

Article

Application and Mechanism of Anionic Collector Sodium Dodecyl Sulfate (SDS) in Phosphate Beneficiation

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Abstract: Phosphate ore is a valuable strategic resource. Most phosphate ore in China is collophane. Utilization of mid-low grade collophane is necessary to maintain social sustainable development. The gravity-flotation combination separation process can be utilized to separate mid-low grade collophane, but the process consumes a large quantity of acid in the reverse stage. Sodium dodecyl sulfate (SDS) was used as a dolomite collector in this study to reduce the acid consumption of collophane flotation. SDS effectively removed dolomite from the gravity concentrate when no other reagents were present. Flotation test results showed that, compared to the conventional gravity-flotation process, the proposed SDS-based process reduced phosphoric acid dosage from 6.1 kg/t to 3.9 kg/t with similar separation results. The SDS action mechanisms on dolomite were further investigated by zeta potential analysis, single mineral flotation tests, infrared spectrum detection, and theoretical analysis. The results indicate that the SDS adsorption on dolomite is mainly physical adsorption, and that favorable separation effects between collophane and dolomite may be attributed to physical adsorption and entrainment. In addition, it also indicates that the physical adsorption can be utilized to remove dolomite from phosphate on account of zeta potential differences when the separate feed is coarse.

Keywords: mid-low grade; collophane; SDS; dolomite; acid consumption; adsorption mechanisms

1. Introduction

Phosphate ore, a non-renewable resource, forms a critical component of the chemical fertilizer industry, and is one of most important strategic resources in China [1,2]. Its development and utilization directly relates to national food security. It is also an essential component in phosphorous-based chemicals [3–5]. China's cumulative reserves of phosphorite comprise approximately twenty billion tons, mainly distributed across Hubei, Guizhou, Yunnan, Szechwan, and Hunan province [6,7].

China is one of the world's largest producers and consumers of phosphate ore resources. Alongside the rapid development of the chemical fertilizer industry in China, phosphate ore consumption has grown tremendously and now threatens to exhaust the country's rich phosphate ore resources [8,9]. To realize the sustainable development and utilization of phosphorite, the focus must shift from rich ore to mid-low grade phosphate ore [10]. Over 75% of the phosphate ore resources in China are mid-low grade collophane (implicit crystal, microscopic cryptocrystalline

apatite) [11], thus, the reasonable utilization and economic exploitation of mid-low grade collophane is of great significance.

Mid-low grade collophane is difficult to utilize directly. It must be upgraded to meet subsequent processing requirements [12–14]. Chinese collophane is characterized by fine grain and close association with gangue minerals, making it particularly challenging to separate [15]. The gangue minerals can be roughly divided into two categories: silicate minerals and carbonate minerals [16–18]. The direct-reverse flotation process, in which the siliceous minerals are discharged by direct flotation while the calcareous minerals are discharged by reverse flotation, is a popular approach to separation [19,20] but one that comes with several drawbacks, including high reagent consumption, high flotation temperature, and severe environmental pollution. The gravity-flotation combination beneficiation of mid-low grade collophane has been proven effective [21,22], but the high acid consumption of the reverse flotation stage remains problematic [23].

In an effort to address this problem, researchers at the Lianyungang Chemical Mine Design and Research Institute attempted to utilize sodium dodecyl sulfate (SDS) as a dolomite collector to separate Yichang phosphate assaying 50% dolomite and 19.25% P_2O_5 with no other reagents through a rougher, cleaner, and scavenger; they ultimately obtained a concentrate with a grade of 30.7% P_2O_5 at a recovery of 82.86% [24,25]. Though successful to some extent, the severe entrainment and excessively stable foam in this process restricted its further application. These issues arose due to the small particle size of the separation feed of mid-low grade collophane, and have largely discouraged researchers from further pursuing SDS as a collector to remove dolomite from collophane.

The objective of this work is to reduce the acid consumption in the conventional gravity-flotation combination beneficiation of mid-low grade collophane via SDS. The feasibility of the proposed process was investigated by comparison against the conventional process. The proposed technique was found to be effective in significantly reducing acid consumption compared to traditional flotation techniques. In addition, the SDS action mechanisms on dolomite have been investigated.

2. Materials and Methods

2.1. Materials

Phosphate ore was obtained from Yichang, Hubei Province, China. The ore was crushed to a grain size of 0–3 mm with a jaw crusher (model XPC-60 × 100) (Wuhan Boshan Machinery Co. Ltd., Wuhan, China) and a double-roll crusher (model HLXPS-Φ250 × 150) (Wuhan Exploring Machinery Factory, Wuhan, China), then wet ground to −0.074 mm accounting for 70% in a laboratory ball mill (HLXMQ-Φ 240 × 90) (Wuhan Hengle Mineral Engineering Equipment Co. Ltd., Wuhan, China) at 50 wt % solids. The ground ore is referred to from here on as “separation feed”.

