Mechanism of Novel K₂SO₄/KCl Composite Roasting Additive for Strengthening Vanadium Extraction from Vanadium–Titanium Magnetite Concentrate

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Abstract: In this paper, a novel K₂SO₄/KCl composite roasting additive was used to extract vanadium from vanadium–titanium magnetite concentrate. Further, the mechanism of K₂SO₄/KCl for extracting vanadium was studied. The results indicate that the vanadium leaching efficiency reached 82.04%, an increase of 7.43% compared to that of single K₂SO₄ and 10.05% compared to single KCl under the following conditions: a total dosage of K₂SO₄/KCl of 7 wt% with a mass ratio of 6/4, a roasting temperature of 950 °C, a roasting time of 1 h, a leaching temperature of 95 °C, a sulfuric acid concentration of 10% (v/v: volume percentage), and a leaching time of 1.5 h with a liquid-to-solid ratio of 3 mL/g. Moreover, crystal chemistry analyses indicated that the essence of the vanadium extraction with roasting was the conversion of cubic crystal systemic vanadium-bearing magnetite (FeO(Fe,V)₂O₃) to trigonal crystal systemic hematite (α-Fe₂O₃), and as most Fe(V)–O bonds were broken with the reconstructed conversion, the dissociation of V(III) occurred. Furthermore, the main decomposition products of K₂SO₄/KCl were K₂O, SO₂, and Cl₂. X-ray diffraction (XRD) and related SEM-EDS analyses indicated that there were mainly three aspects in the mechanism of K₂SO₄/KCl for extracting vanadium. Firstly, activated K₂O could combine with vanadium to generate soluble KVO₃ rather insoluble Ca(VO₃)₂; secondly, SO₂ could react with CaO to form CaSO₄ to prevent the generation of acid-consuming Ca(VO₃)₂, which was beneficial to the dissolution of vanadium-bearing sphene (Ca(Ti,V)SiO₄O); thirdly, Cl₂ could destroy the structure of hematite (Fe₂O₃) to reduce its wrapping extent to KVO₃.

Keywords: vanadium–titanium magnetite; vanadium extraction; composite roasting additives; K₂SO₄/KCl; mechanism

1. Introduction

Vanadium is an important rare metal that plays important roles in the steel, aviation, chemical, battery, medicine, and other industries due to its superior characteristics [1–5]. China’s vanadium resources mainly exist in two forms: vanadium-containing shale and vanadium–titanium magnetite [6]. Vanadium–titanium magnetite is widely distributed in China with a huge reserve and thus has a high utilization value [7].
In recent years, many new vanadium–titanium magnetite deposits were found in Chao-yang, China. Because it has unique features for its higher grade of vanadium and titanium and lower grade of iron [8], it is more suitable for the direct vanadium extraction process rather than the traditional direct iron-making and indirect vanadium extraction process [8–11].

The roasting process is essential to the release and extraction of vanadium, and the effect of the roasting process influences the recovery of vanadium [12,13]. Generally, in order to strengthen the effect of the roasting process, roasting additives are introduced [14]. However, there are many problems with traditional sodium salt and calcium salt additives [15–17].

To solve the abovementioned problems, in our previous work, novel potassium salt roasting additives were proposed, which proved to be significantly more efficient than traditional sodium and calcium salts in extracting vanadium from the vanadium–titanium magnetite concentrate; in particular, K$_2$SO$_4$ worked the best [18]. The generation of insoluble Ca(VO$_3$)$_2$ led to the lower vanadium leaching efficiency of calcium salt roasting, and the stronger reactivity of K$_2$O compared to Na$_2$O resulted in the higher vanadium leaching efficiency of potassium salt roasting than sodium salt roasting [18–20]. However, the optimal vanadium leaching efficiency was merely 71.37% of single K$_2$SO$_4$ salt roasting under suitable conditions [18]. Thus, there is still a great possibility of improving the vanadium leaching efficiency. Generally, compared to a single additive, composite additives have been considered to work better in extracting vanadium due to the synergistic effect [14,21]. Furthermore, the deeper mechanism of vanadium extraction needs to be explained, such as the essence of vanadium extraction with roasting and the rule of vanadium migration and transformation.

