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The Distribution Regularity and Flotation Study of Niobium-Bearing Minerals in Baiyun Obo

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Abstract: The characteristics of Baiyun Obo niobium-bearing minerals are complex physicochemical properties that make the beneficiation of niobium minerals extremely difficult. In this paper, X-ray diffraction, X-ray fluorescence and mineral liberation analyzer (MLA) systems were used to study the niobium occurrence state and distribution of niobium-bearing minerals in the samples from Baiyun Obo. The results show that the chemical and mineral compositions of the sample are complex, with a Nb_2O_5 grading of 0.24%. There are many kinds of niobium minerals, including ilmenorutile, nioboaeschynite-Nd, baotite, latrappite, euxenite-Y, fergusonite and columbite-Mn, and the highest mass fraction of 0.55% is achieved with Nb in nioboaeschynite-Nd, followed by the mass fraction of ilmenorutile (0.33%). All of the niobium-containing minerals demonstrate a low degree of dissociation. Flotation experiments explored the optimal flotation conditions for HOBA (1-hydroxyoctyl-1,1-bisphosphonic acid) as a flotation collector for Baiyun Obo niobium minerals, which is able to increase the grade of Nb_2O_5 in the concentrate to 1.31%. The optimal use conditions of the reagent are pH 3.5–4.5, and the amount of the collector is 1000 g/t. By further optimizing the beneficiation process and reagent system, ilmenorutile and nioboaeschynite-Nd were significantly enriched in the concentrate, which suggested that HOBA can efficiently increase the grade of Nb_2O_5 in the concentrate.

Keywords: MLA; distribution regularity; flotation; niobium; Baiyun Obo

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1. Introduction

Niobium (Nb) is widely used for a variety of applications, such as steel, medical, superconducting magnets and aerospace, because of its advantages of high melting point, high temperature resistance and superconductivity [1–6]. Brazil is home to 85% of the world's niobium reserves, supplying 93% of niobium in the world market [7]. The niobium resources distributed in the Baiyun Obo mining area constitute the biggest reserves found in China. However, due to the complex nature of its ore body, niobium is not a commonly used mineral; this means that about 90% of China's niobium resources rely on imports [8,9]. Due to the growing demand for high-purity niobium metals and minerals, the reasonable utilization of Baiyun Obo niobium ore resources has received increasing research attention.

The ores from the Baiyun Obo mining area include large-scale iron, rare-earth minerals and niobium polymetallic-associated ore. Oxide ores are the main type of niobium-containing minerals in this deposit, including nioboaeschynite-(Nd){(Nd,Ce)$(Nb,Ti)_2(O,OH)_6$}, ilmenorutile {(Ti,Nb,Fe)O_2}, pyrochlore ($CaNb_2O_6F$), columbite {(Fe, Mn)Nb_2O_6}, etc. [10]. Moreover, the composition of niobium-containing minerals may vary among different mining areas in Baiyun Obo, and the properties of the minerals change with the location and depth of mining. The characteristics of the niobium ores include a low niobium-containing grade, a particle size of fine, embedded niobium mineral, high degree of dispersion and mixed niobium mineral types, which lead to poor selectivity of niobium resources, difficulty in extraction and difficulty in smelting. The paragenesis of iron-niobium-rare earth elements (REE) in the Baiyun Obo deposit is complex. In addition to association and continuation, there are widespread difficulties regarding homogeneity, separation and enrichment. Because of the coexistence of various elements and a complex embedded structure, the sorting, enrichment and smelting of Baiyun Obo niobium ore are extremely difficult [11,12].

At present, the distribution regularity and physical characteristics of Baiyun Obo niobium ore have not been comprehensively studied, and the problem of niobium selection has not yet been effectively solved [13]. Therefore, a systematic method of determining the mineral composition, occurrence state and distribution of minerals is essential for the efficient recovery of Baiyun Obo niobium ore.

Flotation is a very efficient and cost-effective enrichment method used to address the complexity of the Baiyun Obo niobium ore, and the flotation reagent is one of the key factors in the flotation process. Flotation is based on the difference between the physical and chemical properties of different minerals on the surface, through their different effects on the liquid and gas of the slurry to achieve separation [14]. The reagents added to the pulp can be selected to adsorb on the surface of specific minerals, which increases the hydrophobic difference between the surfaces of different minerals, providing them with different abilities to interact with air bubbles and become sorted [15].

The reasonable use of a flotation reagent can efficiently and flexibly control the flotation process and realize the separation and enrichment of target minerals [16–20]. Notably, collectors play a crucial role in the flotation process [21]. According to reports, the collectors commonly used for the flotation of niobium ore are types of hydroxamic acid and arsine acid, such as salicylic hydroxamic acid and benzyl arsine acid [22]. However, the low selectivity and stability for hydroxamic and arsine acid collectors remains a problem [23]. Ren et al. [24,25] reported the effects of benzyl arsine acid, $C_{7–9}$ alkyl hydroxamic acid and bisphosphonic acid on the harvesting of ilmenorutile, fersmite and niobite, and the results show that bisphosphonic acid is a good collector of three valuable niobium-containing minerals. Furthermore, its comprehensive recovery ability was the strongest. Zheng et al. [26] also found that bisphosphonic acid is a very good collector, with a good harvesting and selection performance in fersmite flotation. However, bisphosphonic acid as the flotation reagent was not systematically applied to the flotation application of complex Baiyun Obo niobium-containing ore. Because there are widespread problems of associated and contiguous niobium-bearing minerals in Baiyun Obo, many effective flotation reagents for some kinds of niobium minerals may be not appropriate for Baiyun Obo minerals. Therefore, the feasibility of bisphosphonic acid as a flotation collector used for Baiyun Obo niobium ore should be studied.

In this study, the mineral composition, niobium distribution regularity and distribution status of Baiyun Obo niobium ore samples were carefully analyzed using a mineral liberation analyzer (MLA) and X-ray fluorescence. Then, a flotation reagent synthesized by our group, 1-hydroxyoctyl-1,1-bisphosphonic acid (HOBA), was efficiently and systematically applied to the flotation of Baiyun Obo niobium minerals. Additionally, the optimal working conditions of HOBA as a collector of Baiyun Obo niobium-bearing minerals were also explored. The further optimization of the flotation process and reagent system improved the Nb_2O_5 grade in the concentrate. Finally, MLA was used to analyze the sample composition of Baiyun Obo niobium-bearing minerals and concentrate, and the main niobium-bearing minerals, which contained ilmenorutile and nioboaeschynite-Nd, were enriched in the concentrate. The results imply that some types of niobium minerals from this kind of Baiyun Obo niobium-bearing ore samples could be effectively separated with HOBA as the flotation reagent. More importantly, it may provide a guide for choosing proper flotation reagents to solve difficult flotation problems of complex niobium ores in Baiyun Obo.

2. Materials and Methods

2.1. Materials and Reagents

In this study, all the mineral samples of Baiyun Obo niobium ore, terpineol and $(NH_4)_2SiF_6$ were donated by Baogang Group Mining Research Institute Co., Ltd. Carboxymethyl cellulose (CMC) was purchased from Macklin and used to inhibit silicon-containing minerals in the flotation process. NaOH and H_2SO_4 for pH adjustment were purchased from General-Reagent. $Pb(NO_3)_2$ was purchased from Sigma-Aldrich. The salicylic hydroxamic acid and alkyl isohydroxamic acid used in the flotation process were purchased from Aladdin and Macklin, respectively.

