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Migration and Enrichment of Rare Earth Elements in the Flotation Process of Rare Earth-Bearing Collophanite

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Abstract: Rare earth elements (REEs) are important strategic resources, widely used in various technological fields, especially heavy rare earth elements (HREEs). China has extensive rare earth deposits, with diverse mineral types and a complete range of rare earth elements, characterized by a "heavy south, light north" resource distribution pattern. The rare earth-bearing collophane in the Zhijin area of Guizhou is a typical marine sedimentary phosphorite deposit with large reserves and a high heavy rare earth content. This study investigates the rare earth-bearing collophane in the Zhijin area using X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) to analyze its mineral composition and occurrence characteristics. In terms of flotation, a reverse flotation process for magnesium removal was adopted. By optimizing the flotation parameters, including grinding fineness, collector dosage, pH regulator dosage, and depressant dosage, the optimal flotation conditions were determined. A further mineralogical analysis was conducted on both the flotation concentrate and tailings. The results show that the main minerals in the rare earth-bearing collophane of Zhijin are fluorapatite and dolomite, with dolomite as the primary gangue mineral, and rare earth elements are mainly hosted in fluorapatite. The optimal flotation conditions were achieved when the grinding fineness was −74 μm with an 83% passing rate, XF-1 was used as the collector at a dosage of 300 g/t, sulfuric acid (H_2SO_4) as the pH regulator at 6 kg/t, and phosphoric acid (H_3PO_4) as the depressant at 3 kg/t. By employing an optimal reagent regime and implementing a reverse flotation process consisting of one roughing and one scavenging stage, a phosphate concentrate was obtained with a P_2O_5 grade of 31.61% and an REO content of 0.161%. The P_2O_5 recovery reached 84.22%, while the REO recovery was 78.65%. Compared to the raw ore, the P_2O_5 grade increased by 11.52 percentage points, and the REO content improved by 0.051 percentage points. Mineralogical analysis of the flotation concentrate and tailings revealed that dolomite was effectively removed by reverse flotation, while rare earth elements were successfully enriched in the phosphate concentrate. In conclusion, this study provides an efficient flotation separation process for rare earth-bearing collophane and dolomite, while also offering technical support for the efficient recovery of rare earth resources. This research has significant theoretical and practical implications.

Keywords: Zhijin; rare earth-bearing collophane; reverse flotation; flotation process; rare earth recovery

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1. Introduction

Rare earth elements (REEs) are important strategic resources, especially heavy rare earth elements (HREEs), which play a crucial role in aerospace, military, metallurgy, and new material industries due to their unique optical, electrical, and magnetic properties [1,2]. In recent years, the rare earth industry has faced significant challenges due to increasing market demand and supply chain instability [3,4].

China has abundant sedimentary phosphate deposits, some of which contain high concentrations of REEs. In certain phosphorite deposits, HREEs account for more than 30% of the total REE content, making these deposits valuable for industrial development [5]. The recovery and utilization of associated rare earth resources from phosphate deposits can not only improve the comprehensive utilization of mineral resources and achieve high-value, efficient exploitation [6,7] but also mitigate the environmental pollution and ecological damage caused by the mining of ion-adsorbed rare earth deposits in Southern China. Additionally, phosphate rock deposits rich in REEs are expected to become important reserves for HREE resources [8].

The REE-rich phosphorite in Zhijin, Guizhou, is a typical marine sedimentary phosphorite deposit from the Early Cambrian Xiaotan Stage. The primary minerals in this deposit are fluorapatite and dolomite, and the mineralization process occurred during sedimentation and diagenesis [9,10]. One of the significant differences between this deposit and the Kunyang phosphorite of Eastern Yunnan is the enrichment of rare earth elements and yttrium. According to the Comprehensive Exploration Report on Phosphate (Rare Earth) Deposits in the Zhijin Area, Guizhou Province [11], the total rare earth oxide (RE_2O_3) resource in the Zhijin area exceeds 3.5 million tons, with an average grade of 0.1036%. The deposit contains abundant heavy rare earth elements, making it comparable to a super-large rare earth deposit [12–14].

Dolomite is the primary gangue mineral in phosphate ore, and it has surface properties similar to fluorapatite, making their separation challenging [15,16]. Flotation is the most commonly used method for separating fluorapatite from dolomite. In recent years, many researchers have conducted extensive studies on the flotation separation of apatite and dolomite. Zhang et al. [17] used sodium oleate (NaOL) as a collector to investigate the separation effect of collophane and dolomite when using H_2SO_4, H_3PO_4, and a sulfur–phosphorus mixed acid as depressants. The results showed that SO_4^{2-} and $H_2PO_4^-$ were responsible for the depression of collophane, and the combined use of H_3PO_4 and H_2SO_4 was significantly more effective than using them individually. Wei et al. [18] studied the influence of citric acid (CA) on the flotation behavior of apatite and dolomite. Their findings indicated that in a flotation system using NaOL as the collector, CA exhibited stronger adsorption on the apatite surface than on the dolomite surface. The strong chelation between CA and Ca^{2+} on the apatite surface hindered NaOL adsorption on apatite. Similarly, Kang et al. [19] used polyaspartic acid (PASP) as a selective depressant for separating apatite and dolomite in a NaOL-based flotation system. The mechanism of action was that PASP chelated with exposed Mg^{2+} and a certain amount of Ca^{2+} on the dolomite surface, thereby inhibiting NaOL adsorption on apatite. Wang et al. [20] used tara gum (TG) as a depressant and NaOL as a collector for apatite, achieving the direct flotation separation of dolomite and apatite. Their study revealed that TG exhibited a weak physical adsorption on apatite but strong chemical adsorption on dolomite. Kun et al. [21] compared the separation efficiency of sodium dodecyl sulfate (SDS), NaOL, and a fatty acid-based collector (ZY-1) as dolomite collectors in collophane separation. The results showed that for gravity concentrate, SDS provided the best separation performance when H_3PO_4 was used as a depressant for collophane.

Due to the amorphous nature of sedimentary phosphorites and their frequent association with calcareous impurities and amorphous phosphates [22], reverse flotation is commonly used to remove carbonate and silicate gangue minerals from collophane ores. Typically, for medium- to low-grade calcareous collophane ores with an initial P_2O_5 content of around 20%, the reverse flotation process can increase the P_2O_5 grade to 28.23%, with a recovery rate of 87.46% [23]. For rare earth-bearing calcareous collophane, the initial RE_2O_3 content ranges from 0.070% to 0.1190%, and after flotation, it can be enriched to 0.133–0.1861%, with a recovery rate exceeding 80% [24–26]. However, in low-grade rare earth phosphate ores (P_2O_5 < 16%), due to the low initial P_2O_5 content, high gangue mineral content, and complex mineral phases, the final phosphate concentrate also has a relatively low P_2O_5 grade [27]. Except for industrial test samples with an excessively high MgO content, other flotation products have met the acid-grade phosphate rock standards required for phosphoric acid production [28].