In this paper, several other roasting additives were mixed with K$_2$SO$_4$ to obtain composite roasting additives to further improve the vanadium leaching efficiency. Also, crystal chemistry analyses were performed to explain the essence of vanadium extraction with roasting, and phase transformation analyses were also studied to determine the mechanism of composite additives for strengthening vanadium extraction from vanadium–titanium magnetite concentrate.

2. Experimental

2.1. Materials

The vanadium–titanium magnetite ore used in the experiment was from Chao-yang, China. After crushing and grinding, the particle size of the ore was $\sim$0.074 mm, accounting for 65% of the total particle size. The ore was concentrated by weak magnetic separation according to our previous work [8] to obtain the concentrate. All reagents (K$_2$SO$_4$, K$_2$CO$_3$, KCl, and sulfuric acid) used in the test were of analytical grade.

The results of the main chemical composition of the concentrate are illustrated in Table 1, and chemical phase analyses of vanadium in the concentrate, which was measured by sequential extraction procedures [22], are illustrated in Table 2. The X-ray diffraction (XRD) pattern of the concentrate is illustrated in Figure 1. Table 1 shows that the iron grade of the concentrate is low, while the grade of vanadium and titanium is relatively high, and the grade of vanadium is above 1%. Table 2 shows that the main vanadium-bearing minerals are magnetite (FeO(Fe,V)$_2$O$_3$) and sphene (Ca(Ti,V)SiO$_4$O) [8]. Figure 1 also shows that the main minerals in the concentrate include magnetite, ilmenite, and sphene.

| Table 1. Analyses of main chemical composition of the concentrate wt %. |
|-----------------|---------|---------|---------|---------|---------|---------|---------|---------|
| Element         | V$_2$O$_5$ | TiO$_2$ | TFe     | SiO$_2$ | Al$_2$O$_3$ | CaO     | MgO     | SO$_3$  | P$_2$O$_5$ |
| Content         | 1.10     | 19.72   | 44.2    | 9.85    | 3.14       | 4.71    | 0.78    | 0.065   | 0.062      |

| Table 2. Chemical phase analyses of vanadium in the concentrate wt %. |
|-----------------|---------|---------|---------|
| Vanadium Phase  | Magnetite (Fe$_2$O$_4$) | Ilmenite (FeTiO$_3$) | Sphene (CaTiSiO$_4$O) |
| Content         | 63.54   | 5.47    | 30.99    |
2.2. Procedure and Methods

The experimental procedure has been clearly illustrated in our previous work [18].

The content of vanadium in the leachate was determined by the ferrous volumetric method [23], and the vanadium leaching efficiency was calculated according to the following equation:

$$\beta = \frac{C_{Vl} \times V}{C_{Vs} \times M}$$  \hspace{1cm} (1)

where $\beta$ is the vanadium leaching efficiency (%), $C_{Vl}$ is the vanadium content in the leachate (g/mL), $C_{Vs}$ is the grade of vanadium in the concentrate (%), $V$ is the volume of the leachate (mL), and $M$ is the mass of the concentrate (g).

The main chemical composition of the concentrate was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Thermo Elemental, Boston, MA, USA).

Phase compositions were obtained by XRD (D/MAX2500PC, Rigaku, Tokyo, Japan) with Cu-K$\alpha$ radiation.

Microscopic observation and elemental analyses (SEM with EDS) were conducted by using a JEOL IT 300 scanning electronic microscope (JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS, X-Act, Oxford, London, UK).

3. Results and Discussion

3.1. Effect of Different Composite Additives and Their Mass Ratio on Vanadium Leaching Efficiency

According to our previous work, the effects of potassium salt additives were significantly more efficient than sodium and calcium salt additives and K$_2$SO$_4$ worked best [18]. Thus, in order to further increase the vanadium leaching efficiency, composite roasting additives were obtained by mixing several other potassium salts with K$_2$SO$_4$.

