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Geopolymerization of Coal Ash to Produce Cementless Binders†

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A B S T R A C T

The main objective of this study was to evaluate geopolymer concrete made from coal combustion by-products, disposed of in landfills, as a potential substitute for the ordinary Portland cement (OPC), which is responsible for 5-8% of the total CO_2 emissions in the world.

In this study, a coal fly ash sample from the Carolinas was used in a chemical process known as geopolymerization to produce a "geopolymer" binder. The developed geopolymer binder could competently substitute the OPC binder in regular concrete applications. An experimental design program was conducted to optimize parameters of the geopolymerization affecting the strength of the final cementless concrete product. Mortar and concrete samples were made to compare the strength of geopolymer with OPC concrete. The results showed that the compressive strength of geopolymer-based products were more than 6700 psi for mortars and 5750 psi for concrete samples, which could effectively compete with OPC concrete. This paper presents the results of the experiments and discusses the effectiveness of the produced cementless binder.

A R T I C L E I N F O

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1. Introduction

In 2015, about 117 million tons of coal combustion by-products (CCBs) was generated in the United States. However, only about 61 million tons of CCBs was consumed in different applications including the concrete industry, agriculture, structural fills, road base and subbase, soil modification, roofing granules, and mining applications (American Coal Ash Association [ACAA], 2015). The remainder of the CCBs was disposed of in landfills and ponds, which could be a hazard to the environment and to drinking water resources. This has led to short- and long-term effects on the communities surrounding these ponds. There have also been several coal ash spills into the rivers that maintain the drinking water supply for downstream communities. Some main coal ash leakages include the spill in Roane County, TN, in December 2008 and in Eden, NC, in February 2014.

Ordinary Portland cement (OPC), which is widely used in the construction industry, is responsible for ~7% of the total CO_2 emissions in the world (Intergovernmental Panel on Climate Change, 2005). The main part of Portland cement production is the pyroprocessing system in which the raw materials are transformed into clinkers. During this process, substantial amounts of CO_2 are generated and released into air. Depending on the conditions of the reactions, production of 1 ton of OPC releases ~0.85 to 1.35 tons of CO_2 into the atmosphere. In addition, other volatile organic pollutants such as CO are emitted during pyroprocessing (U.S. Environmental Protection Agency, 1995).

The cement production and construction industries have made significant progress in reducing CO_2 emissions since it has been one of the main priorities. Improving the reactions in pyroprocessing and partially substituting Portland cement with alternative cementious materials, including fly ash, bottom ash, and boiler slag, are some of the attempts that have been made (Lovell et al., 1997;

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Naik et al., 1997; Korcak, 1998; ACAA, 2015; Kumar and Stewart, 2003a, b; Higgins, 2009). There have also been significant developments in finding new binders that can completely replace Portland cement binder in concrete (Rangan, 2008). Geopolymer binder is one of the binders that has been the focus of studies to substitute OPC binder in concrete applications.

The geopolymer concept was first introduced by Joseph Davidovits in 1979 when he explained that alkaline metals react with high Al-Si–rich materials and produce a three dimensional alumino-silicate complex with a strong bindery network of Al-Si elements. The raw materials for making geopolymer binder could be any high Al-Si material including natural minerals such as kaolinite and clays and wastes such as fly ash, bottom ash, red mud, and rice-husk. Equation 1 shows a polymerization in which Al-Si elements react with alkaline metals and produce a polymer product:

$$\text{Si-Al materials} + \text{activators (NaOH, Na}_2\text{SiO}_3\text{, KOH)} + \text{water} \rightarrow \text{geopolymer binder} + \text{water} \quad (1)$$

Because the raw materials are inorganic, the new product and reaction were named geopolymer and geopolymerization, respectively (Davidovits, 1988). Geopolymer is one of the introduced solutions to two above-mentioned environmental issues, i.e., disposal of CCBs in ponds and high CO_2 emissions of OPC production. Different raw materials that are rich in Al-Si, such as fly ash, bottom ash, and slags, have been used to generate geopolymer binders to replace OPC in concrete application in the construction industry (Xu and Van Deventer, 2000). This leads to reduction in OPC consumption and consequently to a decline in the CO_2 emissions. Other advantages of geopolymers include reduction in waste materials such as fly ash and bottom ash, less water consumption in comparison to OPC, less mining activities and natural minerals use, and higher resistance to fire and corrosion. Successful use of geopolymer concrete in different applications such as building products, reinforced concrete beams, fire resistance materials, railway sleepers, encapsulation of toxic metals, and high-temperature materials has been reported by many researchers (Balaguru et al., 1997; Palomo et al., 2004; Hardjito and Rangan, 2005; Wallah and Rangan, 2006; Komnitsas and Zaharaki, 2007; Diaz et al., 2009; Akbari et al., 2013). Some challenges faced by geopolymer products are lack of long-term durability data, lack of standard methods that measure the performance of geopolymers, and the conservative nature of the construction industry (Duxson et al., 2007). In this study, a coal fly ash sample from the Carolinas, a high Al-Si–rich material, was used to produce geopolymer binder that could replace OPC binder in concrete applications.

