Rapid Vanadium Extraction from Roasted Vanadium Steel Slag via a \( \text{H}_2\text{SO}_4-\text{H}_2\text{O}_2 \) System: Process and Mechanism

Shugen Liu, Yue Chen, Shuo Yu, Dongdong Zhang*, and Gang Xie

ABSTRACT: A \( \text{H}_2\text{SO}_4-\text{H}_2\text{O}_2 \) system was developed to enhance the efficacy of vanadium extraction from roasted vanadium steel slag. The optimum parameters and the behavior of vanadium extraction were investigated systematically. When 1 mL of \( \text{H}_2\text{O}_2 \) per gram of vanadium slag was added to a leaching mixture at 50 °C, along with 30% \( \text{H}_2\text{SO}_4 \), 80.5% of vanadium extraction was achieved within 15 min. However, without \( \text{H}_2\text{O}_2 \), only 58.5% of vanadium extraction was achieved at the same leaching time. The \( \text{H}_2\text{SO}_4-\text{H}_2\text{O}_2 \) system facilitated the dissolution of metallic ions in a short time and then triggered the production of strong oxidizing substances, such as \( \text{HO}^+ \) and \( \text{O}_2^{-} \), via the Fenton reaction and Fenton-like reaction. Subsequently, the low-valence vanadium, existing in the leaching solution or located on the surface of the particle, was converted to pentavalent vanadium by strongly oxidizing substances, such as \( \text{H}_2\text{O}_2 \) and its derivatives \( \text{HO}^+ \) and \( \text{O}_2^{-} \). The complex oxides on the surface of the particle were destroyed, after which the vanadium inside the particle was gradually exposed to the acid leaching solution. The vanadium was oxidized to pentavalent vanadium, which then entered the leaching solution. Finally, a pathway of vanadium extraction via the \( \text{H}_2\text{SO}_4-\text{H}_2\text{O}_2 \) system was proposed to gain insight into rapid vanadium leaching.

1. INTRODUCTION

Vanadium is regarded as a “vitamin of modern industry,” and it is widely used in various fields, such as aerospace, chemistry, and steel manufacturing, because of its excellent physical and chemical properties.\(^1\)\(^2\) Vanadium is widely distributed on Earth but in small proportions. In particular, black shale and vanadium titanomagnetite are two essential sources available for vanadium extraction.\(^3\) As vanadium titanomagnetite is used in the steel-making process, a large amount of vanadium steel slag is produced, and the \( \text{V}_2\text{O}_3 \) content can be enriched in the range of 12−21% according to different smelting processes and raw materials.\(^4\)

At present, the traditional method for vanadium extraction from steel slag involves alkaline salt roasting, followed by acid leaching and ammonium precipitation.\(^5\) However, it has some disadvantages, such as high energy consumption and large high-salinity wastewater discharge.\(^5\)\(^6\) Although technologies such as calcium roasting, direct leaching, and bioleaching\(^7\)−\(^9\) have made significant progress, most of them have seldom been applied in practical production owing to their inherent limitations. Considering that high-valence vanadium compounds favor vanadium extraction from the solution,\(^1\)\(^0\) sodium salt roasting is adopted before vanadium leaching. However, this process produces chlorine, hydrogen chloride, and other harmful gases, resulting in equipment corrosion and environmental pollution if not controlled.\(^1\)\(^0\) Recent research revealed that \( \text{CaF}_2 \) could facilitate the process of alkaline salt roasting at a low temperature of 700−750 °C,\(^1\)\(^1\) and vanadium extraction under atmospheric acid leaching increased by 7.4% when \( \text{NaCl} \) was added as an auxiliary agent. In addition, Li et al.\(^1\)\(^0\) developed a novel method of nonsalt roasting that showed high vanadium recovery, and the oxidation of vanadium spinel was conducted in the following steps: (1) destruction of vanadium spinel and formation of \( \text{Fe}_2\text{O}_3\text{V}_2\text{O}_5 \); (2) subsequent oxidation of trivalent vanadium compounds; and (3) formation of high-valence vanadates such as \( \text{Mn}_3\text{V}_2\text{O}_7 \) and \( \text{Mg}_2\text{V}_2\text{O}_7 \).

To enhance the efficacy of vanadium extraction, a leaching process has currently gained increasing research interest. In the method developed by Li et al.,\(^1\)\(^0\) ammonium bicarbonate leaching was achieved after nonsalt roasting, whereby 85.1% of vanadium leaching was achieved at 50 °C, with an \( \text{NH}_4\text{HCO}_3 \) mass concentration of 35%. However, ammonium salts evaporated and decomposed easily; thus, the treatment for ammonium gas must be addressed. Liu et al.\(^1\)\(^2\) introduced pressure acid leaching to extract vanadium from vanadium steel slag; the maximum leaching rate was 87.8% at an oxygen...
pressures of 1.0 MPa and leaching temperature of 160 °C. In contrast, Wu et al. proposed a pressure leaching process using NaOH solution to coextract vanadium and chromium, in which the vanadium recovery was as high as 98.3%; however, the required conditions were very rigid, such as a leaching temperature of 200 °C and a reaction time of 180 min. In addition, other methods were implemented to improve the vanadium leaching. Oxidizing agents such as MnO2 and KClO3 were added to the leaching solution to oxidize low-valence vanadium to water-soluble vanadates. 13,14 Peng et al. introduced the system of NaOH–H2O2 to recover vanadium and chromium; the leaching efficiency attained through their system exceeded 85%; however, the required NaOH and H2O2 were up to 1.0 g and 1.2 mL per gram residue, respectively. In addition, some researchers also suggested that 8-hydroxyquinoline entrapping vanadium to metal chelate was an efficient means for vanadium extraction. 15,16