HOBA was synthesized by our research group. The structure of HOBA was determined by nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR and ^{31}P NMR chemical shifts were recorded in deuterated dimethyl sulfoxide-d_6 on a 400 MHz Bruker NMR spectrometer. The Fourier-transform infrared (FTIR) spectrum of HOBA was recorded using iS5-Thermo Fisher.

2.2. Wet Sieving Analysis and X-ray Diffraction

Baiyun Obo niobium ore was wet-screened using 100-, 140-, 200-, 250-, 300-, 400- and 500- mesh sieves, and then the content of each grain level was calculated. The phase qualitative analysis of the Baiyun Obo niobium ore was obtained using X-ray diffraction (XRD, Bruker AXS, D8 Advance; Bruker, Billerica, MA, USA).

2.3. X-ray Fluorescence Spectrum

The elemental content in minerals was characterized by an X-ray fluorescence spectrum (XRF, ZSX Primus III+; Rigaku, Tokyo, Japan). The content of Nb_2O_5 was quantitatively measured by standard curves, and the other components were used as values that were relatively close to the true contents, which were not normalized.

2.4. Mineral Liberation Analysis

After spraying platinum on the surface of the inlaid metallographic sample, the micro-energy spectrum analysis of the mosaic sample was carried out using a mineral liberation analyzer (MLA, FEI MLA 250; FEI Company; Hillsboro, OR, USA). Energy-dispersive spectrometer (EDS) analysis was conducted to summarize the mineral composition and content of the sample.

2.5. Flotation Tests

An XFD-III single-slot flotation machine was used as a flotation separator. Due to the low grade of Nb_2O_5 in feed ore, and in order to fully enrich niobium ore more in low-grade minerals, the method of two-stage flotation, which consists of Nb-rough selection and Nb-beneficiation, was used to explore the experimental conditions of HOBA. In other words, a roughing selection was performed on the minerals, followed by a beneficial flotation operation in the concentrate. Due to the large amount of iron in the sample, the flotation of iron was carried out in advance. Then, 500 g of mineral sample and a moderate amount of water were added to the appropriate scale in the 1L flotation tank, and the initial slurry concentration was maintained at about 33%. The pH of the slurry was adjusted to 2, 4, 6, 8, 10 and 12 by H_2SO_4 and Na_2CO_3. In this experiment, $(NH_4)_2SiF_6$ was used as an inhibitor of silicate minerals and $Pb(NO_3)_2$ was used as an activator [27,28]. In the process of iron flotation, $(NH_4)_2SiF_6$ was first added to the pulp as an inhibitor with a conditioning time of 2 min, followed by sodium oleate as an iron collector in the pulp, with a conditioning time of 2 min. In the Nb-rough selection, the pH was first adjusted, and then the inhibitor $(NH_4)_2SiF_6$ and activator $Pb(NO_3)_2$ were added, both with adjustment times of 2 min in the pulp. Then, the collector HOBA was added, and the optimal pH, dosage, adjustment time and pulp temperature were investigated. Finally, terpineol was added as a frother and stirred for 1 min; the flotation scraping time was 2 min. Then the foam products and tailings were collected, filtered, dried and measured for the Nb_2O_5 grade. The process of Nb-beneficiation did not require the addition of terpineol. The conditions of using HOBA are consistent with the Nb-rough selection. The detailed dosages of reagents and experimental procedures are shown in Figure 1. Flotation optimization experiments are based on the consideration of climatic conditions in the Baiyun Obo mine and conditional experiments with slight changes to the flotation process and inhibitors. The purpose of adding CMC in the flotation optimization process is to suppress silicon-bearing minerals, such as quartz, glimmer and other silicates. The detailed dosages of reagents and flotation processes are shown in Figure 2.

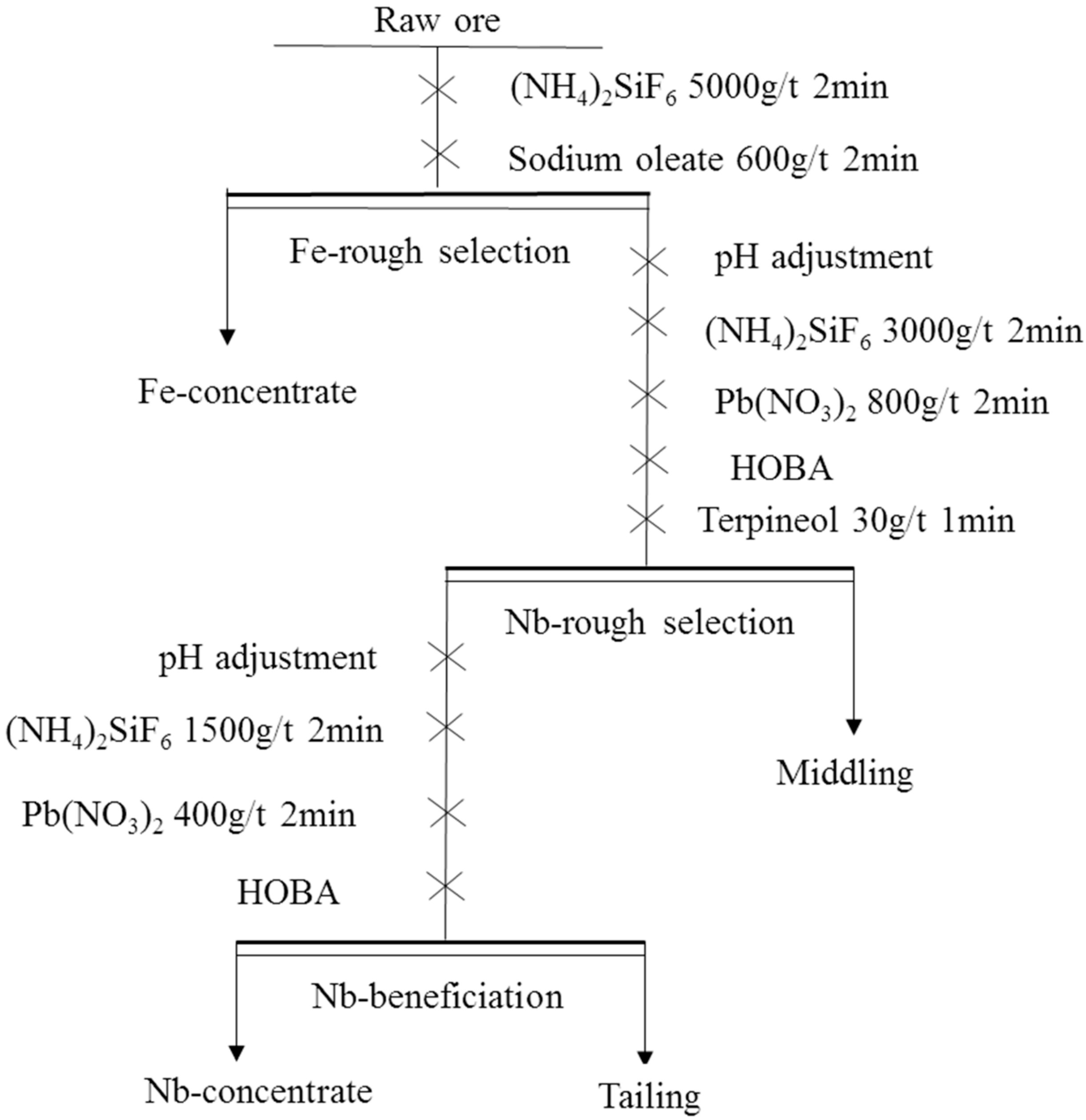

Figure 1. The flowsheet of the flotation of niobium-containing minerals.

