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Characterization and Pre-Concentration of Low-Grade Vanadium-Titanium Magnetite Ore

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Received: 14 July 2017; Accepted: 29 July 2017; Published: 4 August 2017

Abstract: A large number of unexploited low-grade vanadium-titanium magnetite deposits have been found in the Chao-yang area of China in recent years. The reserves are estimated at more than 20 billion tons. A mineralogical study of raw sample indicated that it was a typical low-grade vanadium-titanium magnetite ore with weathering. Most of vanadium-titanium magnetite was replaced by martite and sphene, which would affect the recovery of valuable elements. The intergrowth relationship between vanadium-titanium magnetite and sphene was very complex, and the grain size of sphene was generally fine, and could not be completely liberated even by fine grinding, whereas the content of vanadium and titanium in sphene was higher than that in vanadium-titanium magnetite, resulting in vanadium-titanium magnetite concentrates with characteristics of high vanadium and titanium content. A magnetic separation process was investigated for the pre-concentration of low-grade vanadium-titanium magnetite ore. The results showed that 73.52% of feed ore were directly discarded for reducing the processing capacity of follow-up processing. A vanadium-titanium magnetite concentrate with 1.14% V_2O_5, 22.22% TiO_2, 42.51% Fe and a rough concentrate of ilmenite with 16.05% TiO_2, 20.77% Fe were obtained from low-grade vanadium-titanium magnetite ore which contains 0.050% V_2O_5, 1.67% TiO_2 and 8.53% Fe.

Keywords: pre-concentration; vanadium-titanium magnetite; mineralogical study; martite; sphene; ilmenite; magnetic separation

1. Introduction

Vanadium and titanium are important industrial raw materials, which due to their properties have found applications in various fields [1,2]. Vanadium-titanium magnetite ore is a typical poly-metallic mineral which mainly contains V, Ti and Fe, with a high comprehensive utilization value [3,4]. China is rich in vanadium-titanium magnetite ore, which is mainly distributed in the Pan-xi and Cheng-de area [5]. However, in recent years, a large amount of low-grade vanadium-titanium magnetite ore with 0.03%–0.20% V_2O_5, 1.5%–4.5% TiO_2 and 8%–18% Fe has been found in the Chao-yang area of China, and the reserves are estimated at more than 20 billion tons, which have so far not been exploited and made full use of on a large scale. With the trend of the exhaustion of high-grade and easily processed deposits, it is necessary to utilize this low-grade ore for the future supply of raw materials to society. Furthermore, the grades of V_2O_5 and TiO_2 in vanadium-titanium magnetite concentrates obtained from the low-grade vanadium-titanium magnetite ore of this area are over 1% and 19% respectively, which have an extremely high utilization value for smelting with the characteristics of high vanadium and titanium content, compared with the vanadium-titanium magnetite concentrates from the Pan-xi and Cheng-de area [6–8]. However, because the grade of the valuable elements in vanadium-titanium magnetite ore from the Chao-yang area of China is very low, pre-concentration technology will face the problems of large ore processing capacity, high energy consumption of grinding, and production costs. Hence, economical and efficient pre-concentration technology is the key to ensure a high efficiency comprehensive utilization of vanadium, titanium and iron in low-grade vanadium-titanium magnetite ore in the Chao-yang area of China.

Pre-concentration technology depends on the difference of the separation characteristics between target minerals and gangue minerals. In vanadium-titanium magnetite ore, vanadium mainly occurs in the form of isomorphism in titanium magnetite, whereas titanium mainly occurs in ilmenite, and the main gangue minerals are feldspar and pyroxene [9,10]. The present pre-concentration technology by beneficiation used in vanadium-titanium magnetite ore are the first to recover titanium magnetite by low-intensity magnetic separation, and then recover ilmenite from its tailing [11]. The separation technology of ilmenite includes gravity separation, magnetic separation, flotation and electrostatic separation [12,13]. Although the separation effects of flotation and electrostatic separation are good, they are usually used for the cleaning operation. Moreover, there will be high consumption of reagents in the flotation process and high energy consumption in the electrostatic separation process due to the large ore-processing capacity when the content of the target minerals in raw ore is low [14–16]. Ilmenite concentrate of higher grade can be obtained by gravity separation, but the recovery rate is low. Due to the low-grade vanadium-titanium magnetite ore in the Chao-yang area of China being a newly discovered ore deposit, there are no reports about its properties and the corresponding pre-concentration technology. Thus, it is of great significance to carry out studies on this specific type of mineral resources.

