-2 \mu m$ were added to desired amounts of solution and magnetically stirred for 10 min, and the pH was adjusted using HCl or NaOH. The zeta potential of samples was then measured three times using a Zeta Plus Zeta Potential Meter (Bruker, Karlsruhe, Germany). The average value and the standard deviation of zeta potential were respectively calculated.

2.4. Contact Angle Measurements

The contact angle measurements were performed with sessile drop method using a Digidrop goniometer (GBX, Isere, France). The crystals of apatite and dolomite were embedded in resin and then polished with 500 grit, 1000 grit and 4000 grit alumina sandpapers, successively. For the measurements of minerals in the absence of NaPP, the prepared sample was immersed in a desired concentration NaOL solution for 15 min. For the measurements of minerals in the presence of NaPP, the prepared

sample was firstly immersed in NaPP solution for 15 min and then in NaOL solution for another 15 min. Next, the sample was washed with deionized water and then air dried. A water droplet (about 2 mm in diameter) was introduced onto the sample surface, and then the contact angle results were analyzed by computer software.

2.5. XPS Analysis

The change of surface chemical composition of mineral samples (apatite and dolomite) pretreated with different reagents was determined by X-ray photoelectron spectroscopy (XPS). To prevent extra surface change, the samples were stored in a vacuum drier under the temperature of 25 °C. The XPS measurements were performed on a X-ray photoelectron spectrometer (PHI5000, ULVAC-PHI, Chigasaki, Japan). Firstly, chemical components of the samples were identified by survey scan. Then, high-resolution scans were conducted focusing on certain elements. Sample charging was compensated by taking the C1s peak of background hydrocarbon at 284.8 eV as an internal standard.

3. Results and Discussion

3.1. Micro-flotation Experiments

Figure 3 shows the flotation results of apatite and dolomite as a function of NaOL dosage. It can be seen from Figure 3 that the flotation recoveries of two minerals increased with the increase of NaOL dosage. The recoveries of apatite and dolomite at 60 mg/L dosage NaOL were 80.78% and 93.6%, respectively. Meanwhile, the flotation recovery of dolomite was higher than that of apatite, which implied that NaOL had a better collecting ability to dolomite. Therefore, for the better flotation performance of dolomite, reverse flotation is a proper method to separate apatite from dolomite.

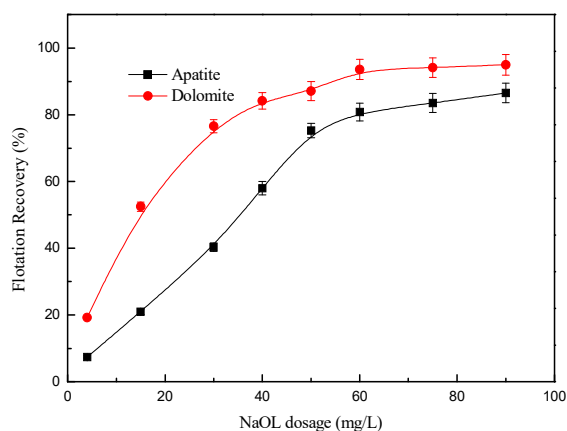


Figure 3. Effect of sodium oleate (NaOL) dosage on the flotation of apatite and dolomite.

The effect of NaPP dosage on the flotation of apatite and dolomite is shown in Figure 4. Our results with single mineral flotation show that while NaPP was an effective depressant for apatite, it had minimal effect on dolomite flotation. At a NaPP dosage of 100 mg/L, apatite was nearly completely depressed while that of dolomite decreased from 93.8% to 84%.

The distinct difference of the flotation recovery makes it possible to separate apatite from dolomite using NaPP as the depressant. Therefore, the flotation tests on the artificial mixed minerals were performed using NaPP as depressant. The flotation results are presented in Table 1.

As can be seen from Table 1 that, the flotation recovery of apatite was improved from 39.4% to 96.5% in the presence of NaPP, while the recovery of MgO slightly increased from 11.3% to 16.3%. Further, the addition of NaPP also resulted in a sharp increase of P₂O₅ grade of concentrate from 26.4% to 34.1% and a decrease of MgO grade of concentrate from 3.8% to 2.9%. The artificial mixed minerals separation reported here suggests that NaPP can be used for separating dolomite from apatite.

