



Selective leaching of vanadium in calcification-roasted vanadium slag by ammonium carbonate



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ABSTRACT

Calcification roasting is a clean way to extract vanadium from the vanadium slag. But the subsequent sulfuric acid leaching brings the impurity of phosphorous into the leach liquor of vanadium and thus inhibits the precipitation of vanadates for vanadium recovery. In this paper, a novel selective leaching method using ammonium carbonate ((NH₄)₂CO₃) has been proposed for the extraction of vanadium in the calcification-roasted vanadium slag. The (NH₄)₂CO₃ leaching can dissolve calcium vanadates with high selectivity while maintaining other impurities including phosphorous in the solid residue. Ammonium vanadate can be precipitated directly by cooling down without pH adjustment or ammonium salt addition, which makes the (NH₄)₂CO₃ leaching cost-effective. The waste water after precipitation can be recycled back to the leaching circuit, showing the friendliness of (NH₄)₂CO₃ leaching method to the environment. With (NH₄)₂CO₃ leaching, 96.0% of vanadium can be dissolved while the corresponding leaching efficiency of phosphorous is 9.2% using the most suitable condition of solid/liquid ratio 1:20, particle size 45–74 μm, leaching temperature 80 °C, (NH₄)₂CO₃ concentration 600 g/L and leaching time 70 min. This work has laid the foundation for the industrial application of ammonium carbonate leaching and provided new insights into selective leaching of valuable elements in complex minerals.

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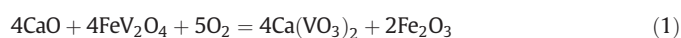
1. Introduction

Vanadium is a nonferrous metal element widely applied in metallurgical and chemical industries due to its special chemical and physical properties (Gupta and Krishnamurthy, 1992; Moskalyk and Alfantazi, 2003). China has the third largest vanadium reserves in the world while most of the vanadium exists as vanadium titano-magnetite ores in Pan-Xi and Chengde areas in China (Moskalyk and Alfantazi, 2003; Zhao et al., 2014). The vanadium titano-magnetite ores are melted in blast furnace to produce vanadium-bearing hot metal, from which vanadium is oxidized and enriched into solid that is called vanadium slag in oxygen blowing converter. The vanadium slag usually contains 5–20% (w/w) V₂O₃ in the form of FeV₂O₄ spinels and is the source for vanadium extraction.

Vanadium can be extracted from the vanadium slag by several methods. Molten NaOH roasting method has been reported to extract vanadium from the vanadium slag. It consumes large amount of energy and expensive NaOH, leading to high production cost (Chen et al., 2013). The method of sub-molten salts can decrease the cost of energy due to the lower production temperature (Liu et al., 2013; Wang et al., 2015). But the requirement of reactors with high corrosion resistance and the large consumption of alkaline limit its wide application. To date, the most cost-effective methods are the roasting – leaching methods, which are widely applied in

the vanadium production industry. The common roasting – leaching method is to roast the vanadium slag with sodium salts to transform the vanadium-bearing spinels into sodium vanadates which are then leached by water. The resultant leach liquor is purified, followed by vanadate precipitation with ammonium salts. The precipitated ammonium polyvanadate is calcined for production of vanadium oxides. Nevertheless, sodium roasting generates corrosive gases, including HCl, Cl₂ and SO₂, which corrode equipment and contaminate the environment severely. Sodium salts with low melting points melt and agglomerate during roasting, which inhibits oxidation of vanadium and thus decreases the extraction of vanadium.

