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Quantitative analysis of crystalline and amorphous phases in pulverized coal fly ash based on the Rietveld method

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ABSTRACT

High proportions of the amorphous phases with minor and variable amounts of crystalline phases (most commonly mullite and quartz) are the main components of pulverized coal fly ash (PCFA). As for the amorphous phase, it can be further subdivided into amorphous aluminum-silicon matrix (AASM) and amorphous silicon (AS), which show different reaction activity during subsequent applications. In the present work, a more comprehensive approach to evaluate the relative content of crystalline and amorphous phases in PCFA was proposed and verified. The results showed that the AS in PCFA can be removed by sodium hydroxide solution under certain leaching conditions, such as NaOH(aq) concentration ($^{<}$15%) and temperature ($^{<}$80 °C). The terminating point of the removal of AS was marked by the forming of hydroxysodalite ($Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$) in desilicated PCFA (De-PCFA). Based on the Rietveld method, the quantitative analysis of crystalline and amorphous phases in PCFA and De-PCFA was performed in turn; then the relative content of crystalline (mullite, quartz) and amorphous (AS, AASM) phases in PCFA can be obtained by calculation.

1. Introduction

Coal fly ash (CFA) produced from coal combustion and coal gasification is one of the largest amounts of industrial solid in the world. > 750 million tons of CFA is generated annually and its resource utilization attracts many researchers' attention [1–4]. So far, several major utilizations of CFA have been elaborated: it can be used for the production of building materials, for the synthesis of zeolites, and for the extraction of valuable elements [2–5]. With the development of these applications, research on the comprehensive understanding of the mineralogical compositions in CFA has been facilitated and developed.

Generally, the mineralogical compositions of CFA are associated with the quality of the coal burned and the technological process used. The most commonly known types of CFA are divided into pulverized coal fly ash, circulating fluidized-bed coal fly ash, and integrated gasification combined cycle coal fly ash, among which the pulverized coal fly ash (PCFA) is one of the most significant part [2,4]. Several studies have showed that high proportions of the amorphous phases with minor and variable amounts of crystalline phases (most commonly mullite and quartz) are the main components of PCFA [3–9]. In these studies, X-ray diffraction (XRD) has been traditionally regarded as a standard tool to investigate the relative content of the crystalline phases as well as of the amorphous content in PCFA. Based on XRD analysis, different methods have been employed to provide semi-quantitative results from the XRD pattern [3,4,10–15]. Especially for the Rietveld method, it was proposed by Hugo Rietveld firstly in 1967 for the characterization of crystalline compounds by neutron diffraction. In the following decades, it allowed one to obtain refined structural data or quantitative information on powder samples through least-squares fitting a calculated pattern to the corresponding experimental pattern [13–15]. During this modeling procedure, the theoretical line profiles are calculated by using structural data (i.e. space group, lattice parameters, atomic positions, etc.) in combination with a line shape model that takes into account the influence of different instrumental and sample-related effects on the peak profile of the diffraction reflections. The contents of each crystalline mineral were determined during this modeling procedure. Meanwhile, the content of amorphous phase is derived from the difference with the total content of the crystalline minerals [13,16,17]. Hence, the Rietveld method can be applied for the quantitative analysis of crystalline and amorphous phases in mixture.

Over the last decades, several works have been performed relied on the Rietveld method to quantitative analysis of the crystalline phases and the amorphous in PCFA. Chancey et al. [18] presented that a Class F fly ash was characterized by a high amorphous content (~77.3%) and

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Table 1
Chemical Compositions of the as-received PCFA sample.

Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	SO_3	MgO	Na_2O	Others
Contents (wt%)	46.20	32.30	4.56	1.99	1.33	1.26	1.02	0.51	0.43	10.4

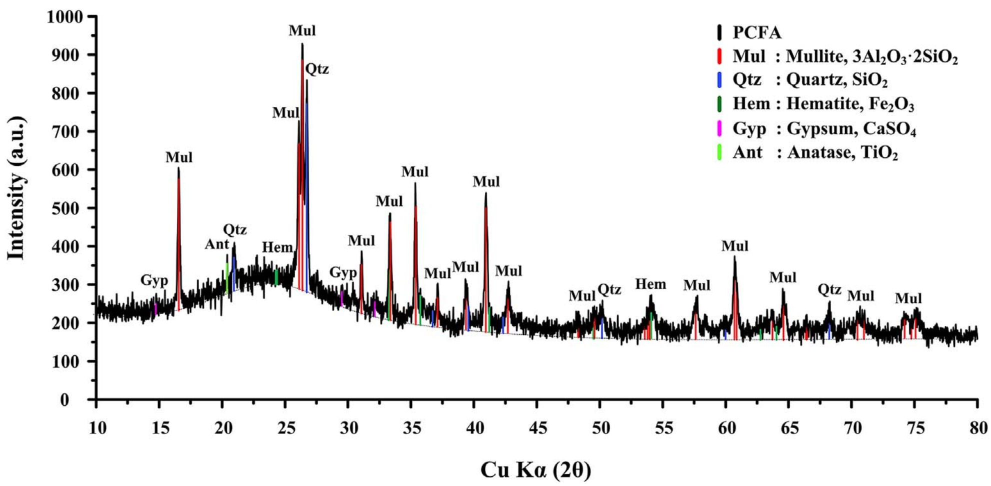

Fig. 1. XRD pattern of the as-received PCFA sample.