This study focuses on rare earth-bearing collophane from the Zhijin area in Guizhou, China. Using X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), we analyzed the mineral composition, chemical composition, and distribution characteristics of the raw ore, flotation concentrate, and flotation tailings. The objective is to investigate the enrichment behavior and efficiency of rare earth elements during the reverse flotation process for magnesium removal.

2. Experimental Section

2.1. Experimental Samples and Reagents

The rare earth-bearing collophane samples used in this study were collected from the fine crushing belt of a phosphate minein Zhijin County, Guizhou Province. The sample had a particle size of 3 mm. After homogenization and splitting, the sample was ground using a conical ball mill (XMQ-Φ240 × 90 model) (Wuhan Locke Grinding Equipment Manufacturing Co., Ltd., Wuhan, Hubei Province, China) before flotation. The flotation collectors used in this study included sodium oleate (NaOL), oxidized paraffin soap (OPS), and XF-1 (which is primarily composed of nitric acid–modified oleic acid). Sulfuric acid (H_2SO_4) was used as the pH regulator, while phosphoric acid (H_3PO_4) was employed as the collophane depressant. The usage, purpose, and properties of the flotation reagents are detailed in Table 1.

Table 1. Usage, purpose, and properties of flotation reagents.

No.	Name	Purity	Usage	Purpose	Dosage (kg/t)
1	NaOL	Analytical	3% aqueous solution	Collector	0.1~1.5 kg/t
2	OPS	Analytical		Collector	0.1~1.5 kg/t
3	XF-1	Industrial		Collector	0.1~1.5 kg/t
4	H_2SO_4	Analytical		pH regulator	5~7 kg/t
5	H_3PO_4	Analytical		Depressant	2~4 kg/t

2.2. Experimental Methods

2.2.1. Reverse Flotation Experiment on Rare Earth-Bearing Collophanite

The reverse flotation test was conducted using an XFD single-cell flotation machine (1 L for the roughing and 0.5 L for the scavenging stage) (Jilin Exploration Machinery Co., Ltd., Changchun, Jilin Province, China). The impeller speed was set to 1992 r/min, and the pulp temperature was maintained at 22 °C to 23 °C. Sequential tests were performed

to evaluate the effects of grinding fineness, collector dosage, pH regulator dosage, and depressant dosage on flotation performance. The flotation process flowchart is shown in Figure 1.

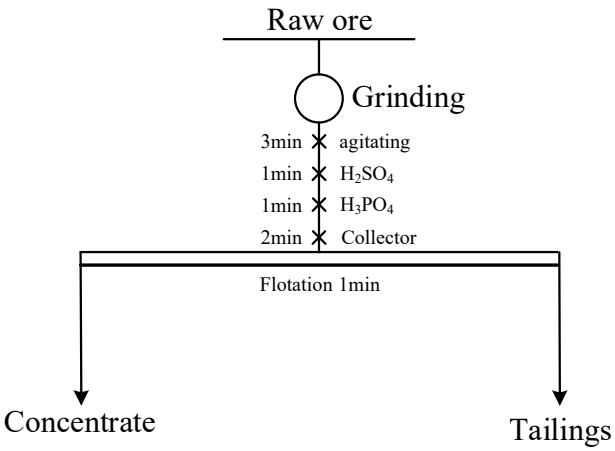


Figure 1. Flowchart of mineral flotation experiment.

2.2.2. X-Ray Powder Diffraction Analysis of Rare Earth-Bearing Collophane

The mineral composition of the rare earth-bearing collophane samples was analyzed using an X-ray powder diffractometer (XRD) from Panalytical (BRUKER AXS GmbH, Karlsruhe, Germany). The main parameters of the instrument were as follows: Cu target, wavelength of 1.54056 Å, scanning speed of 5°/min, and scanning range of 5–90°. The X-ray diffraction patterns were analyzed using HighScore Plus software (version 3.0.5).

2.2.3. X-Ray Fluorescence Spectroscopy Analysis of Rare Earth-Bearing Collophane

An XRF-1800 X-ray fluorescence (XRF) spectrometer from SHIMADZU (Shimane Shimadzu Corporation, 2698 Naoe, Hikawa-cho, Izumo-shi, Shimane, Japan) was used to perform a multi-element analysis on the raw ore, flotation concentrate, and flotation tailings of the rare earth-bearing collophane samples.

2.2.4. Atomic Emission Spectroscopy Analysis

A PerkinElmer Avio 200 inductively coupled plasma optical emission spectrometer (ICP-OES) was used to perform a quantitative analysis of the phosphorus content (expressed as P_2O_5) in the raw ore, flotation concentrate, and flotation tailings. The test temperature was 20 °C, the RF power was 1.3 kW, the plasma gas flow rate was 2 L/min, the auxiliary gas flow rate was 0.2 L/min, and the phosphorus analysis wavelength was 213.617 nm.

2.2.5. Mass Spectrometry Analysis

Due to the low rare earth content in the rare earth-bearing collophane, a PerkinElmer NexION 300X (PerkinElmer, Waltham, MA, USA) inductively coupled plasma mass spectrometer (ICP-MS) was used to determine the rare earth element composition in the raw ore, flotation concentrate, and flotation tailings. The mass-to-charge ratios for element detection are listed in Table 2.

Table 2. Selection of measurement isotopes of 15 rare earth element.

Element	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic mass	89	139	140	141	146	148	153	157	159	163	165	166	169	172	175

2.2.6. Mineral Embedding Characteristics Analysis

The embedding, intergrowth relationships, and elemental distribution of collophane and other gangue minerals in the raw ore, flotation concentrate, and flotation tailings were observed and analyzed using a ZEISS (Carl Zeiss AG, Oberkochen, Baden-Württemberg, Germany) scanning electron microscope and energy-dispersive spectroscopy (SEM-EDS). The samples were first prepared into thin sections or polished sections, followed by Pt coating on the surface. The observation was conducted at a temperature of 23 °C ± 0.5 °C, a working distance of 10 mm, and an operating voltage of 20 kV, using backscattering for observation.

3. Results and Discussion

3.1. Process Mineralogical Study of Rare Earth-Bearing Collophane

3.1.1. Phase and Multi-Element Analysis

The mineral composition of the raw ore was analyzed using X-ray powder diffraction (XRD). As illustrated in Figure 2, the XRD results reveal that the primary mineral phases in the Zhijin rare earth-bearing collophane are fluorapatite and dolomite. Furthermore, based on the intensity of the diffraction peaks, it can be inferred that the dolomite content in the raw ore is relatively high.