On the basis of the existing studies, the effective oxidation of vanadium compounds in vanadium slags to high-valence vanadate and the subsequent transfer to the leaching solution are crucial for vanadium extraction. H2O2 can react with some ions, such as Fe2+, V5+, Ti4+, and Mn2+, under acidic conditions to produce free radicals with strong oxidizing properties. 17 Additionally, the Fenton reagent has been widely used to rapidly decompose these refractory components. Accordingly, this study, for the first time, introduced H2O2 under acidic leaching conditions to enhance the vanadium extraction from roasted vanadium steel slag. The leaching process was straightforward, and the required leaching time was shortened to less than 20 min, which is significantly lower than that required in other leaching processes (2–3 h). In addition to the optimization of technical parameters, the process and mechanism for rapid vanadium leaching were systematically investigated. The results provide valuable support for the practical application of vanadium extraction technology.

2. MATERIALS AND METHODS

2.1. Roasting of Vanadium Steel Slag. The original vanadium steel slag, obtained from a converter steelmaking plant, Kunming Iron and Steel Corporation in Yunnan Province, China, was crushed and ground to less than 150 μm. The obtained vanadium steel slag was mixed with sodium carbonate and calcium fluoride with a mass ratio of 80:20:3.12 The addition of CaF2 can facilitate phase change and realize low-temperature roasting; meanwhile, sodium roasting is helpful for producing water-soluble vanadate. To ensure complete oxidation during the roasting process, the door of the muffle furnace (TC-4-10, ZHONGXING Corp., China) was opened every 10 min for 45 s. After roasting at 700 °C for 60 min, the obtained calcine was crushed to a particle size of <75 μm and then subjected to acid leaching for vanadium recovery.

The elemental compositions of the vanadium steel slags before and after roasting were measured by an X-ray fluorescence analyzer, while the vanadium contents in the slags were determined through an ICP-AES analysis after acid digestion according to the Chinese Standard Method GB/T 6730.58-2017, and the results are listed in Table S1.

2.2. Vanadium Leaching. The leaching experiments were performed at atmospheric pressure, and a 500 mL reactor equipped with a magnetic stirring device (DF-101S, YUHUAA, China) was placed in hot water to maintain a constant leaching temperature. As the temperature of the water bath reached the desired value, 8 g of roasted vanadium steel slag was added to the reactor, and 32 mL of H2SO4 with a volume concentration of 25% was injected into the reactor; the stirring speed was set to 500 rpm. After 1 min, H2O2 (volume concentration, 30%) was supplied to the leaching system, as required. As the mixture was extracted by acid leaching for a certain period, the reactor was rapidly cooled by cold water. Then, the collected filtrate and residue were used for subsequent analysis.

On the basis of the volume and vanadium concentration in the leaching solution, the vanadium extraction can be described as follows:

\[
\text{vanadium leaching (%) = } \frac{\rho_v}{\rho_{v,r}} \times 100 \% (c: \text{ vanadium concentration; } V: \text{ volume of the leaching solution; } \rho_v: \text{ vanadium content in the roasted slag; } m: \text{ mass of the roasted slag}).
\]

2.3. Analysis and Characterization. The oxidation–reduction potential (ORP) and dissolved oxygen (DO) in the leaching system were measured using an ORP meter (PHS-2F, REX, China) and a DO meter (HQ30D, HACH, USA), respectively. An inductively coupled plasma (ICP) analyzer (Iris-Advantage1000, USA) was used to determine the concentrations of metal ions (such as vanadium, manganese, and calcium) in the filtrate. The leaching rate of vanadium extraction was calculated based on the vanadium content and volume of the filtrate.

Tetravalent vanadium was assayed using Benfield solution, and the concentration of pentavalent vanadium in the leaching solution was calculated according to the difference between the total vanadium and tetravalent vanadium. Ferrous and ferric ions were acquired using phenanthroline spectrophotometry.

The solid samples were dried at 100 °C for 12 h and then identified using an X-ray diffractometer (Empyrean, PANalytical Corp., USA). The chemical valence states of iron and vanadium in the solids were analyzed using X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific, USA). All spectra were drawn and analyzed using the XPS peak software.

To investigate the effects of free radicals on vanadium leaching, 1000 μL of DMPO (5,5-dimethyl-1-pyrroline-N-oxide) trapping agent, with a concentration of 0.3 mol L−1, was mixed with 100 μL of leaching mixture. Thereafter, electron paramagnetic resonance (EPR A300-6/1, Bruker Corp., Germany) spectrometry coupled with the spin trapping technique was employed to identify the free radicals.

