

Article

# Vanadium Transitions during Roasting-Leaching Process of Vanadium Extraction from Stone Coal

Yunliang Zhao <sup>1,\*</sup> , Licai Chen <sup>1</sup>, Hao Yi <sup>1</sup>, Yimin Zhang <sup>2,\*</sup>, Shaoxian Song <sup>1</sup> and Shenxu Bao <sup>1</sup>

<sup>1</sup> School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan 430070, China; c13399616706@163.com (L.C.); yihao287@126.com (H.Y.); sxx851215@whut.edu.cn (S.S.); sxbao@whut.edu.cn (S.B.)

<sup>2</sup> School of Resources and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

\* Correspondence: zyl286@whut.edu.cn (Y.Z.); zym126135@126.com (Y.Z.)

Received: 12 January 2018; Accepted: 9 February 2018; Published: 12 February 2018

**Abstract:** The vanadium occurrence in stone coal, water leaching, and acid leaching residue was investigated by energy dispersive spectrometer (EDS) mapping and point analysis, and the vanadium transitions during roasting-leaching of stone coal were revealed. In the roasting process, vanadium-bearing muscovite is converted to K-Na-feldspar, accompanying the liberation of vanadium. Most liberated vanadium reacts with sodium salt to generate water-soluble sodium vanadate, some reacts with calcite in stone coal to form water-insoluble calcium vanadate, and other liberated vanadium exists as free vanadium oxide. However, for coarse muscovite grains, the reaction of muscovite converted to K-Na-feldspar only occurs at the outer margin of muscovite grains, and the vanadium in the interior of muscovite grains is not liberated. During water leaching, the sodium vanadate is leached out. The calcium vanadate and free vanadium oxide are dissolved out in the process of acid leaching, and the vanadium, presenting in muscovite grains surrounded by K-Na-feldspar, still remains in the acid leaching residue. Two suggestions, including optimization of grinding-classification process and adopting microwave roasting, were proposed for improving vanadium recovery according to the vanadium transition rules.

**Keywords:** vanadium; transitions; roasting; leaching; stone coal

## 1. Introduction

Vanadium is an important rare element that has been extensively applied in fields of steel industry, titanium-aluminum alloys, vanadium redox battery, and catalysts [1]. Stone coal is an important vanadium-bearing resource in China. The gross reserve of vanadium in terms of  $V_2O_5$  in stone coal accounts for more than 87% of the domestic reserve of vanadium [2]. However, most vanadium in stone coal exists as V(III) replacing Al(III) from dioctahedral structure as isomorphism in mica group minerals [3], which is generally recovered by roasting with sodium additive at a high temperature [4]. After that, the vanadium is liberated from crystal structure and converted to water or acid soluble vanadate [5], which is subsequently recovered by water leaching and/or acid leaching, ion purification, vanadium precipitation, and calcination [6–8]. For the process of vanadium extraction from stone coal, the vanadium recovery by the roasting-leaching procedure is around 65–75%, while for other procedures, such as ion exchange, solvent extraction, and vanadium precipitation, the vanadium recoveries are more than 97% [9,10]. Therefore, the total vanadium recovery depends on the vanadium recovery of the roasting-leaching step [11]. In order to improve the total vanadium recovery, further vanadium needs to be recovered from the current leaching residue as much as possible. The key is the vanadium occurrence in the leaching residue, which is the reason why the vanadium in the residue cannot be leached out. At present, the researches on vanadium occurrence mostly focus on the raw ore

of stone coal and roasting [12,13]. Hu et al. [14] measured the mineral phase and the vanadium valence of the roasted samples to evaluate the influence of roasting on vanadium recovery. Wang et al. [15] investigated the effect of vanadium occurrence of raw stone coal on the choice of extracting vanadium technology. However, the vanadium occurrence of leaching residue is not involved.

In this work, we investigate the vanadium occurrence, not only in stone coal but also in the water leaching and acid leaching residues, to seek the root of the relatively inferior vanadium recovery during the roasting-leaching process. More importantly, we reveal the vanadium transition rules and the reason why the vanadium in the residue hardly be leached out. Based on it, some suggestions were put forward for optimizing the current roasting-leaching process to improve the vanadium recovery.

## 2. Experimental Section

### 2.1. Materials

The vanadium-bearing stone coal was collected from Teng-da Mining and Metallurgy Co., Ltd., Xiantao, China. It was first decarbonized at 700 °C for 1 h in air using a SXZ-10-B muffle furnace and the decarbonized sample was used for roasting in this study. The chemical composition analysis and mineral composition analysis of the decarbonized sample were described in our previous research [16]. The decarbonized sample is mainly composed of 54.36% SiO<sub>2</sub>, 10.59% Al<sub>2</sub>O<sub>3</sub>, 7.35% CaO, 5.93% Fe<sub>2</sub>O<sub>3</sub>, 4.90% K<sub>2</sub>O, 0.35% Na<sub>2</sub>O, and 0.82% V<sub>2</sub>O<sub>5</sub>. The main minerals are quartz, muscovite, and feldspar. In addition, hematite and a spot of calcite also exist.

