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ALKALI-ACTIVATED CONCRETE

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Abstract: Concrete is the second most used commodity in the world after only water. It is also one of the most polluting materials to the environment. The production process of one ton of Ordinary Portland Cement (OPC) releases approximately 0.84 ton of carbon dioxide. Alkali-Activation has been developed as a technique of combining various latently hydraulic cementitious matrices with an alkali, to produce 'clinker-free' binders in concrete mixes, therefore inhibiting the need for OPC. This study aims at using and comparing results from three different types of cementitious matrices, namely Fly Ash, water quenched Ground Granulated Blast Furnace Slag (GGBFS) and air-cooled Blast Furnace Slag (BFS) with three different concentrations of the alkali-activator, a mix between Sodium Silicate solution and Sodium Hydroxide flakes. A conventional average OPC mix has also been casted to be used as a control mix. It is important to note that all cementitious matrices used are found as byproducts of different industries; both BFS and GGBFS are byproducts of iron production and Fly Ash is produced as a byproduct from burning coal in electric generation power plants. Conventional concrete tests have been performed, as well as the accelerated mortar bar test and accelerated corrosion test. Other tests have also been performed for the cementitious matrices including elemental composition, unit weight and fineness of the granules. Results reveal that Fly Ash activation is the most promising in terms of compressive and flexural strengths. It, however, requires heat curing which may limit its applications to precast, repair works and water plugging.

1 INTRODUCTION

Ordinary Portland Cement Concrete has been widely used since the 1800's. Research estimates that each ton of Cement produced, releases into the environment about 0.84 ton of Carbon Dioxide; directly during decomposition and indirectly because of the energy consumed during production. The total contribution of Cement to global Carbon Dioxide emissions is estimated to be between 5 and 8 percent. Today around 4.2 billion tons of Cement are produced annually with an expected growth rate of 2.5% per annum. Simultaneously, latently hydraulic cementitious matrices such as Fly Ash, Silica Fumes and Slag which are byproducts from various industries have been used as admixtures to replace some of the cement content. This leads to an improvement in concrete properties such as strength and permeability. The presence of cement, however, is required for the cementitious matrices' reaction to occur and produce the binding material in concrete. The idea behind alkali-activation is inhibiting the need for the cement's reaction and 'activating' the unaccompanied cementitious matrices.

1.1 Alkali-Activation

Alkali-Activation has been introduced as a method of initiating the reaction of the cementitious matrices without the need for cement. The process of Alkali-Activation is best demonstrated by the reaction of concrete containing both cement and a cementitious matrix, Fly Ash for example. Two chemical reactions take place. The first is the traditional cement reaction, in which the active components of cement, namely Tricalcium Silicate (C_3S) and Dicalcium Silicate (C_2S) react with water to produce Calcium Silicate (CSH), which is the binding component and Calcium Hydroxide (CH). In the following reaction, Calcium Hydroxide from the first reaction reacts with the Silicon Dioxide (S) present in Fly Ash to produce more Calcium Silicate (CSH). This reaction is represented as follows:

[1] $C_3S/C_2S + H \rightarrow C\text{-}S\text{-}H + CH$

[2] $S+CH \rightarrow C\text{-}S\text{-}H$

The idea behind Alkali-Activation is to externally introduce the Hydroxide ion to replace the Calcium Hydroxide from the first reaction through an alkali activator(s). By doing so, the need for cement in concrete is inhibited. This results in the formation of a 'clinker-free' binder, which both reduces requirement for cement and utilizes byproducts from other industries. The exact details of the chemistry and the exact chemical reactions that occur in Alkali-Activated Concrete (AAC) are not yet fully comprehended. However, the final components of the reaction and the factors affecting the reaction are commonly known. Factors include the chemical composition of the cementitious matrix used, the activator(s) used and their concentrations, as well as external factors such as the curing temperature, fineness of the cementitious matrix granules and mixing time. Commonly activators used include Sodium Silicates, Sodium Hydroxide, Sodium Carbonates, Sodium Alumiosilicates glass, Sodium Sulfate and Potassium Hydroxide. These can be used separately or combined.

