Activation of High Volume Fly Ash Pastes Using Chemical Activators

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ABSTRACT

A number of studies have been conducted on the activation of high volume fly ash pastes (50% fly ash replacement of PC) using chemical activators; sodium sulfate, calcium sulfate and sodium hydroxide at a dosage of 1% wt binder, 10% wt binder and 1 Molar, respectively. Two different temperature regimes were utilised, where samples were treated at (i) 20^oC for 7 days and (ii) 60^oC for the initial 24 hours and 20^0C for the remaining 6 days. Compressive strength was measured at 1, 3 and 7 days. XRD and thermogravimetric analysis (TG) were carried out on samples after 1 and 7 days curing to characterise the hydration products formed. The activation mechanisms of each activator were discussed. Sodium sulfate showed to be the optimum activator when cured at 20^0C whilst calcium sulfate showed to be the optimum activator when cured at 60^0C.

INTRODUCTION

The production of Portland cement consumes a lot of natural resources and energy and emits CO2, SO2 and NOx. These gases can have a detrimental impact on the environment resulting in acid rain and contributing to the Greenhouse effect. Therefore, it is vital that the construction industry react to synthetically utilise resources, especially industrial by-products.

Fly ash has been widely used as a substitute for Portland cement in many applications because of its advantageous on fresh, hardened and durability properties [Lea 1998]. One clear disadvantage in the use of most fly ashes for cement-replacement purposes is that the replacement of cement, especially in high volumes (>40%), decreases rate of early strength development of the concrete.

Numerous investigators have utilised chemical activation to activate fly ash systems. Two different methods commonly utilised include alkali activation and sulfate activation. Alkali

activation involved the breaking down of the glass phases in an elevated alkaline environment to accelerate the reaction [Xu & Sarkar 1991; Ma et al. 1995; Shi 1996; Shi 1998; Fraay & Bejen 1989]. Sulfate activation is based on the ability of sulfates to react with aluminium oxide in the glass phase of fly ash to form sulfates (AFt) that contributes to strength at early ages [Xu & Sarkar, 1991; Shi, 1996; Shi, 1998;]. The possibility of fly ash activation mainly lies in the breaking down of its glassy phases. Fraay considered that the pH value required to dissolve the alumina and silica is about 13.3 or higher. The usual way of achieving a high pH is by the addition of NaOH or other alkaline materials into the fly ash system. Studies carried out by Shi and Day [1996 & 1998] compared the addition of Na_2SO_4 and $CaCl_2$ and found that the addition of both increased the cost of raw materials but the cost per unit strength decreased. The addition of 4% Na_2SO_4 increased both the early and later age strength of paste systems whereas the addition of 4% $CaCl_2.2H_2O$ lowered the early age strength but increased the later strength. Poon [2001] used an addition of 10% of anhydrite to activate a mortar system incorporating 55% fly ash and found that 3 day strengths were improved by about 70%. It also increased the strength at later ages of these mortars.

Another method commonly used by industry to improve early age strengths is to use chemical admixtures. Many commonly available admixtures have the potential to accelerate the hydration of PC systems, whilst also being high range water reducers and superplastiser at the same time. The reduction of free water in the pastes due to the addition of a superplastiser can result in improved strengths [Neville, 2002].This paper presents an exploratory study on the activation of high volume fly ash pastes to achieve improved early age strength using admixture copolymer-based superplasticiser along with three chemical activators (sodium sulfate, calcium sulfate and sodium hydroxide) with accelerated curing.

EXPERIMENTAL

Materials

A normal hardening Portland cement (CEM I 42.5 according to European Standard EN 197-1, 2002) was used for the manufacture of all paste specimens. A Type II fly ash, (EN450 complying with European Standard BS EN206 - Part 1:2000) was used for the manufacture of all paste specimens. The sodium sulfate, calcium sulfate and sodium hydroxide were laboratory grade chemicals. A modified copolymer-based superplasticiser (SP) with dry material content of 40% and relative density at 20^0C of 1.080 was used in the manufacture of mixes. It meets the requirements of BS EN 934-2, 1998.

Mixing and curing.

