



## Role of additives in improved thermal activation of coal fly ash for alumina extraction

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### ABSTRACT

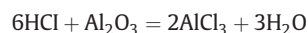
The extraction of alumina from coal fly ash is a good direction for its value-added utilization. The presence of the inert matters with high degree of polymerization, such as mullite and other aluminosilicates, makes the reactivity of coal fly ash very poor. The activation of coal fly ash is necessary before its utilization. The thermal activation calcination with the addition of NaOH and Na<sub>2</sub>CO<sub>3</sub> was carried out in this research. The results showed that the addition of NaOH and Na<sub>2</sub>CO<sub>3</sub> improved the alumina extraction evidently. The maximum alumina extraction reached ~60% when calcination at 600–900 °C with the addition of NaOH and that could reach 82% at 900 °C with the addition of Na<sub>2</sub>CO<sub>3</sub>. Detailed analysis and characterization was carried out by using thermal gravimetric and differential scanning calorimetric analysis (TG-DSC) and X-ray diffraction (XRD). The results indicated that NaOH and Na<sub>2</sub>CO<sub>3</sub> facilitated the decomposition of the polymeric phases. At lower temperatures (<600 °C), NaOH played a main role while Na<sub>2</sub>CO<sub>3</sub> did at higher temperatures (> 700 °C). As a result, the mixed additives containing NaOH and Na<sub>2</sub>CO<sub>3</sub> made alumina extraction attain 95% at 700 °C.

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### 1. Introduction

Coal fly ash (CFA) is generated during high temperature combustion of coal in coal-fired power plants, and also in the smelting, and chemical industries [1]. Currently, about 800 million tons of coal fly ash has been generated in the world [1–3]. In China, electricity generation is majorly from coal-fired power plants. The annual fly ash discharge is more than  $4 \times 10^8$  tons in China [4,5]. The fly ash is the major coal solid waste, beside coal waste and coal slime. Due to the low utilization rate, coal fly ash is generally dumped in lands which pose a serious threat to the environment [6]. Therefore, efficient and safe disposal of CFA is of environmental concern in the whole world.

CFA contains about 10–55 wt.% of Al<sub>2</sub>O<sub>3</sub> [7–11] and is a potential substitute of bauxite for alumina production [12,13]. Extracting Al<sub>2</sub>O<sub>3</sub> from CFA has attracted many researchers' attentions [14–18]. Since the Al/Si weight ratio in CFA is less than 1, acid leaching process other than bayer process or other alkali methods is generally preferred based on its lower cost and lower material consumption [19–21]. The main reactions are as follows (take HCl for instance):



Nevertheless, CFA is formed at very high temperature and it is mainly made up of mullite, quartz and other amorphous phases. The mullite as a major source of aluminum in CFA is considered a non-reactive matter [2]. It is difficult to extract alumina using direct acid leaching method only

after a vigorous treatment through some methods [22–24]. Thermal activation by calcination the samples under high temperature is a common method to motivate the reactivity of CFA to enhance alumina extraction [25]. However, the application of the thermal method is restricted because of the higher calcination temperature and lower activation efficiency. Literatures showed that the addition of certain additives in CFA during the thermal treatment could reduce the calcination temperature and improves alumina extraction [14,26]. Lime and calcium oxide were studied as the common additives. For example, the fly ash mixed with calcium oxide and fine coal, then calcined at 1000–1200 °C, an alumina extraction efficiency of 85% can be achieved using sulphuric acid leaching [14]. In Gabler's study [26] 90% alumina dissolution can be obtained using lime as the additive of low-calcium ashes, calcined at 1100 °C, then leached using sulphuric acid. Although the improved alumina extraction was obtained by using thermal activation, the calcination temperature is still high. In this regard, research on high effective active additive to reduce the calcination temperature is significant to improve Al<sub>2</sub>O<sub>3</sub> extraction from the fly ash using thermal activation.