Particularly, in all leaching experiments, the roasting slag was leached under the following conditions: a leaching temperature of 95 $^\circ$C, a leaching time of 1.5 h, and a sulfuric acid concentration of 10% (v/v) with a liquid-to-solid ratio of 3 mL/g.

The effect of different composite additives and their mass ratios on vanadium leaching efficiency was investigated under the following conditions: the additive total dosage was 7 wt %, the roasting temperature was 950 $^\circ$C, and the roasting time was 1 h. The results are illustrated in Figure 2. As shown in Figure 2, the effect of K$_2$SO$_4$/KCl composite roasting additive is obviously more efficient than K$_2$SO$_4$/K$_2$CO$_3$, which suggests that KCl works better than K$_2$CO$_3$ for vanadium extraction from the concentrate.
Specifically, the decomposition reactions of the above additives are illustrated in Equations (2)–(4).

\[
2\text{K}_2\text{SO}_4 \rightarrow 2\text{K}_2\text{O} + 2\text{SO}_2 + \text{O}_2 \quad (2)
\]

\[
4\text{KCl} + \text{O}_2 \rightarrow 2\text{K}_2\text{O} + 2\text{Cl}_2 \quad (3)
\]

\[
\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2 \quad (4)
\]

3.2. Effect of Additive Dosage on Vanadium Leaching Efficiency

The effect of composite additive K$_2$SO$_4$/KCl with a mass ratio of 6/4, single K$_2$SO$_4$, and KCl dosage on the vanadium leaching efficiency was researched under the following conditions: the roasting temperature was 950 °C and the roasting time was 1 h. The results are illustrated in Figure 3. It can be seen that with the increase of composite additive K$_2$SO$_4$/KCl dosage from 0 to 7 wt %, the vanadium leaching efficiency keeps growing sharply. However, there is little change in the vanadium leaching efficiency when the dosage exceeds 7 wt %. Therefore, the appropriate K$_2$SO$_4$/KCl dosage is identified as 7 wt %.

Compared to single K$_2$SO$_4$ and KCl, the K$_2$SO$_4$/KCl composite additive can effectively improve the vanadium leaching efficiency at the same additive dosage, which indicates that the K$_2$SO$_4$/KCl composite additive has stronger synergy for extracting vanadium from the concentrate.
3.3. Effect of Roasting Temperature and Time on Vanadium Leaching Efficiency

The effect of the roasting temperature and roasting time on the vanadium leaching efficiency was studied under the following conditions: K$_2$SO$_4$/KCl total dosage was 7 wt % with the mass ratio of 6/4. The results are illustrated in Figure 4. As presented in Figure 4, with the increase of the roasting temperature from 700 to 950 °C, the vanadium leaching efficiency increases rapidly. Nevertheless, the vanadium leaching efficiency begins to drop when the roasting temperature exceeds 950 °C. Moreover, the vanadium leaching efficiency decreases when the roasting time exceeds 1 h. Thus, the reasonable roasting temperature is 950 °C and the roasting time is 1 h.

In order to explain why the vanadium leaching efficiency decreases at an extreme roasting temperature and roasting time, the SEM images of the different samples (roasting with 7 wt % K$_2$SO$_4$/KCl with the mass ratio of 6/4 under different roasting conditions) are illustrated in Figure 5. As shown in Figure 5a, the mineral particles are separate from each other and their particle size is small. In contrast, Figure 5b,c shows that the mineral particles bond with each other and their particle size is larger, which indicates that sintering between the materials occurs at these conditions. Related research has implied that the sintered products could wrap the particles and impede the transportation of vanadium into the leaching solution [20,25]. Therefore, sintering under a higher roasting temperature or longer roasting time could result in the decrease of the vanadium leaching efficiency.
3.4. Mechanism of Composite Roasting Additive on Extracting Vanadium

3.4.1. Crystal Transformation of Vanadium-Bearing Magnetite in the Roasting Process

Related research has shown that during the oxidation process of magnetite ($Fe_3O_4$) to hematite ($Fe_2O_3$), there are two possible crystal forms of hematite—$\gamma$-$Fe_2O_3$ and $\alpha$-$Fe_2O_3$—and the conversion process is $Fe_3O_4 \rightarrow \gamma$-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ [26]. Nevertheless, $\gamma$-$Fe_2O_3$ at an unstable phase is translated to the more stable $\alpha$-$Fe_2O_3$ at a high temperature (>550 °C) [26,27]. Therefore, under our experimental conditions (950 °C), the existential form of hematite was $\alpha$-$Fe_2O_3$.

