

# Study of the Dissolution Behavior of Muscovite in Stone Coal by Oxygen Pressure Acid Leaching



NAN-NAN XUE, YI-MIN ZHANG, TAO LIU, and JING HUANG

The dissolution behavior of muscovite in stone coal during the oxygen pressure acid leaching process was studied. The study showed that the dissolution behaviors of V, Al, and K were similar. K was the most easily leached, followed by Al, and then by V during oxygen pressure acid leaching process. When the reaction temperature exceeded 423 K (150 °C), alunite was generated, which led to vanadium losses because of its absorption performance. The dissolution of the muscovite in stone coal mainly depended on H<sub>2</sub>SO<sub>4</sub> concentration and temperature. O<sub>2</sub> had a main effect not on muscovite's dissolution but on the V<sup>3+</sup> oxidation. During the oxygen pressure acid leaching process, (1) the interfacial K in the muscovite lattice was dissolved rapidly, producing a new interface; (2) for charge balance, the interfacial O absorbed hydrogen ions to form hydroxy; (3) the interfacial hydroxy reacted with hydrogen ions and left vacancy as a result of O loss, producing more new surface to expose more Al, V, and Si; (4) the interfacial Al or V was exchanged by hydrogen ions and V<sup>3+</sup> was oxidized to V<sup>4+</sup> and V<sup>5+</sup>; and (5) Si hardly reacted with H<sup>+</sup> and generated high-Si surface.

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## I. INTRODUCTION

STONE coal is a particular vanadium-bearing siliceous shale in China, which mainly formed before the middle Devonian Epoch. Stone coal contains inorganic and organic components, and the content of inorganic is much higher than that of organic materials, which is similar to coal.<sup>[1,2]</sup> The grade of V<sub>2</sub>O<sub>5</sub> is usually lower than 1 pct and the components are complex. The vanadium in stone coal mainly exists of the crystal lattice of muscovite and illite where V(III) replaces Al(III) as isomorphism.<sup>[3,4]</sup>

For extracting vanadium from stone coal, it is essential to break down the structure of muscovite and illite in stone coal. At present, there are two main categories: (1) transforming V(III) into V(IV) or V(V) *via* roasting; and (2) directly disintegrating the crystal lattice of muscovite and illite *via* leaching.<sup>[5–7]</sup>

In recent years, the direct acid leaching process has been getting increased attention, which has resulted in the development of the atmospheric pressure acid leaching process<sup>[8–10]</sup> and the oxygen pressure acid leaching process.<sup>[11–13]</sup> The atmospheric pressure acid leaching process usually needs to add fluoride (like HF,

NaF, NH<sub>4</sub>F, and CaF<sub>2</sub>) or oxidant (like NaClO and MnO<sub>2</sub>) to leach vanadium efficiently.<sup>[14–16]</sup>

The oxygen pressure acid leaching process introduces a pressure field to raise temperature and shorten time. It does not produce air pollution brought by the traditional roasting-leaching process, and there is no need to add the fluoride or oxidant during the whole leaching process. Deng *et al.*<sup>[17]</sup> found that under the conditions of leaching time of 3 to 4 hours, a temperature of 423 K (150 °C), H<sub>2</sub>SO<sub>4</sub> consumption of 25 to 30 pct, liquid-to-solid ratio of 1.2 mL/g, the particle size less than 0.074 mm, FeSO<sub>4</sub> addition of 3 to 5 pct, and oxygen pressure of 1.2 MPa, the vanadium recovery can be more than 92 pct by the method of two-step pressure acid leaching. Fan *et al.*<sup>[18]</sup> also demonstrated that with the increase of FeSO<sub>4</sub> addition, the recovery of SiO<sub>2</sub> was improved in the first leaching stage, but it decreased in the second leaching stage. However, its maximum recovery only attained 0.75 pct. That is, the SiO<sub>2</sub> was difficult to leach.

Oxygen pressure acid leaching is a process of solid-liquid-gas three-phase interfacial reactions. The pressure field can help to raise the reaction temperature and improve the reaction rate. On the one hand, it strengthens the damaging effect of H<sub>2</sub>SO<sub>4</sub> on the structure of aluminosilicate in stone coal for vanadium release. On the other hand, the impurity elements (K, Al, Fe, S, *etc.*) are also leached a lot, which caused numerous problems for the next purification. It is clear that studying the dissolution behavior of aluminosilicate in stone coal is important and helpful for revealing the leaching mechanism of stone coal as well as for exploring selective leaching of vanadium during the oxygen pressure acid leaching process. Therefore, the work of this article focused on the study of the characteristics of stone coal particles before and after oxygen pressure acid leaching and its effect on the

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recovery of V, Al, and K to discuss the behavior of the interfacial dissolution of muscovite in stone coal.