The chemical composition of the raw ore was analyzed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) performed on an IRIS Advantage ER/S instrument (Thermo Elemental, MA, USA). The results were shown in Table 1. The contents of P_2O_5 , SiO_2 , and MgO were 23.98%, 22.14%, and 2.11%, respectively; sesquioxide (Al_2O_3 and Fe_2O_3) content was 6.40%.

Table 1. Chemical composition of raw ore.

Component	P_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Content (%)	23.98	22.14	4.11	2.29	32.02	2.11

The mineral composition of the raw ore was determined via X-ray diffraction (XRD) and microscopy analyses. The XRD analyses were conducted using a Rigaku D/MAX-RB X-ray diffraction (Rigaku, Akishima City, Japan) using Cu $K\alpha$ radiation. The results are shown in Figure 1 and Table 2.

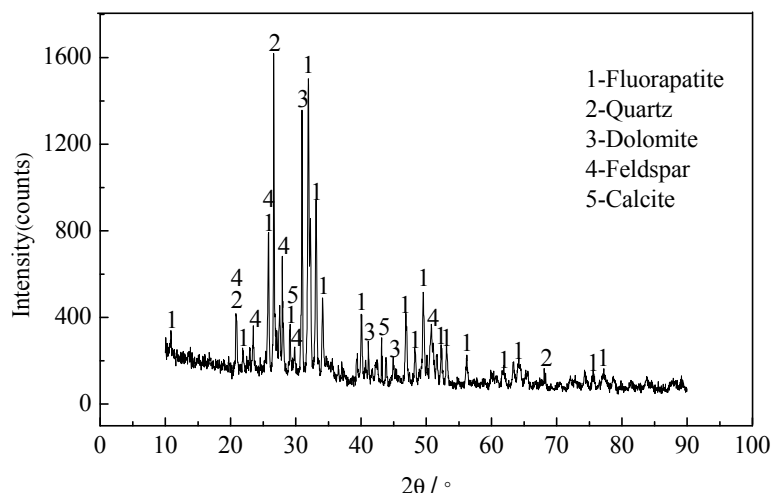


Figure 1. XRD image of raw ore.

Table 2. Mineral composition of raw ore.

Mineral	Collophane	Dolomite	Quartz	Feldspar	Clay	Calcite	Pyrite
Content (%)	56.5	9.5	15.3	3.6	12.8	1.0	1.3

The raw ore mainly contained collophane, dolomite, quartz, feldspar, and clay (56.5%, 9.5%, 15.3%, 3.6%, and 12.8% of the total content, respectively) plus some calcite and pyrite. The collophane was mainly fluorapatite.

Optical microscopy was also performed to determine the main mineral dissemination characteristics. Collophane is characterized by “water chestnut”, polygonal, plate-like, and scattered states. The particles and certain edge portions are mixed with a subtle silica, quartz, and dolomite mixture (Figure 2a,b) and the individual particle is nearly entirely replaced by siliceous rock. Collophane also contains apatite (Figure 2c) embedded in the dolomite fraction, siliceous, and argillaceous pieces, as well as fine-grained pyrite. The particle size of collophane is 0.03–1 mm.

Dolomite has half-automorphic granules, and its aggregates appear to be irregular briquette granules. Most are individually scattered (Figure 2d), while some crystallize or parcel in the collophane and some are distributed as dust-like or fine granules in the collophane and argillaceous fractions. The particle size of dolomite is 0.03–0.15 mm.

Quartz is fine granular, mostly scattered in collophane and argillaceous fractions, and a small fraction are individual scattered states. The particle size of quartz is 0.03–0.4 mm.

Argillaceous fractions are water chestnut or long plates in scattered distribution mainly consisting of illite, sericite, and kaolinite. Some fractions contain quartz powder sand and some appear to be in independent distribution. A small portion appear to have crystallized (Figure 2e) or embedded in the collophane (Figure 2f). The particle size of argillaceous fractions is 0.1–1 mm.

Grain analyses were performed to further observe the characteristics of the separation feed (e.g., differences among size fractions).