However, the availability of utility of this approach has to be demonstrated with “real” complex ores such as those described in the Section 1.

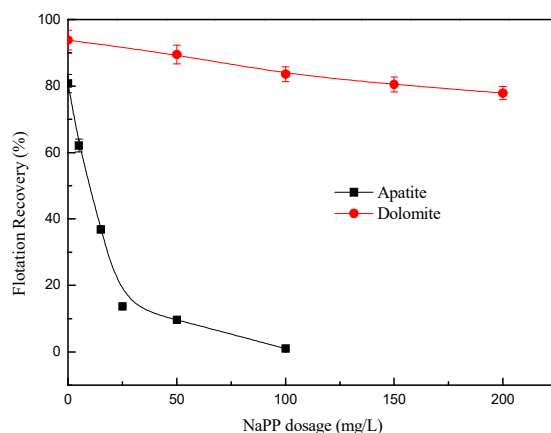


Figure 4. Effect of sodium pyrophosphate (NaPP) dosage on the flotation of apatite and dolomite.

Table 1. Artificial mixed minerals flotation results (NaOL: 60 mg/L).

NaPP (mg/L)	Production	Yield (%)	Grade (%)		Recovery (%)	
			P ₂ O ₅	MgO	P ₂ O ₅	MgO
0	Concentrate	29.4	26.4	3.8	39.4	11.3
	Tailing	70.6	16.9	12.4	60.6	88.7
	Feed	100.0	19.7	9.9	100.0	100.0
100	Concentrate	55.7	34.1	2.9	96.5	16.3
	Tailing	44.3	1.5	18.6	3.5	83.7
	Feed	100.0	19.7	9.9	100.0	100.0

3.2. Zeta Potential Measurements

To reveal the underlying depression mechanism of NaPP, the zeta potential measurements of apatite and dolomite under different reagent conditions were performed as a function of pH, and the results are shown in Figure 5a,b.

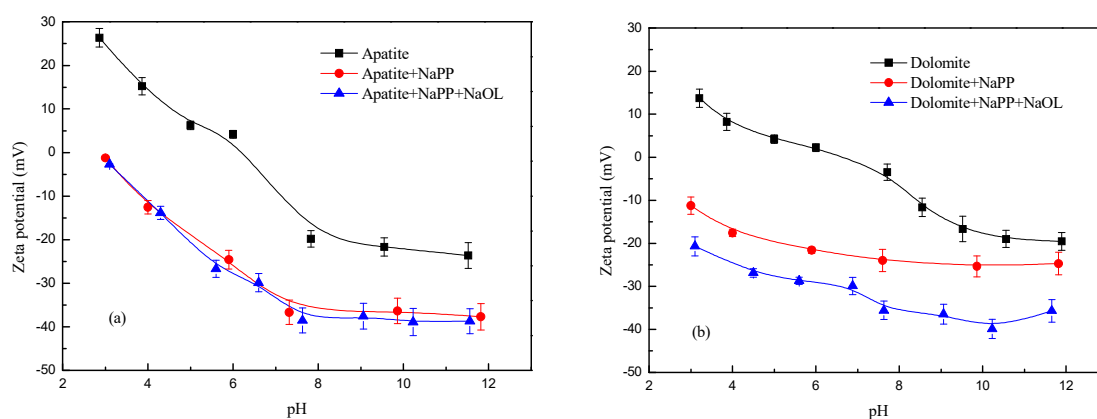


Figure 5. Effect of different reagents on the zeta potential of (a) apatite and (b) dolomite.

Comparing the data in Figure 5a,b, there were obvious potential differences which resulted in the difference in the flotation performance of the two minerals. For apatite, it was positively charged in

the pH range of 3–6, which matched well with other literature. The isoelectric point (IEP) of dolomite was near a pH of 6.5, which was also in agreement with the previous study [15,24].

With the addition of NaPP, zeta potentials of two minerals sharply dropped over the entire pH range, probably due to the adsorption of dissolved NaPP components which were negatively charged. Similar shifts of zeta potentials of both minerals revealed that NaPP interacted intensively with two mineral surfaces.

When NaOL was applied after the addition of NaPP, apatite gave zeta potential which was about the same value obtained for apatite in the presence of NaPP alone. However, the zeta potential of dolomite is more negative compared with that using NaPP alone. The zeta potential results illustrated that the pre-treatment of NaPP prior to NaOL did not prevent the interaction of NaOL with dolomite, but hindered the adsorption of NaOL onto apatite surface. The zeta potential measurements results provided a preliminary understanding of the depressant effect of NaPP.

