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Mechanism of Enhancing Extraction of Vanadium from Stone Coal by Roasting with MgO

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Abstract: In this paper, the extraction of vanadium from stone coal by roasting with MgO and leaching with sulfuric acid has been investigated, and the mechanism analysis of stone coal roasting with MgO was studied. The results indicated that under the conditions that the mass fraction of the particles with grain size of 0–0.074 mm in raw ore was 75%, the roasting temperature was 500 °C, the roasting time was 1 h, MgO addition was 3 wt %, the sulfuric acid concentration was 20 vol %, the liquid-to-solid ratio was 1.5 mL/g, the leaching temperature was 95 °C, and leaching time was 2 h, resulting in a vanadium leaching efficiency of 86.63%, which increased by 7.73% compared with that of blank roasting. The mechanism analysis showed that the degree of calcite decomposition was low and, thus, magnesium vanadate was more easily formed than calcium vanadate below 500 °C. Moreover, magnesium vanadate was easier to dissolve than calcium vanadate during the sulfuric acid leaching process. Thus, the vanadium leaching efficiency was enhanced by using MgO as a roasting additive below 500 °C. Additionally, at high temperature the formation of tremolite would consume calcium oxide produced from the decomposition of calcite, thus, the formation of calcium vanadate was hindered, and V_2O_5 would react with MgO to form magnesium vanadate. Therefore, the vanadium leaching efficiency of roasting with MgO was higher than that of blank roasting at high temperature.

Keywords: stone coal; vanadium; MgO; mechanism analysis

1. Introduction

Vanadium is an important rare metal and has been widely used in ferrous and non-ferrous alloys. Additionally, vanadium also plays a key role in some new industries, such as chemical industry, medicine, vanadium redox batteries, and so on [1,2]. Stone coal is a particular vanadium ore resource in China, and its gross reserves of vanadium account for more than 87% of the domestic reserves of vanadium [3–5]. Therefore, extracting vanadium from stone coal is an important way to obtain vanadium pentoxide.

In general, most of the vanadium in stone coal mainly exists as trivalent vanadium (V(III)) which substitutes for trivalent aluminum (Al(III)) in the octahedral crystal lattice of the mica minerals as an isomorphism [6–8]. The trivalent vanadium in the lattice of the mica minerals cannot be directly dissolved in acid solution, which must be oxidized to a high valence state. Thus, it is necessary to break down the crystal structure of the mica minerals for extracting vanadium from stone coal. One of the effective methods commonly used is roasting [9,10].

Many roasting methods in the vanadium extraction process of low grade vanadium-bearing stone coal have been proposed in the past. Traditionally, the most widely-applied roasting method is sodium roasting. However, sodium roasting produces corrosive gases, including HCl, Cl_2, SO_2, and SO_3, which corrode equipment severely and contaminate the environment [11–14]. These serious disadvantages have limited further development of this roasting method, which has been prohibited by the government in recent years and replaced by some modified roasting methods, such as calcified roasting, oxidizing roasting, and composite additives roasting. Though the exhaust gas pollution is avoided in calcified roasting, the roasting method has high energy consumption and a strong selectivity for minerals, thereby the application of calcified roasting method is limited [15,16]. The oxidizing roasting method can greatly reduce gas pollution, but the leaching efficiency of vanadium is low [17–19]. The composite additives roasting method can decrease the amount of poisonous gas discharge and has a high leaching efficiency of vanadium. However, the method lacks the general applicability of vanadium-bearing minerals [20,21]. Generally speaking, these roasting methods have various problems, such as low vanadium leaching efficiency, high production cost, environmental pollution, and so on. Owing to the increasing environmental concerns, it is essential to research and develop an environmentally-friendly technology with higher recovery of vanadium for extracting vanadium from stone coal.

The aim of this work is to enhance the extraction of vanadium from stone coal by using MgO as roasting additive, which had good function of sulfur fixation and could reduce the release of pollution. This work has certain referential significance for the selection of the additives in the roasting process for extracting vanadium from stone coal.

2. Experimental

2.1. Materials

The stone coal used in this work was obtained from Jiangxi Province, China. The ore was crushed and ground to a certain particle size. The obtained ore was referred to as raw ore throughout this work. All of the reagents used were of analytical reagent grade. The particle size of MgO used is ~0.074 mm. All of the water used in this work was distilled water.

The chemical composition of the raw ore was analyzed through ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) method and the result was given in Table 1. As shown in Table 1, the content of vanadium in terms of V_2O_5 was 0.80% and SiO_2 was the main composition. The mineralogical composition of the raw ore was identified by X-ray diffraction (XRD, Rigaku, Tokyo, Japan) analysis (Figure 1). The electron probe micro-analysis (EPMA) of the raw ore was performed and the result was shown in Table 2. Combined Figure 1 and Table 2, it could be seen that the raw ore was mainly composed of quartz, muscovite, and calcite. Moreover, muscovite was the main vanadium-bearing mineral. Table 3 showed vanadium phase analysis and its valence state in raw ore. It indicated that vanadium mainly existed in silicoaluminate minerals (namely mica minerals) in the form of V(III).

Table 1. Chemical compositions of the raw ore wt %.

Element	V_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	C	S
Content	0.80	65.00	6.78	3.75	3.29	1.53	1.73	0.58	9.21	0.87

Table 2. EPMA result of the raw ore wt %.

Minerals	V	Si	Al	Fe	Ca	Mg	K	O
Quartz	0.00	42.91	0.03	0.00	0.00	0.00	0.00	49.07
Muscovite	0.97	26.57	3.66	0.35	0.03	0.67	1.71	35.06
Calcite	0.01	0.71	0.31	0.00	38.53	0.32	0.25	16.81

Table 3. Vanadium phase analyses and its valence state in raw ore wt %.

