Function of Interface Deposition of Calcium Sulfate in Pressure Acid Leaching of Black Shale-Hosted Vanadium

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Abstract: During pressure acid leaching process of black shale-hosted vanadium, increasing the reaction interface of muscovite dissolution can enhance the vanadium release. In this paper, calcium sulfate (CaSO₄) deposition behavior and its effect on muscovite under K₂SO₄ assistance were focused on for demonstrating the function of CaSO₄ on vanadium leaching from the black shale. Results showed that as K₂SO₄ mediated, the apparent activation energy of vanadium leaching and the apparent reaction order of sulfuric acid decreased from 24.37 kJ/mol to 16.63 kJ/mol and 2.7 to 1.9, respectively. The leaching rate and dependence on pH value were modified. The vanadium leaching acceleration owed to CaSO₄ deposition on muscovite in the black shale. The ion absorption stimulations found that Ca²⁺ is confirmed to be easily absorbed on the six-membered ring cavity of silicon-oxygen tetrahedrons in muscovite structure prior to K⁺ and Na⁺. Meanwhile, SO₄²⁻ provides two oxygen atoms to bond with Ca²⁺ absorbed on muscovite (001) surface. The continuous absorption and bonding create CaSO₄ deposition on muscovite (001) surface which also involves the load transmitting. The stress load transmitting correlates to pore formation in muscovite particles. It was proved that massive micropores initiated and proliferated in the existing pores under K₂SO₄ assistance. The porosity caused by CaSO₄ deposition greatly increased the reaction interface of muscovite dissolution and accelerate internal diffusion of H⁺ to the reaction interface, which can significantly weaken the vanadium leaching dependence on acid.

Keywords: black shale; vanadium extraction; surface deposition; pore propagation

1. Introduction

Facing the increasing market demand for vanadium products and environmental problems [1–4], the efficient and sustainable utilization of vanadium-bearing mineral resources is increasingly necessary and urgent for vanadium industry. Vanadium-bearing black shale has been identified to have enrichments of vanadium, which is distributed in many provinces of China [5,6]. There are vanadium enrichments in black shale elsewhere in the world include United states, Australia, Argentina, and Kazakhstan [7]. The black shale-hosted vanadium deposits have average ore grades that range from 0.1 to 1 weight percent vanadium. In primary black shale, the vanadium can exist mostly as low-valence V³⁺ that replaces Al³⁺ isomorphically in mica or illite lattice [8], which poses a difficulty for vanadium extraction in a green and high-efficiency way.

At present, the roasting–leaching process has become the mainstream technology of vanadium extraction from the black shale in industrial production. It is essential of roasting to activate mica structure and remove the acid-consuming minerals in the black shale, such as pyrite and calcite [9].
Gravity or flotation separation can be combined as pretreatment way to improve the vanadium grade in the black shale [10–13]. In recent years, the direct acid leaching process, characterized by short flow, low energy consumption, easy control of technology conditions and low production cost, is getting increased attention, which has resulted in the development of the atmospheric pressure acid leaching process and the oxygen pressure acid leaching process. The relevant research is always centered on how to disintegrate the crystal lattice of muscovite in a green and high-efficiency way during direct acid leaching.

Muscovite identified as vanadium accumulator is the most common mica minerals in the black shale and weathered to form illite. Muscovite structure undergoes aeolotropic dissolution in acidic solution because of the obvious difference in the response of (001) surface and (hk0) surface to hydrogen ions (H⁺) [14–16]. The (001) surface is the leading reaction interface between muscovite and acidic solution, but due to its high energy requirement for atomic bond fracture, the (001) surface dissolves slowly. Breaking down the (001) surface will be critical to muscovite dissolution.

For the dioctahedral structure possessed by muscovite, the (001) surface is electronegative and can absorb H⁺ to form hydroxy groups with interfacial oxygen after dissolution of interlayer potassium ions in muscovite. The interfacial oxygen atoms of the (001) surface separate from muscovite lattice mainly because adjacent hydroxy groups combine with each other to form water molecule in acidic solution [17]. It is for this reason that the interfacial Al and Si atoms become charge unbalanced, making the (001) surface in an unstable state. Pressure acid leaching is just based on relatively higher temperature to reinforce this structural changes of the (001) surface causing mica dissolution.