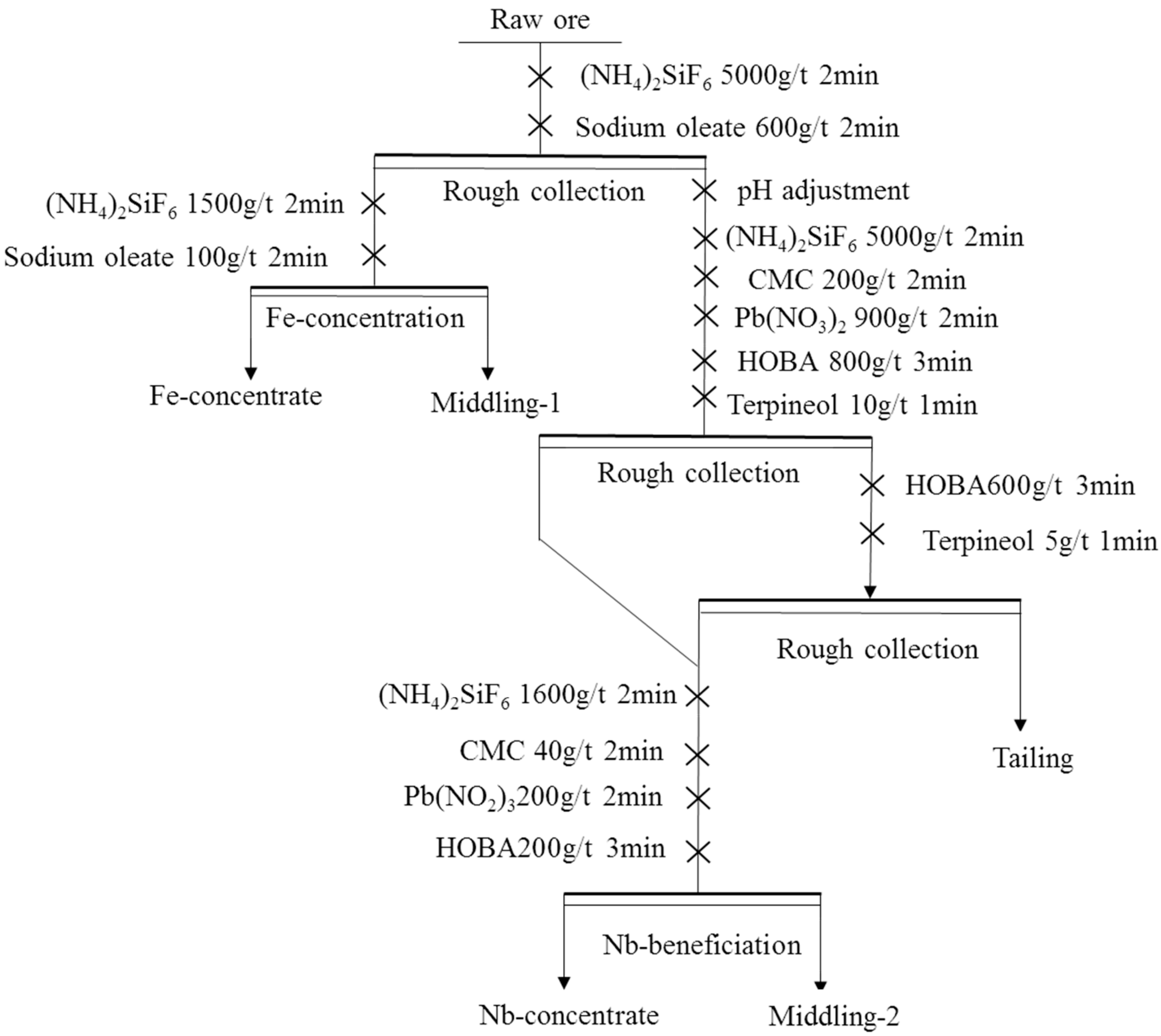

Figure 2. The flowsheet of the flotation optimization experiments.

3. Results and Discussion

3.1. Wet Sieving Analysis and XRD Preliminary Characterization of Baiyun Obo Niobium Ore

The primary wet sieving analysis is shown in Table 1. It reveals that a particle size less than 200 mesh reaches a value of 90.28%. XRD analysis shows that the composition of the sample is consistent with multiple kinds of minerals that contain quartz, hematite, fluorite and other minerals (Figure 3).

Table 1. Niobium ore production statistics of each grain grade.

Number of Meshes	+100	100–140	140–200	200–250	250–300	300–400	400–500	–500
Content wt.%	0.58	0.69	8.45	38.29	19.09	3.26	7.83	21.81

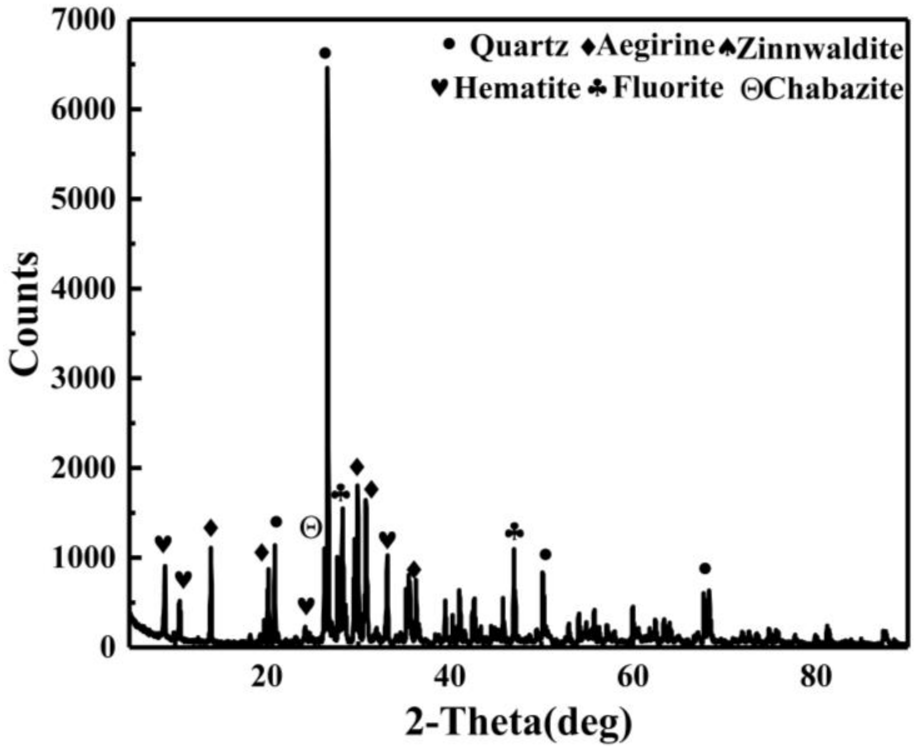

Figure 3. The XRD figure of niobium-bearing minerals in Baiyun Obo.