### 2.2. Procedure

The decarbonized samples were mixed with analytically pure compound additive (6% NaCl and 10% Na<sub>2</sub>SO<sub>4</sub>), then they were ground to 87 wt % minus 74 μm. The mixtures were roasted in a quartz tube furnace at 850 °C for 2 h in air atmosphere.

The roasted sample was first leached by water. The parameters of water leaching operation were temperature of 90 °C, time of 1 h, ratio of water to solid of 4:1 mL/g, and stirring speed of 1000 r/min with JJ-1 electric mixer. Then, the leaching residue was separated from the leachate by SHZ-3 vacuum filtration, and the residue was washed with distilled water several times. After this, the residue was leached by 2.2 wt % hydrochloric acid. The parameters of dilute acid leaching step were the same as the water leaching step, except the leaching temperature was 60 °C. Then, the same vacuum filter was used to separate the solution and residue from the acid leaching system. The vanadium recoveries of the water leaching and acid leaching were calculated by Equations (1) and (2), respectively:

$$R_W = \frac{V_W}{V_R} \times 100\% \quad (1)$$

in which  $R_W$  is the vanadium recovery of water leaching (%),  $V_R$  is the weight of vanadium in roasted sample (g), and  $V_W$  is the weight of vanadium in the water leaching solution (g);

$$R_A = \frac{V_A}{V_R} \times 100\% \quad (2)$$

in which  $R_A$  is the vanadium recovery of acid leaching (%) and  $V_A$  is the weight of vanadium in the acid leaching solution (g). The total vanadium recovery of leaching is the sum of the recoveries of the water leaching and acid leaching.

### 2.3. Measurement Methods

Energy dispersive spectrometer (EDS) analysis of decarbonized stone coal, water, and acid leaching residue was carried out with Inca X-Act EDS (OIMS, Oxford, UK), which was used as attachment configured on the JXA-8230 super electron probe microscopic analyzer (EPMA) (JEOL, Tokyo, Japan). The backscattered electron (BE) detector was used for electronic imaging, and the

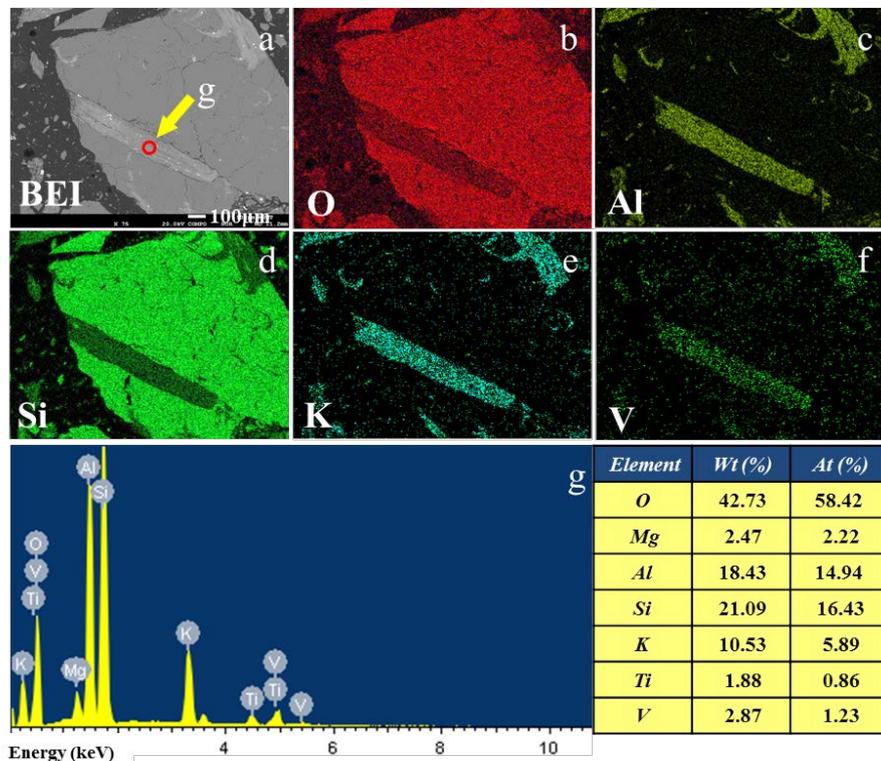
accelerating voltage and beam current was 20 kV and 0.01 mA, respectively. EDS mapping was performed to identify the elemental distribution of the samples.

