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Recovery of vanadium and carbon from low-grade stone coal by flotation

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Abstract: Flotation technology of high-carbon stone coal bearing vanadium was investigated based on mineralogical study. Carbon and vanadium flotation circuits were included in the flotation process for carbon and vanadium mineral concentrates. Carbon and vanadium minerals were efficiently separated via regrinding process in the carbon flotation circuit. The results show that the grade and recovery of V_2O_5 in flotation concentrate are 1.32% and 88.38%, respectively, and the tailings yield is 38.36%. Meanwhile, the grade and recovery of the carbon mineral are 30.08% and 75.10%, respectively, which may be utilized as the fossil fuels directly. The leaching rates of the flotation products are as high as 85%. The results demonstrate that there is no direct adverse effect of flotation process on vanadium leaching. This technology could potentially reduce cost and increase the treatment capacity of vanadium extraction and provide reference to stone coal flotation technology. **Key words:** flotation; low grade; stone coal; vanadium; carbon

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1 Introduction

As an important strategic metal, vanadium has been extensively applied in the fields of steel and alloy materials industries due to their excellent high tensile strength, hardness and fatigue resistance [1,2]. Approximately 80% of the world's vanadium is used in metallurgical purpose in alloy steels, and the other 20% is used in chemical purpose [3]. Vanadium occurs naturally in over 50 different minerals and in fossil fuel deposits rather than in its pure state [3]. Vanadium resources in China primarily exist in vanadium-titanium magnetite ore and stone coal [4]. The gross reserve of V₂O₅ in stone coal is 118 million tons, accounting for higher than 87% of the vanadium reserve in China and exceeding the total vanadium reserve in other countries [5,6]. Therefore, stone coal has aroused considerable attention as an important vanadium-bearing resource.

Currently, vanadium extraction technology from stone coal mainly includes roasting, leaching, ion purification, precipitation and calcinations [2,7]. Due to the low vanadium grade in stone coal (0.13% to 1.2%), traditional vanadium extraction processes face the problems of large ore tonnage, high energy consumption and acid consumption [8]. The market price of V_2O_5 decreased to approximately 75000 CNY per ton in 2013, which is close to its production cost. As the vanadium market price decreases, many vanadium enterprises in China must reduce or cease production. In recent years, a large amount of work has been conducted to improve vanadium recovery and reduce its production cost. Numerous studies have been reported on leaching technologies, such as direct acid, recycling alkali and calcified roasting-carbonate leaching [9]. Meanwhile, some efforts have been emphasized on vanadium beneficiation before being further subjected to melting processing.

If the V_2O_5 grade of stone coal increases by 0.1%, the production cost of 1 t of V₂O₅ would decrease by approximately 4000 CNY, increasing profits by 29% [8]. As a result, only relatively high-grade ore (>0.5% V₂O₅) has economic value and is worth smelting, which only accounts for 40% of the total ore [10]. Most of the mined stone coals are of low grade and require beneficiation to obtain vanadium concentrate. If vanadium beneficiation is successful, a reasonable amount of production cost will be reduced. ZHAO et al [8] attempted to pre-concentrate vanadium value from stone coal by gravity separation with a shaking table after decarbonization, achieving good results. During the decarbonization stage, the carbon thermal energy in the stone coal can be utilized, and the V₂O₅ grade increased to some extent. However, the combustibility of stone

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coal was very poor due to its low carbon content (13.44%) and cannot be directly used as fuel to generate heat in practice. Much information on stone coal beneficiation is available in the literature. XIANG et al [11] investigated the enrichment of vanadium value in stone coal from the Xinjiang Province in China. The results demonstrated that the primary minerals bearing vanadium were muscovite and tourmaline, while the main gangue mineral was quartz. Vanadium concentrate was eventually obtained with a V_2O_5 grade of 3.20% and a recovery of 74.50% using a combination of wet sieving and flotation.

The objective of this work was to pre-concentrate carbon and vanadium from high carbon stone coal obtained from the Shanxi Province, China. Mineralogical studies were performed to confirm the main occurrence of vanadium and carbon and to identify the liberation of these minerals. The designed process flowsheet is composed of a carbon circuit and a vanadium circuit. Flotation condition tests were then conducted to study the effects of particle size, pulp pH and reagent dosage on the recovery and grade of carbon and vanadium.

2 Experimental

2.1 Materials and reagents

The experimental sample of stone coal was obtained from the Shanyang region of Shanxi Province in China. Ore samples were crushed by a laboratory jaw crusher, followed by a roll crusher to less than 3 mm in size. The crushed product was then ground in a ball mill to a pulp density of 70%. The ground product was screened through a 420 μ m sieve to remove oversized material. Mixed oil (MO) and mixed amines (MA) were used as a carbon collector and a vanadium collector, respectively. Sodium silicate (SS) was used as a dispersant, terpenic oil (TO) was used as a frother, and H₂SO₄ was used for pH adjustment.

2.2 Characterization methods

Factors such as mineralogy and particle size distribution are important for choosing suitable concentration methods for stone coal beneficiation. Chemical composition was characterized by X-ray fluorescence spectrometry (XRF) technique using a Philips spectrometer. Mineral phase composition was investigated by powder X-ray diffraction (XRD, D8-ADVANCE, Bruker Co., Germany). Vanadium phase analysis was carried out according to the sequential extraction procedures. Optical microscopy (LEICA DMLB, Leica, Wetzlar, Germany) and scanning electron microscope with energy dispersive spectrometer (SEM–EDS, JSM–6490LV, JEOL Co. Japan) were used to characterize microstructure of the stone coal. Bulk

chemical analysis of the ore was conducted to examine the distribution of vanadium and carbon in each size fraction. The sample was classified into different size fractions i.e., <38, 38–50, 50–74, 74–154, 154–600, 600–1500 and >1500 μ m using standard laboratory sieves.

2.3 Experimental procedure

Flotation was conducted in a Denver laboratory sub-aeration cell. Rougher flotation was performed using a 1.5 L-capacity cell, whereas cleaner flotation was conducted with a 1 L-capacity cell. The flotation process flowsheet of stone coal is shown in Fig. 1. Carbon flotation was performed at 30% pulp density and 1400 r/min at pH 7. Carbon was preferentially floated in virtue of its natural floatability, and then a cleaner flotation was conducted to obtain high carbon recovery. After carbon floatation, vanadium minerals were concentrated using a two-stage flotation process. The flotation products were filtered, thermally dried, weighed and analyzed by XRF.

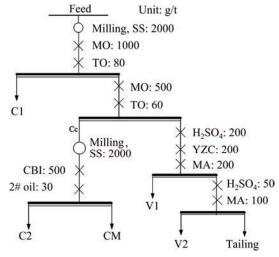


Fig. 1 Process flow-sheet stone coal

3 Results and discussion

3.1 Mineralogical characteristics

3.1.1 Chemical composition analysis

XRF chemical analysis of stone coal indicates that samples contain $0.92\% V_2O_5$, $4.03\% Al_2O_3$, $2.87\% Fe_2O_3$, $2.62\% K_2O$, $69.44\% SiO_2$, $5.42\% SO_3$ and 14.12% C. XRD pattern of the stone coal sample is shown in Fig. 2. According to XRD analysis, the mineral phases presented in the ore samples are quartz, muscovite, pyrite, feldspar and montmorillonite.

3.1.2 Occurrence of vanadium

Muscovite is the primary carrier of vanadium in stone coal. Vanadium generally exists as trivalent vanadium (V(III)), which substitutes for Al^{3+} in the dioctahedron of mica group minerals as an isomorphism,

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