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Phase transformation of iron in limonite ore by microwave roasting with addition of alkali lignin and its effects on magnetic separation

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A B S T R A C T

Phase transformation and magnetic properties of limonite ore with 40.10% Fe via microwave roasting with addition of alkali lignin were investigated by chemical phase analysis and vibrating sample magnetometer (VSM) analysis, respectively. The results of chemical phase analysis indicated that phase compositions and contents of iron in microwave roasted limonite ore were varied with the dosage of alkali lignin, the roasting temperature, the roasting time and the microwave power, and among them the dosage of alkali lignin exerted more significant influence. Iron oxides in limonite ore could be reduced to magnetic iron oxides including γ-Fe_2O_3 and Fe_3O_4 in the following sequence during microwave roasting process by evenly distribution of alkali lignin below 5%: $FeOOH/\alpha\text{-}Fe_2O_3 \rightarrow \gamma\text{-}Fe_2O_3 \rightarrow Fe_3O_4$, accompanied with small amount of FeO, and as the dosage was over 5%, γ-Fe_2O_3 and Fe_3O_4 could be in turn successively transformed into α-Fe_2O_3. Magnetic property studies demonstrated that an iron concentrate containing 88.72% magnetic iron oxides with a maximum saturation magnetization of 41.393 emu/g could be produced from roasted ore which was obtained by microwave roasting at 200 °C and 600 W with 5% alkali lignin for 30 min. In addition, the roasted ore was further used for magnetic separation, and the results showed that combining microwave roasting with addition of 5% alkali lignin could improve the iron recovery from the roasted ore distinctively. It was concluded that the microwave roasting process in the presence of alkali lignin could be a promising approach to effective utilization of limonite ore resources.

1. Introduction

Microwaves are a non-ionizing form of electromagnetic wave with frequency ranging from 300 MHz to 300 GHz. Compared with conventional roasting technology, microwave roasting offers many advantages, such as rapid heating, non-contact heating, selective and volumetric heating, energy transfer, speed of switch on and off, pollution-free environment and compactness of equipment [1]. The microwave heating performances of materials depend greatly on their microwave absorbing properties. Some materials are reflective to microwaves from surface and therefore they can not be heated by microwave irradiation (e.g., metals); transparent (e.g., silica); or excellent absorbers of microwave energy (such as fat and water). Based on these unique performances, so far, microwave heating technology has been widely used in various industry processes such as drying, calcining, and smelting [2–4]. Furthermore, much attention have been paid to the application of microwaves in the ore processing, and series of investigations describing microwave-assisted ore grinding, modification of physical properties, drying and anhydration, extraction processes, roasting and smelting, microwave-assisted carbothermic reduction of metal oxide, pretreatment of refractory gold concentrate, carbon regeneration, and microwave-assisted waste management have been published in different research papers [5–8].

Findings of recent investigations revealed that microwave heating had a significant influence on the magnetic properties of ores, such as hematite [9], pyrite [10], ilmenite [11,12], siderite [13] and chalcopyrite [14]. Omran et al. carried out a comparative study between untreated and microwave roasted iron ores [15]. It was found by high resolution XPS analysis that the peaks for Fe $2p_{3/2}$ and Fe $2p_{1/2}$ were shifted to lower binding energy (BE) as compared to untreated ores, which meant that after microwave irradiation, a

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portion of Fe^{3+} in iron oxide ores were reduced to Fe^{2+} in the form of magnetic phases. Moreover, their study on the effect of microwave pre-treatment on the magnetic properties of iron ores and the quality of iron concentrate by magnetic separation demonstrated that the iron recovery ratio could increase from 39.54% for untreated sample to 97.95% for microwave-roasted sample [9]. Barani et al. studied the effect of microwave roasting on the magnetic properties of four iron ores, and found that magnetic susceptibilities of all the investigated ores increased after microwave treatment. Moreover, the results also demonstrated that an over long period of roasting in microwave field had a negative influence on magnetic properties of ores and an irradiation time of 60 s was enough for the magnetization of the ores [16]. Znamenackova et al. pointed that the magnetic susceptibility of siderite ore increased after being exposed to a microwave power of 900 W for 10 min [13]. The effect of microwave irradiation on the mineralogy and the magnetic processing of a massive deposit of Norwegian ilmenite ore was investigated by S.W. Kingman et al., and they found that a large amount of intergranular fractures were formed after microwave irradiation coupled with an increase in magnetization of ore [17]. Similar findings were also revealed by Song [18]. Rath et al. compared the effects of conventional roasting and microwave roasting on the reduction and beneficiation of a complex Indian iron ore with 57% Fe by magnetic separation, and results indicated that the reduction by microwave roasting could be achieved in a considerably shorter time as compared to conventional roasting, and some undesired non-magnetic iron minerals like fayalite were little observed during microwave roasting process [19].