The vanadium content in leachate of water leaching and acid leaching was measured by ammonium ferrous sulfate titrimetric method (GB/T8704.5, 2007) [17]. The vanadium grade of the roasted sample was determined in accordance with Test Methods of Vanadium in Coal Standard (GB/T 19226-2003) [18].

### 3. Results

#### 3.1. Vanadium Occurrence in Decarbonized Stone Coal

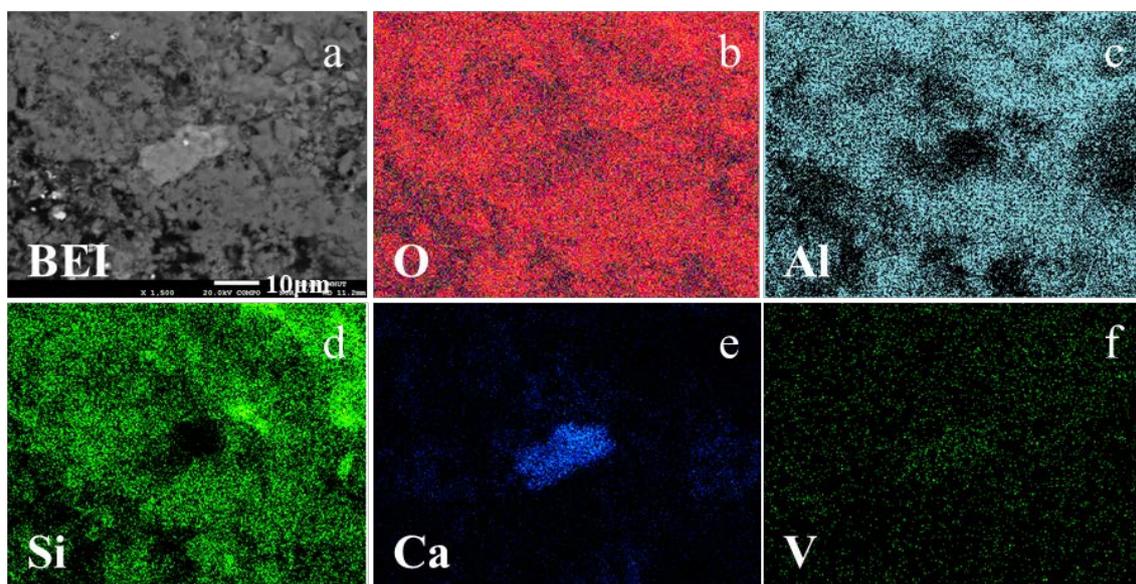
Figure 1 presents the backscattered electron image (BEI) and representative elemental EDS maps of O, Al, Si, K, and V of decarbonized stone coal. As can be seen from Figure 1, the dark gray zones in BEI are composed of Si and O, and it is inferred to be quartz. The light gray zones in BEI belong to potassium-rich aluminosilicate containing O, Al, Si, and K. As mentioned in Section 2.1, in this stone coal, the mineral phases of potassium-rich aluminosilicate are only muscovite and feldspar. The micro-area elemental analysis shows that the Al content of point g in the light gray zone of BEI is 18.43% (Figure 1g). The Al contents of muscovite ( $KAl_2(AlSi_3O_{10})(OH)_2$ ) and feldspar ( $KAlSi_3O_8$ ) are 20.98% and 9.71%, respectively. Hence, it is inferred that the mineral phase in the light gray zone is muscovite. It is observed that the distribution of Al (Figure 1c) and V (Figure 1f) correlates well with the light gray zone of BEI (Figure 1a). Since V(III) and V(IV) have similar ionic radius and electronegativity, and the same coordination number to Al(III); they readily replace Al(III) from dioctahedral structure as isomorphism in muscovite [19]. The correlation between Al and V distribution indicates the vanadium in the stone coal exists as isomorphism in muscovite, which is the most representative and prevalent occurrence of vanadium in stone coal [3].