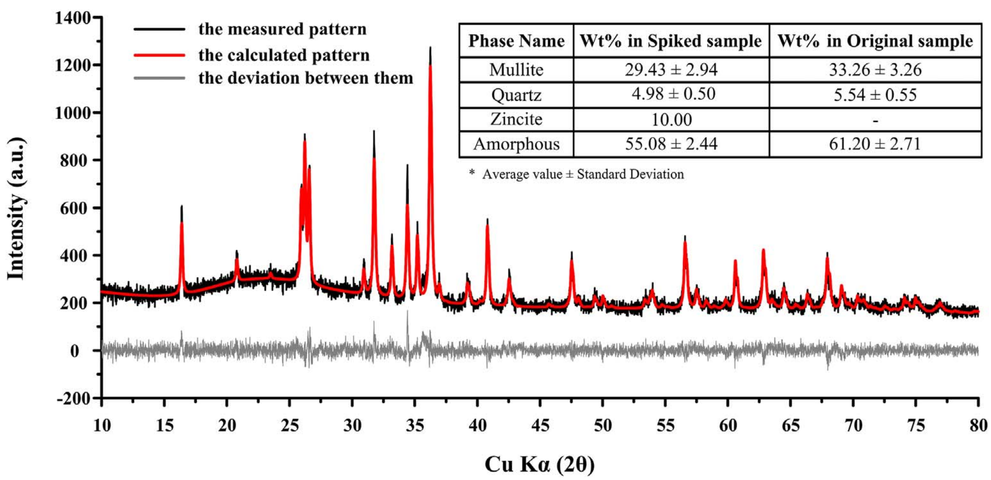

Fig. 2. Quantitative Rietveld analysis of the crystalline and amorphous phases in PCFA (R_{wp} = 7.21%). The amorphous content of this sample was obtained by spiking the sample with a known proportion of ZnO (10.00%) as internal standard.

relatively low contents of quartz (~16.3%), mullite (3.6%), maghemite (~2.1%), etc. [18]. Font et al. [4] and Ibáñez et al. [3] reported that mullite and quartz were the two main crystalline phases in PCFA from Spanish and Dutch, with concentrations up to ~16.3% and ~5%; meanwhile, it is concluded that the amorphous content of the used samples was in the range of 80–97% [3,4,9]. Merwe et al. [6] investigated an ultrafine South African coal fly ash sample and found it was predominantly composed of an amorphous alumina silica glass phase (62.1%), and the two main crystalline phases were mullite (31.8%) and quartz (6.1%) [6]. Cited works showed that the mineralogical composition of PCFA is expressed as high content of amorphous phase and low content of mullite and quartz. However, such researches do not further discern the mineralogical composition and content of the amorphous phase. As a matter of fact, the amorphous phase in PCFA may be mainly classified into two kinds: amorphous aluminum-silicon matrix (AASM) and amorphous silicon (AS). The AASM is the product of the thermal decomposition of clay minerals (most commonly kaolinite, illite and muscovite) in coal; and the AS formed during the further transformation from AASM to mullite. Take kaolinite for instance, the main chemical reactions are as follows:

$$\underset{(Kaolinite)}{Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O} \xrightarrow{500\sim900\ ^\circ C} \underset{\text{(AASM)}}{Al_2O_3{\cdot}2SiO_2}$$

$$\underset{\text{(AASM)}}{\mathrm{Al_2O_3{\cdot}2SiO_2}} \xrightarrow{>1000^\circ C} \underset{\text{(Mullite)}}{\mathrm{3Al_2O_3{\cdot}2SiO_2}} + \underset{\text{(AS)}}{\mathrm{SiO_2}}$$

Generally, the AASM and AS show different reaction activity and strongly influence the phase compositions of reaction product in their subsequent applications. A more comprehensive quantitative analysis of crystalline and amorphous phases in PCFA is of great importance. In this work, the quantitative analysis of the crystalline and amorphous phases in PCFA was performed by the Rietveld method firstly, and then a specific pretreatment was used to remove the AS in PCFA. After that the crystalline and amorphous phases in the prepared sample were also quantitatively analyzed using the identical Rietveld fitting procedure just as performed in PCFA. Based on that, a more comprehensive approach to evaluate the relative content of crystalline and amorphous phase in PCFA was provided.