

RECOVERY OF VANADIUM FROM A HIGH Ca/V RATIO VANADIUM SLAG USING SODIUM ROASTING AND AMMONIA LEACHING

Song Xu, Mujun Long*, Dengfu Chen, Helin Fan, Yuting Chen, Xue Sun
Laboratory of Metallurgy and Materials, College of Materials Science and Engineering,
Chongqing University, Chongqing 400044, P.R. China.
*Email: longmujun@cqu.edu.cn

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Abstract

In order to seek an effective extraction process for vanadium, the recovery of vanadium from a high Ca/V ratio vanadium slag was studied by sodium roasting and ammonia leaching. In the present paper, the oxidation and leaching process of vanadium slag was investigated by X-ray diffraction (XRD), scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS) techniques. The effects of ammonium carbonate concentration, leaching temperature and leaching time on the leaching ratio of vanadium were discussed. As indicated in the experimental result, the optimal $(\text{NH}_4)_2\text{CO}_3$ concentration was 120g/L, leaching temperature was 60°C and leaching time was 20 min. Approximately 92% of the vanadium was recovered under the optimal conditions. Furthermore, by means of X-ray diffraction analysis, the phase transformations of the vanadium slag during roasting and leaching processes were analyzed and discussed.

Introduction

Vanadium is considered as an important rare metal and has been widely used in many fields due to its physical properties such as high tensile strength, hardness, and fatigue resistance [1]. About 85% of vanadium is used in the iron and steel industry [2]. The other 15% is mainly employed in non-ferrous metal industry, chemical industry, electronic industry and so on [3, 4].

Vanadium bearing slag plays a dominant role in the sources of vanadium which accounts for 58% for the production of vanadium [5]. Currently, the most common process to extract vanadium [6,7,8] is to smelt and reduce the vanadic titano-magnetite and produce vanadium-bearing hot metal. Then, the vanadium and iron are separated into vanadium slag and semi-steel by blowing oxygen in LD converter, as shown in Figure 1. Vanadium slag can be treated by several processes such as:

1. Sodium salt roasting-water leaching[8-10],
2. Calcium salt roasting followed by acid or alkaline leaching [11],
3. Acid leaching-solvent extraction [12, 13].

Among these, sodium salt roasting-water leaching technology is the most commonly used for the extraction of vanadium from vanadium slag.

Leaching process is known as a key stage in the process of extracting vanadium from the vanadium slag. The role of leaching process is to dissolve the roasted slag and separated the leachate into solid residues and leaching solution. What's more, the aim of leaching process is to recover as much as possible the vanadates that had been generated during the roasting process.

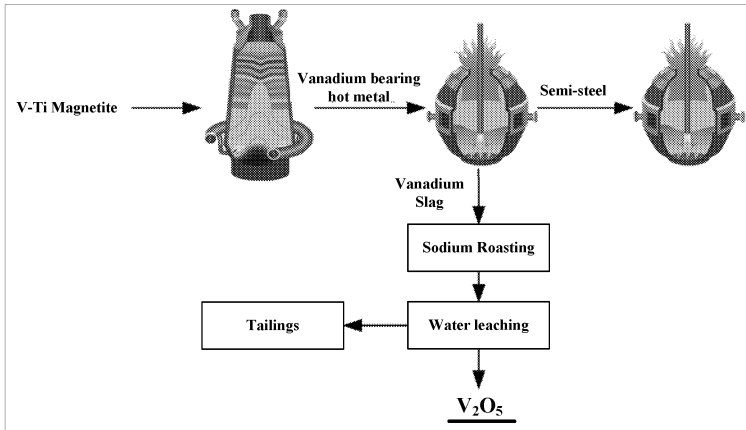


Fig 1. Schematic diagram of vanadium extraction process [8, 14]

Compared with the normal converter vanadium slag, the vanadium slag in the present work has a high Ca/V ratio. In general, high CaO content in the vanadium slag may induce water-insoluble calcium vanadates or calcium-containing vanadium bronze during roasting process [15], leading to difficulties in extraction of vanadium from the high Ca/V ratio slag. The present paper focuses on the feasibility of vanadium recovery from high Ca/V ratio vanadium slag using roasting followed by ammonia leaching (instead of conventional water leaching). Thus, it is necessary to study the ammonia leaching process and to investigate the factors influencing the vanadium extraction. The phase transformations of vanadium slag during the leaching process were also studied with XRD techniques.