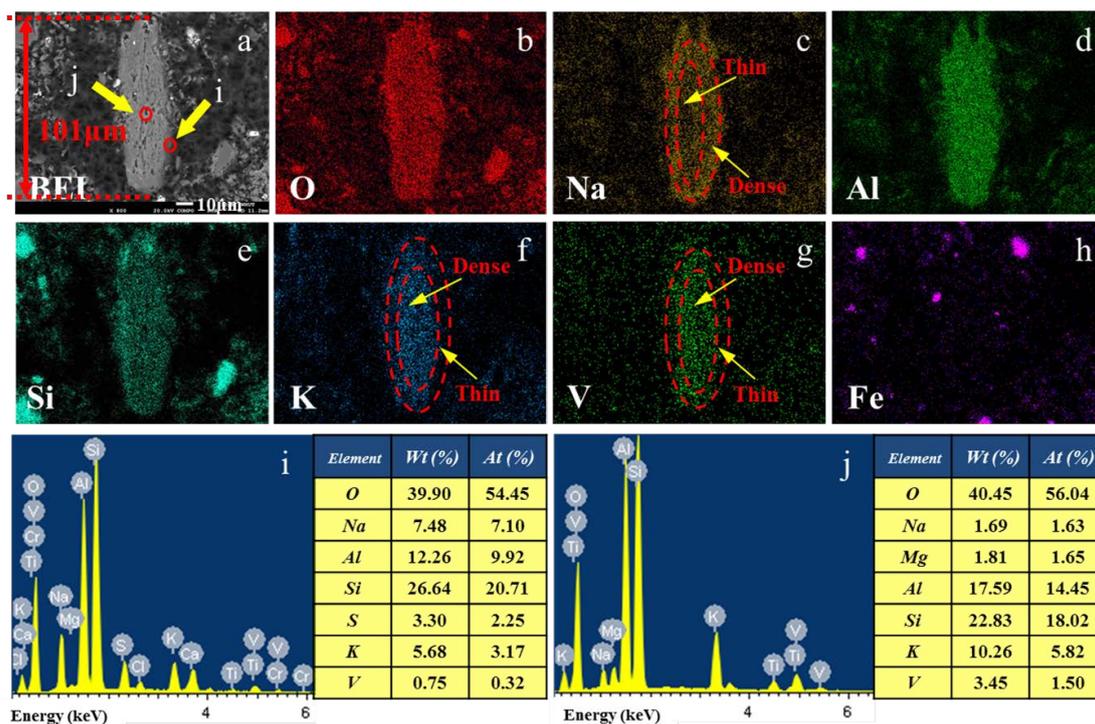
**Figure 1.** (a) BEI of decarbonized stone coal, EDS elemental distribution: (b) O; (c) Al; (d) Si; (e) K; (f) V, and (g) EDS spectra collected from BEI as marked by circle.

### 3.2. Vanadium Occurrence in Water Leaching Residue

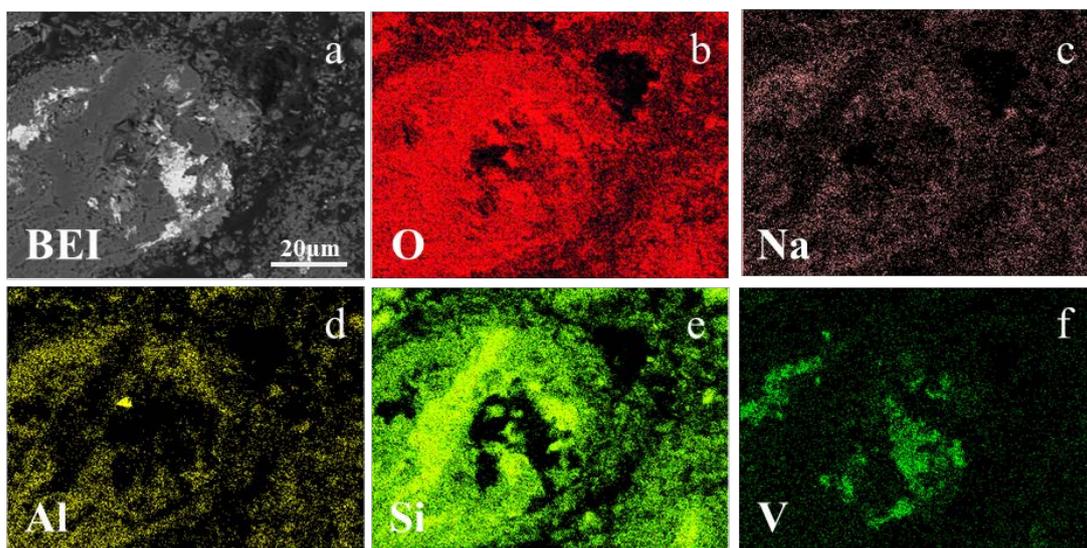
Three types of vanadium occurrence can be identified in water leaching residue. The first type of vanadium occurrence is exhibited in Figure 2. The light gray zone of BEI (Figure 2a) correlates well with the distribution of O (Figure 2b), Ca (Figure 2e), and V (Figure 2f). Considering that there is a spot of calcite in stone coal, it can react with vanadium to generate calcium vanadate during roasting [20]. It is inferred that this type of vanadium presents as calcium vanadate. Figure 3 gives the second type of vanadium occurrence. The distribution of Na, K, and V (Figure 3c,f,g) overlapping with ellipse grain in BEI (Figure 3a) has obvious layering. The distribution of Na is denser in the outer margin and thin in the interior of the ellipse, while the distribution of K and V is thin in the interior and denser in the outer margin of the ellipse. The layering distribution of elements indicates that there are two different kinds of mineral phases, respectively, presenting in the interior and outer margin of the ellipse grain, and the vanadium mainly exists in the inner mineral phase. The micro-area elemental analysis shows that the mineral phase in the outer margin of the ellipse is an aluminosilicate containing both sodium and potassium (Figure 3i), and that in the interior there is a potassium-rich aluminosilicate (Figure 3j). Based on the micro-area elemental composition analysis, it is inferred that the mineral phases in the outer margin and interior of the ellipse grain are K-Na-feldspar and muscovite, respectively. Therefore, the second type of vanadium exists in the muscovite surrounded by K-Na-feldspar. As can be seen from Figure 3a, the particle size of ellipse grain is 101  $\mu\text{m}$ . As for sample with particle size distribution of 87 wt % minus 74  $\mu\text{m}$ , this ellipse grain is coarse, and the particle size of this kind of vanadium-bearing muscovite grain, surrounded by K-Na-feldspar in water residue, is usually around to that of the ellipse grain. The third type of vanadium occurrence is shown in Figure 4. The bright zone in BEI (Figure 4a) correlates with the distribution of V (Figure 4f), and in this bright zone O is also existent (Figure 4b), while there is no distribution of other elements, such as Na, Al, and Si (Figure 4c–e). Hence, the third type of vanadium may appear as free vanadium oxide.



