

## Leaching of Vanadium and Chromium from Residue

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### Abstract

A residue containing 18.80 wt% Cr and 3.11 wt% V was obtained from a wastewater treatment plant. Experiments on vanadium and chromium leaching from the residue were carried out by  $H_2SO_4$ , NaOH and  $H_2O_2$ . It was found that acidic leaching had high leaching efficiency but it was hard to filtrate, while alkaline leaching offered high selectivity for vanadium. The leaching efficiency of vanadium could increase from 62.64% up to 78.69% in the concentrated NaOH solution enhanced by electric field. And also under the specified condition, the leaching efficiency of vanadium and chromium was up to 97.77% and 95.14%, respectively, during the leaching process oxidized with  $H_2O_2$  and electric field.

**Keywords:** Vanadium; Chromium; Acid leaching; Alkaline leaching

### Introduction

Vanadium and chromium are important strategic resources in the industries of iron and steel, non-ferrous metallurgy and chemicals, etc., due to its physical properties such as tensile strength, hardness and fatigue resistance [1]. In China, vanadium is recovered from vanadium-titanium magnetite ore and carbonaceous shale (stone coal) [2]. With an increasing demand in vanadium, the present primary resources seem to be insufficient for domestic need, and vanadium extraction from secondary resources is consequently necessary [3]. The focus had thus been put on fly ashes [4-6] and spent catalysts [3, 7-9]. Many hydrometallurgical processes had been proposed to recover vanadium and chromium, like salt-roasting, hypochlorite leaching, acid leaching, alkali leaching, ammonia leaching and bioleaching [3,4,10-14]. The present work was focused on the leaching process of vanadium and chromium from residue. The residue was formed in the treatment procedure for the wastewater containing  $Cr^{6+}$  and  $V^{5+}$  in some iron and steel companies. Acidic leaching, alkaline leaching, electro-oxidation leaching and alkaline oxidation-leaching were studied.

### Materials and Methods

#### Materials

The residue contained vanadium and chromium, collected from Panzhihua city, Sichuan province, China, was dried in an oven overnight, followed by dry-sieving to obtain particles particle size of < 200 mesh. XRF (X-ray fluorescence) of the residue was shown in Table 1. All the reagents including sulfuric acid, sodium hydroxide, hydrogen peroxide used for leaching and ammonium ferrous sulfate, phosphoric acid, ammonium ferrous sulfate, hexamethylenetetramine, potassium permanganate, and N-phenylanthralinic used in chemical analysis were of analytical grade. Deionized water used in the experiments was produced by water purification system (HMC-WS10).

#### Experimental methods

The dried residue was ground and sieved, and its particle size of < 200 mesh was used in this study. During the leaching process, the entire suspension was maintained at a certain temperature and stirred at an appropriate rate with a thermostatic mixing water bath pot. The leaching procedure was conducted in a stirred beaker which was placed in the water bath equipment. The leaching solution were prepared and then added into the beaker. The residue would be added into the reactor

once the expected temperature was reached. After the required contact time, the filtrate was separated from the residue by vacuum filtration. Titration with ammonium ferrous sulfate was used to determine the concentration of vanadium and chromium in the solution [15].

### Results and Discussions

#### Acidic leaching

The effect of initial sulfuric acid dosage was studied under the optimized conditions: reaction temperature of 90°C, contact time of 2 h, liquid to solid ratio of 4:1 ml.g<sup>-1</sup>. According to the result of experiments illustrated in Figure 1, both the leaching efficiency of vanadium and chromium increased with the increasing of sulfuric acid dosage and reached a maximum value of 90.32% and 99.31%, respectively. As the different occurrence between vanadium and chromium, they were competed in leaching out during the leaching process. The initial sulfuric acid dosage had different effects on the leaching efficiency of vanadium and chromium. At the low initial sulfuric acid dosage, the leaching efficiency of vanadium was only 52.66%, while chromium was 94.28%, in other words, chromium was easier to leach out than vanadium in acidic leaching. More soluble elements were leaching out in the solution during the leaching process, which made the filtrate composition complicated and also brought some trouble in separation of vanadium and chromium. In addition, the silicon in the residue had big trouble in liquid- solid separation during the filtration [13,16].