2 LITERATURE REVIEW

1) Self-Cured Alkali Activated Slag Concrete Mixes an Experimental Study:

In this paper, the Alkali-Activated slag concrete was made using Ground Granulated Blast Furnace Slag (GGBFS) through activation by sodium silicate and sodium hydroxide solution. The effects of Sodium Oxide concentration and the ratio of Silicon Dioxide to Sodium Oxide in the activator on the strength and workability were studied. The results showed that as sodium oxide concentration increases, the compressive and tensile strength increases. However, as the silicon dioxide/sodium oxide ratio increases, the workability decreases. In addition, the effect of using portable or de-ionized water was not significant on the strength of the alkali-activated slag concrete. (Mithun et al, 2014)

2) Performance of Alkali-Activated Slag with Various Alkali Activators:

In this paper, various activators were used to activate the Ground Granulated Blast Furnace Slag and the performance of each mix was studied. The activators used were Sodium Silicate, Sodium Hydroxide and Sodium Carbonate. The workability in addition to the strengths were measured and the results of the mixes were compared. The results showed that the mixes with sodium hydroxide and sodium silicate set quickly. The Sodium Silicate activator yielded the highest compressive and flexural strengths, followed by the Sodium Carbonate and finally the Sodium Hydroxide. (Rajesh et al, 2013)

3) Alkali-Activated Materials, State of the Art RILEM

This book by RILEM (International Union of Laboratories and Experts in Construction, Materials, Systems and Structures) provides a comprehensive study of Alkali-Activated Concrete. It assesses various aspects regarding Alkali-Activation, such as its history, binder chemistry, mix designs standards, testing and potential applications. It refers to several other literature as it discusses the topics of Alkali-Activated Concrete. An important issue discussed in the Fly Ash section is that for Fly Ash to achieve proper strength gain oven curing is required.

4) Handbook of Alkali Activated Cements, Mortars and Concretes

This book gathers various literature on the topic of Alkali-Activated materials in one place, summarizing them under various headings. Topics discussed include chemistry and mix design, properties of Alkali-Activated Concreters, Durability, applications and lifecycle assessment.

3 OBJECTIVES

The main objective of this research is to study Alkali-Activated Concrete as a potential alternative to the ordinary Portland Cement Concrete. This will be done by examining different cementitious matrices with different activator concentrations to possibly highlight potential benefits of Alkali-Activated Concrete.

4 EXPERIMENTAL WORK

4.1 Mix Proportions

Since no specifications or mix design procedures are available, the following criteria were set in developing the mix proportions. These are as follows; the weights of cementitious matrix, coarse aggregates and fine aggregates were all fixed per $1m^3$. The alkali to cementitious matrix ratio was kept almost constant and within the effective range for each type of cementitious matrix. The silicate/hydroxide ratio was changed between the subsequent mixes. It is important to note that the following naming system has been used for the mixes; the letters indicate the material as follows, GGBFS shortened to GG, BFS kept as is and Fly Ash abbreviated to FA. The number following the letters indicates the Silicate to Hydroxide ratio moving from highest to lowest.

4.2 Material Properties

The cementitious matrices used were Type F Fly Ash, quenched (water-cooled) Ground Granulated Blast Furnace Slag (GGBFS), Egyptian air-cooled Blast Furnace Slag (BFS) and OPC. As for the activators, a combination of two activators was used; firstly Sodium Hydroxide Caustic Soda flakes with a purity of 99% and secondly Sodium Silicate solution with Sodium Oxide (Na_2O) content 12%, Silicon Dioxide (SiO_2) content of 32% and a molar ratio of 2.6. Fine aggregates used were well-graded, washed sand. The coarse aggregates used were well-graded washed dolomite.

4.3 Mix Proportions

Table 1: Mix Proportions per $1m^3$

Mix	Cementitious (kg/m^3)	Coarse (kg/m^3)	Fine (kg/m^3)	Sodium Hydroxide (kg/m^3)	Sodium Silicate (kg/m^3)	Water (kg/m^3)	AL/ cement	Silicate/ Hydroxide ratio
OPC	400	1150	620	-	-	192	-	-
BFS 1	350	1150	620	0	65	158	-	-
BFS 2	400	1150	620	16	110	105	-	-
BFS 3	400	1150	620	25	90	120	-	-
GG 1	400	1150	620	15	115	110	0.33	7.667
GG 2	400	1150	620	16	110	105	0.32	6.88
GG 3	400	1150	620	18	120	100	0.35	6.78
GG 4	400	1150	620	30	100	85	0.33	3.33
FA 1	400	1150	620	30	110	45	0.35	3.67
FA 2	400	1150	620	50	130	40	0.45	2.60
FA 3	400	1150	620	53	128	45	0.45	2.42
FA 3'	400	1150	620	53	128	45	0.45	2.42
FA 4	400	1150	620	55	125	47	0.45	2.27

