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Durability of Alkali Activated Blast Furnace Slag

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Abstract. The alkali activation of blast furnace slag has the potential to reduce the environmental impact of cementitious materials and to be applied in geographic zones where weather is a factor that negatively affects performance of materials based on Ordinary Portland Cement. The scientific literature provides many examples of alkali activated slag with high compressive strengths; however research into the durability and resistance to aggressive environments is still necessary for applications in harsh weather conditions. In this study two design mixes of blast furnace slag with mine tailings were activated with a potassium based solution. The design mixes were characterized by scanning electron microscopy, BET analysis and compressive strength testing. Freeze-thaw testing up to 100 freeze-thaw cycles was performed in 10% road salt solution. Our findings included compressive strength of up to 100 MPa after 28 days of curing and 120 MPa after freeze-thaw testing. The relationship between pore size, compressive strength, and compressive strength after freeze-thaw was explored.

1. Introduction

According to the US Geological Survey, 4.18 billion metric tons of cement was produced in 2014 [1]. Due to the sheer size of the concrete market worldwide, the energy and environmental impacts are also large. It has been approximated that 5% of total anthropogenic greenhouse gas emissions stem from cement production [2], [3]. Alkali activated materials are a cementitious material that can be produced from industrial by-products. The chemical composition of the final material is similar to that of Ordinary Portland Cement; however the formation reactions and final chemistry of the two materials differ significantly [4]. This type of material has been identified by the Intergovernmental Panel on Climate Change (IPCC) as a possible alternative to Portland cement that could reduce the environmental impacts of the cement industry [5]. In order for these materials to become a practical

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alternative in the cement market further research is necessary to prove durability and resistance of these materials to weathering.

Previous research in the area of alkali-activated materials has shown varied results in the compressive strength of the alkali activated slag (AAS) materials after exposure to freeze-thaw cycles. Good freeze-thaw resistance is considered to be not losing strength or durability after exposure [6]. One study found that the compressive strength increases after freeze-thaw cycling in AAS material [7]. In Portland cement based materials it has been shown that the properties that effect freeze-thaw resistivity are mostly physicommechanical properties like pore structure, pore saturation and entrained air voids. It is thought that this relationship may be similar for AAMs [6]. This research focuses on the characterization of two design mixes by pore structure analysis, and compressive strength measurements under exposure to freeze-thaw conditions in water and salt water. This research will help to shed light on the relationship between the pores present in the materials and the compressive strength results obtained.

2. Experimental methodology

2.1. Sample materials

The samples utilized potassium hydroxide, ground granulated blast furnace slag (GGBFS), mine tailings, and two types of amorphous silica. The potassium hydroxide was sourced from Brainerd Chemical Co. in Tulsa, Oklahoma. The GGBFS came from St. Mary's Cement Company, based in Burlington, ON, Canada. The composition of the GGBFS is shown in table 1.

The mine tailings were provided by NYCO Minerals, based in Willsboro NY, USA. The mine tailings contain the minerals Garnet, Wollastonite and Pyroxene. The NYCO mine tailings were sifted with a 500 micron sieve before use in samples. The amorphous silica was produced by Evonik Degussa Corporation based in Essen, Germany. The water used in the experiments was tap water from the Rochester, NY municipal water supply.

Table 1. Composition of the slag by weight

Oxide	Percentage of slag by weight
CaO	38.3
SiO ₂	37
Al ₂ O ₃	8
MgO	10.5
Na ₂ O	0.025
K ₂ O	0.043
SO ₃	1.7

2.2. Sample preparation

The activating solution was prepared by dissolving amorphous hydrophilic silica (Aerosil 150) in a 45% KOH solution and water to yield a solution with molar ratios of SiO₂/K₂O =1 and H₂O/K₂O =50. The solution was left to mature for 24 hours before used in sample production. In all samples the mass ratio of slag/activating solution was 2. All of the dry ingredients were carefully weighed and mixed together for 1 minute in the Hobart mixer. Then the activating solution was added to the mixture and all of the reactants were mixed in a Hobart mixer until a homogeneous paste was obtained. The paste was cast into ASTM standard 2 in. cement cubes, vibrated for five minutes and left to mature for one

hour. After this, the cubes were wrapped in plastic and cured in an oven for 24 hours at 45°C. At the end of the curing time, the cubes were de-molded and placed in saturated lime water until testing. Weight proportions of design mixes studied are shown in table 2.