#### Alkaline leaching

As shown in Figure 2, the effect of NaOH dosage on the leaching efficiency was studied while leaching temperature, contact time, liquid

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to solid ratio was kept constant as 90 °C, 2h, 4:1 ml.g<sup>-1</sup>, respectively. As chromium was insoluble in NaOH solution, the leaching efficiency of chromium did not show in Figure 2. Taken into account the optimized vanadium leaching efficiency by H<sub>2</sub>SO<sub>4</sub>, the performance of NaOH was yet to be weakening, which yielded to a best of 62.64%. This could be partially explained by the elution of some chemicals which were responsible for the alkaline consumption such as NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, as the presence of ammonium salts was confirmed by the smell of NH<sub>3</sub> during the alkaline leaching process of the residue [17]. And other way, some vanadium oxides in low valence were insoluble in NaOH, which lead to the low leaching efficiency of vanadium.

Alkaline leaching offered selectivity for leaching vanadium, which was not evident in acid leaching. The result was consistent with the literature [18].

### Electro-oxidation-leaching

The vanadium and chromium in the residue was formed in low valent. Some oxidants and oxidative leaching technologies were applied in the leaching process. Electro-oxidation was an environmental-friendly technology, which could improve the leaching efficiency of vanadium in some ways [18-21]

The leaching efficiency of vanadium effected by current intensity was studied while leaching temperature, contact time, liquid to solid ratio, current intensity was kept constant as 90 °C, 2h, 4:1 ml.g<sup>-1</sup>, 0.6 A, respectively. As chromium was hardly leached out, the leaching efficiency of chromium did not show in the Figure 3. The results shown in Figure 3 described that the leaching efficiency of vanadium firstly increased with the increasing of the current intensity. The maximum leaching efficiency of vanadium was increased from 62.64% to 78.69% intensified by electric field. Firstly, water around the anode could make some strong oxidation activity groups through electrochemical, like .OH groups (showed in Figure 4A and 4B). The vanadium oxides in low valence, V<sup>3+</sup>, V<sup>4+</sup>, might be oxidized to vanadium in high valence, V<sup>5+</sup> (showed in Figure 4B and 4C). Vanadium oxides in high valence had high solubility in alkaline solution which made a contribution to high leaching efficiency.

Element	O	Cr	Si	Na	S	V
Content/wt.%	41.44	18.80	11.30	10.93	10.65	3.11
Element	Ca	Cl	Fe	K	Mg	P
Content/wt.%	1.94	1.06	0.37	0.17	0.13	0.04

Table 1: XRF analysis results of main composition in residue.

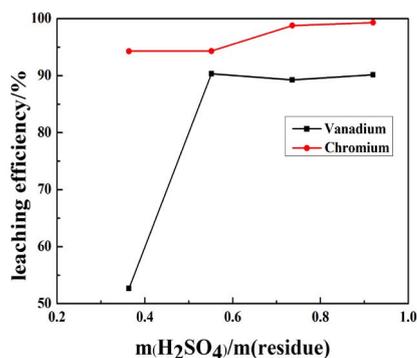


Figure 1: Effects of H<sub>2</sub>SO<sub>4</sub> dosage on the leaching efficiencies of vanadium and chromium.

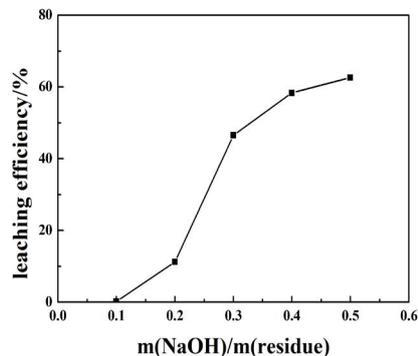


Figure 2: Effects of NaOH dosage on the leaching efficiency of vanadium.

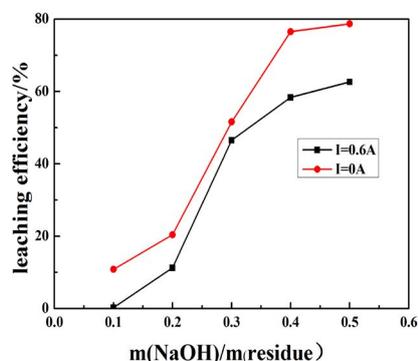


Figure 3: Effects of NaOH dosage and current intensity on the leaching efficiency of vanadium.

