New Insights into the Penetration Depth of Sulfuric Acid and Leaching Effect in the Sulfuric Acid Curing-Leaching Process of Vanadium-Bearing Stone Coal

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ABSTRACT: In the process of sulfuric acid curing-leaching vanadium-bearing stone coal, the curing effect is very important. The main purpose of this study is to capture the difference in the curing effect between coarse and fine stone coal, with a V_2O_5 content of 0.88%. In this work, the effects of various factors such as sulfuric acid concentration, curing time, curing temperature, and different agents for curing on the leaching efficiency of vanadium were investigated by the comparison of the two size fractions. The results showed that the leaching efficiency of vanadium was 87.65% under the optimum curing conditions of 25 wt % sulfuric acid, curing time of 8 h, and curing temperature of 130 °C. It was clearly found that, under the same curing condition, the curing effect of fine stone coal was better than that of coarse stone coal. The penetration part of stone coal particles by sulfuric acid was loose, while the non-penetration part was dense after acid curing. Moreover, the penetration depth of sulfuric acid into the particles was mainly 0.5–0.7 mm on average. There was more sericite/illite in coarse leaching residues, which were mostly dense and hard carbonaceous siliceous slate. Thus, sulfuric acid was difficult to penetrate into and reach the interior of the particle, which resulted in that the leaching efficiency of coarse vanadium-bearing stone coal ore was lower than that of fine vanadium-bearing stone coal ore.

1. INTRODUCTION

According to incomplete statistics, 87% of vanadium resources in China exist in stone coal mine.¹ Stone coal is a unique and advantageous vanadium mineral resource in China with huge reserves, while the reserves of stone coal in other countries in the world are relatively small.² Because of vanadium-bearing stone coal, China ranks first in the world in vanadium reserves. Studies on vanadium extraction from stone coal started from the 1960s in China.³⁴ Traditionally, vanadium is recovered mainly by roasting followed by leaching. However, a large amount of polluting gas is produced during roasting, and a great quantity of energy is consumed. In addition, the traditional roasting-leaching process is highly complicated and results in a low recovery of vanadium. Therefore, it is an urgent need to optimize and upgrade the process.

With the development and progress of vanadium extraction technology, the direct acid leaching method has always occupied a certain proportion in the industry and showed its advantages, which is widely used in many mineral extractions and other fields.⁵⁻¹⁰ However, this process can only adapt to the vanadium-bearing stone coal with high valence and adsorption state of vanadium, and the effect of direct leaching on mica type vanadium-bearing stone coal in China is not very good.¹¹ At present, the sulfuric acid curing-leaching process has become one of the hot spots in vanadium extraction research, which has the advantages of low energy consumption, low pollution, and high efficiency. Using concentrated sulfuric acid as reactants, nickel and cobalt were extracted from the low-grade nickel laterite by the sulfuric acid curing-roasting process and the sulfation degree reached 75% and 90%, respectively.¹² A novel method was proposed to regenerate spent graphite (SG) via a combined sulfuric acid curing, leaching, and calcination process, and the purity of regenerated graphite can reach 99.6%.¹³ The low-grade zinc oxide ore with
high silica was treated through the process of sulfuric acid curing and water leaching, obtaining a zinc recovery of 99.22% and the dissolution of silica of 0.56%, indicating that a good separation of zinc from silica was reached. Therefore, the sulfuric acid curing-leaching process has been found to be the most versatile in most part of the commercial plant.

Especially, the application of the low temperature sulfuric acid curing-leaching process in vanadium-bearing stone coal is a great progress. According to the method, most refractory vanadium-bearing stone coal can be effectively treated by water leaching after heat preservation and curing. The reaction temperature in the curing process is low, with little carbon decomposed and short curing reaction time; thus, the production efficiency can be obviously improved. Therefore, further study on the curing effect of this process is the key.

