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The importance of the network-modifying element content in fly ash as a simple measure to predict its strength potential for alkali-activation

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ABSTRACT

Six different Class F fly ashes were examined to identify the material properties that determine the strength development in geopolymerization. All of the fly ashes displayed typical features of Class F fly ash in chemical and mineral composition, amorphous phase (glass) content, and X-ray diffraction pattern profile; however, the strength developments of the ashes were quite different from each other. The results suggest that the strength is higher under the following configuration: greater content of network modifying elements, greater glass content, lower silicon content, lower intensity of quartz-related ^{29}Si NMR peak, and higher fraction of Al(IV) in the ^{27}Al NMR spectrum. Among the possibilities, the network-modifying elemental content may be the simplest and most accurate measure for strength development of alkali activation of fly ash.

1. Introduction

The demand for the production of concrete continues to increase, even as concerns over global warming and sustainability increase. The cement manufacturing industry releases approximately 0.81.0 ton of CO_2 for every ton of cement clinker produced and is responsible for 7% of total man-made CO_2 emissions [1]. Globally, over 750 million tons of coal fly ash – an industrial by-product waste of coal-fired power plants – are generated annually. Despite increasing consumption by the construction industry as an additive to concrete mixtures, the amount over 40% is still treated as waste, resulting in serious environmental hazards. Thus, the recycling of this waste is of significant importance in terms of sustainability [2].

Alkali activation of an aluminosilicate-rich materials is a sustainable technology that converts the reactive aluminosilicate phase (commonly amorphous or semi-amorphous portion) of the material into a strong binder (called an alkali-activated binder). The development of alkali-activated binders using industrial by-products such as a coal fly ash has gained greater attention from both academia and industry: coal fly ash can replace Portland cement, thereby reducing CO_2 emissions by up to 80% in cement production; in addition, the binders used may be more price competitive than those used in Portland cement [3–5].

The reaction mechanism and products of alkali activation of fly ash are not yet well understood because of the complexity of fly ash in chemical reactions. What is known is that the reaction product is considered to be a geopolymer [3,4,6–8]. Geopolymers are strong alkali-activated amorphous aluminosilicate materials; the term was originally used for the alkali activation of metakaolin [9]. Chemically simpler in oxide composition than fly ash and nearly amorphous, the alkali activations of metakaolins have displayed more consistent results than those of fly ashes [3].

The strength development of alkali-activated fly ash principally depends on the physical and chemical nature of fly ash (e.g., particle size, oxide composition, or amorphous content), activator (e.g., type or dosage of activator), and curing conditions (e.g., temperature, humidity or period) [4,6,10–16]. Most previous works have not focused much on the materials properties of fly ash possibly because the nature of fly ash varies greatly from source to source, and thus, it is very difficult to identify consistent governing factors of fly ash properties that determine the strength of the alkali-activated fly ash matrix.

Attempts to perform quantitative analysis of fly ashes are increasing [12,17,18]; however, there have been only a few efforts to combine the characteristics of fly ashes with the reactivity of alkali activation of fly ashes in terms of mechanical strength

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[10,11,16,19–22] though these are essential to understanding the governing nature of coal fly ashes and for future applications in industry.

The current study examined six different sources of Class F fly ashes, with the aim of identifying the governing factors that determine the mechanical strength of alkali-activated fly ashes. The following methods were employed: X-ray fluorescence, powder X-ray diffraction (XRD), particle size distribution analysis, magic-angle-spinning nuclear magnetic resonance (MAS NMR), and compressive strength testing.

2. Experimental

Six different coal fly ashes (denoted FA1 to FA6) were obtained from six different coal-fired power plant locations in South Korea. The oxide chemical compositions of the raw fly ashes were determined using a Bruker S8 Tiger wavelength dispersive X-ray fluorescence (XRF) spectrometer. The mineralogical composition and weight % of the amorphous phase of fly ashes were tested by powder X-ray diffraction. The X-ray diffraction (XRD) patterns were recorded with a Rigaku high power X-ray diffractometer, employing Cu Kα radiation (λ = 1.5418 Å) with 2θ scanning range of 5–60°. Accurately weighed 10% crystalline Al_2O_3 (NIST RMS 676a, crystalline alumina 99.02% ± 1.11%) relative to fly ash powder was mixed as an internal standard [23] to estimate the content of amorphous phase in the fly ashes. The particle size distributions of the raw fly ashes were determined with a Sympatec HELOS laser diffraction particle size analyzer with a RODOS dispersing unit.

Solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were collected using an AVANCE II 400 MHz Bruker NMR instrument (at KBSI Daegu Center in Korea), with a magnetic field strength of 9.4 T and ZrO_2 4 mm rotors at room temperature. ^{29}Si MAS-NMR spectra were obtained under conditions of proton decoupling with a 30° pulse, a pulse repetition delay of 100 s, which was long enough to differentiate quartz signal, for quantitative analysis and a spinning rate of 10 kHz; ^{27}Al MAS-NMR spectra were acquired with a 30° pulse, a repetition delay time of 3 s for quantitative analysis, and a sample spinning rate of 14 kHz. The recorded chemical shift spectra of ^{29}Si and ^{27}Al were referenced relative to tetramethylsilane (TMS) at 0.0 ppm and 1 M $AlCl_3$(aq.) at 0.0 ppm, respectively.

