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Characterization of geopolymers from compositionally and physically different Class F fly ashes

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ABSTRACT

The alkali-activation technology of coal fly ash is one of several potential solutions to minimize the harmful disposal of fly ash. This study reports high-resolution characterization of the alkali-activated reaction products for two representative Korean Class F fly ashes, which are significantly different in compositional and physical characteristics. The analysis confirms that differences in the network modifying element content, the amorphous phase content, and the particle size lead to large differences in compressive strength. Chabazite-Na and Al-rich chabazite-Na are identified as major crystalline phases in the high strength samples, supporting the favoring formation of ABC-6 family of zeolitic precursors for the higher mechanical strength while the C–S–H formation from the high CaO content (or crystalline CaO) is not a major source of the strength. The XRD analysis shows that the presence of amorphous humps located at 27–29° 2θ is not a sufficient indicator of geopolymeric gel formation. In the ^{29}Si MAS NMR, some portion of −108 ppm Q_4(0Al) peak is not related to quartz, implying that this portion of Si atoms actively participate in geopolymerization. The ^{27}Al MAS NMR spectra exhibit more conversion of Al(V) and Al(VI) aluminum atoms into Al(IV) units in the higher strength sample, which can be an indication of more geopolymeric reaction.

1. Introduction

Coal-fired power plants in South Korea generate approximately 5.29 million tons of fly ash a year. Despite the large consumption of fly ash in cement and concrete industries, a considerable portion of the ash is still buried in landfills in South Korea [1]. The fly ash disposal is potentially seriously harmful to the environment because a significant level of leachable toxic trace elements (e.g., Cd, Cu, As, etc.) in fly ashes may contaminate the water reservoir, soil or ocean, and thus the re-utilization of fly ashes is one of the top environmental issues [2].

Geopolymer has shown a superior potential as an environmentally alternative to portland cement since the binder gains comparable mechanical properties with a considerable reduction of CO_2 emission [3]. Geopolymer is synthesized by alkali-activation of an amorphous aluminosilicate material, and the term was firstly given to the alkali-activated metakaolin by Davidovits [4,5]. Typical alkaline activators are sodium hydroxide (NaOH) or sodium silicate [6]. The metakaolin-based geopolymer reaction product is an aluminosilicate gel and often called, 'zeolitic precursor' because the product has many structural and chemical similarities with synthesized zeolites [5].

Since metakaolin is chemically simpler and more amorphous than fly ash, the alkali-activation of metakaolin has yielded more reliable results than that of fly ash. However, the geopolymer production using coal fly ash has gained an elevated interest from construction fields because this can have a strong competitive price over portland cement in a market of concrete production due to the very low supply cost for fly ash [3].

Despite the importance of the alkali-activation of fly ashes, the reaction mechanism and products are not well understood as yet mainly because of the complexity of fly ashes and the amorphous nature of geopolymer to X-ray although the reaction product is believed to be geopolymer [3,7–9].

The inconsistent reactivity is an inevitable outcome of various material characteristics of fly ashes such as in oxide composition, particle size distribution, content of alkaline metals, content of glass phase, which significantly differ between fly ashes. Accordingly, fly ashes with different reactivities are expected to produce diverse reaction products, resulting in different compressive strengths [9]. The reactivity of coal fly ash for geopolymerization varies a lot from source to source or even in different batches from the same source [9,10]. Such a complex heterogeneity of fly ash

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Table 1
Chemical composition of original fly ashes.

Oxide	Weight %	
	FA1 raw fly ash (%)	FA2 raw fly ash (%)
SiO_2	65.2	51.8
Al_2O_3	23.9	20.0
CaO	2.0	10.1
Fe_2O_3	4.2	10.3
BaO	0.2	0.2
K_2O	1.4	1.0
MgO	0.7	2.0
MnO	0.0	0.1
TiO_2	1.0	1.2
P_2O_5	0.4	1.4
Na_2O	0.1	0.6
SO_3	0.3	0.9
SrO	0.1	0.1
ZrO_2	0.1	0.1
Tb_4O_7	0.0	0.2
MoO_3	0.3	0.0