## II. EXPERIMENTAL

### A. Materials

The stone coal used in the study was obtained from Hubei province, South China. The X-ray diffraction pattern of the stone coal is shown in Figure 1. The stone coal mainly consists of quartz, muscovite, illite, calcite, and pyrite, as shown in Figure 1. The chemical composition of stone coal is given in Table I. The mineral constituents of stone coal were tested by microscopic statistical analyses, as given in Table II.

Table I shows that the content of vanadium is 0.43 pct. High contents of Ca, Fe, and S in the stone coal will lead to the increase of acid consumption. As observed in Table II, in addition to quartz, the major minerals in stone coal are muscovite and illite with a content of 15 pct, followed by carbonic matter, calcite, feldspar, a little pyrite, and kaolinite.

The chemical phases of vanadium in stone coal are detected by potentiometric titration,<sup>[19]</sup> and the results are given in Table III. The chemical constituents of the major minerals in stone coal are observed in Table IV and were obtained by electronic probe micro-analyzer (Phoenix, EDAX).

Table III shows that 80.64 pct of total vanadium existed in silicate minerals, 14.75 pct in organic matter

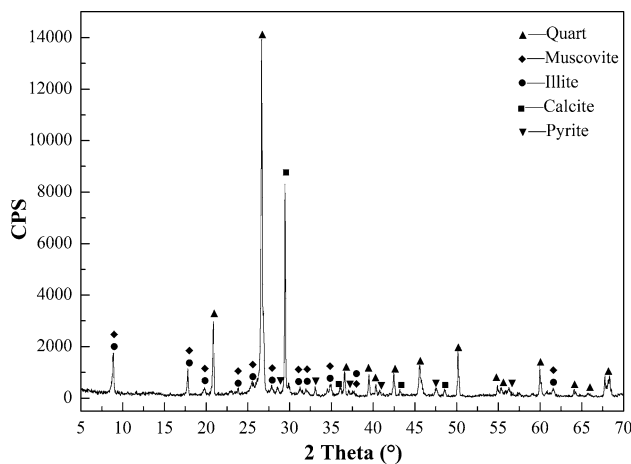


Fig. 1—XRD pattern of the stone coal.

and just 4.61 pct in free oxide. Quartz, pyrite, and calcite did not contain vanadium from Table IV. The vanadium mainly existed in muscovite and illite.

### B. Experimental Setup and Procedure

All experiments were carried out in a pure zirconium autoclave with a volume of 2 L (Model GSH-2) and conducted at a preset temperature that was controlled by a programmable temperature controller with a deviation of  $\pm 276$  K (3 °C). Oxygen was provided from an oxygen cylinder, and the purity of oxygen was 98 pct. Before all experiments, the stone coal was crushed to 0 to 3 mm and then ground by using a ball mill (model XMQL-600) to 0 to 0.074 mm. The ground stone coal is hereafter called “the sample.”

The sample and the prepared H<sub>2</sub>SO<sub>4</sub> solution were first loaded into the autoclave at the liquid-solid ratio of 1.5 mL/g and mixed adequately through mechanical stirring at 350 rpm. The autoclave was first heated without the introduction of oxygen. The heating time was 40 minutes. When the temperature reached the preset value, oxygen was introduced into the autoclave and maintained at a preset pressure. When the reaction period was over, cooling water was inputted through the cooling pipe to cool the slurries. The slurries were filtrated by vacuum suction filter device (model SHB-III), and the leachate and the residue were finally obtained.

### C. Detection Measurement

The content of V, Al, Si, and K in the leachate and the chemical composition of the stone coal and the residues were detected by inductive coupled plasma emission spectrometer (IRIS Advantage Radial, Thermo-Elemental). The X-ray diffraction (XRD) patterns were obtained by using a Rigaku D/MAX-RB X-ray diffraction meter with Cu K $\alpha$  radiation to analyze the mineral compositions in the stone coal and the residues.

Table III. Chemical Phases of Vanadium in Stone Coal (Wt. Pct)

Total V	Chemical Phase		
	V in Free Oxide	V in Silicate Minerals	V in Organic Matter
100	4.61	80.64	14.75
0.43	0.02	0.35	0.06

Table I. Chemical Composition of the Stone Coal (Weight Percentage)

V	Si	Al	Fe	Ca	Mg	K	Na	S	C
0.43	30.38	5.25	3.61	4.16	0.88	2.02	0.10	3.11	13.32

Table II. Mineral Constituents of the Stone Coal (Weight Percentage)

Quartz	Muscovite and Illite	Carbonic Matter	Calcite	Feldspar	Pyrite	Kaolinite	Others	Total
37	15	13	11	10	7	5	2	100

Table IV. EPMA Results of the Major Minerals in Stone Coal (Wt. Pct)

Mineral	V <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
Pyrite		0.06		59.12				
Calcite					1.10	65.94		
Quartz		98.35						
Muscovite	3.48	51.08	27.22	0.23	4.53	0.02	0.07	9.52
Illite	4.14	39.95	23.25	0.14	2.02	0.15	0.08	8.55
Albite	0.09	49.43	6.92	0.08	0.40	0.21	1.97	0.99