3.2. The Chemical Composition of Niobium-Bearing Minerals in Baiyun Obo

The chemical analysis results for some important components in niobium ore are shown in Table 2. These results indicate that the content of Fe_2O_3 is relatively high, at 24.02%, and the content of SiO_2 is 24.40%. The content of the target compound Nb_2O_5 is 0.24%, and it has slightly higher niobium content than diluted tailings (Nb_2O_5 is 0.14%) [10].

Table 2. XRF analysis of some important components of the niobium-bearing minerals in Baiyun Obo.

Components	Nb_2O_5	Fe_2O_3	CaO	MgO	SiO_2	K_2O	Na_2O	SO_3
Content (%)	0.24	24.02	7.26	2.79	24.40	0.61	2.56	0.30
Components	V_2O_5	BaO	ZnO	MnO	Al_2O_3	TiO_2	REO	P_2O_5
Content (%)	0.02	0.37	0.02	0.68	1.43	0.67	1.01	0.62

Therefore, the strategy to increase the content of Nb_2O_5 in the concentrate is to first eliminate the interference of Fe-bearing and Si-containing minerals.

3.3. MLA of Niobium-Bearing Minerals in Baiyun Obo

3.3.1. Mineral Composition and Content of the Sample

MLA is an important method commonly used to analyze mineral composition and distribution [29,30].

The MLA mineral automatic measurement method was used to explore the mineral species and content in sampled niobium-bearing minerals in Baiyun Obo. Table 3 shows that the composition of the sample includes more than 20 kinds of minerals, which are roughly divided into 18 types for ease of analysis and discussion.

Table 3. Mineral composition of the selected niobium ore (area fraction) %.

Nioboaeschynite-(Nd)	Ilmenorutile	Baotite	Latrappite	Euxenite-Y	Fergusonite
0.55	0.33	0.02	0.07	0.18	0.04
Rare-earth minerals	Fluorite	Hematite	Quartz	Other Silicates	Barite
2.82	7.84	14.82	14.9	16.22	0.32
Columbite-(Mn)	Other metal oxides	Sulfide	Carbonate	Riebeckite	Unknown
0.03	0.50	0.05	9.78	31.31	0.22

The gangue minerals in the sample are mainly riebeckite, quartz, barite and carbonate. The iron mineral is mainly hematite with a content of 14.82%. Niobium minerals mainly include ilmenorutile, nioboaeschynite-Nd, baotite, latrappite, euxenite-Y, fergusonite and columbite-Mn. The content values of the minerals are 0.33%, 0.55%, 0.02%, 0.07%, 0.18%, 0.04% and 0.03%, respectively, with a total of 1.22%. The main targets of the sample in beneficiation are ilmenorutile and nioboaeschynite-Nd.

Therefore, it is essential to discuss the occurrence state and physical characteristics of the minerals in detail for the separation and enrichment of Baiyun Obo niobium ore.

3.3.2. MLA Color Plots of the Sample and X-ray Spectra of Niobium-Bearing Minerals by EDS

Figure 5 shows the associated characteristics that demonstrate the relationship between niobium-bearing minerals and other minerals. Most of the fluorite, hematite, riebeckite and quartz in this sample are not associated and embedded with other minerals. Figure 5a,b reveal that nioboaeschynite-(Nd) is associated with other silicate minerals, other metal oxides and riebeckite, as well as being encased in carbonates. The ilmenorutile is associated with other silicates, carbonate, fluorite and other metal oxides (Figure 5c,d). The associated and contiguous conditions of ilmenorutile are the most complex among niobium-bearing minerals.

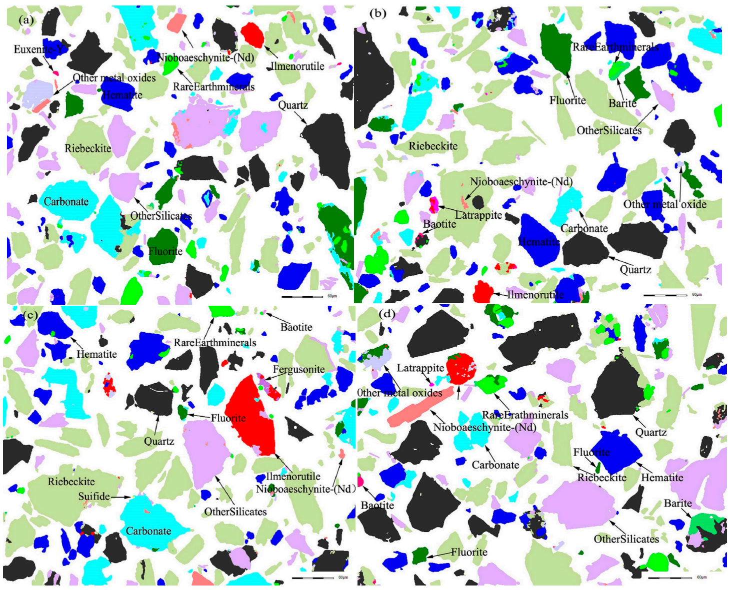

Figure 4. The types of minerals in the samples and the occurrence characteristics of niobium minerals. (**a**): Nioboaeschynite-(Nd) is associated with other silicate minerals and other metal oxides. (**b**): Ilmenorutile and nioboaeschynite-(Nd) are associated with riebeckite, and baotite is associated with quartz and rare-earth minerals. (**c**): Ilmenorutile is associated with other silicates and carbonate, and nioboaeschynite-(Nd) is encased in carbonates. (**d**): Ilmenorutile is associated with fluorite and other metal oxides.

In the MLA system, the EDS was used to identify the niobium-bearing minerals and determine the niobium content in the sample, and the results of X-ray spectra of niobium minerals by EDS are shown in Figure 5. The content of niobium in niobium-bearing minerals is shown in Table 4. The mass fractions of niobium are: columbite-(Mn) (Nb 55.42%), latrappite (Nb 45.54%), fergusonite (Nb 39.65%), euxenite-Y (Nb 29.51%), nioboaeschynite-(Nd) (Nb 23.70%), biotite (Nb 13.92%) and ilmenorutile (Nb 7.81%). Although the Nb content in columbite-(Mn), latrappite, fergusonite and euxenite-Y is higher (>29%), the four minerals are content low in the Baiyun Obo niobium ore (Table 3). The contents of nioboaeschynite-(Nd) and ilmenorutile in this sample are 0.55% and 0.33%, respectively. However, niobium-containing minerals are associated and encased, which is one of the major causes of difficult flotation separation.

