Production of Geopolymer Binder from Coal Fly Ash to Make Cement-less Concrete

Hamid Akbari[1], Robert Mensah-Biney[1], Jonathan Simms[1]

[1] Minerals Research Laboratory, North Carolina State University, 180 Coxe Ave, Asheville, NC 28801

KEYWORDS: coal fly ash, Coal Combustion By-products (CCBs), geopolymer binder, geopolymer concrete, cement-less concrete, Ordinary Portland Cement (OPC) concrete, CO_2 emissions, waste materials, environment.

ABSTRACT

In 2012, more than 100 million tons of Coal Combustion By-products (CCBs) were generated in the USA out of which more than 50% was disposed of in ponds and landfills as tailing materials that could be hazardous to the environment. The other environmental issue is related to Ordinary Portland Cement (OPC), a raw material for construction industry, which is responsible for 5-8% of the total CO_2 emissions in the world. Production of one ton OPC generates one ton of CO_2, a greenhouse gas affecting global warming. Therefore, the main objectives of this study were to address these two environmental challenges through finding a new application for CCBs stored in landfills, and replacing OPC by a new binder to reduce CO_2 emissions. "Geopolymer" or cement-less concrete is the solution to these challenges.

In this study, a coal fly ash sample from Carolina was used in a chemical process known as geopolymerisation to produce a new binder named geopolymer. The developed geopolymer binder could competently substitute the OPC binder in regular concrete application. An experimental design program was conducted to optimize parameters of the geopolymerisation process affecting the strength of the final cement-less 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 at the 60^{th} day could be more than 6600 psi for mortars and 5700 psi for concrete samples which effectively compete with OPC. This paper presents the results of the experiments and discusses the effectiveness of the new cement-less binder.

INTRODUCTION

In 2012, around 110 million tons of Coal Combustion By-products (CCBs) were generated in the US. However, only about 52 million tons of CCBs were consumed in different applications including concrete industry, agriculture, structural fills, road base and sub-base, soil modification, roofing granules, mining application, etc[1]. The remainder CCBs were disposed of in landfills and ponds which could be hazarding the environment and 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 which maintain the drinking water for downstream communities. Some main coal ash leakages include the spill in Roane County, Tennessee in December 2008 and in Eden, North Carolina in February 2014.

Ordinary Portland Cement (OPC), which is widely used in construction industry, is responsible for about 7% of the total CO_2 emissions in the world[2]. 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 is generated and released into air. Depending on the conditions of reactions, production of one ton of OPC releases about 0.85 to 1.35 tons of CO_2 into the atmosphere[3]. In addition, other volatile organic pollutants such as CO are emitted during the pyroprocessing system[3]. 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 system and partially substituting Portland cement by alternative cementious materials including fly ash, bottom ash, and boiler slag are some of the attempts have been made[1, 4, 5, 6, 7, 8, 9]. There have also been significant development in finding new binders which can completely replace Portland cement binder in the concrete[10]. "Geopolymer" binder is one of the new binders that have been focused especially in recent years to substitute OPC binder in concrete applications.

"Geopolymer" concept was first introduced by Joseph Davidovits in 1979 when he explained that alkaline metals react with high rich Al-Si materials and produce a three dimensional alumino-silicate complex with a strong bindery network of Al-Si element. 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, rice-husk, etc. Equation 1 shows the polymerization process in which Al-Si elements react with alkaline metals and produce a polymer product. Because the raw materials are inorganic, the new product and the reaction were named "Geopolymer" and "Geopolymerization", respectively[11].

$$\mathrm{Si-Al\ Materials + Activators\ (NaOH, Na_2SiO_3, KOH) + Water \rightarrow Geopolymer\ binder + Water} \quad (1)$$

Geopolymer is one of the recently introduced solutions to two above-mentioned environmental issues, i.e. disposal of CCBs in ponds and high CO_2 emissions of OPC production. During past years, different raw materials which are rich in Al-Si such as fly ash, bottom ash, and slags, have been used to generate geopolymer binders in order to replace OPC in concrete application in construction industry[12]. This leads to reduction in OPC consumption and consequently, 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 utilization, 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, high temperature materials, etc., has been reported by many researchers[13, 14, 15, 16, 17, 18]. Some challenges that are faced by this new technology are lack of long term durability data, lack of standard methods which measure the performance of geopolymers, and conservative nature of construction industry[19]. In this study, the coal fly ash from Carolina, a high rich Al-Si material, was used to produce geopolymer binder which could replace OPC binder in concrete application.