Category	Total Vanadium	Vanadium Phase			Valence State		
		Bound to Free Oxide	Silicoaluminate	Bound to Organics	V(III)	V(IV)	V(V)
Percentage	100	7	89	4	73	27	0
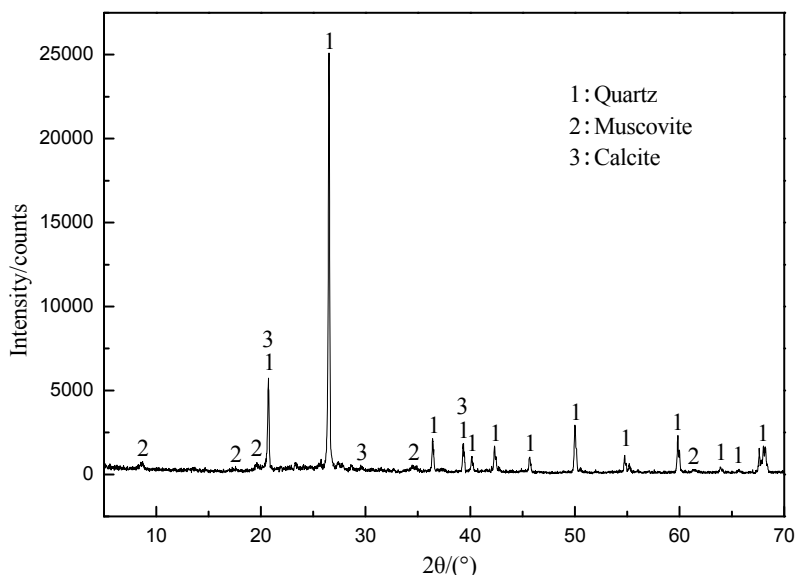
Figure 1. XRD pattern of the raw ore.

2.2. Procedure and Methods

Every experiment adopted forty grams raw ore. The sample, which was composed of the raw ore and a certain amount of magnesium oxide, was put in a crucible and heated in a muffle furnace for a certain period of time. During the roasting process the door of the muffle furnace was kept open to maintain an oxidizing atmosphere.

The leaching experiments were performed at an atmospheric pressure in a magnetic stirrer capable of heating and stirring. In all the leaching experiments, the roasted sample was leaching in 20 vol % sulfuric acid solution according to the liquid-to-solid ratio of 1.5 mL/g at temperature of 95 °C for 2 h. The liquid-to-solid ratio referred to the ratio of the sulfuric acid solution volume (mL) and raw ore quality (g), which meant that the volume of sulfuric acid solution was kept constant at 60 mL during the leaching process. At the end of each leaching test, the leaching slurry was filtered by vacuum filtration and the leaching solution and leaching residue were obtained. The amount of vanadium pentoxide in the leaching solution was determined by ferrous ammonium sulfate titration method [22].

The chemical composition of the raw ore was determined by ICP-AES performed on the IRIS Advantage ER/S instrument (Thermo Elemental, Boston, MA, USA).

X-ray diffraction (XRD) patterns were obtained by using a Rigaku D/MAX-RB X-ray diffraction (Rigaku, Tokyo, Japan) with Cu Kα radiation.

A JAX-8230 electronic probe micro-analyzer (EPMA) was applied for quantitative elementary analysis and mineralogical composition.

Microscopic observation and elemental analysis (SEM with EDS) was conducted by using a JEOL JSM-6610 scanning electronic microscope (JEOL, Tokyo, Japan) equipped with a BRUKER QUANTAX200-30 energy dispersive spectrometer (BRUKER, Karlsruhe, Germany).

The apparent density was determined by using a SK-1002 loose density tester (Qunlong, Xiamen, China).

3. Results and Discussion

3.1. Effect of Roasting Temperature on Vanadium Leaching Efficiency

The effect of roasting temperature from 400 to 900 °C on vanadium leaching efficiency was investigated under the conditions that MgO addition was 0 or 3 wt % and roasting time was 1 h. The mass fraction of the particles with grain size of 0–0.074 mm in raw ore was 75%. The result was presented in Figure 2.

As illustrated in Figure 2, roasting temperature had a significant effect on vanadium leaching efficiency. The vanadium leaching efficiency reached the maximum value (namely 86.63%) at around 500 °C. The vanadium leaching efficiency decreased when the roasting temperature was below or above 500 °C. In particular, the vanadium leaching efficiency of blank roasting decreased obviously after 800 °C. However, the vanadium leaching efficiency of roasting with MgO decreased obviously after 900 °C. It could also be seen from Figure 2 that under the same roasting temperature the vanadium leaching efficiency could be improved by adding MgO in the roasting process. Furthermore, the difference of vanadium leaching efficiency between roasting with MgO and blank roasting was more obvious at high temperature. Therefore, the optimum roasting temperature should be 500 °C.
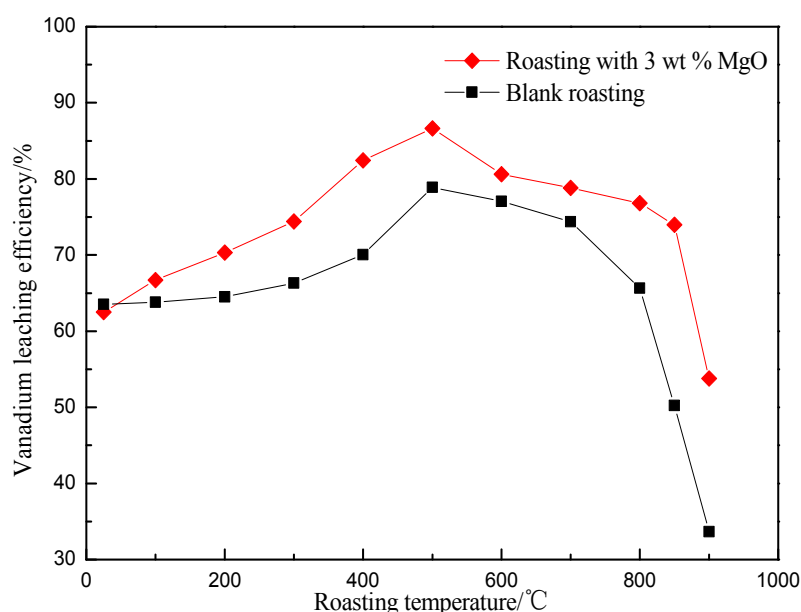