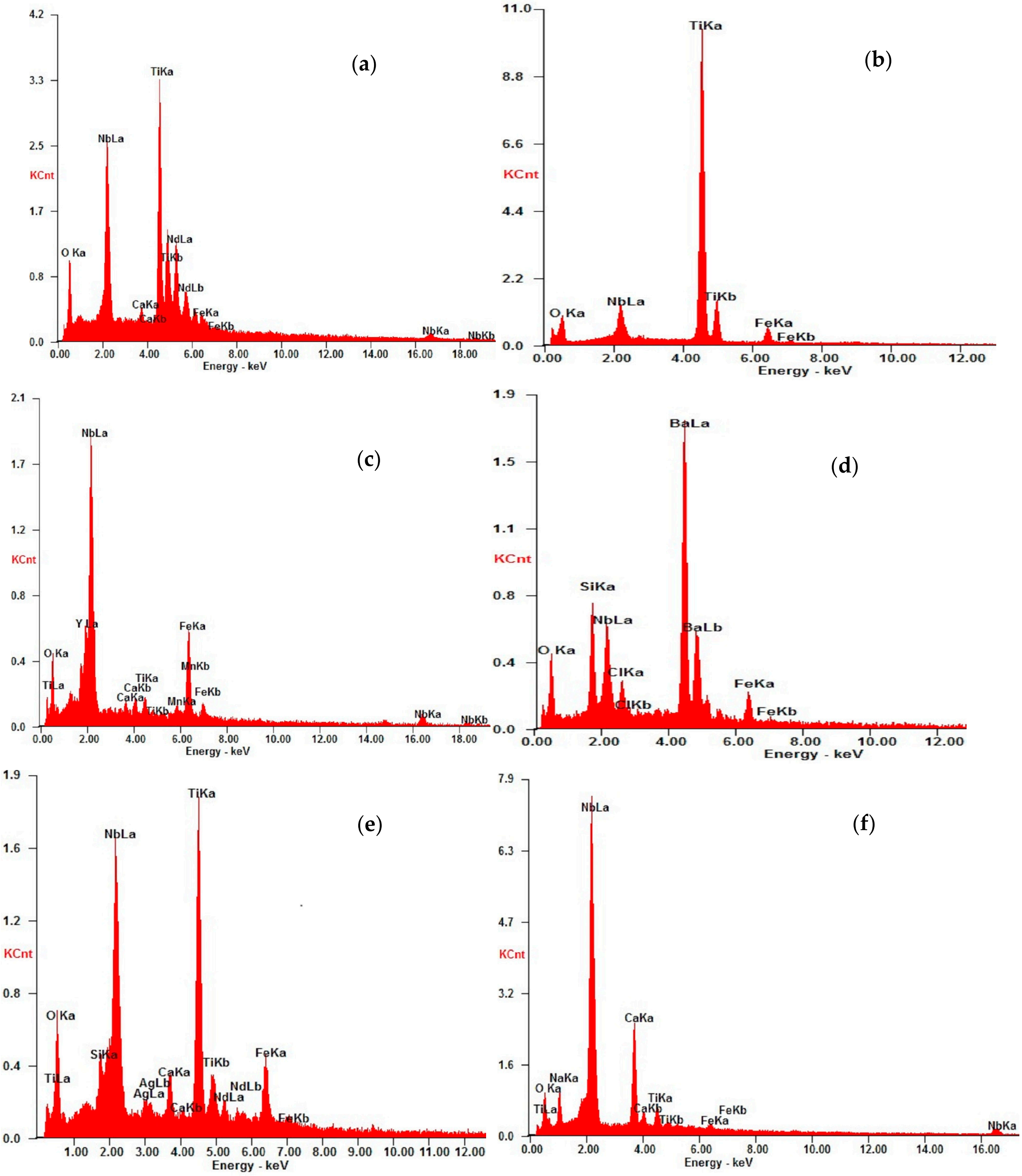

Figure 5. *Cont.*

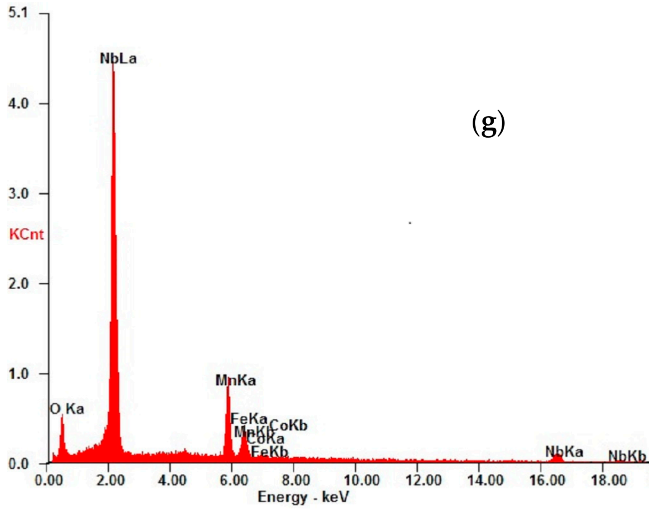

Figure 5. X-ray spectra of niobium minerals by EDS. (**a**): Nioboaeschynite-(Nd); (**b**): ilmenorutile; (**c**): fergusonite; (**d**): baotite; (**e**): euxenite-Y; (**f**): latrappite; (**g**): columbite-(Mn).

Table 4. Mass fraction of niobium in mineral phase (%).

Nioboaeschynite-(Nd)	Latrappite	Ilmenorutile	Fergusonite	Columbite-(Mn)	Baotite	Euxenite-Y
23.70	45.54	7.81	39.65	55.42	13.92	29.51

3.3.3. Granular Composition and Dissociation Characteristics of Niobium-Bearing Minerals

The particle size distributions of nioboaeschynite-Nd, ilmenorutile, columbite-Mn, baotite, fergusonite, latrappite and euxenite-Y are shown in Figure 6 and Table 5. Figure 6 shows that the niobium-bearing mineral particles are fine overall, and all niobium-bearing minerals have a cumulative distribution of 100% at 90 µm, indicating that their particle sizes are less than 90 µm. Table 5 shows that the particle sizes of columbite-Mn, baotite and fergusonite are all less than 38 µm. There are coarse particles in nioboaeschynite-Nd and ilmenorutile, accounting for 77.23% and 81.45% of particles less than 38 µm, respectively. The particle sizes of latrappite and euxenite-Y are less than 38 µm, accounting for 73.7% and 86.04%, respectively. In summary, the particle size of niobium minerals in the Baiyun Obo selection niobium ore is relatively fine.

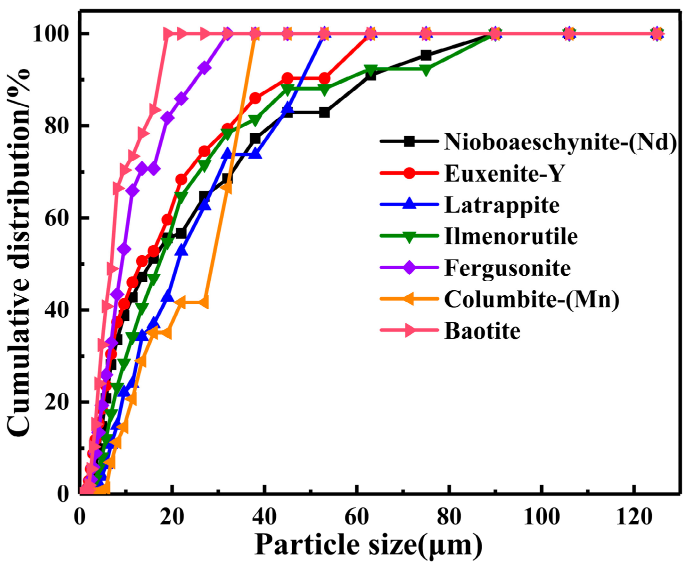

Figure 6. Cumulative particle size distributions of niobium-bearing minerals.

Table 5. Particle size distributions of niobium-bearing minerals (%).