Table 2. Design mix composition.

Material	Design mix G1	Design mix G5
Slag	2	2
Activating solution	1	1
Mine tailings	2	2
Amorphous Hydrophobic silica (Aerosil R972)	0	0.05

2.3. Characterization of samples

The design mixes were tested at 1.7 and 28 days after curing for compressive strength in a Tinius Olsen Electromatic universal testing machine. Each testing day three cubes of each design mix were tested per ASTM standards.

Samples were stored in saturated lime water for 28 days before the beginning of the freeze-thaw cycling. Samples were placed in a plastic tray. Water was then poured into the tray filling the tray to approximately two cm above the bottom. In the 10% salt water case, the water was mixed with common road salt in a large container and then poured into the tray in solution. The cubes were cycled from -10 °C to 4 °C in 50 cycle intervals using an environmental chamber. The cubes were left for one hour at each reference temperature.

It is known that the pore structure of cementitious materials influences their physical properties and stability[6]. To study this effect, both design mixes were tested after 28 days using two different techniques. In the first technique the porosity of the samples was characterized by the nitrogen adsorption method in a Quantachrome Nova 1000e machine. In the second technique, transmission electron microscopy was used.

In order to evaluate the capacity of the samples to retain strength after being exposed to high temperatures, a thermal shock test was conducted. The cubes were dried in a convection oven at 45 °C for 24 hours. After this, one cube of each design mix was exposed to temperatures of 200 °C, 400 °C, 600 °C, and 800 °C for one hour. After temperature exposure two different cooling techniques were evaluated. One cube was cooled in still air, and another was quenched in water. Once the samples reached room temperature, the compressive strength was measured.

The samples were analysed using a Scanning Electron Microscope (SEM). In this work we have used SPI-MODULE Sputter Coater for both design mixes with gold-palladium under a vacuum of 10 Pa. Once the specimens were ready, their images were taken in a JEOL JSM-6400V SEM. Images were capture at a 7kX magnification using a 20kV bean voltage. Moreover, elemental analysis and mapping were also obtained using energy dispersive X-Ray spectroscopy (EDS) on the specimens. Elemental analysis was conducted at four different points on design mixes G1 and G5 cracks and four other points on the nearby surface. The elemental analysis and mapping were collected from Noran System Six software, which is connected to the EDS X-Ray detector.

Transmission electron microscopy (TEM) was done using a JEOL 2010 electron microscope operating at 200 kV. Specimens for electron diffraction were prepared by grinding the paste to a fine powder with a mortar and pestle, dispersing in isopropyl alcohol, sonicating, and then applying a 10

microliter drop to a standard carbon-film covered copper TEM grid and allowing to air dry. At the microscope, thin sections were used to capture powder diffraction patterns, from which d spacings were obtained. The latter were then compared to known spacings of mineral phases that might form under our preparation conditions. Likewise, images of thin sections were obtained for analysis of porosity. ImageJ was used to measure the diameter of the pores.

3. Results and Discussion

3.1. Compressive strength

Compressive strength results over time for design mixes G1 and G5 are shown in figure 1. For each design mix respectively, the strength increases over time. G1 has a higher early compressive strength, but levels out faster over time. Design mix G5 starts out with a lower compressive strength than G1. However, over time G5 gains strength reaching an average of 106 MPa at 28 days.

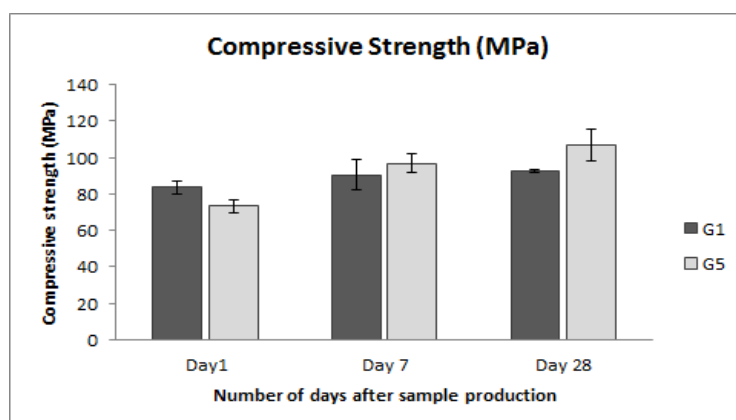


Figure 1. Compressive strength development for design mixes G1 and G5 at days 1, 7 and 28. Error bars are given as one standard deviation.