Na-containing substances, such as NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaCl, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, have good chemical reactivity. They are often used as the fluxing agent for aluminosilicate minerals or ashes to form eutectoid [27–30] or as a solvent to extract minerals from slag [31–33]. The researches proved that Na-containing substances can motivate the chemical reactivity of the aluminosilicate or the slag. Literatures showed that the Na-containing substances such as NaOH and Na<sub>2</sub>CO<sub>3</sub> are also often used to motivate the activity of the CFA [4,34–36]. It has been reported that NaOH or Na<sub>2</sub>CO<sub>3</sub> as the sintering additives was used to improve the extraction of aluminum or silicon in the water or alkaline leaching processes [37–39]. These researches

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proved that NaOH and Na<sub>2</sub>CO<sub>3</sub> can be used as a chemical activator for the CFA. However, few researchers focus the attentions on Na-containing substances as the calcination additive in acid leaching processes for alumina extraction. Our previous study showed that NaOH as the calcination additive of coal fly ash improved the alumina extraction and decreased the thermal activation temperature greatly when using hydrochloric acid as the leachant [40]. Our recent work showed that an improved Al<sub>2</sub>O<sub>3</sub> extraction from the fly ash was also achieved using Na<sub>2</sub>CO<sub>3</sub> as the calcination additive in the same acid leaching process. But the mechanisms of the effect of NaOH and Na<sub>2</sub>CO<sub>3</sub> on the transformation of the phases and the influence on the Al<sub>2</sub>O<sub>3</sub> extraction are still unclear. Information in this regard is of importance to develop the alumina extraction technique from coal fly ash economically and effectively.

In this paper, alumina extraction from coal fly ash using hydrochloric acid as the leachant was performed. The research focused on the effect of Na<sub>2</sub>CO<sub>3</sub> and NaOH additives on the thermal activation efficiency. Based on thermal gravimetric and differential scanning calorimetric analysis (TG-DSC), X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis techniques, the mechanisms on coal fly ash activation, aluminum extraction and phase transformation during activation were discussed in detail.

## 2. Experimental

### 2.1. Materials

Coal fly ash (CFA) samples are collected from the electrostatic precipitator of the First Coal-fired Power Plant in Taiyuan, Shanxi. The chemical compositions are shown in Table 1.

Analytical grade reagents: Ca(OH)<sub>2</sub> (Xudong Chemical Factory in Chaoyang District, Beijing), NaOH (Hengxing Chemical Reagent Co., Ltd. Tianjin), aqueous ammonia (Chemical Fertilizer Plant Reagent Factory in Taiyuan), Hydrochloric acid (Chemical Plant in Beijing), ethylene diamine tetraacetic acid (EDTA, Taixing reagent Factory in Tianjin), CuSO<sub>4</sub> (Chemical Plant, Jiaozuo City in He'nan), oxalic acid (Tianda Chemical Reagent in Dongli District, Tianjin), NaAc (Tianjin chemical Regent Co., Ltd.), Pyridine-azo naphthol (PAN, Shanghai Reagent plant), sulfosalicylic acid (Beijing chemical Plant).

Na<sub>2</sub>CO<sub>3</sub> is industrial soda (Qinghai alkali Industry).

### 2.2. Methods and processes

#### 2.2.1. The activation of coal fly ash

Coal fly ash was activated by thermal activation and thermal treatment with the addition of additives before leached using hydrochloric acid. The samples were made and denoted respectively as FA (the as-received coal fly ash without any treatment before acid leached), FA-Cal(-T) (coal fly ash was activated thermally at a desired temperature (T denote the calcination temperature, below is the same)), FA-Na<sub>2</sub>CO<sub>3</sub>(-T) (the sample was activated thermally with the addition of Na<sub>2</sub>CO<sub>3</sub>), FA-NaOH(-T) (the sample was activated thermally with the addition of NaOH) and FA-Na<sub>2</sub>CO<sub>3</sub> + NaOH(-T) (the sample was activated thermally with the addition of NaOH and Na<sub>2</sub>CO<sub>3</sub> at a weight ratio of 1:1). Among them, the proportion of coal fly ash and additives was 1:1 (weight ratio).

The coal fly ash samples were calcined in a muffle furnace (SX2-12-10) at the desired temperature for 2 h.