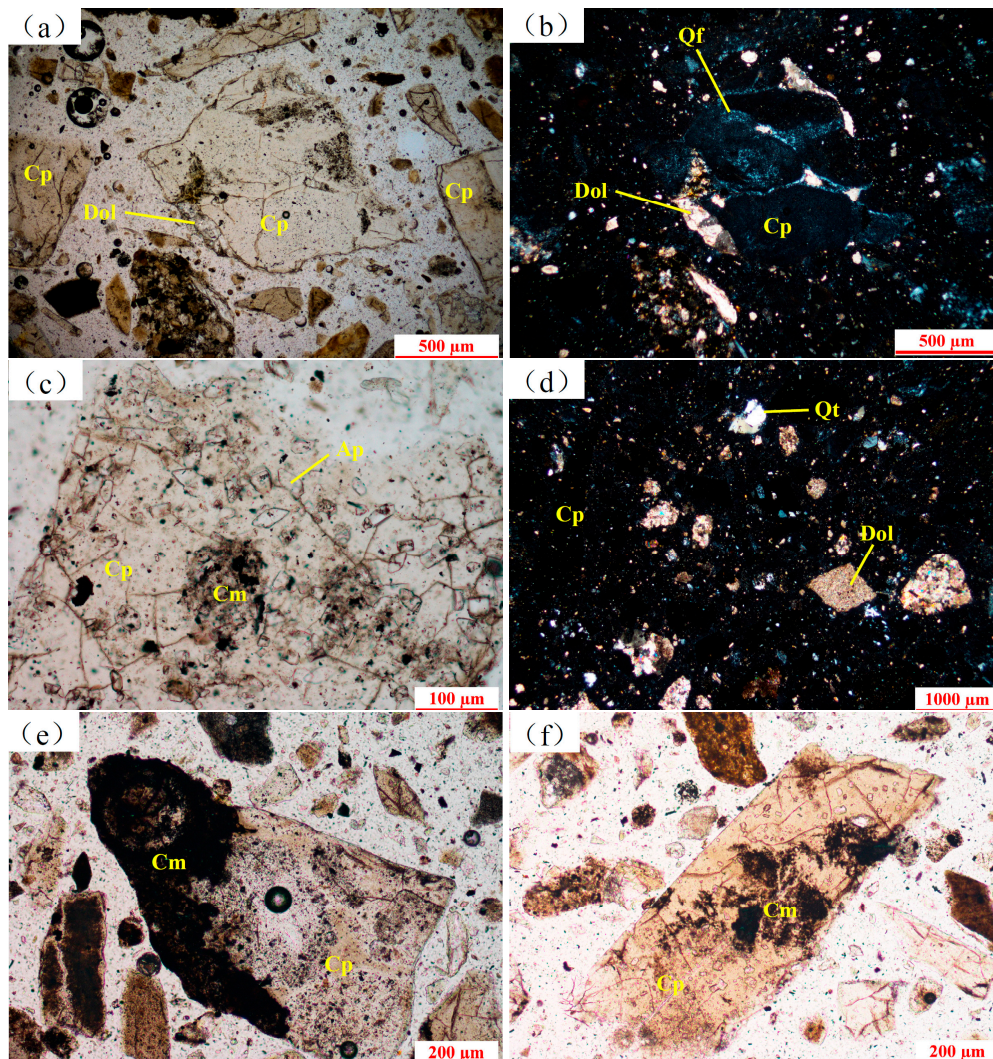


Figure 2. Optical microscopy images of raw ore observed with: (a,c,e,f) plane-polarized light; (b,d) cross-polarized light (Cp: collophane; Ap: apatite; Qf: Quartz and feldspar minerals aggregate Qt: quartz; Cm: clay minerals; Dol: dolomite).

The results in Table 3 showed that phosphorus was concentrated in coarse size fractions, which might be related to mineral properties: (1) The particle size of collophane is larger than dolomite and quartz; and (2) Argillaceous fractions are easy to grind. Meanwhile, the density of collophane is slightly greater than dolomite, quartz, and clay [20], so the ore can indeed be concentrated by gravity separation (and, thus, separated by a gravity-flotation combination process).

Table 3. Grain analyses of separation feed.

Size Fraction (mm)	Yield (%)	Grade (%)		Distribution (%)	
		P ₂ O ₅	MgO	P ₂ O ₅	MgO
+0.15	1.40	28.16	0.60	1.66	0.40
−0.15+0.074	28.69	26.31	1.21	31.78	16.41
−0.074+0.045	23.64	25.20	2.19	25.08	24.47
−0.045+0.038	7.65	24.00	2.76	7.73	9.98
−0.038+0.025	6.12	22.62	3.20	5.83	9.26
−0.025	32.50	20.40	2.57	27.92	39.48
Separation Feed	100.00	23.75	2.11	100.00	100.00

2.2. Methods

2.2.1. Gravity Separation Tests

Owing to the small density differences among the minerals in the raw ore and fine-grained separation feed, a spiral chute ($P/D = 0.36$) was selected for separation [20,26]; 3 kg of separation feed was processed with a five-turn laboratory spiral chute at a pulp density of 18 wt % solids. Tests were conducted under the condition of 215 L/h feed rate and no wash water. The products of gravity separation included concentrate and tailing.

