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Extraction of vanadium from stone coal by roasting in a fluidized bed reactor

Xi Zeng [a], Fang Wang [b], Huifeng Zhang [a,c], Lijie Cui [c], Jian Yu [a,*], Guangwen Xu [a,*]

[a] State Key Laboratory of Multi-Phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China
[c] University of Chinese Academy of Sciences, Beijing 100039, China

HIGHLIGHTS

- The new roasting process consists of two fluidized bed reactors.
- Experimental conditions were optimized on a laboratory fluidized bed reactor.
- Fluidized roasting and impregnating additive on stone coal had better results.

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ABSTRACT

In order to improve leaching efficiency of vanadium pentoxide (V_2O_5) from stone coal and to reduce its connected environmental pollution, this article investigated the oxidizing roasting of stone coal in a laboratory fluidized bed reactor to optimize the roasting method and conditions. The examined parameters included reaction temperature, reaction time and amount and mixing method of additive. The removal of Cl from the generated effluent gas was implemented using CaO as the adsorbent, and comparison was made between the fluidized bed roasting and static roasting in a muffle oven. The results show that the fluidized roasting is more favorable to leach V_2O_5 from stone coal, which can shorten roasting time for reaching the maximal leaching rate, while the realized leaching rate is also higher. Comparing the mixing method applied to stone coal and additive, the impregnation method of additive on stone coal not only increased the leaching rate and shortened the roasting time for reaching the maximal leaching rate, but also reduced the amount of additive required. Adding CaO in stone coal roasting sharply decreased the content of Cl-containing gases in flue gas, which can greatly alleviate the possible environmental pollution. The optimal conditions for fluidized bed roasting were found to be impregnating 6 wt.% additive on coal, adding 3 wt.% CaO and performing roasting at 800 °C for 0.75 h.

1. Introduction

Vanadium and its compounds are important strategic resources and are playing important roles in many industries such as ferrous and non-ferrous metallurgy, chemical production, and electron and battery manufacture [1,2]. Apart from vanadium titano-magnetite, stone coal is another important vanadium-bearing resource. In China, the gross reserve of vanadium in stone coal is estimated to be about 1.18 million tons. In terms of V_2O_5 amount, it takes more than 87% of China's total domestic reserve of vanadium. In recent years, the V_2O_5 extracted from stone coal has reached 40% of the totally produced V_2O_5 in China [3]. With the increasing market demand for vanadium products and the shortage of high-grade ores, it becomes more and more necessary and urgent to exploit and utilize the low-grade stone coal resource for V_2O_5 production.

In stone coal, vanadium exists dominantly as trivalent vanadium (V(III)) in addition to very little as quadrivalent (V(IV)) and quinquevalent vanadium (V(V)). The presence ratio of these different valent states is closely related to the reduction atmosphere for forming the stone coal [4]. Since V(III) and V(IV) have the ionic radius, electronegativity and coordination number similar to those of Al(III), they usually replace Al(III) in dioctahedral structure to form isomorphism in mica and clay minerals [5]. This sort of vanadium is most prevalent and representative in stone coal but it is difficult to be extracted. Besides, the ore containing vanadium in stone coal is always complicatedly combined with carbon, which further increases the difficulty for extracting vanadium form stone coal.

* Corresponding authors. Tel.: +86 10 82544885.
E-mail addresses: yujian@ipe.ac.cn (J. Yu), gwxu@ipe.ac.cn (G. Xu).

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China has started to extract vanadium from stone coal since 1960s, whose fundamental principle is oxidizing the acid- and water-insoluble V(III) to V(IV) and/or V(V), and then precipitating and separating V(IV) from the leaching solvent [6]. Up to now, dozens of technologies have been proposed according to the properties of raw stone coal ore in different regions, and some of them have been applied to industrial productions. These technologies can be divided into two categories, direct acid leaching and acid leaching after roasting [7–10]. The direct acid leaching is adopted only by limited companies because of its inherent disadvantages such as poor feedstock adaptability, low vanadium recovery ratio, large consumption of H_2SO_4, difficulty in separating and concentrating vanadium from many impurities (Fe, Al, Mg, K, Na, etc.), and serious environmental pollution [11,12].

Now, most of the companies producing vanadium from stone coal adopt first roasting and then acid leaching. The representative process is roasting with sodium chloride under oxidizing conditions to convert vanadium in stone coal to acid-soluble salt [13]. In this process, the roasting plays a critical role in oxidizing V(III) to V(IV) and V(V), which is determinative to the available total vanadium recovery ratio and is thus the rate-limiting step. The roasting reactors popularly used include flat kiln, shaft kiln and rotary kiln. All of them, however, have the limitations of low treatment capacity, long roasting time, insufficient heat and mass transfer efficiency in reactors and difficulty in scale-up [6]. The common additive used in the traditional roasting technologies is NaCl, thus bringing about serious emission of poisonous gases of HCl and Cl_2 [14]. In recent years, the Chinese government has banned several hundreds of production lines that adopted the direct acid leaching technology. It is consequently urgent to develop new roasting technology with high recovery of vanadium and having as well controlled pollution to environment for extracting vanadium from stone coal.