Figure 2. Effect of roasting temperature on vanadium leaching efficiency.

3.2. Effect of Roasting Time on Vanadium Leaching Efficiency

The effect of roasting time from 0.5 to 2 h on vanadium leaching efficiency was studied under the conditions that MgO addition was 0 or 3 wt % and roasting temperature was 500 °C. The mass fraction of the particles with grain size of 0–0.074 mm in raw ore was 75%. The result was illustrated in Figure 3.

The vanadium leaching efficiency without roasting process was only 62.52%. It could be observed that roasting time had influence on vanadium leaching efficiency. The vanadium leaching efficiency increased with the rise of roasting time. While the roasting time is short, the transformation of vanadium from low valence to high valence was not complete. However, when roasting time was above 1 h, the vanadium leaching efficiency remained unchanged, which might be due to the fact that the oxidation reaction of vanadium reached equilibrium. Figure 3 also showed that under the same roasting time the vanadium leaching efficiency could be improved by roasting with MgO. Thus, roasting time of 1 h was found to be optimum for roasting process.
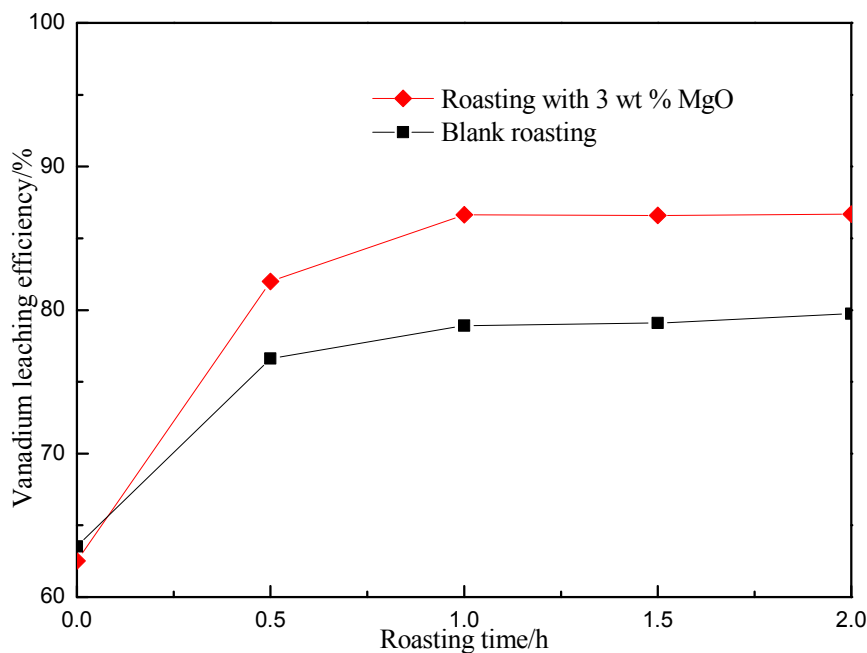
Figure 3. Effect of roasting time on vanadium leaching efficiency.

3.3. Effect of MgO Dosage on Vanadium Leaching Efficiency

The effect of MgO dosage on vanadium leaching efficiency was investigated under the conditions that roasting temperature was 500 °C and roasting time was 1 h. The mass fraction of the particles with grain size of 0–0.074 mm in raw ore was 75%. The result was shown in Figure 4.

The vanadium leaching efficiency of blank roasting was 78.90%. Figure 4 indicated that the vanadium leaching efficiency increased significantly with the increase of MgO dosage. Nevertheless, while MgO dosage exceeded 3 wt %, the increase of vanadium leaching efficiency was not obvious. Hence, MgO dosage of 3 wt % was chosen as the optimal condition for roasting process.
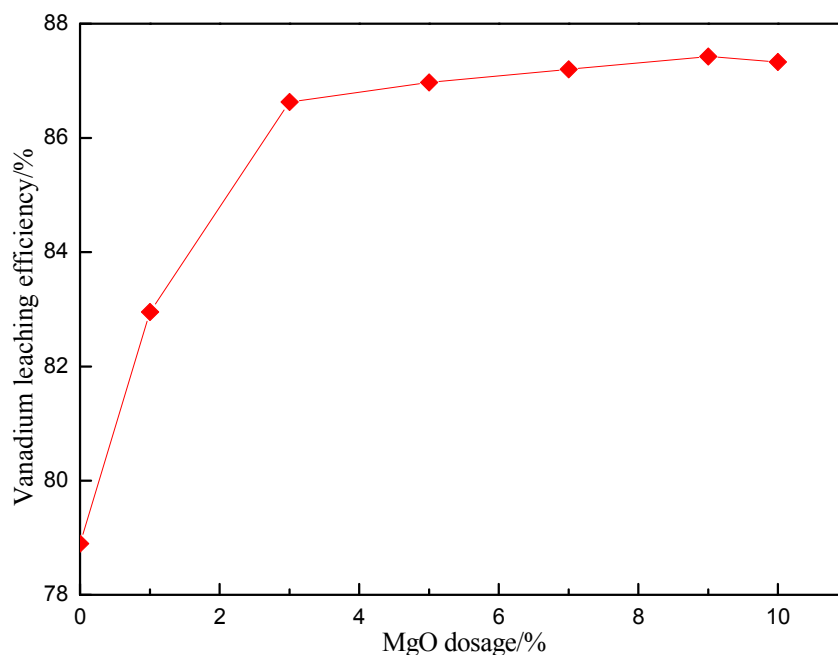