4.4 Specimen Preparation

The reaction between the activators, namely sodium silicate and sodium hydroxide produces large amounts of heat. The activators were, therefore, separately mixed together first according to the required proportions and left to cool down for 15 minutes before being added to the remaining components of the mix in the mixer (cementitious matrix, coarse and fine aggregates, and water). Alkali-activated mixes were used to cast 15x15x15 cm cubes and 15x15x75 cm beams. The GGBFS and BFS mixes were kept in the molds in room temperature for 48 hours, then were demolded and cured in air in room temperature until testing. The Fly Ash mixes were kept in the molds at room temperature for 72 hours, then demolded, wrapped with plastic and cured in the oven at 90 ^{0}C for 24 hours. Afterwards, the specimens were left in room temperature until testing. In order to examine the importance of the oven curing for Fly Ash, the specimens from one of the Fly Ash mixes (FA 3'), which had the same mix proportions as mix (FA 3), was cured in air in normal room temperature.

4.5 Methodology

As aforementioned, tests were performed on the cementitious matrices, on fresh concrete and on hardened concrete.

4.5.1 Material Properties

- Elemental Composition (EDX): The Energy-dispersive X-ray Spectroscopy test, is an analytical test that identifies the elemental composition and percentages of elements present in materials.
- Density
- Blaine Fineness: the Blaine Fineness test was performed using the Blaine Permeability Apparatus and is used to determine the material fineness.

4.5.2 Fresh Concrete

- Slump
- Air content
- Unit Weight
- Temperature

4.5.3 Hardened Concrete

- Compressive strength (7, 28 Days)
- Three Point Flexural strength for reinforced beams (7, 28 Days): performed on beams with a steel cage of 4 steel bars (10mm diameter each) and 4 stirrups (8 mm diameter each).
- Accelerated Corrosion test: to examine the effect of alkali-activation on reinforcement corrosion.
- Accelerated Mortar Bar Test: to test for Alkali-Aggregate Reaction in case of alkali-activation.

5 RESULTS

5.1 Material Properties

5.1.1 EDX

The EDX results show a difference in the chemical composition of the three materials. Besides Oxygen, Fly Ash is rich in Silicon and Aluminum and this classifies it as low Calcium content cementitious matrix. On the other hand, GGBFS and BFS are classified as high Calcium cementitious matrix because of their high Calcium content.

Table 2: Chemical Composition of the Cementitious Matrices

Element / Percentage (%)	BFS	GGBFS	Fly Ash
O	32.9	46.1	51.3
Si	4.9	8.5	26.0
Ca	32.6	40.3	2.5
Fe	23.2	2.2	5.4
Al	1.1	2.2	9.9