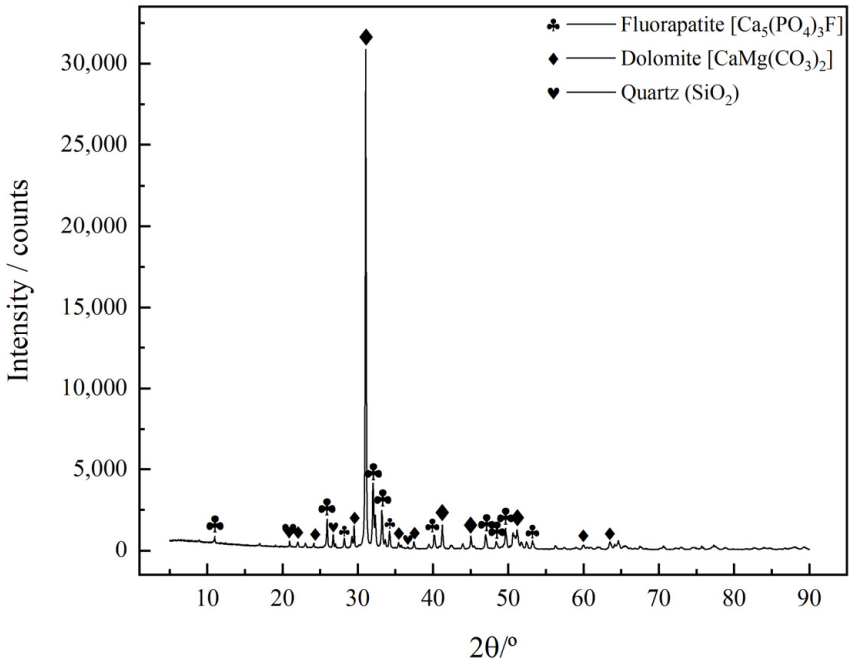


Figure 2. XRD pattern of rare earth-containing collophane.

The results obtained from X-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Figure 3) indicate that the P_2O_5 content in the raw ore is 20.09%, while the MgO content is relatively high at 9.8%, and the F content is relatively low at 2.9%. Combined with the XRD phase analysis, it can be inferred that Mg is primarily hosted in dolomite, whereas F is mainly present in fluorapatite.

Figure 4 presents the analysis of the rare earth element (REE) composition and distribution in the rare earth-bearing collophane. The total REE content in the raw ore is 0.11%, with heavy rare earth element Y having the highest proportion at 32.2% of the total REE content. This is followed by light rare earth element La, which accounts for 21%. Together, Y and La constitute more than 50% of the total REE content. Additionally, the contents of

Nd and Ce are relatively high, at 15.5% and 13.7%, respectively, while the remaining rare earth elements have relatively lower concentrations, all below 10%.

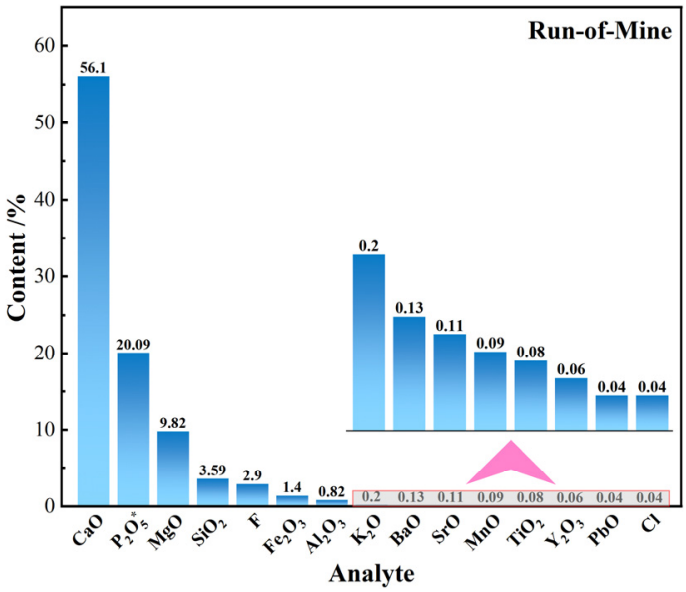


Figure 3. Multi-element analysis of rare earth-containing collophane. * denotes quantitative analysis by ICP-OES.

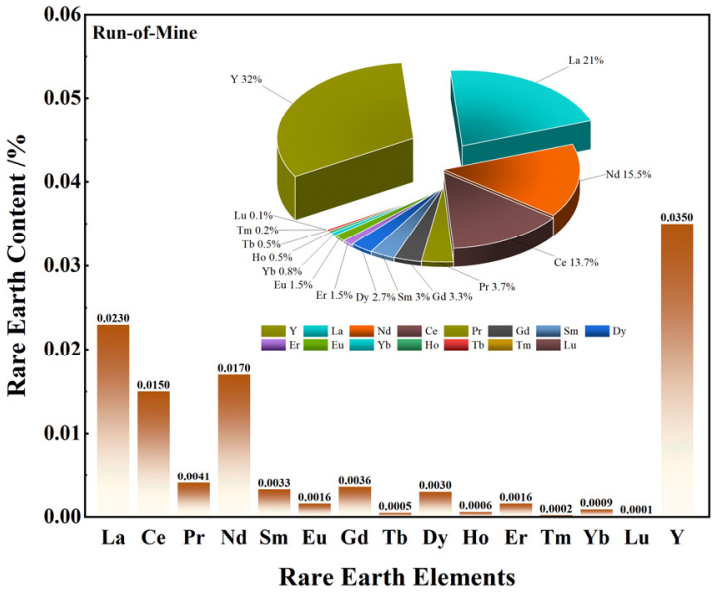


Figure 4. Analysis of rare earth content in rare earth-containing collophane.

3.1.2. Mineral Embedding Characteristics and Composition Analysis

The automated process mineralogy analysis system (BPMA) was used to assess the degree of monomer liberation and the embedding characteristics of the Zhijin rare earth-bearing collophane, with a tested particle size of 100% < −1.5 mm. As shown in Figure 5a,b, apatite rarely occurs as monomers and is predominantly associated with dolomite in the form of intergrowths. Additionally, a small proportion of apatite, dolomite (calcite), and quartz (feldspar) form ternary intergrowths. Furthermore, a minor amount of mica is interwoven with calcite and apatite. Some apatite grains also contain fine inclusions of dolomite, calcite, feldspar, and other minerals.

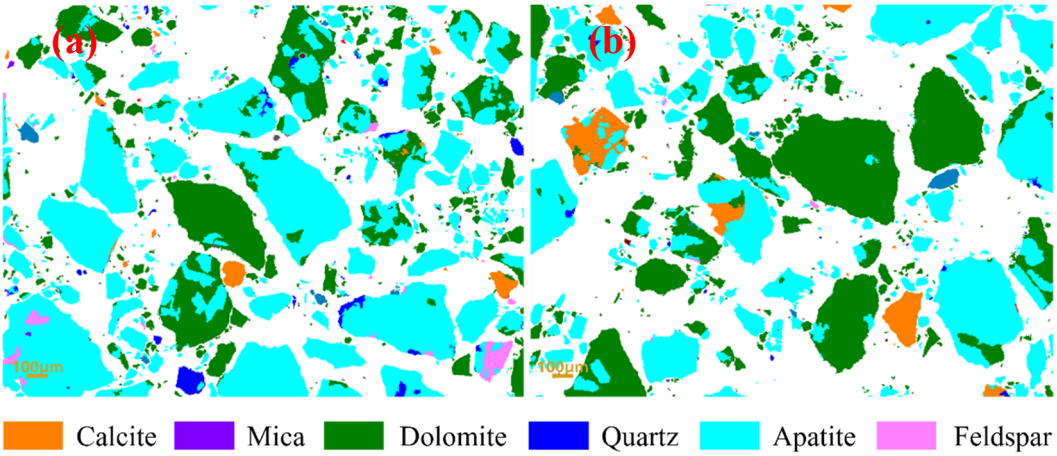


Figure 5. BPMA image of rare earth-bearing collophanite.

