

Article

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_2SO_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_2O compared to Na_2O 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_2SO_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_2SO_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 -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_2SO_4 , K_2CO_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 ($FeO(Fe,V)_2O_3$) and sphene ($Ca(Ti,V)SiO_4O$) [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_2O_5	TiO_2	TFe	SiO_2	Al_2O_3	CaO	MgO	SO_3	P_2O_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_3O_4)	Ilmenite ($FeTiO_3$)	Sphene ($CaTiSiO_4O$)
Content	63.54	5.47	30.99

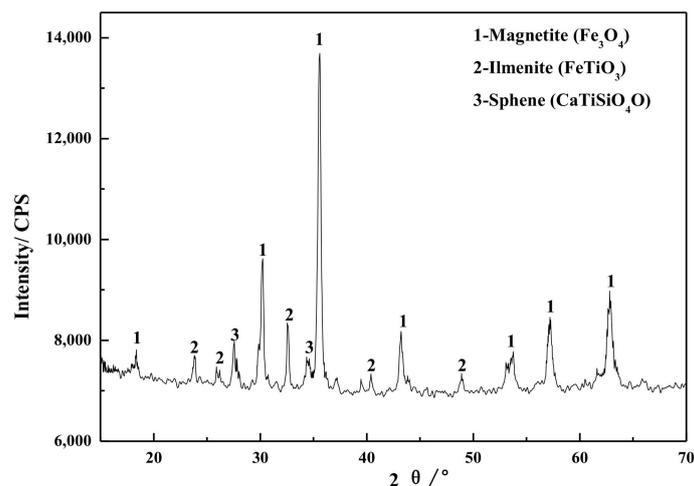


Figure 1. XRD pattern of the concentrate.

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:

$$\beta = \frac{C_{VI} \times V}{C_{Vs} \times M} \quad (1)$$

where β is the vanadium leaching efficiency (%), C_{VI} 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 α 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_2SO_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_2SO_4 .

Particularly, in all leaching experiments, the roasting slag was leached under the following conditions: a leaching temperature of 95 °C, a leaching time of 1.5 h, and a sulfuric acid concentration a 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 °C, and the roasting time was 1 h. The results are illustrated in Figure 2. As shown in Figure 2, the effect of K_2SO_4 /KCl composite roasting additive is obviously more efficient than K_2SO_4 / K_2CO_3 , which suggests that KCl works better than K_2CO_3 for vanadium extraction from the concentrate.

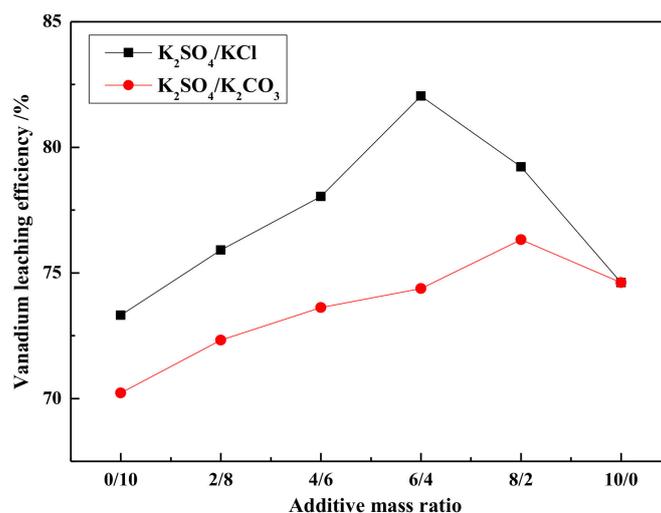
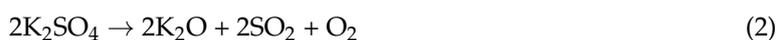


Figure 2. Effect of different composite additives and their mass ratio on vanadium leaching efficiency.

In general, the decomposition of the roasting additive will occur at a high temperature [24]. Specifically, the decomposition reactions of the above additives are illustrated in Equations (2)–(4). K_2SO_4 works best for its decomposition product (SO_2), which can react with CaO (in the concentrate) to generate $CaSO_4$ [18,19] to inhibit the formation of acid-consuming $Ca(VO_3)_2$ and then further facilitate the dissolution of vanadium-bearing sphene ($Ca(Ti,V)SiO_4O$) to release vanadium in the leaching process [18]. KCl works efficiently for its decomposition product (Cl_2), which can destroy the structure of the vanadium-bearing mineral to release vanadium [24]. K_2CO_3 does not work as efficiently for its decomposition product (CO_2), which cannot easily participate in chemical reactions because of its stable properties. Therefore, the optimal composite roasting additive is K_2SO_4/KCl .