Figures 2 (in water) and 3 (in salt water) present the compressive strength of both design mixes after thermal cycling in an environmental chamber. In the first experiment (figure 3) design mix G1 lost approximately 15% of the original compressive strength after 100 cycles but design mix G5 showed a 10% increase in strength under the same conditions (final average of 117.64 MPa) after 100 cycles. With the objective of replicating road conditions in New York, the same set of experiments was conducted in a 10% salt water solution. As seen in figure 3, in both cases an unexpected behaviour was observed. Design mix G1 increased 8% of strength (final average of 92.7 MPa) while design Mix G5 increased by 6% (final average of 112.7 MPa) after 100 cycles. This increase in compressive strength under freeze-thaw testing agrees with previous results obtained by Kukko and Mannonen [7].

Figure 4 presents a summary of the residual compressive strength for the samples after thermal shock. As a general trend, the loss in compressive strength is higher for samples quenched in water than those cooled in still air. Samples cooled in still air retained approximately 50% of the original compressive strength up to 600°C but they retained only 30% when quenched in water at the same temperature. The compressive strength retention was insignificant for all cases at 800°C. Thermogravimetric Analysis (TGA) was performed for both design mixes. In both cases the derivative of the weigh curve shows 3 relevant peaks centered at around 80°C, 370°C and 660°C. The first peak is attributed to the evaporation of adsorbed water and dehydroxilation of C-S-H phase, the second is attributed to the decomposition of Ca(OH)_2 and the last one is associated with the decomposition of CaCO_3 .

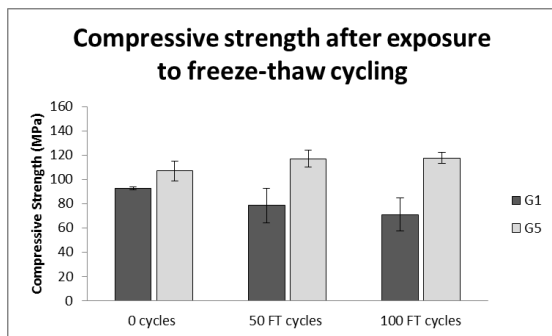


Figure 2. Compressive strength of design mixes G1 and G5 at 50 and 100 thermal cycles in water.

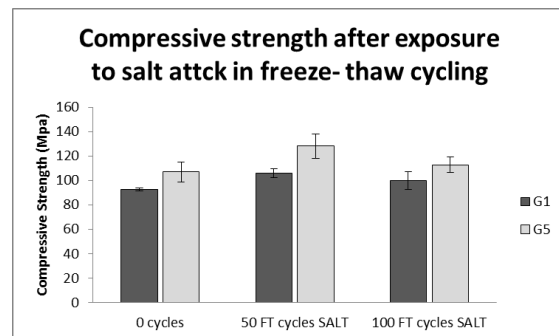


Figure 3. Compressive strength of design mixes G1 and G5 at 50 and 100 thermal cycles in 10% salt water.