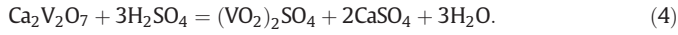
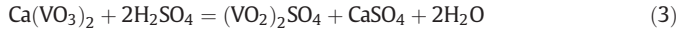
Calcification roasting is a clean alternative to sodium roasting, during which vanadium slag is roasted with lime or limestone to transform vanadium-bearing spinels into calcium vanadates. In the vanadium slag, vanadium exists as FeV₂O₄ spinels which are wrapped by the olive phase Fe₂SiO₃ (Zhang et al., 2012). After calcification roasting, the olive phase Fe₂SiO₄ is decomposed and transformed to CaSiO₃ and Fe₂O₃, and subsequently the spinel phase FeV₂O₄ is oxidized and transformed to Ca₂V₂O₇ and Ca(VO₃)₂ according to Reaction (1)–(2) (Li and Xie, 2012; Yang et al., 2014).



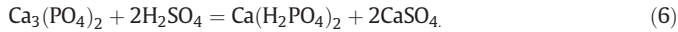
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The calcification-roasted vanadium slag is traditionally leached with sulfuric acid, during which calcium vanadates react with H_2SO_4 to produce soluble $(\text{VO}_2)_2\text{SO}_4$ according to Reactions (3)–(4) (Yang et al., 2014).



The calcification roasting is environment-friendly due to the elimination of pollutant gas and it is also cost-effective due to the inexpensiveness of lime and limestone. However, during calcification roasting, the phosphorus in vanadium slag is transformed to calcium triphosphate which can react with sulfuric acid and dissolve into the leach liquor of vanadium (Reactions (5)–(6)).



In the resultant leach liquor, the phosphate ions combine with vanadate ions to produce heteropolyacid anions, which inhibits precipitation of ammonium vanadates and thus decreases the recovery of vanadium. Especially when utilizing the product line coupling the removal of phosphorus and the production of vanadium slag, the resulted vanadium slag contains high content of calcium phosphates (Fang et al., 2015). If it was pretreated with calcification roasting followed by acid leaching, the recovery rate of vanadium and the purity of vanadium products would be extremely low. In addition, during sulfuric acid leaching, CaSiO_3 react with H_2SO_4 to produce H_2SiO_3 colloid which inhibits leaching of vanadates. Meanwhile, Fe_2O_3 and manganese-bearing phases are easily leached by the acid, resulting in the impurities of iron and manganese elements in vanadium products. It can be concluded that the calcification roasting is an environment-friendly roasting but the subsequent acid leaching brings problems of low recovery rate and low purity of vanadium products due to interference of phosphorus. Therefore, it is a pressing need to leach vanadium selectively from the calcification-roasted vanadium slag, which still remains a challenge in industrial operations.

In this work, the novel method of ammonium carbonate leaching is proposed to selectively leach vanadium into the liquor from calcification-roasted vanadium slag but maintain phosphorus in the solid phase, according to the difference in reactivity of calcium vanadates and calcium phosphate with ammonium carbonate. The vanadium extraction can be as high as 96.0% while the phosphorus extraction is as low as 9.2%. This work has laid the foundation for the industrial application of ammonium carbonate leaching and provided new insights into selective leaching of valuable elements in complex minerals.

2. Materials and methods

2.1. Materials and apparatus

The original vanadium slag was provided by Pan Steel, China. The chemical compositions of the original vanadium slag and the calcification-roasted vanadium slag are shown in Table 1. All chemical reagents used are of analytical grade. Deionized water was produced by Millipore Aquelex 5.

Table 1
Chemical composition of slags.

Oxide composition (% w/w)	FeO	SiO ₂	TiO ₂	V ₂ O ₅	MnO	CaO	MgO	P ₂ O ₅
Original slag	36.09	18.86	11.45	15.44	6.67	2.87	3.53	0.55
Roasted slag	33.43	16.26	9.89	14.43	5.59	9.01	3.12	0.48

Note: The compositions are obtained by the X-ray fluorescence spectrometry.

Chemical composition of slags were determined by X-ray Fluorescence spectrometry (XRF, Shimadzu XRF-1800). Concentrations of vanadium and phosphorous elements in the leach liquor were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Thermo Scientific iCAP 6300 Duo). Phase compositions of solid samples were identified by X-ray diffraction analysis (XRD, Rigaku D/MAX 2500PC) using $\text{Cu K}\alpha$ radiation. Microscopic observation and elemental analysis were conducted by scanning electron microscopy (SEM, TESCAN VEGA III) equipped with energy disperse X-ray spectrometry (EDS or EDX, INCA Energy 350).