At the same time, it can be observed that with the increasing mass ratio of K_2SO_4/KCl , the vanadium leaching efficiency first increases and then decreases, achieving the maximum when the mass ratio of K_2SO_4/KCl is 6/4. Thus, the reasonable mass ratio of K_2SO_4/KCl should be 6/4.



3.2. Effect of Additive Dosage on Vanadium Leaching Efficiency

The effect of composite additive K_2SO_4/KCl with a mass ratio of 6/4, single K_2SO_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_2SO_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_2SO_4/KCl dosage is identified as 7 wt %.

Compared to single K_2SO_4 and KCl , the K_2SO_4/KCl composite additive can effectively improve the vanadium leaching efficiency at the same additive dosage, which indicates that the K_2SO_4/KCl composite additive has stronger synergy for extracting vanadium from the concentrate.

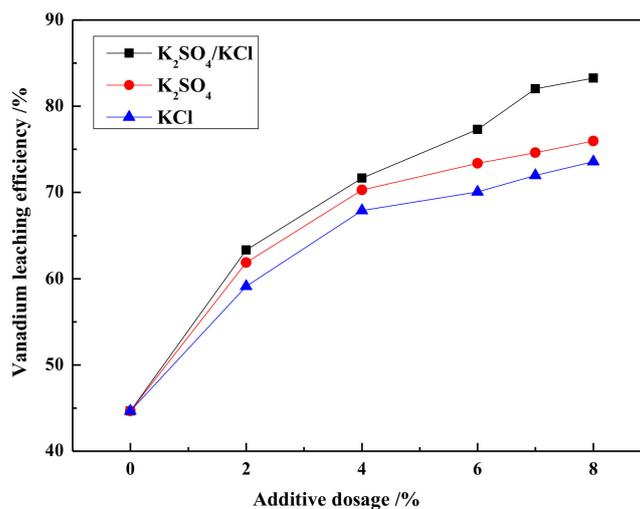


Figure 3. Effect of additive dosage on vanadium leaching efficiency.

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: K₂SO₄/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.

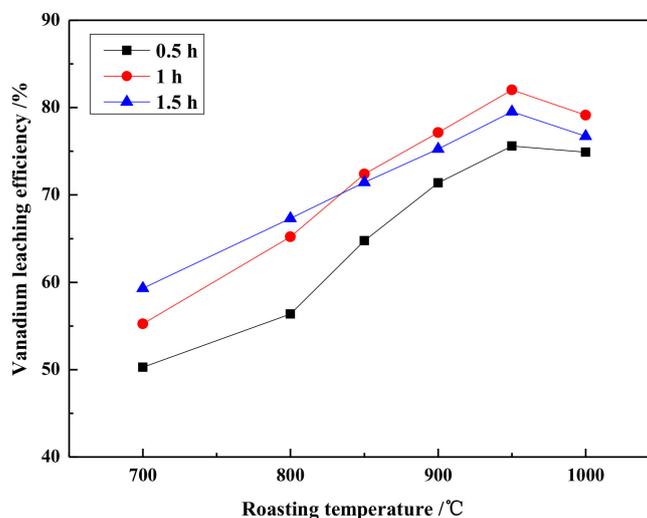


Figure 4. Effect of roasting temperature and time on vanadium leaching efficiency.

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 % K₂SO₄/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.

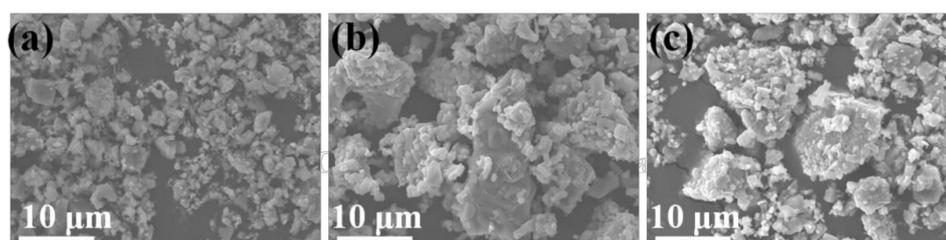


Figure 5. SEM images of different samples (a) roasted at 950 °C for 1 h; (b) roasted at 1000 °C for 1 h; (c) roasted at 950 °C for 1.5 h.