Figure 6 presents the degree of mineral liberation of the rare earth-bearing collophane. According to the figure, 66.4% of the apatite particles have a liberation degree exceeding 90%. Among the major gangue minerals, the proportion of particles with a liberation degree greater than 90% is 49.6% for dolomite, 41.3% for calcite, and 36.8% for quartz.

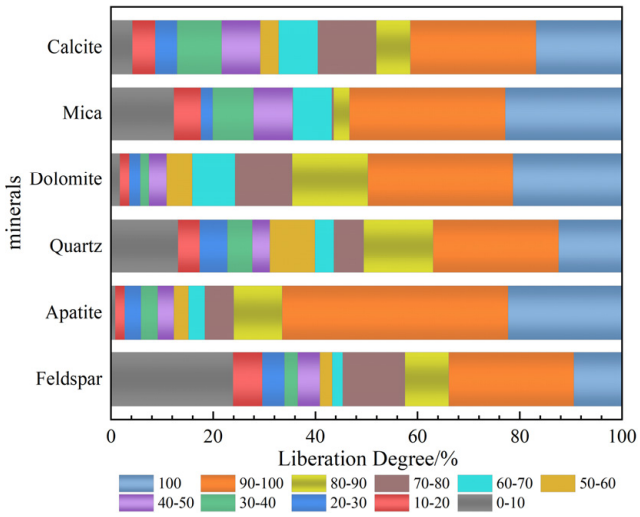


Figure 6. Dissociation degree diagram of rare earth-bearing collophanite.

According to Figure 7, which illustrates the degree of embedding of rare earth-bearing collophane, apatite–dolomite intergrowths have the highest occurrence, accounting for 24.2%. This is followed by apatite–quartz intergrowths, with a proportion of 2.2%. Additionally, dolomite is most commonly associated with apatite, with an intergrowth ratio of 27.8%.

Using scanning electron microscopy and energy-dispersive spectroscopy (SEM-EDS) to analyze the mineral embedding relationships and rare earth element distribution, the Mg element mapping in Figure 8a,b indicates that dolomite fills the spaces between collophane fragments in a cementing form. The P element mapping confirms that phosphorus is primarily associated with collophane, which exhibits rod-like, arcuate, and massive distributions. Meanwhile, the Y element distribution overlaps with that of P, suggesting that rare earth elements are hosted within collophane, with no presence of independent rare earth minerals or other rare earth elements. The Si element mapping reveals that a small amount of quartz occurs as rounded grains, forming sand–silt-sized quartz inclu-

sions within collophane. Additionally, in Figure 8b, an elliptical-shaped collophane grain contains fine-grained dolomite inclusions approximately 10 μm in size.

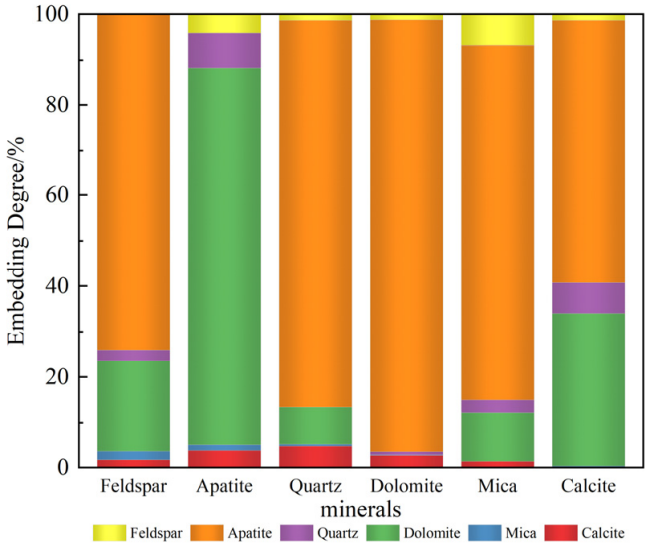


Figure 7. Embedding Degree Diagram of Rare Earth-Bearing Collophanite.

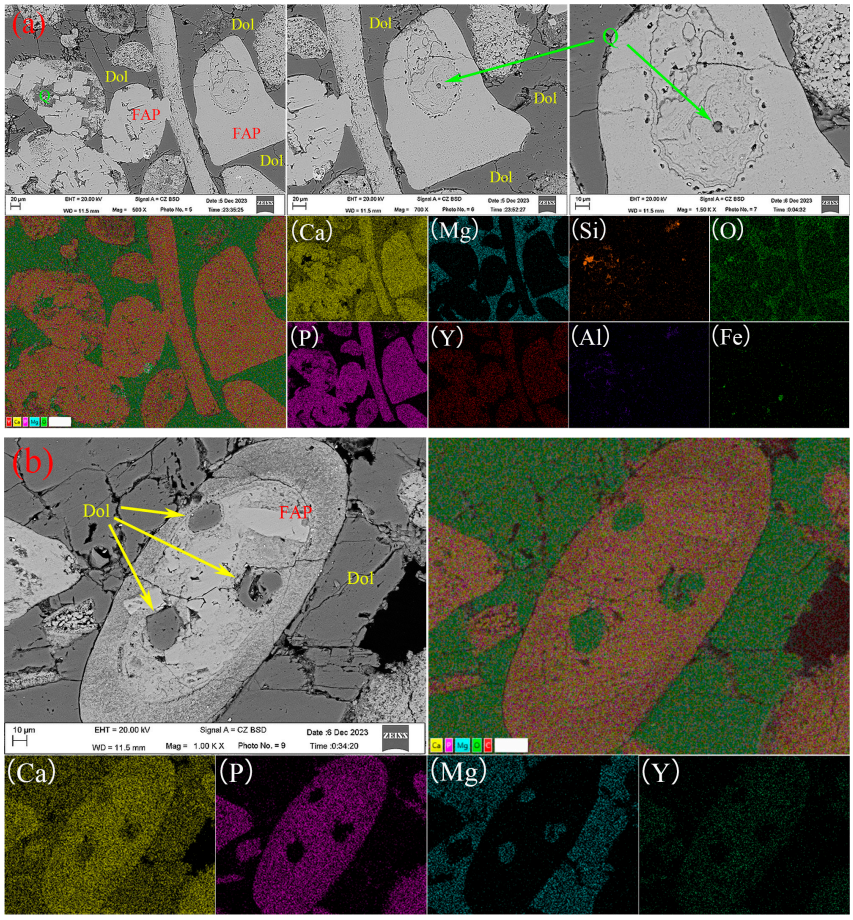


Figure 8. SEM-EDS image of rare earth-bearing collophanite. Q—quartz, Dol—dolomite, FAP—fluorapatite.