Experimental

Vanadium Slag Specification

The prepared vanadium slag samples were ground and screened through 74 μ m sieve prior to leaching. The chemical composition was analyzed using X-ray fluorescence spectroscopy (XRF, model XRF1800, SHIMADZU, Japan), and the results are presented in Table I, where the vanadium oxide was analyzed as V₂O₅ for

convenience. Compared with the common converter vanadium slag [8], the vanadium slag in this work has a lower content of vanadium and a higher Ca/V ratio.

Table I. Chemical composition of vanadium slag (main fraction, %)

V ₂ O ₅	FeO	SiO ₂	MnO	TiO ₂	CaO	MgO	Cr ₂ O ₃	Al ₂ O ₃	P ₂ O ₅
13.60	36.80	18.30	8.60	8.30	4.40	3.85	4.02	1.34	0.45

The mineralogical analysis of the samples was investigated using X-ray diffraction (XRD), which was performed with a Rigaku D/MAX 2500PC using Cu K α radiation. An X-ray diffraction pattern of the vanadium slag is presented in **Figure 2**. It can be observed that the major phases in this slag were vanadium-containing spinel (Mn,Fe)(Cr,V)₂O₄, olivine phase (Fe,Mg)₂SiO₄, pyroxene phase Ca(Fe,Mg)Si₂O₆, and some iron oxide Fe₃O₄.

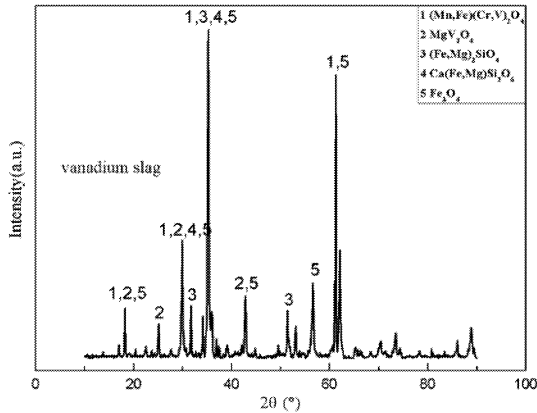


Fig 2. XRD pattern of raw vanadium slag

Sample Preparation

The sample that would be used for leaching experiments was prepared by the following sodium roasting process. The ground vanadium slag was thoroughly mixed with a prior determined mass of sodium carbonate. Then the mixture was put into an electric muffle furnace where the roasting experiments were carried out. A proportional-integral-differential (PID) controller ($\pm 5K$) was employed to control the temperature, and the furnace was kept with free access to air in order to maintain an oxidizing atmosphere during roasting process so as to obtain a maximum efficiency in the conversion of the vanadium. After a determined roasting time, the samples were taken out and cooled down to the room temperature rapidly. Then, the roasted samples were ground to the size of $-74\mu\text{m}$ and saved for further processing.

Experimental Leaching Procedure

The prepared roasted samples were leached with an ammonia carbonate leaching solution which was prepared with analytical reagent $(\text{NH}_4)_2\text{CO}_3$ and distilled water. The leaching procedure was performed in a stirred three-neck flask which was placed in a water bath. At the end of the leaching time the leachate was separated from the solid residues by means of vacuum filtration. Vanadium concentration in the leachate was analyzed by the ammonium ferrous sulfate titration, which is a standard analytical method.

Leaching ratio (η) of sodium salt roasting process was defined as Eq.(1).

$$\eta = \frac{[V_s]}{[V_t]} \quad (1)$$

where $[V_t]$ is the mass of total vanadium in the raw slag before roasting, and $[V_s]$ is the mass of vanadium in the leaching solution.

(1) Characterization of the sample

The crystalline phases of raw vanadium slag and roasted slag were characterized by powder X-ray diffraction. Scanning electron microscopy (SEM) and energy disperse X-ray spectrometry (EDS) were also used, to investigate the surface morphologies and surface compositions.