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— $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ —and the conversion process is $\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ [26]. Nevertheless, $\gamma\text{-Fe}_2\text{O}_3$ at an unstable phase is translated to the more stable $\alpha\text{-Fe}_2\text{O}_3$ at a high temperature ($>550\text{ °C}$) [26,27]. Therefore, under our experimental conditions (950 °C), the existential form of hematite was $\alpha\text{-Fe}_2\text{O}_3$.

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 ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$) to hematite ($\alpha\text{-Fe}_2\text{O}_3$) is illustrated in Figure 6.



The crystal structure of magnetite ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$) is a cubic crystal system, and the unit cell parameters are: $a = b = c = 0.8375\text{ nm}$, $\alpha = \beta = \gamma = 90^\circ$. The crystal structure of hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a trigonal crystal system, and the unit cell parameters are: $a = b = 0.5038\text{ nm}$, $c = 1.3756\text{ nm}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. 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 ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$) to hematite ($\alpha\text{-Fe}_2\text{O}_3$) 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 ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$) 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.

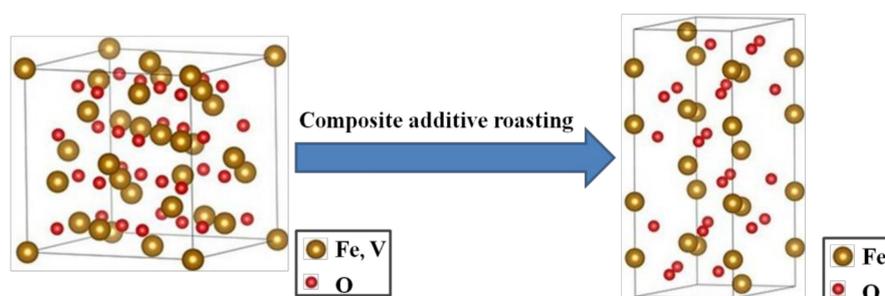


Figure 6. Crystal transformation relationship of vanadium-bearing magnetite ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$) to hematite (Fe_2O_3).

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_2O_3) was transformed from vanadium-bearing magnetite ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$); therefore, it can be speculated that KVO_3 exists in the area and the grain is hematite (Fe_2O_3). Further, it can be concluded that the reason why soluble KVO_3 could not be leached was that insoluble hematite (Fe_2O_3) wrapped KVO_3 , so that only KVO_3 in the surface layer of hematite (Fe_2O_3) could be dissolved out and not in the inner layer.

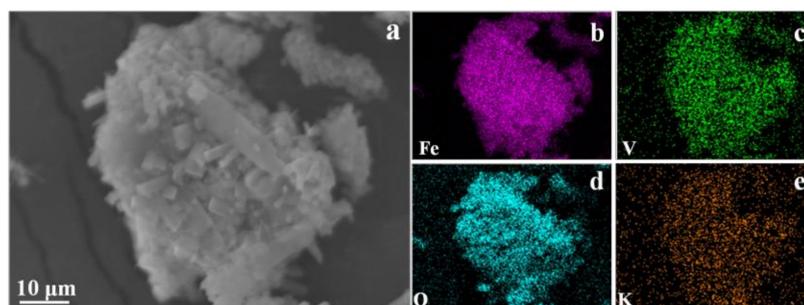


Figure 7. (a) SEM image of leaching slag (optimal conditions); EDS elemental distribution: (b) Fe; (c) V; (d) O; (e) K.

According to Equations (2) and (3), the main decomposition products of the $\text{K}_2\text{SO}_4/\text{KCl}$ composite roasting additive were K_2O , SO_2 , and Cl_2 . According to our previous work on the mechanism of single K_2SO_4 for extracting vanadium from the concentrate, the effect of K_2O and SO_2 were determined [18]. Therefore, the key to explaining the mechanism of the $\text{K}_2\text{SO}_4/\text{KCl}$ 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_2SO_4 roasting slag (the dosage of K_2SO_4 was 4.2 wt %), and $\text{K}_2\text{SO}_4/\text{KCl}$ roasting slag (the dosage of K_2SO_4 was 4.2 wt % and the dosage of KCl was 2.8 wt %, which was that the total dosage of $\text{K}_2\text{SO}_4/\text{KCl}$ 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.

