Cleaner and effective process for extracting vanadium from vanadium slag by using an innovative three-phase roasting reaction

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Yilong Ji [a,b], Shaobo Shen [a,*], Jianhua Liu [b], Yuan Xue [a]

[a] *State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083, China*
[b] *Engineering Research Institute, University of Science and Technology Beijing, Beijing, 100083, China*

A B S T R A C T

The traditional industrial practice for extracting vanadium from vanadium slag involves a Na_2CO_3-Na_2SO_4-NaCl-added pellet roasting at 800 °C followed by a water leaching. Some chlorine and hydrogen chloride are emitted by this process. About 80% of vanadium and 5% of chromium can be extracted in this case. The disposal of this leaching residue containing high contents of chromium and vanadium is still an unsolved environmental problem so far. A complete extraction of vanadium and chromium from vanadium slag might be an ultimate solution. In order to efficiently extract vanadium from vanadium slag, an innovative NaOH-added pellet was applied in this work to replace traditional Na_2CO_3-Na_2SO_4-NaCl-added pellet. It was found that the volume of NaOH-added pellet increased by 144% and many cavities were formed spontaneously throughout the pellet during the roasting at 700 °C. A solid phase (dry slag minerals), a liquid phase (molten liquid drops of NaOH with low viscosity) and a gas phase (O_2) were involved in a three-phase reaction occurred inside the pellet. The spontaneously formed cavities created good kinetic conditions for the three-phase reaction. The V extraction was thus increased from traditional 80% at 800 °C to current 99% at 700 °C. The V extraction was increased by 39% when a NaOH-added pellet sample was used instead of a NaOH-added powder sample. The roles of porous pellet and liquid NaOH drops were explored. The V extraction dramatically increased with increasing temperature in the temperature range of 400 °C to 600 °C and reached a maximum at 700 °C. The V extraction dramatically increased with time within the first 15 min at 700 °C. The optimal roasting temperature, time and R(Na/Cr) value for the V extraction were 700 °C, 15 min and 7.67, respectively. The V extraction was 99.2% under the optimal conditions. The cooling rate of the roasted pellet had no significant effect on V extraction. The vanadium from the vanadium slag was mainly contained in a vanadium-containing spinel phase $(Mn, Fe)(V, Cr, Ti)_2O_4$. The oxidation of V^{3+} probably went through the following process: $(Mn, Fe)(V, Cr, Ti)_2O_4 \rightarrow (Cr_{0.15}V_{0.85})_2O_3 \rightarrow NaVO_2 \rightarrow Na_3VO_4$. This process avoided the emission of toxic gas.

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1. Introduction

About 88% of vanadium worldwide is extracted from vanadium-containing titaniferous magnetites while the rest is extracted from other minerals such as stone coal or secondary resources such as spent catalyst (Moskalyk and Alfantazi, 2003; Li et al., 2013). Most of vanadium in titaniferous magnetites is first reduced into hot metal by coke in blast furnace and then oxidized in converter and enriched into steel slag, which is usually called as vanadium slag (Gustafsson and Wang, 1985; Kim et al., 2016; Liu et al., 2013;

Lundkvist et al., 2013; Song et al., 2014; Vanvuuren and Stander, 2001; Zhao et al., 2014; Zheng et al., 2012). About 5–8 wt % of vanadium and 2–5 wt % of chromium are contained in the vanadium slags (Chen et al., 2015; Jia et al., 2014; Kim et al., 2016; Li et al., 2016; Lundkvist et al., 2013; Song et al., 2014; Yang et al., 2014; Zhang et al., 2016a,b). Cr^{6+} is a well-known carcinogenic substance (Ananpattarachai and Kajitvichyanukul, 2016). The significant health problems thought to be associated with atmospheric exposure of volatile vanadium-containing substances have been reported (Olopade and Connor, 2011). The carcinogenic, immunotoxic and neurotoxic effects of volatile and soluble vanadium (V^{4+} and V^{5+}) have been documented (Olopade and Connor, 2011; Zwolak, 2014). Thus both soluble vanadium (V^{4+} and V^{5+}) substances and chromium (Cr^{6+}) substances are toxic heavy-metal

substances and vanadium slag is a potential toxic solid. The current traditional industrial practice for extracting vanadium from vanadium slag involves a Na_2CO_3-Na_2SO_4-NaCl-added oxidation roasting in air at about 800 °C followed by water leaching (Sadykhov, 2008; Li et al., 2011; Vanvuuren and Stander, 2001; Yang et al., 2014; Song et al., 2014). The melting points of Na_2CO_3, Na_2SO_4 and NaCl are 851 °C, 884 °C and 801 °C, respectively. For the pellet composed of vanadium slag and the mixture of Na_2CO_3, Na_2SO_4 and NaCl, basically there is no cavity formed throughout the pellet. Therefore, the traditional process is basically regarded as a two-phase reaction between a solid pellet (V slag solid plus sticky liquid mixture of Na_2CO_3-Na_2SO_4-NaCl with high viscosity) and a gas (O_2). It is usually thought that insoluble V^{3+} from V slag was converted to soluble V^{5+} or V^{4+} during the oxidation roasting and the exacted vanadium exists in the leaching solution (Yang et al., 2014; Zheng et al., 2012). The vanadium extraction for above traditional process is about 80% and less than of 5% of chromium is also extracted simultaneously (Liu et al., 2013; Zheng et al., 2012). The high chromium content in the leaching residue posed a big environmental problem unsolved so far in China. In addition, the vanadium extraction is far from satisfied. Moreover, some toxic gases such as chlorine and hydrogen chloride are also produced during the roasting (Jia et al., 2014; Song et al., 2014; Yang et al., 2014; Zheng et al., 2012). Thus, a novel method is required to solve these three problems.