### Alkaline oxidation-leaching

The alkaline oxidation-leaching was carried out to remove any chromium surface layers encapsulating vanadium phases, while leaching temperature, contact time, liquid to solid ratio was kept constant as 90 °C, 2h, 4:1 ml.g<sup>-1</sup>, respectively. H<sub>2</sub>O<sub>2</sub> as an oxidant was used to oxidize vanadium and chromium in low valent. As shown in Figure 5, the leaching efficiency of vanadium and chromium increased with the addition of H<sub>2</sub>O<sub>2</sub>, but the lack of effect on vanadium dissolution indicated that there were no chromium surface layers encapsulating vanadium phases. With the addition of H<sub>2</sub>O<sub>2</sub>, the leaching efficiency of chromium had a significant increase, it was up to 95.14%, and vanadium was 97.77%.

### Residue morphology before and after leaching

XRD (X-ray diffraction) analysis of the raw residue and leaching residues were conducted to analyze the change. Figure 6 showed the XRD traces of raw residue (A), residue after acid leaching (B) and residue after alkaline oxidation-leaching (C). From Figure 7, it was clear that the characteristic peaks of the main contents phases disappeared leaving a residue composed primarily of SiO<sub>2</sub> after leaching.

The morphology of raw particles before and after leaching was examined by SEM (scanning electron microscope) shown in Figure 8. The morphology had no big differences between raw residue and residue after leaching, but the composition and color had big differences that could be seen from Figures 6 and 7. The filtrate after acid leaching was black and contained Cr<sup>3+</sup>, V<sup>3+</sup>, VO<sup>2+</sup> etc. While the filtrate after alkaline oxidation leaching was yellow and it contained CrO<sub>4</sub><sup>2-</sup>, VO<sub>3</sub><sup>-</sup>. The VO<sub>3</sub><sup>-</sup>

could be precipitated with ammonium salt like ammonium sulfate and  $\text{CrO}_4^{2-}$  was left behind in the solution.

### Conclusions

The present work was focused on the leaching process of vanadium and chromium from a residue precipitated from the waste water of a steel mill. Various methods were adopted to perform the leaching procedure. The best leaching performance was showed by the acidic leaching, in which process, the residue was leached with  $\text{H}_2\text{SO}_4$  at  $90^\circ\text{C}$  for 2 h with the liquid–solid ratio of  $4:1 \text{ ml.g}^{-1}$ . The leaching efficiency of vanadium and chromium could reach a maximum value of 90.32% and 99.31%, respectively. It was, however, not recommended as an advisable technique because of the highest consumption of acid and more soluble elements, which would need a correspondingly high investment to separate and recover the metals. The solution containing chromium could be a potential feedstock for ferrochromium production, but further separation and purification would be required before this could happen. In the alkaline leaching process, high selectivity for vanadium was observed, but the highest leaching efficiency was only 62.64%. In order to increase the dissolution of vanadium and chromium in NaOH solution, electro-oxidation technology and  $\text{H}_2\text{O}_2$  were introduced. The leaching efficiency of vanadium could increase from 62.64% up to 78.69% in the concentrated NaOH solution enhanced by electric field. The electricity could replace the consumption of chemicals and achieve energy conservation and emissions reduction. It would be promoted in the future. Under the specified conditions, the leaching efficiency of vanadium and chromium was up to 97.77% and 95.14%, respectively, during the leaching process oxidized with  $\text{H}_2\text{O}_2$ .

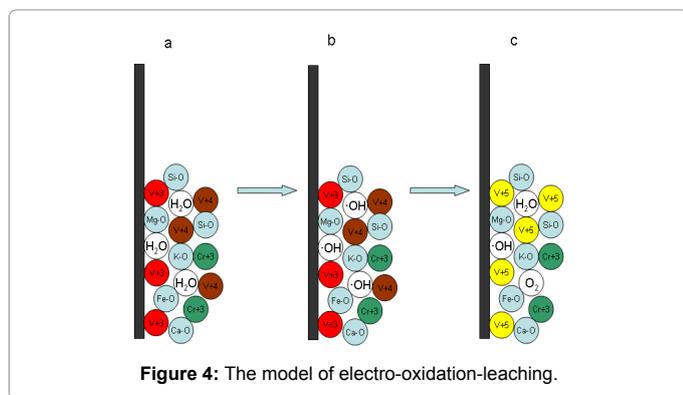


Figure 4: The model of electro-oxidation-leaching.