2. Materials and Methods

2.1. Sample collection and characterization

A coal fly ash sample was collected from a coal-fired power plant in the Carolinas and brought to the Minerals Research Laboratory of North Carolina State University located in Asheville. The X-ray fluorescence (XRF) analysis was conducted to characterize the fly ash sample. The results of the XRF test are shown in Table 1; they clearly show that the sample was rich in aluminum oxide and silica, making it a suitable raw material for geopolymerization. Moreover, the ratio of silica to aluminum oxide was ∼2, an ideal value for concrete applications.

Table 1
X-ray fluorescence (XRF) analysis results of the Carolinas fly ash sample

	Component						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	LOI[1]
Analysis (%)	46.15	22.13	17.72	2.80	0.64	1.95	4.06

[1] The loss on ignition (LOI) is measured with the ASTM procedure rather than by XRF.

2.2. Geopolymer binder production

The collected fly ash sample was used to produce geopolymer binder to replace the OPC binder in commercial concrete. To evaluate the suitability of the Carolinas fly ash sample as a construction material, preliminary tests were conducted to determine the important parameters affecting geopolymerization. There are more than 20 parameters that affect the final geopolymer product; five were selected to be the most important variables. The experimental design program was used to determine critical parameters affecting the strength of the final geopolymer product. Sodium silicate (Na_2O, 14.7%; SiO_2, 27.4%; H_2O, 55.95%) and sodium hydroxide were applied as the alkaline activators in this study. In the first phase, 5.08-cm (2-inch) mortar cubes of geopolymer composites were prepared and tested to obtain their compressive strength. The fine sand–to–fly ash mass ratio for these cubes was 2.75, with an alkaline liquid–to–fly ash mass ratio of 0.35. To prepare the mortar cubes, fly ash and fine sand were first dry mixed in a concrete mixer for 3 minutes. Then, sodium silicate and sodium hydroxide, already mixed before starting the tests, were added gradually to the dry mixture along with water and mixed for another 10 minutes. The mixture was poured into 5.08-cm molds to form mortar cubes. After molding samples, the cubes were put in an oven with varying temperatures for curing and then at ambient temperature for aging. In addition, mortar cubes were made with OPC to compare their compressive strength with geopolymer samples. The optimized formulation used to make OPC mortar cubes was obtained from previous studies. These cubes were cured in water at ambient temperature.

Furthermore, concrete cylinders with a diameter of 10.16 cm (4 inches) and a height of 20.32 cm (8 inches) were made using coarse and fine aggregates to further compare geopolymer and OPC binders in concrete application. The design of these cylinders is shown in Table 2. Figure 1 shows some cubes and cylinders made in this study.

Table 2
Design of concrete cylinders for comparison of geopolymer and ordinary Portland cement (OPC) binders

Composition	OPC concrete (%)	Geopolymer concrete (%)
OPC	13.7	–[1]
Fly ash	–	12.8
Fine aggregate (sand)	33.6	33.8
Coarse aggregate	44.7	47.4
Water	8.0	1.5
NaOH (19 M)	–	1.3
Na_2SiO_3	–	3.2
Total concrete	100.0	100.0

[1] – = the compound is not present or it is 0.

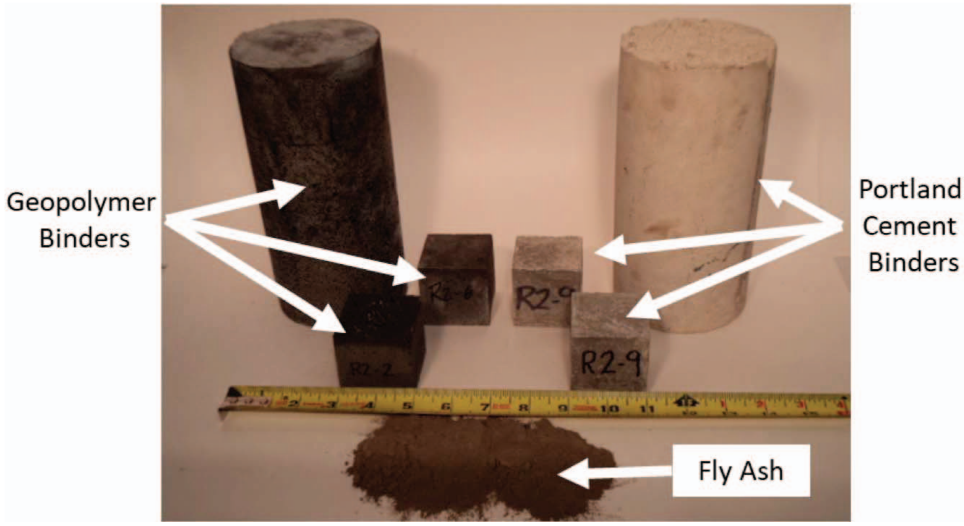

Fig. 1. Geopolymer binders made from the Carolinas fly ash vs. ordinary Portland cement binders.