Granularity Range/μm	Nioboaeschynite-Nd	Ilmenorutile	Columbite-Mn	Baotite	Fergusonite	Latrappite	Euxenite-Y
>75	4.73	7.68	-	-	-	-	-
>45~75	12.35	4.21	-	-	-	16.27	9.71
>38~45	5.69	6.66	-	-	-	10.03	4.25
<38	77.23	81.45	100	100	100	73.7	86.04

The monomer dissociation degree of nioboaeschynite-Nd, ilmenorutile, columbite-Mn, baotite, fergusonite, latrappite and euxenite-Y was analyzed using a free bare surface area method, and the treatment results are shown in Table 6. These results reveal a low degree of dissociation for niobium-bearing minerals. The highest degree of monomer dissociation is seen from nioboaeschynite-Nd, and its value is 39.14%. This is followed by ilmenorutile, with a monomer dissociation degree of 34.82%, and the lowest degree of monomer dissociation is for baotite, with a value of 8.45%. The low dissociation degree of monomers of niobium-bearing minerals means that the flotation separation of niobium-bearing minerals is difficult.

Table 6. Liberation degree of important niobium minerals in Nb-bearing minerals (%).

Mineral Name	Nioboaeschynite-(Nd)	Ilmenorutile	Baotite	Latrappite	Euxenite-Y
Nioboaeschynite-(Nd)	39.14	0.21	0.00	0.04	0.94
Ilmenorutile	0.63	34.82	0.00	0.05	0.21
Baotite	0.16	7.08	8.45	0.00	0.31
Latrappite	7.65	4.55	0.00	12.14	1.10
Euxenite-Y	9.81	2.33	0.20	0.11	31.60
Fergusonite	0.92	6.19	0.00	0.08	1.66
Columbite-(Mn)	0.14	5.32	0.01	0.57	0.98
Mineral name	**Hematite**	**Barite**	**Carbonate**	**Riebeckite**	**Quartz**
Nioboaeschynite-(Nd)	6.22	0.20	16.94	11.82	4.03
Ilmenorutile	18.38	0.73	2.79	9.95	3.66
Baotite	2.75	2.83	1.97	17.77	18.52
Latrappite	27.55	0.26	5.51	17.85	2.58
Euxenite-Y	5.08	2.41	3.17	18.60	7.33
Fergusonite	22.12	0.17	3.11	19.11	6.46
Columbite-(Mn)	18.12	0.01	0.32	8.02	18.02
Mineral name	**Fergusonite**	**Columbite-(Mn)**	**Fluorite**	**Other minerals**	**Rare-earth minerals**
Nioboaeschynite-(Nd)	0.13	0.01	6.27	9.99	4.06
Ilmenorutile	0.62	0.53	2.90	20.62	4.06
Baotite	0.03	0.05	0.88	31.60	7.60
Latrappite	1.47	2.19	8.10	6.26	2.79
Euxenite-Y	1.04	0.19	1.19	9.29	7.65
Fergusonite	28.19	0.85	0.46	8.39	2.29
Columbite-(Mn)	2.46	20.46	0.90	10.33	14.34

3.4. Flotation Tests

HOBA is a type of α-hydroxy-substituted alkyl bisphosphonic acid. Figure 7a,b show the detailed information of HOBA [31]. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.41 (s, 9H), 2.31 (d, J = 14.8 Hz, 1H), 1.77 (d, J = 14.1 Hz, 2H), 1.52 (s, 2H), 1.22 (d, J = 16.4 Hz, 7H), 0.86 (t, J = 6.4 Hz, 3H)) and ^{31}P NMR (162 MHz, DMSO-d_6): δ 20.27 (s).

The FTIR spectrum of HOBA is presented in Figure 8, which illustrates that the stretching vibration peaks of –OH appear at around 3536 cm^{-1}. The C–H vibration bands of –CH_2– and –CH_3 groups appear at around 2956 cm^{-1}, 2925 cm^{-1} and 2930 cm^{-1}. The peaks at around 1174 cm^{-1} and 921 cm^{-1} are separately assigned to stretching vibration bands of P=O and P–OH [32].

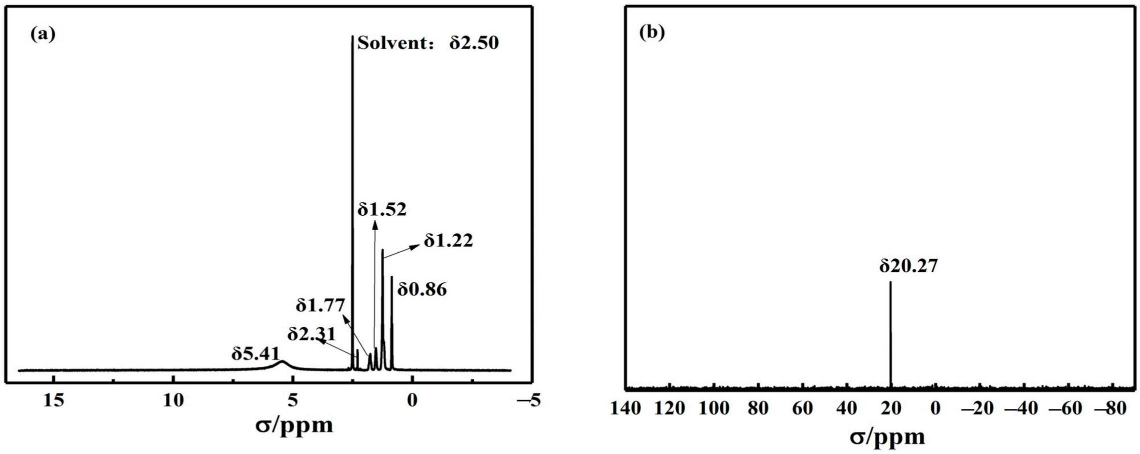

Figure 7. ^{1}H NMR and ^{31}P NMR of HOBA (**a**): ^{1}H NMR; (**b**) ^{31}P NMR.

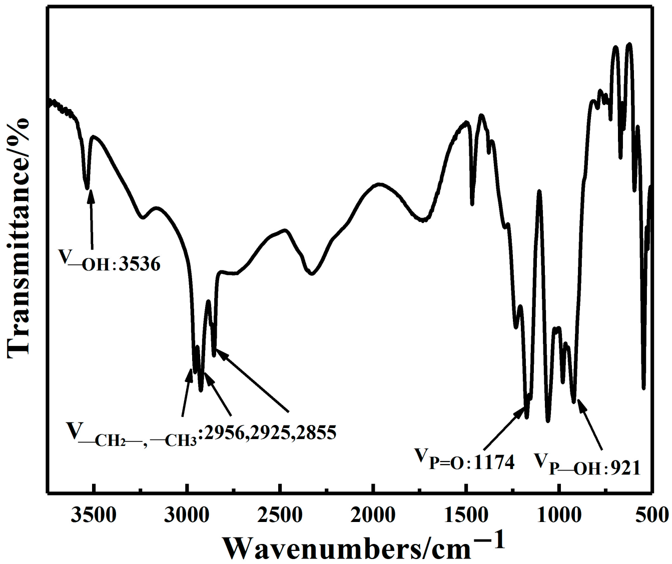

Figure 8. The FTIR spectrum of HOBA.

The flotation results of HOBA as a collector for Baiyun Obo niobium ore are shown in Figure 9. Figure 9a illustrates the influence of pH on the Baiyun Obo niobium ore flotation using HOBA as the collector. It is evident that the Nb_2O_5 grade in concentrate decreases with the increase in pH, and the recovery of concentrate first increases and then decreases. In a pH range from 3.5 to 4.5, HOBA demonstrated excellent harvesting ability of Baiyun Obo niobium ore and showed that the maximum flotation recovery of concentrate (73.2%) could be achieved.