Paste cubes of size 50mm were manufactured in accordance with BS EN 196-3: 2005. The superplasticiser (SP) was added to the mixing water of the mixes prior to mixing at a dosage of 0.4% weight of cementitious material. Sodium sulfate and sodium hydroxide were also dissolved in the mixing water prior to mixing. Anhydrite was added and pre-blended with the PC and fly ash in the mixer prior to mixing. The temperature of the mixing water was also controlled and in each case was kept at 20.5^0C ($\pm$ 0.5).

The following is a description of the mixes manufactured with the mix identity used in the presentation of data in brackets following descriptions;
(I) 50% PC + 50% Fly ash + SP (**Sika**), (II) 50% PC + 50% Fly ash + SP + 1% Sodium sulfate (1% weight of binder) (**Sika + 1**), (III) 50% PC + 50% Fly ash + SP + 10% Calcium sulfate (10% weight of binder) (**Sika + 2**), (IV) 50% PC + 50% Fly ash + SP + 1 Molar Sodium hydroxide (**Sika + 3**)

Two different curing regimes were used in this study. To ensure that the AFt phase will not convert to AFm phase and hence resulting in potential Delayed Ettringite Formation (DEF), 60°C was used for thermal curing. Thus, the following two regimes were considered: (1) 20^{0}C for 7 days and (2) 60^{0}C for 1 day and 20^{0}C for 6 days. All samples were kept in the moulds and placed in constant temperature (20°C or 60°C) environments for the first 24 hours. After 24 hours the cubes were demoulded. 50mm cubes not required for 1 day testing were wrapped in damp hessian cloth and sealed in plastic bags and then placed back in 20^{0}C (± 0.5) curing environment until required for testing.

Stopping hydration and powder sample preparation

At the dates of testing, three paste cubes were crushed for obtaining the compressive strength. The average was reported as compressive strength at each age. The debris of the cubes were then fractured into pieces and soaked in acetone to stop the hydration. Before the XRD and TG test, the acetone was filtered and the samples were dried in a desiccator under vacuum. The dried fragments were then crushed and ground in an agate mortar to pass 63 µm. The powder samples passing 63 µm were used in the XRD and TG analyses.

Sample analysis

Standard consistence tests were used to identify the water demand for each mix to achieve standard consistence, which were carried out on fresh paste according to BS EN 196-3:2005 using the Vicat apparatus. XRD analysis was run on a PANalytical XPert PRO X-ray diffractometer operating at 2^0/min and a step size of 0.02^0 between 5-65^0. Thermogravimetric analysis (TG) was carried out using a Simultaneous Thermal Analyser STA 449C Jupiter. The TG test was run with a heating profile of 30 - 1000^{0}C at 10^{0}C/min in a flowing atmosphere of nitrogen. The compressive strength was determined in accordance with BS EN 12390-3: 2002.

RESULTS

X-ray diffraction (XRD)

XRD analysis was carried out on powder samples and the description of how the powder samples were prepared and information on XRD diffractometer is described in the following paragraphs. To improve clarity of presenting XRD data, sections of the full scans (5-65^0 2θ) will be presented in this paper.

Key: 1 - Ettringite, 2 - Gypsum,
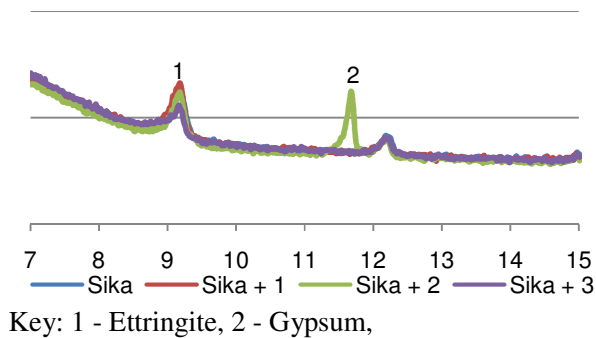
Fig. 1. XRD patterns of PFA mixes treated at 20°C at 1 day (7-15° 2θ).