3. RESULTS AND DISCUSSION

3.1. Vanadium Extraction in the Leaching System. 3.1.1. Effect of H2O2 on Vanadium Leaching. H2O2 is widely used as a typical strong oxidant in wastewater treatment. In this study, 8 mL of H2O2 (volume concentration, 30%) was added to the leaching system, which contained 8 g of roasted vanadium steel slag and 32 mL of H2SO4. Other technical parameters were as follows: leaching temperature of 50 °C, H2SO4 concentration of 25% (volume concentration), and stirring speed of 500 rpm. As shown in Figure 1, the vanadium extraction in the leaching system with H2O2 was 70.5% at 10 min, which increased to 80.5% at 15 min, followed by no significant increase. In contrast, vanadium leaching in the control system without H2O2 was less than 60% before 15 min, which gradually increased from 66.7% at 30 min to 74.2% at 120 min. Therefore, the addition of H2O2 effectively enhanced the rapid vanadium extraction from the leaching system. The optimal leaching time in the conventional acid leaching process

ACS Omega 2022, 7, 25580–25589
http://dx.doi.org/10.1021/acsomega.2c02744
ACS Omega 2022, 7, 25580–25589
25581
is 2–3 h. However, in this study, the time required for vanadium extraction, with the addition of H$_2$O$_2$, was only 15 min. In addition, the leaching rate was significantly improved.

### 3.1.2. Vanadium Extraction at Different Reaction Temperatures

The effects of temperature on vanadium extraction were investigated in the test and control leaching systems, and the leaching time was 15 min. Other parameters were the same as above. When the reaction temperature increased from 30 to 50 °C, vanadium leaching in the H$_2$O$_2$ system exhibited a gradual increase; however, it presented a moderate decrease from 80.5% at 50 °C to 73.9% at 60 °C (Figure 2). For the leaching system without H$_2$O$_2$, the vanadium extraction increased gradually from 44.1 to 62.9% in the range of 30–60 °C. Nevertheless, the leaching rate at any temperature in the leaching system was lower than that in the test system.

In general, increasing the temperature can accelerate the rate of chemical reaction; therefore, vanadium leaching in the control system showed an increasing trend at the temperature of 30–60 °C. However, for the test system, the addition of H$_2$O$_2$ to the acidic mixture intensified the leaching reaction, and the higher temperature was not helpful for vanadium extraction. Moreover, H$_2$O$_2$ rapidly decomposed with increasing temperature, while the water in the leaching system likely evaporated at high temperatures, which led to less vanadates entering the leaching solution at the lower liquid–solid ratio. Thus, 50 °C was selected as the suitable ambient temperature for this study.

### 3.1.3. Mutual Effects of H$_2$SO$_4$ Concentration and H$_2$O$_2$ Dosage

This study investigated the effects of H$_2$SO$_4$ and H$_2$O$_2$ on vanadium extraction. On the basis of the previous tentative experiments, the typical parameters were as follows: the leaching time was 15 min, reaction temperature was 50 °C, volume concentration of H$_2$SO$_4$ varied from 10 to 30%, and H$_2$O$_2$ dosage was 0–1.5 mL/g. Vanadium leaching increased with acid concentration and showed no significant increase as the volume concentration of H$_2$SO$_4$ exceeded 25% (Figure 3). Although acid leaching is an important step for vanadium extraction, a high acid concentration may reduce the oxygen solubility in the solution and decrease the oxidation of vanadium, which is unfavorable for vanadium extraction.

As shown in Figure 3, the leaching system exhibited higher vanadium extraction after the addition of H$_2$O$_2$ to the mixture of H$_2$SO$_4$ and vanadium steel slag. As the acid concentration was 25%, the test systems, with their respective H$_2$O$_2$ dosage of 1.0 and 1.5 mL/g, maintained a relatively higher vanadium extraction than the leaching system with a H$_2$O$_2$ dosage of 0.5 mL/g. However, the vanadium leaching only presented a slight increase when the H$_2$O$_2$ dosage increased from 1.0 to 1.5 mL/g. On the basis of the above experiment results, the suitable acid concentration and H$_2$O$_2$ dosage were 25% and 1.0 mL/g, respectively.