Liu et al. extracted vanadium and chromium from vanadium slag by submerging vanadium slag in a liquid molten salt composed of NaOH, $NaNO_3$ and dissolved O_2 at about 400 °C (Liu et al., 2013). Because the solubility of O_2 in the molten salt was very low at 400 °C, $NaNO_3$ was thus added to act as an alternative oxidant in this process (Liu et al., 2013). The optimal conditions are as follows. The weight ratio of liquid molten salt to slag was 4 to 1. The weight ratio of NaOH to $NaNO_3$ was 1 to 1. The reaction temperature was 400 °C. The flowrate of O_2 was 0.5 L/min. The reaction time was 6 h. The extractions of vanadium and chromium were 93.7% and 88.2%, respectively, under the optimal conditions. This process is basically regarded as a two-phase reaction between liquid solution (molten salts and the submerged vanadium slag powder) and gas (O_2), because the solubility of O_2 in the liquid solution is very low.

NaOH was used in this work to replace the salts of Na_2CO_3, Na_2SO_4 and NaCl, which is used in the traditional process. To the best of our knowledge, this is a novel process for extracting V from vanadium slag. The optimal conditions for extracting V from the vanadium slag by this process were studied. The mechanisms involved in this reaction process were also investigated.

2. Experimental

2.1. Materials

About 30 kg of vanadium slag from one steel-making plant of China was used in this work. The slag was crushed, dried and sieved. The dried slag samples were kept in a desiccator before use. Unless otherwise specified, the slag sample with a particle size of 49–74 μm was used in the experiments. The chemical analysis of the vanadium slag was shown in Table 1. The contents of V_2O_3 and SiO_2 from the slag were 12.2 wt% and 19.54 wt%, respectively.

Table 1
Main chemical composition of the original vanadium slag.[a]

Elements	V_2O_3	Cr_2O_3	FeO	SiO_2	TiO_2	MnO	Al_2O_3	MgO	CaO
wt.%	12.22	5.14	38.48	19.54	10.82	5.72	2.22	2.95	2.23

[a] Particle size of the original vanadium slag ranged from 49 to 74 μm.

2.2. Experimental procedure

In order to make the pellets used in this work, about 0.20 g of deionized water was added into a powder mixture composed of about 2.20 g of the vanadium slag (49–74 μm) and 1.10 g of solid NaOH in most of cases unless otherwise specified. The molar ratio of NaOH to V was 7.67 in this case. The mixture thus obtained was pressed into a cylinder pellet with a diameter of 15 mm and a height of 8 mm under a pressure of 0.5 MPa. This pellet was placed in a corundum boat of 30 mL. The boat was then put in a Muffle furnace already set at a temperature of 400–850 °C. The interior room of the Muffle furnace was connected to outside air in many places such as the jack of the thermocouple. In addition, the door of the Muffle furnace was slightly opened during the roasting process. Thus the pellet sample was basically exposed to the atmosphere with a partial pressure of oxygen of 0.21 atm. The Muffle furnace was kept at the set temperature for a period of time. After that, the boat was taken out from the Muffle furnace and then cooled to the room temperature. The boat with the content was placed in a glass beaker of 500 mL. About 250 mL of deionized water was added to the beaker to immerse the boat. The water in the beaker was raised to 90 °C for 5 min by a heating plate. The mixture was occasionally stirred using a glass stick during the water leaching. In this way, the content of the boat could be completely taken out and transferred into the water in the beaker. After the solution was cooled to room temperature, it was filtered through a Whatman GF-A membrane with a pore diameter of 0.4 μm. The filtrate was analyzed with ICP-AES (SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH) to measure the concentration of chromium. The solid residue and the membrane were dried at 105 °C for 4 h. Then the solid leaching residue was removed from the membrane and weighed.

The percentage of extracted vanadium was calculated on the basis of the following:

$$V\text{extraction}(\%) = \frac{[V]V}{W_V} \times 100 \tag{1}$$

where W_V is the weight of vanadium in milligrams from the sample, $[V]$ the concentration of vanadium from the filtrate in milligrams per liter, and V the volume of the filtrate in liters.

2.3. Chemical analysis and characterization

About 0.3000 g of weighed dried slag sample or leaching residue sample was put in a platinum crucible and mixed with alkaline lithium metaborate ($LiBO_2$), lithium fluoride (LiF) and lithium bromide (LiBr) solution. Then the crucible was put in a Muffle oven already set at 1200 °C for about 25 min. After that, the hot content of the crucible was transferred to a glass beaker containing a solution of HNO_3 and HCl. Finally a clear digestion solution was obtained and the metal concentrations in the solution were analyzed by ICP-AES (SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH). Apart from vanadium and chromium, the contents of the other elements from the vanadium slags were determined by X-ray florescence Spectrometer (XRF-1800, Shimadzu).

The X-ray diffraction (XRD) patterns of the fine sample powders with particle size between 58 μm and 74 μm were recorded with a Rigaku TTRIII X-ray diffractometer equipped with a Cu Kα radiation source (λ = 0.15405 nm). The diffraction patterns of XRD were analyzed using the softwares of both Crystallographica Search-Match and X'pert HighScore plus. A compound was assigned until its three strongest peaks were found. The SEM sample was normally prepared by pouring a liquid composed of epoxy, thylenediamine and dibutyl phthalate on the sample powder placed at the bottom of a plastic mold. After standing for 12 h, a solidified sample