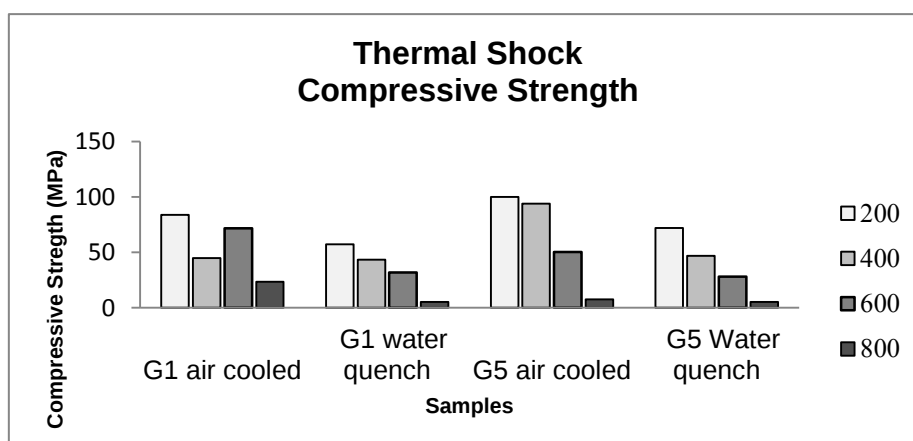


Figure 4. Residual compressive strength for design mixes G1 and G5 after thermal shock at 200°C, 400°C, 600°C and 800°C.

3.2. Pore size analysis

Table 3 presents the summary of the pore analysis by the Barret-Joyender-Halenda Method for both design mixes. It can be seen that for both mixes the total pore volume is approximately the same as well as the radius of the mesopores (21Å). However there is a significant difference in the total surface area of both design mixes with G5 being the largest. This suggests that design mix G5 may have a larger number of small pores compared to design mix G1.

Table 3. BJH desorption summary.

	Design mix G1	Design mix G5
Surface Area (m ² /g)	31.925	44.837
Pore Volume cc/g	0.052	0.065
Pore Radius Dv(r) (Å)	21.428	21.671

An alternative method for measuring the pore size distribution via Transmission Electron Microscopy (TEM) was evaluated. Images of thin sections were used along with ImageJ to directly measure the pore diameter. The results are shown in figures 8 and 9. Both design mixes show a peaked distribution in the 4 to 6 nm diameter range, with that for G5 being slightly broader.

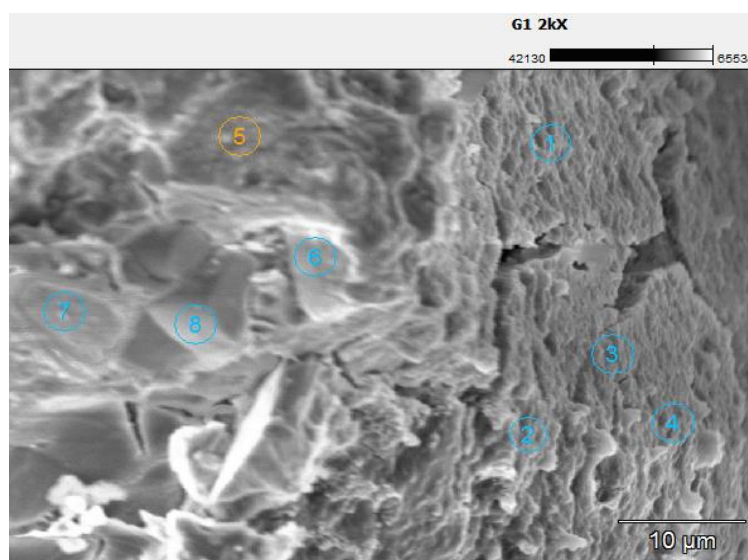


Figure 5. SEM image of G1 showing the interior surface of a crack (right side) and the adjacent surface (left side). The numbers indicate the points where EDS analysis was done (1 through 4 in the crack and 5 through 8 on the surface).

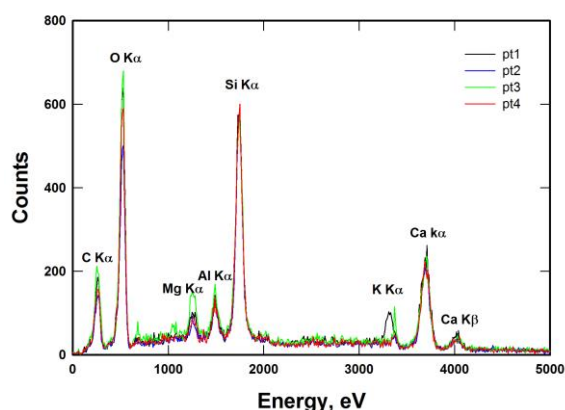


Figure 6. A comparison the EDS spectra for four randomly points in a crack wall of G1. Spectra have been normalized so the Si peak intensity is the same in all four spectra.