However, numerous H⁺ are inevitable during pressure acid leaching process because of limited reaction interface of muscovite dissolution. The conventional auxiliaries, such as fluoride, chlorinated oxidizers, or fluosilicic acid can prompt vanadium leaching through participating in muscovite dissolution reaction. Differently, the sulfate is an intermediary to induce the common ion effect, thus causing a chain reaction between CaSO₄ and CaSO₄·2H₂O. At the temperature below 100 °C, the common ion effect of K₂SO₄ produces the first conversion of CaSO₄(aq)→CaSO₄·2H₂O(s); Once the temperature beyond 100 °C, the second conversion of CaSO₄·2H₂O(s)→CaSO₄(s) becomes a spontaneous action [18]. CaSO₄ produced by the dissolution of calcite or dolomite in the black shale is usually taken as useless product. As K₂SO₄ mediates in pressure acid leaching process, CaSO₄ can be utilized through the conversions to strengthen vanadium leaching from the black shale, which should be attributed to the deposition of CaSO₄ on muscovite particles [19]. However, to date, it is a pity that the deposition essence of CaSO₄ and its function on muscovite dissolution have not been reported in details.

Therefore, in this work, the vanadium leaching kinetics of black shale, variation of the surface environment and pore structure of muscovite particles during pressure acid leaching of black shale were studied under K₂SO₄ assistance, and the absorption ways of Ca²⁺ and SO₄²⁻ on muscovite (001) surface was simulated basing on first-principles density-functional theory (DFT), aiming at revealing the deposition process of CaSO₄ and its promotion on vanadium quick release from muscovite. This research will reveal a different mechanism of strengthening vanadium release during pressure acid leaching of black shale.

2. Materials and Methods

The black shale used in this study comes from Hubei province, South China. The ICP-AES (IRIS Advantage Radial, USA) results and the SEM-EDS patterns of the black shale are shown in Table 1 and Figure 1. The black shale has a vanadium grade of 0.72% and a high calcium content of 5.82%. The vanadium valences in the black shale were analyzed by potentiometric titration and are summarized in Table 2. According to Figure 1 and Table 2, 75% of vanadium should exist mostly as low-valence V³⁺ that replaces Al³⁺ isomorphically in muscovite. Vanadium-rich muscovite in the black shale is represented by muscovite hereinafter.
Each leaching experiment is carried out in a zalium reaction vessel with a volume of 2 L and adopts PID temperature controller with a deviation of ±3 °C. The test ore samples are obtained after crushed and ground to 85% passing 74 microns. The sulfuric acid solution is chosen as leaching agent and prepared with deionized water at molarity from 1 to 4 M respectively. Then, 150 g of the test ore samples and the sulfuric acid solution are fed into the reaction vessel at the liquid to solid ratio of 1.5 mL/g and then the sulfate is added in. After sealing the reaction vessel, the 1.0 Mpa oxygen is inlet and it starts to heat up. The oxygen purity is 98%. The leaching temperature should be reached in 45 min by adjusting heater voltage. When the leaching temperature reaches the set value, the timing is started. After experiment, the leaching residues and leachate can be separated by vacuum filter. The experiments are replicated for three times. The dynamic leaching experiments are carried out within a time period, from 1 h to 5 h.