(2) Optimization of ammonia leaching parameters

The roasted slag used for the leaching experiments was prepared under optimal roasting conditions determined in a previous study [16]: addition amount of sodium carbonate of 19%, roasting temperature of 800°C, roasting time of 2 hour. Effects of $(\text{NH}_4)_2\text{CO}_3$ amount, leaching temperature and leaching time on the leaching ratio of vanadium were also investigated by single-factor experimental analysis. During the leaching process, the liquid to solid ratio was kept at a constant 8.0 ml/g. Scheme of the single-factor experiments is illustrated in Table II.

Table II. Scheme of the single-factor leaching experiments

Factors studied	$(\text{NH}_4)_2\text{CO}_3$ concentration, g/L	Leaching temperature, °C	Leaching time, min
$(\text{NH}_4)_2\text{CO}_3$ concentration	80,100,120,140,160	50	20
Leaching temperature	120	30,40,50,60,70	20
Leaching time	120	50	10,15,20,25, 30,40

(3) Phase transformation during roasting and leaching process

It is of importance to understand the leaching mechanism by investigating the phase transformations occurring during the leaching process. The phases present in the roasted slag and leaching residue under optimized conditions were studied using XRD.

Results and Discussion

Characterization of the Sample

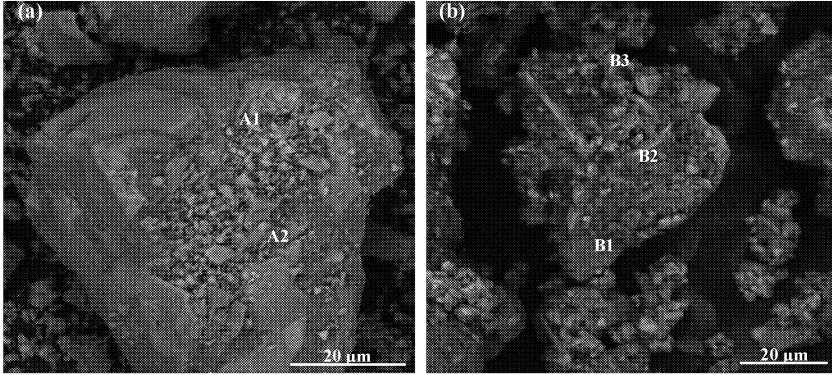


Fig 3. SEM images of slag samples: (a) raw vanadium slag, (b) roasted slag

The SEM images of slag samples are presented in Fig.3. **The EDS analyses of the areas marked in Fig. 3 are given in Table III.** As shown in Fig. 3(a), there were some smaller and brighter grains (shown in area A1) which were dispersed irregularly in the matrix phase. Based on the results of XRD and EDS analysis, these grains were the vanadium spinel (see the analysis data for area A1 in Table III). The matrix phase was olivine. It can be seen from Table III that V, Ti and Cr were mainly concentrated in the spinel grains (A1), while Al, Si and Ca existed mainly in the olivine (silicate) phase (A2). Fe and Mn existed in both phases.

As shown in Fig. 3(b), it can be seen from the SEM image of the roasted sample that some particles cohered together and presented a flower pattern. Results from EDS and XRD analysis demonstrate that the oxidized vanadium spinel had reacted with the Na_2CO_3 to produce sodium vanadates (shown in areas B1, B2 and B3, with the corresponding analyses in Table III). It was worth noting that there was a certain content of Mg and Ca in areas B1 and B3.

Figure 4 illustrates the XRD patterns of the sample before and after roasting process. Compared with the XRD pattern of raw vanadium slag (which has also been presented earlier in Fig. 2), the peaks of Fe_2O_3 , acmite ($\text{NaFeSi}_2\text{O}_6$) and sodium pyroxene ($\text{NaTiSi}_2\text{O}_6$) appeared in the XRD pattern of roasted slag, while the characteristic peaks of $(\text{Mn,Fe})(\text{Cr,V})_2\text{O}_4$ disappeared. Meanwhile, the water-soluble sodium vanadates such as NaVO_3 and NaV_3O_8 were generated owing to the oxidizing reaction between the sodium carbonate and vanadium oxide. Some minor material phases such as MgV_2O_4 and $\text{Mg}_3(\text{VO}_4)_2$ were also generated which are water-insoluble substances. As a consequence, it is worthwhile to carry out experiments to recover the vanadium from these water-insoluble compounds by the ammonia leaching process.