Currently, muscovite is the primary vanadium-bearing mineral in stone coal with $V^{5+}$ substituting $Al^{3+}$ from the dioctahedral structure as isomorphism in muscovite. Therefore, in order to extract vanadium, the muscovite structure must be destroyed with sulfuric acid curing and then release vanadium. At a certain temperature and acidity, hydrogen must be destroyed with sulfuric acid curing and then release dioctahedral structure as isomorphism in muscovite. There-
as the temperature increased from 130 to 150 °C. When the temperature was 130 °C, vanadium leaching efficiency was 87.31%, producing the best conditions for vanadium leaching. Therefore, the optimal temperature is selected to be 130 °C.

It can also be seen from Figure 2 that the grade and recovery of the +1.5 mm leaching residue were considerably higher than those of the −1.5 mm leaching residue across the whole temperature range tested. The results indicate that temperature also had different curing effects on the coarse and fine stone coal. Obviously, the curing effect of coarse grains is slightly worse.

2.1.3. Effects of Curing Time. Figure 3 shows the effect of different curing times on vanadium leaching. As the curing time ranged from 5 to 8 h, the leaching efficiency of vanadium increased gradually, whereas the leaching efficiency decreased slightly as the time was prolonged to 11 h. The rapid increase in vanadium leaching efficiency was mainly due to the high curing temperature and sufficient sulfuric acid, which ensured the rapid diffusion of sulfuric acid to sericite particles, which was conducive to the decomposition of sericite/illite and the release of V(III). When the curing time is extended to 8 h, as long as the external conditions do not change, this balance will not be broken, and the macro-performance is that the vanadium leaching efficiency does not change significantly with the extension of time. This is because the cured samples could be dried in a prolonged time, which decreases the activity of the cured samples and makes the metal ions difficult to leach. Almost the leaching efficiency of vanadium reached the highest value at a curing time of 8 h, which could be selected as the optimal curing time.

Equally, both the grade and recovery of the +1.5 mm leaching residue were considerably higher than those of the −1.5 mm leaching residue across the whole curing time range tested. Even if the curing time was prolonged properly, sulfuric acid was difficult to get inside the coarse particles to react, which may be due to the dense internal structure of coarse particles. The curing time of leaching vanadium from stone coal is one of the important factors affecting vanadium conversion. If the curing time is too short, the conversion of low valent vanadium is not enough; if the curing time is too long, the energy consumption will be increased and the production efficiency will be affected.

2.1.4. Effects of Different Additives for Curing. In recent years, fluorides such as HF and CaF₂ have been proposed as leaching aids for sulfuric acid leaching.HF and CaF₂ can markedly boost the efficiency and accelerate the rate of vanadium leaching from stone coal. To investigate the effect of different additives for curing, experiments were carried out by adding 2 wt % HF (the concentration of HF is 40 wt %) and 3 wt % CaF₂.

As shown in Figure 4, when HF was introduced into the leaching system, the leaching efficiency could reach 88.45%, which was 0.81% slightly higher than that of H₂SO₄ (87.64%) alone. Also, the leaching efficiency was 87.27% while CaF₂ was added. The results implicate that there was no obvious change in the leaching efficiency of vanadium with additives. Hence, there is no need to add extra agents in the curing process.

2.2. Analysis of Leaching Efficiency of Vanadium with Different Size Fractions under the Optimum Conditions. From the above curing tests, it can be seen that the grade and recovery of the coarse leaching residue were generally lower than those of the fine leaching residue, which indicates that the curing effect of the coarse-grained leaching residue was worse than that of the fine-grained leaching residue. According to the investigation and discussion above, the optimum curing conditions were as follows: initial curing H₂SO₄ concentration of 25 wt %, curing temperature of 130 °C, and curing time of 8.0 h. Under the above optimum curing conditions, the curing-leaching test was carried out, and the leaching residue was screened and analyzed. The results (excluding residue yield loss) are shown in Figure 5. It is

![Figure 2](https://doi.org/10.1021/acsomega.1c02109)
Figure 2. Effect of curing temperature on vanadium leaching (m(ore) = 910.0 g, m(water) = 90.0 g, C(H₂SO₄) = 25%, t = 8 h).

