

Behaviors of impurity elements Ca and Fe in vanadium-bearing stone coal during roasting and its control measure



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ARTICLE INFO

Article history:

Received 10 August 2014

Received in revised form 16 November 2015

Accepted 22 January 2016

Available online 30 January 2016

Keywords:

Roasting

Calcium

Iron

Stone coal

Reducing impurities

ABSTRACT

The behaviors of impurity elements Ca and Fe in vanadium-bearing stone coal during roasting were investigated in two aspects: combining with vanadium and reacting with other phases. As compared to Na, Ca was more easily combined with vanadium generating water-insoluble calcium-bearing vanadate during roasting. The phase distribution calculated by FactSage showed that Ca reacted with quartz and albite to form amorphous phases, resulting in the entrapment of vanadium, thereby decreasing vanadium recovery markedly. In contrast, Fe in stone coal did not affect vanadium recovery as it did not combine with vanadium and not react with other phases during roasting. In order to decrease the negative effects derived from the impurity elements such as Ca, a control measure of concentrating vanadium and reducing impurities treatment was carried out to decrease the dosage of Na₂SO₄ and improve vanadium recovery.

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1. Introduction

The gross reserve of vanadium in stone coal which is a unique vanadium-bearing resource in China (Li et al., 2010) accounts for more than 87% of the domestic reserve of vanadium (Bin, 2006). Most vanadium in stone coal is V³⁺ substituting for Al³⁺ in the dioctahedral structure of mica group minerals (Zhang et al., 2011; Zhao et al., 2013a), which is necessary to be extracted by roasting with sodium additive at high temperature (He et al., 2007; Wang et al., 2008; Zhang et al., 2012). Through roasting, the vanadium is liberated from the crystal structure of mica and converted to water-soluble sodium vanadate (Chen et al., 2010; Hu et al., 2012) which is subsequently recovered by leaching, ion purification, precipitation and calcination (El-Nadi et al., 2009; Li et al., 2013; Moskalyk and Alfantazi, 2003; Zeng et al., 2009).

Two mica-type stone coals collected from the same place were ever investigated by Hu et al. (2009) and Han et al. (2012) respectively, showing differing vanadium recoveries (70% vs. 50%) in the process of water leaching under the same roasting condition. Based on the comparison of the chemical composition of the two stone coals, it is found that the only difference is the CaO and Fe₂O₃ contents, which seems to be the reason for the different vanadium recoveries of water leaching (VRWLs). In addition, Chen et al. (2008) conjectured that during roasting Ca and Fe may react with vanadium to generate water-insoluble calcium vanadate and ferric vanadate, respectively, resulting in a decrease in the VRWL. In order to reduce the detrimental effect of

Ca in stone coal on VRWL, Na₂SO₄ is always used as the roasting additive to inhibit the formation of water-insoluble calcium vanadate through depleting calcite in stone coal by forming gypsum (Han et al., 2012), i.e. Eqs. (1) and (2).



In fact, the root cause of the impurity elements decreasing the VRWL is that they are capable of combining with vanadium over the sodium in the competition. However, the proposed mechanisms of the impurity elements affecting VRWL just remain at the speculative stage at present, and the investigation of the competition between impurity elements and sodium in combination with vanadium is not involved. In addition, although the addition of Na₂SO₄ to inhibit the generation of calcium vanadate can improve the VRWL to some extent, this process consumes a large amount of Na₂SO₄, resulting in a significant increase of cost. Hence, this study focuses on the behaviors of impurity elements Ca and Fe during roasting to investigate the mechanisms of Ca and Fe affecting VRWL. Moreover, a permanent cure for reducing the negative effect of impurity elements on the VRWL is also achieved.

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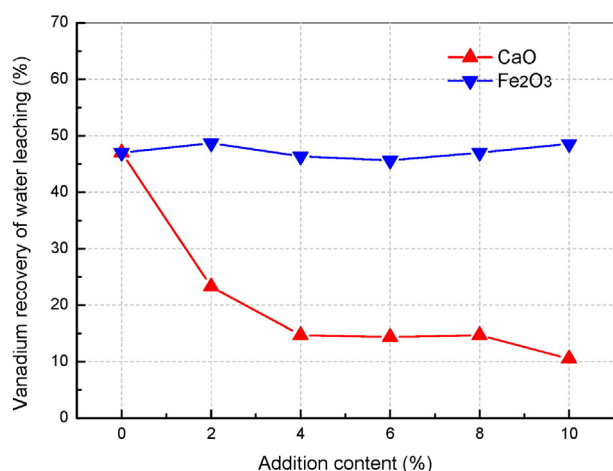


Fig. 1. Effect of CaO and Fe₂O₃ addition on VRWL of roasted sample.

2. Experimental

2.1. Materials

The mica-type stone coal was obtained from Teng-da Mining and Metallurgy Co. Ltd., Hubei, PR China. The chemical composition and mineral composition of the sample were analyzed in the previous research (Zhao et al., 2013a). It is mainly composed of 54.36% SiO₂, 10.59% Al₂O₃, 7.35% CaO, 5.93% Fe₂O₃ and 0.82% V₂O₅. The main mineral phases are quartz, muscovite and feldspar, respectively. In addition, a spot of hematite and calcite also exist.