MATERIALS AND METHODS

Sample collection and characterization. A coal fly ash sample was collected from a coal-fired power plant in Carolina and brought to the North Carolina State University Minerals Research Laboratory (MRL) located in Asheville, North Carolina. The XRF analysis was conducted to characterize the fly ash sample. The results of the XRF test is shown in Table 1. It is clear from Table 1 that the sample is rich in aluminum oxide and silica making it a suitable raw material for the geopolymerisation process. Moreover, the ratio of silica to aluminum oxide is around 2 which is ideal for concrete applications.

Table 1: The XRF analysis results of the Carolina fly ash sample.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	L.O.I.
Analysis (%)	46.15	22.13	17.72	2.80	0.64	1.95	4.06

Geopolymer Binder Production. The collected fly ash sample was used to produce geopolymer binder in order to replace OPC binder in commercial concrete. To evaluate the suitability of Carolina fly ash sample as a construction material, preliminary tests were conducted to determine the important parameters affecting geopolymerisation process. There are more than 20 parameters that affect the final geopolymer product out of which five were selected to be the most important variables. Experimental design program was used to determine critical parameters affecting the strength of 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, 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 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 2-inch molds to form mortar cubes. After molding samples, the cubes were put in an oven with varying temperature for curing and then at ambient temperature for aging. Additionally, mortar cubes were made with OPC to compare their compressive strength with geopolymer samples. The OPC cubes were cured in water at ambient temperature.

In addition, concrete cylinders with diameter of 4 inch and height of 8 inch were made using coarse and fine aggregate to further compare geopolymer and OPC binders in concrete application. The design of these cylinders are shown in Table 2.

Table 2: The design of concrete cylinders for comparison of geopolymer and OPC binders.

Composition	Ordinary Portland Cement Concrete (%)	Geopolymer Concrete (%)
Ordinary Portland Cement	13.7	-
Fly Ash	-	12.8
Fine Aggregate (Sand)	33.6	33.8
Coarse Aggregate	44.7	47.4
Water	8.0	1.5
NaOH (19M)	-	1.3
Na_2SiO_3	-	3.2
Total Concrete	100.0	100.0

RESULTS AND DISCUSSION

Geopolymer binder is a product of geopolymerisation process in which high Si-Al materials react with alkaline metals to generate a very strong bindery network of Si and Al elements. To optimize the parameters of geopolymerisation process, an experimental program was designed and used. Preliminary tests showed that five parameters including sodium hydroxide concentration, sodium silicate to sodium hydroxide mass ratio, water to sodium oxide mass ratio, curing temperature, and curing time are the important parameters affecting the final geopolymer product. A fractional factorial design was used to determine the critical process parameters among these five factors. Figure 1 shows the cubes and cylinders made in this study. The results of experimental program showed that sodium hydroxide concentration, curing temperature, and water to sodium oxide mass ratio were the most critical parameters in geopolymerisation process.

Figure 1: Geopolymer binders made from Carolina fly ash vs. OPC binders.

Mortar cubes and concrete cylinders were tested for different days to establish the curves showing relation between compressive strength and age. Figure 2 compares the results of compressive strength tests conducted on mortar cubes of geopolymer and OPC binders. Figure 2 clearly shows that the strength of both geopolymer and OPC cubes increases by aging. Moreover, the compressive strength of geopolymer or cement-less binder is always higher than that of the regular cement binder. For example, at the 63rd day, geopolymer showed a compressive strength of 6700 psi in comparison to 5800 psi for OPC.

