Evaluation the potential of recovering various valuable elements from a vanadiferous titanomagnetite tailing based on chemical and process mineralogical characterization

Jinsheng Liu (✉ 1910515@stu.neu.edu.cn)  
Northeastern University School of Metallurgy  https://orcid.org/0000-0001-6221-212X

Zhenxing Xing  
Northeastern University

Jianxing Liu  
Northeastern University

Xueyong Ding  
Northeastern University

Xiangxin Xue  
Northeastern University

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Abstract

In order to evaluate the potential of recovering various valuable elements from vanadiferous titanomagnetite tailing (VTMT), the chemical and process mineralogical characterization of VTMT were investigated in this study by various analytical techniques such as XRF, XRD, optical microscope, SEM, EDS and AMICS et al. It was found that VTMT is coarser powder in general, about 50% of the particle size is greater than 54.30 µm. The total iron content of the VTMT was 22.40 wt.%, and its TiO$_2$ grade is 14.45 wt.%, even higher than those found in natural ilmenite ores. The majority of iron and titanium were located in ilmenite and hematite, 62.84% of hematite and 90.27% of ilmenite were present in monomeric form. However, there is still a portion of ilmenite and hematite embedded in gangue such as anorthite, diopside, and serpentite et al. For the recovery of valuable fractions such as Fe and TiO$_2$ from VTMT, a treatment process including ball milling – high-intensity magnetic separation – one roughing and three refining flotation was proposed. Finally, a concentrate with TiO$_2$ grade of 47.31% and TFe grade of 35.44% was produced, TiO$_2$ and TFe had recovery rates of 57.71% and 28.23%, respectively. The recovered product is absolutely adequate as a raw material for the production of rutile. This study provides a reference and a new research direction for the recycling and comprehensive utilization of VTMT.

Introduction

Vanadiferous titanomagnetite tailing (VTMT) is a typical by-product generated during the mining and mineral processing of vanadiferous titanomagnetite ore. Statistically, processing one ton of vanadiferous titanomagnetite concentrate produces approximately 1.5 tons of VTMT, and the volume of tailing yield will increase as the grade of the original ore drops (Li et al., 2020). Thus, a large quantity of VTMT have been generated in China at locations such as Panxi, Chengde and Chaoyang, the major areas where vanadiferous titanomagnetite ore are mined and processed (Xiao and Zhang, 2019; Xu et al., 2017; Yu et al., 2021). So far, due to the lack of advanced processing technology, the majority of VTMT are simply stockpiled in the form of waste products today, creating many tailing ponds (Gan et al., 2022; Kang et al., 2020). It not only occupies large amounts of land and pollutes the environment, but also risks tailing dam failure, threatening the safety of people's property and health (Liu et al., 2019; Yu et al., 2014). Thus, such large-scale VTMTs need to be dealt with urgently, in order to recycle and environmentally manage industrial waste resources (Ciarpica et al., 2019; Wang et al., 2018).

Recently, preparation of lightweight foamed ceramics by using VTMT as raw material along with other tailings such as feldspar tailings and kaolinite-type pyrite tailings, has been proposed (Li et al., 2020; Zhu et al., 2021). However, it causes the waste of valuable metal elements in the VTMT, and Li et al. also demonstrated that the chemical composition of CaO and SiO$_2$ in VTMT has a negative impact on the bulk density and open porosity of foamed ceramics (Li et al., 2022a). These are not conducive to the treatment and utilization of VTMT on a large scale. Thus, it is preferred to extract further valuable metals such as iron, titanium, vanadium and scandium from the VTMT by means of advanced metallurgical and mineral processing techniques (Xiao et al., 2021), similar to those used in raw vanadiferous titanomagnetite ore (Gao et al., 2020; Han et al., 2021; Li et al., 2022b; Sukmara et al., 2022). Meanwhile, whether directly preparing new materials or extracting valuable elements from VTMT, a detailed process mineralogical analysis is an important prerequisite and an effective method to improve the availability of VTMT (Baum, 2014; Brough et al., 2013; Kelvin et al., 2022; Xu et al., 2021; Zhang et al., 2014). And, as testing tools continue to be developed and upgraded, more and more methods are being used to conduct process mineralogical analysis of a variety of refractory ores and tailings (Guanira et al., 2020; Lotter, 2011; Mahieux et al., 2010; Xu et al., 2019). Which not only improves the utilization of ores and tailings, but also avoids a lot of unnecessary resources and energy wastage by using process mineralogy to evaluate the potential of comprehensive tailings utilization (Barik et al., 2022; Simonsen et al., 2020). However, little literature reports on the process mineralogy of VTMT have been published, which is perhaps an important reason for the failure to fully utilization of the VTMT (Abdollahi et al., 2020; Alfonso et al., 2022; Ospina-Correa et al., 2018).