From Fig. 1 it can be seen that the fly ash mix activated with sodium sulfate produced the highest ettringite peak after 1 day curing followed by calcium sulfate and sodium hydroxide activated mixes. Ettringite formation can contribute to the early strength development in the OPC/fly ash composite [Roy & Silsbee; Katz, 1998; Xu & Sarkar, 1991; Ma et al., 1995; Shi, 1996;].Ettringite was formed due to the reaction of sulfate from the chemical activator and the gypsum added in the OPC with aluminate present in the mix. These findings match well with work reported by Poon, 2001. A gypsum peak is visible in the calcium sulfate mix at approximately 11.7^{0}.


Key: 3 - Calcium hydroxide, 4 - Tri-calcium silicate, 5 - Anhydrite,
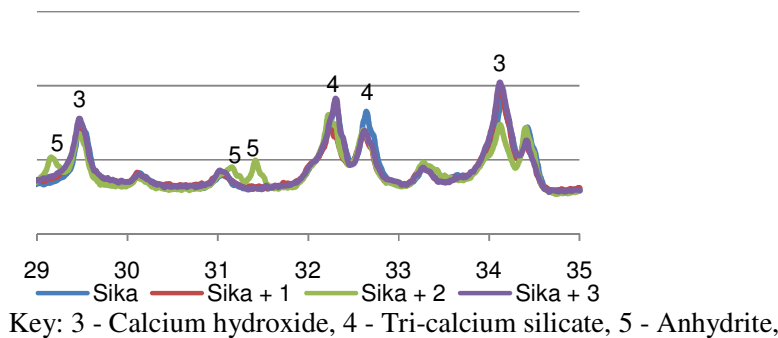
Fig. 2. XRD patterns of PFA mixes treated at 20°C at 1 day (29-35° 2θ)

The anhydrite peaks are obvious in the calcium sulfate mix in Fig. 2. It is also noticeable that the largest tri-calcium silicate peaks were identified in the Sika and Sika + 3 mixes. This would suggest that sodium hydroxide had not activated the PC to the same extend as sodium sulfate and calcium sulfate. This trend fits with the ettringite results presented in Fig. 1. Anhydrite peaks are also visible in the calcium sulfate activated mix (Sika + 2).

Key: 1 - Ettringite, 2 - Gypsum, 6 - Calcium aluminate hydrate
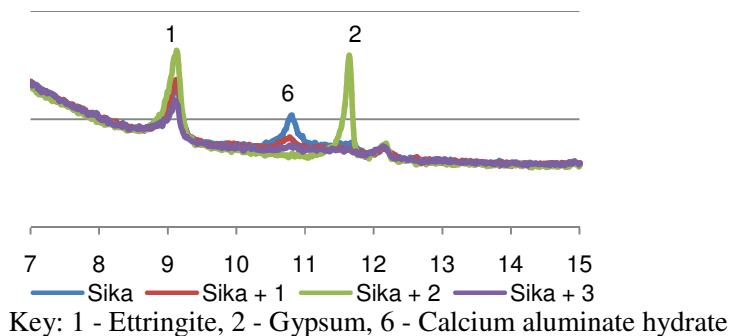
Fig. 3. XRD patterns of PFA mixes treated at 20°C at 7 days (7-15° 2θ)

After 7 days curing at 20^{0}C, ettringite is most predominant in the calcium sulfate activated mix. A lower ettringite peak was identified in the sodium sulfate and sodium hydroxide mixes respectively. Calcium aluminate hydrate was identified in the un-activated Sika mix and to a certain extent in the sodium sulfate mix. This peak was not identified after 1 day curing. The alumina may have been liberated from fly ash after its glassy structure was broken down. Calcium aluminate hydrate may not have been present in the activated mixes as the aluminium may have been consumed in the formation of ettringite (calcium aluminium sulfate hydroxide hydrate). A large gypsum peak was also identified in the matrix activated with anhydrite after 7 days curing which suggests a large quantity of unreacted sulfate was still present in the paste after 7 days curing.