The morphology of leaching residues is observed by scanning electron microscope (JSM-IT300, Jeol, Tokyo, Japan). The pore structure of leaching residues is tested by automatic mercury porosimeter (AutoPore IV 9500, Micromeritics, Norcross, GA, USA) and automatic surface area and pore-size analyzer (ASAP 2020, Micromeritics, Norcross, GA, USA). The pore volume and pore surface area are derived via integration of the mercury injection and nitrogen adsorption curves. The surface chemical state of Al2p in the leaching residues was detected by X-ray photoelectron spectrometer (Multilab 2000, Thermo Fisher Scientific, Waltham, MA, USA). Vanadium concentration in leachate is measured by chemical titration with ferrous ammonium sulfate. The vanadium concentration in leachate is measured by chemical titration with ferrous ammonium sulfate. Vanadium concentration in leachate is measured by chemical titration with ferrous ammonium sulfate. Vanadium leaching efficiency is taken as index and calculated using Equation (1).

\[
\alpha = \frac{CL}{\eta M} \cdot 100
\]  

where \( \alpha \) is the vanadium leaching efficiency (%), \( \eta \) is the vanadium grade in black shale (%), \( C \) is the vanadium concentration in leachate (g/L), \( L \) is the leachate volume, and \( M \) is the feeding mass of black shale (g).

All periodic DFT calculations are performed with the Vienna ab initio simulation package (VASP) [20,21]. The exchange-correlation energy is approximatively treated by the generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof parameterization (PBE) [22].
approximation (GGA) with the function of PBE-version [22,23], and the electron–ion interactions are described by the projector augmented wave (PAW) method [24,25]. A kinetic energy cutoff value of 800 eV and a $3 \times 3 \times 1$ mesh of Γ-point-centered k-points is adopted in the calculation of the muscovite (001) surface. The geometry optimization is convergent when the total energy change and the forces is less than 10-5 eV and 0.05 eV/Å, respectively. Moreover, the van der Waals force correction and a dipole correction along the z-direction are applied in all calculations.

The initial crystal structure of muscovite is taken from the optimized geometrical model with $a = 5.29$ Å, $b = 9.12$ Å, $c = 20.26$ Å, and $\beta = 95.83^\circ$ [26]. The muscovite (001) surface is modeled using one TOT slab with a $2 \times 1 \times 1$ supercell. Meanwhile, a vacuum boundary of 20 Å is added to ignore the interactions between slabs. The two rows of bottom atoms are fixed for considering the influence of internal atoms on the surface reaction. Full calculations are performed without the constraint of the space group symmetry.

3. Results

3.1. Effect of Sulfate Type and Dosage on Vanadium Leaching

The three common sulfates ($K_2SO_4$, $Na_2SO_4$, and $KAl(SO_4)_2\cdot12H_2O$) were investigated and the leaching results are shown in Figure 2. The vanadium leaching efficiency can maintain at 85% after calcite in black shale was removed by hydrochloric acid in advance. The three sulfates can increase the vanadium leaching efficiency beyond 90%. The sulfates are directly related to the calcium phase in the black shale. The vanadium leaching efficiency firstly increased and then decreased with sulfate dosage. When adding $K_2SO_4$ at the dosage of 7wt.%, the vanadium leaching efficiency topped out at 95.60%. $K_2SO_4$ was chosen as assisted-leaching agent for investigating the vanadium leaching kinetics of black shale.

![Figure 2](image_url)

Figure 2. Variation of vanadium leaching efficiency as a function of the three sulfate dosages with leaching temperature of 150 °C, leaching time of 5 h and acid concentration of 4 M.

3.2. $K_2SO_4$-Assisted Pressure Acid Leaching Kinetics

Variations of the vanadium leaching efficiency over time under $K_2SO_4$ assistance are compared with no assistance in Figure 3a and Figure 5a. At the same leaching time, temperature and sulfuric acid concentration, the vanadium leaching efficiency was much higher under $K_2SO_4$ assistance than
no assistance. The K2SO4-assisted pressure acid leaching of the black shale may have an advantage of vanadium leaching rate.

![Variations of vanadium leaching efficiency as a function of leaching time with acid concentration of 4 M and K2SO4 dosage of 7 wt% at 110 °C, 130 °C, 150 °C, and 170 °C, respectively (a) and linear-fitting curves of Equations (2)–(4) (b–d) basing on the data in (a). The dashed lines and hollow points represent the vanadium leaching efficiency and corresponding linear-fitting curves without K2SO4 addition, other leaching parameters being equal.