This work focused on the application of a high efficiency, low cost and environmentally friendly magnetic separation technology to recover vanadium-titanium magnetite concentrate and pre-concentrate rough concentrate of ilmenite, which provides high quality raw materials for flotation from low-grade vanadium-titanium magnetite ore in the Chao-yang area of China based on a mineralogical study. The reason why the vanadium-titanium magnetite concentrates in this area have the characteristics of high vanadium and titanium content was discovered. A new process is proposed, which will significantly reduce the cost of the comprehensive utilization of low-grade vanadium-titanium magnetite in the Chao-yang area of China.

2. Experimental

2.1. Materials

The vanadium-titanium magnetite ore samples used in this work were collected from Chao-yang, Liaoning Province, China. Around 300 kg of representative ore samples were crushed to below 2 mm size with a two-stage jaw crusher (model XPC-60 × 100) (Wuhan Bo-shan Machinery Co. Ltd., Wuhan, China) and a one-stage roll crusher (model HLXPS-Φ250 × 150) (Wuhan Exploring Machinery Factory, Wuhan, China). The crushed samples were then uniformly mixed and divided into 2 kg samples for characterization and pre-concentration studies.

2.2. Procedure and Test Methods

The crushed materials were firstly wet-ground in a laboratory ball mill (model HLXMQ-Φ240 × 90) (Wuhan Heng-le Mineral Engineering Equipment Co. Ltd., Wuhan, China) at 50 wt % solids, until a particle size below 1 mm was achieved. The ground product was referred to as separation feed and subjected to separation by a wet high-intensity magnetic separator (model XCSQ-50 × 70) (Wuhan Heng-le Mineral Engineering Equipment Co. Ltd., Wuhan, China), which required a particle size less than 1 mm for pre-discarding tailing. The tailing of wet high-intensity magnetic separation was rejected as waste ore. Low-intensity magnetic separation tests were carried out with a magnetic drum (model CRIMM-Φ400 × 300, Changsha Research Institute of Mining and Metallurgy Co. Ltd., Changsha, China) on magnetic minerals that were the concentrate from pre-discarding tailing by wet high-intensity magnetic separation. The products of low-intensity magnetic separation included vanadium-titanium magnetite concentrate and weakly magnetic minerals. Then, wet high intensity magnetic separation experiments were conducted again to obtain a rough concentrate of ilmenite from weakly magnetic minerals.

The analysis methods were as follows:

1. Chemical composition was detected by ICP-AES (inductively-coupled plasma atomic emission spectrometry) performed on an IRIS Advantage ER/S instrument (Thermo Elemental, Waltham, MA, USA).
2. X-ray diffraction (XRD) analysis was conducted using a Rigaku D/MAX-RB X-ray diffraction (Rigaku, Akishima, Japan) using Cu Kα radiation. The phases were identified by comparison of the peak positions and d values with data published by the International Centre for Diffraction Data (ICDD).
3. Optical microscopy (Leica, Wetzlar, Germany) and a scanning electron microscope (JSM-6610) (JEOL Co., Tokyo, Japan) with an energy dispersive spectrometer (BRUKER, Karlsruhe, Germany) were used to characterize the microstructure of the vanadium-titanium magnetite ore.
4. The determination of the vanadium grade was measured in accordance with the test methods of vanadium in vanadium-bearing slag by ferrous ammonium sulfate titration using 2-(phenylamino)-benzoic acid as an indicator (GB/T 8704.5-2007) [17].
5. Sizing analysis was conducted on the feed sub-samples by using laboratory wet and dry screening methods. Dry screening was carried out by a standard vibration sieve machine (HLSDB-Φ200, Wuhan Hengle Mineral Engineering Equipment Co., Wuhan, China).

3. Results and Discussion

3.1. Characterization Studies

3.1.1. Chemical Composition Analysis

The main chemical composition of raw sample is presented in Table 1, which shows that the main component in the sample is SiO_2. Not only is the content of the V_2O_5 only 0.050%, but there is also a low TiO_2 and Fe content of 1.67% and 8.53%, respectively. It is a typical low-grade vanadium-titanium magnetite ore.