**Figure 2.** (a) BEI of the first type of vanadium-bearing grain in water leaching residue, EDS elemental distribution: (b) O, (c) Al, (d) Si, (e) Ca, and (f) V.



**Figure 3.** (a) BEI of the second type of vanadium-bearing grain in water leaching residue, EDS elemental distribution: (b) O, (c) Na, (d) Al, (e) Si, (f) K, (g) V, (h) Fe, and EDS spectra collected from BEI as marked by circle (i) at the outer margin and (j) at the interior of grain.

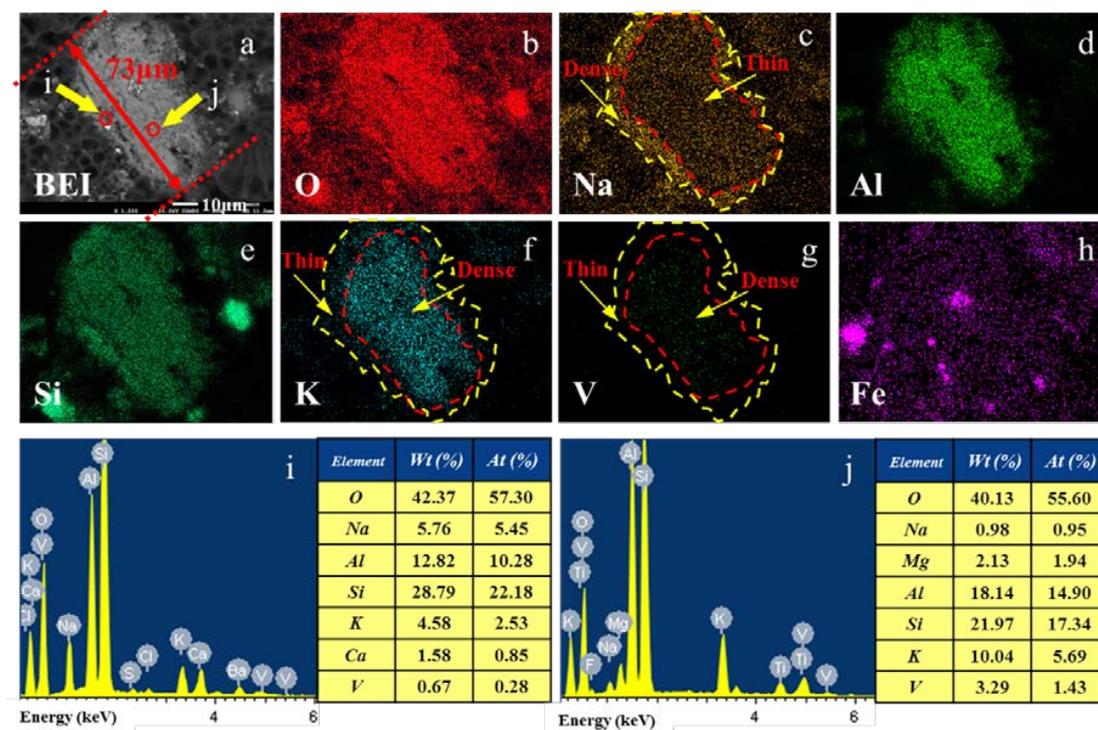


**Figure 4.** (a) BEI of the third type of vanadium-bearing grain in water leaching residue, EDS elemental distribution: (b) O, (c) Na, (d) Al, (e) Si, and (f) V.

