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A novel approach for pre-concentrating vanadium from stone coal ore

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ABSTRACT

Stone coal, a kind of important vanadium-bearing resources in China, accounts for about 87% of the domestic reserves of vanadium. But the currently developed techniques to extract vanadium from stone coal are all confronted with environmental problems. For example, large quantities of caustic or greenhouse gases discharged in the oxidizing roast process, enormous consumptions of acid or alkali in the leaching step and massive tailings containing toxic V^{5+} ions.

With a view to solve those problems, an innovative process for pre-concentration of vanadium from stone coal was designed and confirmed on a laboratory scale. The distinct features of this design are as follows. Firstly, the environment-friendly Fe_2O_3 is selected as a capturer of vanadium. Secondly, the natural reducing property of stone coal is utilized to promote the formation of magnetic V-rich phase, Fe_2VO_4. Thirdly, a high-grade vanadium concentrate is obtained by magnetic separation method.

The practicability of this design was confirmed using industrial stone coal on a laboratory scale. When 10 mass% Fe_2O_3 relative to stone coal was added and roasted at 1200 °C for 3 h, a high-grade concentrate containing vanadium higher than 14 mass% was obtained, and more than 91% of the total vanadium in stone coal was recovered.

1. Introduction

Vanadium, as an important transition metal, is widely used in diverse areas ranging from high strength steels, Ti-V-Al alloys, vanadium-REDOX storage battery, catalysts, specialized ceramics to low density-high intensity magnets (Moskalyk and Alfantazi, 2003; Vijayakumar et al., 2011; Yamamura et al., 2011; Aboelfetoh and Peistchnig, 2014). From 2001, the world production of vanadium is about 58,000 metric tons per year, and China's vanadium output accounts for more than 38%. In China, about 87% of vanadium is reserved in stone coal ore (Dai et al., 2012; Ketris and Yudovich, 2009). Hence, to extract vanadium from stone coal efficiently and environmentally is of significance for the sustainable supply of vanadium in China as well as in the world.

Stone coal is a type of shallow marine sediment that is formed from lower organisms and colloidal silica or clay in a reducing environment after a long time of metamorphism and digenesis (Dai et al., 2017). It mainly consists of mica group minerals, as well as a small amount of calcite, pyrite and carbonaceous. The mica minerals are mainly comprised of illite, muscovite and biotite etc. And the main chemical compositions of stone coal are SiO_2, Al_2O_3, CaO, MgO, FeS_2, C and a small amount of TiO_2, V_2O_5, K_2O and Na_2O etc. The vanadium grade is generally in the range of 0.13–1.2 mass% (Zhang et al., 2011).

Vanadium in stone coal is generally found as V^{3+}, V^{4+} and V^{5+}, among which V^{3+} is dominant because stone coal originates from the reducing environment (Wang et al., 2008). The V^{3+} and partial V^{4+} substitute for Al^{3+} from the dioctahedral structure in mica minerals as an isomorphism, while some V^{4+} and a small amount of V^{5+} occur in an absorbed state on the surface of kaoline and pyrite (Hu et al., 2012; Wang et al., 2013). These dispersive occurrences greatly increase the difficulties of pre-concentrating and extracting vanadium from stone coal. Firstly, vanadium cannot be pre-concentrated effectively by the conventional flotation, gravity and magnetic separation methods. For example, Liu et al. used the gravity separation method to treat the stone coal ore, the V_2O_5 grade can be improved from 0.81% to 1.02% and the recovery rate was 89.6% (Liu et al., 2016). Zhao et al. proposed a modified gravity separation method, although some minerals that consume acid can be removed, the grade of V_2O_5 was not improved obviously (Zhao et al., 2013). Wang et al. proposed the desliming-flotation method to pre-concentrate the vanadium from low-grade stone coal, in which the V_2O_5 grade was 0.68%. The V_2O_5 grade in the final concentrate can reach 1.88% with the recovery rate of 76.58% (Wang et al., 2014b). Form the above given results, it can be seen evidently

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that the conventional methods of beneficiation are ineffective to obtain high-grade concentrate from the stone coal ore. Secondly, vanadium cannot be leached directly, since the trivalent vanadium, V^{3+}, embedded in the crystal lattice of mica minerals is insoluble in acid and water.

In order to extract vanadium from stone coal, the well-known salt roasting-water leaching technique, which was originally used to extract vanadium from vanadium minerals, was transplanted in the 1970s. Although many improved techniques have been developed, such as the blank roasting-acid leaching, the calcified roasting-carbonate leaching and the low salt roasting-cyclic oxidation technique etc, the basic principle for extracting vanadium is unchanged (Zhang et al., 2011; Li et al., 2009; Wang et al., 2014a, 2014b; Liu et al., 2010; Li et al., 2010; He et al., 2007; Zhu et al., 2012). That is, the V^{3+} is converted to V^{5+} and/or V^{4+} compounds by roasting with additives under the oxidizing conditions, and then the soluble vanadate is leached. In fact, this principle doesn't match the mineral properties of stone coal. Firstly, stone coal is a kind of ore formed in the reducing environment and with the reducing property, so the oxidizing roast is in essence against its natural property, which will inevitably cause low roasting efficiency, high-energy consumption and high emission. Secondly, the stone coal ore is directly used as the feed for the leaching process. This causes the problems, such as the huge amount of feedstock, the excessive acid consumed by gangue minerals, as well as the large amount of the resulting effluents (Seredin, 2012; Chen et al., 2014; Yang et al., 2011; Li et al., 2014). Therefore, aimed at extracting vanadium from stone coal efficiently and greenly, an innovative process to pre-concentrate vanadium is designed and verified as the first step.