A new fluidized bed two-stage roasting process consisting of a fluidized bed (FB) reactor and a transport bed reactor has been proposed in Institute of Process Engineering (IPE), Chinese Academy of Sciences (CAS). As shown in Fig. 1, stone coal is first autothermally roasted in the fluidized bed reactor for partial decarbonization, and its products are in turn forwarded to the transport bed reactor to implement complete decarbonization and deep oxidation of vanadium through adding an additive. In the transport bed, the produced poisonous gases, such as HCl and Cl_2 are removed through injecting an adsorbent that is likely CaO. The big particles of stone coal that are not adequately roasted in the transport bed reactor is collected by a cyclone and then returned to the fluidized bed reactor for further roasting. While large particles, usually stone, are withdrawn from the bottom of the transport bed, the roasted fine particles carried with hot flue gas are collected by another cyclone and further cooled and collected for acid leaching. By integrating the advantages of fluidized bed and transport bed reactors [15], the new two-stage roasting process is not only applicable to powder feedstock (e.g., powder stone coal), but enables also large treatment capacity in comparison with the kiln reactors.

By simulating the practically possible conditions for the process illustrated in Fig. 1, a small laboratory batch fluidized bed reactor was used to test how the roasting process affects the downstream acid leaching. The results were compared with the traditional fixed bed roasting to demonstrate the technical feasibility and advantages of the new proposal. The effects on leaching rate for V_2O_5 were systematically examined for the parameters including roasting temperature and time, additive type and amount, mixing method between additive and stone coal. Moreover, the chlorine removal from the generated flue gas by CaO was also investigated. As a consequence of this study, a roasting process is finally proposed to ensure the high-efficiency recovery of vanadium from stone coal.

2. Experimental section

2.1. Roasting apparatus and test

As shown in Fig. 2, the fluidized bed roasting apparatus consists of a fluidized bed reactor (FB), an electric furnace, a gas supply section, a feeding hopper, a cyclone and a gas cleaning system. The FB reactor was made of high purity quartz glass and was 50 mm in inner diameter (I.D.). Its reaction zone was 300 mm long between a bottom gas preheating section of 300 mm long and an expanded freeboard of 100 mm in inner diameter and 150 mm in length. Experiment was started by heating the reactor to a desired temperature, such as 800 °C, and then high-purity air at a specified rate was fed into the reactor to form the roasting atmosphere. The roasting was initiated by feeding exactly 30 g stone coal or its mixture with the adopted additive into the reactor through a hopper-like feeder. The generated gas, with fly ash as well, passed through a cyclone and several washing bottles of sodium hydroxide solution immersed in an ice-water bath to remove the poisonous gas components, mainly HCl and Cl_2. After experiment, the reactor was taken out from the electric furnace to quickly cool it to the room temperature. The roasted stone coal collected from the cyclone and reactor was taken to analyze its content of V_2O_5 according to the measurement method depicted in the Section 2.2.

The static roasting of stone coal was conducted in a muffle furnace, and the result was compared with that from the fluidized bed roasting in terms of the available extraction efficiency of vanadium. At a desired temperature, the mixture of stone coal and additive was loaded into a ceramic crucible, and this crucible was in turn put into the muffle furnace to implement the roasting in air atmosphere. After reaching the roasting time, the ceramic crucible was taken out and cooled quickly to the room temperature, and the roasted sample in the crucible was similarly analyzed as for that from the fluidized bed roasting.

2.2. Material and measurement

Raw stone coal used in this study was taken from Sansui county, Guizhou Province of China. Prior to experiment, the stone coal was crushed and sieved to the sizes of 0.1–0.15 mm, and then dried in an oven at 105 °C for 2 h. Table 1 shows the results of industrial analysis and ultimate analysis for the stone coal and the contents of major components in its ash. The content of vanadium in terms of V_2O_5 is up to 1.26 wt.%, a prospective value for application development of vanadium leaching. On the other hand, the fixed carbon in stone coal is about 15%, which can seriously hinder the release of vanadium from stone coal due to its strong surface energy and ability of adsorption. The roasting tests used a commercial additive with its effective components being Na_2CO_3, NaCl and some other species.

Two methods were adopted to mix stone coal and additive, physical mixing method by mechanical agitation and "impregnation" method by blending stone coal into a solution of additive containing 15 wt.% water and then aging the coal for about 5 min. All percents cited for additive were against the mass of dry stone coal. Measurement of V_2O_5 in the roasted stone coal was performed via the following procedure. A certain amount of the roasted stone coal (via either fluidized bed or static roasting) was dissolved into a sulfuric acid in a conical flask, and the resulting solution was in turn heated with a water-bath preset at 40 °C under 2-h continuous stirring and further filtered. The vanadium concentration in the filtering solution was determined according to the method of Chinese National Standard of YB/T 5328-2006 based on ferrous ammonium sulfate titration using N-phenylanthranilic acid as an indicator [16].