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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 leaching process of vanadium from vanadium-chromium reducing residue in alkaline medium with MnO_2. The effects of serval parameters like reaction time, reaction temperature, dosage of MnO_2, dosage of NaOH, and liquid-to-solid ratioon the leaching process had been studied. The results indicated that MnO_2 was an efficient oxidant for vanadium leaching out. The leaching efficiency of vanadium was up to 97.25% at reaction temperature of 90 °C, 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 and its compounds were called "vitamins of modern industry" and widely used in many fields, like catalyst, steel and petrochemical industry, catalyst, iron steel [1-6]. The vanadium valence could be +2, +3, +4 and +5 due to its electronic configuration of $[Ar]3d^34s^2$, and +5 was 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 and formed the precipitate containing low valence chromium and vanadium, which was usually called vanadium-chromium reducing residue (VCRR). More than 500 thousand tons of the VCRR were 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]. Above 95% vanadium could be leached out with hazardous gas or toxic tailings. But some problems like high alkaline consumption, high energy cost and equipment corrosion were still unsolved. The treatment of VCRR was still a waste resource and also resulting in environmental pollution.

In this paper, MnO_2 as an oxidant was used to enhance the alkaline leaching process of vanadium. 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. Experimental

2.1. Imental Materials

The VCRR was collected from 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.

The experimental process was the same as the recent studies [11]: 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:

$$\eta = \frac{V \cdot C}{m\omega} \times 100\% \tag{1}$$

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.

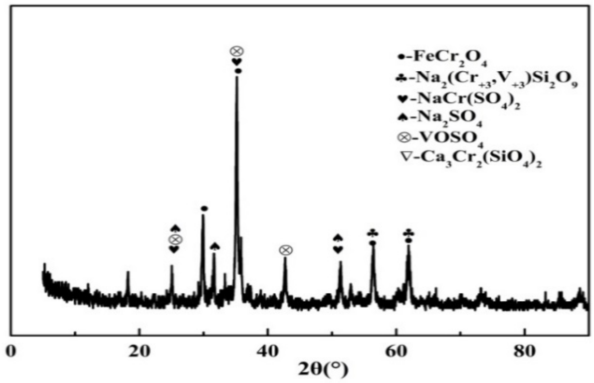

Figure 1. The XRD pattern of the original residue

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 Discussions

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 to oxidize low valence vanadium 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 ΔG 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.

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

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

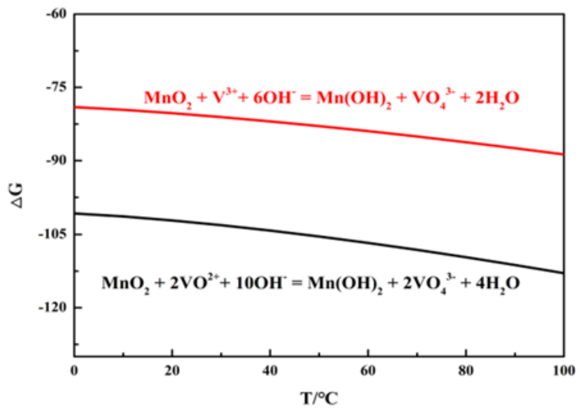

Figure 2. Relationship between △G and temperature of oxidation of vanadium with MnO_2

3.2. *Effect of Dosage of MnO_2*

Based on the above, the oxidation reaction of low valence vanadium and MnO_2 was easy to happen in thermodynamics. 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.

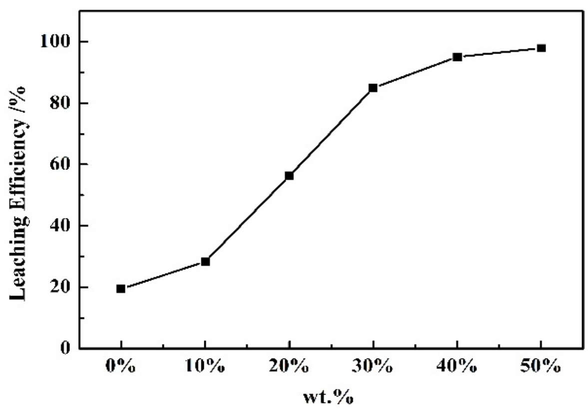

Figure 3. Effect of dosage of MnO_2 on the leaching efficiency of vanadium

The leaching efficiency of vanadium was increased linearly with the increase of 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 was oxidized to high valence 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 to high valence and contributing to high leaching efficiency of vanadium.

3.3. *Effect of Dosage of NaOH*

Results shown in Figure 4 summarized the effect of dosage of NaOH on the leaching process as the other reaction conditions kept as: reaction time at 60 min, reaction temperature of 90 °C, 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.%.