3.2.1. Apparent Activation Energy of Vanadium Leaching

Assuming the pressure acid leaching process of black shale conforms to the shrinking core model, when the leaching rate is controlled by interior diffusion, Equation (2) can be used to describe the leaching kinetics of the process [27].

\[ k_D(t - t_0) = 1 - 3\left(1 - \frac{1}{1 - a_0}\right) + 2\left[1 - (1 - a_0)^\frac{3}{2}\right](\alpha - a_0) = f_D(\alpha, t) \]  (2)

When the leaching rate is controlled by the interfacial chemical reaction, Equation (3) is employed to describe the leaching kinetics [27].

\[ k_C(t - t_0) = 1 - \left(1 - \frac{1}{1 - a_0}\right)^\frac{1}{2} = f_C(\alpha, t) \]  (3)

When the leaching rate is under mixed control, Equation (4) may be used [28].

\[ k(t - t_0) = \frac{1}{3}(1 - a_0)^\frac{3}{2}\ln\left(1 - \frac{1}{1 - a_0}\right) - 1 + \left(1 - \frac{1}{1 - a_0}\right)^\frac{3}{2} = f_m(\alpha, t) \]  (4)
In these equations, $t$, $\alpha$, $k_D$, $k_c$, and $k$ refer to the leaching time (s), fractional leaching efficiency of vanadium, and apparent rate constants of internal diffusion, chemical reaction, and mixed control, respectively. In the leaching experiments, the test sample experienced a temperature-rising stage where the leaching of V has already been taking place for a certain time. Considering the starting time of the leaching process, it is evident that the leaching efficiency ($\alpha_0$) calculated for the holding time of 0 h ($t_0$) is not zero and should not be ignored in Equations (2)–(4).

The time-dependent leaching data in Figure 3a was fitted by Equations (2)–(4) and the fitting results are shown in Figure 3b–d. The linear fitting curves of Equation (4) can pass though the origin and the correlation coefficients $R^2$ were higher than the required coefficient (0.9196) when the confidence is 99%. The vanadium leaching rate can be judged under mixed control. The apparent rate constants from the linear fitting results of Equation (4) was chosen to be substituted into the Arrhenius equation, as shown in Figure 4. The apparent activation energy ($E_a$) of vanadium leaching process is calculated from the slope of the Arrhenius plot. Comparing with no assisted leaching, the apparent activation energy of K$_2$SO$_4$-assisted leaching declined from 24.37 kJ·mol$^{-1}$ to 16.63 kJ·mol$^{-1}$, which marked the increasing vanadium leaching rate.

$$\ln k = \ln A - \frac{E_a}{RT} + n \ln C_{H_2SO_4}$$

where $k$ is the apparent rate constant, $E_a$ is the apparent activation energy of leaching (kJ·mol$^{-1}$), $C_{H_2SO_4}$ is the acid concentration (mol/L), $n$ is the apparent reaction order of sulfuric acid and $T$ is the leaching temperature (K).

![Figure 4. Linear fitting curve of Arrhenius equation under mixed control.](image-url)
weakened as \( K \) with or without \( K \) from 2.7 to 1.9 under \( K \) of the aqueous concentrations of the metals present in the mineral itself [29]. So, the \( H^+ \) pH but independent of the aqueous concentrations of the metals present in the mineral itself [29]. So, the \( H^+ \) can be considered at far from equilibrium and have been traditionally interpreted to be a function of minerals.

According to the line slope in Figure 6, the apparent reaction order (\( n \)) of sulfuric acid decreased from 2.7 to 1.9 under \( K_2SO_4 \) assistance, which means that the pH dependence of Equation (6) has been weakened as \( K_2SO_4 \) mediated in pressure acid leaching of the black shale. \( K_2SO_4 \) indirectly prompted Equation (6), which should be attributed to the conversions between \( CaSO_4 \) and \( CaSO_4\cdot2H_2O \).

\[
KAl_2(AlSi_3O_{10})(OH)_2 + 10H^+ = 3Al^{3+} + K^+ + 3H_2SiO_4
\]  

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Figure 5. Variations of vanadium leaching efficiency as a function of leaching temperature of 150 °C and \( K_2SO_4 \) dosage of 7 wt% at acid concentrations of 1 M, 2 M, 3 M, and 4 M, respectively, (a) and linear-fitting curves of Equation (4), (b) based on the data in (a). The dashed lines and hollow points represent the vanadium leaching efficiency and corresponding linear-fitting curves without \( K_2SO_4 \) addition, other leaching parameters being equal.