In this study, in order to thoroughly understand the physicochemical properties of VTMT and to evaluate the potential of recovering various valuable elements from it, the chemical and process mineralogical characterization of VTMT were
investigated in detail by various analytical techniques. Finally, according to the results of chemical and process mineralogical analysis, proposing a process flow for the recovery of valuable fractions such as Fe and TiO$_2$ from VTMT. This study provides a reference and a new research direction for recycling and comprehensive utilization of VTMT.

**Materials And Methods**

**Sampling and preparation**

The materials used in this study were VTMT samples from a mining plant located in northwest area of Liaoning Province, China. Figure 1 shows the process flow diagram of VTMT source. The raw vanadiferous titanomagnetite ore was obtained from the vanadiferous titanomagnetite mining area in northwest of Liaoning, where the original ore is shallowly buried, severely weathered, and with a low content of valuable elements. The raw vanadiferous titanomagnetite ore from open pit mining was crushed by jaw and toothed roll crushing, the crushed product was screened by 12 mm sieve next. Then, the larger particle ore (+ 12 mm) was sent back to previous stage for further crushing, the smaller grain ore was sorted by a section of dry magnetic roller (magnetic field strength 0.3 T), and about 50% the non-magnetic gangue minerals were discarded to obtain dry concentrate. The dry concentrates were ground to -74 µm particle size content of 50% ~ 60%, followed by medium-intensity magnetic separation using a cylinder magnetic separator with a magnetic field strength of 0.7 T, and the magnetic concentrate and weakly magnetic minerals were obtained. The weakly magnetic ore was subjected to strong magnetic separation with a magnetic field strength of 1.0 T, resulting in the magnetic concentrate and the non-magnetic minerals. In this study, the VTMT samples used in the following analysis operations are the non-magnetic minerals and.

**Chemical composition**

For chemical characterization, 100 g VTMT was dried in vacuum dryer (DZF-6050, Gongyi Yuhua Instrument Co. Ltd., Zhengzhou, China) at 105 °C for 4 h and then grounded into fine powder (-0.074 mm) by a laboratory-scale three head agate grinding machine (XPM 120×3, Jiangxi Longzhong Machinery Equipment Co. Ltd., Ganzhou, China). The chemical composition of the samples was obtained with the help of an X-ray fluorescence spectrometer (XRF-1800, Shimadzu Corporation, Kyoto, Japan) using a powder pressed method to prepare the samples.

**Particle size distribution**

The grinding operation of VTMT was carried out in a laboratory-scale damp mill (XMQ150/50, Jiangxi Zhengchang Mineral Processing Equipment Co., Ganzhou, China) with an internal diameter and an internal volume of 0.5 m and 0.1 m$^3$ respectively, and grinding speed was 48 r/min, the feed mass was 300 g, and 128.5 ml of water was added as a grinding aid at a solid–liquid ratio of 7/3. Then, the particle size distribution was measured by a laser particle size analyzer (Mastersizer 3000, Malvern Panalytical Co. Ltd., Malvern, UK) with an effective measurement range of 0.01 to 3500 µm, the particle size analyzer was calibrated with mono-dispersed particle size standards, and all particle size distribution data were calibrated with the obtained calibration curves.