2.2.2. Flotation Separation Tests

Flotation tests were carried out with a 0.5/0.75L XED-IV single cell flotation machine (Jilin Prospecting Machinery Factory, Changchun, China). Tests were conducted at a solid content of 33%, pulp temperature of 298 K, and impeller speed of 1725 rpm. Chemical reagents were added to the cell at different time points. Sodium carbonate, water glass, and ZY-1 (fatty acid) served as regulator, depressant, and collector, respectively, during the direct flotation tests, and phosphoric acid served as regulator and depressant during reverse flotation. As discussed above, SDS served as a dolomite collector during reverse flotation.

2.2.3. Zeta Potential Analysis Tests

A suspension containing 0.01 wt % single apatite or dolomite particles ground to -2 mm in an agate mortar was prepared in KCl solution (10^{-3} M). The pH value of the suspension was adjusted to the desired value using HCl or NaOH solution. The suspension was stirred with magnetic stirrer for 5 min to prepare samples for analysis. The samples were placed into a zeta analyzer (Malvern Instruments Ltd., Malvern, UK) to measure the zeta potential of the mineral surfaces at 298 K. The tests were run in three replicates and the average is reported as the final value.

2.2.4. Single Mineral Flotation Tests

Single mineral flotation tests were carried out in a XFGC II flotation machine (Wuhan Hengle Mineral Engineering Equipment Co. Ltd., Wuhan, China) with a 40 mL flotation cell. Four grams of single collophane or dolomite (particle size 0.038–0.074 mm) and 40 mL of distilled water were added to the flotation cell, then HCl or NaOH was added to adjust the pH and the pulp was stirred for 1 min. A moderate amount of the collector was then added to the flotation cell followed by stirring for another 2.5 min, then the pH values were measured with a precise pH meter (PHS-3C). Tests were conducted at a pulp temperature of 298 K and impeller speed of 1500 rpm. The flotation time was 5 min and the froth was manually scraped. The froths obtained were dried and weighed to calculate the yield, which was reported here as the sample recovery.

2.2.5. FTIR Spectrum

The infrared spectra were obtained on a NEXUS670 spectrometer (Thermo Nicolet, MA, USA). The FTIR (Fourier Transform Infrared Spectroscopy) spectra of samples were recorded in the range from 400 to 4000 cm^{-1} . Collophane or dolomite (0.15 g, -0.045 mm) was equilibrated with 100 mL of the SDS solution at a concentration of 20 mg/L and pH of 7.5. The solution was stirred at 250 rpm for 6 h, then gently washed three times with deionized water and air-dried after conditioning. Fifty milligrams of the sample was mixed with 100 mg of KBr powder in an agate mortar, then the mixture was ground to further reduce the particle size and complete the mixing process. The powdered mixture was then pressed into a thin plate for FTIR analysis.

3. Results and Discussion

3.1. Gravity Separation Test Results

The results of our gravity separation tests on the separation feed were obtained.

Table 4 illustrated where obvious concentration effects were observed during the experiment. Gravity concentrate with P_2O_5 28.95%, MgO 2.08%, and recovery of 57.62% P_2O_5 was obtained. The removal of Mg by gravity separation was so weak that the gravity concentrate failed to meet the requirements for subsequent processing. The weak effect of removing Mg may be the result of small density differences between collophane and dolomite. A sketch of the phenomenon observed in the experiment was shown in Figure 3, where the grain size of the gravity concentrate was much larger than the gravity tailing.

Table 4. Gravity separation results.

Products	Yield (%)	Grade (%)		Recovery (%)	
		P_2O_5	MgO	P_2O_5	MgO
Gravity concentrate	47.43	28.95	2.08	57.62	46.61
Gravity tailing	52.57	19.21	2.15	42.38	53.39
Separation feed	100.00	23.83	2.12	100.00	100.00

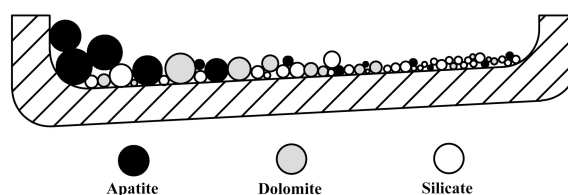


Figure 3. Gravity separation phenomenon.

To quantify the differences of the grain size of gravity products, grain analyses were performed.

Figure 4 further illustrated the large differences in grain size between the gravity concentrate and gravity tailing, where +0.045 mm size fractions accounted for 77.12% in the gravity concentrate and −0.025 mm size fractions accounted for 53.36% in the gravity tailing. Theoretically, the density differences among the minerals in phosphorus ore are small, which can lead to a wide disparity in grain size of gravity products. Obviously, the test results are consistent with the theory.