**Table 1**  
Chemical composition of local fly ash.

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	Loss on ignition
Contents (wt.%)	48.52	33.59	5.66	2.12	0.39	1.57	1.48	0.18	0.31	5.22

#### 2.2.2. Alumina extraction from coal fly ash

The as-received and activated coal fly ash samples as shown in Section 1.2.1 were used to extract alumina. The leaching processes as follows: 20 wt.% hydrochloric acid solutions were added in a 4-mouth flask with coal fly ash at a solid–liquid weight ratio of 1:3. The flask was heated to 100 °C in an electric jacket and stirred for 2 h. After stood for 2 h, the flask was cooled to room temperature. Then the mixture was filtered and washed with deionized water for many times until Cl<sup>-</sup> could not be detected from the filtrate using AgNO<sub>3</sub>. After that, the filtrate and insoluble residue were collected.

The content of Al<sup>3+</sup> was determined using copper salts back-titration [41]. The dissolution of Al<sup>3+</sup> in hydrochloric acid solution was the indicator to evaluate the activation efficiency of coal fly ash. The method of copper salts back-titration is described as follows: an excessive amount of standard Ethylene diamine tetra acetic acid (EDTA) solution was added into the filtrate. Pyridine-azo naphthol (PAN) was added as an indicator. CuSO<sub>4</sub> solution was added until the color of the filtrate changed from green to purple. It is needed to note that the filtrate contains a large amount of Fe<sup>3+</sup> in addition to Al<sup>3+</sup>. The presence of Fe<sup>3+</sup> would disturb the determination of Al<sup>3+</sup> by coordinating with EDTA. To exclude the interference of Fe<sup>3+</sup>, Fe<sup>3+</sup> need to be coordinated with EDTA firstly with sulfosalicylic acid as an indicator before the measurement of Al<sup>3+</sup>. The alumina extraction ( $\omega(\text{Al}_2\text{O}_3)$ ) was calculated according to Eq. (1).

$$\omega(\text{Al}_2\text{O}_3) = \frac{m_{\text{F}}(\text{Al}_2\text{O}_3)}{m_{\text{CFA}}(\text{Al}_2\text{O}_3)} = \frac{[c(\text{EDTA}) \cdot V(\text{EDTA}) - c(\text{CuSO}_4) \cdot V(\text{CuSO}_4)] \times 27 \times \frac{102}{54}}{M(\text{Al}_2\text{O}_3)} \quad (1)$$

Where,  $m_{\text{F}}(\text{Al}_2\text{O}_3)$  and  $m_{\text{CFA}}(\text{Al}_2\text{O}_3)$  denoted the mass of Al<sub>2</sub>O<sub>3</sub> in the filtrate and in coal fly ash respectively, c and V denoted the concentration and volume of the reagent. M(Al<sub>2</sub>O<sub>3</sub>) denoted the molecular weight of Al<sub>2</sub>O<sub>3</sub>.

The insoluble residue needs to be dried and collected. Corresponding to the marks of the coal fly ash samples, the residues were denoted as R-FA, R-FA-Cal(-T), R-FA-Na<sub>2</sub>CO<sub>3</sub>(-T), R-FA-NaOH(-T) and R-FA-Na<sub>2</sub>CO<sub>3</sub> + NaOH(-T).

### 2.3. Sample characterization

The phase analysis of the coal fly ash was performed by using an X-ray diffraction analyzer (D/MAX2500PC XRD analyzer of Tokyo Rigaku Co.). The accelerate voltage was 40 kV, the electrical current was 100 mA and scan ranges from 10° to 80° at the speed of 4°/min.

Thermal gravimetric and differential scanning calorimetric analysis (TG-DSC) analysis was carried out in a thermo gravimetric analyzer (TGA92, SETARAM, France) in an argon atmosphere. The sample loading was 10 mg and the heating rate was 3 °C/min. The weight changing with time was recorded on a personal computer.

Chemical compositions of CFA and its acid-leached residues were analyzed by X-ray fluorescence analyzer spectrometer (Simultix 12 XRF spectrometer of Tokyo Rigaku Co.). The voltage was 50 kV, the electrical current was 40 mA and the integral time was 40 s.

## 3. Results and discussion

### 3.1. Effect of activation on the alumina extraction

#### 3.1.1. Alumina extraction from as-received and calcined coal fly ash

Fig. 1 shows the alumina extraction from the as-received and the calcined coal fly ash (CFA) samples using hydrochloric acid (HCl). The calcined CFA sample was obtained by calcination the as-received CFA at 900 °C for 2 h. The alumina extraction from the as-received CFA was very low and the value was less than 5% even though the concentrated hydrochloric acid was used. For the calcined CFA, the

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