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Aluminum release from microwave-assisted reaction of coal fly ash with calcium carbonate

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ABSTRACT

Coal fly ash (CFA) is a potential aluminum resource alternative to bauxite. Because most aluminum in CFA exists in an inert mullite phase, the way in which CFA can be activated is becoming important. Thermal activation with the addition of calcium carbonate ($CaCO_3$) is a common method for recovering aluminum from CFA; however, the lower energy efficiency of conventional heating has limited its application. In this investigation, microwave irradiation (MWI) was found to be an energy-saving method for CFA activation, and 95 wt% of aluminum was released from the specimen treated by MWI at 800 °C for 60 s. Compared to conventional thermal activation, MWI reduced the sintering temperature by nearly 400 °C and shortened the reaction time by 20 times. Anisothermal reactions, which occurred due to the selective heating of the microwave, controlled the decomposition rate of $CaCO_3$ and the formation rate of anorthite. MWI also accelerated the formation of fused phase and contributed to the formation of well-ordered hexagonal anorthite.

1. Introduction

Coal fly ash (CFA) is an industrial by-product of coal-fired power stations [1,2]. Statistics from the Ministry of Environmental Protection in China showed that 470 million tons of CFA was generated in 2010, 68% of which was used in civil engineering and building materials; the remaining ash was stockpiled. The two largest coal-producing provinces in China, i.e., Inner Mongolia and ShanXi, generated a large amount of high aluminum-containing CFA (alumina equivalent: 40 wt%–50 wt%) [3]. Recovering alumina from this CFA was thus officially encouraged under the newly revised regulations for the comprehensive utilization of CFA.

Recovering alumina from a sintered mixture of CFA and lime was first proposed in 1960s [4], and alkali and acid processing technologies have since been developed [5,6]. The alkali processing technology includes lime-sintering and lime-soda-sintering processes. The mixture is sintered at a high temperature to produce aluminates, and the aluminum is then leached with sodium carbonate solution. The acid processing technology includes direct acid leaching and pre-sintering processes. Because most aluminum in CFA exists in mullite, less than 60 wt% of aluminum can be leached by direct acid leaching, except for concentrated sulfuric acid leaching at a temperature of 300 °C [7–9]. Transforming mullite to a chemically active product under sintering has also been adopted in acid technology, i.e., the pre-sintering process. After mixing CFA with Na_2CO_3 and NaOH at a weight ratio of 1:0.5:0.5 and sintering at 700 °C for 2 h, 95% of aluminum was leached using hydrochloric acid solution [10]. Matjie [11] sintered the mixture of 50 wt% of fly ash, 40 wt% of fine coal and 10 wt% of lime at the temperature range of 1000–1200 °C and leached 85 wt% of aluminum using sulfuric acid solution.

Studies on leaching aluminum from CFA over the past 50 years have shown that the additive-sintering process is a potentially competitive method for recovering aluminum. However, the large amounts of additive and the high energy consumption during the sintering process has hindered its development of large-scale applications. In previous work, we developed a new additive-sintering method with a higher aluminum leaching ratio than 85 wt%. In this method, the amount of additive decreased to less than 40 wt% of CFA. However, the decrease in energy consumption was not very effective due to the lower energy efficiency of conventional heating (CH).

Microwave irradiation (MWI) technology has been frequently applied in energy-saving sintering processes due to its many advantages such as lower energy consumption, a faster heating rate and less processing time [12–15]. MWI is a process in which electromagnetic field couples with materials and then converts into thermal energy [16]. MWI has been reported to enhance the diffusion and mass transportation in solids [17–19], i.e., MWI can lower the reaction energy barrier. Therefore, this study was designed to investigate the effects of MWI on the reaction of CFA and $CaCO_3$. A single mode microwave

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applicator was used to treat specimens to ensure the accuracy and reliability of this experiment.

2. Experimental section

2.1. Materials

CFA was collected from Wujing Power Plant in Shanghai, China. The chemical compositions of CFA were analyzed by X-ray fluorescence (XRF) spectrometry (ARL ADVANT 3600, Thermo Fisher Scientific, America), and the results are shown in Table 1. The X-ray diffraction (Rigaku D/MAX 2550 VB with Cu target, run at 2θ steps of 0.02°) analysis showed that the major minerals in CFA were mullite and quartz.

A commercially available AR grade $CaCO_3$ was used as the CFA additive.

2.2. MWI equipment

A single mode microwave applicator assembled in our laboratory was used for heating specimen [20]. The surface temperature of the specimen was continuously monitored by an IR camera. During the MWI, the input power (forward power) and the output power (reflected power) were also measured using a power monitor. The absorbed microwave power used to heat the specimen was the difference between the input and output powers.