![Figure 3](https://doi.org/10.1021/acsomega.1c02109)
Figure 3. Effect of curing time on vanadium leaching (m(ore) = 910.0 g, m(water) = 90.0 g, T(curing) = 130 °C, C(H₂SO₄) = 25%).

![Figure 4](https://doi.org/10.1021/acsomega.1c02109)
Figure 4. Effect of different additives for curing on vanadium leaching (m(ore) = 910.0 g, m(water) = 90.0 g, C(H₂SO₄) = 25%, C(HF(40%)) = 2%, C(CaF₂) = 3%, t = 8 h).
clearly found that the leaching efficiency of vanadium tended to increase with the decrease in particle size, which was consistent with the change in vanadium grade of raw ore, contrary to the change in vanadium grade of the leaching residue. This detailed result shows that, for coarse-grained vanadium ore, maybe it was difficult for sulfuric acid to reach the inside of the particles during curing, resulting in poor leaching effect. Hence, it is necessary to continue to analyze the root cause of the low leaching efficiency of vanadium.

2.3. Distribution Relationship between Vanadium and Sericite/Illite in the Leaching Residue with Different Particle Sizes.

In view of the fact that sericite/illite in −3 mm leaching residues is difficult to observe, the −6+3 mm leaching residue and +6 mm leaching residue were detected and analyzed by SEM. Figure 6 shows the results. It can be seen from Figure 6 that the vanadium grade in +6 mm leaching residue was mainly carbonaceous siliceous slate just because it was dense and hard to crush, and the mineral composition was mainly quartz, followed by sericite/illite, barite, etc.

As displayed in Table 1, there was just only 0.02% vanadium in Figure 6a,b while 0.08% and 0.07% in Figure 6c and Figure 6d, respectively, which shows that there was relatively more vanadium where there was sericite/illite, while there was less vanadium where sericite/illite was absent. Thus, the content of vanadium was closely related to the distribution of sericite/illite. This also confirms that vanadium existed in sericite/illite in isomorphic form. Furthermore, the destruction of the sericite/illite structure represents the leaching of vanadium.

2.4. Change in Vanadium Content in Coarse Leaching Residue Particles.

Because sericite/illite was unevenly distributed and a few particles were observed, the leaching residue particles with a size of +10 mm were continuously observed and analyzed by SEM. Then, the observed sericite/illite was analyzed by EDS several times. The results are shown in Figure 7 and Table 2.

![Figure 5. Comparison of leaching results of vanadium-bearing stone coal with different particle sizes.](image1)

![Figure 6. SEM of leaching residues with different particle sizes: (a, b) −6+3 mm and (c, d) +6 mm leaching residues.](image2)

Table 1. EDS Analysis Results of Leaching Residues with Different Particle Sizes (wt %)

| elements | O   | Al  | Si  | K   | V   | remark            |
|----------|-----|-----|-----|-----|-----|------------------|
| Figure 6a| 50.07 | 0.50 | 49.33 | 0.09 | 0.02 | almost no sericite/illite could be found |
| Figure 6b| 49.22 | 0.52 | 50.14 | 0.10 | 0.02 |
| Figure 6c| 50.01 | 0.55 | 49.24 | 0.12 | 0.08 | sericite/illite could be found |
| Figure 6d| 49.55 | 0.51 | 49.73 | 0.14 | 0.07 |

![Figure 7. BSE of the +10 mm leaching residue: (a−d) +10 mm leaching residue.](image3)