In this process, the environment-friendly Fe_2O_3 was used as an additive. It captures vanadium, and magnetic V-rich Fe_2VO_4 phase is formed by roasting under the controlled conditions. Then, the V-rich phase is separated by magnetic separation method. The advantages are as follows: (1) the reducing roast is coincident with the reducing property of stone coal; (2) the magnetic V-rich phase can be separated effectively and greenly; (3) a high-grade vanadium concentrate can be obtained without leaving any unexpected substance in the tailings.

2. Details of the process

The sequence of this process is shown schematically in Fig. 1. It can be summarized as three key steps. First, the stone coal ore is ground with Fe_2O_3 and carbon homogeneously, and then pelleted. Second, the pellets are roasted under the controlled reducing conditions. The iron oxide reacts with vanadium and magnetic V-rich phase is formed. Third, the roasted pellets are ground into powder, and the V-rich phase is separated by magnetic method. Here, the carbon is used on one hand to reduce Fe_2O_3 to FeO, and on the other hand maintain the reducing conditions in the roasting step. Therefore, the quantity of carbon additive is determined by the contents of Fe_2O_3 and the carbon in stone coal.

During the reducing roast step, the added Fe_2O_3 is reduced and prone to reacting with the components in stone coal. Since the

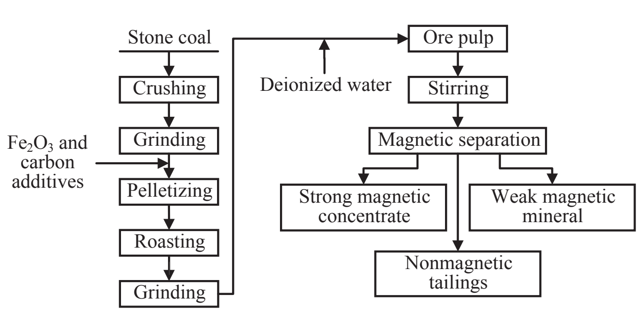

Fig. 1. Flowchart of the new process to pre-concentrate the vanadium in stone coal.

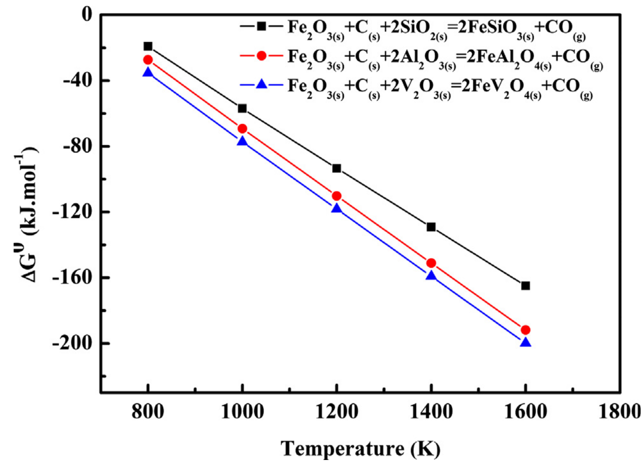

Fig. 2. The changes of standard Gibbs energy of the reactions between iron oxide and V_2O_3, SiO_2, as well as Al_2O_3.

dominant minerals in stone coal are mica, which are composed mainly of SiO_2 and Al_2O_3, the chemical affinities of FeO to V_2O_3, SiO_2 and Al_2O_3 were compared, respectively. In Fig. 2, the changes of standard Gibbs energy of the reactions are presented. It can be seen that the change of Gibbs energy to form iron vanadate spinel, FeV_2O_4, is the most negative one. This means that the iron vanadate spinel, FeV_2O_4, is more prone to be formed than the other two compounds.

Concerning the spinel structural compound formed between iron oxide and V_2O_3, FeV_2O_4 and Fe_2VO_4 are reported. FeV_2O_4 possesses the normal spinel structure, in which the oxygen ions are in face-centered cubic close packing, Fe^{2+} ions are on the tetrahedral interstices of oxygen ions, and V^{3+} ions are on octahedral sites. Fe_2VO_4 has the inverse spinel structure similar to Fe_3O_4, in which half of the iron ions exhibit as divalent, whereas the other half of iron ions are trivalent (Yang et al., 2009; Wakihara et al., 1971; Pool et al., 2015). The chemical affinity to form Fe_2VO_4 should also be compared in Fig. 2. But, it is unfortunate that no thermodynamic data of Fe_2VO_4 are available.

Although the preliminary thermodynamic analysis demonstrates that it is feasible to use Fe_2O_3 as the capturer of vanadium, the practicability of the new designed process should be ultimately confirmed by experiments. Therefore, in the following sections, vanadium in industrial stone coal was pre-concentrated according to the designed process.

3. Experimental

3.1. Characterization of stone coal ore

The raw stone coal ore used in the present study was taken from Yichang City in Hubei province of China. It was crushed, ground and sieved by a standard test sieve whose pore size was 0.074 mm in diameter. The particle size was all less than 0.074 mm. Then, X-ray diffraction analyzer (Bruker D8 Advance) and X-ray fluorescence analyzer (Shimadzu XRF-1800) analyses were used for mineralogical and chemical analysis, respectively.

The XRD pattern of stone coal ore is shown in Fig. 3. As seen, it mainly consists of quart, dolomite, roscoelite, illite, orthoclase and pyrite. The contents of the elements measured by XRF are presented in Table 1. The total content of carbon determined by combustion method is about 5.7 mass%, in which about 5 mass% comes from carbonate and the rest is amorphous carbon. The occurrence state of vanadium was observed through SEM measurements. It mainly occurs in illite and roscoelite, and a small amount of vanadium can also be found in pyrite and orthoclase mineral.