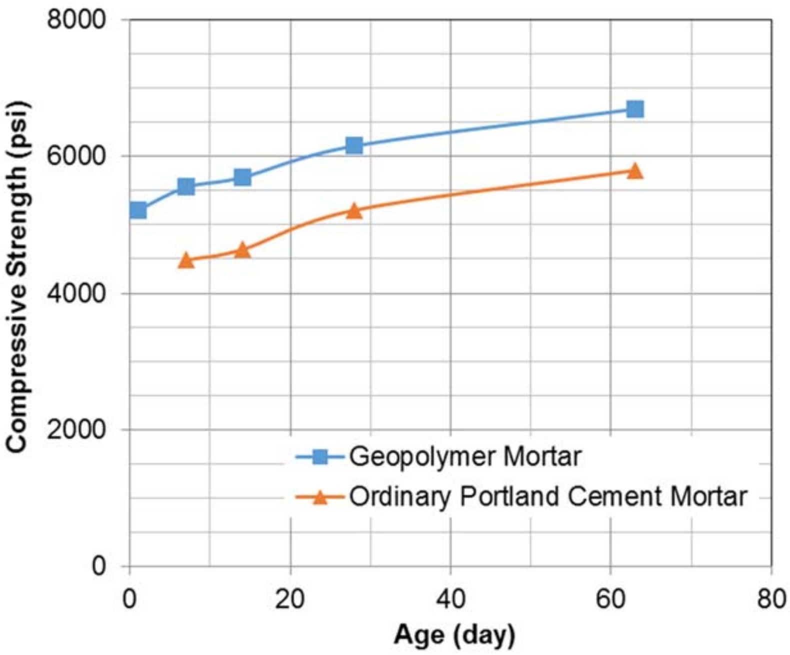

Figure 2: Comparison between geopolymer and OPC binders in 2-inch mortar cubes.

Promising results obtained from mortar cubes led to the next phase of this study which was producing concrete cylinders with diameter of 4 inch and height of 8 inch by adding coarse and fine aggregates to the mixtures. In this phase, preliminary concrete cylinders were made and tested for their strength. Figure 3 shows the results of compressive strength tests conducted on cylinders made with geopolymer composites and compares them with OPC. As exhibited in Figure 3, 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. For example, at the 60th day, compressive strength of geopolymer and OPC concrete reached 5750 psi and 6550 psi, respectively. These preliminary data showed that geopolymer could successfully compete with OPC. These results clearly support the hypothesis of this study which is to prove the suitability of the Carolina fly ash in producing strong geopolymer binders. However, more tests are needed in order to optimize all the parameters affecting the strength of the final geopolymer product.

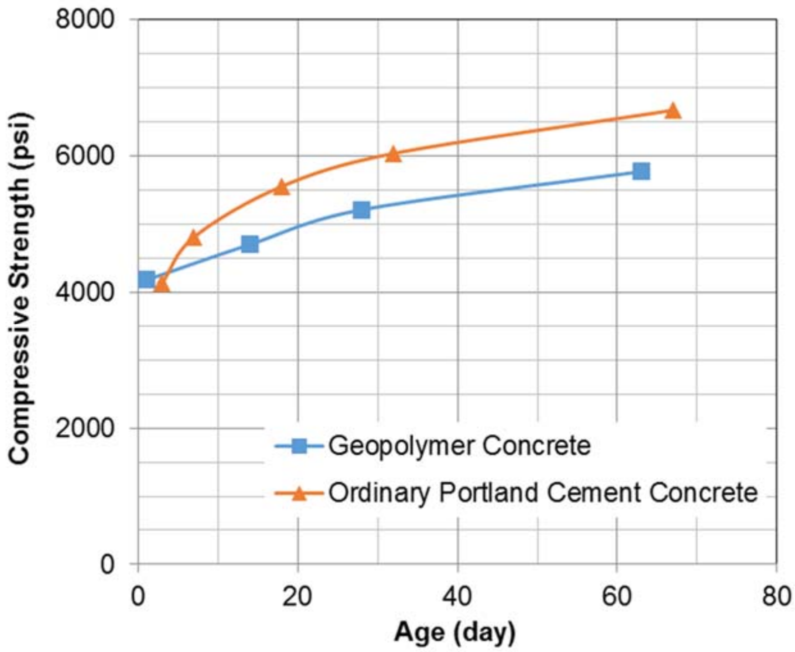

Figure 3: Comparison between geopolymer and OPC binders in concrete cylinders.

CONCLUSION

In this study, a fly ash sample from a coal-fired power plant in Carolina was collected and tested to investigate its suitability in producing geopolymer binder to replace Ordinary Portland Cement (OPC) binder in concrete application.