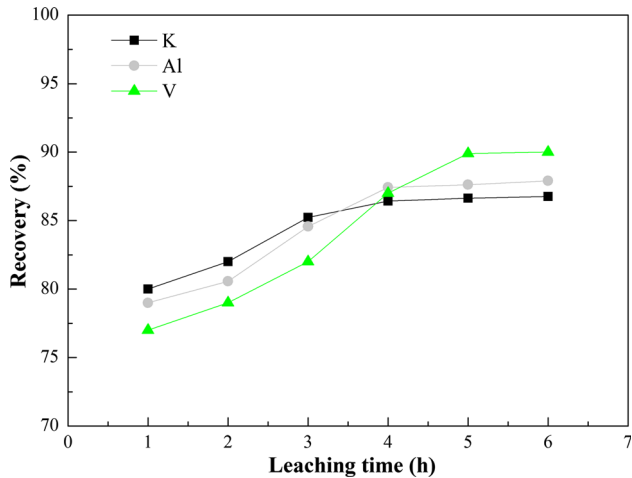


Fig. 2—Variations of the recovery of V, Al, and K over leaching time.

### III. RESULTS AND DISCUSSION

#### A. Effect of Leaching Time on the Leaching of V, Al, and K

The variations of the recovery of V, Al, and K over leaching time were investigated under the conditions of 423 K (150 °C), 20 pct(vol) H<sub>2</sub>SO<sub>4</sub>, 1.5 MPa O<sub>2</sub>. As Figure 2 shows, the recovery of K, Al, and V first increased and then started to be stable, respectively, at 3, 4, and 5 hours. To ensure the high recovery of vanadium, 5 hours was chosen to be a standard for the length of the experiment. It could be also suggested that K was most easily leached, followed by Al, and then by V during the oxygen pressure acid leaching process. This was due to the different locations of K, Al, and V in the muscovite lattice. The K was located between the unit layer structure of the muscovite lattice in stone coal for valence compensation, whereas the Al and the V were located in the unit layer structure, which was stable.

#### B. Effect of Reaction Temperature on the Leaching of V, Al, and K

The variations of the recovery of V, Al, and K with the increase of reaction temperature were investigated under the conditions of 5 hours, 20 pct(vol) H<sub>2</sub>SO<sub>4</sub>, 1.5 MPa O<sub>2</sub>. As shown in Figure 3, the recovery of V, K, and Al reached the maximum at 423 K (150 °C) and then declined rapidly with the increasing reaction temperature. Hence, the samples after leaching at 423 K, 443 K, and

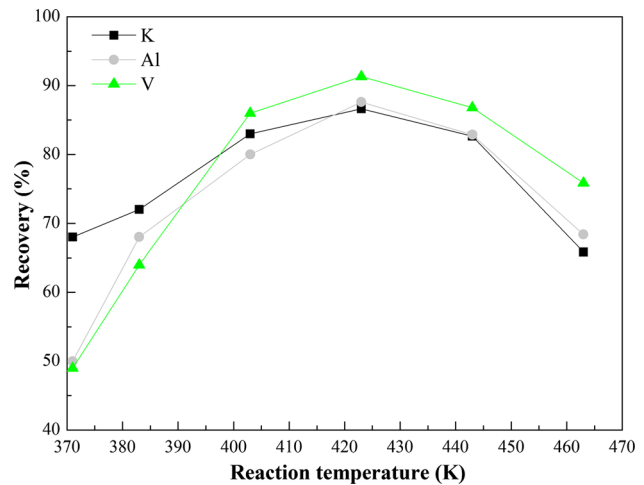
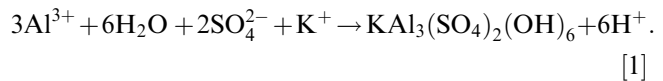


Fig. 3—Variations of the recovery of V, Al, and K with the increase of reaction temperature.

463 K (150 °C, 170 °C, and 190 °C) were examined using an X-ray diffractometer (Figure 4). Four obvious diffraction peaks of alunite (KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) appeared at both 443 K and 463 K (170 °C and 190 °C), and the diffraction peaks of the muscovite disappeared after leaching at both 443 K and 463 K (170 °C and 190 °C). According to the chemical Eq. [1], alunite was formed by Al<sup>3+</sup> hydrolysis:



Meanwhile, the peaks' intensity of alunite at 463 K (190 °C) was higher than at 443 K (170 °C), which suggested that the increasing reaction temperature promoted Al<sup>3+</sup> hydrolysis, with the result that more alunite was generated and led to vanadium loss because of its absorption performance.