Key: 2 - Gypsum, 3 - Calcium hydroxide, 4 - Tri-calcium silicate, 5 - Anhydrite,
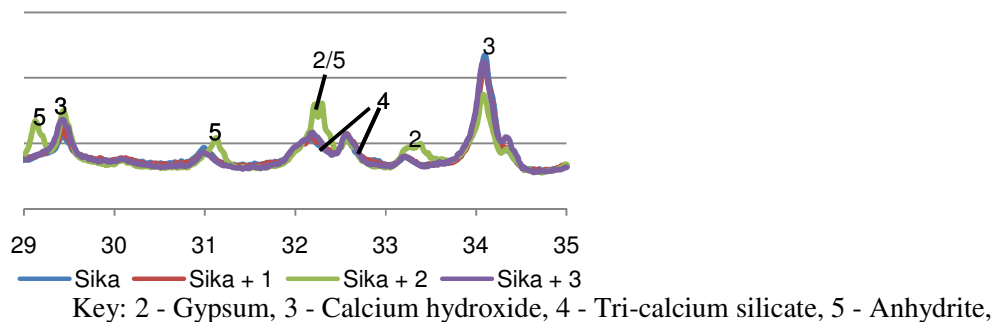
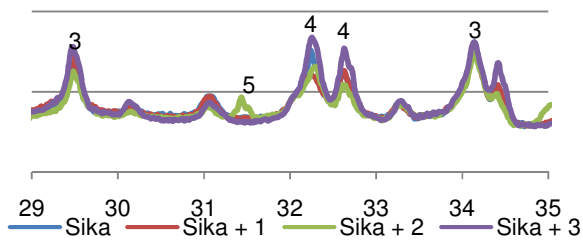**Fig. 4. XRD patterns of PFA mixes treated at 20°C at 7 days (29-35° 2θ)**

The obvious difference between the scans at 1 and 7 days in Figs 2 and 4 respectively is that tri-calcium silicate is reduced which is expected with the continued hydration of PC. There is a new peak however in the calcium sulfate activated mix at approximately 32.3^0 which is not tri-calcium silicate. It would seem that this peak correlates to anhydrite. Unreacted anhydrite and gypsum are also identified in the same scan. Similar to 1 day results, the calcium sulfate activated mix showed the lowest peak for calcium hydroxide which would suggest that calcium sulfate has been more successful in activating the fly ash when compared to the other chemical activators.
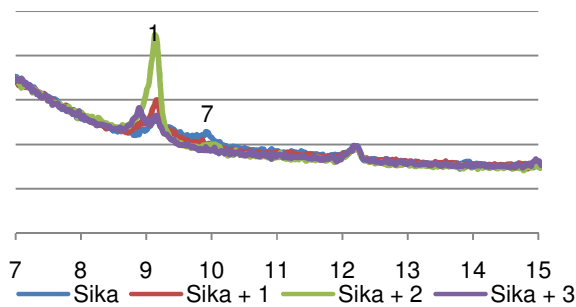
Key: 1 - Ettringite, 7 - Mono-sulfate,

Fig. 5. XRD patterns of PFA mixes treated at 60°C at 1 day (7-15° 2θ)

Fig. 5 shows that in the presence of high temperature a large ettringite peak was formed in the calcium sulfate activated mix. There is no evidence of a gypsum peak in the calcium sulfate mix treated at 60^{0}C which may suggest the majority of anhydrite has been consumed in the first 24 hours under the elevated temperatures. A small mono-sulfate peak was identified in the un-activated Sika mix which suggests high temperature curing has converted ettringite to mono-sulfate. Taylor [1997] highlights that this may lead to delayed ettringite formation at later ages.

Key: 3 - Calcium hydroxide, 4 - Tri-calcium silicate, 5 - Anhydrite,

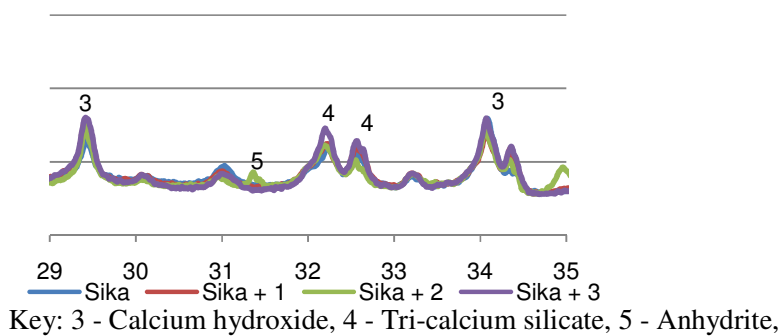**Fig. 6. XRD patterns of PFA mixes treated at 60°C at 1 day (29-35° 2θ)**

Fig. 6 shows that calcium hydroxide and tri-calcium silicate levels are reduced for the calcium sulfate activated mix. With this and the fact that ettringite peaks were increased for the same mix suggest that calcium sulfate has indeed activated the fly ash. The peaks from unreacted anhydrite are also reduced in the mix treated at 60^{0}C when compared to the mix treated at 20^{0}C (Fig. 2).