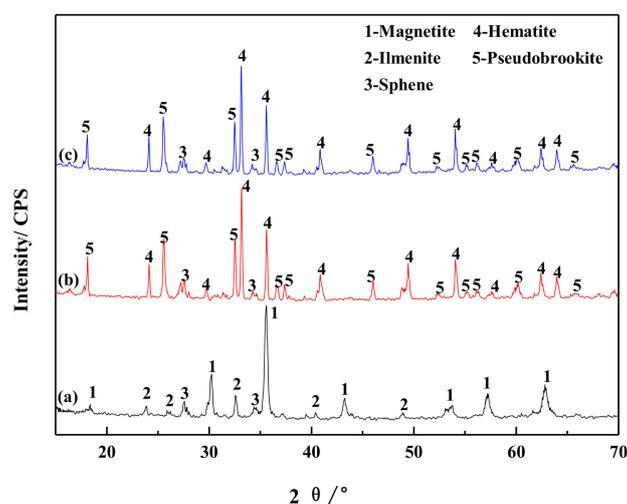


Figure 8. XRD patterns of different samples (a) concentrate; (b) single K_2SO_4 roasting slag; (c) $\text{K}_2\text{SO}_4/\text{KCl}$ roasting slag.

As presented in Figure 8a,b, it can be observed that the diffraction peaks of the magnetite phase (Fe_3O_4) completely disappear when the strong diffraction peaks of the hematite phase (Fe_2O_3) appear. Therefore, it can be concluded that single K_2SO_4 roasting can fully destroy the structure of vanadium-bearing magnetite ($\text{FeO}(\text{Fe},\text{V})_2\text{O}_3$) 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 (Fe_2O_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 (Fe_2O_3). Related research has declared that hematite (Fe_2O_3) can react with Cl_2 to generate FeCl_3 at a high temperature ($>800\text{ }^\circ\text{C}$) [12,29,30], and the relevant reaction is illustrated in Equation (6). Particularly, the boiling point of FeCl_3 is $315\text{ }^\circ\text{C}$; therefore, under our experimental conditions ($950\text{ }^\circ\text{C}$), it volatilizes in the form of gas. Thus, it can be concluded that the occurrence of Equation (6) resulted in the weakness of the intensity of the hematite phase (Fe_2O_3).



Based on the above analyses, a possible explanation was proposed. The possible mechanism of Cl_2 that strengthens vanadium extraction was that Cl_2 could react with hematite (Fe_2O_3) to generate volatile FeCl_3 to reduce the extent of hematite (Fe_2O_3) wrapping KVO_3 , facilitating the dissolution of vanadium. Further, compared to single K_2SO_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.

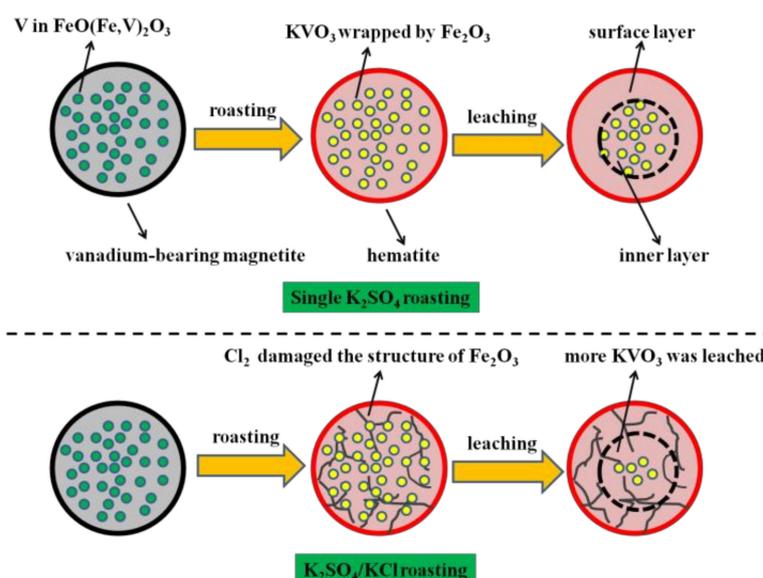


Figure 9. Mechanism schematic of $\text{K}_2\text{SO}_4/\text{KCl}$ for strengthening vanadium extraction from the concentrate.