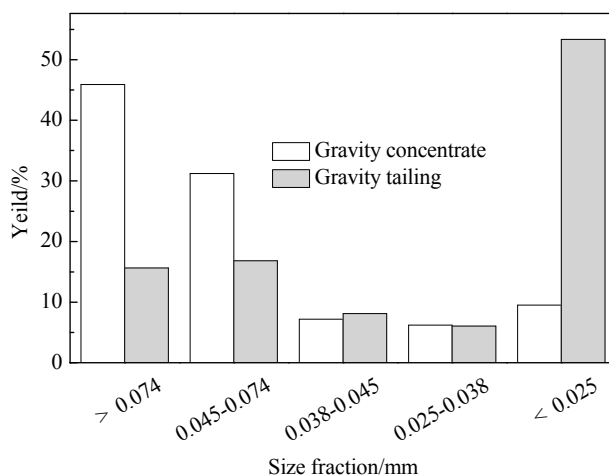


Figure 4. Grain analyses of gravity products.

3.2. Flotation Separation Test Results

A flow chart of the gravity-flotation combination process was drawn based on the flotation test results as shown in Figure 5. The rougher tests were conducted in 0.75 L flotation cell, and the cleaner tests and reverse tests were conducted in 0.5 L flotation cell. Concentrate with a grade of 31.29% P_2O_5 at a recovery of 89.10% was attained under the optimum reagent dosage conditions. From here on, this process is referred to as the “conventional gravity-flotation combination process”. The conventional gravity-flotation combination process comes at relatively low processing cost due to the relatively minimal quantity of direct flotation feed necessary, but the high acid consumption in the reverse flotation stage is problematic.

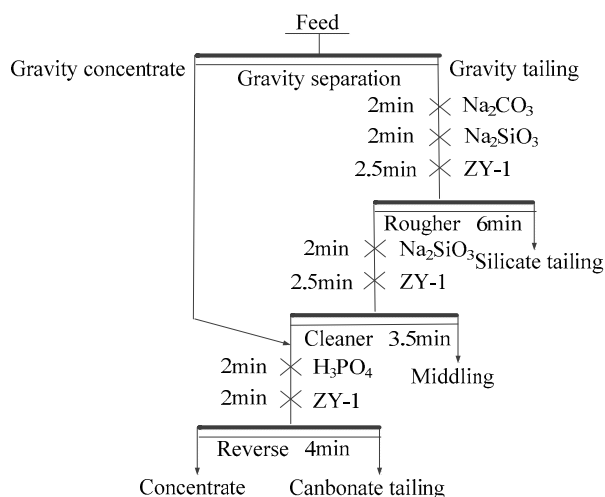


Figure 5. Conventional gravity-flotation combination process.

As discussed in the introduction, SDS has been reported as an efficient collector for dolomite removal under the condition that no other reagents are present, but it resulted in severe entrainment and excessively stable foam. Considering that the particle size of gravity concentrate was coarse, SDS was tested here as a reverse collector to remove the dolomite from gravity concentrate in the absence of any other reagents.

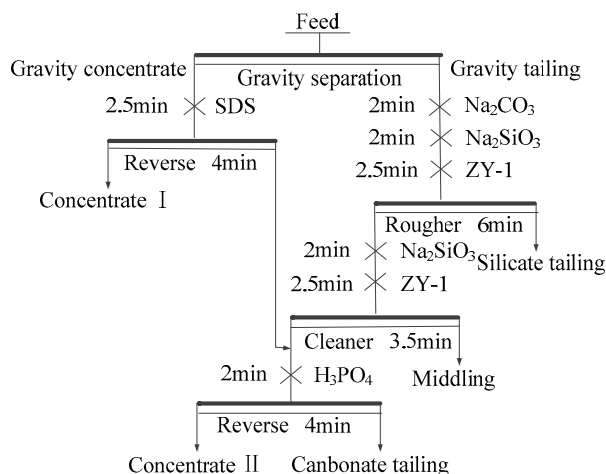
3.2.1. SDS Separation Performance

SDS reverse flotation tests were run to test SDS as a collector to float dolomite in the absence of any other reagents. The tests were conducted in 0.75 L flotation cell and the operating time was 2.5 min. The results indicated excellent defoaming properties of the froth product, high separation efficiency, and good separation effects overall. On the other hand, SDS was also replaced by ZY-1 and sodium oleate in subsequent tests to separate the gravity concentrate for the sake of comparison.

As shown in Table 5, the separation effect of SDS was optimal with similar concentrate yields. Moreover, SDS has better resistances to hard water and low temperature compared to ZY-1 or sodium oleate, which is beneficial to flotation. Therefore, the gravity concentrate was determined to be separated by SDS in the absence of any other reagents. A test flowchart was drawn based on these results (Figure 6). From here on, this process is referred to as the “improved gravity-flotation combination process” (or simply “improved process”).