**Process mineralogical characterization**

**Mineral phases**

Mineral phase analysis of the crushed products in -0.075 mm size fractions were carried out by an X-ray powder diffractometer (X’Pert Pro, PANalytical B.V., Almelo, Netherlands). The XRD parameters were as follows: Cu Kα radiation, 40 keV accelerating voltage, 30 mA current, 5–90° scanning range, and 0.1 s/step (0.01°/step) scan speed. The minerals phases were determined by comparing peak locations and d values to data from the International Centre for Diffraction Data (ICDD).

**Morphology and distribution characteristics**
Mineral particle morphology and distribution characteristics in VTMT were analyzed by an optical microscopy (DM6000M, Leica Microsystems Inc., Wetzlar, Germany) and a scanning electron microscope (ULTRA PLUS, German Zeiss Microscope Co., Oberkochen, Germany) equipped with an energy dispersive spectrometer (Bruker QUANTAX 400 – 10, Bruker Scientific Instruments Co., Billerica, USA).

Mineral liberation

In order to gain a more detailed understanding of the particle size distribution and correlation of the various mineral phases present in the VTMT, an advanced mineral identification and characterisation system (AMICS), equipped with back-scattered scanning electron microscopy (Sigma 300, German Zeiss Microscope Co., Oberkochen, Germany), energy dispersive X-ray analysis (Quantax 400, Bruker Scientific Instruments Co., Billerica, USA) and AMICS software, was used to analyze the liberation of various metallic and non-metallic mineral phases in the VTMT.

Results And Discussion

Chemical composition

Chemical composition of VTMT is listed in Table 1. The VTMT used in this research was composed of Fe, Ti, Si, Al, Ca, Mg and contained small amounts of K, Na, V, S and P. The grades of Al₂O₃, CaO, MgO and SiO₂ are 4.68 wt.%, 8.71 wt.%, 5.65 wt.%, and 34.69 wt.%, respectively, which may imply that gangue are silicate and aluminosilicate minerals containing calcium and magnesium, and the content is large. The grade of Fe³⁺ is 10.20 wt.%, which presumably contains amount of hematite in VTMT. Significantly, it is noticed that the content of TiO₂ is fairly high, which is 14.4 wt.%, even higher than those found in natural ilmenite ores (Zhai et al., 2020). Therefore, the VTMT has a high recycling and utilization value.

<table>
<thead>
<tr>
<th>Element</th>
<th>TFe</th>
<th>Fe³⁺</th>
<th>Fe²⁺</th>
<th>TiO₂</th>
<th>V₂O₅</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₂</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>22.40</td>
<td>10.20</td>
<td>11.54</td>
<td>14.45</td>
<td>0.08</td>
<td>34.69</td>
<td>4.68</td>
<td>8.71</td>
<td>5.65</td>
<td>0.23</td>
<td>0.85</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Particle size distribution analysis

Figure 2 shows the particle size distribution of the VTMT. It can be easily seen from this that the size of the VTMT particles is significantly concentrated between 18 and 163 µm. The largest distribution rate of particle size occurred around 60 µm, reaching 9.72%. Moreover, the fitted geometric average size of VTMT particle is 75.84 +/- 0.53 µm, which indicates that the VTMT sample is coarser powder in general. The accumulation curves show values of 54.30 µm and 93.54 µm for d₅₀ and d₉₀ (Fig. 2(b)), respectively, which further confirms the coarse particle characteristics of the VTMT. Therefore, the processing of necessary grinding is very important to separate and recover valuable elements from the VTMT.

In order to analyze the distribution regularity of each element in different size fractions, the chemical composition analysis of each size fraction was carried out by XRF, and the results are listed in Table 2. By comparing and analyzing the content of a certain element in each size fraction, the elements had three kinds of distribution behaviors. Ca, Mg, Al, Si and K had the same distribution behaviors that the contents in the + 74 µm size fractions were much higher than that in the – 74 µm size fractions. On the contrary, the content of Ti in + 74 µm size fraction were much lower than that in the – 74 µm size fractions. It can be inferred that the VTMT has been partially enriched in elements, and the separation of the valuable metal Ti from other elements can be achieved by suitable screening operations. In addition, Fe, Mn, Na, Zn, and P are uniformly distributed in each particle size without obvious aggregation. The difference is that the content of Fe is significantly higher.
than the others. Therefore, some grinding and modification treatment seems necessary to achieve effective recovery of valuable metals in VTMT.

