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SODIUM SILICATE ACTIVATED SLAG-FLY ASH CEMENT

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This research examines an alternative binder, Alkali Activated Cement (AAC), examining the fresh and hardened mechanical properties of twelve AAC mortar mixes with varying mixture proportions of blast-furnace slag, fly ash, sodium silicate (the alkali activator), and additional water. In addition to the Slag-Fly Ash mortars, nine mixtures with blast-furnace slag, silica fume, aluminum hydrate, sodium silicate, and water were tested. For all mortars, the compressive strength was exponentially related to the water/activator-solids ratio. Mortar strengths at 28 days ranged from 5 MPa to 20 MPa. Increasing the slag to binder-solids ratio from 0.1 to 0.2 increased the strength with water to binder ratios from 0.2 to 0.4. However, rapid or almost instantaneous setting times were observed for a slag to binder-solids ratio of 0.2. The research concluded that using a carefully chosen mix design can prevent quick setting while still achieving high strength and acceptable workability. It is suggested the CaO to binder-solids ratio remain below 0.07; a sodium silicate to binder solids ratio of around 0.25 is optimal; a water to binder-solids ratio should be around 0.3. When replacing fly ash, a Si/Al ratio above 2 is recommended. This research concluded that other solids (Silica Fume and Aluminum Hydrate) could replace Slag and/or Fly Ash if the overall chemical balance of the system is maintained.

Keywords: Alkali-activated cement, Workability, Binder, Activator solids ratio, Blast-furnace slag, Compressive strength.

1 BACKGROUND

There has been extensive research on Alkali Activated Cement (AAC) and its microstructure, strength development, durability and setting characteristics (*cf*. Caijun et al. 2006). Lu (1989) researched Alkali Activated Slag-Fly Ash cement, and concluded that the two main hydration products are Calcium Silicate Hydrates (CHS) and Alkali Aluminosilicate gel. CHS is the main hydration product of Ordinary Portland Cement, while Alkali Aluminosilicate Gel is the main hydration product of Geopolymer. By varying the mix composition’s chemical balance or by changing the mineralogy of the mix solids, it is possible to influence the abundance and the chemical makeup of these two hydration products.

The alkali activator used in AAC influences the mix design being employed. Caijun et al. (2006) noted that different activators have dissimilar chemical properties and therefore differing effects on the cement solids. Therefore, depending on the activator, the optimal mineralogy and chemical balance of the cement solids will be different. This explains why research on Sodium Silicate Activated Slag-Fly Ash Cement by Ionescu and Ispas (1986) and Bijen and Waltje (1989) contradict each other.

Bijen and Waltje (1989) noted that Sodium Hydroxide Activated Cement is stronger than Sodium Silicate Activated Cement, while Ionescu and Ispas (1986) observed the opposite. This highlights that mix guidelines need to be formulated based on the activator used.

The chemical balance of the cement solids, i.e., Calcium, Silicon, and Aluminum, will influence the microstructure of the final product. Calcium is incorporated into the C-S-H phase while Aluminum is built into the Alkali Aluminosilicate gel. Silicon is needed in both phases of the final product. Research by Pacheco-Torgal et al. (2008) indicated that when the Calcium Oxide content of the cement solids exceed 9%, the strength of the final product is reduced because of competition between the two hydration products. Therefore the mix constituents need to be selected so that the CaO content does not exceed 9%. The optimal chemical balance for the Alkali Aluminosilicate Gel is also known because of the extensive research on geopolymers. Gourley et al. (2011) recommends that the Si/Al ratio of the geopolymer should be kept around 2 for best results.

A key issue identified in the research is the quick setting times of Sodium Silicate Activated Cement. Caijun et al. (2006) and Duran Atiş et al. (2009) noted that the settings times are not affected by the dosage of the Sodium Silicate Activator but by the modulus of the Sodium Silicate. The modulus is the ratio of SiO_2 to Na_2O. When this ratio is close to 1, setting times of around 30 minutes have been observed. Decreasing the ratio below 1 or increasing it past 1.5 can extend the setting times significantly. The problem is that this also decreases the final strength of the hardened cement.

2 EXPERIMENTAL PROGRAM

This research consisted of two stages. Stage one of the experimental programs examined Slag-Fly Ash mixes, while stage two assessed the effect of replacing Fly Ash with a mix of Silica Fume and Aluminum Hydrate. Details of the mix compositions are found in Tables 1 and 2. The mixing regime was the same for all mixes, and consisted of 2 minutes dry mixing followed by the addition of liquid components, and another 4 minutes of wet mixing. Following the mixing, part of the mix was separated to use in assessing the setting time, while the remaining material was cast into molds conforming to ASTM 1009C 50 mm molds specifications. During curing the samples were stored in a climate-controlled room. In this room the samples were air cured at a constant temperature of approximately 25°C until the time of testing.