3.3. Contact Angle Measurements

The advancing contact angle of the two minerals before and after interaction with NaPP as a function of NaOL dosage was measured to reveal the changes of surface wettability of the two minerals. As can be seen from Figure 6, surface hydrophobicity of both minerals in the absence of NaPP was dramatically improved with the increase of NaOL dosage, which indicated the increasing adsorption of NaOL onto the minerals surface. In addition, the contact angle values of apatite and dolomite were in accord with the flotation recoveries presented in Figure 3. After interaction with NaPP, the contact angle of apatite was significantly decreased. However, as for dolomite, the insignificant change of contact angle showed little influence of NaPP on its surface hydrophobicity. The different effects of NaPP on the surface hydrophobicity of apatite and dolomite revealed that NaPP could restrict the adsorption of NaOL onto apatite while hardly affect NaOL adsorption onto dolomite. Therefore, the decrease of NaOL adsorption onto apatite resulted in the depression of its flotation performance.

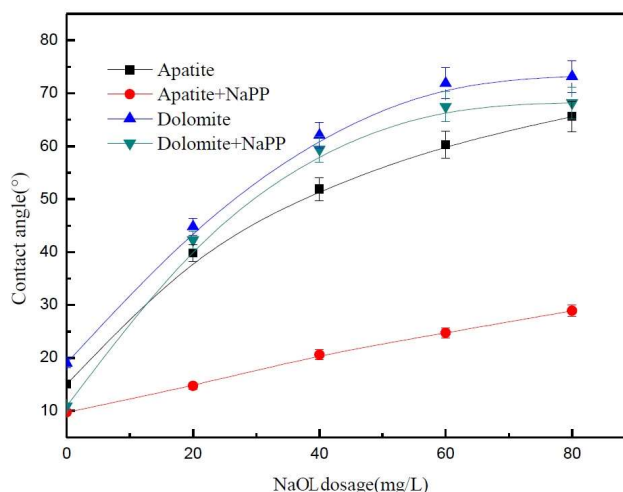


Figure 6. Contact angle of the minerals before after interaction with NaPP as a function of NaOL dosage.

3.4. XPS Analysis

To further investigate the interaction mechanism between NaPP and the two minerals (apatite and dolomite), XPS analyses of apatite and dolomite in the absence and presence of NaPP were conducted, and the fitted results are shown Figure 7. With reference to data from United States National Institute of Standards and Technology (NIST), the binding energy of 133.39 eV and 133.80 eV corresponds to $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and $\text{Ca}_2\text{P}_2\text{O}_7$, respectively. As can be seen from Figure 7a, only the peak of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ was observed in the absence of NaPP, whereas the P2p peaks could be decomposed into two P2p-P2p_{3/2} doublets, indicating the existence of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and $\text{Ca}_2\text{P}_2\text{O}_7$ in the presence of NaPP. Furthermore,

after adding NaPP, the P2p atomic concentration increased from 10.84% to 11.69%, which also showed NaPP successfully chemisorbed onto the apatite surface, and thus depressed the flotation of apatite.

As for dolomite, the Ca2p and Mg1s peaks with and without NaPP are also fitted to confirm the chemical information of surface species. It could be seen from Figure 7b, the Ca2p peak of single dolomite appeared at 347.00 eV, in which the peak of 347.00 eV was assigned to CaCO_3 . After the addition of NaPP, a new Ca2p3/2 peak for $\text{Ca}_2\text{P}_2\text{O}_7$ was observed and the characteristic P was also detected on dolomite surface. However, the Mg1s binding energy did not change in the presence of NaPP. All these changes offered good evidence that NaPP adsorbed onto dolomite surface, and selectively reacted with active Ca sites rather than Mg sites.