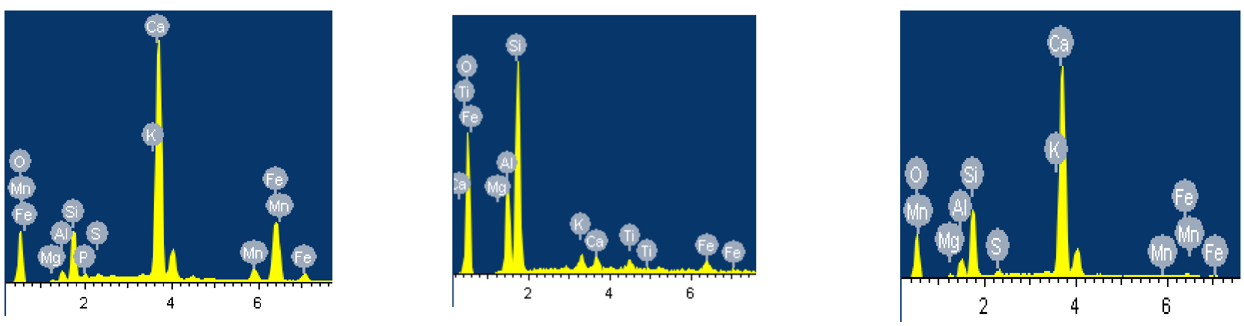


Figure 1: Results from EDX, from left to right BFS, GGBFS, Fly Ash

5.1.2 Density & Blaine Fineness

Density results show that the Fly Ash and GGBFS had considerably lower densities than OPC. OPC and Fly Ash, which were both supplied in powder form, had the highest fineness. GGBFS and BFS were supplied as large granules and lumps respectively and had to be grinded to achieve a lower fineness. Fineness was performed to ensure that the grinded material has a roughly uniform fineness after grinding.

Table 3: Blaine fineness and Density of the Cementitious Matrices

Cementitious Matrix	Blaine Fineness (cm^2 / g)	Density (g / cm^3)
OPC	3508	3.22
GGBFS	3171	2.81
BFS	2912	3.18
Fly Ash	3752	2.38

5.2 Ordinary Portland Cement Concrete Fresh and Hardened Results

Table 4: Fresh Concrete Results

Mix	Slump (mm)	Air Content (%)	Temperature (°C)	Unit Weight (kg/m^3)
OPC	20	1.3	31	2447

Table 5: Hardened Concrete Results

	7 Days		28 Days	
Mix	Compressive (MPa)	Flexural (MPa)	Compressive (MPa)	Flexural (MPa)
OPC	28.8	17.6	39.1	24.6

5.3 Air Cooled BFS Fresh and Hardened Concrete Results

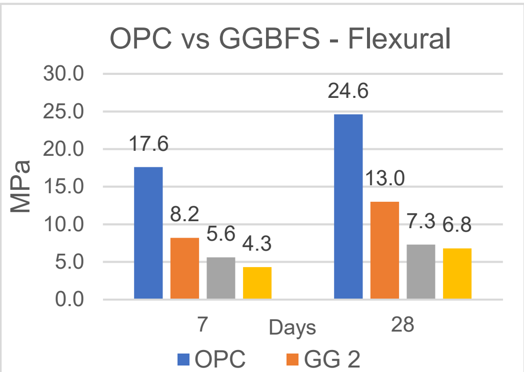
BFS yielded very poor results for both fresh and hardened tests. The mixes did not develop any cohesion with the paste surrounding the aggregates only. The setting behavior of the concrete was also abnormal, with the mix suddenly in one cycle of the mixer becoming very unworkable. Hardened concrete achieved very low strengths. The mixes were therefore excluded from further analysis and comparison.

5.4 Water Quenched GGBFS Fresh and Hardened Concrete Results

Table 6: GGBFS Fresh Concrete Results

Mix	Slump (mm)	Air Content (%)	Temperature (°C)	Unit Weight (kg/m^3))
GG 1	20	5.5	23	2091
GG 2	Collapse	2.5	25	2267
GG 3	30	4.0	24	2360
GG 4	10	5.0	26	2298

All the GGBFS mixes were unworkable except mix GG2, which was highly workable. Also, all the GGBFS mixes had lower temperatures than the conventional OPC concrete mix performed.



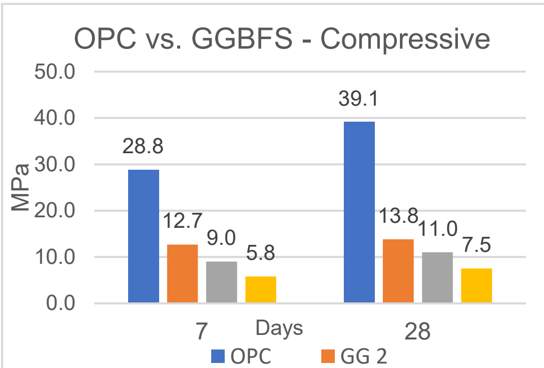


Figure 2: OPC vs GGBFS Compressive and Flexural Strengths

Mix GG1 showed extremely low compressive and flexural strength compared to the other mixes, most likely because of an error during mixing. Its results are excluded from further analysis. All GGBFS mixes showed lower 7 and 28 days compressive and flexural strength compared to the conventional OPC mix. Compressive and flexural strength of the GGBFS concrete decreases as the ratio Silicate/Hydroxide decreases. For example, mix GG4 which has the lowest Silicate / Hydroxide content, yielded the lowest compressive and flexural strength. Green formations with a distinctive smell were noticed over the surfaces and inside the GGBFS casted beams and cubes. Samples of these formations were biologically tested four times on four different media with no conclusion reached.