The amount of collector plays an important role in the flotation experiments. As HOBA presented a strong collecting ability for niobium ore flotation at pH from 3.5 to 4.5, the effects of collector dosage on niobium ore flotation were tested. As shown in Figure 9b, the flotation recovery of concentrate increases with a higher collector dosage and achieved a 71.6% flotation recovery of concentrate at 1000 g/t HOBA. The Nb_2O_5 grade in concentrate shows a similar trend to the recovery. Taking into account the recovery rate and grade, the most applicable amount of HOBA is 1000 g/t.

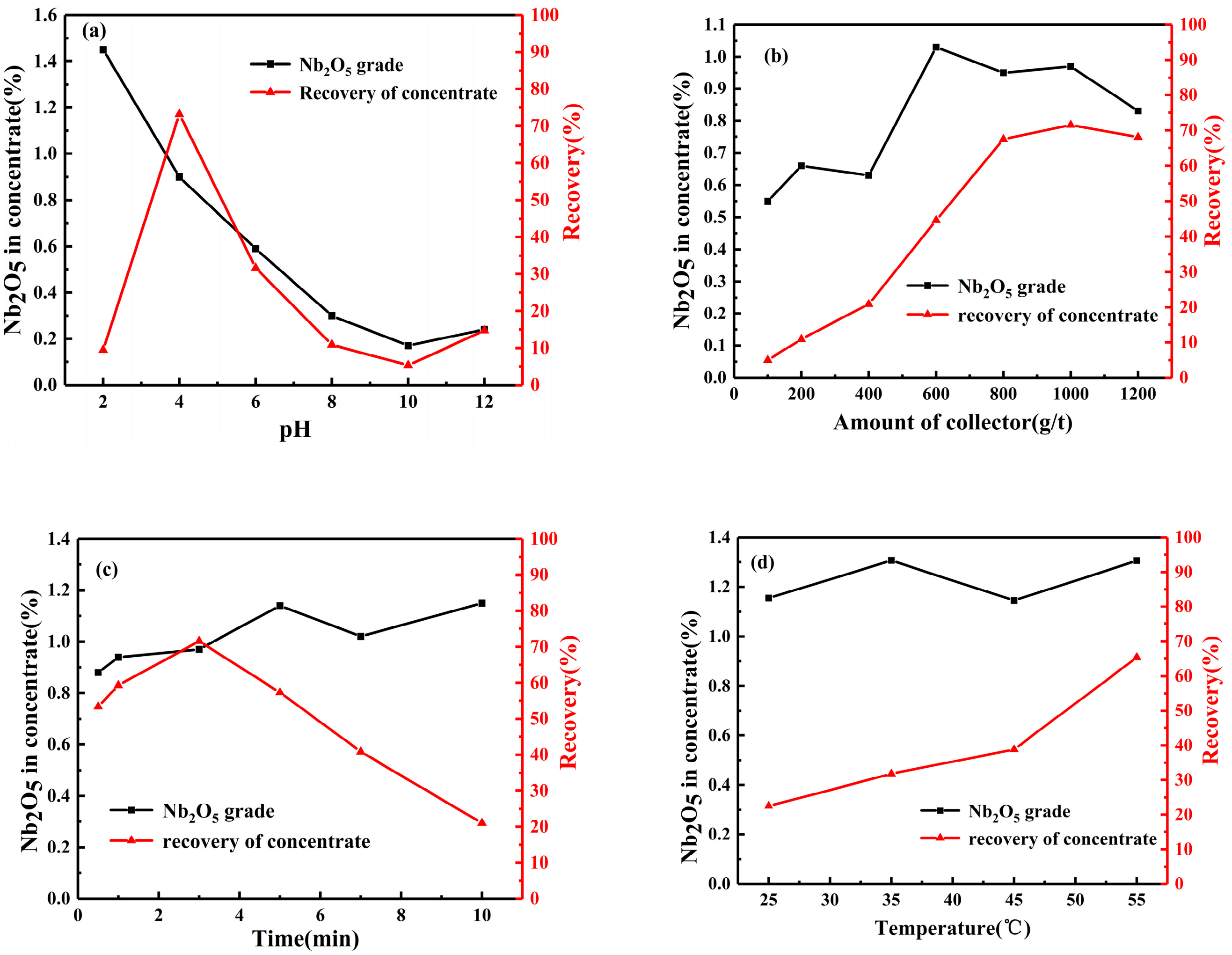

Figure 9. Experimental results of HOBA as a collector for Baiyun Obo niobium ore. (**a**) The Nb_2O_5 grade and recovery of flotation concentrate as a function of pH (flotation conditions: 800 g/t collector dosage, room temperature, and the harvesting time of the collector is 3 min). (**b**) The Nb_2O_5 grade and recovery of flotation concentrate as a function of the collector dosage (flotation conditions: 3.5 < pH < 4.5, room temperature, and the harvesting time of the collector is 3 min). (**c**) The Nb_2O_5 grade and recovery of flotation concentrate as a function of the collector harvest time (flotation conditions: 3.5 < pH < 4.5, 1000 g/t collector dosage, and room temperature). (**d**) The Nb_2O_5 grade and recovery of flotation concentrate as a function of slurry temperature (flotation conditions: 3.5 < pH < 4.5, 1000 g/t collector dosage, and the harvesting time of the collector is 3 min).

Figure 9c,d confirm that both harvesting time of the collector and slurry temperature have an impact on the flotation effect. The Nb_2O_5 grade and recovery of flotation concentrate as a function of the collector harvest time is displayed in Figure 9c, the recovery of concentrate increases to maximum, and then decreases with the increase in collector harvest time; the Nb_2O_5 grade in concentrate changes from 0.881% to 1.15%. As shown in Figure 9d, the recovery of concentrate increases with increasing temperature, and the Nb_2O_5 grade in concentrate changes from 1.16% to 1.31%. It can be seen that the temperature has a low effect on the grade of Nb_2O_5 in the concentrate, and the recovery rate increases with the increase in temperature. The results show that the optimal harvest time of the collector is 3 min, and 55 °C is the optimum slurry temperature.

The pH condition of HOBA, as the flotation of niobium feed ore in Baiyun Obo, is 3.5–4.5, which is convenient for industrial implementation. The dosage of the reagent is

1000 g/t, the optimal flotation action time is 3 min, and the optimal temperature of the flotation slurry is 55 °C.

Two typical collectors of octyl isohydroxamic acid and salicylic hydroxamic acid were compared with HOBA under the same conditions described above, and the results are shown in Figure 10. Under the same flotation conditions, the recovery rate of the concentrate after octyl isohydroxamic acid was highest, but the grade of Nb_2O_5 in the concentrate was at a minimum, indicating that its ability of selectivity was poor. The grade of Nb_2O_5 in the concentrate after the action of salicylic hydroxamic acid was highest, but the recovery rate was at a minimum, indicating that its recovery capacity was not strong. Both the grade and recovery of the concentrate after HOBA were high, indicating that its selectivity and recovery ability were superior to octyl isohydroxamic acid and salicylic hydroxamic acid under the above flotation conditions.