Table 1. Main chemical composition of raw sample (wt %).

Element	V_2O_5	TiO_2	TFe	SiO_2	Al_2O_3	CaO	MgO	P	S
Content	0.050	1.67	8.53	47.25	12.89	10.32	5.96	0.06	0.01

3.1.2. Mineral Composition Analysis

The raw sample observed by the unaided eye presents khaki or light grey coloration, a granular and powdery texture, and serious weathering. The results of optical microscopy indicate that the main minerals are feldspar and pyroxene. In addition, magnetite, martite and ilmenite are also detected. The composition and content can be seen from Table 2 on the basis of microscopy and scanning electron microscope analysis, and the specific susceptibility of the minerals are also tabulated in Table 2 [18], which shows that the content of metallic minerals, including magnetite, martite and ilmenite, is less than 10%. The specific susceptibility to differences among various minerals was taken into account for mineral separation. Magnetic separation may be an appropriate method.

Table 2. Mineral composition of raw sample (wt %).

Mineral	Magnetite	Martite	Ilmenite	Sphene	Feldspar
Content	0.87	6.33	1.94	1.37	51.78
Specific Susceptibility (10^{-8} m^3/kg)	>4000	60~440	280~450	5~10	−1~5
Mineral	**Pyroxene**	**Amphibole**	**Talc**	**Montmorillonite**	**Else**
Content	22.34	4.00	5.03	5.34	1.00
Specific Susceptibility (10^{-8} m^3/kg)	20~400	50~300	−1~5	-	-

3.1.3. Occurrence of Valuable Elements

The chemical phase of the valuable elements in the raw sample were analyzed through sequential extraction procedures [19]. Iron phase analyses (Table 3) indicated that the iron mainly existed in martite and silicate minerals, in which the distribution rate of the form of silicate minerals was 39.08%. The former is possible to get effective recovery by high intensity magnetic separation, and the latter is the key object that needs to be removed in the process of beneficiation. It can be known from the titanium phase (Table 4), that the occurrence of titanium is relatively dispersed, but ilmenite is the main form of Ti-containing mineral. Moreover, the distribution rate of the form of silicate minerals is 20.24%. The results of the vanadium phase are presented in Table 5, which shows that vanadium mainly occurred in iron minerals and silicate minerals in which the distribution rate of the form of silicate minerals was 42.20%. Therefore, the theoretical recovery of Fe, TiO_2 and V_2O_5 from metallic minerals is 58.69%, 79.76% and 57.80%, respectively.

Table 3. Chemical phase analysis of iron in raw sample (wt %).

Phase	Magnetite	Martite	Ilmenite	Carbonate	Silicate	Total
Mass fraction	0.58	3.76	0.66	0.19	3.33	8.52
Distribution	6.81	44.13	7.75	2.23	39.08	100.00

Table 4. Chemical phase analysis of titanium in raw sample (wt %).

Phase	Ilmenite	Iron Minerals	Rutile	Silicate	Total
Mass fraction	0.97	0.35	0.02	0.34	1.68
Distribution	57.74	20.83	1.19	20.24	100.00

Table 5. Chemical phase analysis of vanadium in raw sample (wt %).

Phase	Iron Minerals	Ilmenite	Silicate	Total
Mass fraction	0.0273	0.0016	0.0211	0.0500
Distribution	54.60	3.20	42.20	100.00

3.1.4. Alteration of Vanadium-titanium Magnetite

Secondary changes of the vanadium-titanium magnetite were very strong, and most of the vanadium-titanium magnetite experienced varying degrees of alteration. The replacement of vanadium-titanium magnetite by martite and sphene are the two main alteration types [20]. To develop a visual comprehension of the form of alteration in the vanadium-titanium magnetite, SEM images of vanadium-titanium magnetite replaced by martite (H) and sphene (Sp) are presented in Figures 1 and 2.