3.2. Flotation Study of Rare Earth-Bearing Collophane

3.2.1. Collector Comparison Test

The SEM-EDS analysis revealed that yttrium (Y), a rare earth element, is primarily hosted within collophane, with no independent rare earth minerals detected. Therefore, the flotation test conditions were evaluated based on phosphate concentrate grade (expressed as P_2O_5 content) and recovery rate.

Under the conditions of a −74 μm particle size accounting for 83%, pulp concentration of 25%, flotation machine impeller speed of 1992 r/min, collector dosage of 300 g/t, pH regulator (H_2SO_4) dosage of 6 kg/t (pH = 5), and depressant (H_3PO_4) dosage of 3 kg/t, a collector comparison test was conducted. This test aimed to evaluate the collecting performance of different collectors for rare earth-bearing collophane under identical flotation conditions. The test results are shown in Figure 9.

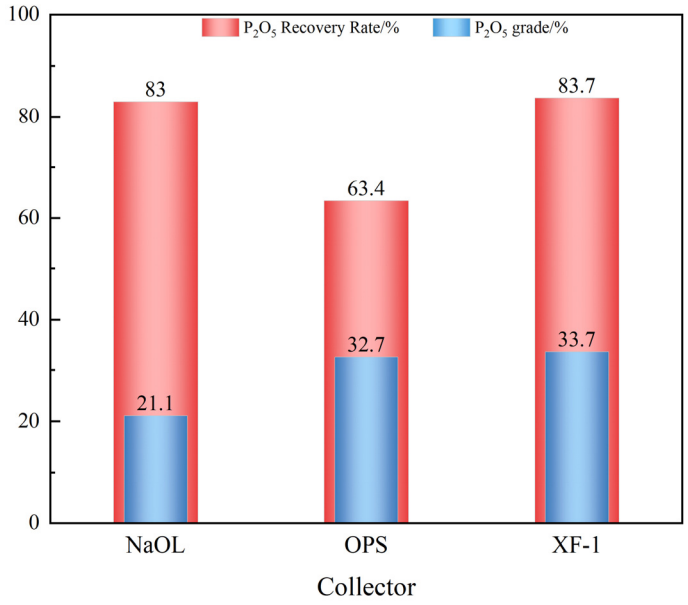


Figure 9. Comparative test of collectors for rare earth-bearing collophanite.

The experiment compared the concentrate grade and recovery rate of P_2O_5 in rare earth-bearing collophane ore using sodium oleate, oxidized paraffin soap, and XF-1 as collectors. As shown in Figure 9, when sodium oleate was used as the collector, the recovery rate was comparable to that of XF-1; however, the concentrate grade was 12.6 percentage points lower. The P_2O_5 enrichment ratios were 1.05 and 1.67, respectively, indicating that the enrichment ratio with XF-1 was 59% higher. When oxidized paraffin soap was used as the collector, the concentrate grade was 1 percentage point lower than that obtained with XF-1, and the P_2O_5 enrichment ratio was 1.63, representing a 2.5% reduction compared to XF-1. Although the difference in P_2O_5 enrichment was relatively small, the recovery rate was 20.3 percentage points lower. Therefore, XF-1 was ultimately selected as the collector for the reverse flotation desilication of rare earth-bearing collophane ore.

3.2.2. Grinding Fineness Test

Under the conditions of a 25% pulp concentration, flotation machine impeller speed of 1992 r/min, XF-1 collector dosage of 300 g/t, pH regulator (H_2SO_4) dosage of 6 kg/t (pH = 5), and depressant (H_3PO_4) dosage of 3 kg/t, a grinding fineness test was conducted (Figure 10). This test aimed to evaluate the effect of different grinding fineness levels on flotation performance and determine the optimal grinding fineness for flotation.

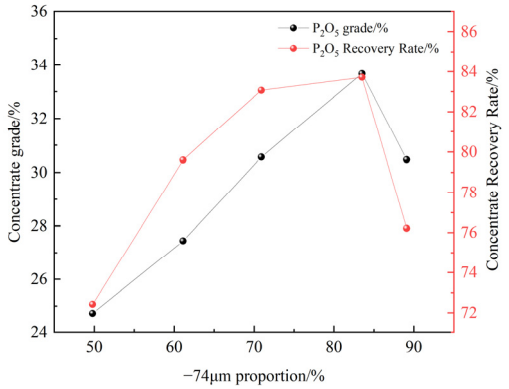


Figure 10. The effect of grinding fineness on flotation.

As shown in Figure 10, with the increase in grinding fineness, both the concentrate grade and recovery rate gradually improved. This indicates that finer grinding enhances the degree of liberation of collophane, leading to an increase in both concentrate grade and recovery. However, when the −74 μm fraction reached 89%, a decline in concentrate grade and recovery was observed. This suggests that excessive grinding caused severe mineral overgrinding and slime formation, which negatively affected flotation performance. Therefore, the optimal grinding fineness for flotation was determined to be 83% passing −74 μm.

3.2.3. Collector Dosage Test

Under the optimal grinding fineness condition (−74 μm, 83.5%), while keeping the dosages of the depressant and pH regulator unchanged, the collector dosage was varied to evaluate its effect on concentrate grade and recovery rate. The test results are shown in Figure 11.

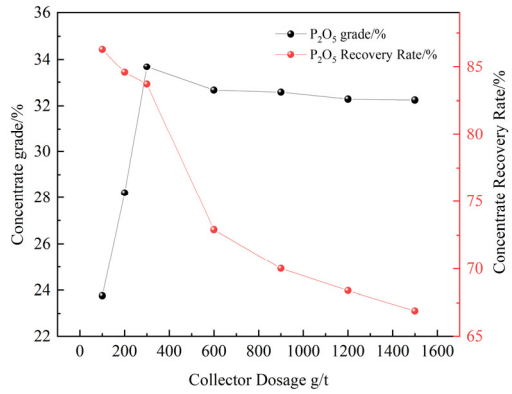


Figure 11. The effect of collector dosage on flotation.

As observed in Figure 11, with the increase in collector dosage, the concentrate grade initially increased and then gradually stabilized, while the recovery rate showed a continuous decline. This indicates that an excessive collector dosage resulted in the unintentional flotation of collophane along with dolomite, leading to a reduction in concentrate recovery. Based on these findings, the optimal collector dosage was determined to be 300 g/t.

3.2.4. pH Regulator Dosage Test

Under the optimal conditions of a −74 μm particle size accounting for 83% and collector dosage of 300 g/t, while keeping other parameters unchanged, the dosage of the pH regulator (H_2SO_4) was varied to evaluate its effect on concentrate grade and recovery rate. The test results are shown in Figure 12.