### Table 2 Chemical composition of each size fraction in VTMT (wt.%)

<table>
<thead>
<tr>
<th>Size fraction/µm</th>
<th>Fe</th>
<th>Ti</th>
<th>Si</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Mn</th>
<th>K</th>
<th>Na</th>
<th>Zn</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTMT</td>
<td>24.48</td>
<td>16.74</td>
<td>10.11</td>
<td>3.49</td>
<td>2.74</td>
<td>2.21</td>
<td>0.45</td>
<td>0.13</td>
<td>0.07</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>+150</td>
<td>23.20</td>
<td>4.48</td>
<td>16.84</td>
<td>5.09</td>
<td>3.40</td>
<td>4.36</td>
<td>0.52</td>
<td>0.32</td>
<td>0.06</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>-150+96</td>
<td>20.67</td>
<td>5.01</td>
<td>18.12</td>
<td>5.12</td>
<td>3.67</td>
<td>4.25</td>
<td>0.37</td>
<td>0.36</td>
<td>0.06</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>-96+74</td>
<td>20.48</td>
<td>7.49</td>
<td>16.82</td>
<td>5.40</td>
<td>3.78</td>
<td>3.52</td>
<td>0.34</td>
<td>0.29</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>-74+48</td>
<td>23.98</td>
<td>14.82</td>
<td>11.45</td>
<td>4.23</td>
<td>2.90</td>
<td>2.12</td>
<td>0.46</td>
<td>0.15</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>-48+38</td>
<td>25.93</td>
<td>19.57</td>
<td>8.27</td>
<td>2.89</td>
<td>2.35</td>
<td>1.52</td>
<td>0.50</td>
<td>0.10</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>-38</td>
<td>26.45</td>
<td>18.05</td>
<td>8.75</td>
<td>3.22</td>
<td>2.38</td>
<td>1.62</td>
<td>0.51</td>
<td>0.10</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### Qualitative mineral compositions

In general, the grinding quality of an ore is highly reliant on the mineral phase composition. Thus, the main minerals of VTMT were determined by X-ray Diffraction (XRD), the results are shown in Fig. 3. VTMT is mainly composed of several metallic minerals and pyroxene phases, characterized by a few powerful diffraction peaks distributed between 22.5° and 60° of 2-theta. The main metallic minerals are ilmenite (FeTiO$_3$), maghemite (γ-Fe$_2$O$_3$) and hematite (Fe$_2$O$_3$), pyroxene phases minerals are diopside ferrian (Ca$_{1.018}$(Mg$_{0.733}$Fe$_{0.293}$)((Si$_{1.67}$Fe$_{0.304}$)O$_6$)), anorthite (Ca(Al$_2$SiO$_8$)). And, small amounts of amorphous phases are also probably present, because there is an unshaped diffusive hump ranging between 5° and 20° of 2-theta. Further investigation of the qualitative mineral composition of VTM by advanced mineral identification and characterisation system (AMICS) is shown in Table 3. It indicates that the VTM consists 9.00 wt.% serpentine, 1.36 wt.% feldspar, 5.15 wt.% quartz and 1.18 wt.% titanite, apart from the significant mineral phases identified by XRD.

### Table 3 Mineral composition of the LVTC wt.%

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ilmenite</th>
<th>Maghemite</th>
<th>Hematite</th>
<th>Diopside</th>
<th>Quartz</th>
<th>Serpentine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>31.71</td>
<td>3.43</td>
<td>7.88</td>
<td>10.40</td>
<td>5.15</td>
<td>9.00</td>
</tr>
</tbody>
</table>

### Micromorphology and distribution characteristics analysis

As target minerals for recovery, the morphology and distribution characteristics of several major metallic minerals were analyzed by optical microscopy and scanning electron microscope (SEM). In addition, the composition of minerals was analyzed by X-ray energy dispersive spectrometer (EDS).