Setting times where assessed every 10 minutes by measuring the time taken for 200 mL of mortar to flow through a funnel. This test was stopped when the mix failed to flow through the funnel. Compressive strength was tested at 1, 14, 28 and 42 days.

3 RESULTS

3.1 Compressive Strength

The presentation of results obtained from the compressive testing is limited to the 28-Day data for this paper format. The 14-Day and 42-Day data show the same trends as the ones visible in the 28-Day data. The 1-Day data is very scattered and in most cases a trend is not clearly observable.

Table 1. Stage one mortar mix compositions.

Mix Name	Blast furnace Slag (g)	Fly Ash (g)	Activator	Extra Water (g)
A1X	186	1671	421	136
A2X	157	1409	355	271
A3X	135	1219	307	370
A2Y	167	1503	758	78
A3Y	143	1288	649	210
A3Z	152	1366	1033	30
B1X	376	1503	426	138
B2X	316	1265	359	274
B3X	273	1092	310	373
B2Y	338	1350	765	78
B3Y	289	1155	655	212
B3Z	306	1226	1042	30

Table 2. Stage two mortar mix compositions.

Mix Name	Blast-furnace Slag (g)	Silica Fume (g)	Aluminum Hydrate (g)	Activator	Extra Water (g)
2A1X	156	483	401	354	166
2A1Y	160	487	419	483	103
2A1Z	164	492	438	620	36
2A2X	154	501	369	348	164
2A2Y	157	506	386	476	101
2A2Z	161	512	403	610	36
2A3X	152	517	342	344	162
2A3Y	155	523	357	470	100
2A3Z	159	529	373	602	35

3.1.1 *Water to activator solids ratio and the reactive fraction*

The effect on compressive strength at 28 days of water to activator solids ratio and the reactive fraction (SiO_2 + Al_2O_3 + CaO fraction of Total Binder Solids) is shown in Figures 1 and 2 respectively. The water to activator solids ratio and the reactive fraction form a trend that is not highly sensitive to the effects of other mix factors. So even though the slag addition and water content varies considerably between the mixes, the trend of decreasing strength with increasing water/activator solids, and increasing strength for increasing reactive fraction, are evident, though with a lower correlation seen in the reactive fraction.

3.1.2 *Slag content*

Figure 3 shows the effect of increasing the slag content of the binder-solids. It can be seen that increasing the slag content from a ratio of slag/binder-solids of 0.1 to 0.2 increases the strength significantly. However it should be noted that increases beyond this point would have resulted in a reduction of strength (Pacheco-Torgal et al. 2008). It can be seen that the compressive strength increases exponentially with decreasing water content. This is analogous to OPC, as adding water to the mix increases initial porosity and therefore decreases strength (Caijun et al. 2006).

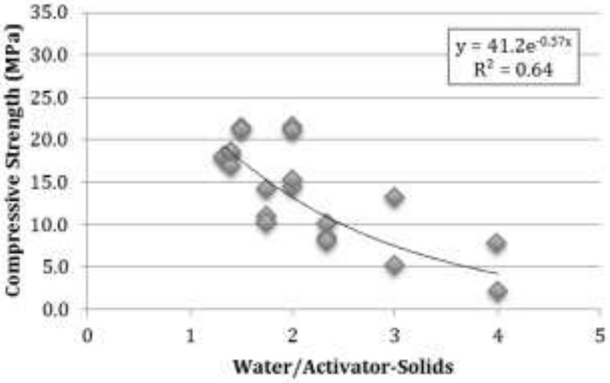

Figure 1. Mortar 28-Day compressive strength trend with water/activator solids.

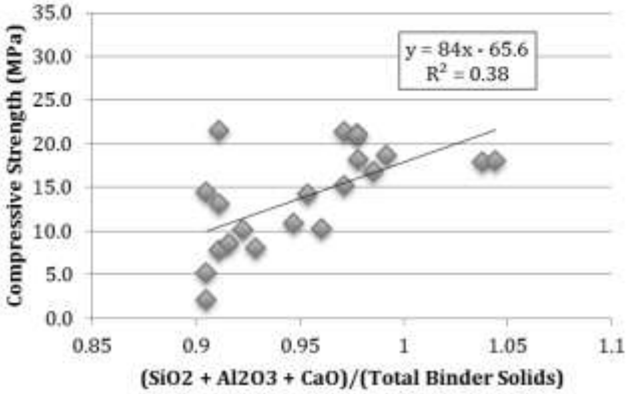

Figure 2. Mortar 28-Day compressive strength trend with reactive fraction.

