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Oxidative Leaching of Vanadium from Vanadium-Chromium Reducing Residue with MnO$_2$

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Abstract: This paper focused on the oxidative leaching process of vanadium from vanadium-chromium reducing residue in alkaline medium with MnO$_2$. The effect of experimental parameters including reaction time, reaction temperature, dosage of MnO$_2$, dosage of NaOH, and liquid-to-solid ratio on the leaching efficiency of vanadium had been studied. The results indicated that MnO$_2$ was an efficient oxidant for leaching out of vanadium. The leaching efficiency of vanadium was up to 97.25% under optimal reaction conditions: reaction temperature of 90 ℃, reaction time of 60 min, dosage of MnO$_2$ at 50 wt.%, concentration of NaOH at 30 wt.% and liquid-to-solid at 5:1 mL/g.

1. Introduction

The vanadium compounds as important national strategy resources were widely used in petrochemical industry, catalyst, iron steel, due to its excellent physicochemical properties and also it was called as "vitamins of modern industry" [1-6]. As it had an electronic configuration of $[Ar]3d^34s^2$, the vanadium valence could be V(II), V(III), V(IV) and V(V) the most common oxidation states [7]. In China, the main sources of vanadium were vanadium-titan magnetite ore [8] and stone coal [9] and the vanadium was almost existed in low valence. In the vanadium producing process, a large amount wastewater containing V(V) and Cr (VI) was produced. The wastewater was reduced with Na$_2$SO$_3$ or iron scurf to form the precipitate containing Cr (III), V (IV) and V (III), which was usually called vanadium-chromium reducing residue. In which, vanadium mainly occurs as V (IV) and V (III). In China, every year more than 500 thousand tons of the vanadium-chromium reducing residue was produced. The handling of these residues had become a thorny problem in many plants in China

Many hydrometallurgy technologies had been investigated to recover vanadium from the vanadium-chromium reducing residue, directing leaching with NaOH [10], alkaline leaching with electric field [11, 12]. The sub-molten salt (SMS) technology had been successfully applied to leach out vanadium in concentrated alkaline solution[13-16]. The leaching efficiency of vanadium could reach up to 95% and no hazardous gas or toxic tailings were discharged during the process. But the process needed high alkaline consumption, high energy cost and the equipment corrosion was a big challenge due to the high causticity of the reaction medium (usually above 70 wt%). The vanadium-chromium reducing slag had not been treated effectively, resulting in a waste of vanadium and chromium resources as well as environmental pollution.

In this paper, MnO$_2$ was used to oxidize the low valent vanadium during the alkaline leaching process. The effect of reaction time, reaction temperature, dosage of MnO$_2$ dosage of NaOH and liquid-to-solid ratio on the leaching efficiency of vanadium were investigated.

2. Materials and Methods

2.1 Materials

The vanadium-chromium reducing residue was precipitated from a waste water contained vanadium and chromium in low valence in an iron and steel mill from Pan gang Group Co., Ltd., Panzhihua, Sichuan Province, China. Before the experiment, the residue dried and grounded to suitable particles. The chemical composition of the residue was listed in Table 1 and the phase composition was detailed in **Figure 1**. All the reagents used in the experiments were analytical grade.

2.2 Experimental procedure

All experiments were performed in a glass beaker with a thermostatic mixing water bath pot [11, 17, 18].

A predetermined amount of NaOH and deionized water was added to the beaker to produce homogeneous slurry under constant stirring. The slurry was heated to a predetermined temperature. Next, the residue was added to the reactor, and then the amount of MnO_2 was added. After the required contact time, the filtrate was separated from the residue by vacuum filtration. The concentration of vanadium in the filtrate was determined by inductive couple plasma-optical mission spectrometry (ICP-3000).

The leaching efficiency of vanadium (η_V) was calculated in Equation (1), as followed:

$$\eta = \frac{V \cdot C}{m\omega} \times 100\%$$

(1)

Where, C is the concentration of vanadium in the filtrate, g/L; V is the volume of the filtrate, mL; ω is the mass fraction of vanadium in the vanadium-chromium reducing residue; m is mass of the vanadium-chromium reducing residue used in the leaching experiments, g.
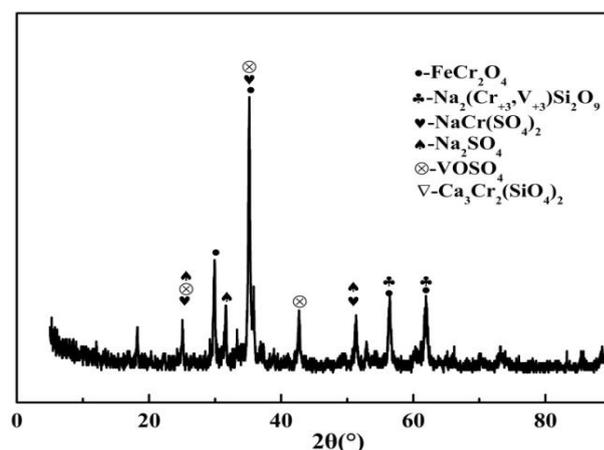