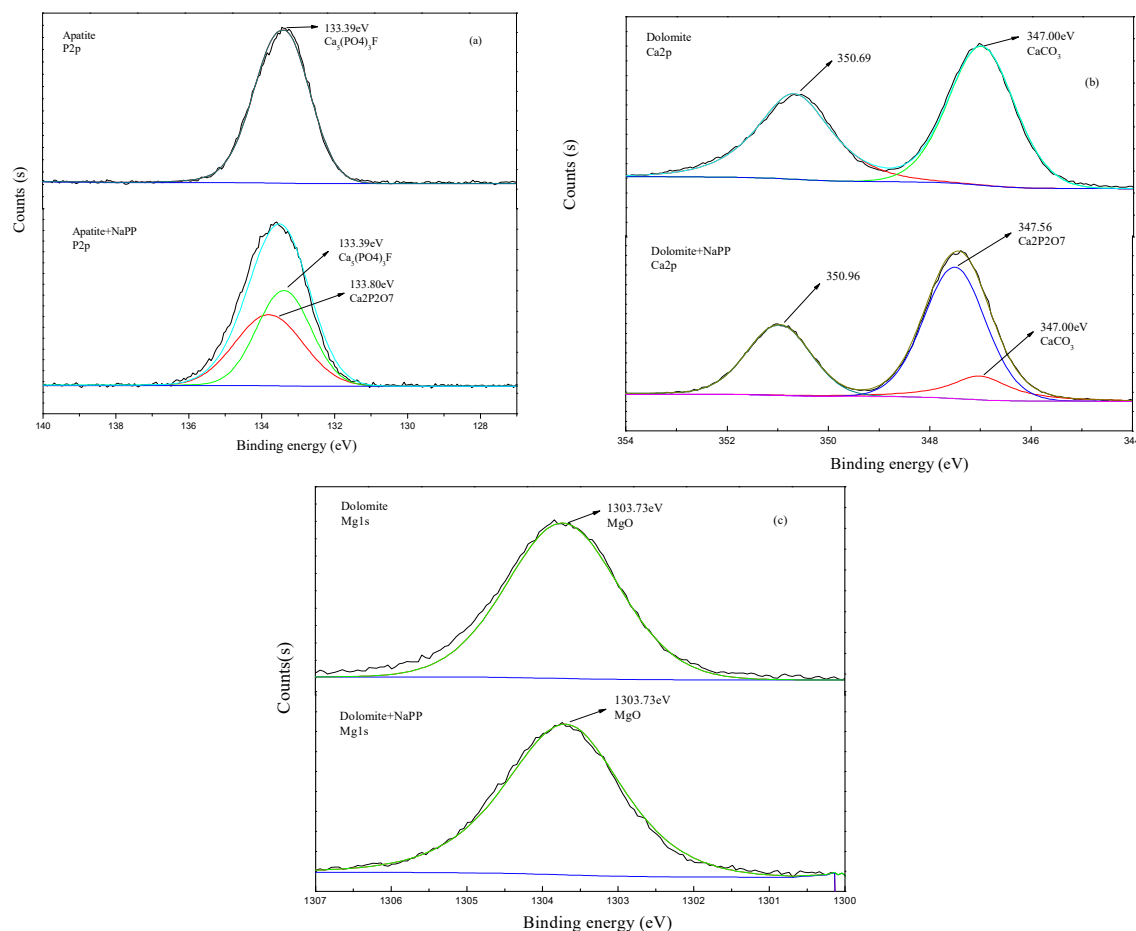


Figure 7. Fitting of X-ray photoelectron spectroscopy (XPS) spectra of (a) P2p of apatite, (b) Ca2p of dolomite and (c) Mg1s of dolomite before and after treatment with NaPP.

In addition, to obtain more detailed information about the selective depression of NaPP on apatite flotation, broad scan XPS analyses of apatite and dolomite under different reagent conditions were also employed, and the results are shown in Figure 8 and Table 2. Generally, an obvious shift of binding energy indicates variations of chemical environment. From Table 2 we can see that after apatite was treated with NaOL, the binding energy of Ca2p decreased by 0.51 eV, which revealed a chemical interaction between apatite and NaOL. For the chemical adsorption of NaOL onto apatite surface, apatite was hydrophobic. After apatite was treated with both NaPP and NaOL, the binding energy of Ca2p shifted by 0.05 eV, which was much smaller than that treated with single NaOL, indicating that the interaction between apatite and NaOL was obviously suppressed by NaPP. Meanwhile, according to Figure 7 we deduced that active Ca sites strongly interacted with both NaPP and NaOL. When

NaPP was added before NaOL, NaPP chemisorbed onto apatite surface and thus restricted the reaction of Ca with NaOL. Thus, the flotation of apatite was depressed by NaPP.