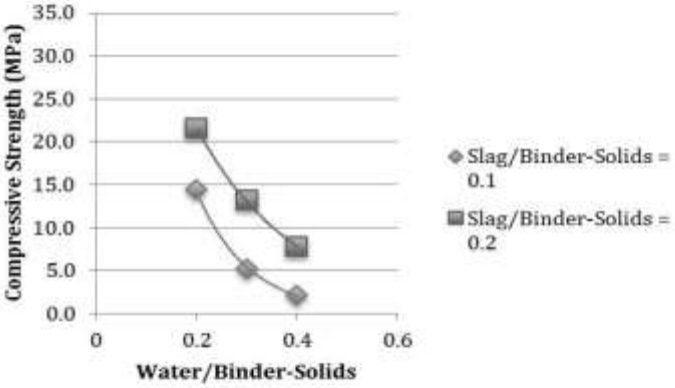

Figure 3. Slag-based mortar mixtures, 28-Day compressive strength trend with water to binder solids.

3.1.3 *Stage two: Silica fume and aluminum hydrate*

Figure 4 shows the results gained during stage two of this research. In stage 2 of the research, a mix of silica fume and aluminum hydrate replaced the fly ash used in stage one. The water content was static at 0.35 and the slag addition static at 0.15. In Figure 4 it can be seen that the replacement of fly ash slightly reduces strength.

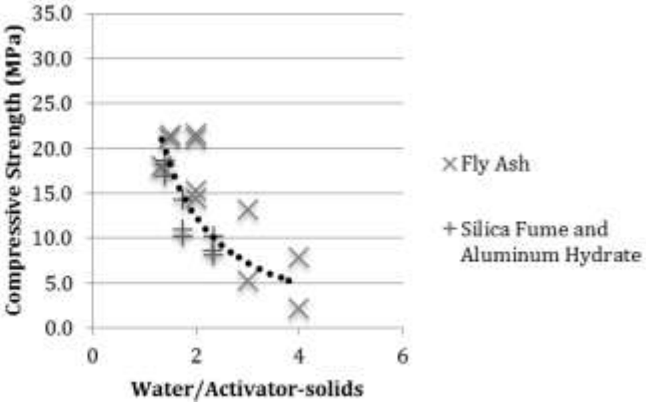

Figure 4. Fly ash and silica fume + aluminum hydrate based mortar mixtures, 28-Day compressive strength trend with water to activator solids.

3.2 Setting Time

It was observed in all cases that a slag to binder-solids ratio of 0.2 leads to a very quick setting mortar that is unsuitable for use outside of a laboratory environment. Flow times through the funnel were an order of magnitude of 3 times longer (140 to 160 minutes) for a slag/binder solids ratio of 0.1 compared to 0.2. Increasing the water content of the mix can increase the setting time. When activator-solution to binder-solids ratio increases, the setting time is also increased. Also observable was that the increase in setting times is larger when more slag was added to the mix.

4 CONCLUSION

4.1 Mixture Design Guidelines

Maintain CaO to Binder-Solids Ratio below 0.07 in order to keep setting times high. If highest strength is required and setting times are unimportant, this ratio can be increased.

Minimize Water to Sodium Silicate ratio as much a possible, as long as workability is not impaired due to low Water to Binder-Solids Ratio.

Aim for a Sodium Silicate to Binder Solids ratio of 0.25. This can be lowered to 0.2 when high 1-Day strength or a cheaper mix is required but setting rates and ultimate strength will be negatively impacted. The ratio can also be increased to 0.30 when CaO content is below 0.07, and higher late-age strength is required, but low-age strength and workability will be negatively impacted. Water to Binder-Solids ratio should be around 0.30.

When a stronger mix is required a higher Sodium Silicate content should be considered before lowering the water content. Lowering the water content has a larger influence on workability than increasing Sodium Silicate content, and a higher Sodium Silicate content can extend setting times.

When replacing Fly Ash with another material, aim for a Si/Al ratio slightly above 2 but below 0.25. Preserve the ratio of (SiO_2 + Al_2O_3 + CaO) to Binder-Solids as high as possible.

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