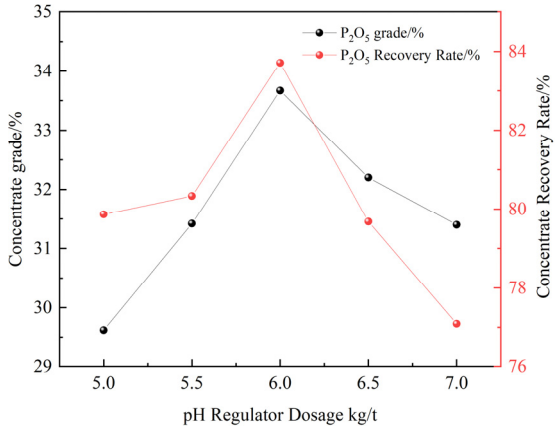


Figure 12. The effect of pH modifier dosage on flotation.

As shown in Figure 12, with the increase in the pH regulator dosage, both concentrate grade and recovery rate initially increased and then began to decline. This indicates that an excessive pH regulator dosage reduces the collecting performance of the collector, negatively impacting flotation efficiency. Based on the results, the optimal dosage of the pH regulator (H_2SO_4) was determined to be 6 kg/t.

3.2.5. Depressant Dosage Test

Under the optimal conditions of a −74 μm particle size accounting for 83.5%, collector dosage of 300 g/t, and pH regulator (H_2SO_4) dosage of 6 kg/t, the depressant (H_3PO_4) dosage was varied to evaluate its effect on concentrate grade and recovery rate. The test results are shown in Figure 13.

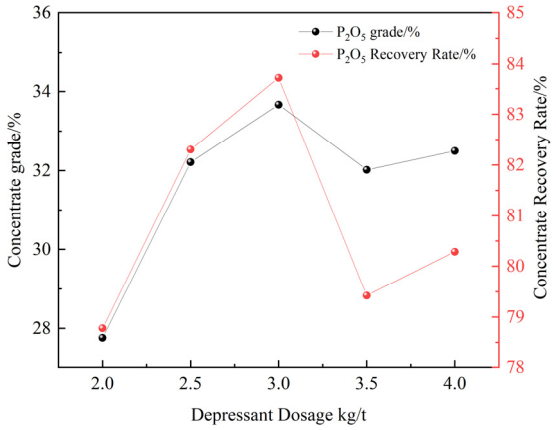


Figure 13. The effect of depressant dosage on flotation.

As observed in Figure 13, with the increase in depressant dosage, both concentrate grade and recovery rate initially increased and then began to decline. This indicates that, during the reverse flotation process, an excessive amount of depressant enhances the suppression of gangue minerals but simultaneously reduces the concentrate grade and recovery. Based on these findings, the optimal depressant (H_3PO_4) dosage was determined to be 3 kg/t.

3.2.6. Closed-Circuit Experiment

Using the optimal grinding fineness and flotation reagent scheme determined from the conditional tests, a "one rougher–one scavenger" closed-circuit flotation test was conducted. The mass balance flowchart is shown in Figure 14.

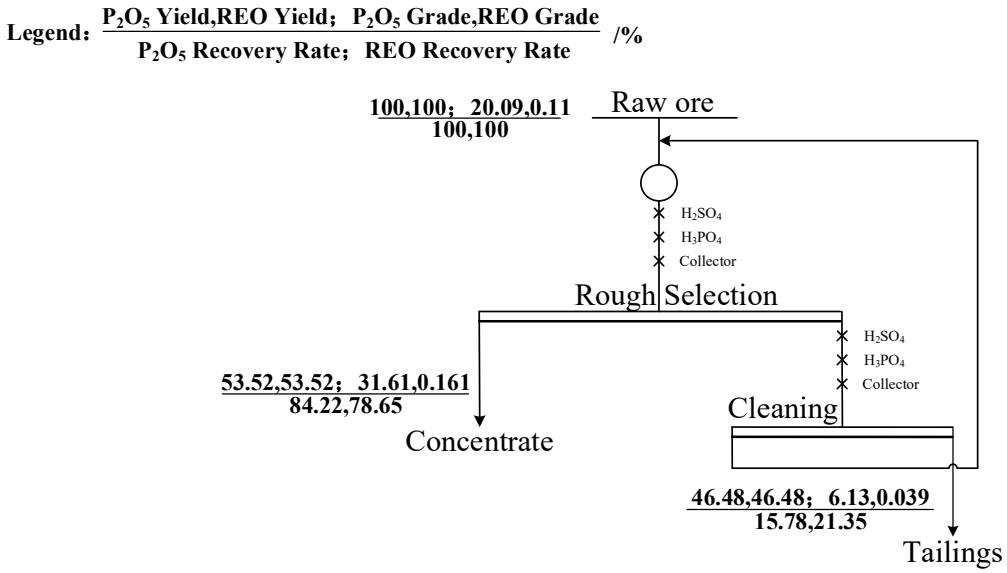


Figure 14. Flowchart of mass balance for one roughing and one scavenging stage.

Through a single roughing and a single scavenging stage, the final phosphate concentrate achieved a P_2O_5 content of 31.61% and an REO content of 0.161%, with P_2O_5 and REO recovery rates reaching 84.22% and 78.65%, respectively.

3.3. Mineral Composition and Chemical Analysis of Flotation Concentrate and Tailings

3.3.1. Phase and Multi-Element Analysis

To investigate the mineral composition of the flotation concentrate and tailings, XRD, XRF, and ICP-MS analyses were conducted. The results are presented in Figures 15–19.

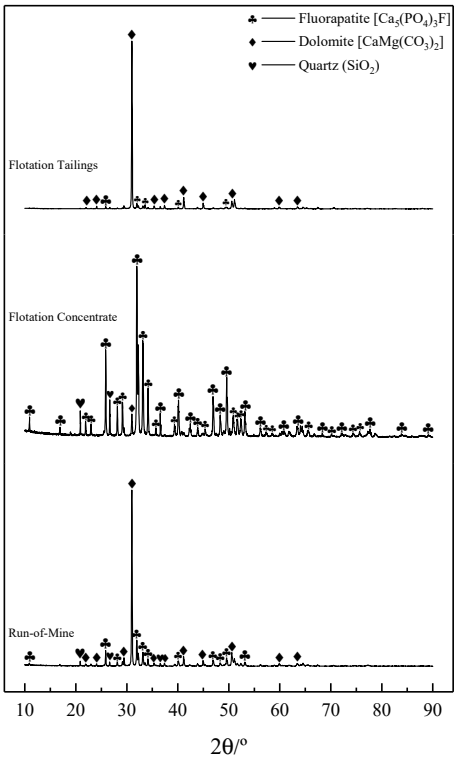


Figure 15. XRD patterns of flotation concentrate and tailings.