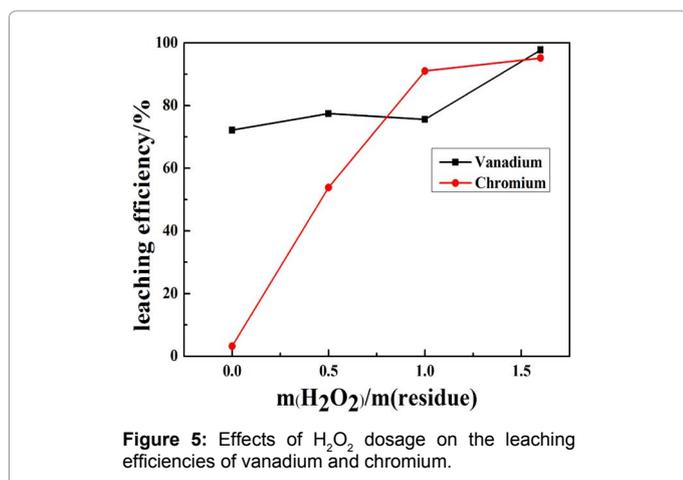


Figure 5: Effects of  $\text{H}_2\text{O}_2$  dosage on the leaching efficiencies of vanadium and chromium.

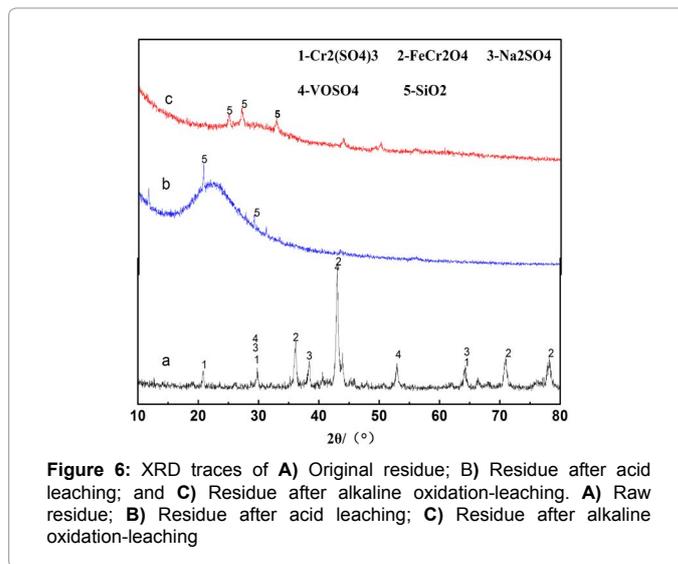


Figure 6: XRD traces of A) Original residue; B) Residue after acid leaching; and C) Residue after alkaline oxidation-leaching. A) Raw residue; B) Residue after acid leaching; C) Residue after alkaline oxidation-leaching



Figure 7: Image of A) Raw residue; B) Residue after acid leaching; C) Residue after alkaline oxidation-leaching.

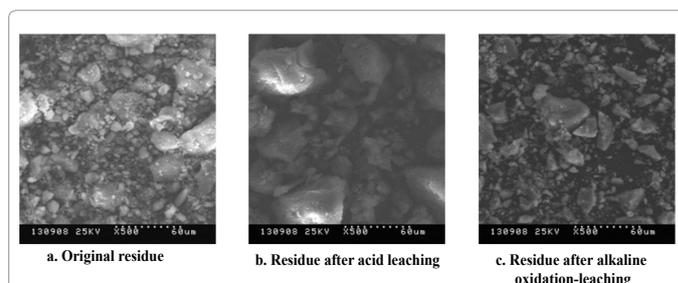


Figure 8: SEM image of A) Raw residue; B) Residue after acid leaching; C) Residue after alkaline oxidation-leaching.

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