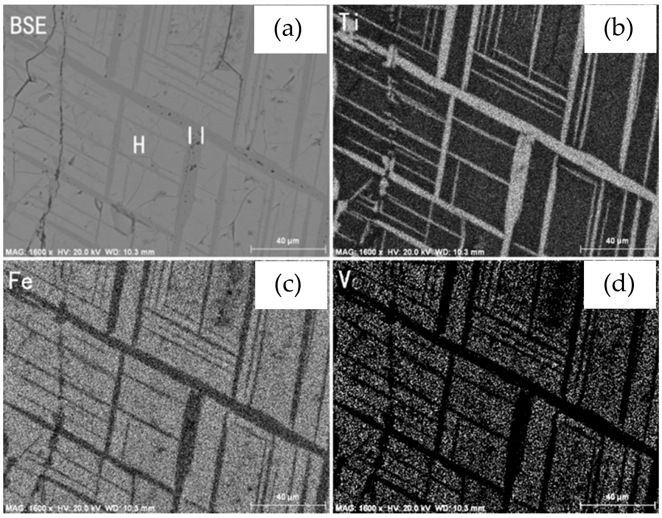

Figure 1. SEM images of vanadium-titanium magnetite replaced by martite: (**a**) Back-scattered electron image; (**b**) Ti element mapping; (**c**) Fe element mapping; (**d**) V element mapping.

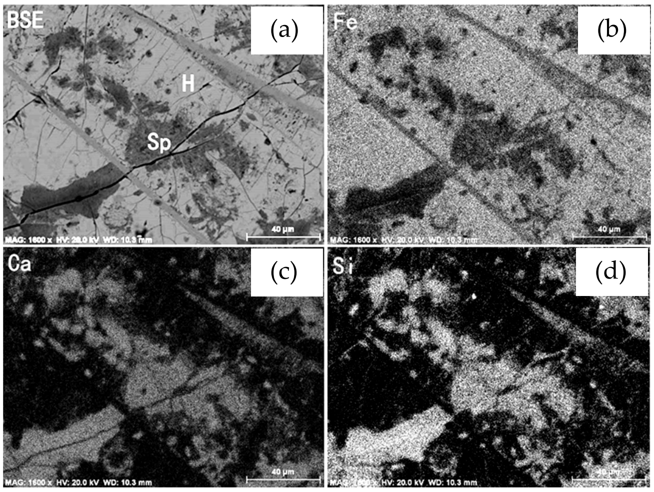

Figure 2. SEM images of vanadium-titanium magnetite replaced by sphene: (**a**) Back-scattered electron image; (**b**) Fe element mapping; (**c**) Ca element mapping; (**d**) Si element mapping.

As shown in Figure 1, fine grid shaped ilmenite lamellae formed by the separation of solid solutions can be found in the grains. Meanwhile, the V and Fe have good relevance in the view fields from the SEM images. Obviously, the martite is formed by the oxidation of vanadium-titanium magnetite, which weakens the susceptibility of vanadium-titanium magnetite. The relevance of Ca and Si in Figure 2 are quite good, illustrating that vanadium-titanium magnetite is replaced by sphene [21]. Combined with the above conclusion, SEM-EDS analyses were conducted and the results indicate that the chemical composition of vanadium-titanium magnetite and ilmenite are homogeneous. However, the chemical composition content of sphene varies greatly with V_2O_5, TiO_2 and Fe content ranging from 0.92% to 2.74%, 19.58% to 30.31%, and 5.56% to 33.89%, respectively. The reason for this phenomenon may be that the sphene is a transitional product which is formed in the process of the replacement of vanadium-titanium magnetite by sphene. The results on average of raw sample by SEM-EDS analyses (Table 6) indicate that the vanadium occurs in an isomorphism state in vanadium-titanium magnetite and sphene, which will have effects on the quality of vanadium-titanium magnetite concentrate, and the vanadium content of sphene is relatively high. However, the differences between the separation characteristics of sphene and pyroxene are not significant [18,22], which will be lost together in tailing, thus affecting the recovery of vanadium. Hence, the target minerals that need to be enriched in the pre-concentration process are iron minerals and ilmenite. Meanwhile, utilizing the specific susceptibility differences of minerals to separate iron minerals and ilmenite from gangue minerals could realize the enrichment of valuable elements, such as V, Ti and Fe.

Table 6. The results of average of raw sample by SEM-EDS analyses (wt %).