As we known, limonite ores are a common and widely distributed iron oxide ore resources in the world. However, there is little substantially breakthrough in the beneficiation technique of making extensive use of these plentiful iron ore resources due to their high-water content, loose structure and sliming, etc. Therefore, limonite ores have been regarded as one of the most refractory iron ore resources. Although many techniques such as suspension magnetization roasting-magnetic separation [20], sodium-carbonate-added carbothermic reduction-magnetic separation [21], and direct reduction roasting followed by magnetic separation [22] have been tentatively used for recovering iron from limonite ores nowadays, the separation indexes and/or treatment cost were far from satisfactory. Based on this situation, it is imperative to propose and develop an efficient and economic beneficiation technique for exploiting and utilizing these abundant refractory limonite ore resources. This work investigated the effect of microwave irradiation on the phase transformation and the magnetic properties of limonite ore under reductive condition and the recovery ratios of iron from microwave roasted ore by magnetic separation were also studied in hopes that the results of this paper would help in ascertaining the feasibility of recovering iron from limonite ores by the proposed alkali-lignin-added microwave-assisted magnetization roasting-magnetic separation process.

2. Materials and experimental methods

2.1. Materials

Limonite ore sample was obtained from Yongzhou City, Hunan Province, China. Alkali lignin was used as reducing agent with a particle size below 200 mesh and was supplied by Shandong Tranlin Group, China. The alkali lignin was composed of about 53% alkali lignin, 12% reductive substances, 18% caustic alkali and 17% low molecular weight organics and inorganic salts, which was used without further treatment. All the chemical reagents used in this experiment were of analytical grade, which were purchased from Taishan, China.

The ore sample was first crushed and ground to a particle size smaller than 0.25 mm (+60 mesh) in a ball grinder. Table 1 and Fig. 1 present the main chemical components and the X-ray diffraction (XRD) pattern of ore sample, respectively. It can be seen from Table 1 that although Fe_2O_3 content was approximately 57.31%, the contents of MnO_2, Al_2O_3 and SiO_2 were relatively high in the ore sample, which would be detrimental to its effective utilization. The XRD pattern of the limonite ore shown in Fig. 1 indicated that the raw ore was mainly goethite (FeO(OH)), hematite (α-Fe_2O_3), jacobsite ($MnFe_2O_4$), and kaolinite ($Al_2Si_2O_5(OH)_4$). The phase compositions of iron in ore sample were analyzed by chemical phase analysis, which are listed in Table 2. It was obvious that iron minerals mainly consisted of goethite (FeO(OH)) and hematite (α-Fe_2O_3), small amount of iron silicate (Fe-Si minerals), siderite ($FeCO_3$) and pyrite (FeS_2). In addition, the dissemination relationship between iron minerals and gangue minerals in raw ore sample was observed by scanning electron microscopy (SEM) image, and the maps of main element distribution were obtained by an energy dispersive spectrometer in SEM microscope. The results were shown in Fig. 2, which demonstrated that the iron in ore sample was mixed with a considerable amount of Mn, Al and Si in the form of fine grained dissemination, therefore, it was difficult to liberate iron grains just through the milling process.

2.2. Microwave roasting of limonite ore

A MAS-II microwave reaction apparatus was used for all roasting experiments. Twenty grams of limonite ores were employed for each experiment. The mixture of ore and alkali lignin was first put into a 100-ml corundum crucible covered with a lid and then subjected to microwave irritation in microwave reaction apparatus (in term of roasting experiment for raw ore, alkali lignin was not added.). In microwave field, the mixture obtained was rapidly heated to a designated temperature. The temperature inside the crucible was instantly controlled by varying the microwave power automatically according to a feedback control signal given by the temperature measured by an infrared temperature probe. After the roasting process was completed, the roasted ore remaining in the capped crucible was cooled to room temperature in microwave reaction apparatus. Then, the roasted ore was characterized by chemical phase analysis to study the phase transformation of iron during microwave roasting process. Meanwhile, the magnetic properties of the roasted ore were measured using vibrating sample magnetometer (VSM).

2.3. Magnetic separation of roasted ore

Prior to magnetic separation experiment, 10 g of the cooled roasted ore were wet ground in a laboratory scale ball mill (model: XMQ-ϕ240 $\times$ 90) at a pulp density of 50% solids to a particle size below -45 μm (+325 mesh). The obtained slurry was then separated at room temperature by a Davies magnetic tube (model: XCGS-φ50) with a setting working electrical current which is related to magnetic field strength. In this study, the magnetic field strength was varied from 1 kOe from 4 kOe. After magnetic separation, the magnetic fraction (magnetic iron concentrate) obtained was filtered, dried and weighted. The drying process was conducted in an oven at 80 °C. The recovery ratio of iron was used to evaluate the efficiency of microwave roasting, which was calculated based on the following equation:

$$\varepsilon = (\beta \times m)/(\beta_0 \times m_0) \quad (1)$$

where ε is the recovery ratio of iron, β is the iron grade in the magnetic iron concentrate, m is the mass of magnetic iron