Mechanism of vanadium slag roasting with calcium oxide

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ABSTRACT

Thermodynamic analyses, XRD characterization and non-isothermal oxidation kinetic analyses were conducted to find the mechanism of vanadate formation when vanadium slag was roasted with calcium oxide. The effects of heating rate, added amount of CaO, holding temperature and holding time on oxidation efficiency were investigated. Thermodynamic calculations show that the fayalite is more likely to be oxidized than vanadium spinel, formation of calcium vanadates is easier than that of $Mn(VO_3)_2$ and $Mg(VO_3)_2$ and the oxidation of Fe^{2+} in augite is hindered by the presence of diopside. TGA results show that lowering the heating rate can improve the oxidation efficiency of vanadium. The maximum vanadium recovery of 93.3% was achieved when the vanadium slag with a ratio of $m(CaO)/m(V_2O_5)$ of 0.42 was roasted at 850 °C for 2.5 h. Dynamic heating experiments indicate that oxidations of vanadium spinel and augite overlap within 608–959 °C with a heating rate of 3 °C·min^{-1}, while only oxidation of spinel occurs within 657–914 °C at 5 °C min^{-1}. The oxidation was controlled by a 3/2 reaction and a third order reaction, with corresponding overall apparent activation energy values of 140.3 and 247.8 kJ·mol^{-1} for the heating rates of 3 °C·min^{-1} and 5 °C·min^{-1}, respectively.

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1. Introduction

Vanadium, as a very important transition metal, is widely used in various fields (Liao and Bo, 1985; Moskalyk and Alfantazi, 2003). At present, the primary vanadium resources are vanadium slag, stone coal, steel slag and spent catalyst. Vanadium slag which is a by-product of vanadium titanomagnetite accounted for more than 38% of the world's overall vanadium production in 2009 (Polyak, 2011). Processes comprising roasting, leaching, purification of aqueous solution, and precipitation steps are commonly employed in vanadium extraction from vanadium slag to produce vanadium pentoxide, of which, roasting plays a more important role in the whole process chain of vanadium.

Since problems like difficulties in sodium salt recovery, utilization of tailings, and environmental pollution, exist in the conventional roasting process with sodium salts (*i.e.* Na_2CO_3, NaCl and Na_2SO_4), this process is not favored; hence, it is essential to develop some new processes for the clean production of vanadium oxide. Sub-molten salt (Liu et al., 2013), carbonate salt (Li et al., 2011) and compound salt roasting for vanadium extraction can decrease the amount of poisonous gas discharge; however, they cannot eliminate the hazard of sodium or potassium in the tailings and waste water. Calcium salt roasting was firstly proposed by the

Russia Tula factory in 1970s and it was not applied commercially due to lower recovery of vanadium compared with sodium salt roasting (Liao and Bo, 1985). However, it does have benefits of lower cost of additive, no emission of pollutional gas, and no sodium or potassium contained in tailings and waste water, so this process is of increasing interest.

Vanadium slag roasting with calcium oxide is an oxidation process. Vanadium embedded in the slag presents as V^{3+}, and with roasting, V^{3+} is oxidized to V^{4+} and V^{5+} and converted to vanadate which can be dissolved in a subsequent leaching step. Many investigations (Cao, 2012; Li et al., 2012; Li, 2011) have focused on the effects of roasting parameters, including the ratio of $m(V_2O_5)/m(CaO)$, roasting temperature and roasting time, on the vanadium recovery. Van Vuuren and Stander (1995) studied the oxidation kinetics of synthetic FeV_2O_4 over the temperature range of 200–580 °C and the oxidation of synthetic FeV_2O_4 in a sodium carbonate mixture (Van Vuuren and Stander, 2001). Voglauer et al. (2004) investigated the reaction kinetics of vanadium roasting process in steel slag. In this paper, the thermodynamics of a converter vanadium slag roasting process with calcium oxide was analyzed. Effects of heating rate, added amount of CaO, holding temperature and holding time on oxidation and recovery of vanadium, and experimentally the relationships between the heating rate and the optimum holding temperature were studied. The roasted samples prepared under different roasting conditions were characterized by X-ray diffraction (XRD). The oxidation kinetic equations and apparent activation energy values for a vanadium slag roasting process in the presence of calcium

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oxide were obtained using differential scanning calorimetry and thermal gravimetric (DSC–TG) methods.

2. Experimental

2.1. Materials

The chemicals used in this study (CaO, H_2SO_4, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, $C_{13}H_{11}NO_2$, H_2NCONH_2, $NaNO_2$ and $KMnO_4$) were all of analytical grade (Sinopharm Chemical Reagent Co., Ltd, purity >98%). CaO was used as the additive for vanadium slag roasting and was dried in an oven at 120 °C for 24 h before use. The other chemicals were used to determine vanadium content in the slag with ammonium ferrous sulfate titration method. Water used in experiments was deionized one time. Vanadium slag was supplied by Sichuan Weiyuan Iron & Steel Co., Ltd. China (after magnetic separation). The mass fraction of the raw slag with particle size larger than 250 μm was 16.3%, and after screening, the slag with particle size within 48–75 μm was chosen for roasting experiments in this study. The mineralogical and chemical analyses of this slag were conducted using X-ray diffraction (XRD, X'Pert Pro MPD, PAnalytical B.V. of Netherlands), SEM-EDS (SSX-550, Shimadzu Corporation), X-ray fluorescence spectroscopy (S-MAX, Rigaku) and ICP-OES (Optima 4300DV, American PerkinElmer Company). Chemical compositions of the slag were listed in Table 1 and the X-ray diffraction pattern was shown in Fig. 1. The backscatter image and EDS analysis results of the slag were given in Fig. 2 and Table 2, respectively.