In the case of dolomite, after treatment with NaOL, the binding energy of Ca2p and Mg1s shifted by -0.63 eV and -0.29 eV, respectively. These changes suggested that both Ca and Mg were active sites for chemical reaction with NaOL [5,25]. Moreover, the shift of Ca2p binding energy of dolomite was larger than that of apatite, revealing that the interaction between Ca of dolomite and NaOL was more intensive, which was in accordance with the flotation results of Figure 3 and the contact angle measurements of Figure 6. Interestingly, after dolomite was treated with both NaPP and NaOL, the binding energy of Ca2p and Mg1s changed by -0.07 eV and -0.56 eV, respectively. These results demonstrated that for dolomite both Ca and Mg were active sites that reacted with NaOL. The presence of NaPP restricted the interaction between active Ca sites and NaOL, but enhanced the interaction between Mg sites and NaOL. Thus, Mg became predominant active sites for NaOL adsorption. Thus, these changes did not affect the adsorption of NaOL and maintained the flotation performance of dolomite with the addition of NaPP.

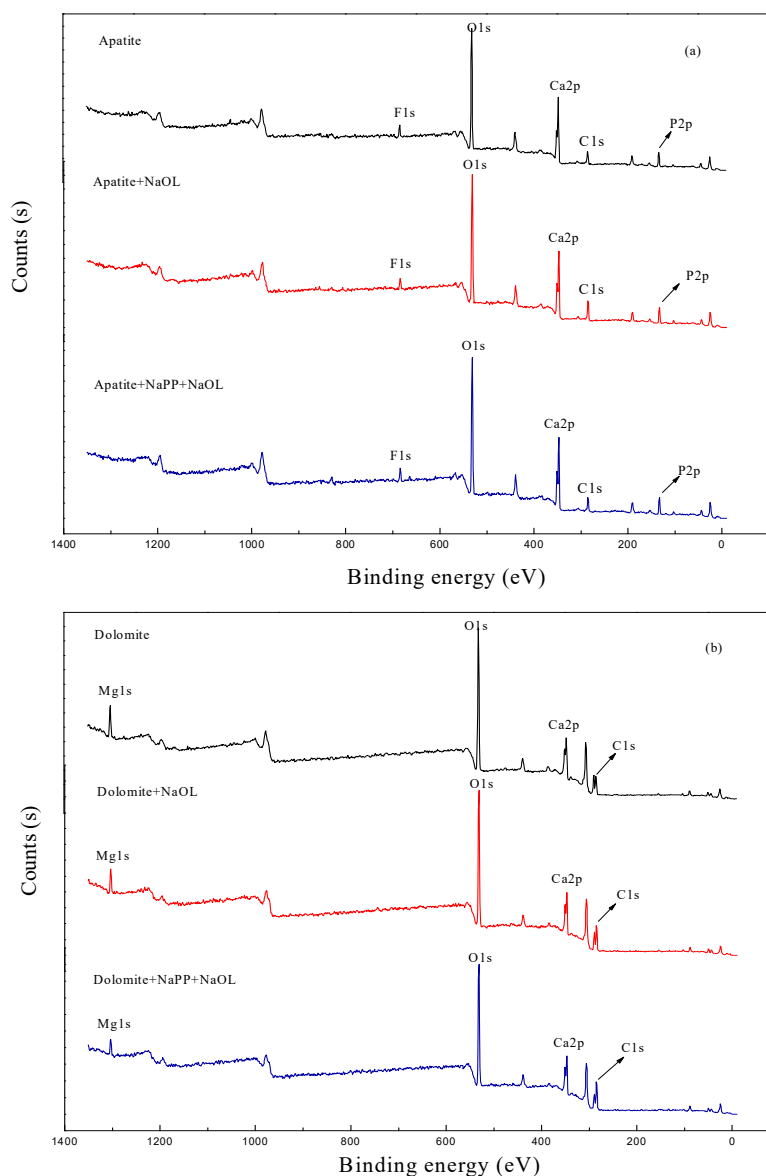


Figure 8. Broad scan XPS spectra of (a) apatite and (b) dolomite before and after treatment with NaPP or NaPP + NaOL.