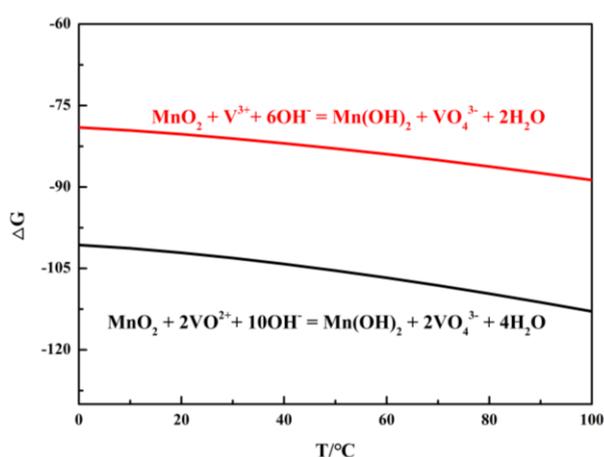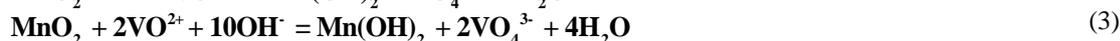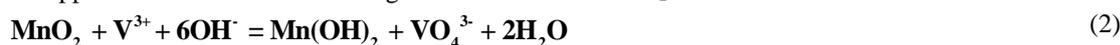Figure 1 The XRD pattern of the original residue

Table 1 Composition of the original vanadium and chromium residue (%, wt)

Component	O	Cr	Si	Na	S	V
Amount (wt.%)	41.44	18.80	11.30	10.93	10.64	3.11
Component	Ca	Cl	Fe	K		
Amount (wt.%)	1.94	1.06	0.37	0.17		

3. Results and Discussion

3.1 Reaction mechanism

The vanadium existed as low valent in vanadium-chromium reducing residue according to the results showed in **Figure 1**, and it was hard to leach out in alkaline medium [10]. It was known that $E^0_{MnO2/Mn2+} = 1.21$ V and $E^0(VO_2^+/VO^{2+}) = 1.00V$, and therefore MnO_2 might be used as the oxidizing agent to oxidize V(IV) in the leaching process [19, 20]. Thus, the main reaction during the oxidative leaching process was between the low valent vanadium and MnO_2 like Equation (2) and (3). The ΔG_T^θ of Equation (2) and (3) at different temperatures could be calculated with $\Delta_f H_{298}^\theta$, S_{298}^θ and C_p at 298 K [21, 22]. The results showed in

Figure 2 showed that the △G was negative which indicated that the reaction of Equations (2) and (3) were easy to happen and the oxidative leaching of vanadium with MnO_2 was feasible.

$$MnO_2 + V^{3+} + 6OH^- = Mn(OH)_2 + VO_4^{3-} + 2H_2O \tag{2}$$
$$MnO_2 + 2VO^{2+} + 10OH^- = Mn(OH)_2 + 2VO_4^{3-} + 4H_2O \tag{3}$$

Figure 2 Relationship between △G and temperature of oxidation of vanadium with MnO_2