### 3.3. Vanadium Occurrence in Acid Leaching Residue

The BEI and representative elemental EDS maps of acid leaching residue are shown in Figure 5. The distribution of Na, K, and V, as marked by irregular polygon, is heterogeneous (Figure 5c,f,g). The distribution of Na is denser in the outer margin and thin in the interior of the grain, while distribution of K and V are thin in the interior and denser in the outer margin of the grain. The micro-area elemental analysis at the outer margin and interior of the grain was carried out.

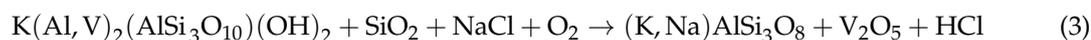
It is observed that the elemental composition at the outer margin is with values of 42.37%, 5.76%, 12.82%, 28.79%, and 4.58% for O, Na, Al, Si, and K, respectively (Figure 5i), which is close to the chemical composition of K-Na-feldspar, and it is inferred as K-Na-feldspar. Similarly, the mineral phase in the interior of the grain is identified as muscovite. Consequently, the vanadium in acid leaching residue presents in the muscovite surrounded by K-Na-feldspar, which is in good agreement with the second type of vanadium occurrence in water leaching residue.



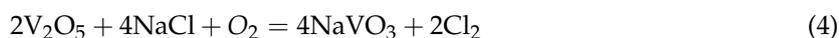
**Figure 5.** (a) BEI of acid leaching residue, EDS elemental distribution: (b) O, (c) Na, (d) Al, (e) Si, (f) K, (g) V, (h) Fe, and EDS spectra collected from BEI as marked by circle (i) at the outer margin and (j) at the interior of grain.

#### 4. Discussion

According to the results from the EDS analysis, there are three types of vanadium occurrence in the water residue: (1) calcium vanadate, (2) existing in muscovite surrounded by K-Na-feldspar, and (3) free vanadium oxide. In the process of roasting, vanadium-bearing muscovite can react with quartz and sodium salt to generate K-Na-feldspar as follows [21,22]:



Equation (3) shows vanadium is liberated from crystal structure of muscovite during the reaction of muscovite converted to K-Na-feldspar. Most liberated vanadium reacts with sodium salt to generate water-soluble sodium vanadate, and the reaction is expressed as:

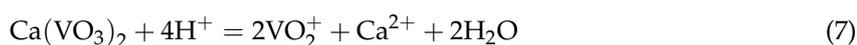


Some liberated vanadium reacts with calcite in stone coal to form water-insoluble calcium vanadate, and the reaction is given as:

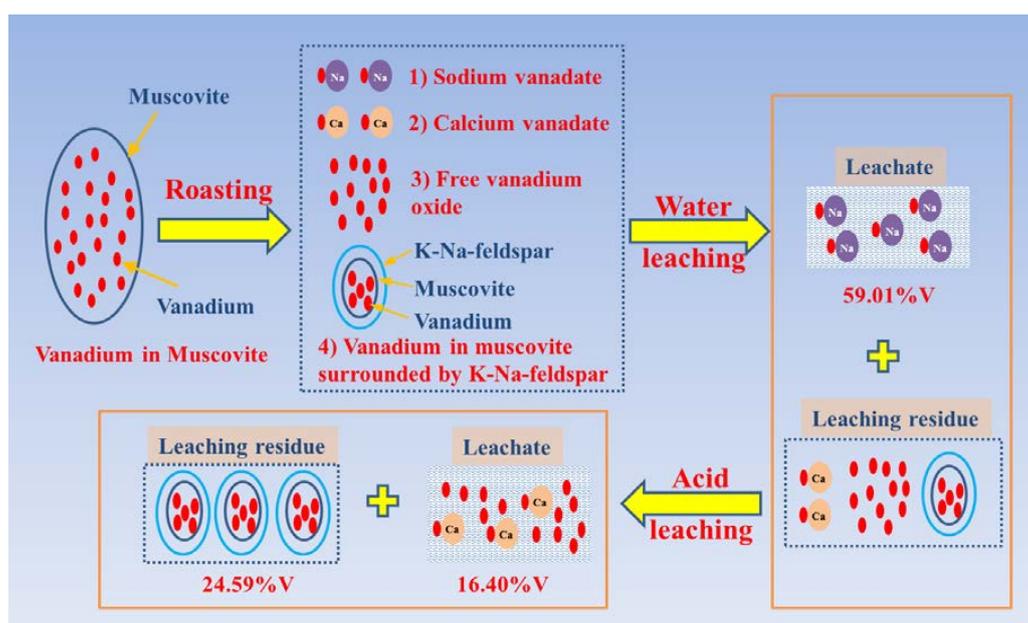


Additionally, other liberated vanadium is unreacted and exists as free vanadium oxide. However, for some coarse muscovite grains, only the outer margin of muscovite grain is converted to K-Na-feldspar, and the reaction does not occur in the interior of the grain. Hence, the vanadium in the interior of the grain is not liberated and remains in muscovite, which is surrounded by K-Na-feldspar.