As displayed in Figure 7, sericite/illite (the white area) can be clearly observed in the leaching residue, which was white, slender, and flaky in Figure 7. Therefore, it is obvious that the vanadium-bearing minerals in the residue particles were mainly sericite/illite, which was mostly in the form of small scales, with a slice diameter of <0.01 × 0.005 mm and a maximum of 0.04 × 0.01 mm in some cases. They were very unevenly distributed among quartz grains, wrapped in quartz, or...
Table 2. EDS Analysis Results of Sericite/Illite in +10 mm Leaching Residue Particles (%)

| elements | O   | Al  | Si  | K   | V   |
|----------|-----|-----|-----|-----|-----|
| Figure 7c spot 1 | 47.42 | 4.24 | 41.30 | 1.92 | 5.12 |
| spot 2    | 45.73 | 4.49 | 43.71 | 2.53 | 3.54 |
| spot 3    | 48.22 | 8.85 | 38.30 | 3.74 | 0.90 |
| average   | 47.57 | 4.76 | 41.30 | 2.39 | 3.98 |
| Figure 7d spot 1 | 46.40 | 4.24 | 41.26 | 3.03 | 5.08 |
| spot 2    | 38.40 | 7.11 | 44.59 | 5.68 | 4.22 |
| spot 3    | 47.57 | 4.76 | 41.30 | 2.39 | 3.98 |
| average   | 44.15 | 5.32 | 42.35 | 3.70 | 4.48 |

distributed along rock fissures and voids. The distribution of sericite/illite was not uniform, and the particle size was very fine. In order to dissociate vanadium-bearing minerals with associated minerals, higher grinding fineness is needed.

In addition, the EDS results of sericite/illite (Table 2) show that the sericite/illite generally contained vanadium, but the content varied from 0.30% to 13.33%. It shows that the leaching effect of the coarse leaching residue was not good enough. Meanwhile, fine sericite/illite distributed among quartz grains had different vanadium contents in different parts of the same grain. Quantitative analysis by EDS shows that the white area (spot 1, spot 2, and spot 3) in Figure 7c consisted of O, Al, Si, K, V, and V with contents of 5.12%, 3.54%, and 0.9%, respectively; similarly, in the white area (spot 1, spot 2, and spot 3) in Figure 7d, V with contents of 5.08%, 4.22%, and 3.98%, respectively. We can clearly observe this finding from Figure 7, which was the higher the vanadium content, the brighter the white color.

2.5. Depth Analysis of Sulfuric Acid Permeated the Curing Granules. In order to find out the depth of sulfuric acid entering into the curing particles, the +6 mm leaching residue particles were specially selected, and the samples were prepared by grinding under the condition of drying (to prevent the loss of sulfuric acid). Then, the penetration depth of sulfuric acid was observed and measured by SEM.

It can be seen from the results in Figure 9 that the penetration depth of sulfuric acid varies greatly, about 140–2000 μm, and most of them are 500–700 μm. In Figure 9, the green scale was the penetration depth of sulfuric acid. Obviously, the permeated part of stone coal particles by sulfuric acid was loose, while the non-permeated part was dense. This difference can be clearly observed in Figure 9 through the depth of color. In addition, there was a few or almost no vanadium-bearing sericite/illite in the sulfuric acid penetration parts. However, the dissemination characteristics of vanadium-bearing minerals were the same as those of raw ore and leaching residue particles in the part not permeated or partially permeated.

In order to analyze the element difference between the loose and dense parts, the EDS was carried out. Table 3 shows that the content of S in the loose part permeated by sulfuric acid is 9.14%, while it is 0.39% in the dense part and the part almost without sulfuric acid penetration, which shows that the loose part has been permeated by sulfuric acid, and the dense part has not been permeated. Therefore, in order to leach vanadium from vanadium-bearing minerals, sulfuric acid needs to completely permeate in the particles. However, it is very difficult because the carbonaceous siliceous slate was dense and hard, and the particle size of vanadium-bearing minerals is very fine.

Combined with the above results, the +1.5 mm coarse leaching residue was mostly dense carbonaceous siliceous slate with low vanadium content. During the curing process, sulfuric acid permeated in particles for 0.5–0.7 mm on average, so the effective crushing particle size should be less than 1.5 mm.

