Full Length Article

Reaction characteristics and evolution of constituents and structure of a gasification slag during acid treatment

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ABSTRACT

Gasification slag is a potential resource of high value, which can be utilized as a porous material by acidification. To have a deep understanding of the composition and structural characteristics of the acidified slag, the gasification slag was treated using different concentrations of acetic acid (HAc) and HCl, respectively. The slag samples, in both an untreated and an acidified form, were characterized by AAS, XRD, FT-IR, BET, and TG. The results show that the reaction between the slag and a higher concentration of HAc could generate crystal minerals like alumohydrocalcite ($CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$) and aluminum acetate hydroxide (($CH_3COO)_2Al(OH)$). Meanwhile, HAc treatment results in an increase of crystallinity, but HCl treatment exerts the opposite effect. In addition, compared to the untreated, the specific surface area of the slag treated by HAc and HCl increases 20 times and 86 times, respectively. Acid treatment would make more mesoporous due to the extraction of Ca.

1. Introduction

Coal plays an indispensable role in the fields of energy and chemicals in China [1]. Yet most of coal as a fossil fuel is hard to consume efficiently and cleanly [2]. Hopefully, coal gasification technology as a most promising technological approach can achieve high efficient and environmental friendly coal conversion. Ash agglomerating fluidized bed (AFB) coal gasification technology developed by the Institute of Coal Chemistry of Chinese Academy Sciences can handle the coal with higher ash content and ash fusion temperature [3], and produces partly molten slag that is agglomerated to spherical particles [1,4]. As we know, the waste slag can be reused as a secondary resource according to its own characteristics [5]. However, most of the slag was conducted in cement production (48.5%), reclamation of low lying area (12.73%), roads and embankments construction (11.65%), mine filling (8.26%), brick manufacture (6.30%) [6], which may cause the contamination of soil and groundwater, disrupt ecological cycles and set off ambient environmental hazards [7,8]. Accordingly, a comprehensive utilization of the waste slag is becoming an urgent issue.

Acid-leaching is expected to assist in the potential applications of the slag, leading to the partial removal of Al, Fe and Ca, causing surface erosion and collapse, leaving behind a framework possessing a large surface area to produce a porous matter, which can be used for CO_2 capture [9,10], insulation materials [11–13], adsorption [14–16] and catalysis [17,18]. Although much attention has been given to the application of acidified slag, less research has been conducted on its structure, and the relationship between acid reaction and the chemical structure remains unclear. The delineation of such a composition and structure of acidified slag not only permits a better understanding of the nature of the acid treatment but also provides an insight into its application to practical production. In this paper, the strong inorganic acid HCl compared with the weak organic acid HAc are chosen to modify the slag. Depending on most of the impurities (Fe_2O_3, CaO, and others) in fly ash, different acids have been used, such as HCl, H_2SO_4, and HNO_3, moreover, HCl is typically selected as the preferred ash pretreatment [19,20]. On the other hand, acetic acid, a more environmentally friendly and relatively cheap acid, has been used as a proxy for disposing of solid wastes due to its high selectivity to the Ca and Fe [21,22], during which useful inorganic salts are obtained, like calcium acetate and iron acetate that can be used as deicers [23]. Therefore, the evolution of the composition and structure of the slag generated from AFB gasifier by treatment with HAc and HCl was systematically investigated respectively, so as to provide a basis for its high-value use.

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2. Experimental

2.1. Preparation of raw slag

The slag was sampled from the AFB gasification pilot plant using Shenmu pulverized semi-coke (Sub-bituminous coal char with 76.00% C, 1.31% H, 0.77% N, 0.31% S, 4.53% O (wt%); 8.53% Volatile matter, 10.68% Ash, 6.40% Moisture (air dry basis)) at 950 °C and 2.0 MPa. Before the experiments, the slag was dried at 110 °C in a drying oven for 12 h, ground to below 74 μm and calcined at 660 °C (the calcination temperature was firstly determined by TG) in an air atmosphere to remove the carbon, which is used as a raw material. The major components of raw slag were Si, Al, Fe and Ca, which added up to more than 93.7% (Table 1). Thus, the elements of Si, Al, Fe and Ca were mainly discussed in the following experiment.