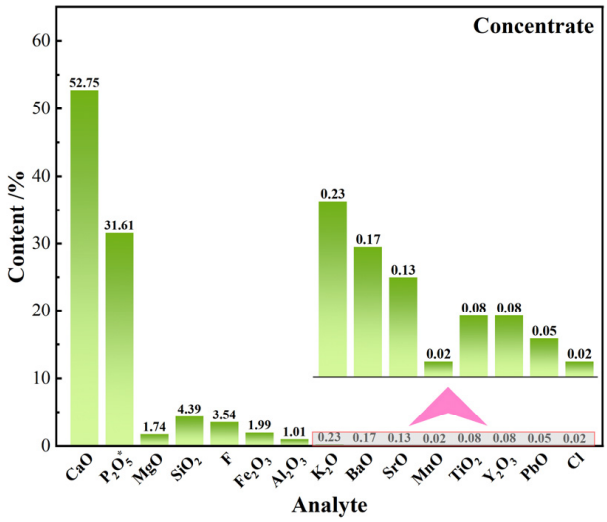


Figure 16. Multi-element analysis of flotation concentrate. * denotes quantitative analysis by ICP-OES.

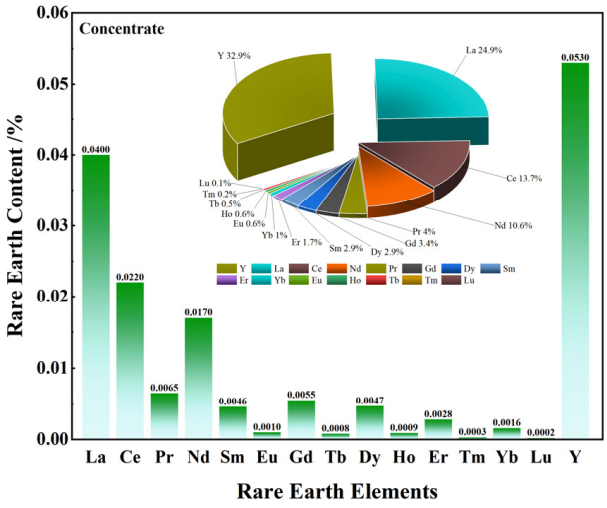


Figure 17. Rare earth content analysis of flotation concentrate.

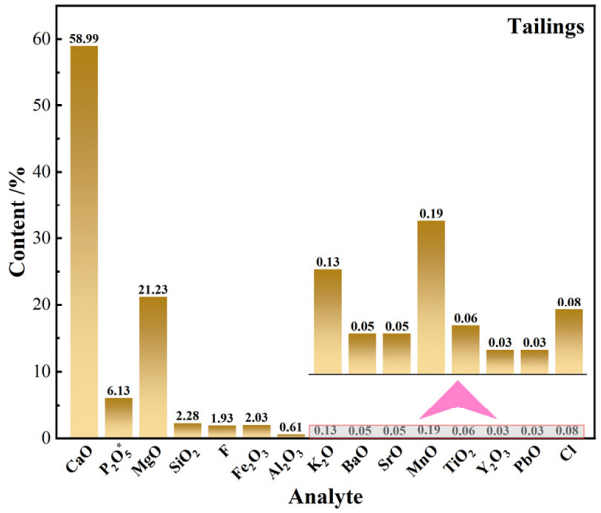


Figure 18. Multi-element analysis of flotation tailings. * denotes quantitative analysis by ICP-OES.

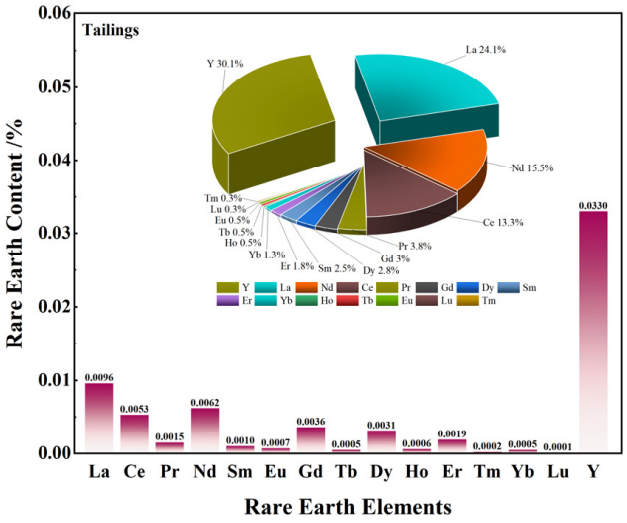


Figure 19. Rare earth content analysis of flotation tailings.

A comparative XRD analysis of the raw ore, flotation concentrate, and flotation tailings revealed that the primary mineral phases in the raw ore are collophane, dolomite, and a small amount of quartz, with dolomite being the dominant gangue mineral. After reverse flotation, the dolomite content in the concentrate decreased significantly, while the quartz content showed a slight increase. This is attributed to XF-1, a fatty acid-modified collector, which does not adsorb onto the quartz surface, resulting in a relative increase in quartz content in the flotation concentrate. The flotation tailings mainly consist of dolomite with a small amount of collophane.

Figures 16 and 17 present the XRF analysis and rare earth content analysis of the flotation concentrate from rare earth-bearing collophane. As shown in Figure 16, the P_2O_5 content in the flotation concentrate increased from 20.09% in the raw ore to 31.61%, an improvement of 11.52 percentage points, with an enrichment ratio of 1.46. Meanwhile, the MgO content decreased from 9.82% in the raw ore to 1.74%, a reduction of 8.08 percentage points. Combined with the phase analysis results, this confirms that Mg is primarily hosted in dolomite, indicating that the flotation process effectively removed dolomite. According to Figure 17, the rare earth elements (REEs) were enriched along with collophane in the flotation concentrate. The total rare earth oxide (REO) content increased from 0.11% in the raw ore to 0.161%, an increase of 0.051 percentage points, with an enrichment ratio of 1.57. The two most abundant rare earth elements, Y and La, increased by 0.018 and 0.017 percentage points, respectively. The distribution of rare earth elements remained nearly unchanged compared to the raw ore, with Y and La together accounting for more than 50% of the total REEs.

The multi-element analysis of the flotation tailings from rare earth-bearing collophane (Figure 18) shows that the P_2O_5 content decreased from 20.09% in the raw ore to 6.13%, a reduction of 13.96 percentage points. Meanwhile, the MgO content increased from 9.82% in the raw ore to 21.22%, an increase of 13.14 percentage points. Figure 19 presents the REE content analysis of the flotation tailings. The total rare earth oxide (REO) content decreased from 0.11% in the raw ore to 0.039%, a reduction of 0.071 percentage points. The content of heavy rare earth element Y and light rare earth element La decreased by 0.003 percentage points and 0.013 percentage points, respectively. The REE distribution remained almost unchanged, with Y and La together accounting for more than 50% of the total rare earth elements.

3.3.2. Analysis of Mineral Intergrowth Relationships in Flotation Concentrate and Tailings

The mineral intergrowth relationships and rare earth element distribution in the flotation concentrate and tailings were analyzed using SEM-EDS. The results are shown in Figures 20 and 21.