Figure 8. Statistical chart of sericite/illite in leaching residue particles with a size of +6 mm.
Figure 9. BSE of sulfuric acid penetration depth analysis of cured particles. Note that dark gray (scale) refers to the permeated part of sulfuric acid; light gray refers to the non-penetration part of sulfuric acid, the same below: (a−h) +6 mm leaching residue.

Table 3. EDS Analysis of Different Parts in Leaching Residue Particles (%)

| elements                        | O   | Na | Mg | Al  | Si  | S   | Cl  | K   | Ca  | Cr  | Fe  |
|---------------------------------|-----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|
| relatively loose (the part penetrated by H₂SO₄) | 35.33 | 0.76 | 1.28 | 2.98 | 42.43 | 9.14 | 1.25 | 1.02 | 3.20 | 3.09 | 2.43 |
| relatively dense (the site unreached by H₂SO₄)   | 46.17 | 0.00 | 0.07 | 7.85 | 45.21 | 0.39 | 0.00 | 0.00 | 0.18 | 0.07 | 0.07 |
3. FURTHER DISCUSSION

The curing process is done at atmospheric pressure, and the acid mist can be recycled by recycling, so it has a good development prospect. The sulfuric acid curing-leaching method has been utilized in vanadium separation of vanadium-bearing stone coal, which mainly occurs in mica aluminosilicate minerals. There are many influencing factors on curing, which is closely related to the leaching efficiency of vanadium. According to the results of the curing process, it is found that the leaching efficiency of coarse vanadium-bearing stone coal ore was lower than that of fine vanadium-bearing stone coal ore. Regarding the difference of leaching efficiency between coarse and fine vanadium-bearing stone coal, a graphical representation (Figure 10) reveals a possible curing process of sulfuric acid on vanadium-bearing stone coal ore with different particle sizes based on both the acid leaching results and the SEM analysis.

In the curing, sulfuric acid first contacted the surface of vanadium-bearing mineral particles and then gradually penetrated in them. For fine particles, sulfuric acid can approach or reach the center of the particles after a long time of heat preservation at 130 °C. As a result, the leaching effect of vanadium was better and the leaching efficiency was higher. However, for coarse particles, sulfuric acid cannot reach the center of particles, resulting in poor leaching effect and low leaching efficiency of vanadium; hence, more sericite/illite can be observed. The reason might be that most of the coarse leaching residues were carbonaceous siliceous slate, which was dense and hard, which made it difficult for sulfuric acid to penetrate into and reach the interior of the particles. Therefore, in order to improve the leaching efficiency, we need to reduce the crushing fineness. However, considering the cost, it is not economical. Therefore, maybe we need to think of other ways to strengthen and optimize the curing process.

4. CONCLUSIONS

Based on the results of this investigation, the following conclusions can be drawn:

1. In this study, sulfuric acid curing and water leaching were used to treat vanadium-bearing stone coal. The results show that the optimum curing conditions were as follows: initial curing H₂SO₄ concentration of 25 wt %, curing temperature of 130 °C, and curing time of 8.0 h, while the leaching efficiency of vanadium is 87.64%.
2. The penetration part of stone coal particles by sulfuric acid was loose, while the non-penetration part was dense. Furthermore, the content of S in the loose part was higher than that in the dense part. The penetration depth of sulfuric acid into particles was 0.5–0.7 mm on average. Thus, the effective crushing particle size should be less than 1.5 mm.
3. Where there was sericite/illite in the leaching residue, there was vanadium. Also, there was more sericite/illite in the coarse leaching residue. Most of the coarse leaching residues were carbonaceous siliceous slate, which was dense and hard, which made it difficult for sulfuric acid to penetrate into and reach the interior of the particles. Therefore, the leaching efficiency of coarse vanadium-bearing stone coal ore was lower than that of fine vanadium-bearing stone coal ore.