V_2O_5	TiO_2	Fe	CaO	MgO	Al_2O_3	SiO_2	Mineral
0.59	5.21	63.46	0.00	0.45	1.37	0.48	V-Ti Magnetite
0.10	51.64	36.73	0.00	0.66	0.00	0.00	Ilmenite
1.53	25.53	22.05	18.50	0.70	3.09	19.15	Sphene

3.1.5. Grain-Size Distribution of Metallic Minerals in Raw Sample

The composition and distribution of the grain size of metallic minerals play an essential role in determining the grinding fineness and the methods of mineral processing. The grain size distribution of metallic minerals in the raw sample (Figure 3) indicates that iron minerals and ilmenite are both medium and fine grained and the difference in grain size is small. The cumulative distribution rates of iron minerals and ilmenite are 82.02% and 82.55%, respectively, when the grain size is over 0.15 mm. In terms of disseminated grain size, more than 80% of iron minerals and ilmenite can be liberated at the grinding fineness of −0.15 mm. The particle size distribution rate with −0.074 mm is about 60% at this point. Particles usually need to be broken as finely as possible in order to increase liberation. However, the energy consumption of grinding will be greatly increased with the decrease in the size of particle, and fine particles are more difficult to separate. Thus, a grinding fineness of −0.074 mm, accounting for about 60%, is suggested to treat the low-grade vanadium-titanium magnetite ore from the Chao-yang area in order to make sure that over 80% of the iron minerals and ilmenite can be liberated.

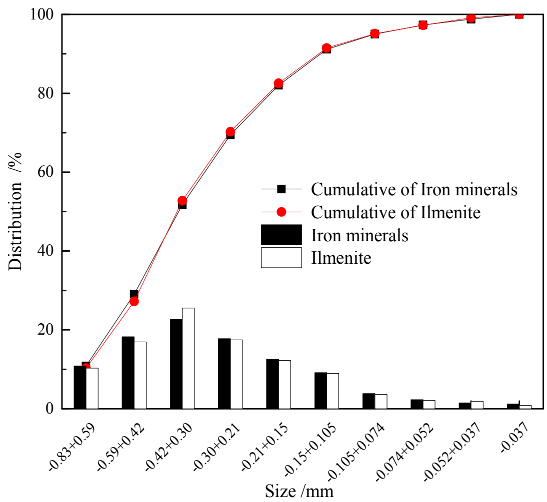

Figure 3. Grain size distribution of metallic minerals in raw sample.

3.2. *Pre-Discarding Tailing*

Pre-discarding tailing by wet high-intensity magnetic separation was taken into account to reduce the ore processing capacity and the production cost, due to the content of valuable elements in the raw sample being very low, and feldspar—which accounts for more than half of the raw sample—being a non-magnetic mineral. It can be seen from Figure 4 that magnetic intensity has a significant effect on the recovery of valuable elements in pre-discarding tailing. The yield and recovery of valuable elements increases with increasing magnetic intensity. The recovery of TiO_2, V_2O_5 and Fe are 82.26%, 67.08% and 55.28%, respectively, which are near the theoretical recovery of valuable elements recovered from metallic minerals combined with the results of chemical phase analyses when the magnetic intensity is 1.0 T. Meanwhile, the waste ore, which accounts for 73.52% of the raw sample, is discarded. Therefore, 1.0 T is considered as the most suitable magnetic intensity for pre-discarding tailing.

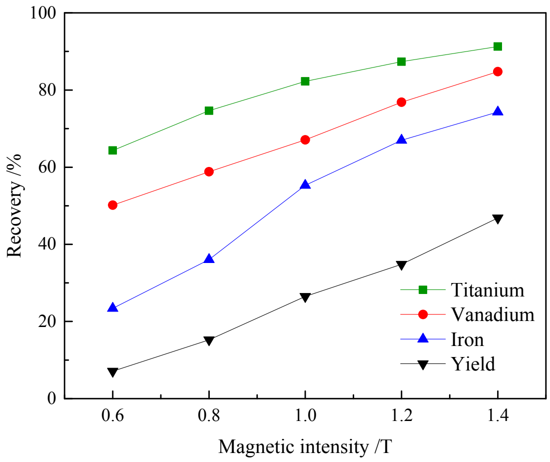

Figure 4. The effect of magnetic intensity on the pre-discarding tailing.

3.3. Low-Intensity Magnetic Separation

From the mineralogical study of the raw sample, it is known that vanadium is mainly distributed in iron minerals. Due to the iron minerals without oxidation and with a low degree of oxidation being strongly magnetic minerals, it is feasible to separate them by low-intensity magnetic separation. The grade and recovery of valuable elements in vanadium-titanium magnetite concentrate were investigated at different levels of grinding fineness with a magnetic intensity of 0.13 T.