### Micromorphology of ilmenite

Several typical optical microscope images and scanning electron microscopy (SEM) images about micromorphology and distribution of ilmenite in VTMT are shown in Fig. 4, and the elemental content of point A-C was also analyzed by energy dispersive spectroscopy (EDS). According to the elemental composition analysis in the EDS, the areas represented by points
A, B and C are identified as ilmenite, anorthite and titanite, respectively. Microscopically, ilmenite, hematite and gangue such as anorthite take up the major areas in VTMT.

The VTMT contains a lot of ilmenite, which is the main recovered target mineral in this study, and the majority of it are produced in the form of granular and irregular flake monomers (Fig. 4a, Fig. 4d and Fig. 4f). Which demonstrates the feasibility of recovering ilmenite from the VTMT to provide raw material for rutile production. A small amount of ilmenite is associated with gangue (Fig. 4b, Fig. 4e), and a few fine grained ilmenite is occasionally seen wrapped by gangue or associated with hematite (Fig. 4b, Fig. 4c). Trace ilmenite is distributed as flakes and grids in hematite. Therefore, the key to improving the grade of the recovered product is to realize the dissociation of ilmenite from other minerals as far as possible.

**Micromorphology of hematite**

In terms of physical and chemical properties, hematite is most similar to ilmenite in VTMT, and it is also the main major factor hindering ilmenite recovery. Therefore, the micromorphology and distribution of hematite also have been investigated in detail by the optical microscope, SEM and EDS, and some results are shown in Fig. 5.

According to the above qualitative mineral compositions analysis, apart from non-magnetic hematite, a few powerful magnetic hematite is also present in VTMT. However, the low volume and fine particle size of maghemite result in its insignificant appearance in optical microscope images and SEM images. Similar to ilmenite, the majority of hematite are produced in the form of granular and irregular flake monomers (Fig. 5d, Fig. 5e and Fig. 5f). A few hematite is associated with gangue (Fig. 5b), and rarely fine hematite even embedded in it (Fig. 5b, Fig. 5c). Little hematite is produced in association with ilmenite (Fig. 5a). However, in terms of particle size, hematite is obviously smaller than ilmenite. Which further implies that separate recovery of ilmenite and hematite can be achieved from the VTMT by appropriate mineral processing.

**Specific dissociation characteristics**

For clarification of the specific degree of mineral dissociation, the dissociation characteristics of ilmenite and hematite in optical microscope images and SEM images were counted by a line section method, and the results are shown in Table 4 and Table 5, respectively. 1/4, 1/2 and 3/4 in the table represent a region where 25%, 50% and 75% of the ilmenite or hematite particles are embedded in the gangue, respectively. The number of ilmenite particles in the monomer is significantly more than that of hematite, by almost 30%. Which is beneficial to the separate recovery of the two minerals and improves the grade of the recovered product. In terms of trends in the degree of embedding with the gangue, the two minerals are very similar. Minerals embedded in veinstones over large areas are the maximum amount, and the number of particles decreases as the embedded area drops. There is 5.01% ilmenite and 13.93% hematite particles, and more than 3/4 of the area of these mineral particles is embedded in gangue. Which implies that the association of hematite with gangue is much more complex than that of ilmenite. This also means that it is more difficult to recover hematite from VTMT than ilmenite. At the same time, the interconnection between ilmenite and hematite occurred seldom.

<table>
<thead>
<tr>
<th>Monomers Embedded in gangue</th>
<th>Embedded in hematite</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 3/4</td>
<td>1/2 ~ 3/4</td>
<td>1/4 ~ 1/2</td>
</tr>
<tr>
<td>90.27</td>
<td>5.01</td>
<td>1.75</td>
</tr>
<tr>
<td>28.62</td>
<td>1.59</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Table 4

Dissociation characteristics results of ilmenite %
### Table 5

Dissociation characteristics results of hematite %

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Embedded in gangue</th>
<th>Embedded in ilmenite</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt; 3/4</td>
<td>1/2 ~ 3/4</td>
<td>1/4 ~ 1/2</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>62.84</td>
<td>13.93</td>
<td>9.78</td>
<td>5.37</td>
</tr>
<tr>
<td>7.11</td>
<td>1.58</td>
<td>1.11</td>
<td>0.61</td>
</tr>
</tbody>
</table>