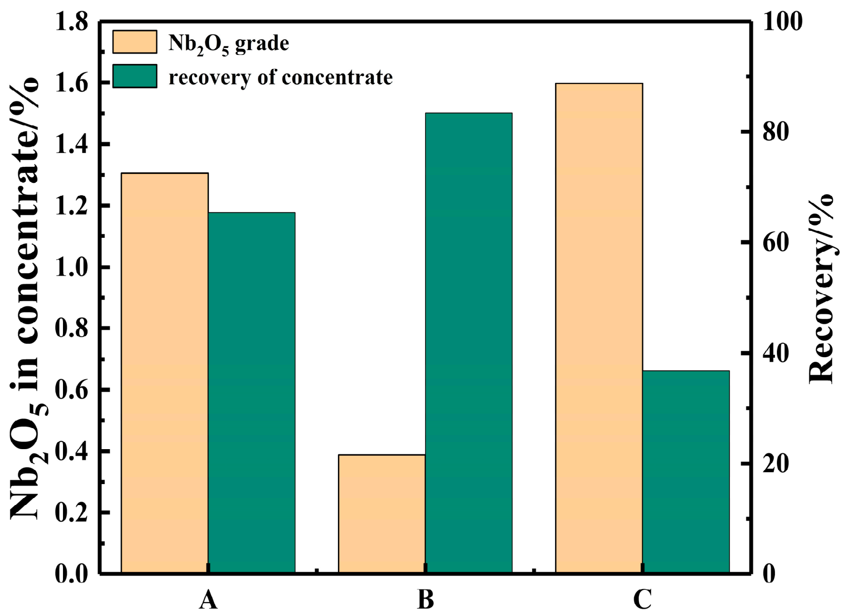

Figure 10. Comparison of flotation effects of three flotation collectors. (A: HOBA; B: octyl isohydroxamic acid; C: salicylic hydroxamic acid).

In order to improve the grade of Nb_2O_5 in the concentrate and make HOBA more suitable for industrial use, the process flow and regent system were optimized. The use of iron selection is the same as that used in the above conditional experiments; after a rough selection and selection operation, the grade of Fe_2O_3 in the iron concentrate was 77.5%, and the recovery rate was 53.7%. To reduce the influence of silicon-containing minerals on the flotation process, CMC was added to the slurry as an inhibitor of silicate minerals [33,34]. Based on the consideration of on-site flotation in Baiyun Obo mine, the flotation temperature was set to room temperature. The niobium selection process was carried out with two rough selections and one beneficiation, in which the amount of HOBA reagent was reduced in order to cut costs as much as possible, and the pH of flotation was maintained between 3.5 and 4. Table 7 shows the results of the flotation optimization experiment; the grade of Nb_2O_5 in niobium concentrate can reach 1.38%, followed by Nb_2O_5 in middling-1 and middling-2 at 0.34% and 0.32%, respectively. Thus, the addition of CMC can indeed inhibit silicate minerals and improve the grade of Nb_2O_5 in concentrate. The recovery rate of niobium concentrate is 30.4%, which is higher than the results of the conditional experiment at 25 °C (Table 7 and Figure 9d). Based on the complexity of the Baiyun Obo niobium mine, the current optimization process needs to be further explored.

Table 7. Flotation optimization experimental results.

Products	Yield/%	Nb_2O_5	
		Grade/%	Recovery/%
Iron concentrate	22	0.15	13.8
Niobium concentrate	5.39	1.38	30.4
Middling-1	9.42	0.34	13.2
Middling-2	21.3	0.32	27.8
Tailing	41.9	0.09	14.9

The composition of niobium minerals in concentrate was detected using MLA, and the comparison results with feed ore, as shown in Table 8, clarify that niobium minerals are enriched in concentrate. Ilmenorutile, nioboaeschynite-Nd, baotite, latrappite, euxenite-Y, fergusonite and columbite-Mn were enriched by 4.30, 5.76, 5.00, 8.57, 4.33, 3.00 and 3.33 times, respectively. Ren et al. found that it was relatively difficult to enrich ilmenorutile [35]. The enrichment ratio of ilmenorutile is lower than that of nioboaeschynite-Nd because its structure is more complex, and the associated and continuous conditions are far more intricate than other niobium-containing minerals. Ilmenorutile and nioboaeschynite-Nd were clearly enriched in the concentrate, suggesting that HOBA can improve the grade and recovery of Nb_2O_5 in concentrate.

Table 8. Comparison of niobium mineral composition in concentrate and feed ore (%).

	Nioboaeschynite	Ilmenorutile	Baotite	Latrappite	Euxenite-Y	Columbite-(Mn)	Fergusonite
Feed Ore	0.55	0.33	0.02	0.07	0.18	0.03	0.04
Concentrate	3.17	1.42	0.10	0.60	0.78	0.10	0.12

4. Conclusions

In this study, a mineral dissociation analyzer (MLA) was used to systematically study the mineralogy of the samples of niobium-bearing minerals in Baiyun Obo. The HOBA synthesized by our research group was applied systematically to the flotation of Baiyun Obo niobite ore, and the most suitable flotation conditions for industrial application were obtained through a series of conditional experiments. Through the optimization of the flotation process and the pharmaceutical regime, CMC was able to inhibit silicate minerals, and it was surprising that HOBA showed superior selectivity and capture ability. The main conclusions of this study are as follows:

1. The target element (in terms of Nb_2O_5) in the Baiyun Obo niobium-bearing mineral samples was 0.24%. After MLA analysis, seven kinds of niobium minerals were found in the sample: ilmenorutile, nioboaeschynite-Nd, baotite, latrappite, euxenite-Y, fergusonite and columbite-Mn. Among them, the contents of nioboaeschynite-Nd and ilmenorutile were 0.55% and 0.33%, respectively. Other niobium minerals are low in content, so ilmenorutile and nioboaeschynite-Nd should be the main targets for the flotation of niobium-bearing minerals.
2. The occurrence state of niobium-containing minerals in this sample is relatively complex. Most of the fluorite, hematite, riebeckite and quartz in this sample exist in their independent forms. The results of the monomer dissociation analysis show that the dissociation degree of niobium-bearing minerals is very low and is mainly associated with riebeckite and silicate minerals. The ilmenorutile has the most complex associated structure which is related to other silicates, carbonate, fluorite and other metal oxides.
3. The results of flotation experiments show that the best effects for industrial application are presented when the pH of the slurry is 3.5–4.5, the temperature is 55 °C, the dosage of HOBA is 1000 g/t and the capture time is 3 min. Compared to the grade of 0.24% in the raw ore, the grade of Nb_2O_5 in the concentrate can be increased to 1.31%, and thus enriched by approximately 5.5 times. In the optimization experiment, the addition of CMC significantly increased the grade of Nb_2O_5 in the concentrate, indicating

that it effectively inhibits silicate minerals. Ilmenorutile and nioboaeschynite-Nd are enriched in the concentrate, which suggests that HOBA can effectively promote the separation and enrichment of niobium-containing minerals in Baiyun Obo during the flotation process. Additionally, the detailed mechanisms of typical niobium-containing minerals' surfaces with HOBA are being systematically investigated. In view of the complex embedding and difficult extraction of Baiyun Obo niobium ore, maximizing the effect of HOBA in terms of flotation requires the full optimization of the reagent system and flotation process. Our research group is currently conducting in-depth research on optimization steps to obtain better results in the future.

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