Figure 5 shows that the recovery of vanadium, titanium, and iron obviously decrease with increased grinding fineness, whereas the grade of Fe increases slowly, the grade of titanium decreases slightly in general, and the grade of SiO_2 decreases slowly. However, the grade of V_2O_5 decreases when the particle size distribution rate with −0.074 mm is above 85.2%. Thus, the vanadium-titanium magnetite concentrate at a grinding fineness with −0.074 mm particle size, accounting for 94.8% was studied by XRD and SEM analysis.

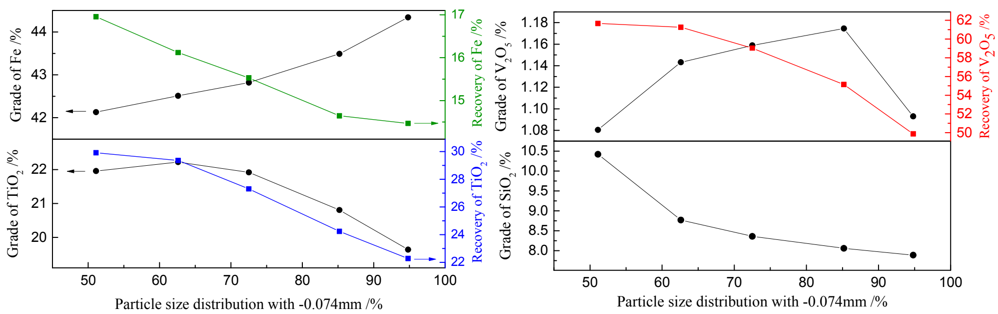

Figure 5. The effect of grinding fineness on low-intensity magnetic separation.

As shown in Figure 6, the diffraction peaks of sphene also appear in the vanadium-titanium magnetite concentrate, in addition to magnetite and ilmenite, and the sphene content obtained by semi-quantitative analysis of XRD was 19.8%. Figure 7 indicates that the intergrowth relationship between vanadim-titanium magnetite (M) and sphene (Sp) is very complex. Furthermore, the grain size of sphene and ilmenite (Il) lamellae are generally fine. Obviously, sphene and ilmenite cannot be completely liberated even by fine grinding. Combined with the results of SEM-EDS analyses (Table 6), it can be seen that the vanadium and titanium content in sphene is higher than in vanadium-titanium magnetite, illustrating that the replacement of vanadium-titanium magnetite by sphene leads to vanadium-titanium magnetite concentrates with the characteristics of high vanadium and titanium content, besides the complex association between vanadium-titanium magnetite and ilmenite lamellae formed by the separation of solid solutions resulting in a high titanium content in vanadium-titanium magnetite concentrates. Hence, considering the comprehensive recovery of valuable elements and the energy consumption of grinding, the particle size distribution rate with −0.074 mm of 62.6% was chosen as the optimal grinding fineness, with which a vanadium-titanium magnetite concentrate with 1.14% V_2O_5 grade, 22.22% TiO_2 grade, 42.51% Fe grade, and 61.27% V_2O_5 recovery, 29.36% TiO_2 recovery, 16.12% Fe recovery was obtained.

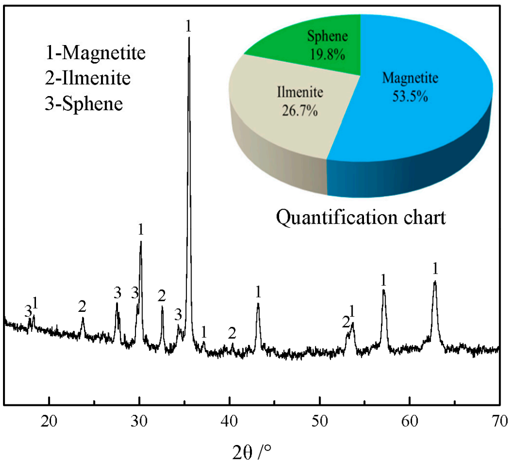

Figure 6. XRD patterns of the vanadium-titanium magnetite concentrate.