In order to verify the above hypothesis, the SEM images and relative EDS analyses of single K_2SO_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 V, O, K, and Fe, which indicates that the distribution of KVO_3 and hematite (Fe_2O_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 (Fe_2O_3) and KVO_3 is wrapped by it. Moreover, the grain has a relatively dense structure in the single K_2SO_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 (Fe_2O_3) to some extent compared to single K_2SO_4 roasting, which is consistent with the XRD analyses. Further, with the destruction of hematite (Fe_2O_3), its wrapping degree to KVO_3 decreased, which was conducive to the dissolution of vanadium and provided more evidence to support the hypothesis in Figure 9.

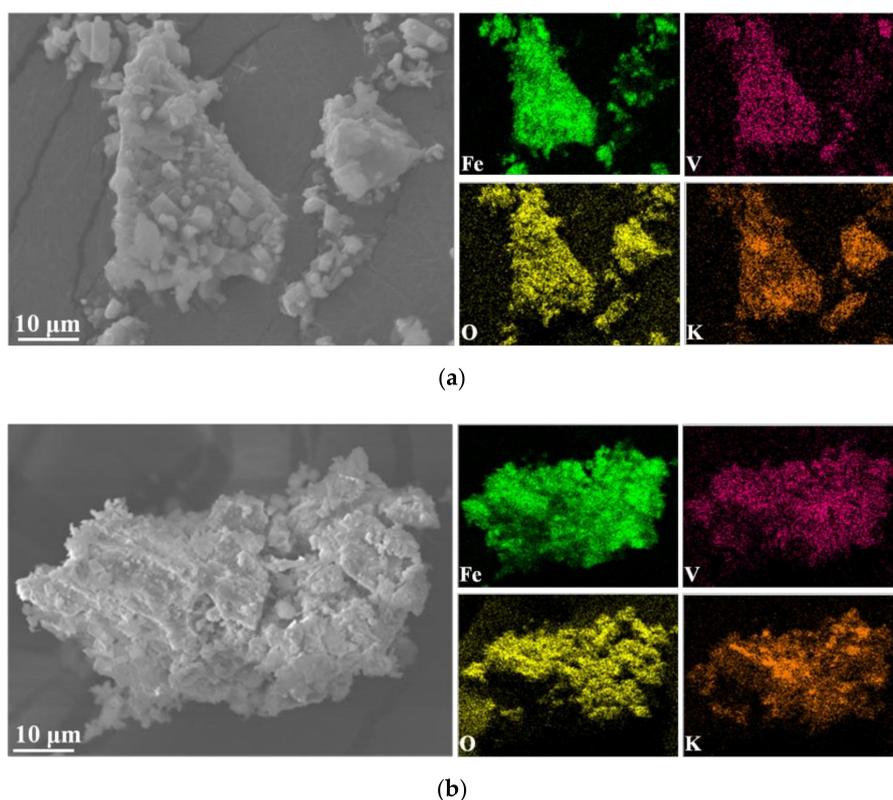


Figure 10. SEM images and relative EDS analyses of different samples (a) single K_2SO_4 roasting slag; (b) K_2SO_4/KCl roasting slag.

Integrating the above analyses, the mechanism of the K_2SO_4/KCl composite roasting additive on extracting vanadium was mainly reflected in three aspects. Firstly, highly active K_2O 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 ($Ca(Ti,V)SiO_4O$), facilitating the release of vanadium. Thirdly, Cl_2 could react with hematite (Fe_2O_3) to generate volatile $FeCl_3$ to reduce the extent of hematite (Fe_2O_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_2SO_4 and 10.05% compared with single KCl under the following conditions: the total dosage of K_2SO_4/KCl was 7 wt % with the mass ratio of 6/4, the roasting temperature was 950 °C, the roasting time was 1 h, the leaching temperature was 95 °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 ($FeO(Fe,V)_2O_3$) to trigonal crystal systemic hematite ($\alpha-Fe_2O_3$), 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_2SO_4/KCl composite roasting additive were K_2O , SO_2 , and Cl_2 . Meanwhile, the mechanism of K_2SO_4/KCl for facilitating vanadium extraction was mainly reflected in three aspects. Firstly, highly active K_2O 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 CaSO₄ to inhibit the formation of acid-consuming Ca(VO₃)₂, which is favorable to the dissolution of vanadium-bearing sphene (Ca(Ti,V)SiO₄O); thirdly, Cl₂ could react with hematite (Fe₂O₃) to generate volatile FeCl₃ to reduce the extent of hematite (Fe₂O₃) wrapping KVO₃.