5. MATERIALS AND METHODS

5.1. Raw Materials. Vanadium-bearing stone coal used in this study was generated by crushing and grinding (0–3 mm) from ore dressing Plant, Shaanxi Province, China. The obtained ore with a grain size of ~3 mm was the sample used in this work, which was referred to as raw ore throughout this study. Concentrated sulfuric acid (Offered by Qiming Chemical Co., Ltd., China) used was industrial grade throughout this study.

Photos of vanadium-bearing ore are listed in Figure 11. Vanadium mainly existed in purplish red argillaceous slate and gray white argillaceous slate and relatively small in (containing) carbonaceous siliceous slate.

The chemical composition of the raw ore was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 4300DV, PerkinElmer, Boston, MA, USA). The results are listed in Table 4. The vanadium content in raw ore (based on V₂O₅, the same below) was 0.88%. The main gangue component was SiO₂ with a content of 79.35%.

| SiO₂ | K₂O | Na₂O | Al₂O₃ | CaO | MgO | TiO₂ |
|------|------|------|--------|-----|-----|------|
| 79.35 | 1.13 | 0.01 | 3.75 | 2.72 | 1.49 | 0.21 |
| SO₂ | BaO | TiO₂ | MnO | P₂O₅ | V₂O₅ | LOI |
| 0.72 | 1.91 | 3.00 | 0.01 | 0.51 | 0.88 | 4.86 |

The phase and valence state of vanadium are presented in Table 5 and Table 6, respectively. We can see from Table 5...
that vanadium mainly existed in aluminosilicate, then in free oxide, and little in carbonaceous. Moreover, as seen in Table 6, the results show that V(III) was dominant, accounting for 77.72%, V(IV) accounted for 22.28%, and V(V) was not found in the raw ore, which was basically consistent with the results in the existing literature. V(III) was distributed in the form of isomorphism in aluminosilicate sericite/illite, followed by limonite, montmorillonite, kaolinite, and vanadium titanium ore.

The pattern analysis was identified by X-ray diffraction (XRD, D/MAX 2500PC, Rigaku, Tokyo, Japan) using Cu-Kα radiation. Figure 12 indicates that the main minerals in the vanadium-bearing shale were quartz, sericite/illite, and clay minerals (montmorillonite and kaolinite). Figure 13 shows the screening results of the raw ore sample.

5.2. Experimental Procedure. Schematic diagram of the experimental setup of the V leaching process is shown in Figure 14. The procedure is described as follows.

5.2.1. Curing. First, 910 g of the raw ore (dry weight) and a certain amount of water were placed in a corundum crucible with a volume of 2 L and mixed completely. Next, the crucible was placed in a muffle furnace, and the curing experiment was conducted at a required temperature for a certain period of time. After curing, the cured product was placed at room temperature for a period of time, and the cured ore was obtained.

5.2.2. Water Leaching. The cured ore was leached in water of 600 mL for 1.0 h at a temperature of 55 °C. After leaching for 1.0 h, the slurry was filtered and washed with water four times, and then solid–liquid separation was carried out to obtain the leaching residue. Then, the leaching residue was screened with a 1.5 mm sieve to obtain +1.5 mm and −1.5 mm leaching residues. Finally, the leaching residues of +1.5 mm and −1.5 mm were sent to test the vanadium content.

5.3. Experimental Mechanism. In aluminosilicate minerals, V(III) usually takes the place of Al(III) and Fe(III) in the silicon oxygen tetrahedral “complex network layer” and aluminum oxygen octahedral “single network layer” in the form of isomorphism to enter the mica lattice. The purpose of roasting is to transform the non-water-soluble V compounds to water-soluble vanadate. At high temperatures, a certain concentration of sulfuric acid can destroy the structure of mica and let hydrogen ions into the mica lattice under the condition of heat preservation, thus changing the ion radius and releasing vanadium in the lattice. Moreover, in the oxidation atmosphere, V(IV) and V(V) were further converted into soluble V(IV) and V(V) to obtain vanadium-containing solutions so as to achieve the purpose of leaching vanadium from ore.