### 3.2. Characteristics of the Leaching Process

#### 3.2.1. Variations of Ferric and Vanadic Components in the Solution

To reveal the characteristics of the leaching system, the concentrations of typical metal ions, such as V$^{5+}$/V$^{4+}$ and Fe$^{3+}$/Fe$^{2+}$, were determined under the conditions mentioned in section 3.1. In the acid leaching system without H$_2$O$_2$, the concentration of total vanadium gradually increased during the entire leaching process. The pentavalent vanadium fluctuated from 3897 to 4588 mg/L, and the tetravalent vanadium moderately increased from 973 mg/L at 10 min to 4588 mg/L...
at 120 min (Figure 4a). Conversely, the vanadium extraction in the H$_2$O$_2$ system showed a moderate increase before 15 min, following which it exhibited minor fluctuations. Moreover, the concentrations of tetravalent and pentavalent vanadium presented the same variations (Figure 4b). During the leaching process, the H$_2$O$_2$ system maintained a stable ratio of tetravalent vanadium to total vanadium, which slightly fluctuated between 13.5 and 20.3%. In addition, it obtained relatively higher concentrations of total vanadium and pentavalent vanadium compared to the control system. This result is consistent with the vanadium extraction derived from the two systems. For the acid leaching system without H$_2$O$_2$, the Fe$^{3+}$ ion and total iron concentrations exhibited an increasing tendency as the leaching time increased. Fe$^{3+}$ ions were predominant in the solution, and the proportion of Fe$^{2+}$ ions was less than 3.5% (Figure 4c). In contrast, the concentration of Fe$^{2+}$ ions gradually increased from 2227 mg/L at 10 min to 3234 mg/L at 45 min, and the percentage of Fe$^{2+}$ to total iron was approximately 58–60%. As the leaching time was extended to 120 min, Fe$^{2+}$ ions rapidly declined to 668 mg/L, whereas the concentration of Fe$^{3+}$ ions increased to 5700 mg/L (Figure 4d), which was 89.5% of the total iron. The variations of ferric ions in the two leaching systems indicated that adding H$_2$O$_2$ to the acid leaching system may facilitate the dissolution of ferrous ions, leading to an increase in the total iron of the leaching solution. In the vanadium extraction process, vanadium in the mineral exists primarily as iron vanadium oxide and surrounds the matrix of olivine phases (Fe$_2$SiO$_4$), and the high-valence vanadate is more easily dissolved in the leaching solution. Although alkaline salt roasting may be helpful for vanadium extraction, the roasted slag or the leached residual still contains a certain amount of low-valence vanadium compounds. Thus, the effective conversion of low-valence vanadium to water-soluble vanadates is crucial for vanadium extraction. After H$_2$O$_2$ was added to the leaching system, it reacted with Fe$^{2+}$ under acidic conditions and produced HO• via the Fenton reaction. The strong oxidizing potential, derived from H$_2$O$_2$ and its derivatives HO• and O$_2$, oxidized the low-valence vanadium in the leaching solution or on the surface of the vanadium-bearing particle, after which the tetravalent vanadium in the liquid phase decreased. However, the total vanadium and pentavalent vanadium maintained relatively higher concentrations (Figure 4a,b). The addition of H$_2$O$_2$ facilitated the dissolution of ferrous compounds (such as Fe$_2$SiO$_4$ and Na$_4$FeO$_3$) and caused a significant increase in the Fe$^{2+}$ ion and total iron concentrations (Figure 4c,d), thereby accelerating vanadium leaching (Figure 4b) as more enveloped vanadium was exposed. At a later stage of the leaching reaction, the promotion of vanadium leaching was no longer evident because of the decomposition of H$_2$O$_2$, and the total iron increased moderately under acid leaching for a long time. However, the Fe$^{2+}$ ion could be oxidized by high-potential substances, such as O$_2$ and vanadate. Thus, the ferrous
concentration in the H₂O₂ leaching system decreased from 3234 mg/L at 45 min to 668 mg/L at 120 min (Figure 4d).

3.2.2. Chemical Phase Analysis of the Solid. Four types of solid samples were subjected to XRD analysis. The first was the roasted vanadium steel slag, and the second was residual 1 collected at a leaching time of 15 min in the control system. The remaining two samples were residuals 2 and 3 collected at 15 and 120 min, respectively, in the H₂SO₄−H₂O₂ system. Section 3.1.1 describes the technical parameters. As shown in Figure 5a, the diffraction peaks observed in the XRD patterns of the roasted vanadium steel slag are complex, but the solid sample presents distinct diffraction peaks of iron vanadium oxides, such as FeVO₄, Fe₃V₁₂O₂₃, and FeV₂O₅. Furthermore, Fe₃O₄, NaFeTiO₄, (TiO₃)·V₂O₅, and Fe₂SiO₄ (fayalite) appeared in the solid. In addition to pentavalent vanadium, low-valence vanadium, such as in FeV (fayalite) appeared in the solid. In addition to pentavalent vanadium, low-valence vanadium was oxidized to the V⁵⁺ species by high-potential reagents, such as HO• (E⁰ (HO•/H₂O) = 2.85 V), H₂O₂ (E⁰ (H₂O₂/H₂O) = 1.763 V), and O₂ (E⁰ (O₂/H₂O) = 1.229 V), making the peak of V⁵⁺ species relatively weak (Figure 6c,d). As for the existence of iron compound, the binding energy Fe 2p peaks at 709.8–710.4 eV correspond to Fe²⁺−O bonds, whereas those at 711.4–712.5 eV correspond to Fe⁴⁺−O bonds. The Fe²⁺ and Fe⁴⁺ species presented characteristic peaks, as demonstrated in Figure 6b–d. The percentage of Fe⁴⁺ species was 28.9% in residual 1, whereas it changed to 22.9% in residual 2 and then decreased to 14.3% in residual 3, which was collected at 120 min in the H₂O₂ leaching system. The results indicate that adding H₂O₂ to the leaching system enhanced the dissolution of ferric compounds. This finding was also supported by the high concentration of Fe²⁺ ions in the H₂O₂ system (Figure 4d).

3.2.3. Free Radicals in the H₂SO₄−H₂O₂ Leaching System. EPR spectrometry coupled with the spin trapping technique was employed to investigate the generation of radicals in the control system and the H₂SO₄−H₂O₂ leaching system. According to the characteristic peaks of the EPR spectra, hydroxyl radicals (HO•) and superoxide anion radicals (O₂•⁻) can be detected simultaneously in the H₂SO₄−H₂O₂ leaching system, but neither of them exists in the control system without H₂O₂. According to the principle of chemical reaction, the Fenton reaction can trigger the production of free radicals such as HO• and HO₂⁻; O₂•⁻ is also a potential reactive oxygen species produced by the following reaction:

\[ \text{HO}^- + \text{HO}_2^- = \text{O}_2^{-} + \text{H}_2\text{O} \]

It was not surprising that HO• and O₂•⁻ appeared in the H₂SO₄−H₂O₂ system. The reactive oxygen species have strong oxidizing properties; for example, the standard electrode potential of HO•/H₂O is up to 2.85 V, which provides a favorable external environment for the oxidation of low-valence vanadium compounds. Thus, the H₂SO₄−H₂O₂ system maintained lower tetravalent vanadium and higher total vanadium than the control system. The results revealed that these reactive oxygen species are beneficial for rapid vanadium leaching from roasted vanadium steel slag.