Table 5. Concentrate indexes of reverse flotation tests.

Collector	Dosage (kg/t)	Yield (%)	P ₂ O ₅ Grade (%)	MgO Grade (%)
SDS	0.40	71.86	30.36	0.84
ZY-1	0.33	71.65	29.43	1.17
Sodium oleate	0.36	71.49	29.32	1.21

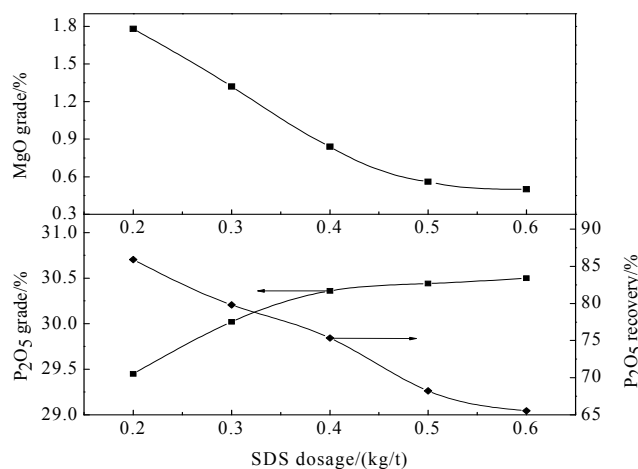
**Figure 6.** Improved gravity-flotation combination process.

3.2.2. SDS Reverse Flotation Tests for Gravity Concentrate

Flotation tests were further run to determine the feasibility of the improved process. SDS reverse flotation tests of the gravity concentrate were conducted under various SDS dosages.

Figure 7 showed that the removal of Mg was substantial as the SDS dosage increases, but when SDS dosage reached 0.5 kg/t, the MgO content varied slightly. Excessive SDS collects more apatite, especially fine-grain apatite, while the entrainment of fine grain apatite grows severe as the SDS dosage increases. Hence, 0.4 kg/t can be considered the optimum SDS dosage.

Under these conditions, on the basis of raw ore, concentrate with P₂O₅ 30.36%, MgO 0.84%, and recovery of 43.42% P₂O₅ was successfully obtained. The froth product with P₂O₅ 25.35%, MgO 5.25% was regarded as the middling.

**Figure 7.** Effect of SDS dosage on concentrate separation indices.

3.2.3. SDS Action Mechanism

As discussed above, zeta potential analysis tests and flotation tests on single cellophane and dolomite were conducted to investigate the SDS adsorption mechanism on dolomite.

Figure 8 showed where the zeta potential differences between collophane and dolomite were substantial at various pH values. Within the range of 3.0 to 9.0, higher pH decreased the zeta potential. The points of zero charge (PZC) of collophane and dolomite were about 4.7 and 6.5, respectively. The results were calculated as follows [27]:



$$K_a = \frac{[\text{H}^+][\text{DS}^-]}{[\text{HDS}_{(\text{aq})}]} \quad (2)$$

$$\text{pH} - \text{pK}_a = \lg \frac{[\text{DS}^-]}{[\text{HDS}_{(\text{aq})}]} \quad (3)$$

$$\text{pK}_a < \text{pH} < \text{PZC} \quad (4)$$

where pH is the effective pH range for electrostatic mineral collection. HDS is a strong acid [27], so $\text{pH} < \text{PZC}$ is the effective pH range. The effective pH ranges for SDS on collophane and dolomite by electrostatic forces were $\text{pH} < 4.7$ and $\text{pH} < 6.5$, respectively.

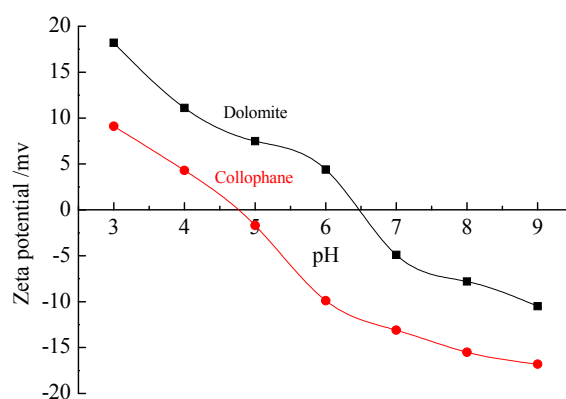


Figure 8. Effect of pH on zeta potential.