Figure 6. Plot of \( \ln k \) as a function of sulfuric acid concentration.

As shown in Figure 5a, the sulfuric acid concentration greatly affects the vanadium leaching efficiency with or without \( K_2SO_4 \) addition. Muscovite dissolution reaction in sulfuric acid solution can be considered at far from equilibrium and have been traditionally interpreted to be a function of pH but independent of the aqueous concentrations of the metals present in the mineral itself [29]. So, the \( H^+ \) concentration directly affects the reaction rate of Equation (6). \( K_2SO_4 \) does not participate in Equation (6) but can be involved in a chain reaction between \( CaSO_4 \) and \( CaSO_4\cdot2H_2O \) as shown in Table 3.

\[
KAl_2(AlSi_3O_{10})(OH)_2 + 10H^+ = 3Al^{3+} + K^+ + 3H_2SiO_4
\]  

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Table 3. A chain reaction from CaSO₄·2H₂O to CaSO₄.

| Temperature | Reactions |
|-------------|-----------|
| T < 100 °C  | \[
\text{CaCO}_3(s) + \text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2
\]
|           | \[
\text{Ca}^{2+} + \text{SO}_4^{2-} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} = \text{K}_2\text{Ca(SO}_4\text{)}_2\text{·H}_2\text{O}
\]
|           | \[
\text{K}_2\text{Ca(SO}_4\text{)}_2\text{·H}_2\text{O} + \text{H}_2\text{O} = \text{CaSO}_4·2\text{H}_2\text{O(s)} + \text{K}_2\text{SO}_4
\]
| T > 100 °C | \[
\text{CaSO}_4·2\text{H}_2\text{O(s)} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}
\]
|           | \[
\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4(s)
\]

The apparent activation energy and the apparent reaction order of sulfuric acid are plugged into Equation (4), which obtained a mathematical model for the pressure acid leaching of the black shale as follows.

\[
\frac{1}{3}(1 - \alpha_0)^{1/3} \ln \left( \frac{1 - \alpha}{1 - \alpha_0} \right) - 1 + \left( \frac{1 - \alpha}{1 - \alpha_0} \right)^{-1/3} = 5.92 \exp \left( \frac{-4 \times 10^3}{T} \right) C_{\text{H}_2\text{SO}_4}^{1.9} t
\]  (7)

The vanadium leaching efficiency was forecasted with this model by iterative computation. To test the accordance between the experimental values and the calculated values from Equation (7), a plot of these values was drawn. As can be seen in Figure 7, a good coincidence was achieved between the calculated and the experimental values. The relative error is controlled in 10%.

![Figure 7. Comparison of experimental and calculated values of the vanadium leaching efficiency.](image)

3.3. Surface Condition of Muscovite after K₂SO₄-Assisted Leaching

The morphology of the K₂SO₄-assisted leaching residues (KLR) and non-assisted leaching residues (NLR) was analyzed by SEM-EDS and shown in Figure 8.

It was observed that CaSO₄ crystals were deposited on muscovite and disintegrated muscovite particles in the KLR. Rod-like CaSO₄·2H₂O crystals were observed below 100 °C in Figure 8a. Tiny CaSO₄ crystals with longitudinal growth concentrated upon muscovite surface when the temperature initially rising to 150 °C (seen in Figure 8b) and transformed into lateral growth over time (seen in Figure 8c,d). This transformation of crystal shape was accompanied with muscovite surface cracking and decomposing.