Unless otherwise specified, the compound additive with 6 wt.% NaCl and 10 wt.% Na₂SO₄ was used as roasting additive in this study, which has been previously found to be the optimal addition (Zhao et al., 2013b). Both NaCl and Na₂SO₄ with analytical grade were purchased from Tianjin Kemio Chemical Regent Ltd. CaO, Fe₂O₃, V₂O₅ and NaVO₃ (all analytical grade) were purchased from Sinopharm Chemical Reagent Corp.

2.2. Procedures

The stone coal samples were mixed with additives mentioned above and a certain content of CaO (i.e. 0%, 2%, 4%, 6%, 8%, 10%) or Fe₂O₃ (i.e. 0%, 2%, 4%, 6%, 8%, 10%) to investigate the effect of Ca and Fe on the VRWL. Subsequently the mixtures were ground to $-150\ \mu\text{m}$ by a vibration mill (HLXZM-100). The roasting system has been confirmed in our

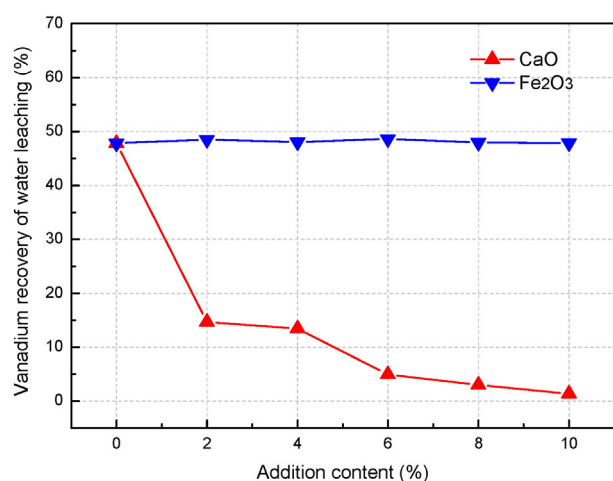


Fig. 2. Effect of CaO and Fe₂O₃ addition on VRWL of sample roasted again.

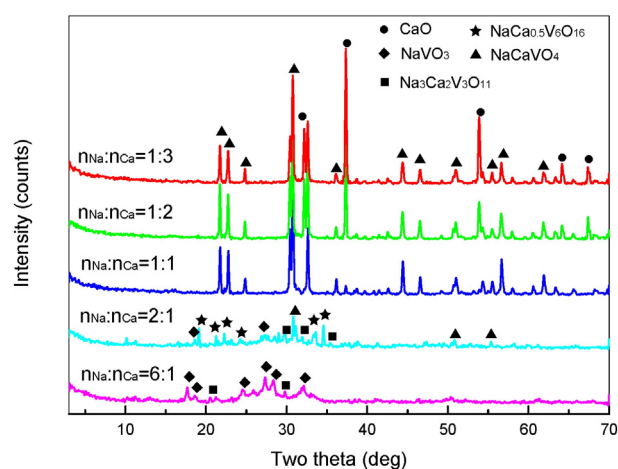


Fig. 3. XRD patterns of samples with different molar ratios of Na to Ca in the NaVO₃-CaO system.

previous research (Zhao et al., 2013b). The mixture in a muffle furnace (SXZ-10-B) experienced three stages: heating up (from room temperature to 850 °C, heating rate 14 °C/min), roasting (850 °C for 2 h) and nature cooling (from 850 °C to 500 °C). Then the roasted sample was taken out and leached in water. The water leaching parameters were as follows: temperature of 90 °C, time of 1 h, water to solid ratio of 4:1 mL/g and stirring speed of 1000 r/min with JJ-1 electric mixer. The VRWL is defined as Eq. (3):

$$\text{VRWL} = \frac{\text{Vanadium in water leaching solution}}{\text{Vanadium in roasted sample}} \times 100\%. \quad (3)$$

2.3. Analytical methods

X-ray diffraction (XRD) analysis was conducted for the roasted samples using Rigaku D/Max-RB X-ray diffractometer with Cu-K α radiation, voltage of 40 kV, current of 30 mA and at the scanning rate of 15°/min from 3° to 70°.

The vanadium content in water leaching solution was measured by ammonium ferrous sulfate titrimetric method (GB/T 8704.5-2007). The vanadium, iron and calcium grades in samples were determined in accordance to the methods of GB/T 19226-2003, GB/T 6730.5-2007 and GB/T 19281-2003, respectively.

The phase distributions of the roasted samples with different CaO and Fe₂O₃ addition were calculated by the thermodynamic software

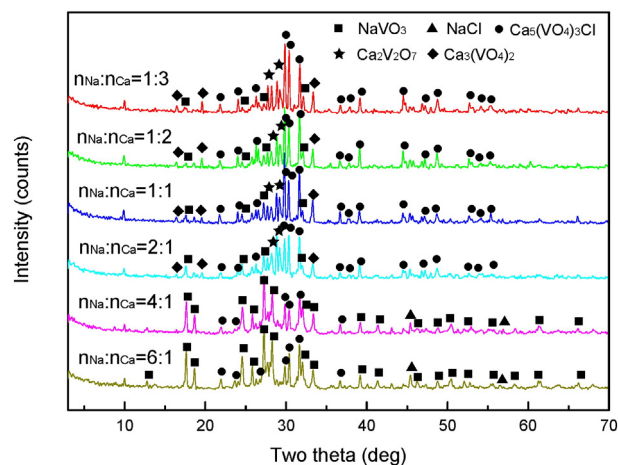


Fig. 4. XRD patterns of samples with different molar ratios between Na and Ca in the NaCl-CaO-V₂O₅ system.

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