#### C. Effect of Acid Concentration on the Leaching of V, Al, and K

The variations of the recovery of V, Al, and K with the increase of H<sub>2</sub>SO<sub>4</sub> concentration were investigated under the conditions of 5 hours, 423 K (150 °C), 1.5 MPa O<sub>2</sub>. As shown in Figure 5, the recovery of V, Al, and K rose rapidly at first and then started to level off at 20 pct H<sub>2</sub>SO<sub>4</sub>. The main chemical compositions of the samples before and after leaching are given in

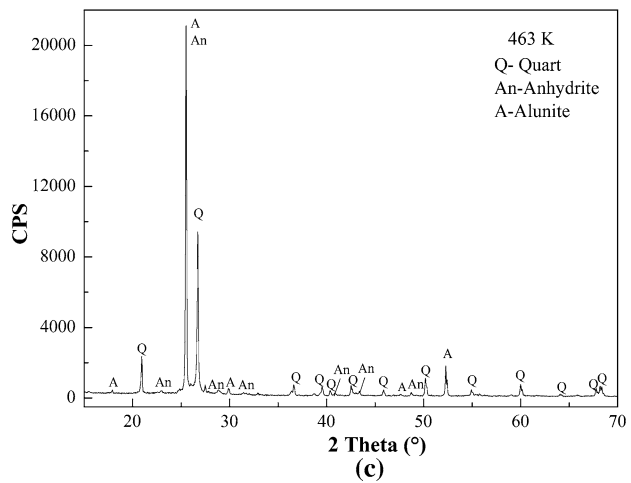
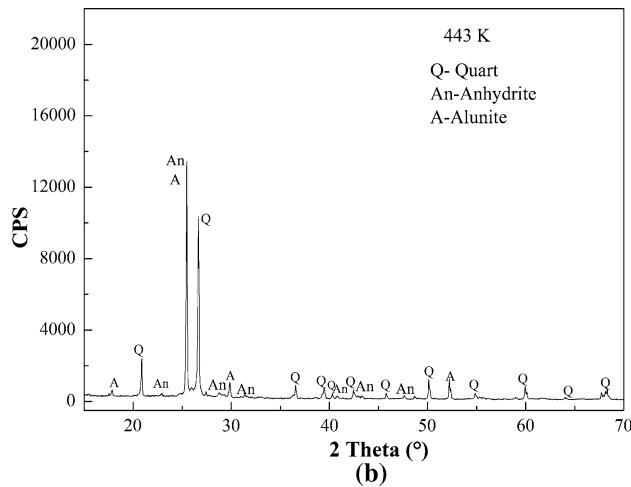
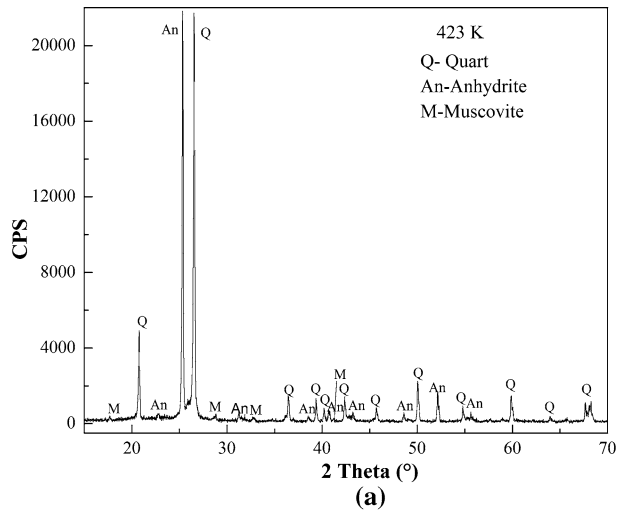


Fig. 4—XRD patterns of the samples after leaching at (a) 423 K (150 °C), (b) 443 K (170 °C), and (c) 463 K (190 °C).

Table V. The content of V, Al, and K after leaching at 20 pct H<sub>2</sub>SO<sub>4</sub> was very low. In the stone coal, the molar ratio of V to Al was 1:25. About 3.85 pct of the hydrogen ions that reacted with the muscovite and illite in stone coal were used for the exchange with V, 96.15 pct for the exchange with Al by calculation.

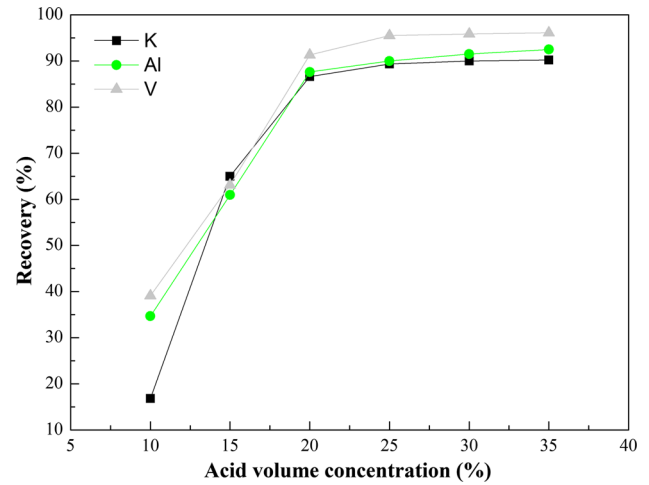


Fig. 5—Variations of the recovery of V, Al, and K with the increase of H<sub>2</sub>SO<sub>4</sub>.

