



Review

A cleaner vanadium extraction method featuring non-salt roasting and ammonium bicarbonate leaching



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ABSTRACT

A cleaner method featuring non-salt roasting and ammonium bicarbonate leaching has been studied for the extraction of vanadium from vanadium slag. Compared to the traditional alkaline salt roasting followed by water leaching process, chromium spinel in the raw vanadium slag will not be converted to carcinogenic chromate salts and exhaust gas will not be produced in the non-salt roasting process. The soluble salt, NH_4VO_3 , can be easily crystallized directly by cooling. The wastewater from vanadate precipitation can be recycled in the leaching process. The leaching residue can be comprehensively utilized in conjunction with an iron-making process. The oxidation mechanisms of vanadium spinel were analyzed using XRD and SEM-EDS. Additionally, the effects of leaching variables, including ammonium bicarbonate concentration, roasted vanadium slag particle size, and leaching temperature, were examined. Finally, the leaching thermodynamics and leaching kinetics have been studied.

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Contents

1. Introduction	207
2. Materials and method	207
2.1. Materials	207
2.2. Procedure	208
2.2.1. Non-salt roasting	208
2.2.2. Ammonium bicarbonate leaching	208
3. Results and discussion	208
3.1. Roasting mechanisms	208
3.2. Leaching mechanisms	211
3.3. Effects of main leaching parameters	211
3.3.1. Influence of roasted vanadium slag particle size	211
3.3.2. Influence of ammonium bicarbonate solution concentration	211
3.3.3. Influence of reaction temperature	212

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3.4.	Morphology of the residues	212
3.5.	Kinetics analysis	213
3.5.1.	The first stage	213
3.5.2.	The second stage	214
3.5.3.	Activation energy	214
3.6.	XRD and microscope analysis of leached residues	215
4.	Conclusions and perspectives	216
	Acknowledgements	216
	References	216

1. Introduction

Vanadium (V) is a strategic metal and its major products include V_2O_5 , V_2O_3 , VN, ferrovanadium, and the Ti–Al–V alloy, which are widely applied in the metallurgical, material, and industrial chemical fields due to their unique physical and chemical properties (Moskalyk and Alfantazi, 2003). Usually, vanadium titanomagnetite is the main resource for vanadium recovery in the world. Vanadium slag is enriched with vanadium basically in the form of a vanadium spinel and is generated during the iron and steel-making process using vanadium titanomagnetite (Jia et al., 2014) as the raw material. In addition, vanadium titanomagnetite contains about 9–12 wt% TiO_2 and the titanium was mainly gone to blast furnace slag in the iron-making process (Chen and Chu, 2014). The blast furnace slags typically contain approximately 20–30 wt% TiO_2 and many researchers have used the titanium dioxide in the blast furnace slag to produce photocatalytic materials, glass ceramics, and silicon titanium alloys in recent years (Chen et al., 2015). However, researchers in the field of toxicology find that TiO_2 nanoparticles can cause adverse health impacts in the human body (Zhen et al., 2014).

The common way to extract vanadium from vanadium slag is by alkaline salt roasting followed by water leaching and ammonium precipitation (Wang et al., 2015). Vanadium spinel in the vanadium slag reacts with sodium salts (one or a combination of NaCl, Na_2CO_3 or Na_2SO_4) as well as oxygen during roasting process to produce sodium vanadate which can be easily dissolved by water (Li et al., 2015). However, in the alkaline-roasting process, sodium salts produce chlorine, hydrogen chloride, sulfur dioxide and sulfur trioxide, which can corrode equipment and harm the environment if not controlled (Skocaj et al., 2011). In addition, chromium spinel, which is usually intergrown with vanadium spinel, can partially be simultaneously oxidized to hexavalent chromate salts under an alkaline roasting condition. The hexavalent chromate salts can be easily leached into the leaching solution, resulting in accumulation of toxic CrO_4^{2-} in the solution and the leaching residues (Moskalyk and Alfantazi, 2003). The removal of chromate is via reduction using sulfur or sulfur dioxide followed by precipitation generating a large amount of chromium sludge. There are about 50,000 t of chromium sludge produced in China each year by the vanadium industry. Consequently, the sludge represents a severe threat to the environment (Liu et al., 2015). Further, in order to precipitate the vanadium, approximately 30–50 t of high-salinity ammonia wastewater containing Na_2SO_4 , $(NH_4)_2SO_4$ and/or NH_4Cl will be generated per t of V_2O_5 product (Deng et al., 2012). Even though evaporation could be utilized to treat the wastewater, the mixed salts obtained cannot be recycled or sold. Therefore, the salts or salt solutions can only be stored on land or deeply buried, becoming potential future environmental threats (Guo et al., 2015).

In order to solve the problems associated with the sodium salt roasting technology, lime or limestone has been utilized in the process of roasting to produce calcium vanadate, producing

$Ca(VO_3)_2$, $Ca_3(VO_4)_4$, and $Ca_2V_2O_7$ (Hao and Liu, 2009; Wu et al., 2015), followed by sulfuric acid leaching, precipitation and calcination to obtain vanadium pentoxide (Gabra and Malinsky, 1981). Compared with the sodium salt roasting technology, calcium roasting does not release harmful kiln gases. Further, high salinity, ammonia-containing wastewater will not be generated in the leaching process as well. However, this process suffers from operation difficulty, causing low vanadium recovery. In addition, during acid leaching, calcium sulfate will be generated and accumulated in the leaching residues, preventing further utilization of the residues as iron-making raw materials (Li and Xie, 2012). Because the high S residue contains a small amount of calcium chromate, which is carcinogenic, the safe and economical handling of such residue has become a great challenge for the calcium-roasting process (Yang et al., 2014).

In view of the foregoing, it is clear that the development of new approaches to extract vanadium from vanadium slag with minimum environmental impact is of great urgency. In this study, a novel method featuring non-salt roasting and ammonium leaching (NRAL) has been proposed and the new process has the following features. Firstly, as no salts are added during the roasting process, chromium spinel in the vanadium slag cannot be converted to carcinogenic chromate salts, avoiding the cost and disposal of chromium waste. Secondly, vanadium is converted to vanadate compounds through non-salt roasting, which can be directly leached out in the form of NH_4VO_3 by an ammonium bicarbonate reagent. Moreover, after cooling crystallization, NH_4VO_3 can be easily separated as a product and the solution can be recycled for further leaching operations, avoiding the discharge of process water. More importantly, the leaching residue after the vanadate extraction does not contain alkali metals, consequently, can be easily utilized as iron-making feed material.

The main focus of this research is to study the roasting mechanisms as well as the leaching kinetics by systematically examining the phase change of vanadium slag. Finally, the effect of the roasted vanadium slag particle size, ammonium bicarbonate concentration, and leaching temperature on the leaching ratio of vanadium were also studied.

2. Materials and method

2.1. Materials

The vanadium slag (which was supplied by Chengde Iron and Steel Group Co., Ltd., Hebei, China) was ground using a laboratory-type planetary ball mill (Fritsch Pulverisette 5) then dried in an oven overnight. Particles of less than 200 mesh were then collected via dry sieving for the experiments. The chemical composition of the slag was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer Optima 7,300 V), and the results are presented in Table 1. Phase compositions were determined by X-ray diffraction analysis (XRD, PANalytical

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