Table III. EDS analysis of raw vanadium slag and roasted samples (mass fraction, %)

Area	O	Na	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe
A1	26.15	-	-	-	-	-	7.31	21.79	9.06	5.74	29.95
A2	48.93	-	-	3.38	23.88	8.81	-	-	-	5.00	10.01
B1	44.47	18.84	-	-	2.75	1.59	1.90	13.59	2.85	3.21	10.79
B2	41.37	20.91	-	-	2.47	-	-	11.29	-	3.25	20.71
B3	38.19	13.37	2.69	-	8.55	7.62	2.99	9.21	-	2.25	15.13

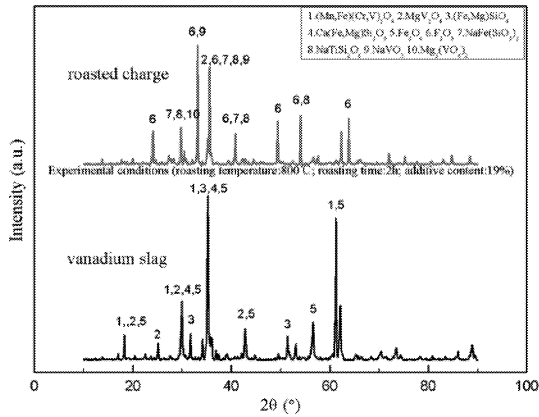


Fig 4. XRD patterns of raw vanadium slag and roasted slag

Parameters of Ammonia Leaching Process

The main aim of leaching process is to extract vanadates from the roasted charge to the greatest extent possible. Hence, in present paper, the effects of $(\text{NH}_4)_2\text{CO}_3$ concentration, leaching temperature and leaching time on the leaching ratio of vanadium were investigated by single-factor experimental analysis.

Effect of Ammonia Carbonate Concentration

Figure 5 illustrates the effect of $(\text{NH}_4)_2\text{CO}_3$ concentration on the leaching ratio of vanadium. This increased with the increment of $(\text{NH}_4)_2\text{CO}_3$ concentration at low concentrations, however it decreased slightly when the concentration of $(\text{NH}_4)_2\text{CO}_3$ exceeded 120 g/L. This phenomenon may be attributable to carbonate precipitation which occurred at high $(\text{NH}_4)_2\text{CO}_3$ concentrations, and tended to block the reaction.

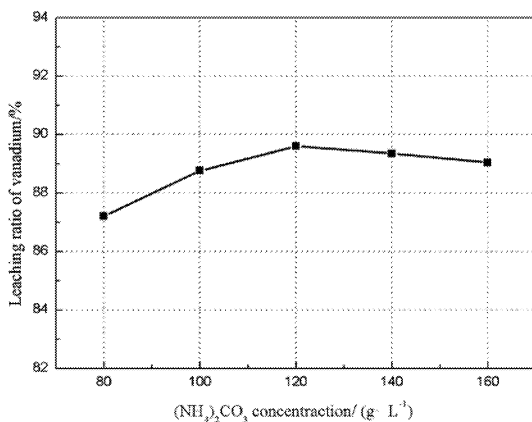


Fig 5. Effect of (NH₄)₂CO₃ concentration on the leaching ratio of vanadium
Temp 50°C, time 20 min

Effect of Leaching Temperature

The leaching ratio of vanadium versus leaching temperature is shown in Figure 6. Increasing leaching temperature played a significant role in the recovery of vanadium. However, the extraction of vanadium increased only slowly as the leaching temperature varied from 60 to 70°C. A maximum extraction of 91.2% was achieved at 70°C, yet there was only a 0.3% differential with the temperature at 60°C. Therefore, considering that higher temperature would accelerate the hydrolyzation of the (NH₄)₂CO₃ solution, 60°C was chosen as the optimum leaching temperature in present work, also saving energy.