Key: 1 - Ettringite, 7 - Mono-sulfate,
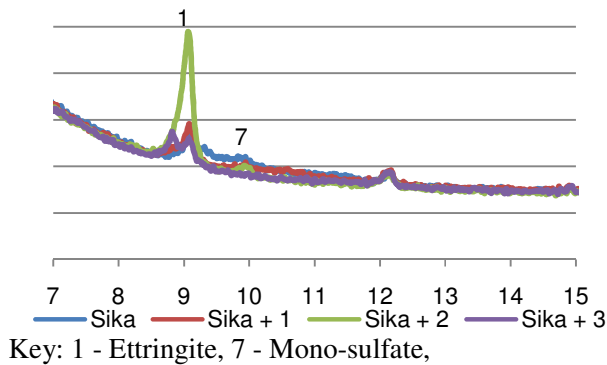
Fig. 7. XRD patterns of PFA mixes treated at 60°C at 7 days (7-15° 2θ)

Ettringite peaks for the un-activated Sika mix and the sodium sulfate and sodium hydroxide activated mixes are similar after 1 and 7 days curing. The ettringite peak identified in the calcium sulfate mix after 7 days curing has increased when compared to the peak obtained after 1 day curing which suggests that calcium sulfate has continued to activate fly ash after 1 day. There is also some mono-sulfate still identifiable in the un-activated Sika mix after 7 days curing.

The data presented in Fig. 8 for mixes treated at 60°C for 24 hours after 7 days curing are quite similar to the data presented in Fig. 6 for the same mixes after 24 hours curing. A reduction in the tri-calcium silicate peaks is obvious and this is due to the continued hydration of PC. No significant change in the calcium hydroxide peaks has occurred between 1 and 7 days. A slight reduction in unreacted anhydrite can be seen. When compared with the same mixes treated at 20°C (Fig. 4) there is significantly less unreacted anhydrite in the calcium sulfate mixes cured at 60°C for the first 24 hours.

Key: 3 - Calcium hydroxide, 4 - Tri-calcium silicate, 5 - Anhydrite,

Fig. 8. XRD patterns of PFA mixes treated at 60°C at 7 days (29-35° 2θ)

Derivative thermogravimetric analysis (DTG)
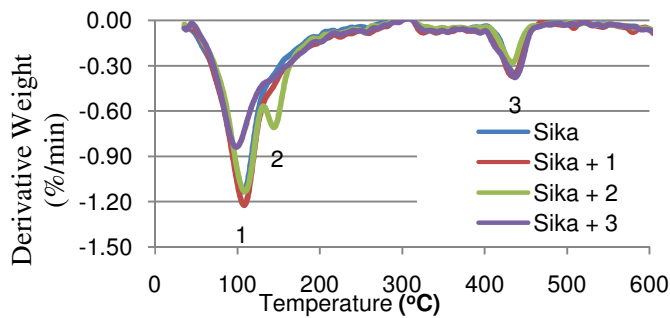
Key: 1 - CSH/Ettringite, 2 - Gypsum, 3 - Calcium hydroxide

Fig. 9. DTG curves for mixes treated at 20^{0}C for 1 day (50-600^{0}C)