According to our previous work, the main chemical reaction of vanadium extraction in the roasting process [18] is illustrated in Equation (5). It can be inferred that the essence of vanadium extraction with roasting was the conversion of vanadium-bearing magnetite to hematite, and the crystal transformation relationship of vanadium-bearing magnetite ($FeO(Fe,V)_2O_3$) to hematite ($\alpha$-$Fe_2O_3$) is illustrated in Figure 6.

$$FeO(Fe,V)_2O_3 + K_2SO_4 + CaO + O_2 \rightarrow Fe_2O_3 + KVO_3 + CaSO_4 \quad (5)$$

The crystal structure of magnetite ($FeO(Fe,V)_2O_3$) is a cubic crystal system, and the unit cell parameters are: $a = b = c = 0.8375$ nm, $a = \beta = \gamma = 90^\circ$. The crystal structure of hematite ($\alpha$-$Fe_2O_3$) is a trigonal crystal system, and the unit cell parameters are: $a = b = 0.5038$ nm, $c = 1.3756$ nm, $a = \beta = 90^\circ$, $\gamma = 120^\circ$. In general, the phase transformation can be divided into reformed transformation and reconstructed transformation [28]. For the reformed transformation, the disconnection and reconstruction of chemical bonds will not occur, and a new crystal structure will not be formed. For the reconstructed transformation, chemical bonds will be broken over a large area, and then new crystal structures appear [28,29]. The conversion of magnetite ($FeO(Fe,V)_2O_3$) to hematite ($\alpha$-$Fe_2O_3$) in the roasting process should be a reconstructed transformation because a new crystal structure is produced. Thus, it can be found that most Fe(V)–O bonds in vanadium-bearing magnetite ($FeO(Fe,V)_2O_3$) were broken and the dissociation of V(III) occurred with its reconstructed transformation. Then, the dissociated V(III) could be further oxidized and transformed to soluble vanadate.

![Crystal transformation relationship of vanadium-bearing magnetite ($FeO(Fe,V)_2O_3$) to hematite ($Fe_2O_3$).](image)
3.4.2. Synergistic Effect of Composite Roasting Additive

In order to explore the existence of vanadium which could not be leached, the SEM image and relevant EDS analyses of the leaching slag (the previous optimal conditions) are illustrated in Figure 7. As shown in Figure 7, there is still some relevance of Fe, V, O, and K. The previous analyses have explained that hematite (Fe$_2$O$_3$) was transformed from vanadium-bearing magnetite (FeO(Fe,V)$_2$O$_3$); therefore, it can be speculated that KVO$_3$ exists in the area and the grain is hematite (Fe$_2$O$_3$). Further, it can be concluded that the reason why soluble KVO$_3$ could not be leached was that insoluble hematite (Fe$_2$O$_3$) wrapped KVO$_3$, so that only KVO$_3$ in the surface layer of hematite (Fe$_2$O$_3$) could be dissolved out and not in the inner layer.

![Figure 7](image)

**Figure 7.** (a) SEM image of leaching slag (optimal conditions); EDS elemental distribution: (b) Fe; (c) V; (d) O; (e) K.

According to Equations (2) and (3), the main decomposition products of the K$_2$SO$_4$/KCl composite roasting additive were K$_2$O, SO$_2$, and Cl$_2$. According to our previous work on the mechanism of single K$_2$SO$_4$ for extracting vanadium from the concentrate, the effect of K$_2$O and SO$_2$ were determined [18]. Therefore, the key to explaining the mechanism of the K$_2$SO$_4$/KCl composite roasting additive on strengthening the vanadium extraction from the concentrate was to investigate the effect of Cl$_2$.