By contrast in Figure 8e,f, CaSO₄ crystals were not found on muscovite which still had a rough but intact surface in the NLR, indicating that muscovite was dissolved in a way of peeling off particle surface layer by layer without assistance.
The chemical states of Al2p in the KLR and the NLR were also studied by XPS and the results are shown in Figure 9. There are four-coordinated Al and six-coordinated Al in the black shale. The four-coordinated Al exists in muscovite and feldspar while the six-coordinated Al just exists in muscovite. So, the six-coordinated Al content can trace muscovite surface. The four-coordinated Al in aluminum-oxygen tetrahedron has a binding energy of about 73.4–74.55 eV and the six-coordinated Al in aluminum-oxygen octahedron has a binding energy of about 74.1–75.0 eV. As seen in Figure 9a, the Al2p fine spectrum of the black shale was split into three peaks, two of which at 74.46 eV and 73.67 eV belongs to the six-coordinated Al and the four-coordinated Al, respectively.

Figure 9. XPS fine spectrums of Al2p in (a) the black shale, (b) the NLR and (c) the KLR obtained after leaching with 4 mol/L H2SO4 and 7wt% K2SO4 at 150 °C for 5 h.
Under K$_2$SO$_4$ assistance, the Al2p fine spectrum peaked at the binding energy of 74.00 eV that belonged to the four-coordinated Al. Without assistance, the Al2p fine spectrum was split into three peaks, two of which at 74.70 eV and 73.67 eV belonged to the 6-coordinated Al and the four-coordinated Al, respectively. Moreover, it cannot be ignored that the peaks with binding energies of 72.20 eV and 72.77 eV in Figure 9a,b disappeared in Figure 9c. Based on XRD analysis (Figure 10), the four-coordinated Al in the KLR should be located in microcline. So the peaks with binding energies of 72.20 eV and 72.77 eV belonged to [AlO$_4$] in muscovite structure and disappeared in the KLR, indicating the disorganization of muscovite structure.

![Figure 10. XRD patterns of the NLR (a) and the KLR (b) obtained after leaching with 4 mol/L H$_2$SO$_4$ and 7 wt% K$_2$SO$_4$ at 150 °C for 5 h.](image)

3.4. Pore Distribution in the KLR and the NLR

The pores in the black shale ore can be classified using pore classification of Xiaotb [30] as ultra-large pores (>100 μm, including microcracks), large pores (1 μm < d < 100 μm), mesopores (100 nm < d < 1 μm), transition pores (10 nm < d < 100 nm), and micropores (d < 10 nm). In terms of the micropores and transition pores, the relationship between the pore size and mercury-injection pressure cannot follow Washburn equation, leading to a distortion of pore size–pore volume distribution. The mercury intrusion method is not suitable for testing the micropores and transition pores. So, the combined method of nitrogen adsorption and mercury intrusion was adopted to analyze the pore structure of KLR and the results are shown in Figures 11 and 12, and Table 4.

![Figure 11. Pore to throat ratio of the KLR obtained after leaching at 45 min, 1 h, and 5 h with 4mol/L H$_2$SO$_4$ and 7 wt% K$_2$SO$_4$ under 150 °C (r$_p$ and r$_t$ respectively represent the pore size and the pore throat size that is the diameter of the thinnest part in porous channel).](image)
were higher than the large pores and mesopores. It was noted that the micropores in surface
The mesopores did not present the most probable distribution, marking a wide pore size range of the
As shown in Figure 11, the KLR had a narrow pore to throat ratio ($R_{pt}$) range from 30 to 45 at the
leaching time of 45 min. However, the $R_{pt}$ went up and broadly ranged from 33 to 70 at the leaching
time of 1 h, which indicated that the pore throat size decreased and the pore size increased. It can be
deduced that massive pores initiated and proliferated in the existing pores within one-hour leaching.
This change will bring about the increasing of muscovite–acid interface. As the leaching time reached
five hours, the $R_{pt}$ obviously dropped off and just ranged from 9 to 21, which manifested that the pore
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throat size was approaching the pore size. The pores should be expanded as a result of interfacial
reaction of muscovite dissolution.