The DTG curves presented in Fig. 9 show three significant dips in the curves which represent weight loss. Taylor [1997] stated that the peaks for 115-125°C represents calcium silicate hydrate (CSH), 135-140°C represents ettringite, 145-165 ^{o}C represents gypsum and 530-550 ^{o}C represents calcium hydroxide. The first significant weight loss occurs at approximately 110^{0}C. This would signify CSH from Taylor [1997]; however peaks from thermal analysis might shift due to the variation of CSH gel formed or the crystallisation degree of the crystals. As a result, different researchers [Taylor, 1997; Bye, 1999] have reported slightly different temperatures. The TG analysis was run at 10°C/min, so it would be very difficult to differentiate the peaks between CSH and ettringite as both occur at a similar temperature range. Therefore, they might overlap. As a result the peak at approximately 110^{0}C can be attributed to CSH/ettringite. In Fig. 9 it is evident that the sodium sulfate activated mix had the most CSH gel (the main strength-giving hydration products) and ettringite and this mix was closely following by the calcium sulfate activated mix, the un-activated Sika mix and finally the sodium hydroxide activated mix. The second significant dip occurred in the calcium sulfate activated mix at approximately 150^{0}C and this was accounted to be gypsum [Borrachero et al. 2008]. Calcium hydroxide is accounted to the third significant dip in the curves at approximately 450^{0}C [Taylor, 1997]. The sodium hydroxide mix contained the most calcium hydroxide, followed closely by the sodium sulfate activated mix and un-activated, with the calcium sulfate activated mix having the least amount of calcium hydroxide. These results compare almost perfectly with XRD results so the main observations will be presented only for the remaining DTG graphs.
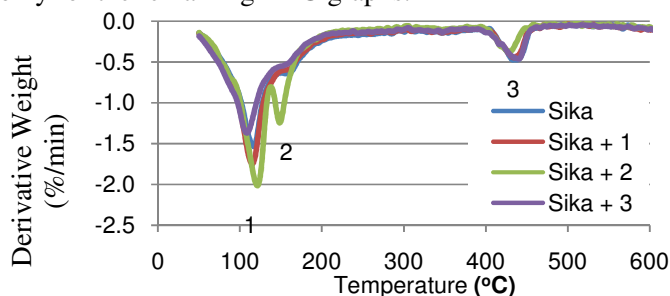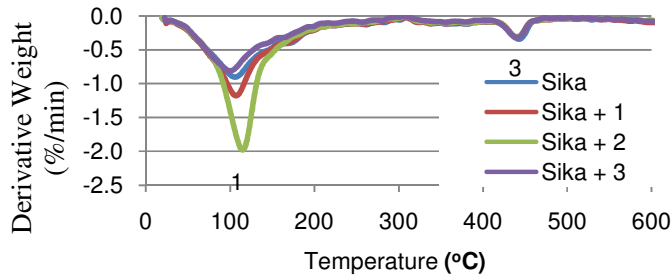

Key: 1 - CSH/Ettringite, 2 - Gypsum, 3 - Calcium hydroxide

Fig. 10. DTG curves for mixes treated at 20^{0}C for 7 days (50-600^{0}C)

Similar DTG data was obtained after 7 days however a higher quantity of CSH/ettringite was obtained in the calcium sulfate activated mix. The un-activated mix showed to have the most calcium hydroxide. This is an ideal match for ettringite with XRD data (Figs 3 and 4).

Key: 1 - CSH/Ettringite, 3 - Calcium hydroxide

Fig. 11. DTG curves for mixes treated at 60^0C for 1 day (50-600^{0}C)

DTG data presented in Fig. 11 show the quantity of CSH /ettringite decreased in mixes in the following order; calcium sulfate < sodium sulfate < un-activated < sodium hydroxide. The CSH/ettringite content of the calcium sulfate mix was significantly larger than the other mixes. The sodium hydroxide activated mix provided the largest amount of calcium hydroxide but was only marginally greater than the other mixes.
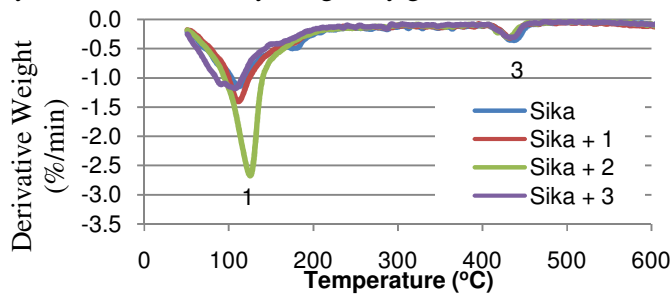

Key: 1 - CSH/Ettringite, 3 - Calcium hydroxide

Fig. 12. DTG curves for mixes treated at 60^0C for 7 days (50-600^{0}C)