2.2. Experimental procedure

2.2.1. Calcification roasting

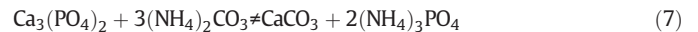
The vanadium slag was milled and the portion in particle size $<74 \mu\text{m}$ was collected. The collected portion of vanadium slag was mixed with calcium oxide (CaO) in mass ratio of 100:7.2 (V/Ca molar ratio 1:1.1) in a ceramic evaporation dish. The mixture was heated in a muffle furnace at 900°C for 2 h and stirred occasionally to inhibit agglomeration. The calcification-roasted vanadium slag was cooled down to room temperature by air.

2.2.2. Ammonium carbonate leaching

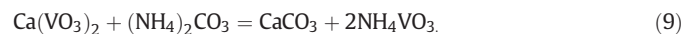
The calcification-roasted vanadium slag was milled and screened to different size portions ($<45 \mu\text{m}$, $45\text{--}74 \mu\text{m}$, $74\text{--}95 \mu\text{m}$, $95\text{--}180 \mu\text{m}$ and $>180 \mu\text{m}$). The roasted slag was then leached by 50–600 g/L ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) at solid/liquid ratio of 1:2–25 (60–300 mL $(\text{NH}_4)_2\text{CO}_3$ and 10–30 g roasted slag). The pH of $(\text{NH}_4)_2\text{CO}_3$ solution varied from 9.1 to 9.4 with concentration increasing from 50 g/L to 600 g/L. The leaching experiments were performed at atmospheric pressure in three-neck flask with plug to maintain concentrations of reactants and products. The reaction mixture was stirred with magnetic stirrer at 100 rpm and heated in water bath at $30\text{--}90^\circ\text{C}$ in commercial magnetic stirring water bath pot (Type DF-101, Gongyi Electric Equipment Corp., China).

3. Chemical principles

Ammonium carbonate can leach vanadium selectively from the calcification-roasted vanadium slag and eliminate phosphate dissolution. During leaching with $(\text{NH}_4)_2\text{CO}_3$ aqueous solution, insoluble $\text{Ca}_3(\text{PO}_4)_2$ cannot react with $(\text{NH}_4)_2\text{CO}_3$ to produce soluble ammonium phosphate. This is due to the fact that the solubility product constant (K_{sp}) of $\text{Ca}_3(\text{PO}_4)_2$ (2.07×10^{-29} at 25°C) is much smaller than K_{sp} of CaCO_3 (2.8×10^{-9} at 25°C) and thus Eq. (7) cannot take place (Speight, 2005).



However, the K_{sp} of $\text{Ca}_2\text{V}_2\text{O}_7$ (1.1×10^{-7}) and $\text{Ca}(\text{VO}_3)_2$ (3.70×10^{-5}) at 25°C is remarkably larger than the K_{sp} of CaCO_3 (2.8×10^{-9}), which leads to the transformation of $\text{Ca}_2\text{V}_2\text{O}_7$ and $\text{Ca}(\text{VO}_3)_2$ into more insoluble CaCO_3 and soluble NH_4VO_3 according to Reactions (8)–(9):



In this way, vanadium is leached from the roasted slag into the leach liquor in the form of NH_4VO_3 which has high solubility in aqueous solution at high temperature. After leaching, NH_4VO_3 precipitation can be easily obtained by cooling the leach liquor without pH adjustment or ammonium salt addition. In addition, the waste water after NH_4VO_3 precipitation can be recycled into the procedure of ammonium leaching, which saves the production cost and eliminates the discharge of waste water (Fig. 1). Furthermore, the production of colloidal H_2SiO_3 is inhibited

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