3. Results and Discussion

Geopolymer binder is a product of geopolymerization in which high Si-Al-rich materials react with alkaline metals to generate a very strong bindery network of Si and Al elements. To optimize the parameters of geopolymerization, an experimental program was designed and used. Preliminary tests showed that five parameters—sodium hydroxide concentration, sodium silicate-to-sodium hydroxide mass ratio, water-to-sodium oxide mass ratio, curing temperature, and curing time—were the important parameters affecting the final geopolymer product. A fractional factorial design was used to determine the critical process parameters among these five factors. The results of the experimental program (Figure 2) indicated that the mass ratio of water to sodium oxide and sodium silicate to sodium hydroxide were the most critical parameters affecting the compressive strength of the geopolymer concrete.

Mortar cubes and concrete cylinders were tested on different days to establish the curves, showing the relation between compressive strength and age. Figure 3 compares the results of compressive strength tests conducted on mortar cubes of geopolymer and OPC binders. Figure 3 also shows that the strength of both geopolymer and OPC cubes increased by aging. Moreover, the compressive strength of geopolymer or cementless binder was always higher than that of the regular cement binder. After 63 days, geopolymer binder showed a compressive strength of 6700 psi in comparison to 5800 psi for OPC (Figure 3).

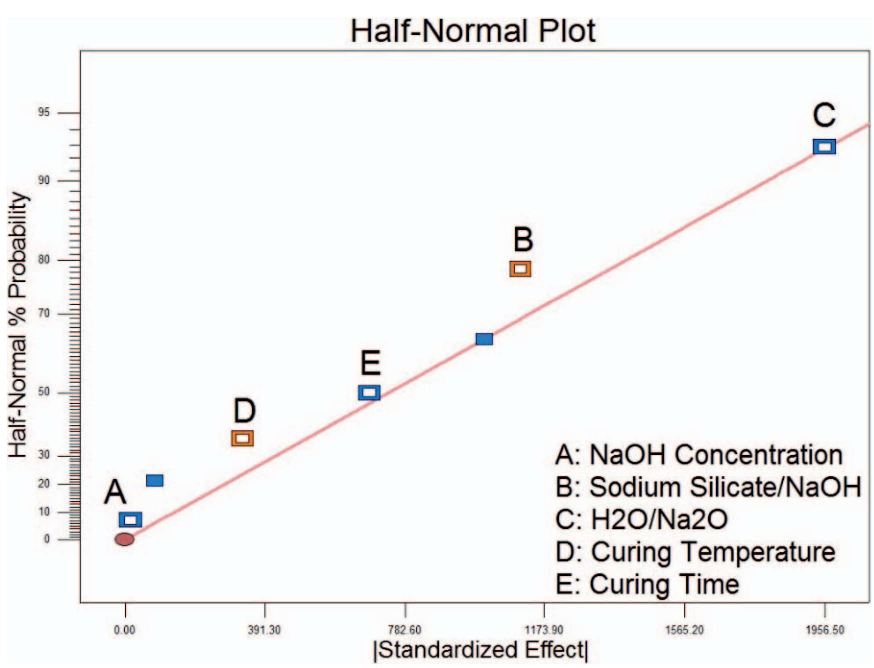

Fig. 2. Critical parameters affecting the compressive strength of geopolymer concrete.

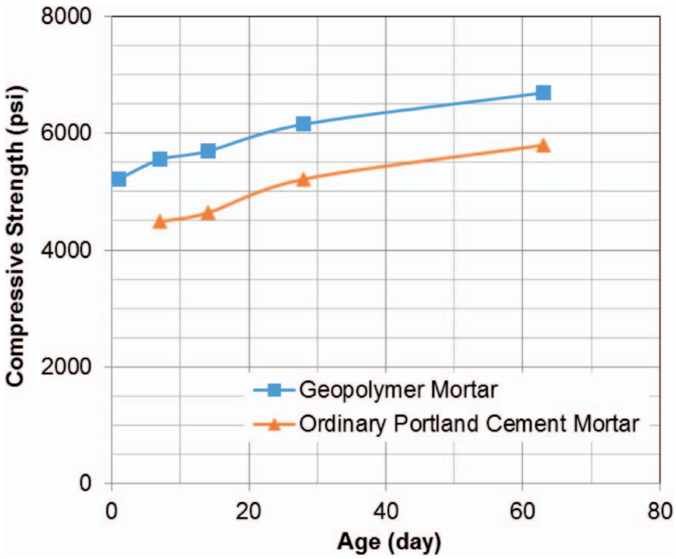

Fig. 3. Comparing the geopolymer and ordinary Portland cement mortar samples.