5.5 Fly Ash Fresh and Hardened Concrete Results

Table 7: Fresh Concrete Results

Mix	Slump (cm)	Air Content (%)	Temperature (°C)	Unit Weight (kg/m^3)
FA 1	0	1.8	40	2380
FA 2	Poor fresh concrete status			
FA 3	0	1.5	42	2312
FA 3'	0	1.5	42	2312
FA 4	Collapse	1.2	44	2360

All the Fly Ash mixes showed very low workability except mix FA 4, which was highly workable. Mix FA2 was extremely unworkable and very sticky to the extent that it was impossible to perform any of the fresh concrete tests for it and no beams were cast for this mix. All the Fly Ash mixes had higher temperatures than the conventional OPC concrete mix.

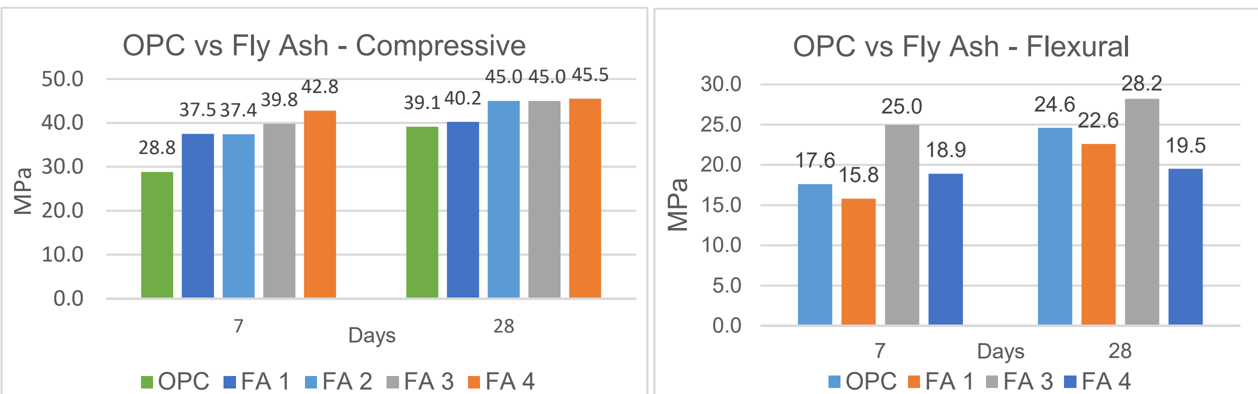


Figure 3: OPC vs Fly Ash Compressive and Flexural Strengths

The Fly Ash mixes showed higher 7 and 28 days compressive strengths compared to the conventional OPC mix. They also showed similar 7 and 28 days flexural strength compared to OPC. As the ratio of Silicate/Hydroxide decreased, the 7 days compressive strength of the Fly Ash concrete increased. For example, mix FA4 which had the lowest Silicate/Hydroxide content, had the highest 7 days compressive strength. At 28 days, the effect of this Silicate/Hydroxide became negligible; 28 days strength was approximately 45 MPa for most mixes. Moreover, Fly Ash mixes gained a much higher percentage of their 28-days strength by day 7 compared to the conventional mix.

5.5.1 Oven-Curing versus Air-Curing for Fly Ash Activated Concrete

Mixes FA 3 and FA 3' have the exact mix proportions but mix FA 3 was oven cured, while FA 3' was air cured. As the results show, the compressive and flexural strengths of the air cured mix were extremely lower than those of the oven cured mix. It can therefore be concluded that oven curing is essential for Fly Ash's strength gain.