Figure 4. Effect of MgO dosage on vanadium leaching efficiency.

3.4. Effect of the Particle Size of Raw Ore on Vanadium Leaching Efficiency

The effect of the particle size of raw ore on vanadium leaching efficiency was investigated under the conditions that roasting temperature was 500 °C, MgO addition was 3 wt % and roasting time was 1 h. The result was shown in Figure 5.

As shown in Figure 5, the vanadium leaching efficiency increased with the decrease of the particle size of raw ore. While the mass fraction of the particles with the grain size of 0–0.074 mm exceeded 75%, the vanadium leaching efficiency began to decline. The reason might be that the viscosity of leaching slurry increased when the particle size of raw ore was too small, which hindered the leaching process. Thus, the mass fraction of the particles with the grain size of 0–0.074 mm in raw ore should be 75%.
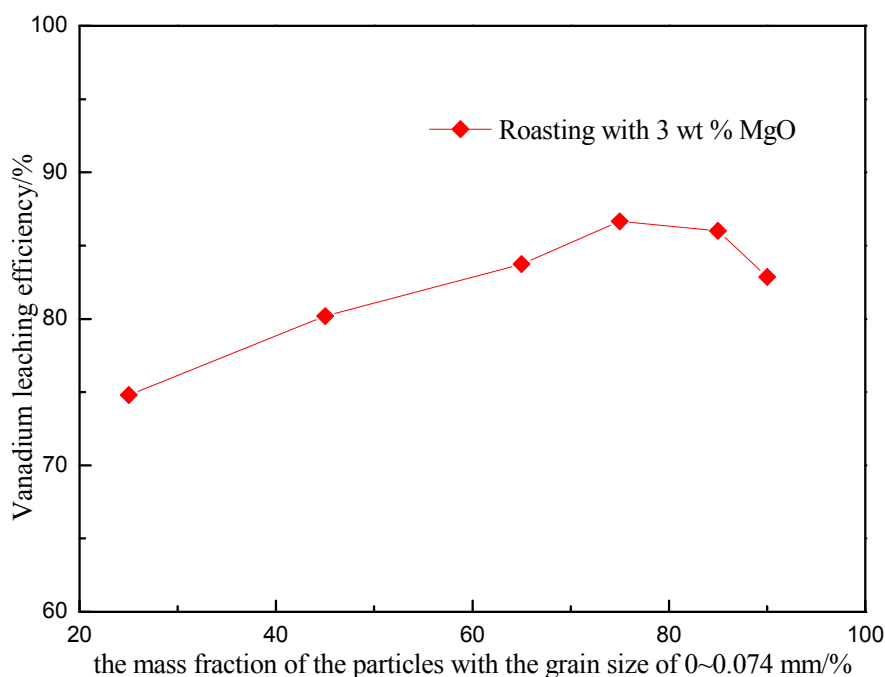

Figure 5. Effect of the particle size of raw ore on vanadium leaching efficiency.

3.5. The Mechanism Analysis of Stone Coal Roasting with MgO

The phase transformation of the samples roasted with 3 wt % MgO at different roasting temperatures for 1 h were analyzed by XRD. The XRD patterns were presented in Figure 6.

It could be seen that the diffraction peaks of calcite could not be identified when the roasting temperature increased to 700 °C. Meanwhile, the diffraction peaks of muscovite were weakened with the increase of roasting temperature and then disappeared at 900 °C, indicating that during the roasting process the structure of muscovite was destroyed, and then the vanadium in the octahedron crystal lattice of muscovite could be released and oxidized into high valence vanadium. Hence, below 500 °C the vanadium leaching efficiency was improved with the increase of roasting temperature.

It could also be observed from Figure 6 that two new mineral phases, sanidine and tremolite, appeared at 900 °C. To confirm the existence of tremolite, the SEM image and corresponding EDS analysis of the sample roasted with 3 wt % MgO at 900 °C for 1 h were conducted. The results were shown in Figure 7.