Promising results obtained from mortar cubes led to the next phase of this study, which was producing concrete cylinders with a diameter of 10.16 cm and a height of 20.32 cm by adding coarse and fine aggregates to the mixtures. In this phase, preliminary concrete cylinders were made and tested for their strength. Figure 4 shows the results of compressive strength tests conducted on cylinders made with geopolymer composites and OPC. The compressive strength of both geopolymer and OPC concrete increased with age; however, OPC showed a sharper increase during the first 14 days. After that, the strength of both geopolymer and cement concrete increased at almost the same rate. Finally, after 60 days, the compressive strength of geopolymer and OPC concrete reached 5750 and 6550 psi, respectively (Figure 4). These results showed that geopolymer could successfully compete with OPC and also clearly support the objective of this study: to show the suitability of the Carolinas fly ash in producing strong geopolymer binders.

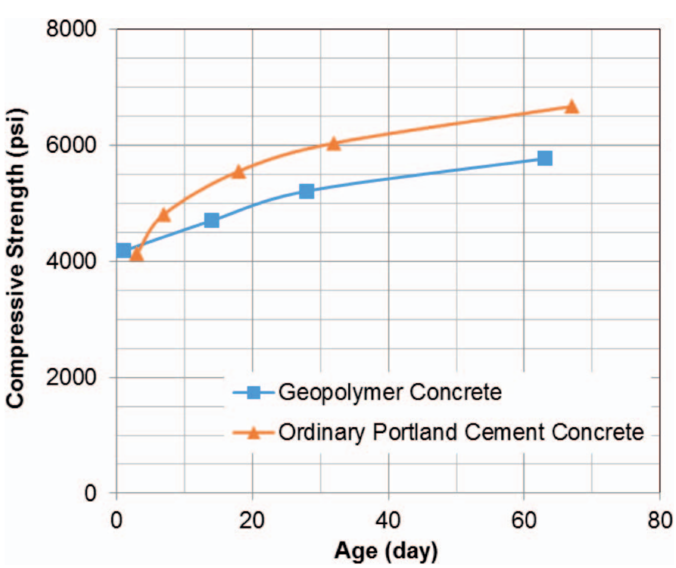

Fig. 4. Comparing the geopolymer and ordinary Portland cement concrete samples.

The geopolymer concrete cylinders showed a slightly lower compressive strength than OPC, whereas the same result was not observed for geopolymer mortar cubes. As mentioned, there are more than 20 parameters affecting the geopolymerization reaction through which the Si-Al binder is generated. Therefore, the strength of the final geopolymer product is directly affected by the process parameters and their interactions. In this study, the most important parameters were investigated and optimized and the values for other less important parameters were assumed from previous studies. Moreover, the addition of coarse aggregate in the concrete cylinders might affect the geopolymerization reaction and consequently the strength of the final binder. It should be noted that the main objective of this study was to evaluate the competency of the geopolymer concrete in substituting the OPC in some applications. The results of mortar cube and concrete cylinder tests showed that the compressive strength of geopolymer and OPC samples varied in the range of less than 16%, indicating that the geopolymer binder could successfully compete with the OPC.

4. Conclusions

In this study, a fly ash sample from a coal-fired power plant in the Carolinas was collected and tested to investigate its suitability in producing geopolymer binder to replace OPC binder in concrete applications. An experimental design program was applied to determine the critical parameters of geopolymerization affecting the compressive strength of the final geopolymer binder used in concrete applications. The tests identified that the mass ratio of water to sodium oxide and sodium silicate to sodium hydroxide to be the most critical geopolymerization parameters. Compressive strength tests conducted on mortar cubes showed that geopolymer binders reached a value of 6700 psi after 63 days, which was more than that for OPC binder with a value of 5800 psi. Moreover, the results of concrete cylinders showed that the compressive strength of geopolymer and OPC cylinders at the 60th day was 5750 and 6550 psi, respectively. These findings revealed that the compressive strength of the geopolymer and OPC samples varied in the range of less than 16%, indicating the suitability of the Carolinas fly ash in making the geopolymer or cementless concrete to compete with the OPC concrete.

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