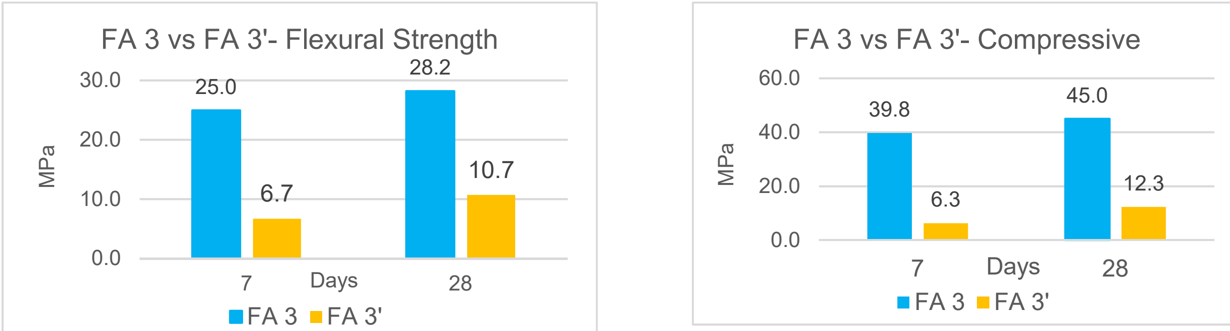


Figure 4: FA 3 (Oven cured) vs FA 3’ (Air-cured) Compressive and Flexural Strength

5.6 Accelerated Corrosion Test

The Accelerated Corrosion Test was conducted only on OPC and Fly Ash. Special beams were cast with 3 steel bars extruding from the sides. A Sodium Chloride solution with 20% concentration was used to accelerate the corrosion rate. Current was measured once every week for 3 weeks between the top and bottom bars. As per test standards, the lower the current, the better the resistance to corrosion. The results showed that Fly Ash has better resistance to corrosion than the conventional concrete since a lower current was measured from the Fly Ash beam compared to that measured from the OPC beam.

Table 8: Accelerated corrosion Results

	Current (mA)		
	week 1	week 2	week 3
OPC	0.036	0.045	0.050
Fly Ash	0.026	0.029	0.032

Figure 5: Corrosion beams with extruding reinforcement

1.2 Accelerated Mortar Bar Test

Special OPC and Fly Ash bars were casted (25mmx25mmx285mm) with the required gradation and testing procedures according to ASTM C1260. The results show that the specimens experienced minor shrinkage whereas the standards anticipate expansion. It can be concluded that since no expansion occurred, the threat of alkali-aggregate is not expected to occur.

Table 9: Accelerated mortar bar results

Material	% Change in length
OPC	0.02
FA	0.04

Figure 6: Mortar bar specimens

6 ANALYSIS

6.1 6.1 7/28 Days Compressive Strength Ratio

The compressive strength 7/28 days ratios for the water quenched GGBFS yielded an average of 84% and the oven-cured Fly Ash an average of 90%. These are considerably higher than the 74% of the conventional concrete mix, showing that GGBFS and Fly Ash had higher initial strength gain compared to the conventional mix. Some oven-cured Fly Ash mixes almost gained maximum compressive strength after 7 days. After 7 days, the air-cured Fly Ash mix gained only 51% of its maximum compressive strength which is very low. This further proves that heat curing is a must for the Fly Ash.

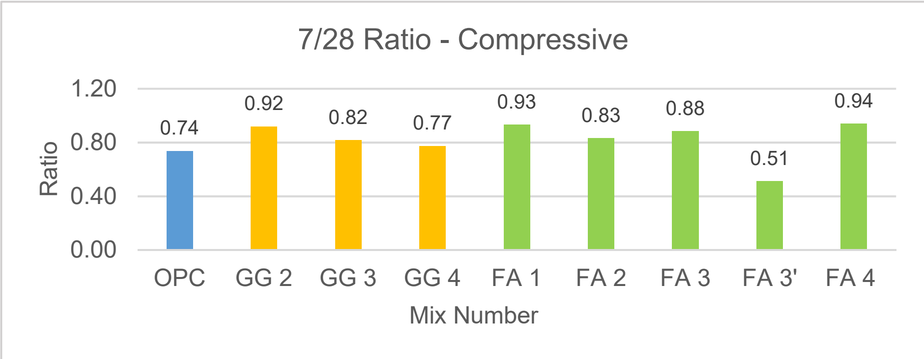


Figure 8: Compressive strength 7/28 ratio

6.2 Compressive Strength and Silicate/Hydroxide Ratio

The compressive strength versus the Silicate to Hydroxide ratio was plotted for both the GGBFS and Fly Ash mixes. The trends show that for GGBFS, as the Sodium Silicate to Sodium Hydroxide ratio decreases, the compressive strength decreases. For the Fly Ash, however, as this ratio decreases, the compressive strength of the Fly Ash increases.