To study the role that Cl$_2$ played in extracting vanadium from the concentrate, the phase transformation between the concentrate, single K$_2$SO$_4$ roasting slag (the dosage of K$_2$SO$_4$ was 4.2 wt %), and K$_2$SO$_4$/KCl roasting slag (the dosage of K$_2$SO$_4$ was 4.2 wt % and the dosage of KCl was 2.8 wt %, which was that the total dosage of K$_2$SO$_4$/KCl was 7 wt % with the mass ratio of 6/4) was analyzed by XRD, and the XRD patterns are illustrated in Figure 8. These roasting slags were obtained at roasting conditions of 950 °C for 1 h.

![Figure 8](image)

**Figure 8.** XRD patterns of different samples (a) concentrate; (b) single K$_2$SO$_4$ roasting slag; (c) K$_2$SO$_4$/KCl roasting slag.
As presented in Figure 8a,b, it can be observed that the diffraction peaks of the magnetite phase \( \text{Fe}_3\text{O}_4 \) completely disappear when the strong diffraction peaks of the hematite phase \( \text{Fe}_2\text{O}_3 \) appear. Therefore, it can be concluded that single \( \text{K}_2\text{SO}_4 \) roasting can fully destroy the structure of vanadium-bearing magnetite \( \text{FeO(Fe,V)}_2\text{O}_3 \) and complete the transformation from magnetite to hematite in the roasting process. As shown in Figure 8b,c, their main phase compositions are consistent. However, compared to Figure 8b, the intensity of the hematite phase \( \text{Fe}_2\text{O}_3 \) in Figure 8c is weakened to some extent, which indicates that \( \text{K}_2\text{SO}_4/\text{KCl} \) roasting can partly destroy the structure of hematite (\( \text{Fe}_2\text{O}_3 \)). Related research has declared that hematite (\( \text{Fe}_2\text{O}_3 \)) can react with \( \text{Cl}_2 \) to generate \( \text{FeCl}_3 \) at a high temperature \((>800 \, ^\circ\text{C})\) \([12,29,30]\), and the relevant reaction is illustrated in Equation (6).

\[
2\text{Fe}_2\text{O}_3 + 6\text{Cl}_2 \rightarrow 4\text{FeCl}_3 + 3\text{O}_2 \tag{6}
\]

Based on the above analyses, a possible explanation was proposed. The possible mechanism of \( \text{Cl}_2 \) that strengthens vanadium extraction was that \( \text{Cl}_2 \) could react with hematite (\( \text{Fe}_2\text{O}_3 \)) to generate volatile \( \text{FeCl}_3 \) to reduce the extent of hematite (\( \text{Fe}_2\text{O}_3 \)) wrapping \( \text{KVO}_3 \), facilitating the dissolution of vanadium. Further, compared to single \( \text{K}_2\text{SO}_4 \), the hypothetical mechanism schematic of \( \text{K}_2\text{SO}_4/\text{KCl} \) for strengthening vanadium extraction from the concentrate is illustrated in Figure 9.

![Figure 9. Mechanism schematic of \( \text{K}_2\text{SO}_4/\text{KCl} \) for strengthening vanadium extraction from the concentrate.](image)