Table V. Main Chemical Composition of the Samples Before and After Leaching (Weight Percentage)

Sample	V	Si	Al	K
Before leaching	0.43	30.38	5.25	2.02
After leaching at 10 pct H <sub>2</sub> SO <sub>4</sub>	0.26	29.43	3.43	1.68
After leaching at 15 pct H <sub>2</sub> SO <sub>4</sub>	0.16	29.63	2.05	0.70
After leaching at 20 pct H <sub>2</sub> SO <sub>4</sub>	0.04	29.84	0.65	0.27

Hence, the hydrogen ions used to exchange with Al greatly increased the acid consumption in addition to the acid dissolution of pyrite and calcite. As shown from this analysis, the H<sub>2</sub>SO<sub>4</sub> concentration had a significant influence on the dissolution of muscovite and illite in stone coal.

#### D. Effect of O<sub>2</sub> Partial Pressure on the Leaching of V, Al, and K

The variations of the recovery of V, Al, and K with the increase of O<sub>2</sub> partial pressure were investigated under the conditions of 5 hours, 423 K (150 °C), 20 pct(vol) H<sub>2</sub>SO<sub>4</sub>. As shown in Figure 6, the recovery of K and Al changed a little with O<sub>2</sub> partial pressure. The recovery of V increased 5.67 pct with increasing O<sub>2</sub> partial pressure to 1.5 MPa and then leveled off. The XRD patterns of the samples after leaching at 0, 0.5, 1, and 1.5 MPa were shown in Figure 7. It was worth noting that the diffraction peaks of the muscovite basically unchanged with the increase of O<sub>2</sub> partial pressure and the pyrite disappeared. The pyrite was oxidized and decomposed by O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, based on Reference 20. It was therefore concluded that O<sub>2</sub> had no remarkable influence on the muscovite dissolution. V<sup>3+</sup> in the muscovite lattice can be easy to leach only if it is oxidized into V<sup>4+</sup> or V<sup>5+</sup>. [21] As shown in Figure 7, when the O<sub>2</sub> partial pressure was below 1.5 MPa, only the recovery of V was affected by O<sub>2</sub> partial pressure, which indicated that O<sub>2</sub> had a main effect on the V(III) oxidation.

E. Interface Dissolution Behavior of Muscovite in Stone Coal

Oxygen pressure acid leaching of stone coal is a process of gas-liquid-solid three-phase interfacial reactions. The sample after leaching under the condition of

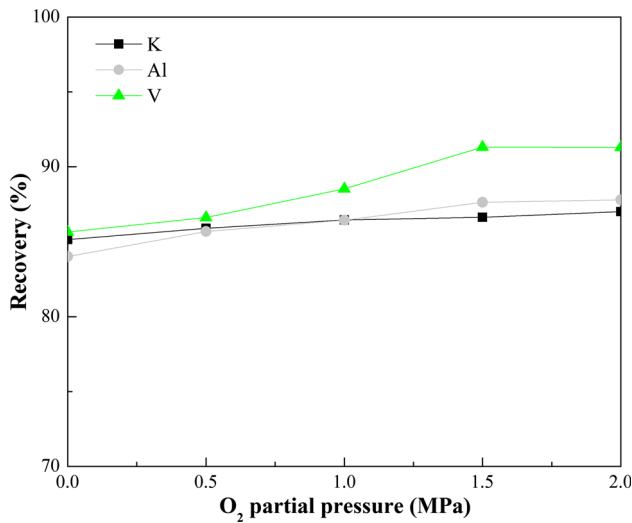


Fig. 6—Variations of the recovery of V, Al, and K with the increase of O<sub>2</sub> particle pressure.

423 K(150 °C), 20 pct(vol) H<sub>2</sub>SO<sub>4</sub>, 5 hours, 1.5 mL/g(l/s), 1.5 MPa O<sub>2</sub> was tested, respectively, with scanning electron microscopy (JSM-5610LV, Jeol, Japan) and specific surface area analyzer (F-sorb3400, App, Beijing). The SEM images (Figure 8) indicated that the particle surface of the residue was more rough and had holes and cracks, as well as flaky exfoliation, as shown in Figure 8(b). The results of the specific surface area (Table VI) showed the increase of specific surface area of the residue, which suggested that oxygen pressure acid leaching can cause the formation of a new interface.