As shown in Figure 9, when the pH ranged from 3.0 to 9.0, the recovery of dolomite gradually decreased. Namely, higher zeta potential improved the recovery, so it could be inferred that physical adsorption occurred in our experiment. Under the optimal SDS reverse flotation test conditions described above, the pulp pH is 7.5. The FTIR spectra obtained under this pH condition, as shown in Figures 10 and 11, indicated that there was no apparent chemical adsorption between collophane and dolomite. In short, the SDS adsorption on dolomite is mainly physical.

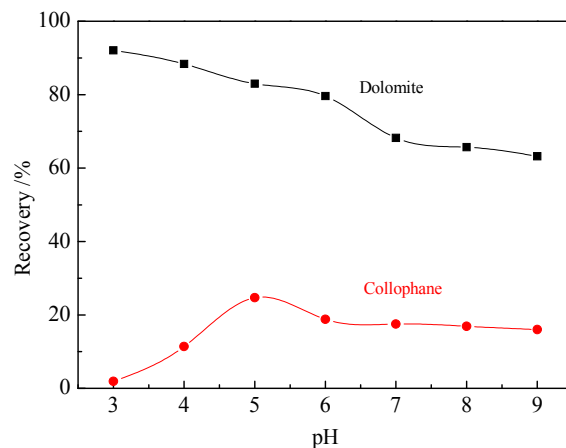


Figure 9. Effect of pH on recovery (SDS dosage is 3×10^{-4} mol/L).

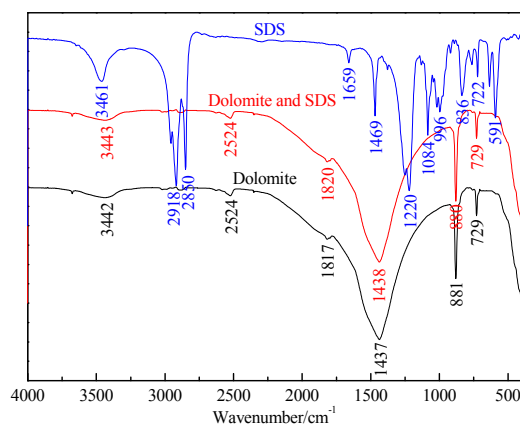


Figure 10. FTIR spectra of before and after action between dolomite and SDS.

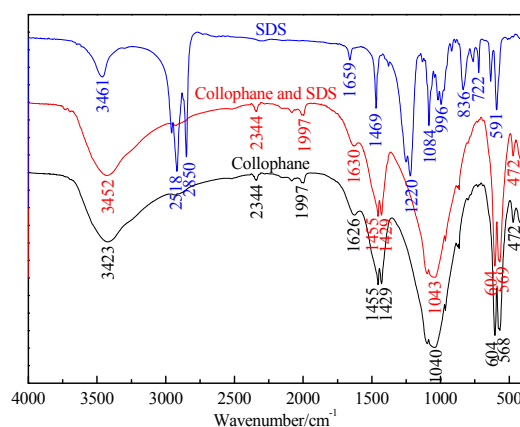


Figure 11. FTIR spectra of before and after action between collophane and SDS.

The K_{sp} values of $Mg(DS)_2$ and $Ca(DS)_2$ were obtained as follows [28,29]:



$$K_{sp}^1 = [Mg^{2+}][DS^-]^2 = 2.29 \times 10^{-10} \quad (6)$$



$$K_{sp}^2 = [Ca^{2+}] [DS^-]^2 = 1 \times 10^{-9.7} \quad (8)$$

The ratio is $\frac{K_{sp}^1}{K_{sp}^2} = 1.15$, which indicates that the chemical adsorption differences between collophane and dolomite are theoretically very small. This also indicates that favorable dolomite separation effect is not attributable to chemical absorption, but to physical adsorption.

As reported in Table 3, the average particle size of dolomite was smaller than collophane; the density differences between them is very small [20], so dolomite is more readily entrained than collophane. An entrainment phenomenon was also observed in the SDS reverse flotation tests. To this effect, the separation effect may be partly attributed to entrainment.

In summary, the SDS adsorption on dolomite is mainly physical and the favorable separation effect between collophane and dolomite can be attributed to physical adsorption and entrainment. In addition, it is inferred that the physical adsorption can be utilized to remove dolomite from phosphate on account of the zeta potential differences when the separate feed is coarse.

3.3. Quantity-Quality Flow-Sheet

The quantity-quality flow-sheet was drawn based on the flotation results.

As depicted in Figure 12, after the gravity concentrate was separated by the SDS, 75.36% of the phosphorus had been recovered and the separation feed of follow-up reverse flotation decreased by up to 44.12%. To this effect, the proposed method readily solved the problem of overweight dolomite in the gravity concentrate. Concentrate I and concentrate II were merged as the final concentrate, thus, under the optimum reagent dosage conditions, final concentrate with P_2O_5 31.31%, MgO 0.88%, and 89.23% recovery of P_2O_5 was obtained.