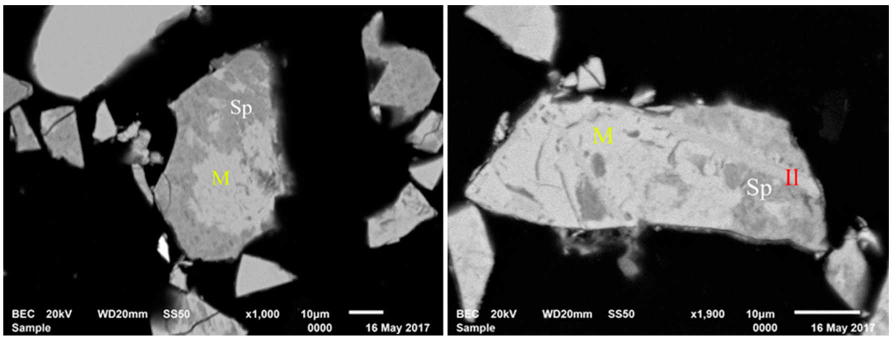

Figure 7. SEM images of the vanadium-titanium magnetite concentrate.

3.4. High Intensity Magnetic Separation

Although ilmenite is a weakly magnetic mineral, it has a slightly stronger susceptibility compared with other gangue minerals, which are more likely to be pre-concentrated by a wet high-intensity magnetic separation process from low-intensity magnetic separation tailing. The results of magnetic intensity tests (Table 7) show that when the magnetic intensity is 0.6 T, a rough concentrate of ilmenite with 16.05% TiO_2 grade, 20.77% Fe grade, and 64.86% TiO_2 recovery, 20.57% Fe recovery is obtained. The mineral particles are subjected to weaker magnetic forces when the magnetic intensity is less than 0.4 T. The magnetic force of the mineral particles at a magnetic intensity of 0.4 T is weaker than that of the mineral particles at a magnetic intensity of 0.6 T, resulting more difficulty in getting rid of the shackles of mechanical force. Therefore, the TiO_2 and Fe grade of the concentrate at a magnetic intensity of 0.4 T are 10.98% and 18.24%, respectively, which are lower than that of the concentrate at a magnetic intensity of 0.6 T. The grade of the valuable elements decreased due to some gangue minerals that are magnetized into the concentrate when the magnetic intensity exceeds 0.6 T. Hence, 0.6 T was chosen as the optimal magnetic intensity to separate ilmenite from gangue minerals.

Table 7. The results of magnetic intensity tests by high-intensity magnetic separation.

Magnetic Intensity/T	Products	Yield (wt %)	Grade			Recovery		
			V_2O_5	TiO_2	Fe	V_2O_5	TiO_2	Fe
0.4	Concentrate	7.78	0.113	10.98	18.24	16.73	21.57	8.86
	Tailing	92.22	0.048	3.37	15.82	83.27	78.43	91.14
	Feed	100.00	0.053	3.96	16.01	100.00	100.00	100.00
0.6	Concentrate	15.88	0.091	16.05	20.77	27.37	64.86	20.57
	Tailing	84.12	0.045	1.65	15.13	72.63	35.14	79.43
	Feed	100.00	0.052	3.95	16.03	100.00	100.00	100.00
0.8	Concentrate	42.71	0.075	7.26	17.92	61.34	78.10	47.78
	Tailing	57.29	0.035	1.52	14.60	38.66	21.90	52.22
	Feed	100.00	0.053	3.97	16.02	100.00	100.00	100.00

3.5. Flow-Sheet Test

The flow-sheet for the pre-concentration of low-grade vanadium-titanium magnetite ore (Figure 8) shows that the grade of V_2O_5, TiO_2 and Fe in the waste ore is only 0.022%, 0.40% and 5.19%, respectively, which has no utilization value. The rejection rate is up to 73.52%, which greatly reduces the ore processing capacity of follow-up processing. The V_2O_5 grade of vanadium-titanium magnetite concentrate and the TiO_2 grade of ilmenite rough concentrate are much higher than that of the tailing. The total recovery of V_2O_5, TiO_2 and Fe in vanadium-titanium magnetite concentrate and the rough concentrate of ilmenite obtained from low-grade vanadium-titanium magnetite ore by a pre-concentration process are 48.21%, 61.84% and 18.45%, respectively. However, the recovery of V_2O_5, TiO_2 and Fe will be 71.87%, 75.18% and 33.38%, respectively, if calculated from magnetic minerals that are obtained from pre-discarding tailing by a wet high-intensity magnetic separation. Hence, the pre-concentration process by magnetic separation can not only greatly improve the grade of valuable elements, but also effectively recover vanadium and titanium in metallic minerals.