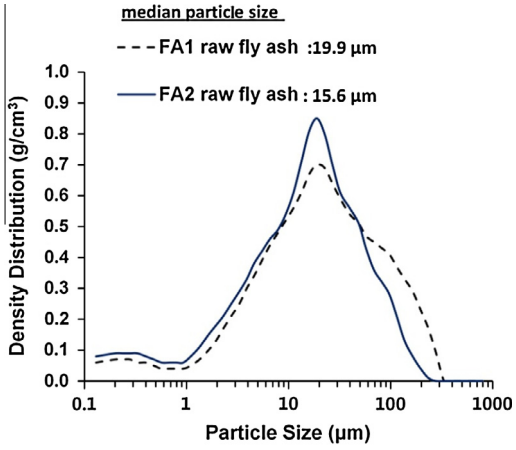


Fig. 2. Density distribution of particle size for fly ashes with median sizes.

leading to difficulties of quality control has been one of obstacles to commercial implementation of alkali-activated fly ash binders.

This study selected commercially representative two Class F fly ash sources in South Korea to explore the effects of the compositional and physical differences of the fly ashes on alkali-activated reaction products using powder X-ray diffraction (XRD), compressive strength testing, particle size distribution analysis, X-ray fluorescence (XRF), solid-state magic-angle-spinning nuclear magnetic resonance (MAS NMR) and synchrotron transmissive X-ray microscopy.

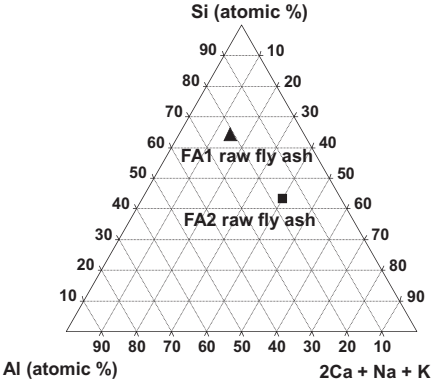
2. Experimental

Two Class F coal fly ashes (denoted FA1 and FA2) used in the present study were supplied from the largest coal-fired power plants, which are about 220 km apart each other, in South Korea.

The chemical compositions of the raw coal fly ashes are given in Table 1, determined by X-ray fluorescence spectrometer (Bruker S8 Tiger). The equivalent elemental compositions for major elements were graphically summarized in Fig. 1.

Although the use of sodium silicate as an activator generally produces much stronger matrices, it generally causes the reaction products to be more amorphous to X-ray, which makes it difficult to analyze the XRD results [11,12]; thus, this study activated the ashes using only NaOH solution with a relatively high curing temperature of 60 °C to increase the crystallinity of the hardened ashes.

The fly ashes were alkali-activated with 5M (denoted '5M' in the sample label) NaOH solution made from a reagent grade of NaOH pellets (Sigma–Aldrich). The solution to solid binder weight ratio (s/b) of samples was fixed to 0.6 to attain suitable consistency



In-let table of composition

Element	Atomic %	
	FA1 raw fly ash	FA2 raw Fly ash
Si	58.6%	40.9%
Al	19.4%	15.7%
Ca	3.9%	15.7%
Fe	9.0%	18.7%
Mg	0.5%	1.7%
Na+K	3.2%	2.3%
2Ca+Na+K+2Mg	12.1%	37.3%
Si/Al (atomic ratio)	3.0	2.6
Ca/Si (atomic ratio)	0.1	0.4

Fig. 1. Triangular compositional plot for original fly ashes used in this investigation.

Table 2
Compressive strengths of hardened samples.

Fly ash	Sample label (fly ash-solution-temp.)	Solution/fly ash (wt./wt.)	NaOH solution (M)	Curing temperature (°C)	1-day Curing		28-day Curing	
					Strength (MPa)	Stdev[a] (MPa)	Strength (MPa)	Stdev[a] (MPa)
FA1	FA1-5M-60C	0.6	5.0	60	1.3	0.3	8.7	2.2
FA2	FA2-5M-60C	0.6	5.0	60	6.6	0.9	41.6	12

[a] Stdev: standard deviation of strength test results.