As shown in Figure 12, the KLR was mostly large pore based. The two peaks of large pore
distribution concentrated in the pore size ranges from 1 μm to 5 μm and from 5 μm to 20 μm, respectively.
The mesopores did not present the most probable distribution, marking a wide pore size range of the
mesopores in the KLR. The transition pores and micropores were much less than the large pores and
mesopores, but the two broad peaks respectively occurred in the pore size ranges from 2 nm to 4 nm
and from 10 nm to 80 nm.

According to Table 4, the proportion of large pores decreased over time while the mesopores,
transition pores and micropores increased, indicating that the proliferation of smaller pores involved
in the mesopores, transition pores, and micropores. The surface areas of transition pores and micropores
were higher than the large pores and mesopores. It was noted that the micropores in surface

Table 4. Pore characteristics of KLR based on the data of Figure 11.

| Pore        | Leaching Time | Proportion/% | Pore Volume/mL·g⁻¹ | Pore Surface Area/m²·g⁻¹ |
|-------------|---------------|--------------|---------------------|-------------------------|
| Large pore  | 45 min        | 75.91        | 0.3807              | 0.3757                  |
|             | 1 h           | 70.97        | 0.3462              | 0.2744                  |
|             | 5 h           | 59.45        | 0.2294              | 0.2037                  |
| Mesopore    | 45 min        | 19.70        | 0.0988              | 0.4788                  |
|             | 1 h           | 24.11        | 0.1176              | 0.6532                  |
|             | 5 h           | 34.21        | 0.1320              | 0.7418                  |
| Transition pore | 45 min    | 3.41         | 0.0171              | 2.8821                  |
|             | 1 h           | 4.18         | 0.0204              | 2.9374                  |
|             | 5 h           | 5.00         | 0.0193              | 3.2427                  |
| Micropore   | 45 min        | 0.98         | 0.0049              | 5.1398                  |
|             | 1 h           | 0.74         | 0.0036              | 3.5296                  |
|             | 5 h           | 1.35         | 0.0052              | 5.3163                  |
area decreased 1.6102 m²/g after leaching for 1 h and increased 1.7867 m²/g after leaching for 5 h, signaling that some micropores at first got blocked because of CaSO₄ nucleation and further increasing time brought about the new micropores born under CaSO₄ growth in situ. This behavior enlarged the reaction interface of muscovite dissolution so that more four-coordinated and six-coordinated Al were exposed on the reaction interface and equipped with high reactivity.

3.5. Mechanism of CaSO₄ Deposition on Muscovite and Its Function

The (001) surface of muscovite structure is the main reaction interface of muscovite dissolution after releasing K⁺. On the basis of VASP software calculation, two potential sites on the (001) surface will be considered for determining the preferential deposition position of CaSO₄. The first potential site is set in the six-membered ring cavity of silicon-oxygen tetrahedrons and the second potential site is set above Al atoms in aluminum-oxygen tetrahedrons, shown in Figure 13a.

![Figure 13. Muscovite (001) surface (a), potential absorption sites of Ca(II), K(I), and Na(I) on muscovite (001) surface (b) and optimized bonding ways of sulfate ion on muscovite (001) surface after Ca(II) absorption (c).](image)

Ca²⁺, K⁺, and Na⁺ are the main unavoidable cations during K₂SO₄-assisted pressure acid leaching of the black shale. The absorption competition among these three cations were investigated. As seen in Figure 13b, no matter locating on the first or second potential site, K⁺ and Na⁺ shared very few electrons with the six-membered ring of silicon-oxygen tetrahedrons. Differently, Ca²⁺ fully shared the electrons with the six-membered ring when positioned on the first potential site. However, once locating on the second potential site, Ca²⁺ barely shared the electrons with the six-membered ring. The electron sharing degree can signify interatomic interactions, which indicates that a strong interatomic interaction between Ca²⁺ and the (001) surface happened. The absorption energy of Ca²⁺ on the first potential site was the lowest of all the data in Figure 14a. So Ca²⁺ is capable of easily absorbing in the six-membered ring cavity of silicon-oxygen tetrahedrons prior to K⁺ and Na⁺.
The structure model of muscovite after Ca$^{2+}$ absorbing in the six-membered ring cavity of silicon-oxygen tetrahedrons was thus built up. Six possible locations were selected to determine the optimal bond-making position of SO$_4^{2-}$ to this structure model. As shown in Figure 13c, the first three locations of SO$_4^{2-}$ are above Ca$^{2+}$ with different location angles while the latter three locations of SO$_4^{2-}$ are in the cavity of six-membered ring of silicon-oxygen tetrahedrons with different location angles.