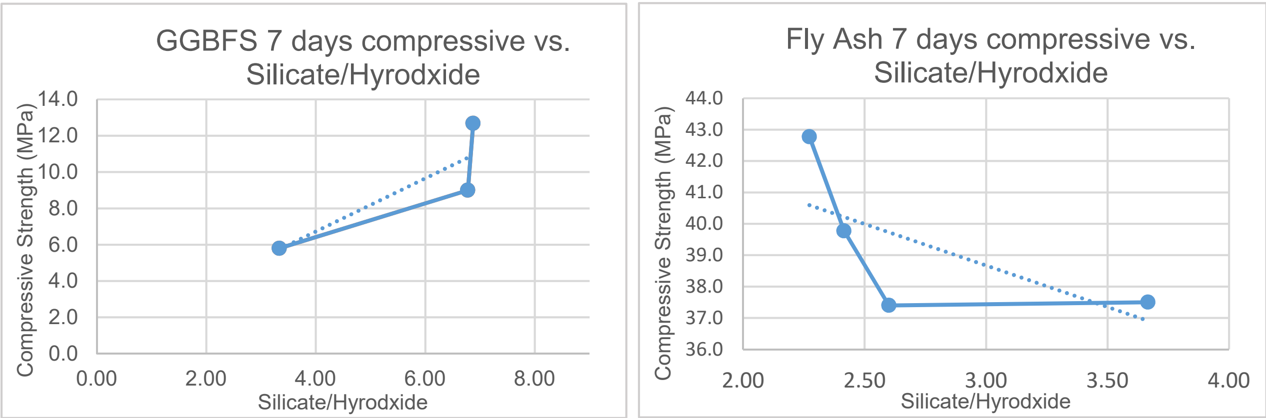


Figure 9: GGBFS and Fly Ash compressive strength vs silicate/hydroxide ratio

7 CONCLUSIONS

This study provides a comparison between three different cementitious matrices namely, BFS, GGBFS and Fly Ash. These were tested with an activator consisting of a combination of sodium silicate and sodium hydroxide. In light of the materials, methodology and results, the following conclusions can be stated:

- The poor fresh and hardened results obtained from air-cooled BFS may be an indication of the inert nature of the crystalline structures formed during the air-cooling process.
- Workability represents a major challenge for Alkali-Activated Concrete, as most mixes did not yield acceptable workability.
- Water Quenched GGBFS yielded lower compressive and flexural strengths after 7 and 28 days compared to conventional concrete. This could be attributed to the poor available quality of GGBFS in Egypt.
- Egyptian air-cooled BFS results show extremely poor results in compressive and flexural strengths.
- Fly Ash achieved higher 7 and 28 days strength than conventional concrete and similar ranges of flexural strengths. It exhibited early strength gain properties, however, heat curing is essential for the strength gain to take place.
- Results from the accelerated corrosion and mortar bar tests most likely eliminated the threat of alkali-aggregate reaction and reinforcement corrosion respectively.

8 RECOMMENDATIONS FOR FURTHER RESEARCH AND APPLICATION

Alkali-Activated Concrete still needs further experimental work in order to both, verify as well as to build upon the findings of this research. The following recommendations are proposed for future experimental work:

- Experiment with a wider set of activators, concentrations and activation techniques.
- Experiment with admixtures and mix proportion modifications for workability.
- Experiment with different activation techniques for BFS.
- Perform compressive and flexural strength tests beyond 28 days.
- Conduct the Mortar Bar Test at further ages.
- Conduct the Chemical Durability Test and permeability test.
- Investigate different curing temperatures and durations for Fly Ash.
- Explore potential use of Fly Ash mixes in steam-cured precast concrete, water and fluid plugging and repair works.

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