3.2.4. Changes in Other Indicators. The indicators DO and ORP were detected in the two comparative leaching systems (Figure 8). The DO values in the H₂SO₄−H₂O₂ system always exceeded the upper limit of detection (22 mg/L), and the reason is related to the fact that abundant oxygen was released into the leaching solution after the decomposition of H₂O₂. For the control system with no addition of H₂O₂, the mechanical agitation and the addition of diluted H₂SO₄ solution resulted in the presence of dissolved oxygen in the leaching solution, and the DO decreased from 7.5 mg/L at startup to 1.0 at 3 min, then gradually increased and maintained a stable value of 7.6 mg/L after 12 min (Figure 8a). In the early stage of acid leaching, ferrous ions rapidly entered the leaching solution and consumed the dissolved oxygen to be oxidized to ferric compounds (shown in Figure 4c,d). Consequently, the DO decreased significantly and maintained a relatively lower value during a leaching time of 1–6 min.

For the control system, the ORP fluctuated moderately between 1020 and 1060 mV. However, the H₂SO₄−H₂O₂
system presented a relatively lower ORP during a leaching time of 15 min. Although the DO was always more than 22 mg/L, the leached ferrous ion in the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}_2$ system was also up to 2227 mg/L at 10 min (Figure 4d), resulting in an ORP value of less than 1000 mV, and varied from 930 mV to 970 mV (Figure 8b).

In addition to the vanadic and ferric compounds, the leaching of other metallic elements was investigated in this study, and the ICP analysis is shown in Table S2. For the control system, the leaching of Mn, Cr, and Ti significantly increased with an increase in leaching time; however, the concentration of Ca$^{2+}$ in the leaching solution moderately decreased due to the formation of CaSO$_4$ (Figure 5). After $\text{H}_2\text{O}_2$ was added to the leaching mixture, the compounds Mn, Cr, and Ti could be leached out in a short time of 15 min; however, there was no significant increase in chromium leaching.

4. CHEMICAL REACTION AND PATHWAY FOR THE RAPID VANADIUM EXTRACTION

To discuss the feasibility of a chemical reaction, the electrode potentials$^{2,26,27}$ were compared in this study. As shown in

---

Figure 6. XPS spectra for the solids: (a) V$^{4+}$/V$^{5+}$ and (b) Fe$^{2+}$/Fe$^{3+}$ in residual 1; (c) V$^{4+}$/V$^{5+}$ and (d) Fe$^{2+}$/Fe$^{3+}$ in residual 2; (e) V$^{4+}$/V$^{5+}$ and (f) Fe$^{2+}$/Fe$^{3+}$ in residual 3.
Table 1, the standard electrode potentials of $\text{HO}^\cdot$/H$_2$O, H$_2$O$_2$/H$_2$O, HO$_2^-$/H$_2$O, O$_2$/H$_2$O, VO$_2^+$/VO$^{2+}$, Fe$^{3+}$/Fe$^{2+}$, and VO$^{2+}$/V$^{3+}$ are 2.85, 1.776, 1.70, 1.229, 1.00, 0.771, and 0.331 V, respectively. Therefore, most of the free radicals have a stronger oxidizing ability, and low-valence metal compounds such as ferrous ions and trivalent or tetravalent vanadium in the leaching system can be oxidized by HO$^\cdot$, H$_2$O$_2$, and O$_2$. In addition, ferrous ions can be oxidized by pentavalent vanadium because of the difference in the electrode potentials. The speed of the oxidation process depends on the chemical reaction rate, which is determined by the strength of the bonds and external factors, such as temperature, concentration, and mass transfer.

On the basis of the principles of physical chemistry and the obtained results, a pathway for vanadium leaching in the H$_2$SO$_4$–H$_2$O$_2$ system was proposed (Figure 9). According to the simulation of the HSC Chemistry 6.0 software, as well as some related references, the potential chemical reactions during vanadium extraction are described in Table 2. In the acid leaching system, the soluble compounds on the outer surface of the particles dissolved in the H$_2$SO$_4$ and entered the leaching solution. The fluorine in the roasted vanadium steel slags accelerated the etching of the outer surface, causing the iron vanadium compounds and others in the inner layer of the particles to gradually be exposed to the acid solution. This process provides the prerequisites for the enhancement of vanadium extraction. However, two factors adversely affected the leaching process; on one hand, silicate compounds such as Fe$_2$SiO$_4$ and MgSiO$_3$ dissolved in highly acidic solution, and they were converted into colloidal H$_2$SiO$_3$, which can absorb positive cations of vanadium such as VO$^{2+}$ or VO$_2^+$. On the other hand, Ca$^{2+}$ reacted with SO$_4^{2-}$ to produce a poorly soluble compound CaSO$_4$ (shown in Figure 5). Both H$_2$SO$_4$ and CaSO$_4$ wrap around the particle or the vanadic compounds, resulting in adverse effects on the dissolution and diffusion of vanadium ions.

After H$_2$O$_2$ was added to the leaching system, the Fe$^{3+}$ leaching increased significantly in a short time (Figure 4d), and the concentrations of Mn and Ti in the solution improved moderately (Table S2). H$_2$O$_2$ facilitated the dissolution of low-valence metallic ions and then triggered the production of strong oxidizing substances (Figure 7), such as HO$^\cdot$ and HO$_2^-$, via Fenton and Fenton-like reactions. Considering that the Fe ion presented a relatively higher concentration than Mn and

Figure 7. EPR spectra of the mixture derived from the H$_2$SO$_4$–H$_2$O$_2$ leaching system (note: 1 - characteristic peaks of O$_2^-$; 2 - characteristic peaks of HO$^\cdot$).