The surface chemical compositions (Table VII) of the samples before and after leaching were detected by X-ray photoelectron spectroscopy (VG Multilab 2000). The surface of the sample after leaching exhibited less elemental content than the surface of the sample before leaching from Table VII. The Al atom percentage reduced from 8.21 to 0.65 pct. K and Na did not exist on the surface of the residue. The Si atom percentage increased from 25.15 to 32.16 pct. The Fe atom percentage reduced from 1.97 to 0.32 pct, and the S atom percentage increased from 0.82 to 2.65 pct. Table VII also showed the changes of the chemical environment of these elements during the acid leaching. Before leaching, Al2p with the binding energy of 73.79 eV existed in aluminosilicate. S2p with the binding energy of 160.87 and 168.07 eV both existed in the carbonic matter. Fe2p

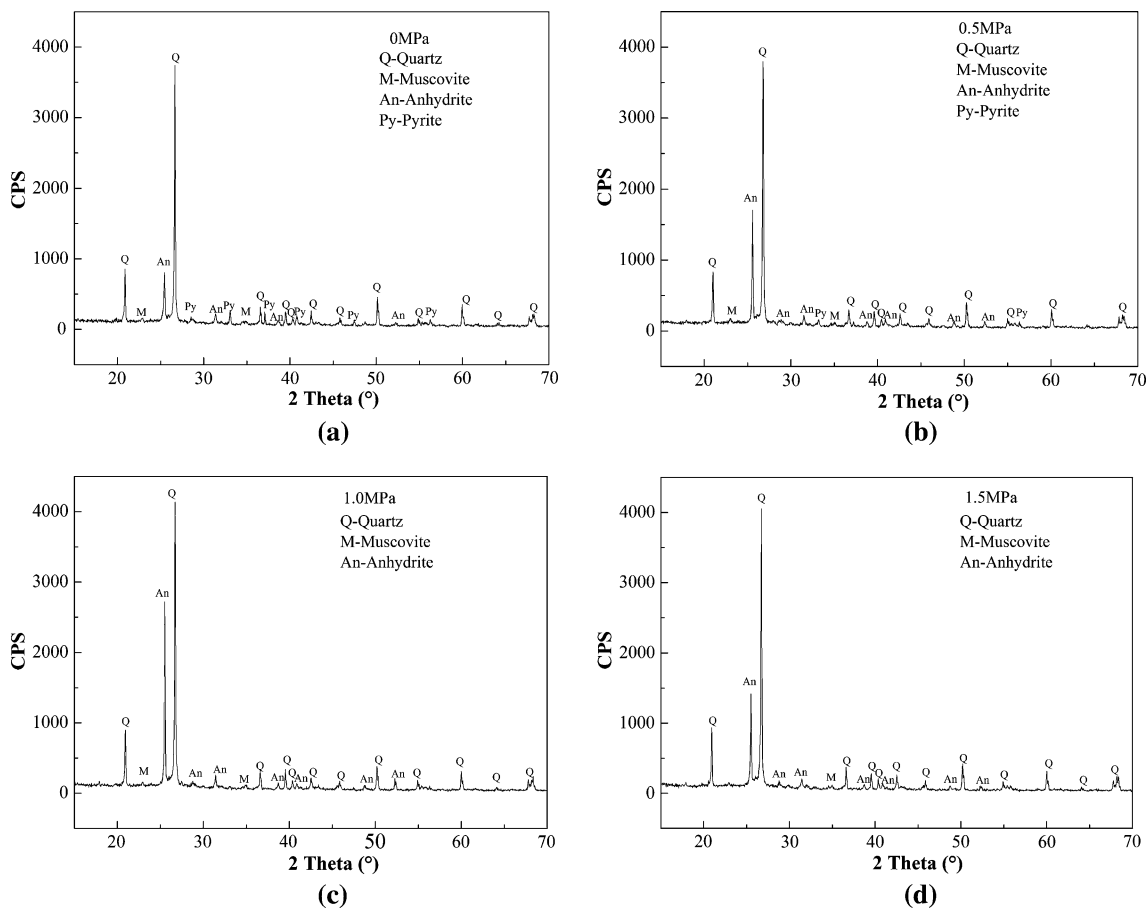
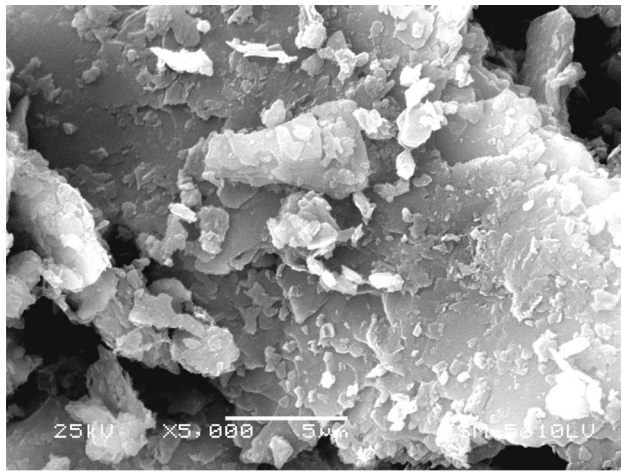
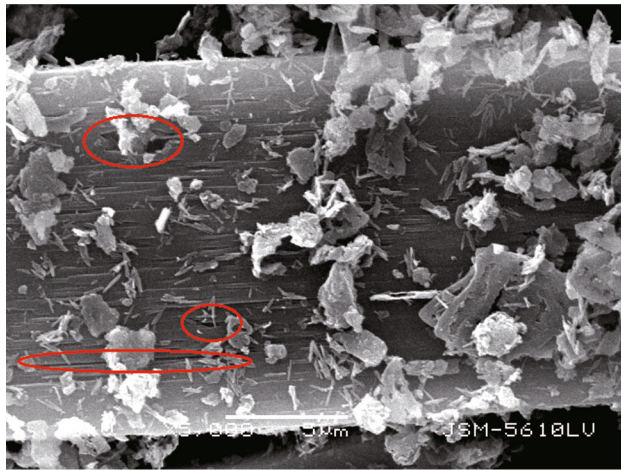