Figure 7 revealed that the elemental distribution of O, Mg, Si, and Ca had obvious relevance. Combined with the XRD patterns of the roasted samples in Figure 6, the tremolite, which had good thermal stability, existed in the sample roasted with 3 wt % MgO at 900 °C for 1 h.
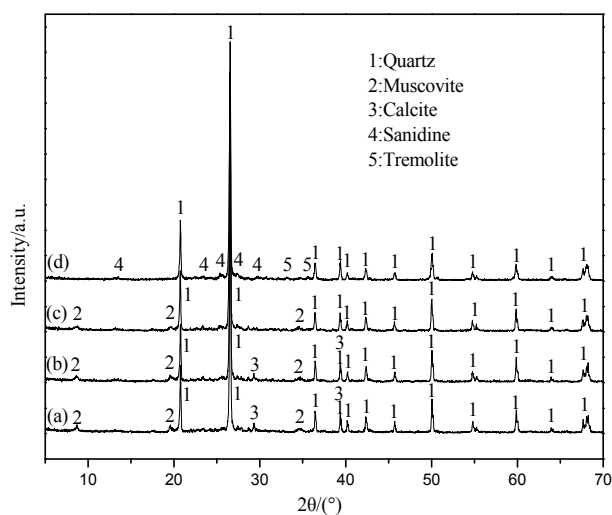
Figure 6. XRD patterns of the samples roasted with 3 wt % MgO at different roasting temperatures for 1 h. (**a**) 400 °C; (**b**) 500 °C; (**c**) 700 °C; and (**d**) 900 °C.
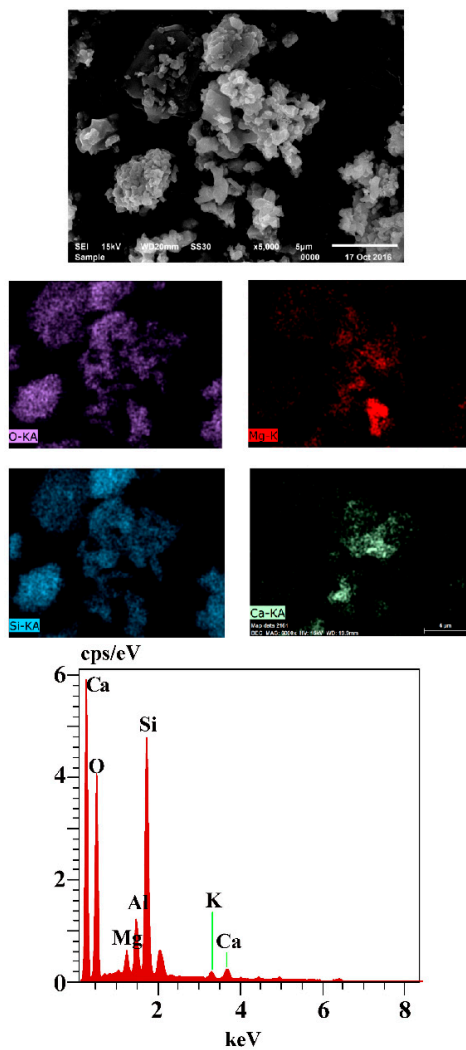

Figure 7. SEM image and corresponding EDS analysis of the sample roasted with 3 wt % MgO at 900 °C for 1 h.

To find out the reason why vanadium leaching efficiency decreased at high temperature, the SEM images of the roasted samples at 850 °C were observed.

As shown in Figure 8a, some particles were bonded to each other and then big molten mass formed after roasting at 850 °C, which indicated that the sample was sintered at 850 °C [23]. A similar situation could also be observed in Figure 8b. Hence, it was reasonable to deduce that the decrease of vanadium leaching efficiency at high temperature might be attributed to that the samples were sintered.
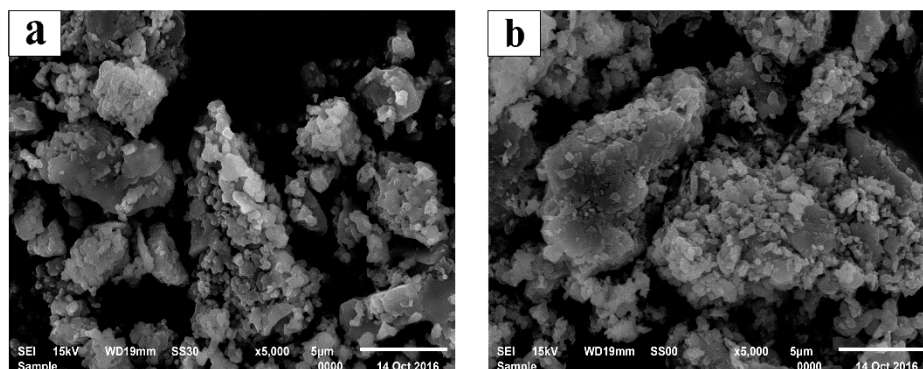

Figure 8. SEM images of the roasted samples at 850 °C: (**a**) Blank roasting; (**b**) Roasting with 3 wt % MgO.

To confirm the deduction that the decrease of vanadium leaching efficiency at high temperature was due to the face that the samples were sintered. The apparent density of the roasted samples at different roasting temperatures was determined and the results are presented in Figure 9.