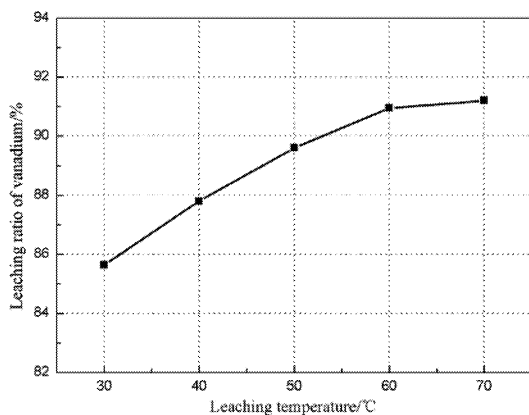


Fig 6. Effect of leaching temperature on the leaching ratio of vanadium.
Conc 120 g/L, time 20 min

Effect of Leaching Time

Figure 7 shows the profile of the leaching ratio of vanadium against the leaching time. It can be observed that the ratio gradually increased with the increasing leaching time up to 25 minutes. From 25 to 40 min there was a small decrease. The vanadates cannot be sufficiently dissolved when the leaching time was too short, nevertheless, it will be a waste of time if the leaching time was too long. Therefore the optimal leaching time was 20 min.

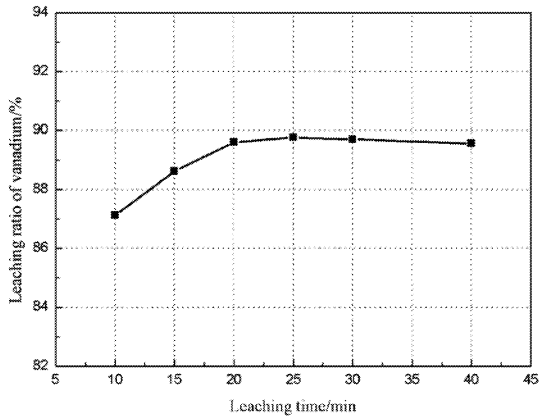


Fig 7. Effect of leaching time on the leaching ratio of vanadium
Conc 120 g/L, temp 50°C

Phases Present Before and After the Ammonia Leaching Process

Under optimized leaching conditions, the leaching residue was analyzed by means of XRD analysis. Figure 8 shows the XRD patterns of roasted slag before and after ammonia leaching process. The results indicated that the major phases of the leaching residue are basically the same as that of the roasted sample except that the sodium vanadates had dissolved away. It is worth mentioning that the minor phase manganese vanadate was not detected in the leaching residue, indicating that the water insoluble vanadates were also leached along with the water soluble sodium vanadates in the ammonia carbonate leaching solution. Therefore the ammonia leaching process is an efficient way to deal with the roasted high Ca/V ratio vanadium slag.

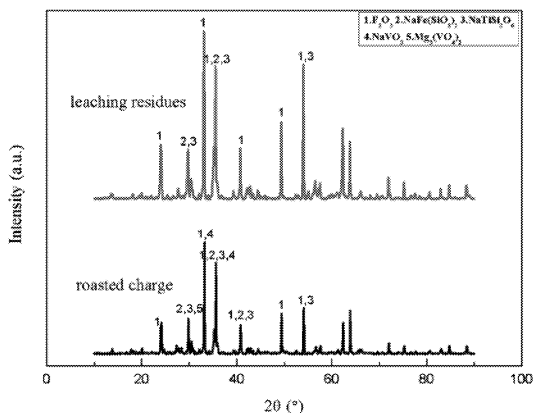


Fig 8. XRD pattern of the roasted slag and leaching residue

Summary

Experiments on extraction of vanadium from a high Ca/V ratio vanadium slag by sodium roasting and ammonia leaching process were carried out in the current study, indicating that the sodium roasting and ammonia leaching process was a practicable method to extract vanadium from a high Ca/V ratio vanadium slag. As shown in the experimental study, the optimal ammonia carbonate concentration was 120g/L, the leaching temperature was 60°C, and the leaching time was 20 min. By means of X-Ray diffraction (XRD) techniques, the phases present in vanadium slag during leaching process under the optimal leaching conditions were analyzed and discussed. Under the ammonia leaching process, most of the vanadates (>90%) were leached to the leaching solution.

Acknowledgements

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