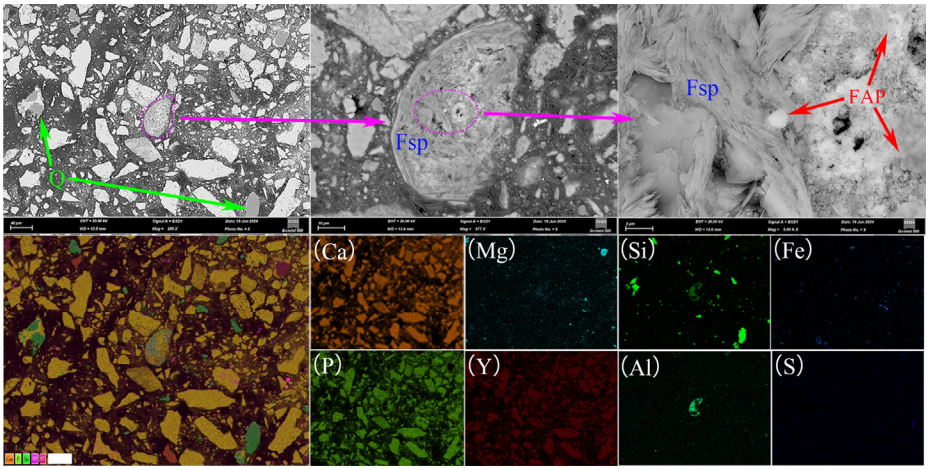


Figure 20. SEM-EDS image of rare earth-bearing collophane flotation concentrate. Q—quartz, Dol—dolomite, FAP—fluorapatite, Fsp—feldspar.

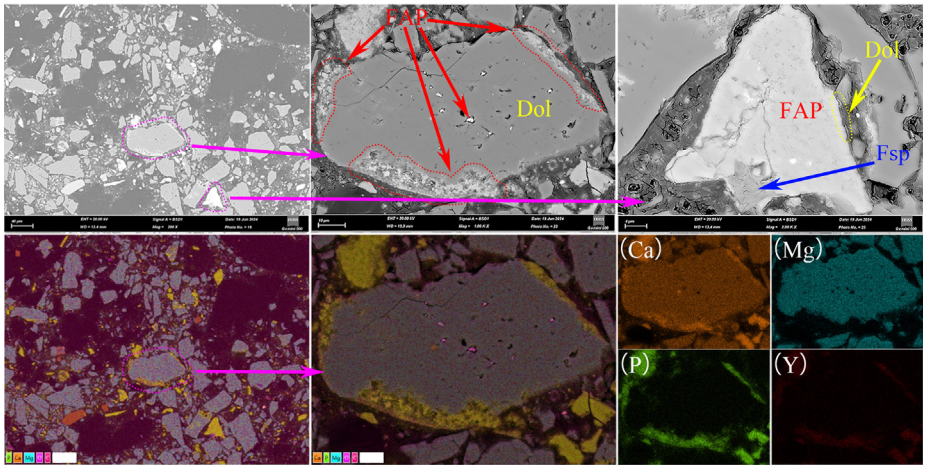


Figure 21. SEM-EDS image of rare earth-bearing collophane flotation tailings. Dol—dolomite, FAP—fluorapatite, Fsp—feldspar.

As observed in Figure 20, the flotation concentrate contains a small amount of fine-grained intergrowths and inclusions of collophane with dolomite and silicate minerals. Based on the elemental mapping of Si, Al, and Mg, collophane forms fine-grained intergrowths with quartz, with particle sizes smaller than 20 μm. Additionally, the feldspar replacement of collophane is evident. According to the elemental mapping of P and rare earth element Y, Y is significantly enriched along with the phosphate concentrate, and no independent rare earth minerals were detected.

As shown in Figure 21, the flotation tailings are primarily composed of dolomite, with a small amount of collophane. Based on the elemental mapping of P and Mg, collophane and dolomite exist as binary intergrowths, as well as ternary intergrowths of collophane, dolomite, and feldspar. During the flotation process, the collector adsorbs onto the dolomite surface, causing it to enter the flotation tailings along with the froth. Additionally, a small amount of heavy rare earth element Y overlaps with the P element, indicating that Y is hosted within collophane and follows unliberated collophane into the flotation tailings.

4. Conclusions

This study focused on the rare earth-bearing collophane from Zhijin, Guizhou, conducting a process mineralogical investigation using XRD, XRF, and SEM-EDS. Subsequently, reverse flotation tests were performed to compare different magnesium removal reagents and optimize the flotation conditions. Finally, the mineralogical characteristics and elemental distribution of the flotation concentrate and tailings were analyzed to determine the migration of phosphorus and rare earth elements. The key conclusions are as follows:

1. The primary mineral phases of the rare earth-bearing collophane from Zhijin are fluorapatite and dolomite, with a P_2O_5 content of 20.09% and a total rare earth oxide (REO) content of 0.11%. Among the rare earth elements, yttrium (Y) has the highest proportion, accounting for 32.2%. SEM-EDS and BPMA analyses revealed that fluorapatite and dolomite primarily exist as intergrowths and inclusions, with rare earth elements hosted in fluorapatite, and no independent rare earth minerals were detected;
2. A comparative test of three collectors (NaOL, OPS, and XF-1) showed that XF-1 had the best magnesium removal performance. Based on this, XF-1 was selected as the collector for subsequent flotation condition tests. The optimal flotation conditions were determined as a grinding fineness of -74 μm (83%), XF-1 collector dosage of 300 g/t, pH regulator (H_2SO_4) dosage of 6 kg/t, and depressant (H_3PO_4) dosage of 3 kg/t. Under these optimal conditions, a closed-circuit flotation test (one rougher–one scavenger) yielded a phosphate concentrate with 31.61% P_2O_5 and a recovery rate of 84.22%, as well as an REO content of 0.161% and a recovery rate of 78.65%;
3. Mineralogical composition and multi-element analysis of the flotation concentrate and tailings showed that the P_2O_5 grade in the flotation concentrate increased by 11.52 percentage points, while the REO content increased by 0.051 percentage points, indicating that rare earth elements were successfully enriched in the phosphate concentrate. In contrast, the P_2O_5 content in the flotation tailings decreased from 20.09% in the raw ore to 6.13%, while the MgO content increased significantly, confirming the effective removal of dolomite as the primary gangue mineral;
4. The study further examined the recovery and enrichment of rare earth elements. According to the ICP-MS analysis, the overall rare earth element recovery in the flotation concentrate reached 78.65%, with a significant enrichment of heavy rare earth element Y and light rare earth element La, increasing by 0.018 and 0.017 percentage points, respectively. Meanwhile, the REO content in the flotation tailings dropped to 0.039%, a decrease of 0.071 percentage points compared to the raw ore, while the distribution ratio of rare earth elements remained largely unchanged.

This research provides an efficient flotation separation process for the recovery of rare earth elements from collophane, offering technical support for the high-value utilization of rare earth resources.

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