An experimental design program was applied to determine the critical parameters of geopolymerisation process affecting the compressive strength of final geopolymer binder used in concrete applications. The tests identified sodium hydroxide concentration, curing temperature, and water to sodium oxide mass ratio to be the most critical geopolymerisation parameters. Compressive strength tests conducted on mortar cubes at the 60th day showed that geopolymer binder revealed a better performance than OPC binder with a strength of about 6650 psi versus 5750 psi, respectively. Moreover, the results of preliminary concrete cylinders showed that the compressive strength of geopolymer and OPC cylinders were 5750 and 6550, respectively, at the 60th day. These results proved the suitability of Carolina fly ash in making geopolymer or cement-less concrete to replace OPC concrete. However, more tests are needed to optimize all the parameters in the case of concrete cylinders to obtain the best geopolymer product with highest performance.

REFERENCES

[1] ACAA (American Coal Ash Association), Coal Combustion Product (CCP) Production and Use Survey Report, 2012, p.1.
[2] IPCC (Intergovernmental Panel on Climate Change), Carbon dioxide capture and storage, Special Report, Cambridge University Press, New York, USA, 2005.
[3] EPA (U.S. Environmental Protection Agency), Compilation of Air Pollutant Emission Factors, 1995, Chapter 11.6, pp. 1-26.
[4] Higgins, D., Portland cement replacement: within-mixer or factory-blend?, Concrete, March 2009, pp.22-24.
[5] Kumar S. and Stewart J., Geotechnical Engineering Characteristics of Illinois PCC Dry Bottom Ash Amended With Bentonite, ASCE Journal of Energy Engineering, to be published in Vol. 129(2), 2003.
[6] Kumar S. and Stewart J., Utilization of Illinois PCC Dry Bottom Ash in Compacted Landfill Barriers, Soil and Sedimentation Contamination: an International Journal, Vol. 12 (3), 2003
[7] Korcak R.F., Agricultural uses of Coal Combustion Byproduct, Wright et al. (Eds.) Agricultural Uses of Municipal, Animal and Industrial Byproducts. USDA-ARS Conservation Res. Rep. No. 44, NTIS, Springfield, VA, 1998.
[8] Lovell C. W., Ke T., Huang W., Lovell J.E., Bottom Ash As Highway Material, Presented at the 70th Annual Meeting of the Transportation Research Board, Washington, D.C., January 1997.
[9] Naik T.R., Banerjee D.D., Kraus R.K., and Singh, S.S., Use of Class F Fly Ash and Clean-Coal Blends for Cast Concrete Products, Proceedings of the 12th ACAA International Symposium, Orlando, Florida, January 26-30, 1997.
[10] Rangan B. V., Fly ash-based geopolymer concrete, Research Report GC 4, Engineering Faculty, Curtin University of Technology, Perth, Australia, 2008.
[11] Davidovits J., Soft Mineralogy and Geopolymers, Proceedings of the Geopolymer 88 International Conference, The Université de Technologie, Compiègne, France, 1988.
[12] Xu Hua, Van Deventer J.S.J., 2000, “The geopolymerisation of alumino-silicate minerals”, International Journal of Mineral Processing (59), pp 247-266.
[13] Balaguru P., Kurtz S., Rudolph J., Geopolymer for Repair and Rehabilitation of Reinforced Concrete Beams, The Geopolymer Institute, 1997.
[14] Palomo A., Fernandez-Jimenez A., Lopez-Hombrados C., Lleyda J.L., Precast Elements Made of Alkali-Activated Fly Ash Concrete, Eighth CANMET/ACI International

Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Las Vegas, USA, 2004.
[15] Hardjito D., Rangan B.V., Development and Properties of Low-Calcium Fly Ash-Based Geopolymer Concrete, Research Report GC1, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2005.
[16] Wallah S.E., Rangan B.V., Low-calcium fly ash-based geopolymer concrete: long-term peroperties, Research Report GC 2, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2006.
[17] Komnitsas K., Zaharaki D., Geopolymerisation: A review and prospects for the minerals industry, Minerals Engineering (20), 2007, pp 1261-1277.
[18] Diaz E.I., Allouche E.N., Eklund S., Factors affecting the suitability of fly ash as source material for geopolymers, Fuel, 2009, Vol 89 (5), pp. 992-996.
[19] Duxson P., Provis J.L., Lukey G.C., Van Deventer J.S.J., The Role of Inorganic Polymer Technology in the Development of Green Concrete, Cement and Concrete Research (37), 2007, pp 1590-1597.