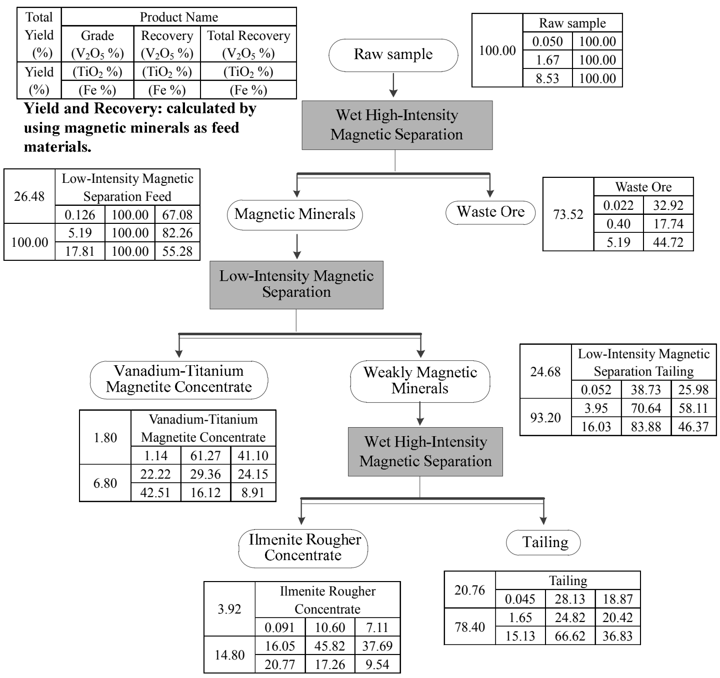

Figure 8. Flow-sheet for the pre-concentration of low-grade vanadium-titanium magnetite ore.

4. Conclusions

1. The mineralogical study of the raw sample indicates that it is a typical, low-grade vanadium-titanium magnetite ore with weathering. Vanadium and iron mainly occur in iron minerals and silicate minerals, and ilmenite is the main form of Ti-containing mineral. Most of the vanadium-titanium magnetite is replaced by martite and sphene. The replacement of vanadium-titanium magnetite by martite weakens the susceptibility of vanadium-titanium magnetite, and the vanadium content of sphene is relatively high. The differences between the separation characteristics of sphene and pyroxene are not significant, and they will be lost together in tailing, thus affecting the recovery of valuable elements.
2. The intergrowth relationship between vanadium-titanium magnetite and sphene is very complex and the grain size of sphene is generally fine, and cannot be completely liberated even by fine grinding, whereas the content of vanadium and titanium in sphene is higher than that in vanadium-titanium magnetite, resulting in vanadium-titanium magnetite concentrates with the characteristics of high vanadium and titanium content.
3. A high efficiency, low cost and environmentally friendly pre-concentration process by magnetic separation was investigated for enriching iron minerals and ilmenite in order to realize the enrichment of valuable elements. Through the process, 73.52% of the feed ore are directly discarded, greatly reducing the ore processing capacity of the follow-up processing. In addition, a vanadium-titanium magnetite concentrate with 1.14% V_2O_5, 22.22% TiO_2, and 42.51% Fe, and a rough concentrate of ilmenite with 16.05% TiO2 and 20.77% Fe were obtained from a low-grade vanadium-titanium magnetite ore which contained 0.050% V_2O_5, 1.67% TiO_2 and 8.53% Fe. The total recovery of V_2O_5, TiO_2 and Fe were 48.21%, 61.84% and 18.45%, respectively. However, the recovery of V_2O_5, TiO_2 and Fe will be 71.87%, 75.18% and 33.38%, respectively, if the magnetic minerals obtained from the pre-discarding tailing are used as feed materials.

Acknowledgments: This research was funded by the Project in the National Science & Technology Pillar Program of China (No. 2015BAB18B01).

Author Contributions: Chengbao Xu and Yimin Zhang conceived and designed the experiments; Chengbao Xu performed the experiments; Chengbao Xu and Tao Liu analyzed the data; Tao Liu and Jing Huang contributed reagents/materials/analysis tools; Chengbao Xu wrote this paper.

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

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