Fig. 7—XRD patterns of the samples after leaching at (a) 0 MPa O<sub>2</sub>, (b) 0.5 MPa O<sub>2</sub>, (c) 1 MPa O<sub>2</sub>, and (d) 1.5 MPa O<sub>2</sub>.





(a)



(b)

Fig. 8—SEM images of the samples (a) before leaching and (b) after leaching.

**Table VI. Specific Surface Area of the Samples Before and After Leaching (m<sup>2</sup>/g)**

Sample	Before Leaching	After Leaching
SBET	7.662	13.298

with the binding energy of 707.89 eV existed as the Fe(II)-S bond. However after leaching, Al2p with the binding energy of 74.65 eV existed as Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>. S2p with the binding energy of 170.01 eV existed as CaSO<sub>4</sub>. Fe2p with the binding energy of 709.8 eV existed as the Fe(III)-O bond. The binding energy of Si2p increased from 102.07 to 103.28 eV, which indicated that the chemical environment of Si had been closed to the typical Si-O tetrahedron (103.4 eV<sup>[22]</sup>). Accordingly, the main interface changes of stone coal particles before and after leaching were that (1) the dissolution of K, Na, and Al made new high-Si surface generated; (2) Fe(II)-S bond was broken under the coaction of H<sup>+</sup> and O<sub>2</sub>; and (3) S in carbonic matter completely reacted with H<sup>+</sup> and O<sub>2</sub>. The Fourier

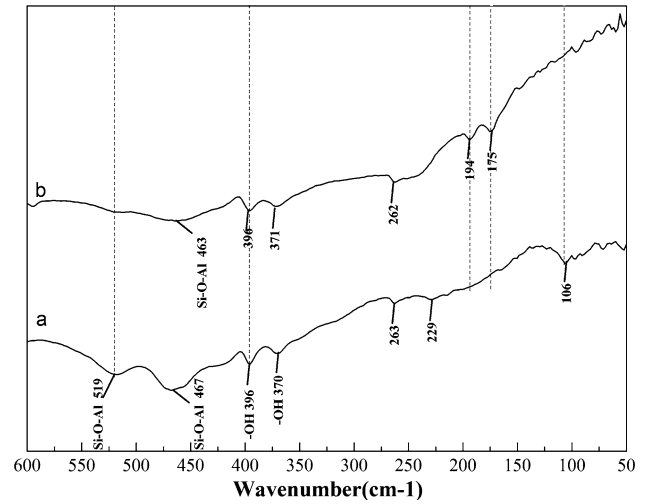


Fig. 9—Far-infrared spectrum of the samples (a) before leaching and (b) after leaching.

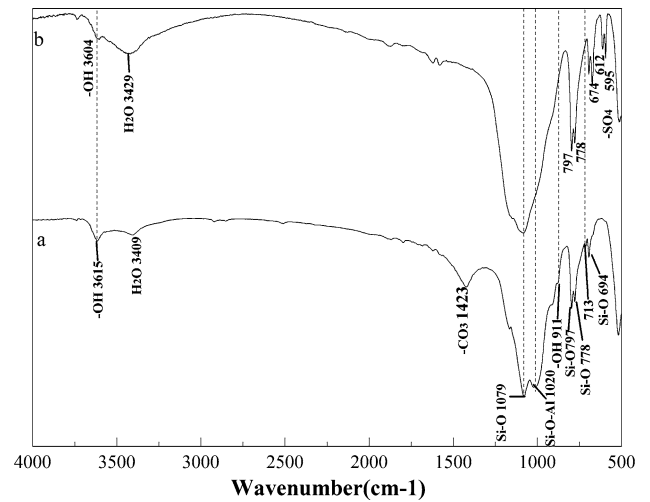


Fig. 10—Mid-infrared spectrum of the samples (a) before leaching and (b) after leaching.