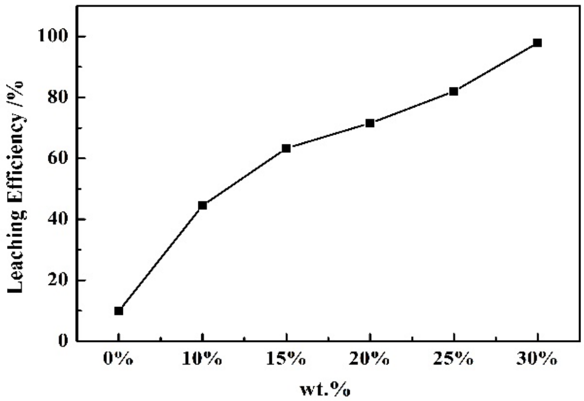

Figure 4. Effect of dosage of NaOH on the leaching efficiency of vanadium

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 low valence vanadium 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 as optimal condition for further experiments.

3.4. Effect of Reaction Temperature

Reaction temperature had significant meaning in the diffusion process. The higher temperature increased the activity of atoms and molecules, and also the reaction rate [23]. Figure 5 summarized the effect of reaction temperature on the leaching efficiency of vanadium on 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 °C and therefore 90 °C was chosen for optimal reaction temperature in further experiments.

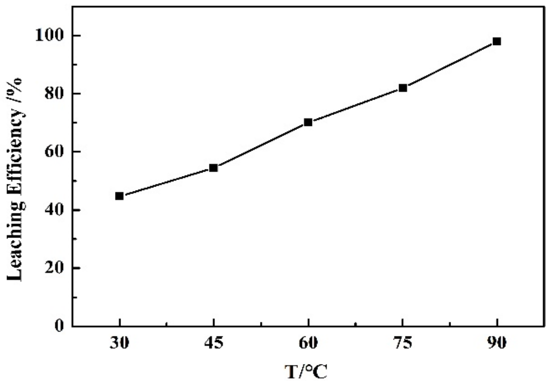

Figure 5. Effect of dosage of reaction temperature on the leaching efficiency of vanadium

3.5. Effect of Reaction Time

Figure 6 showed the leaching efficiency of vanadium as reaction time ranged 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 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.

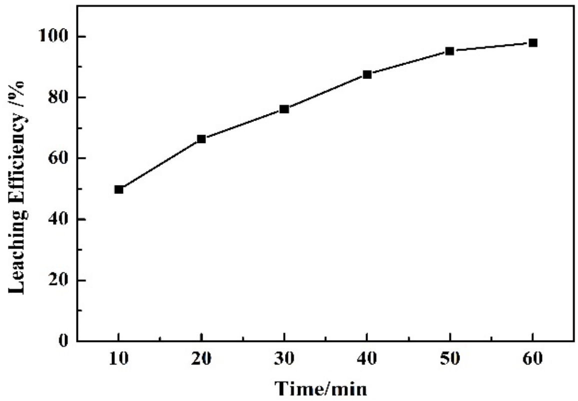

Figure 6. Effect of dosage of reaction time on the leaching efficiency of vanadium

3.6. Effect of Liquid-To-Solid Ratio

The liquid-to-solid ratio showed a significant effect on the leaching process due to the filtrate volume and purpose product concentration in the leaching process [23]. A series of experiments were conducted to investigate the effect of liquid-to-solid ratio on the leaching efficiency of vanadium. The liquid-to-solid ratio was set as 3:1, 4:1, 5:1, 6:1 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.

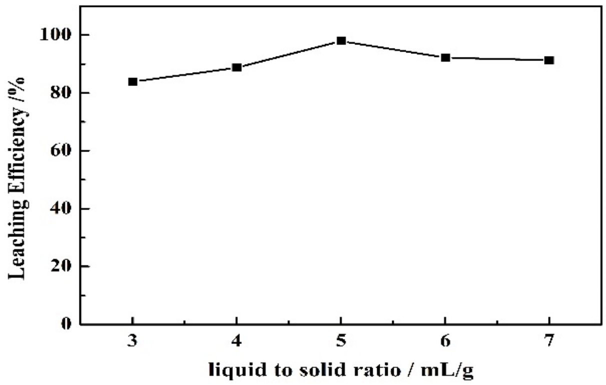

Figure 7. Effect of dosage of liquid-to-solid ratio on the leaching efficiency of vanadium

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 favoured 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 °C, 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. Low valence vanadium was 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 °C, 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.

5. Acknowledgements
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