### Particle size distribution of minerals

Particle size is an important factor influencing the recovery, therefore the particle size distribution of ilmenite and hematite in the VTMT was investigated and the results are shown in Fig. 6. Obviously, the size of ilmenite and hematite in VTMT is predominantly medium to fine grained. The particle size of ilmenite is concentrated between 20 µm and 104 µm, hematite is concentrated between 15 µm and 104 µm, accounting for 79.27% and 80.09% respectively. Specifically, the quantity of hematite is much more than titanite in -74 µm particles. Which also further validates that ilmenite particle size is larger than hematite, providing guidance for recovery and utilization.

### Elements distribution in minerals

Generally, valuable metals are endowed in various mineral resources in the form of mixed mineral phases, and only very few exist as monomers (Gao et al., 2020). Therefore, in order to further determine the feasibility of valuable metal recovery from VTMT, the distribution of valuable elements in minerals was investigated, and the results for iron and titanium are shown in Tables 6 and 7, respectively. Obviously, Fe mainly exist in ilmenite, hematite and diopside, Ti mainly exist in ilmenite, hematite and titanite. Specifically, 30.74 wt.% of Fe and 3.82 wt.% of Ti exist in hematite, which is divided into strongly magnetic maghemite and weakly magnetic hematite, and the magnetic properties of weakly magnetic hematite are similar to those of ilmenite. Which indicates that the valuable elements in VTMT could not be recovered efficiently by a single magnetic separation. In addition, a percentage of the valuable elements present in gangue such as diopside, anorthite and titanite will be lost. Therefore, the theoretical recovery of Fe and Ti from VTMT is 81.57 wt.% and 97.21 wt.%, respectively.

### Table 6

Distribution analysis of Fe element in minerals wt.%

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ilmenite</th>
<th>Maghemite</th>
<th>Hematite</th>
<th>Diopside</th>
<th>Anorthite</th>
<th>Serpentine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction</td>
<td>50.83</td>
<td>8.09</td>
<td>22.65</td>
<td>13.46</td>
<td>4.83</td>
<td>0.13</td>
</tr>
<tr>
<td>Distribution</td>
<td>11.39</td>
<td>1.81</td>
<td>5.07</td>
<td>3.02</td>
<td>1.08</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Table 7

Distribution analysis of Ti element in minerals (wt.%)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ilmenite</th>
<th>Maghemite</th>
<th>Hematite</th>
<th>Titanite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction</td>
<td>93.39</td>
<td>3.59</td>
<td>0.23</td>
<td>2.79</td>
</tr>
<tr>
<td>Distribution</td>
<td>8.10</td>
<td>0.31</td>
<td>0.02</td>
<td>0.24</td>
</tr>
</tbody>
</table>

### Grinding characteristics
Figure 7 shows the particle size distribution of VTMT after grinding for 2 ~ 10 min. When grinding for 2 min, the coarse particles of VTMT (74 ~ 96 µm, 96 ~ 150 µm and > 150 µm) could hardly be found. On the contrary, the number of fine VTMT particles (< 38 µm) increases sharply, and this phenomenon is particularly prominent in the first 6 min of grinding. Above results show that VTMT is an easily ground material, it can be dissociated by simple grinding without significant energy waste. Which is maybe attributed to the mineral composition and desirable conjoining mechanism in the VTMT. In addition, after 4 min of grinding, the number of 48 ~ 38 µm VTMT particles increases from 19.66–33.34%, then decreases with the increase of grinding time. This suggests that VTMT grinding is a step-by-step procedure, with the first 4 min mostly for coarse particles, followed by medium and fine particles. For economic and subsequent recycling purposes, the recommended grinding duration is 4 ~ 6 min.

Proposed flow sheet

The above chemical and process mineralogical analysis results indicate that the VTMT is a very potential by-product to be utilized, containing some amount of valuable metal elements such as titanium and iron. Moreover, the majority of iron and titanium are located in ilmenite and hematite. However, the VTMT also contains a large amount of anorthite, diopside, and serpentine et al., and a portion of ilmenite and hematite is embedded in the gangue, which is the main reason that hinders the utilization of the VTMT. Therefore, in order to obtain an efficient recovery of valuable elements, a treatment process including ball milling – high-intensity magnetic separation – one roughing and three refining flotation was proposed, and the flow chart is shown in Fig. 8.