The main chemical reactions of vanadium extraction from stone coal by sulfuric acid curing-leaching are as follows:

\[
(V_2O_5)X \cdot X + 2H_2SO_4 + \frac{1}{2}O_2 = V_2O_2(SO_4)_2 + 2H_2O + X
\]

\[
V_2O_2(OH)_2 + 2H_2SO_4 = V_2O_2(SO_4)_2 + 4H_2O
\]

\[
V_2O_3 + H_2SO_4 = (VO_2)_2SO_4 + H_2O
\]

where X represents the mica structure in the ore.

H_2O was formed in all the above reactions. H_2O from curing and heat preservation will enhance the permeability of sulfuric acid in aluminosilicate minerals and strengthen the decomposition process. The product of sulfuric acid curing is soluble sulfate. The cured sample was heated by adding water.

Table 5. Analysis Results of Vanadium Phase in Raw Ore (wt %)

| vanadium phase | vanadium in free oxides (V₂O₅) | vanadium in aluminosilicate (V₂O₅) | total |
|---------------|---------------------------------|-------------------------------------|-------|
| content       | 0.31                            | 0.51                                | 0.88  |
| distribution  | 35.23                           | 57.95                                | 100.00|

Table 6. Valence State of Vanadium in Raw Ore (wt %)

| valence state | V(III) | V(IV) | V(V) | total |
|---------------|--------|-------|------|-------|
| content       | 0.68   | 0.19  | 0.19 | 0.87  |
| distribution  | 77.72  | 22.28 | 100  |       |

Figure 12. X-ray diffraction (XRD) analysis of raw ore.
and stirred to leach. Vanadium was transferred into the solution in the form of ion.

5.4. Data Treatment. The curing effect mainly refers to the valence conversion rate of vanadium in the sample, which directly determines the vanadium leaching efficiency. Therefore, the leaching efficiency is generally used as the index to measure the curing effect.

The recovery rate ($\varepsilon_{+1.5}$ and $\varepsilon_{-1.5}$) and the leaching efficiency ($\eta$) were calculated by eqs 4–6, respectively.

$$
\varepsilon_{+1.5} = \frac{\beta_{+1.5}}{\alpha} \times 100% 
$$

(4)

$$
\varepsilon_{-1.5} = \frac{\beta_{-1.5}}{\alpha} \times 100% 
$$

(5)

$$
\eta = 100% - \varepsilon_{+1.5} - \varepsilon_{-1.5} 
$$

(6)

where $\alpha$ is the mass of raw ore (g); $\beta_{+1.5}$ and $\beta_{-1.5}$ are the mass of +1.5 mm and −1.5 mm leaching residues, respectively (g); and $\beta_{+1.5}$ and $\beta_{-1.5}$ are the grade of +1.5 mm and −1.5 mm leaching residues, respectively (%).

5.5. Analytical Methods. 5.5.1. Analysis and Detection Methods of Vanadium. The content of vanadium in the test was analyzed by titration with ammonium ferrous sulfate.28

The solid sample was melted with Na$_2$O$_2$ and then soaked with hot water and boiled with sulfuric acid (the liquid sample was titrated with ammonium ferrous sulfate standard solution).

Potassium permanganate was used to oxidize vanadium to a high valence state. In the presence of urea, excess potassium permanganate was decomposed by sodium nitrite. At last, it was titrated with ammonium ferrous sulfate standard solution with benzo-o-benzoic acid as an indicator.29

5.5.2. Analysis of Micro-Morphology and Micro-Composition. The surface morphologies and elemental analysis of leaching residues were observed by secondary electron imaging and backscattered electron imaging (BSE) using a Quanta 650 scanning electron microscope (FEI, Hillsboro, USA) coupled with a double X-ray spectrometer (AMETEK, Inc., Berwyn, USA) for electron image acquisition and elemental analysis, respectively. The following are the working parameters: acceleration voltage of 30 kV, resolution of 3.0 nm, and magnification of 8–300,000 times.30,31

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