It was demonstrated that, before 900 °C, the apparent density increased slightly with the increase of roasting temperature, which was due to the slight sintering of the samples. After 900 °C the apparent density increased sharply. This suggested that the samples were sintered seriously [24]. At this time some vanadium in the raw ore might be enwrapped in the formed sintered sample, which was hard to be leached by sulfuric acid. Thus, the vanadium leaching efficiency decreased at high temperature. Meanwhile, it could be seen that under the same conditions the apparent density of the sample roasted with 3 wt % MgO was less than that of the blank roasted sample.
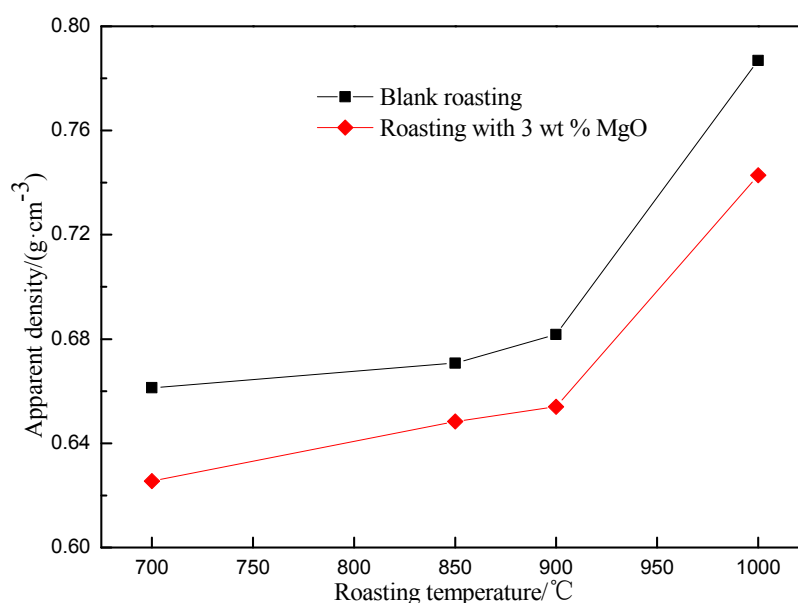

Figure 9. Apparent density of the roasted samples at different roasting temperatures.

To study the function of MgO on vanadium extraction from stone coal, the SEM images and corresponding EDS analysis of the blank roasted sample and the sample roasted with 3 wt % MgO at 500 °C were conducted.

Researchers had proposed that vanadate compounds appeared during the stone coal roasting process [25]. The relevance of V, Ca, and O shown in Figure 10a indicated that the vanadium in the blank roasted sample at 500 °C was probably in the form of calcium vanadate, which was difficult to be leached by the sulfuric acid. Nevertheless, Figure 10b illustrated that the elemental distribution of V, Mg, and O had obvious relevance. Combined with [26,27], it could be deduced that magnesium vanadate existed in the sample roasted with 3 wt % MgO at 500 °C. Moreover, magnesium vanadate was easier to dissolve than calcium vanadate during the sulfuric acid leaching process [28,29]. Therefore, it may be due to the formation of magnesium vanadate that the vanadium leaching efficiency of roasting with MgO was higher than that of blank roasting.
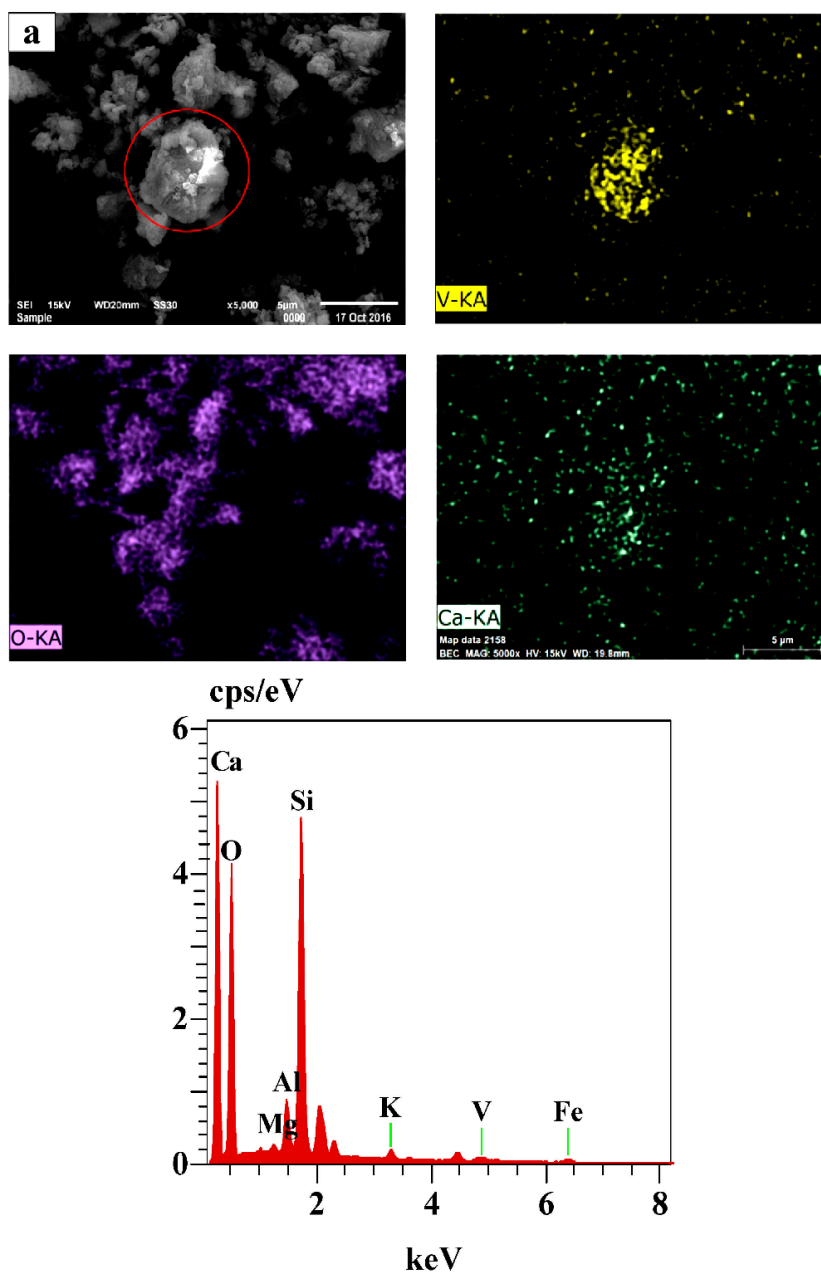