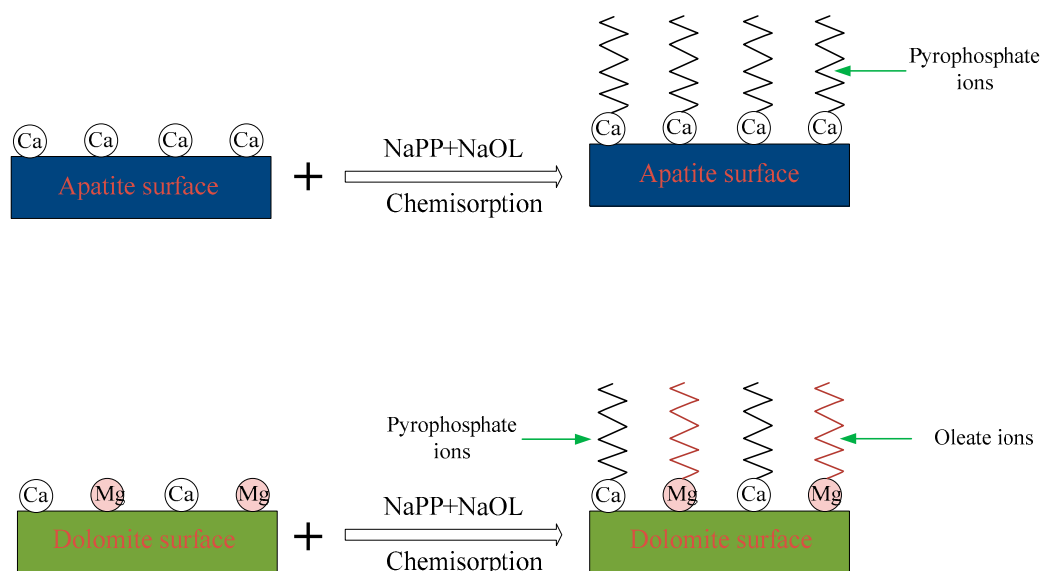
Table 2. Binding energy of elements on the minerals surface under different reagent conditions.

Sample	Binding Energy (eV)		Chemical Shift (eV)	
	Ca	Mg	Ca	Mg
Apatite	347.54	-	-	-
Apatite + NaOL	347.03	-	−0.51	-
Apatite + NaPP + NaOL	347.49	-	−0.05	-
Dolomite	347.14	1303.79	-	-
Dolomite + NaOL	346.51	1303.50	−0.63	−0.29
Dolomite + NaPP + NaOL	347.07	1303.23	−0.07	−0.56

3.5. Depression Mechanism of NaPP

Based on the flotation results, zeta potential and contact angle measurements, and XPS analysis, the possible mechanism about NaPP depression is proposed in Figure 9.

For apatite, Ca provided the only active sites which interacted with both NaPP and NaOL. This led to the competitive adsorption of NaPP and NaOL onto apatite surface. The pre-adsorption of hydrophilic NaPP occupied active Ca sites, restricting the adsorption of NaOL onto apatite surface and thus producing hydrophilia in apatite. However, dolomite has both active Ca and Mg sites for chemical reaction with NaOL. Thus, while NaPP interfered with the interaction of active Ca sites with NaOL, it improved the reactivity of the Mg sites with collector. Thus, the interaction differences resulted in the selective depression of apatite by NaPP.

**Figure 9.** Schematic diagram of potential depression mechanism of NaPP.

4. Conclusions

This study systematically investigated the effect of sodium pyrophosphate on the selective reverse flotation of apatite from dolomite. NaPP showed selective depression of apatite, thus realizing the preferential flotation separation of apatite from dolomite. Based on the results of zeta potential and contact angle measurements, and XPS analyses, it was concluded that NaPP occupied active Ca sites and hindered the adsorption of NaOL onto apatite surface. As for dolomite, although the presence of NaPP interfered with the interaction between active Ca sites and NaOL, it improves the reactivity of active Mg sites with NaOL. Thus, the flotation of dolomite was slightly influenced by NaPP. In this way, the separation of apatite from dolomite was achieved. However, the limitation of the work is that

the test was carried out on pure minerals. The focus of the following work is to confirm the results with dolomitic phosphate ores.

Author Contributions: Y.C. and G.Z. conceived and designed the experiments; Y.C. prepared the samples and performed the experiments; Q.F. and G.Z. contributed reagents/materials/analysis tools; Y.C. analyzed the data; Y.C., R.L., and D.L., wrote and revised the paper.

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

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