The vanadium in acid leaching residue exists in muscovite surrounded by K-Na-feldspar. Comparing the vanadium occurrence in water leaching residue with that in acid leaching residue, it is indicated that the calcium vanadate and free vanadium oxide are dissolved out during acid leaching. The chemical reactions are as follows [23]:



The vanadium recoveries of the water and acid leaching are calculated, which are 59.01% and 16.40%, respectively, and the vanadium content in the acid leaching residue was measured, which is 24.59%. It can be inferred that 59.01% and 16.40% of vanadium were converted to water-soluble vanadate during roasting. 40.99% of vanadium remained in the water residue presenting as calcium vanadate and free vanadium oxide, as well as existing in muscovite surrounded by K-Na-feldspar. 16.40% of the water-insoluble but acid-soluble vanadium, including calcium vanadate and free vanadium oxide, was leached by acid. However, there is 24.59% of vanadium presenting in muscovite surrounded by K-Na-feldspar still in the acid leaching residue. Given the above, the vanadium transitions during roasting-leaching process can be schematically presented as Figure 6. The primary reason that there is vanadium in acid leaching residue is that the vanadium is not liberated from the muscovite for the coarse muscovite grains during roasting, because the reaction of muscovite converted to K-Na-feldspar is hindered when increasing the thickness of the product layer is increased. This vanadium remaining in muscovite cannot be leaching out by water and dilute acid. Hence, to improve the vanadium recovery of leaching, the key is to avoid coarse muscovite grains, and two ways could be proposed. One is guaranteeing the uniformity of particle with suitable grinding-classification process. The other is adopting microwave roasting, which can heat the outer margin and interior of grains simultaneously and result in the fragment of coarse muscovite [24].



**Figure 6.** Schematic diagram of vanadium transitions during roasting-leaching process of vanadium extraction from stone coal.

## 5. Conclusions

During roasting of stone coal, vanadium-bearing muscovite is converted to K-Na-feldspar and around 75% of vanadium is liberated from crystal structure of muscovite. Most liberated vanadium reacts with sodium salt to generate water-soluble sodium vanadate; some reacts with calcite in stone coal to form water-insoluble calcium vanadate, and other liberated vanadium exists as free vanadium oxide. For coarse muscovite grain, only the outer margin of muscovite grain is converted to K-Na-feldspar, and the reaction does not occur in the interior of the grain, in which vanadium is not liberated and surrounded by K-Na-feldspar. The sodium vanadate is leached out in the water leaching process, and the calcium vanadate and free vanadium oxide are dissolved out during acid leaching. The vanadium, which presents in muscovite grains surrounded by K-Na-feldspar, remains in acid leaching residue.

**Acknowledgments:** The financial support for this work from the Natural Science Foundation of Hubei Province of China (2016CFA013) and the Wuhan Science and Technology Bureau (2016070204020156) are gratefully acknowledged.

**Author Contributions:** Yunliang Zhao and Yimin Zhang conceived and designed the experiments; Yunliang Zhao and Licai Chen performed the experiments; Hao Yi and Shenxu Bao analyzed the data; Yimin Zhang and Shaoxian Song contributed reagents, materials, and analysis tools; Yunliang Zhao and Licai Chen wrote the paper.