In order to verify the above hypothesis, the SEM images and relative EDS analyses of single \( \text{K}_2\text{SO}_4 \) roasting slag and \( \text{K}_2\text{SO}_4/\text{KCl} \) roasting slag are illustrated in Figure 10. It can be seen from Figure 10a,b that there is an obvious correlation of \( \text{V, O, K, and Fe} \) which indicates that the distribution of \( \text{KVO}_3 \) and hematite (\( \text{Fe}_2\text{O}_3 \)) is highly related in these roasting slags. Combined with the EDS analyses of leaching slag in Figure 7, it can be speculated that the grain is hematite (\( \text{Fe}_2\text{O}_3 \)) and \( \text{KVO}_3 \) is wrapped by it. Moreover, the grain has a relatively dense structure in the single \( \text{K}_2\text{SO}_4 \) roasting slag and the grain has a loose structure in the \( \text{K}_2\text{SO}_4/\text{KCl} \) roasting slag. Thus, it can be inferred that \( \text{K}_2\text{SO}_4/\text{KCl} \) roasting could damage the structure of hematite (\( \text{Fe}_2\text{O}_3 \)) to some extent compared to single \( \text{K}_2\text{SO}_4 \) roasting, which is consistent with the XRD analyses. Further, with the destruction of hematite (\( \text{Fe}_2\text{O}_3 \)), its wrapping degree to \( \text{KVO}_3 \) decreased, which was conducive to the dissolution of vanadium and provided more evidence to support the hypothesis in Figure 9.
Integrating the above analyses, the mechanism of the K$_2$SO$_4$/KCl composite roasting additive on extracting vanadium was mainly reflected in three aspects. Firstly, highly active K$_2$O could combine with vanadium to generate soluble KVO$_3$ to avoid the formation of insoluble Ca(VO$_3$)$_2$, which was conducive to the recovery of vanadium [18]. Secondly, SO$_2$ could react with CaO to generate CaSO$_4$ to inhibit the formation of acid-consuming Ca(VO$_3$)$_2$, which was favorable to the dissolution of vanadium-bearing sphene (Ca(Ti,V)SiO$_4$O), facilitating the release of vanadium. Thirdly, Cl$_2$ could react with hematite (Fe$_2$O$_3$) to generate volatile FeCl$_3$ to reduce the extent of hematite (Fe$_2$O$_3$) wrapping KVO$_3$, which was beneficial for the dissolution of vanadium. Particularly, the aforementioned effects had a synergistic effect and promoted the extraction of vanadium together.

4. Conclusions

1. The vanadium leaching efficiency of 82.04% was obtained, which increased 7.43% compared with single K$_2$SO$_4$ and 10.05% compared with single KCl under the following conditions: the total dosage of K$_2$SO$_4$/KCl was 7 wt % with the mass ratio of 6/4, the roasting temperature was 950 $^\circ$C, the roasting time was 1 h, the leaching temperature was 95 $^\circ$C, the sulfuric acid concentration was 10% (v/v), and the leaching time was 1.5 h with the liquid-to-solid ratio of 3 mL/g.

2. The essence of the vanadium extraction with roasting was the conversion of vanadium-bearing magnetite to hematite. With the reconstructed transformation of cubic crystal systemic magnetite (FeO(Fe,V)$_2$O$_3$) to trigonal crystal systemic hematite ($\alpha$-Fe$_2$O$_3$), most Fe(V)–O bonds were broken and V(III) was dissociated out, which was then further oxidized and transformed into soluble vanadate.

3. The main decomposition products of the K$_2$SO$_4$/KCl composite roasting additive were K$_2$O, SO$_2$, and Cl$_2$. Meanwhile, the mechanism of K$_2$SO$_4$/KCl for facilitating vanadium extraction was mainly reflected in three aspects. Firstly, highly active K$_2$O could combine with vanadium to generate soluble KVO$_3$ to avoid the formation of insoluble Ca(VO$_3$)$_2$; secondly, SO$_2$ could
react with CaO to generate CaSO$_4$ to inhibit the formation of acid-consuming Ca(VO$_3$)$_2$, which is favorable to the dissolution of vanadium-bearing sphene (Ca(Ti,V)SiO$_4$); thirdly, Cl$_2$ could react with hematite (Fe$_2$O$_3$) to generate volatile FeCl$_3$ to reduce the extent of hematite (Fe$_2$O$_3$) wrapping KVO$_3$.

**Author Contributions:** R.L. and T.L. conceived and designed the experiments; R.L. performed the experiments; R.L. analyzed the data; T.L., Y.Z., and J.H. contributed reagents/materials/analysis tools; R.L. wrote this paper.

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