3.2 Effect of dosage of MnO₂

Based on the above, the oxidation reaction of low valence vanadium and MnO_2 was easy to happen in thermodynamics. It was known that $E^0_{MnO2/Mn2+} = 1.21$ V and $E^0(VO_2^+/VO^{2+}) = 1.00$ V, and therefore MnO_2 could be used for the oxidation of V(IV) during the leaching process. The effect of MnO_2 dosage on the leaching efficiency of vanadium was investigated as other reaction conditions kept as constant: reaction time of 60 min, reaction temperature of 90 °C, liquid-to-solid ratio of 5:1 mL/g, and dosage of NaOH at 30 wt.%. The results were shown in **Figure 3**.
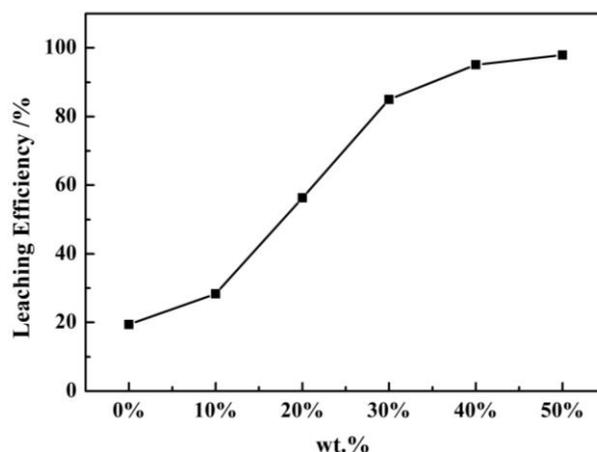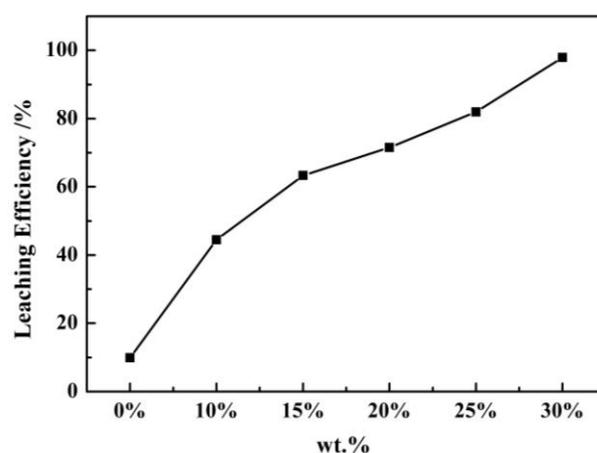

Figure 3 Effect of dosage of MnO_2 on the leaching efficiency of vanadium

The leaching efficiency of vanadium was increased linearly with the increase of dosage of MnO_2. The leaching efficiency of vanadium was increased from 19.38% without MnO_2 to 97.25% at dosage of MnO_2 at 50 wt.%. The vanadium in low valences like V(IV) and V(III) was oxidized to V(V) by MnO_2, and then dissolved in alkaline medium and achieved high leaching efficiency. The results confirmed that MnO_2 could oxidize low valence vanadium ion of V(IV) and V(III) into V(V).

3.3 Effect of dosage of NaOH

Results shown in **Figure 4** summarized the effect of dosage of NaOH on the leaching efficiency of vanadium as the reaction conditions kept as: reaction time at 60 min, reaction temperature of 90 ℃, liquid-to-solid ratio of 5:1 mL/g and dosage of MnO_2 at 50 wt.%. The concentration of NaOH was set as 0 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.% and 30 wt.%.

Figure 4 Effect of dosage of NaOH on the leaching efficiency of vanadium

The leaching efficiency of vanadium was increased with the increasing of dosage of NaOH. About 9.94% vanadium leached out in neutral medium with oxidation of MnO_2. And the leaching efficiency increased up to 97.25% at NaOH of 30 wt.%. The vanadium in low valence was hard to leach out in alkaline medium, while the high valent vanadium was easy to dissolve in alkaline medium and achieve high leaching efficiency. The high concerned NaOH solution was beneficial for high valent vanadium leaching out. As the leaching efficiency had up to 97.25%, thus the dosage of NaOH at 30 wt.% was chosen for optimal condition for further experiments.

3.4 Effect of reaction temperature

Reaction temperature played an important role in the diffusion process. The higher temperature increased the activity of atoms and molecules, and therefore the reaction rate [23]. **Figure 5** summarized the effect of reaction temperature on the leaching process under standard conditions: reaction time of 60 min, liquid-to-solid ratio of 5:1 mL/g, dosage of MnO_2 at 50 wt.% and concentration of H_2SO_4 at 30 wt.%. The leaching efficiency of vanadium was improved by increasing the reaction temperature. 97.25% of vanadium could leach out at a reaction temperature of 90 ℃ and therefore 90 ℃ was chosen for optimal reaction temperature in further experiments.
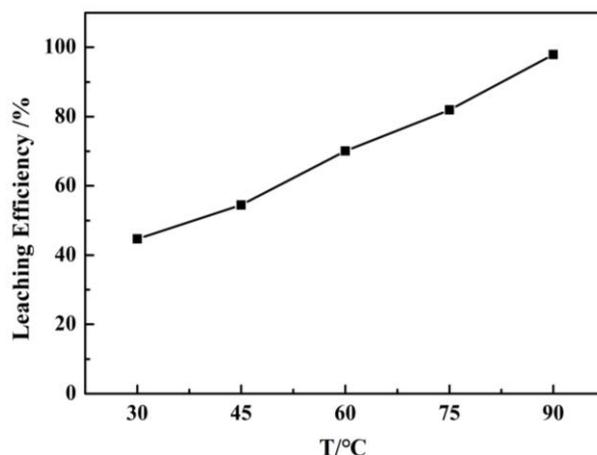
Figure 5 Effect of dosage of reaction temperature on the leaching efficiency of vanadium