Figure 8. Changes in (a) DO and (b) ORP during the leaching process.

Figure 9. Pathway of vanadium leaching in the H$_2$SO$_4$–H$_2$O$_2$ system.

| Electrode Reaction | $E^\theta$/V |
|-------------------|-------------|
| VO$^{2+}$ + 4H$^+$ + 3e$^-$ = V$^{3+}$ + 2H$_2$O | 0.337 |
| H$_2$O$_2$ + H$^+$ + e$^-$ = HO$^\cdot$ + H$_2$O | 0.71 |
| Fe$^{3+}$ + e$^-$ = Fe$^{2+}$ | 0.771 |
| VO$_2^+$ + e$^-$ = VO$^{2+}$ | 1.00 |

Table 1. Redox Potential of the Specific Reaction for the Vanadium Leaching

Figure 7. EPR spectra of the mixture derived from the H$_2$SO$_4$–H$_2$O$_2$ leaching system (note: 1 - characteristic peaks of O$_2^-$; 2 - characteristic peaks of HO$^\cdot$).
Table 2. Potential Chemical Reactions and Equations in the H₂SO₄—H₂O₂ System

| reaction equation (50 ℃) | ΔG | log K | related refs |
|--------------------------|----|------|-------------|
| H₂O₂ + Fe²⁺ = HO₂⁻ + OH⁻ + Fe³⁺ | eq 1 | | |
| H₂O₂ + V⁵⁺ = V⁵⁺ + HO₂⁻ | eq 2 | | |
| H₂O₂ + HO²⁻ = H₂O + HO₂⁻ | eq 3 | | |
| H₂O₂ + Fe³⁺ = Fe³⁺ + HO₂⁻ + H⁺ | eq 4 | | |
| H₂O₂ = O₂ + H₂O | eq 5 | −49.69 | 33.61 | HSC Chemistry 6 |
| HO²⁻ + HO₂⁻ = O₂ + H₂O | eq 6 | | |
| HO²⁻ + Fe³⁺ = OH⁻ + Fe⁴⁺ | eq 7 | −24.46 | 16.56 | HSC Chemistry 6 |
| HO²⁻ + HO²⁻ = H₂O₂ | eq 8 | −44.21 | 30.05 | HSC Chemistry 6 |
| 2HO²⁻ = O₂ + H₂O₂ | eq 9 | | |
| O₂ + 4Fe²⁺ + 4H⁺ = 4Fe³⁺ + 2H₂O | eq 10 | −37.78 | 25.55 | HSC Chemistry 6 |
| VO²⁺ + Fe²⁺ + 2H⁺ = Fe³⁺ + VO²⁺ + H₂O | eq 11 | −4.24 | 2.87 | HSC Chemistry 6 |
| VO²⁺ + SO₄²⁻ = VO₂SO₄⁻ | eq 12 | | |
| VO₂²⁻ + 2Fe²⁺ = V₂O₄ + 2Fe²⁺ | eq 13 | | |
| V⁺⁺ + H₂O = V(OH)⁺⁺ + H⁺ | eq 14 | | |
| V⁺⁺ + O₂ + 2H⁺ = VO²⁺ + H₂O + 3e⁻ | eq 15 | −108.9 | | HSC Chemistry 6 |
| 4FeVO₄ + SO₂ = 2Fe₂O₃ + 4VO₂ | eq 16 | −384.54 | 26.01 | HSC Chemistry 6 |
| VO₂ + H₂SO₄ = (VO₂)₂SO₄ + H₂O | eq 17 | | |
| VO₂ + H₂SO₄ = VOSO₄ + H₂O | eq 18 | −13.82 | 9.34 | HSC Chemistry 6 |
| VO₂ + 2H₂SO₄ + H₂O₂ = 2VOSO₄ + 3H₂O | eq 19 | −94.77 | 64.1 | HSC Chemistry 6 |
| Fe₂SO₄ + 1/2O₂ + H₂O = Fe₂O₃ + H₂SO₄ | eq 20 | −54.49 | 36.85 | HSC Chemistry 6 |
| MgSO₄ + H₂SO₄ = MgSO₄ + H₂SiO₃ | eq 21 | −21.07 | 14.25 | HSC Chemistry 6 |
| Ca⁺⁺ + SO₄²⁻ = CaSO₄ | eq 22 | −7.64 | 5.16 | HSC Chemistry 6 |

Ti ions, the correlation between Fe ions and vanadium extraction was discussed systematically in this paper. In general, the increase in total vanadium in the H₂SO₄—H₂O₂ system is closely related to the oxidation of vanadium compounds with low valence. When no matter exists in the leaching solution or on the surface of the particle, trivalent and tetravalent vanadium can be converted to pentavalent vanadium by strongly oxidizing substances, such as H₂O₂ and its derivatives, HO²⁻ and O₂⁻ (Table 1). Table 2 lists the potential chemical reactions. Furthermore, the vanadium inside the particle gradually is exposed to the acid leaching solution after the complex oxides on the surface of the particle are destroyed and can then be oxidized to high-valence vanadium, which favors vanadium leaching (Figure 1). For the H₂SO₄—H₂O₂ system, the leaching reaction was rapid (performed within 6 min), and it was very difficult to determine the activation energy and chemical reaction rate for this rapid leaching process. Thus, this requires further investigation.