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

References

1. Zhang, Y.M.; Bao, S.X.; Liu, T.; Chen, T.J.; Huang, J. The technology of extracting vanadium from stone coal in China: History, current status and future prospects. *Hydrometallurgy* **2011**, *109*, 116–124. [[CrossRef](#)]
2. Skyllaskazacos, M.; Cao, L.Y.; Kazacos, M.; Kausar, N.; Mousa, A. Vanadium electrolyte studies for the vanadium redox battery—A review. *ChemSusChem* **2016**, *9*, 1521–1543. [[CrossRef](#)] [[PubMed](#)]
3. Han, J.L.; Zhang, Y.M.; Liu, T.; Huang, J.; Xue, N.N.; Hu, P.C. Preparation of Vanadium Nitride Using a Thermally Processed Precursor with Coating Structure. *Metals* **2017**, *7*, 360. [[CrossRef](#)]
4. Bijelic, A.; Aureliano, M.; Rompel, A. The antibacterial activity of polyoxometalates: Structures, antibiotic effects and future perspectives. *Chem. Commun.* **2018**, *54*, 1153–1169. [[CrossRef](#)] [[PubMed](#)]
5. Gumerova, N.; Krivosudsky, L.; Fraqueza, G.; Breibeck, J.; Al-Sayed, E.; Tanuhadi, E.; Bijelic, A.; Fuentes, J.; Aureliano, M.; Rompel, A. The P-type ATPase inhibiting potential of polyoxotungstates. *Metallomics* **2018**, *10*, 287–295. [[CrossRef](#)] [[PubMed](#)]
6. Zhu, X.B.; Li, W.; Tang, S.; Zeng, M.J.; Bai, P.Y.; Chen, L.J. Selective recovery of vanadium and scandium by ion exchange with D201 and solvent extraction using P507 from hydrochloric acid leaching solution of red mud. *Chemosphere* **2017**, *175*, 365–372. [[CrossRef](#)] [[PubMed](#)]
7. Sui, Y.L.; Guo, Y.F.; Jiang, T.; Xie, X.L.; Wang, S.; Zheng, F.Q. Gas-based reduction of vanadium titanomagnetite concentrate: Behavior and mechanisms. *Int. J. Miner. Metall. Mater.* **2017**, *24*, 10–17. [[CrossRef](#)]
8. Xu, C.B.; Zhang, Y.M.; Liu, T.; Huang, J. Characterization and Pre-Concentration of Low-Grade Vanadium-Titanium Magnetite Ore. *Minerals* **2017**, *7*, 137. [[CrossRef](#)]
9. Chen, D.S.; Zhao, H.X.; Hu, G.P.; Qi, T.; Yu, H.D.; Zhang, G.Z.; Wang, L.N.; Wang, W.J. An extraction process to recover vanadium from low-grade vanadium-bearing titanomagnetite. *J. Hazard. Mater.* **2015**, *294*, 35–40. [[CrossRef](#)] [[PubMed](#)]
10. Li, H.Y.; Fang, H.X.; Wang, K.; Zhou, W.; Yang, Z.; Yan, X.M.; Ge, W.S.; Li, Q.W.; Xie, B. Asynchronous extraction of vanadium and chromium from vanadium slag by stepwise sodium roasting—Water leaching. *Hydrometallurgy* **2015**, *156*, 124–135. [[CrossRef](#)]
11. Chen, D.S.; Song, B.; Wang, L.N.; Qi, T.; Wang, Y.; Wang, W.J. Solid state reduction of Panzhihua titanomagnetite concentrates with pulverized coal. *Miner. Eng.* **2011**, *24*, 864–869. [[CrossRef](#)]
12. Hu, Y.J. Study on Roasting and Leaching Mechanism of Vanadium-bearing Shale with High-calcium Mica. Ph.D. Thesis, Wuhan University of Technology, Wuhan, China, 2012. (In Chinese)
13. Zhang, X.F.; Liu, F.G.; Xue, X.X.; Jiang, T. Effects of microwave and conventional blank roasting on oxidation behavior, microstructure and surface morphology of vanadium slag with high chromium content. *J. Alloys Compd.* **2016**, *686*, 356–365. [[CrossRef](#)]
14. Yang, X.L.; Feng, Y.L.; Li, H.R.; Du, Z.W. Optimization Mechanism of Additive of Composite Sodium Salts on Vanadium Oxidation of Siliceous Shale. *Minerals* **2017**, *7*, 103. [[CrossRef](#)]
15. Xiang, J.Y.; Huang, Q.Y.; Lv, X.W.; Bai, C.G. Multistage utilization process for the gradient-recovery of V, Fe, and Ti from vanadium-bearing converter slag. *J. Hazard. Mater.* **2017**, *336*, 1–7. [[CrossRef](#)] [[PubMed](#)]
16. Xiang, J.Y.; Huang, Q.Y.; Lv, X.W.; Bai, C.G. Extraction of vanadium from converter slag by two-step sulfuric acid leaching process. *J. Clean. Prod.* **2018**, *170*, 1089–1101. [[CrossRef](#)]
17. Zhu, X.B.; Li, W.; Guan, X.M. Vanadium extraction from titanomagnetite by hydrofluoric acid. *Int. J. Miner. Process.* **2016**, *157*, 55–59. [[CrossRef](#)]