3.5 Effect of reaction time

Figure 6 showed the leaching efficiency of vanadium by varying the reaction time from 10 min to 60 min under selected conditions: reaction temperature of 90 °C, liquid-to-solid ratio of 5:1 mL/g, dosage of MnO_2 at 50 wt.% and concentration of NaOH at 30 wt.%. Increasing of reaction time could promote the reaction between MnO_2 and low valent vanadium in alkaline medium and achieve high leaching efficiency. The leaching efficiency of vanadium was increased from 49.69% at 10 min to 97.25% at 60 min. which indicated that 60 min was enough to leach out vanadium.
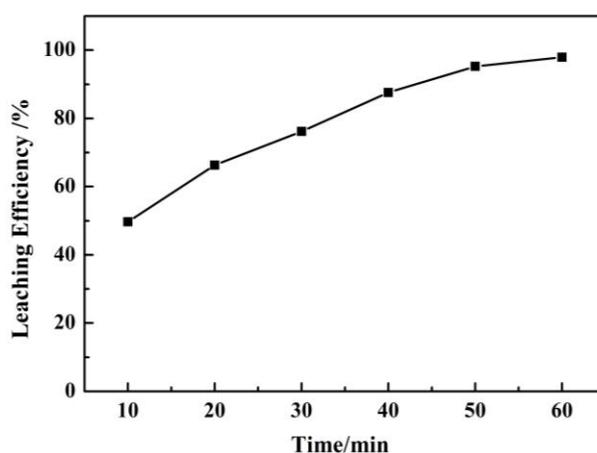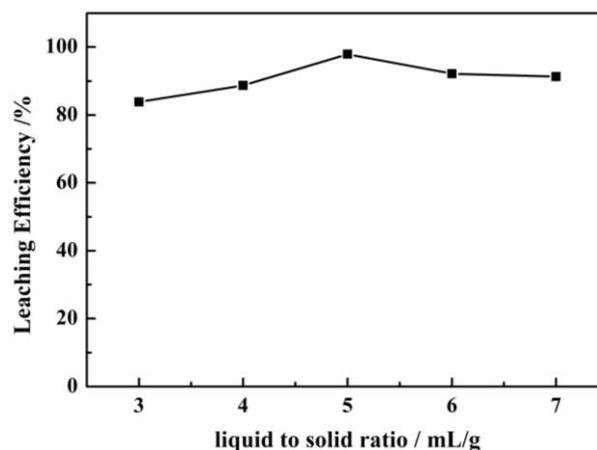

Figure 6 Effect of dosage of reaction time on the leaching efficiency of vanadium

3.6 Effect of liquid-to-solid ratio

The liquid-to-solid ratio showed a significant effect on the volume of filtrate and concentration of purpose product in the leaching process [23]. A series of experiments were conducted to evaluate an optimal liquid-to-solid ratio to achieve high leaching efficiency of vanadium. The liquid-to-solid ratio was set as 3:1 mL/g, 4:1 mL/g, 5:1 mL/g, 6:1 mL/g and 7:1 mL/g, and other reaction conditions were kept as constant: reaction temperature of 90 °C, reaction time of 60 min, dosage of MnO_2 at 50 wt.% and concentration of NaOH at 30 wt.%. The results were shown in **Figure 7**.

Figure 7 Effect of dosage of liquid-to-solid ratio on the leaching efficiency of vanadium

The leaching process was inefficient for low liquid-to-solid ratio as the viscosity of reaction medium was large, just 83.85% of vanadium were leached out in liquid-to-solid at 3:1 mL/g. The leaching process favored higher liquid-to-solid ratio, where 97.25% of the vanadium was obtained at a liquid-to-solid of 5:1 mL/g. While further increase of the liquid-to-solid ratio had negative effect on the leaching process. Therefore, a liquid-to-solid of 5:1 mL/g was recommended for future use.

Based upon the above experimental results, the optimal reaction conditions for vanadium leaching out was: reaction temperature of 90 ℃, reaction time of 60 min, dosage of MnO_2 at 50 wt.%, concentration of NaOH at 30 wt.% and liquid-to-solid at 5:1 mL/g. The leaching efficiency of vanadium was up to 97.25% under optimal reaction conditions.

4. Conclusions

This paper focused on the oxidative leaching process of vanadium with MnO_2 from vanadium-chromium reducing residue. Vanadium in low valent could be oxidized to high valent by MnO_2 in the alkaline leaching process, which contributed to high leaching efficiency of vanadium and it was up to 97.25% under optimal reaction conditions: reaction temperature of 90 ℃, reaction time of 60 min, dosage of MnO_2 at 50 wt.%, concentration of NaOH at 30 wt.% and liquid-to-solid at 5:1 mL/g.

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