2.2. Acid treatment

10 ± 0.01 g of raw slag was put into a 250 mL beaker together with 90 mL HAc solution or HCl solution respectively, and then the beaker was covered with plastic wrap to avoid volatilization. The experiments were carried out at different concentrations of HAc (1–9 M) and HCl (1–6 M) respectively at 80 °C in a water bath with continuous stirring for 2 h (pre-experiment had shown that 2 h was sufficient for the acid treatment). After acid treatment, the residue was washed thoroughly with distilled water and dried at 110 °C for 12 h, and then ground again to below 74 μm and finally sealed in a transparent plastic bag for standby. The slag acidified by HAc and HCl are labeled as AS (acetic acid treated slag) and HS (hydrochloric acid treated slag), respectively. Besides, the samples of AS and HS under different concentrations are labeled as HAc-iM (i = 1–9) and HCl-jM (j = 1–6), respectively.

The total leaching rate x is calculated by the formula:

$$x = (m_0 - m_1)/m_0 \tag{1}$$

where m_0 represents the mass of the raw slag before acid treatment; m_1 is the non reacted mass during acid treatment.

2.3. Characterization

The proximate and ultimate analyses were performed according to the Chinese National Standards GB/T 212-2008, GB/T 476-2001, respectively. The ash chemical compositions (except for SiO_2 and P_2O_5) in coal char ash or the slag were conducted following MT/T 1014-2006, and the content of SiO_2 and P_2O_5 were conducted following GB/T 1574-2007.

Atomic absorption spectroscopy (AAS) analysis was performed using a SENPU analyzer model 6810 to quantitate Ca, Al and Fe.

X-ray diffraction (XRD) analysis was carried out on a Bruker AXS D8 Advance powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) over a scanning interval (2θ) from 5° to 80° at a scanning speed of 0.02°/min and the accelerating voltage of 40 kV, tube current of 40 mA.

Fourier transform infrared spectroscopy (FT-IR) analysis was performed with a Nicolet IS50 FT-IR spectrometer at room temperature over the range 4000–400 cm^{-1} after 32 scans at 4 cm^{-1} resolution, where the samples were prepared using the KBr pellet method with the mass fraction of KBr and the sample is 200 mg: 1 mg.

The specific surface area, and pore diameter and volume were measured by the nitrogen adsorption and desorption analysis at 77 K using a JWGB analyzer (model JW-BK132F) and following the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods.

Thermogravimetric (TG) curves were obtained in a nitrogen atmosphere with 100 mL/min over the temperature range from 5 to 800 °C at 10 °C/min by a Setaram thermogravimetric analyzer (model APE2651B).

3. Results and discussion

3.1. Slag leaching behavior with acids

As shown in Fig. 1, the leaching rate of HS is higher than that of AS at the same concentration because the hydrogen ions become completely ionized in HCl solution and are free to react with Ca, Al and Fe, but HAc is not completely dissociated as it is a weak acid [24]. The total leaching rate of AS increases first then decreases as HAc concentration increases, and reaches a maximum of 38% at 4 M, whereas that of HS abruptly increases to 61% and then grows less when the concentration of HCl increases beyond 3 M.

To give an explanation for the downward trend in leaching rate of AS, an additional TG experiment was fulfilled. Fig. 2(a) shows the weight loss curves, which can be broadly divided into two categories. The first category is for the samples acidified by different concentrations of HAc ranging from 1 to 6 M, whose curves have the same shape, and there is no significant change during the heating process. The second category is for the samples treated by various concentrations of HAc ranging from 7 to 9 M whose peaks at 260 °C reach a maximum that can be ascribed to the decomposition of aluminum acetate hydroxide [25] and alumohydrocalcite [26,27]. The total weight loss of these samples is in the range of 17.4–19.0% at 600 °C, and no longer

Table 1
Chemical composition of the coal char ash, raw slag, AS and HS (wt.% expressed as equivalent oxide).

Mineral type	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	TiO₂	SO₃	K₂O	Na₂O	P₂O₅
Coal char ash	31.98	11.99	7.10	34.58	0.96	0.43	6.93	0.32	0.91	0.24
Raw slag	34.69	14.50	9.48	35.10	0.94	0.60	0.35	0.46	0.66	0.32
HAc-4M	56.64	16.62	10.56	11.33	0.82	0.67	0.03	0.74	0.70	0.41
HCl-4M	79.80	9.83	4.02	2.34	0.32	0.62	0.05	0.83	0.53	0.09