5. CONCLUSION

H₂O₂ is an effective reagent for enhancing vanadium leaching in a short time. The vanadium extraction in the H₂SO₄—H₂O₂ system improved by 22%, compared to that in a control system with no addition of H₂O₂. The leaching time in the proposed system reduced to 15 min owing to the addition of H₂O₂. H₂O₂ and its derivatives have high redox potentials and can oxidize Fe²⁺ ions and low-valence vanadium. Because of the rapid dissolution of metallic ions and complex compounds, vanadium in the inner particle begins to be exposed to the acid leaching solution, following which it can be oxidized to pentavalent vanadium, resulting in a significant increase in the total vanadium.

In the H₂SO₄—H₂O₂ system, the metallic ions of Mn, Cr, and Ti were leached out simultaneously, but there was no significant increase in chromium leaching. The leaching reaction was rapid, and the potential chemical reactions were speculated based on the obtained results and the simulation of the HSC chemistry. The determination of the activation energy and chemical reaction rate for this rapid leaching process requires further investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02744.

Two tables: one is elemental compositions of the vanadium steel slags before and after roasting, and the other is ICP analysis of the leaching solution (PDF).

AUTHOR INFORMATION

Corresponding Author

Dongdong Zhang — Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China; Email: 20120054@kust.edu.cn
Shugen Liu — Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China
Yue Chen — Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China
Shuo Yu — Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China
Gang Xie — Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China; State Key Laboratory of Pressure Hydrometallurgical Technology of Associated Nonferrous Metal Resources, Kunming 650503, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02744

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was financially supported by the State Key Laboratory of Pressure Hydrometallurgical Technology of Associated Nonferrous Metal Resources (yy2016004) and the Reserve Talents of Young and Middle-aged Academic and Technical Leaders in Yunnan Province (202105AC160096).