transform infrared spectrometer (Nexus, Thermo Nicolet, America) was used to confirm the bonding structure of Al, Si, and K (Figures 9 and 10). According to Reference 23, Al<sub>2</sub>OH vibration was located at 3615, 911 cm<sup>-1</sup>; the bands at 396, 371 cm<sup>-1</sup> belonged to the swing and translation of the hydroxy. After leaching, the band at 911 cm<sup>-1</sup> disappeared; the band at 3615 cm<sup>-1</sup> shifted to 3604 cm<sup>-1</sup> and weakened; the division of two bands at 396 and 371 cm<sup>-1</sup> became shallow. The bands' changes proved the breakdown of the Al-OH bond, which indicated that the tetrahedron and the octahedron in the muscovite lattice separated along the top surface of the tetrahedron because the hydroxy in the muscovite lattice is located on the top surface of the tetrahedron.

According to Reference 23, the bands at 467, 519 cm<sup>-1</sup> belonged to Si-O-Al<sup>IV</sup> bending vibration; the bands at 1020, 1079, 797, 778, 713 cm<sup>-1</sup> all belonged to the

**Table VII. Surface Chemical Compositions of the Samples Before and After Leaching (at. pct)**

Chemical State	Before Leaching		After Leaching	
	$X_B$ /pct	$E_B$ /eV	$X_B$ /pct	$E_B$ /eV
O1s	59.97	531.05	64.35	532.58
K2p	1.33	292.88	0	—
Na1s	0.82	1072.07	0	—
Si2p	25.15	102.07	32.16	103.28
Al2p	8.21	73.79	0.26	74.65
Fe2p	1.97	707.89	0.32	709.8
Ca2p	2.47	346.75	1.35	348.59
S2p	0.21	160.87	2.65	170.01
	0.61	168.07		

stretching vibration of Si(Al<sup>IV</sup>)-O and Si-O-Si(Al<sup>IV</sup>), of which the band at 713 cm<sup>-1</sup> was considered the Si-O-Al<sup>IV</sup> in-plane stretching vibration. After leaching, on the one hand, the bands at 713, 519, 1020 cm<sup>-1</sup> disappeared and the band at 467 cm<sup>-1</sup> broadened. On the other hand, the bands at 1079, 797, 778 cm<sup>-1</sup> strengthened, which indicated that the stretching vibration of the Si-O bond was enhanced. So the bands' changes indicated the breakdown of the Al<sup>IV</sup>-O bond in the muscovite lattice.

The loss of the band at 106 cm<sup>-1</sup>, which has been related to the potassium content of muscovite<sup>[24]</sup> indicated the loss of potassium by muscovite in stone coal during the leaching. The bands appearing at 194 and 175 cm<sup>-1</sup> after leaching, which are related to the nonpotassium muscovite structure,<sup>[24]</sup> also proved the loss of potassium.

Overall it could be revealed that during oxygen pressure, the acid leaching process on the interface (1) K in the muscovite lattice was dissolved rapidly, producing a new surface; (2) for charge balance, the interfacial O absorbed H<sup>+</sup> to form hydroxy; (3) the interfacial hydroxy reacted with H<sup>+</sup> and left vacancy as a result of O loss, producing more new surface to expose more Al, V, and Si; (4) the interfacial Al or V was exchanged by H<sup>+</sup> and V<sup>3+</sup> was oxidized by O<sub>2</sub> into V<sup>4+</sup> and V<sup>5+</sup>; and (5) Si hardly reacted with H<sub>2</sub>SO<sub>4</sub> and was left to generate a high-Si surface.

#### IV. CONCLUSIONS

From the results of this study, the following conclusions can be drawn:

1. The dissolution behaviors of V, Al, and K were similar. K was the most easily leached, followed by Al, and then by V during the oxygen pressure acid leaching process. When the reaction temperature exceeded 423 K (150 °C), alunite was generated, which led to vanadium losses because of its absorption performance. The dissolution of the muscovite in stone coal mainly depended on H<sub>2</sub>SO<sub>4</sub> concentration and temperature. O<sub>2</sub> had a main effect not on muscovite's dissolution but on the V<sup>3+</sup> oxidation.
2. During the oxygen pressure acid leaching process, on the interface, (1) K in the muscovite lattice was

dissolved rapidly, producing a new surface; (2) for charge balance, the interfacial O absorbed hydrogen ions to form hydroxy; (3) the interfacial hydroxy reacted with hydrogen ions and left vacancy as a result of O loss, producing more new surface to expose more Al, V, and Si; (4) the interfacial Al or V was exchanged by hydrogen ions and V<sup>3+</sup> was oxidized to V<sup>4+</sup> and V<sup>5+</sup>; and (5) Si hardly reacted with H<sub>2</sub>SO<sub>4</sub> and was left to generate a high-Si surface.

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