Table 1 shows that Fe is the richest element in the slag and then decreasing in concentration are V, Si, Ca, Mn, and Ti successively. The main mineral phases in the converter slag are vanadium spinel, fayalite and augite as shown in Fig. 1. According to the EDS analysis results (Table 2) it is known that the white area in Fig. 2 is the vanadium bearing phase-vanadium spinel [(Mn, Fe) (V, Cr)$_2$O$_4$]; the gray area and the black area are the matrix phases–fayalite (Fe$_2$SiO$_4$) and augite [Ca (Fe, Mg)Si$_2$O$_6$], respectively–dispersed around the spinel phase. The silicon content in augite is higher than in fayalite; the dark gray areas (D and E) are Ca$_3$P$_2$O$_8$ and Ca$_2$P$_2$O$_7$. Since the content of P in slag is only 0.22%, calcium phosphate phases occupy a small fraction of the sample surface area. The volume fractions of vanadium spinel, fayalite and augite are 32.74%, 49.52% and 17.74% respectively.

2.2. Experimental apparatus

Roasting tests were carried out in a vertical tube furnace controlled by a Shinaden SR-53 temperature programmed instrument with molybdenum disilicide heating elements as shown in Fig. 3. The isothermal section was about 90 mm long and the temperature variation was within ±1 °C. Leaching experiments were conducted in glass vessels centered in a thermostatic water bath (HH-4, China Changzhou Sino Instrument Co., LTD) and the pH values were measured by a pH-meter (OHAUS Starter 3C). The dynamic oxidation experiments were carried by TG–DSC (STA409CD, NETZSCH German).

2.3. Experimental procedure

The vanadium slag (48–75 μm) was mixed with additive of CaO and prepared into Φ 8–10 mm pellets. In the roasting experiments, only a few pellets were put in the corundum crucible and the two ends of
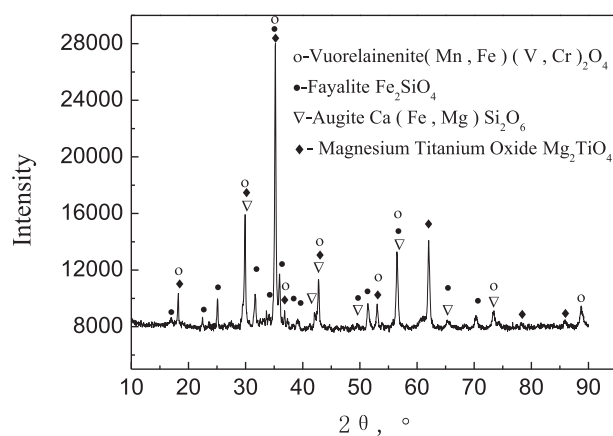

Fig. 1. X-ray diffraction pattern for vanadium slag.

the corundum work tube were directly open to atmosphere to ensure that the pellets were thoroughly exposed to air. The pellets were heated according to a preset heating system. When the holding time was completed, the roasted pellets were quenched to room temperature. The roasted pellets were ground to fine powder and characterized by XRD. Roasting efficiency was expressed by vanadium recovery upon leaching, and the leaching conditions were liquid to solid ratio of 4:1, temperature of 65 °C, time of 1 h, pH of 2.5, and stirring speed of 500 rpm. The vanadium recovery was calculated by the following equation:

$$\eta, \% = \frac{m_0 w_0 - m_1 w_1}{m_0 w_0} \times 100\%$$

where η represents the vanadium recovery, m_0 is the mass of roasted slag, w_0 is the mass fraction of vanadium in the roasted slag, m_1 is the mass of the tailing after leaching and w_1 is the mass fraction of vanadium in the tailing.

The mass fraction of vanadium in the roasted slag and in the tailing was determined by ammonium ferrous sulfate titration.

3. Thermodynamic analysis for roasting process

Vanadium spinel surrounded by matrix phases—fayalite and augite, is the main vanadium-bearing phase in converter vanadium slag. In order to obtain a high oxidation efficiency of vanadium, the structure of the binding phases should be destroyed firstly to liberate the vanadium spinel and then it is easier for oxygen to contact with vanadium spinel directly. The trivalent vanadium is oxidized into pentavalent vanadium and then converted to dilute acid soluble vanadate.
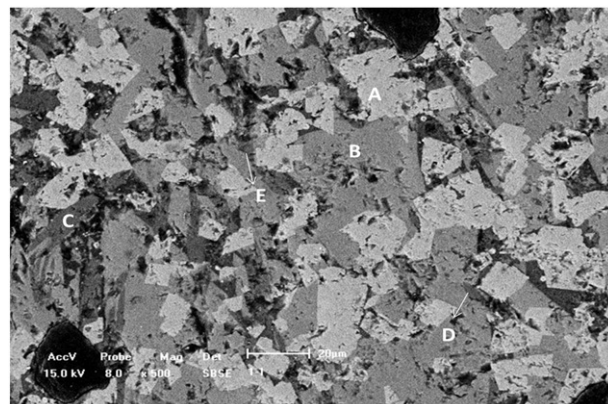
Table 1
Chemical composition of vanadium slag (mass fraction, %).

V$_2$O$_5$	FeO	MFe	SiO$_2$	CaO	MnO	TiO$_2$	Cr$_2$O$_3$	MgO
14.3	24.84	2.29	14.3	9.9	8.5	7.4	4.4	3.7
Al$_2$O$_3$	P$_2$O$_5$	SO$_3$	Na$_2$O	K$_2$O				
2.1	6.4 × 10^{-1}	1.9 × 10^{-1}	1.0 × 10^{-1}	3.9 × 10^{-2}				

Fig. 2. Backscattered micrograph of the vanadium slag.