Figure 10. *Cont.*
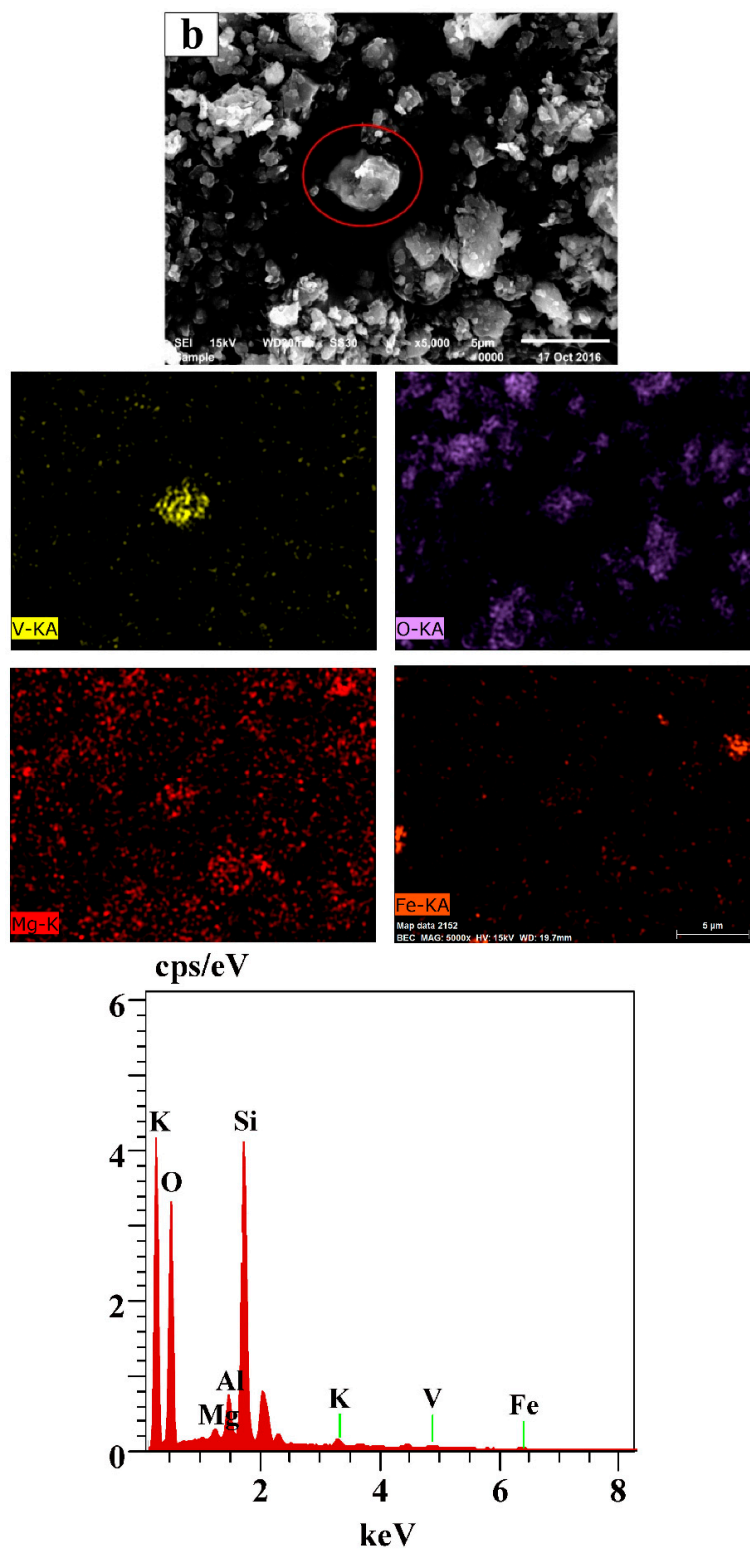
Figure 10. SEM images and corresponding EDS analysis of the blank roasted sample (**a**) and the sample roasted with 3 wt % MgO (**b**) at 500 °C.

From the above experiments and analysis, it could be concluded that the stone coal roasting process was a complex chemical reaction process. The main chemical reactions that occurred during stone coal roasting process were shown in Table 4. HSC Chemistry software (Outokumpu Research OY,

Pori, Finland) was designed for various kinds of chemical reactions and equilibria calculations [30–32]. The standard Gibbs free energy changes ΔG^{Θ} for each reaction at different temperatures could be obtained by HSC Chemistry software. The results are shown in Figure 11.

Table 4. The main chemical reactions during stone coal roasting process.