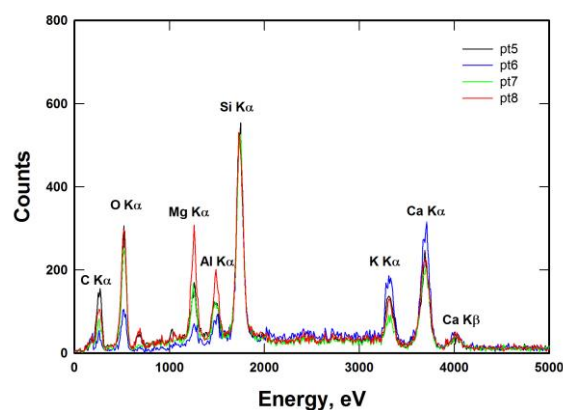


Figure 7. A comparison the EDS spectra for four randomly points on the surface of G1. Spectra have been normalized so the Si peak intensity is the same in all four spectra.

Elemental analysis using EDS was done on both G1 and G5. Figure 5 shows an SEM image of a crack and the adjacent surface area for G1. Spectra were collected from four random points in both the crack and the surface areas. These are compared in figures 6 and 7. The most noticeable difference was that the O peak was much higher for the spectra from the crack (figure 6) than from the nearby surface (figure 7). An identical study on G5 showed smaller differences in the O peak height between the two areas.

Histogram G1 100k

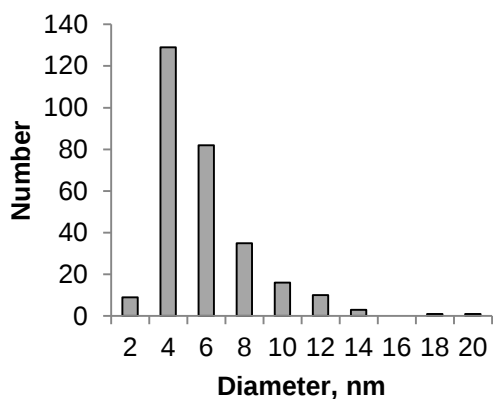


Figure 8. Histograms showing the pore diameter distribution as measured by TEM for G1.

Histogram G5 100k

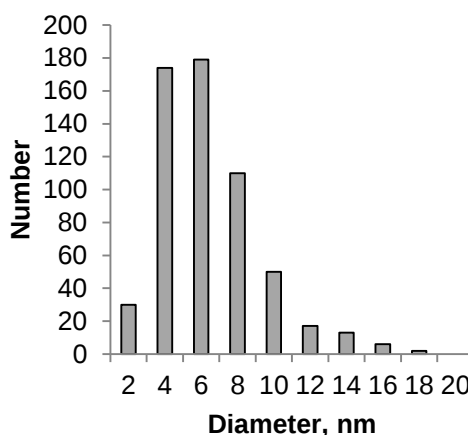


Figure 9. Histograms showing the pore diameter distribution as measured by TEM for G5.

4. Conclusions

A high compressive strength cementitious material was obtained by the alkali activation of blast furnace slag with mine tailings. The average 28 day compressive strength was 92.6 MPa. The addition of amorphous silica in the design mix increased the compressive strength to 106.8 MPa on average, although one sample reached 114 MPa. Both design mixes used 80% by mass of industrial by-products. When exposed to thermal cycling they both increased their compressive strength, reaching an average of 128 MPa after 50 freeze-thaw cycles in a 10% salt water solution. Under thermal shock when the samples are cooled in still air they retained approximately 50% of the original compressive strength up to 600°C. However, the samples retained only 30% when quenched in water at the same temperature. The compressive strength retention was insignificant for all cases at 800°C. Results from pore size analysis via Nitrogen adsorption and Transmission Electron Microscopy show that for both mixes the majority of the mesopores are in the range 4 – 6 nm in diameter but there are differences in the mesopore distributions. Moreover, the effect of pore size and distribution in the final compressive strength and durability is inconclusive at this moment.

Overall the preliminary pore analysis via BET support the literature [6] in suggesting that the increase in compressive strength under freeze thaw by the design mix with additional 5% amorphous silica could be caused by the presence of smaller pores. Further research is underway to support this claim.

5. References

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