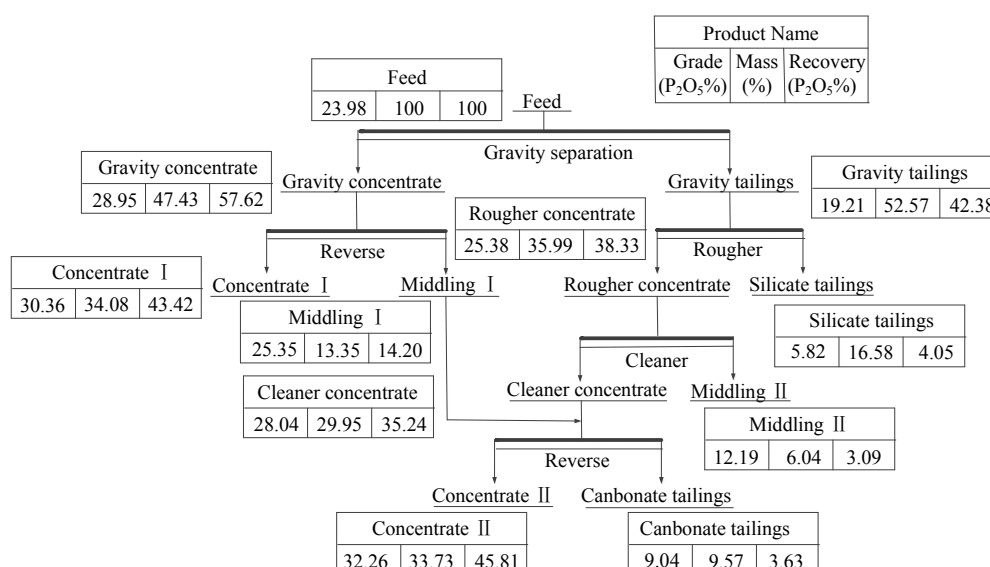


Figure 12. Quantity-quality flow-sheet of improved process.

3.4. Comparison between Different Processes

To research the effects of the improved process in greater detail, the optimum reagent dosages and corresponding concentrate indices of the improved and conventional processes were compared.

Tables 6 and 7 indicated that compared to the conventional process, the improved process reduced the dosage of phosphoric acid from 6.1 kg/t to 3.9 kg/t with similar separation results. The improved process can save 8.1 CNY/t in raw ore costs according to reagent prices current as of October 2016. In addition, the decline in acid consumption also can slows down the acid corrosion of equipment, further enhancing the economic benefits of the improved process.

Table 6. Optimum reagent dosages of two processes.

Process	The Optimum Reagents Dosage (kg/t)				
	Sodium Carbonate	Water Glass	Collector	Phosphoric Acid	SDS
Conventional process	1.4	0.9	0.5	6.1	0
Improved process	1.4	0.9	0.4	3.9	0.2

Table 7. Concentrate indices of two processes.

Process	The Corresponding Indices of Concentrate (%)			
	Yield	P ₂ O ₅ Grade	MgO Grade	P ₂ O ₅ Recovery
Conventional process	67.87	31.29	0.93	89.10
Improved process	67.81	31.31	0.88	89.23

4. Conclusions

1. The separation effect of SDS was optimal when SDS, ZY-1, and sodium oleate served as collectors to remove dolomite from gravity concentrate in the absence of other reagents.
2. The proposed gravity concentrate is suitable for flotation by SDS by virtue of its excellent defoaming properties, high separation efficiency, and good separation effects. Gravity concentrate containing 28.95% P₂O₅ and 2.08% MgO was separated by SDS, ultimately yielding concentrate with P₂O₅ 30.36%, MgO 0.84%, and 75.36% recovery of P₂O₅.
3. The improved gravity-flotation combination process was proven effective in reducing the acid consumption from 6.1 kg/t to 3.9 kg/t with similar separation results compared to the conventional gravity-flotation combination process. The improved process can also save 8.1 CNY/t raw ore and slow down the acid corrosion of equipment.
4. Our analysis of the SDS action mechanism indicates that the SDS adsorption on dolomite is mainly physical, and that the favorable separation effect between collophane and dolomite can be attributed to physical adsorption and entrainment.
5. The physical adsorption can be utilized to remove dolomite from phosphate on account of zeta potential differences when the separate feed is coarse.

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Author Contributions: Kun Sun and Tao Liu conceived and designed the experiments; Kun Sun, Bo Wang, and Chengbao Xu performed the experiments; Xin Liu and Yimin Zhang analyzed the data; Tao Liu and Yimin Zhang contributed reagents/materials/analysis tools; and Kun Sun wrote this paper.

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

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