The purpose of ball milling is to increase the dissociation of target minerals such as ilmenite and hematite from the gangue as much as possible, and then to separate the gangue and weak magnetic minerals by high-intensity magnetic separation. The grades of TiO$_2$ and TFe in the obtained magnetic minerals were increased to 20.02% and 24.80%, respectively. Then, the following flotation is to separate and recovery minerals such as TiO$_2$-rich ilmenite and Fe-rich hematite. After a roughing flotation step, the content of TiO$_2$ and TFe were significantly improved, reached 35.96% and 31.04%, respectively. However, the roughing tailings yield is unimpressive, indicating that there is potential for continued improvement. After three refining flotation steps, a concentrate with TiO$_2$ grade of 47.31% and TFe grade of 35.44% was produced. Finally, TiO$_2$ and TFe had recovery rates of 57.71% and 28.23%, respectively.

Conclusions

In this study, the chemical and process mineralogical characterization of VTMT were investigated in detail by various analytical techniques such as XRF, XRD, optical microscope, SEM, EDS and AMICS et al. It was found that VTMT is coarser powder in general, about 50% of the particle size is greater than 54.30 µm. The total iron content of the VTMT was 22.40 wt.%, and its TiO$_2$ grade is 14.45 wt.%, even higher than those found in natural ilmenite ores. The majority of iron and titanium were located in ilmenite and hematite, 62.84% and 90.27% of hematite and ilmenite were present in monomeric form. However, there is still a portion of ilmenite and hematite embedded in gangue such as anorthite, diopside, and serpentine et al., which is the main reason that hinders the utilization of the VTMT. Then, for the recovery of valuable fractions such as Fe and TiO$_2$ from VTMT, a treatment process including ball milling – high-intensity magnetic separation – one roughing and three refining flotation was proposed. Finally, a concentrate with TiO$_2$ grade of 47.31% and TFe grade of 35.44% was produced. Meanwhile, TiO$_2$ and TFe had recovery rates of 57.71% and 28.23%, respectively.

Declarations

Ethics approval We declare that current research fully abides by both local and international guidelines of ethical research regulations.

Consent to participate Not applicable
Consent for publication All authors have explicit consent to publish this article submitted to ESPR.

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions Jinsheng Liu: investigation, writing—original draft, data collection and validation; Zhenxing Xing: data analysis; Jianxing Liu: resources and methodology; Xueyong Ding: project administration and supervision; Xiangxin Xue: conceptualization, project administration and supervision. Both authors read and approved the final manuscript.

Data availability The data is publically available, and all source of data used in this research is given in the manuscript.

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References


**Figures**

Figure 1

Process flow diagram of VTMT source
Figure 2

Particle size distribution of VTMT: (a) differential curve, (b) cumulative curve

A: Anorthite (Ca(Al₂SiO₈))  
D: Diopside ferrian, syn (Ca₁.₀₁₈(Mg₀.₇₃₃Fe₀.₂₈₆)(Si₁.₆₇₇Fe₀.₃₀₄)O₆))  
H: Hematite (Fe₂O₃)  
I: ilmenite (FeTiO₃)  
M: Maghemite-C, syn (γ-Fe₂O₃)

2-Theta, degree
Figure 3

X-ray diffraction patterns of VTMT

Figure 4

Micromorphology and distribution of ilmenite in VTMT; (a)-(c) optical microscope images, (d)-(f) SEM images, and EDS of point A-C
Figure 5

Micromorphology and distribution of hematite in VTMT; (a)-(c) optical microscope images, (d)-(f) SEM images, and EDS of point A-C
Figure 6
Particle size distribution of ilmenite and hematite; (a) content of distribution, (b) cumulative amount.

Figure 7
Particle size distribution of VTMT after grinding for different times
Figure 8

Numerical quality flow chart of recovery valuable elements from VTMT