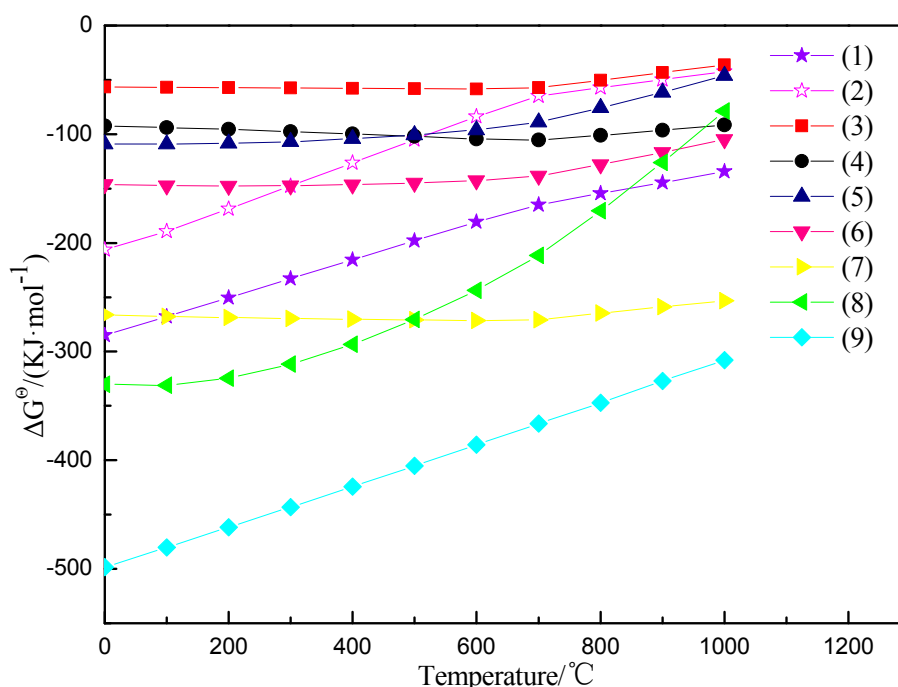| No.	Chemical Reactions
(1)	$V_2O_3 + O_2 = V_2O_5$
(2)	$2V_2O_4 + O_2 = 2V_2O_5$
(3)	$MgO + V_2O_5 = MgV_2O_6$
(4)	$2MgO + V_2O_5 = Mg_2V_2O_7$
(5)	$3MgO + V_2O_5 = Mg_3(VO_4)_2$
(6)	$CaO + V_2O_5 = CaV_2O_6$
(7)	$2CaO + V_2O_5 = Ca_2V_2O_7$
(8)	$3CaO + V_2O_5 = Ca_3V_2O_8$
(9)	$2CaO + 5MgO + 8SiO_2 + H_2O = Ca_2Mg_5Si_8O_{22}(OH)_2$

Figure 11. Standard Gibbs free energy changes for main chemical reaction at different temperatures during the stone coal roasting process.

As presented in Figure 11, the standard Gibbs free energy changes ΔG^{Θ} for all of the main chemical reactions were negative over the temperature range of 100–1000 °C, which indicated that the formation of various vanadate compounds and tremolite, and the oxidation of vanadium, were thermodynamically feasible. ΔG^{Θ} values for reactions (1) and (2) were negative, indicating that V(III) and V(IV) could be oxidized to V(V) during the stone coal roasting process, and V_2O_5 would react with other oxides to form vanadate.

ΔG^{Θ} values for reactions (6)–(8) were more negative than those for reactions (3)–(5) and this meant that the formation of calcium vanadate was easier than that of magnesium vanadate when enough calcium oxide was present. Based on [29,33,34], below 500 °C the degree of calcite decomposition was low. Due to the deficiency of calcium oxide, magnesium vanadate was more easily formed at temperatures lower than 500 °C. Moreover, the solubility of magnesium vanadate was relatively large. Thus, the vanadium leaching efficiency was enhanced by using MgO as roasting additive.

$\Delta G^{\ominus}$ value for reaction (9) was the most negative, which indicated that in the presence of calcium oxide this reaction was the easiest to happen. When the roasting temperature was higher than 500 °C, calcium oxide produced from the decomposition of calcite increased gradually with the increase of temperature. However, due to the introduction of MgO during stone coal roasting process, tremolite appeared at high temperature. The formation of tremolite would consume calcium oxide and, thus, the formation of calcium vanadate was hindered. As a result, V_2O_5 would react with MgO to form magnesium vanadate. Accordingly, the vanadium leaching efficiency of roasting with MgO was higher than that of blank roasting at high temperature.

4. Conclusions

In this study, vanadium was extracted from stone coal by roasting with MgO and leaching with sulfuric acid, and the function of MgO during stone coal roasting process was analyzed. The following conclusions can be drawn:

(1) The vanadium leaching efficiency of 86.63% was obtained under the experimental conditions that the particle size of raw ore was ~0.074 mm accounting for 75%, the roasting temperature was 500 °C, the roasting time was 1 h, the MgO addition was 3 wt %, the sulfuric acid concentration was 20 vol %, the liquid-to-solid ratio was 1.5 mL/g, the leaching temperature was 95 °C, and leaching time was 2 h. However, under the same conditions only 78.90% of vanadium was leached during blanking roasting and the sulfuric acid leaching process. Thus, the vanadium leaching efficiency increased by 7.73% by using MgO as the roasting additive.

(2) During the roasting process the formation of calcium vanadate was easier than that of magnesium vanadate when enough calcium oxide was present. Below 500 °C the degree of calcite decomposition was low. Due to the deficiency of calcium oxide which was produced from the decomposition of calcite, magnesium vanadate was more easily formed. Moreover, magnesium vanadate was easier to be dissolved than calcium vanadate during the sulfuric acid leaching process. Hence, the vanadium leaching efficiency was improved by using MgO as roasting additive below 500 °C. Additionally, tremolite appeared at high temperature, which would consume calcium oxide produced from the decomposition of calcite. As a result, the formation of calcium vanadate was hindered and V_2O_5 would react with MgO to form magnesium vanadate. Accordingly, the vanadium leaching efficiency of roasting with MgO was higher than that of blank roasting at high temperature.

Author Contributions: Fang Chen and Yimin Zhang conceived and designed the experiments; Fang Chen performed the experiments; Fang Chen and Nannan Xue analyzed the data; Yimin Zhang, Jing Huang contributed reagents/materials/analysis tools; and Fang Chen wrote the paper.

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

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