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

## References

1. Mirazimi, S.M.J.; Rashchi, F.; Saba, M. A new approach for direct leaching of vanadium from LD converter slag. *Chem. Eng. Res. Des.* **2015**, *94*, 131–140. [[CrossRef](#)]
2. Zhao, Y.; Zhang, Y.; Bao, S.; Chen, T.; Xiang, L. Effect of Stone Coal Chemical Composition on Sintering Behavior during Roasting. *Ind. Eng. Chem. Res.* **2014**, *53*, 157–163. [[CrossRef](#)]
3. 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](#)]
4. Zhao, Y.; Zhang, Y.; Bao, S.; Chen, T.; Han, J. Calculation of mineral phase and liquid phase formation temperature during roasting of vanadium-bearing stone coal using FactSage software. *Int. J. Miner. Process.* **2013**, *124*, 150–153. [[CrossRef](#)]
5. Cai, Z.; Feng, Y.; Li, H.; Du, Z.; Liu, X. Co-recovery of manganese from low-grade pyrolusite and vanadium from stone coal using fluidized roasting coupling technology. *Hydrometallurgy* **2013**, *131–132*, 40–45. [[CrossRef](#)]
6. Cai, Z.; Feng, Y.; Li, H.; Zhou, Y. Selective separation and extraction of Vanadium(IV) and Manganese(II) from co-leaching solution of roasted stone coal and pyrolusite via solvent extraction. *Ind. Eng. Chem. Res.* **2013**, *52*, 13768–13776. [[CrossRef](#)]
7. Liang, L.; Bao, S.; Zhang, Y.; Tang, Y. Separation and recovery of V(IV) from sulfuric acid solutions containing Fe(III) and Al(III) using bis(2-ethylhexyl)phosphoric acid impregnated resin. *Chem. Eng. Res. Des.* **2016**, *111*, 109–116. [[CrossRef](#)]
8. Ye, P.; Wang, X.; Wang, M.; Fan, Y.; Xiang, X. Recovery of vanadium from stone coal acid leaching solution by coprecipitation, alkaline roasting and water leaching. *Hydrometallurgy* **2012**, *117–118*, 108–115. [[CrossRef](#)]
9. Li, X.; Wei, C.; Deng, Z.; Li, M.; Li, C.; Fan, G. Selective solvent extraction of vanadium over iron from a stone coal/black shale acid leach solution by D2EHPA/TBP. *Hydrometallurgy* **2011**, *105*, 359–363. [[CrossRef](#)]
10. Li, W.; Zhang, Y.; Liu, T.; Huang, J.; Wang, Y. Comparison of ion exchange and solvent extraction in recovering vanadium from sulfuric acid leach solutions of stone coal. *Hydrometallurgy* **2013**, *131–132*, 1–7. [[CrossRef](#)]
11. Zhao, Y.; Zhang, Y.; Song, S.; Chen, T.; Bao, S. Behaviors of impurity elements Ca and Fe in vanadium-bearing stone coal during roasting and its control measure. *Int. J. Miner. Process.* **2016**, *148*, 100–104. [[CrossRef](#)]
12. Li, M.; Wei, C.; Fan, G.; Li, C.; Deng, Z.; Li, X. Extraction of vanadium from black shale using pressure acid leaching. *Hydrometallurgy* **2009**, *98*, 308–313. [[CrossRef](#)]
13. Zhu, X.; Zhang, Y.; Jing, H.; Tao, L.; Yi, W. A kinetics study of multi-stage counter-current circulation acid leaching of vanadium from stone coal. *Int. J. Miner. Process.* **2012**, *114–117*, 1–6. [[CrossRef](#)]

14. Hu, Y.J.; Zhang, Y.M.; Bao, S.X.; Liu, T. Effects of the mineral phase and valence of vanadium on vanadium extraction from stone coal. *Int. J. Miner. Mater.* **2012**, *19*, 893–898. [[CrossRef](#)]
15. Wang, M.; Xiang, X.; Zhang, L.; Xiao, L. Effect of vanadium occurrence state on the choice of extracting vanadium technology from stone coal. *Rare Met.* **2008**, *27*, 112–115. [[CrossRef](#)]
16. Zhao, Y.; Zhang, Y.; Liu, T.; Chen, T.; Bian, Y.; Bao, S. Pre-concentration of vanadium from stone coal by gravity separation. *Int. J. Miner. Process.* **2013**, *121*, 1–5. [[CrossRef](#)]
17. *Ferrovandium-Determination of vanadium content-The ammonium ferrous sulfate titrimetric method*; GBT 8704.5–2007; Bureau of Quality and Technical Supervision of China: Beijing, China, 2007.
18. *Determination of vanadium in coal*; GBT19226–2003; Bureau of Quality and Technical Supervision of China: Beijing, China, 2003.
19. Lin, H.; Fan, B. Study on mechanism of phase transformation during roasting and extracting vanadium from fangshankou bone coal. *Chin. J. Rare Met.* **2001**, *25*, 273–277.
20. Shu, B.; Wang, Z.; Li, Q.; Zhang, Y. Review of vanadium extraction from stone coal by roasting technique with sodium chloride and calcium oxide. *Chin. J. Rare Met.* **2010**, *34*, 291–297.
21. Chen, T.J.; Qiu, G.Z.; Zhu, D.Q. Experiment study on new technology of extracting vanadium from stone coal with cyclic oxidation. *J. China Coal Soc.* **2008**, *33*, 454–458.
22. Zhao, Y.; Wang, W.; Zhang, Y.; Song, S.; Bao, S. In-situ investigation on mineral phase transition during roasting of vanadium-bearing stone coal. *Adv. Powder Technol.* **2017**, *28*, 1103–1107. [[CrossRef](#)]
23. Li, M.; Wei, C.; Qiu, S.; Zhou, X.; Li, C.; Deng, Z. Kinetics of vanadium dissolution from black shale in pressure acid leaching. *Hydrometallurgy* **2010**, *104*, 193–200. [[CrossRef](#)]
24. Song, S.; Campos-Toro, E.F.; López-Valdivieso, A. Formation of micro-fractures on an oolitic iron ore under microwave treatment and its effect on selective fragmentation. *Powder Technol.* **2013**, *243*, 155–160. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).