18. Li, R.M.; Liu, T.; Zhang, Y.M.; Huang, J.; Xu, C.B. Efficient Extraction of Vanadium from Vanadium–Titanium Magnetite Concentrate by Potassium Salt Roasting Additives. *Minerals* **2018**, *8*, 25. [[CrossRef](#)]
19. Zhu, X.B.; Zhang, Y.M.; Liu, T. Experiment and Mechanism Study on Vanadium Extraction from Stone Coal by Activation Roasting. *Chin. J. Rare Met.* **2013**, *37*, 284–288. (In Chinese)
20. Chen, F.; Zhang, Y.M.; Huang, J.; Liu, T.; Xue, N.N. Mechanism of Enhancing Extraction of Vanadium from Stone Coal by Roasting with MgO. *Minerals* **2017**, *7*, 33. [[CrossRef](#)]
21. Wang, B.; Liu, T.; Zhang, Y.M.; Huang, J. Effect of CaF₂/CaO Composite Additive on Roasting of Vanadium-Bearing Stone Coal and Acid Leaching Kinetics. *Minerals* **2017**, *7*, 43. [[CrossRef](#)]
22. Beijing General Research Institute of Mining & Metallurgy. *Chemical Phase Analyses*; Metallurgical Industry Press: Beijing, China, 1979; pp. 141–150. (In Chinese)
23. Gao, Y.M. Determining vanadium content in vanadium-bearing slag with ferrous iron volumetric method. *Ferro-Alloys* **2003**, *3*, 44–46.
24. Zhao, Y.L.; Kang, S.C.; Wang, W.; Zhang, Y.M.; Song, S.X.; Bao, S.X. Decomposition characteristics of compound additive and effect of roasting atmosphere on vanadium extraction from stone coal. *Asia-Pac. J. Chem. Eng.* **2017**, *12*, 374–380. [[CrossRef](#)]
25. Yuan, Y.Z.; Zhang, Y.M.; Liu, T.; Chen, T.J. Comparison of the mechanisms of microwave roasting and conventional roasting and of their effects on vanadium extraction from stone coal. *Int. J. Miner. Metall. Mater.* **2015**, *22*, 476–482. [[CrossRef](#)]
26. Chen, C. Transformation Mechanism of Iron Minerals in Oolitic Hematite Magnetic Roasting. Master's Thesis, Northeastern University, Shenyang, China, 2013. (In Chinese)
27. Babay, S.; Mhiri, T.; Toumi, M. Synthesis, Structural and spectroscopic characterizations of maghemite γ -Fe₂O₃ prepared by one-step coprecipitation route. *J. Mol. Struct.* **2015**, *1085*, 286–293. [[CrossRef](#)]
28. Liao, L.B. *Crystal Chemistry and Crystal Physics*; Geological Press: Beijing, China, 2000; pp. 107–109. (In Chinese)
29. Zhao, Y.L. Theoretical Investigation on Roasting Process of Low-Grade Mica-Type Vanadium-Bearing Shale. Ph.D. Thesis, Wuhan University of Technology, Wuhan, China, 2014. (In Chinese)
30. Zhang, Y.M.; Hu, Y.J.; Bao, S.X. Vanadium emission during roasting of vanadium-bearing stone coal in chlorine. *Miner. Eng.* **2012**, *30*, 95–98. [[CrossRef](#)]



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