REFERENCES

(1) Peng, H.; Liu, Z. H.; Tao, C. Y. A Green Method to Leach Vanadium and Chromium from Residue Using NaOH-H₂O₂. Sci. Rep. 2018, 8, 426.
(2) Wang, Z.; Zheng, S.; Wang, S.; Qin, Y.; Du, H.; Zhang, Y. Electrochemical Decomposition of Vanadium Slag in Concentrated NaOH Solution. Hydrometallurgy 2015, 151, 51–55.
(3) 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. Min. Met. Mater. 2012, 19 (10), 893–898.
(4) Ye, G. H.; Tong, X.; Lu, L. Resource Characteristics of Vanadium-Bearing Steel Slag and Progress in Extracting Vanadium. Chin. J. Rare Metals 2010, 34 (5), 769–775 (in Chinese).
(5) Wu, K. H.; Wang, Y. R.; Wang, X. R.; Wang, S. N.; Liu, B.; Zhang, Y.; Liu, B.; Co-Extraction of Vanadium and Chromium from High Chromium Containing Vanadium Slag by Low-Pressure Liquid Phase Oxidation Method. J. Clean. Prod. 2018, 203, 873–884.
(6) Liu, H. B.; Du, H.; Wang, D. W.; Wang, S. N.; Zheng, S. L.; Zhang, Y. Kinetics Analysis of Decomposition of Vanadium Slag by KOH Sub-Molten Salt Method. Trans. Nonferrous Met. Soc. China 2013, 23 (5), 1489–1500.
(7) Gomes, H. I.; Funari, V.; Mayes, W. M.; Rogerson, M.; Prior, T. J. Recovery of Al, Cr and V from Steel Slag by Bioleaching: Batch and Column Experiments. J. Environ. Manag. 2018, 222 (15), 30–36.
(8) Li, J. X.; Zhang, B. G.; Yang, M.; Lin, H. Bioleaching of Vanadium by Acidithiobacillus Ferrooxidans from Vanadium-Bearing Resources: Performance and Mechanisms. J. Hazard. Mater. 2021, 416, 125843.
(9) Zhu, Y. G.; Zhang, G. F.; Feng, Q. M.; Lu, Y. P.; OU, L. M.; Huang, S. J. Acid Leaching of Vanadium from Roasted Residue of Stone Coal. Trans. Nonferrous Met. Soc. China 2010, 20, 107–111.
(10) Li, M.; Wei, C.; Fan, G.; Wu, H. L.; Li, C.; Li, X. Acid Leaching of Black Shale for the Extraction of Vanadium. Int. J. Miner. Process 2010, 95 (1), 62–67.
(11) Wang, J. Vanadium Extraction from Vanadium-Containing Steel Slag and Its Application for Wet Desulfurization. Master Thesis, Kunming University of Science and Technology, Kunming, 2019 (in Chinese).
(12) Liu, S. G.; Ding, E. M.; Ning, P.; Xie, G.; Yang, N. Vanadium Extraction from Roasted Vanadium-Bearing Steel Slag via Pressure Acid Leaching. J. Environ. Chem. Eng. 2021, 9 (3), 105195.
(13) Yang, K.; Zhang, X. Y.; Tian, X. D.; Yang, Y. L.; Chen, Y. B. Leaching of Vanadium from Chromium Residue. Hydrometallurgy 2010, 103 (1–4), 7–11.
(14) Chen, X. Y.; Lan, X. Z.; Zhang, Q. L.; Ma, H. Z.; Zhou, J. Leaching Vanadium by High Concentration Sulfuric Acid from Stone Coal. Trans. Nonferrous Met. Soc. China 2010, 20, 123–126.
(15) Naeemullah; Tuzen, M.; Kazi, T. G.; Citak, D.; Soylak, M. Pressure-Assisted Ionic Liquid Dispersive Microextraction of Vanadium Coupled with Electrothermal Atomic Absorption Spectrometry. J. Anal. At. Spectrom. 2013, 28, 1441.
(16) Wadhwa, S. K.; Tuzen, M.; Kazi, T. G.; Soylak, M. Graphite Furnace Atomic Absorption Spectrometric Detection of Vanadium in Water and Food Samples after Solid Phase Extraction on Multiwalled Carbon Nanotubes. Talanta 2011, 86, 205–209.
(17) Czapski, G.; Samuni, A.; Meisel, D. Reactions of Organic Radicals Formed by Some “Fenton-Like” Reagents. J. Phys. Chem. 1971, 75 (21), 3271–3280.
(18) Liu, X. Y.; Guan, H. L. Inquiry into Analytical Method for Vanadium in Benfield Solution. Chem. Fertilizer Ind. 2005, 32 (4), 49–51 (in Chinese).
(19) Williams, A. G. B.; Scherer, M. M. Spectroscopic Evidence for Fe(II)-Fe(III) Electron Transfer at the Iron Oxide-Water Interface. Environ. Sci. Technol. 2004, 38 (18), 4782–4790.
(20) Ma, A. J.; Liu, S. G.; Li, K.; Ning, P.; Xie, G.; Yang, N. Novel Technology for Hydrogen Sulfide Purification via the Slurry Prepared from Roasted Vanadium Steel Slag. Chem. Eng. J. 2020, 394, 124905.
(21) Li, T.; Liu, S. G.; Yao, X. F. Addition of Reactive Oxygen Scavenger to Enhance PH₂Biopurification: Process and Mechanism. Process Saf. Environ. Prot. 2020, 142, 118–120.
(22) Li, H.-Y.; Wang, K.; Wang, C.; Lin, M.; Xie, B. Atomic Atmosphere: A Way to Understand Phase Evolution during Vanadium Slag Roasting at the Atomic Level. Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater 2019, 75 (6), 927–932.
(23) Wang, Z. H.; Chen, L.; Aldahrbi, T.; Li, C.; Liu, W. Z.; Zhang, G. Q.; Yang, Y. H.; Luo, D. M. Direct Recovery of Low Valence Vanadium from Vanadium Slag: Effect of Roasting on Vanadium Leaching. Hydrometallurgy 2020, 191, 105156.
(24) Khachatryan, L.; Dellingier, B. Environmentally Persistent Free Radicals (EPFRs)-2. Are Free Hydroxyl Radicals Generated in Aqueous Solutions? Environ. Sci. Technol. 2011, 45 (21), 9232–9239.
(25) Wang, Y. J. Sample Pretreatment Analysis Technology Based on Fe-ZSM-5 Ultrasonic-Fenton Reaction. Master Thesis, Shanghai Jiao Tong University, Shanghai, 2014 (in Chinese).
(26) Huang, K. L. Inorganic Chemistry; Science Press: Beijing, 2007 (in Chinese).
(27) Jiang, Z. P. Environmental Engineering; Higher Education Press: Beijing, 2005 (in Chinese).
(28) Walling, C.; Johnson, R. A. Fenton’s Reagent. V. Hydroxylation and Side-chain Cleavage of Aromatics. J. Am. Chem. Soc. 1975, 97 (2), 363–367.
(29) Nizova, G. V.; Kozlov, Y. N.; Shul’pin, G. B. Effect of Acetoneitrile on the Catalytic Decomposition of Hydrogen Peroxide by Vanadium Ions and Conjugated Oxidation of Alkanes. Russ. Chem. Bull. 2004, 53 (10), 2330–2333.
(30) Pignatello, J. J. Dark and Photoassisted Iron(3+)-Catalyzed Degradation of Chlorophenoxyl Herbicides by Hydrogen Peroxide. Environ. Sci. Technol. 1992, 26 (5), 944–951.
(31) He, D.; Feng, Q.; Zhang, G.; Luo, W.; Ou, L. Study on Leaching Vanadium from Roasted Residue of Stone Coal. Mining Metall. Explor. 2008, 25 (4), 181–184.
(32) Lu, Z. L. Investigation and Industrial Practice on Extraction of V₂O₅ from Stone Coal Containing Vanadium by Acid Process. Hydrometall. China 2002, 21 (4), 175–183 (in Chinese).
(33) Li, M.; Liu, B.; Zheng, S. L.; Wang, S. N.; Du, H.; Dreisinger, D. B.; Zhang, Y. A Cleaner Vanadium Extraction Method Featuring Non-Salt Roasting and Ammonium Bicarbonate Leaching. *J. Clean. Prod.* 2017, 149, 206–217.

(34) Li, H. Y.; Wang, C. J.; Yuan, Y. H.; Guo, Y.; Diao, J.; Xie, B. Magnesiation Roasting-Acid Leaching: A Zero-Discharge Method for Vanadium Extraction from Vanadium Slag. *J. Clean. Prod.* 2020, 260, 121091.

(35) Yang, Z.; Li, H. Y.; Yin, X. C.; Yan, Z. M.; Yan, X. M.; Xie, B. Leaching Kinetics of Calcification Roasted Vanadium Slag with High CaO Content by Sulfuric Acid. *Int. J. Miner. Process* 2014, 133, 105–111.