As found in Figure 14b, the binding energy of SO$_4^{2-}$ and Ca$^{2+}$ reached the minimum at the second location of SO$_4^{2-}$, closely followed by the third location and the first location. The binding energy of SO$_4^{2-}$ and Ca$^{2+}$ at the latter three locations was obviously higher than at the first three locations. So SO$_4^{2-}$ tends to providing two oxygen atoms to bond with Ca$^{2+}$ in order to form a stable new structure. Muscovite (001) surface gives CaSO$_4$ deposition a suitable interfacial environment, which was validated by the experimental phenomenon in Figure 8d.

We can conclude that as the temperature exceeded 100 °C, CaSO$_4$·2H$_2$O was bound to decompose into Ca$^{2+}$ and SO$_4^{2-}$, so Ca$^{2+}$-enriched environment happened to be formed. In this situation, the absorption and bonding of Ca$^{2+}$ and SO$_4^{2-}$ can be continuous to get CaSO$_4$ crystals deposited and growth on muscovite (001) surface. In the deposition process, CaSO$_4$ crystals pass the stress load to muscovite, which is the reason for causing the porosity of muscovite particles in the leaching process of black shale. Strong tensile stress shall start with the six-membered ring cavity on muscovite (001) surface, thus breaking muscovite structure and then exposing more reaction interface. These reaction interfaces are full of dangling bonds, which makes the interfacial free energy increase. Equation (6) can be driven vastly on the reaction interface, which inevitably triggers muscovite structural dissolution.

4. Conclusions

In this study, it was shown that K$_2$SO$_4$ assistance was the most effective to the vanadium release from the black shale. When K$_2$SO$_4$ mediated the pressure acid leaching process, the vanadium leaching rate was still controlled by interior diffusion of H$^+$ and muscovite–acid interfacial reaction, but the apparent activation energy of vanadium leaching decreased from 24.37 kJ/mol to 16.63 kJ/mol, which is a signal of the increasing leaching rate. The apparent reaction order of sulfuric acid decreased from 2.7 to 1.9, indicating the weaken leaching dependence on sulfuric acid.

The absorption simulation of Ca$^{2+}$, K$^+$, Na$^+$, and SO$_4^{2-}$ on muscovite (001) surface can well explain the deposition process of CaSO$_4$. Ca$^{2+}$ is confirmed to be easily absorbed on the six-membered ring cavity of silicon-oxygen tetrahedrons in muscovite structure prior to K$^+$ and Na$^+$. Meanwhile, SO$_4^{2-}$ provides two oxygen atoms to bond with Ca$^{2+}$ absorbed on muscovite (001) surface. Such continuous absorption and bonding of Ca$^{2+}$ and SO$_4^{2-}$ creates CaSO$_4$ deposition on muscovite (001) surface which involves the load transmitting. It can be deduced that starting with the six-membered ring cavity on muscovite (001) surface, CaSO$_4$ crystals pass the stress load to the whole structure of muscovite. The stress load transmitting can correlate to pore formation in muscovite particles. The pore analysis helped us to prove that massive micropores initiated and proliferated...
in the existing pores under K₂SO₄ assistance. The porosity caused by CaSO₄ deposition will greatly increase the reaction interface of muscovite dissolution and accelerate internal diffusion of H⁺ to the reaction interface, which can significantly weaken the vanadium leaching dependence on acid and accelerate the vanadium leaching rate.

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