2.3. Methods

2.3.1. CFA activation

CFA and $CaCO_3$ were mixed to comply with the molar ratio of CaO to Al_2O_3 of anorthite. A batch of two samples of 40 g of dry mixture and 20 ml of ethanol were pulverized for 2 h in a planetary ball mill equipped with two 500-ml agate jars. The sample of wet milled was dried in the oven at 105 °C for 24 h and then pressed to form 10 × 8 mm cylindrical specimens.

An input power of 500 W was applied for MWI. The sliding short circuit piston was first adjusted to the position with minimal output power, i.e., the microwave coupled best with the specimen. The piston held still until the specimen was heated to the required temperature. The piston was then adjusted to maintain the required temperature during the holding process. The specimens were treated by MWI at 700 °C and 800 °C for various time. Conventional thermal treatment was conducted in a muffle furnace. The specimens were directly put into the furnace at 800 °C, 1100 °C and 1200 °C and heated for various time; they were then quenched in air.

2.3.2. Aluminum leaching procedure

The activated specimens were milled using an agate pestle to pass through a 45-μm sieve and were then subjected to Al leaching. The milled sample was mixed with hydrochloric acid solution (10 wt%) in a flask with a stirrer at a solid/liquid weight ratio of 1:20 and was leached at 98 °C for 1 h. The concentration of Al^{3+} in the leachate was analyzed using previous methods [21].

Table 1
Composition (wt%) of CFA.

Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	K_2O	MgO	P_2O_5	SO_3	Na_2O	LOI	Total
39.98	50.07	3.14	2.22	1.31	0.96	0.57	0.41	0.32	0.07	1.61	99.93

LOI: loss on ignition.

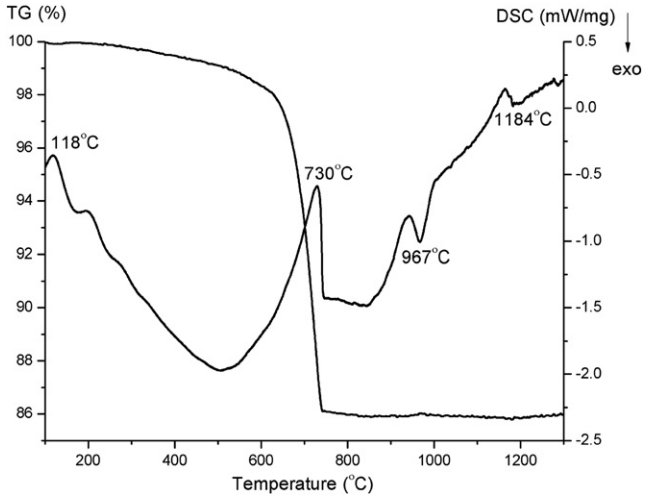

Fig. 1. TG-DSC results for the CFA and $CaCO_3$ mixture.

2.3.3. Normalized intensity ratio (NIR)

To investigate the reaction processes under different heating methods, the heated specimens were analyzed using the normalized intensity ratio (NIR_i) [22]:

$$NIR_i = \left(\frac{I_i - I_{i(back)}}{\sum_{i=1}^{6} \left(I_i - I_{i(back)} \right)} \right)$$

where I_i is the XRD intensity of reaction product and $I_{i(back)}$ is the intensity of XRD background of reaction product. The intensities of (210) of mullite, (011) of quartz, (104) of calcium carbonate, (200) of calcium oxide, (211) of gehlenite and (201) of anorthite were used to calculate the NIR_i.

3. Results and discussion

3.1. Conventional activation of CFA

3.1.1. Thermal behavior of the CFA and $CaCO_3$ mixture

The thermal behavior of the CFA and $CaCO_3$ mixture was analyzed using thermogravimetry and differential scanning calorimetry

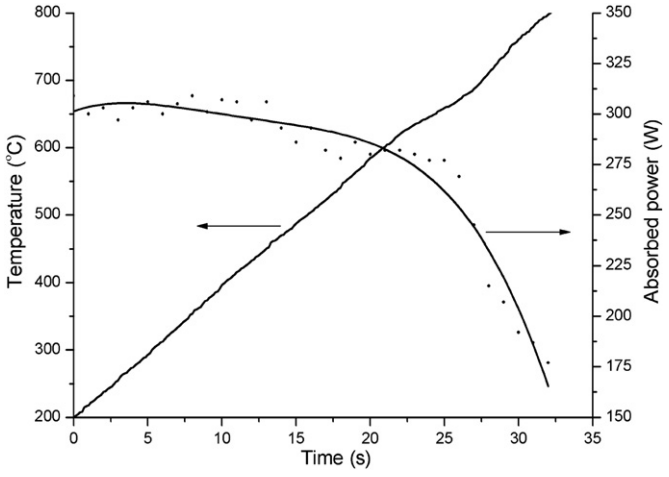

Fig. 2. Variations in the temperature and absorbed power of a specimen containing CFA and $CaCO_3$ under MWI.