The coal fly ashes were alkali activated with 5 M (denoted '5M' in the sample label) and 10 M (denoted '10M' in the sample label) NaOH solutions made from analytical grade NaOH pellets (Sigma–Aldrich). To obtain appropriate consistency of all the pastes, the solution to solid binder weight ratio (s/b) of the samples was set to 0.6. Triplicate paste mixtures were cast in 2.54 × 2.54-cm cylinder molds for each axial compressive strength test. All the samples

Table 2
Chemical composition of coal fly ashes.

Oxide	Weight (%)					
	FA1	FA2	FA3	FA4	FA5	FA6
SiO_2	65.2	51.8	63.2	56.0	62.2	54.1
Al_2O_3	23.9	20.0	19.1	23.9	22.8	23.3
CaO	2.0	10.1	4.0	4.9	3.1	4.6
Fe_2O_3	4.2	10.3	8.3	7.7	6.0	9.7
BaO	0.2	0.2	0.1	0.2	0.1	0.2
K_2O	1.4	1.0	1.2	1.8	1.6	3.0
MgO	0.7	2.0	1.2	1.3	1.0	1.6
MnO	0.0	0.1	0.1	0.1	0.1	0.1
TiO_2	1.0	1.2	1.1	1.3	1.3	1.0
P_2O_5	0.4	1.4	0.3	0.6	0.3	0.2
Na_2O	0.1	0.6	0.4	0.8	0.6	1.3
SO_3	0.3	0.9	0.7	0.7	0.6	0.6
SrO	0.1	0.1	0.1	0.2	0.1	0.1
ZrO_2	0.1	0.1	0.1	0.1	0.1	0.0
Tb_4O_7	0.0	0.2	0.0	0.1	0.0	0.0
MoO_3	0.3	0.0	0.0	0.0	0.0	0.0

Table 1
Mixture proportions and compressive strength testing results of alkali-activated fly ash samples.

Fly ash	Sample label (fly ash-solution-temp.)	Solution/fly ash (wt./wt.)	NaOH solution (M)	Curing temperature for the first 24 h (°C)	Compressive strength (MPa) with standard deviation			
					7-Day	7-day Average	28-Day	28-day Average
FA1	FA1-5M-30C	0.6	5	30	0.0 ± 0.0	0.9	2.7 ± 0.3	2.4
	FA1-5M-60C	0.6	5	60	1.4 ± 0.0		1.8 ± 0.3	
	FA1-10M-30C	0.6	10	30	0.0 ± 0.0		0.9 ± 0.2	
	FA1-10M-60C	0.6	10	60	2.1 ± 0.8		4.3 ± 0.7	
FA2	FA2-5M-30C	0.6	5	30	1.4 ± 0.2	4.1	12.2 ± 2.0	9.4
	FA2-5M-60C	0.6	5	60	7.4 ± 1.6		9.9 ± 1.7	
	FA2-10M-30C	0.6	10	30	1.5 ± 0.2		6.5 ± 1.3	
	FA2-10M-60C	0.6	10	60	6.1 ± 0.8		8.9 ± 1.5	
FA3	FA3-5M-30C	0.6	5	30	0.0 ± 0.0	1.3	1.3 ± 0.1	2.7
	FA3-5M-60C	0.6	5	60	1.6 ± 0.1		2.9 ± 0.4	
	FA3-10M-30C	0.6	10	30	0.3 ± 0.2		1.0 ± 0.2	
	FA3-10M-60C	0.6	10	60	3.5 ± 0.1		5.8 ± 0.4	
FA4	FA4-5M-30C	0.6	5	30	0.0 ± 0.0	2.3	2.7 ± 0.4	3.6
	FA4-5M-60C	0.6	5	60	2.7 ± 1.1		4.9 ± 0.0	
	FA4-10M-30C	0.6	10	30	0.7 ± 0.2		2.7 ± 0.2	
	FA4-10M-60C	0.6	10	60	5.9 ± 0.3		4.2 ± 0.3	
FA5	FA5-5M-30C	0.6	5	30	0.0 ± 0.0	1.5	2.6 ± 0.3	2.8
	FA5-5M-60C	0.6	5	60	3.0 ± 0.7		4.1 ± 0.6	
	FA5-10M-30C	0.6	10	30	0.0 ± 0.0		0.1 ± 0.2	
	FA5-10M-60C	0.6	10	60	3.0 ± 0.3		4.3 ± 0.3	
FA6	FA6-5M-30C	0.6	5	30	0.1 ± 0.1	1.9	7.4 ± 0.5	4.9
	FA6-5M-60C	0.6	5	60	3.4 ± 0.7		5.7 ± 0.3	
	FA6-10M-30C	0.6	10	30	0.0 ± 0.0		2.6 ± 0.3	
	FA6-10M-60C	0.6	10	60	4.3 ± 0.7		4.0 ± 1.0	