After 7 days curing, the quantities of CSH/ettringite increased in the sodium sulfate activated mix and significantly in the calcium sulfate activated mix. The un-activated Sika mix showed to have the largest quantity of calcium hydroxide but again the margin was small. Once again this data correlated very well with the XRD data.
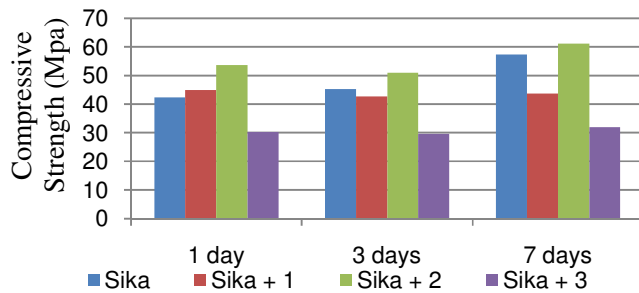
Compressive strength

The compressive strengths of the four mixes treated at the two different curing temperatures and tested at 1, 3 and 7 days are presented in the following Figs.
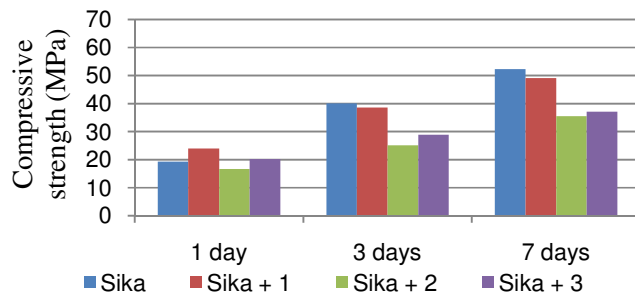
Fig. 13. Compressive strength results for all mixes treated at 20⁰C for up to 7 days

Compressive strength data obtained after 24 hours curing showed that the addition of 1% sodium sulfate was capable of increasing compressive strengths by 25% when compared to the un-activated mix. The increase in compressive strength can be attributed to the increased CSH gel and ettringite in the mix which was identified using XRD and DTG. The sodium hydroxide activated mix provided slightly improved compressive strengths whilst the calcium sulfate mix provided slightly reduced compressive strengths when compared to the un-activated mix. The trends in compressive strength gain after 1 day are similar at 3 and 7 days. The un-activated mix provided better compressive strengths at 3 and 7 days when compared to the activated mixes. This is contrary to XRD and DTG data showing calcium sulfate activated mix to having increased quantities of CSH gel and ettringite at 7 days when compared to the other mixes. Literature suggests however that calcium sulfate and sodium sulfate will continue to activate fly ash after 7 days so improvements in strength may occur at later ages [Roy & Silsbee; Katz, 1998; Xu & Sarkar, 1991; Ma et al., 1995; Shi, 1996].

Fig. 14. Compressive strength results for all mixes treated at 60⁰C for 1 day and 20⁰C for 6 days.

The compressive strength data obtained after mixes were cured in a 60⁰C environment for 24 hours show that both sodium sulfate and calcium sulfate were capable of increasing compressive strengths by 10% and 27% respectively. The sodium hydroxide activated mix provided compressive strengths 25% lower than the un-activated mix. Palacios and Puertas, 2005 stated that in a high alkaline media (pH 13.0 - 13.6) the chemical admixtures may undergo structural change. This may explain the reduction in compressive strength in sodium hydroxide activated mixes. At 3 days, when the samples had returned to a 20⁰C curing

environment there was very little strength gain in the un-activated mix and no increase in any of the activated mixes. At 3 days, only the calcium sulfate activated mix outperformed the un-activated mix. After 7 days of curing again the calcium sulfate activated mix outperformed the un-activated mix by 7%. The sodium sulfate activated mix did not gain any strength after being cured at 60^0C for the initial 24 hours. This was also the case for the sodium hydroxide mix.

CONCLUSIONS

Based on these results the following conclusions can be made;
- The addition of sodium sulfate and calcium sulfate formed significant quantities of CSH gel and ettringite.
- Calcium sulfate activated mixes treated at 20^0C for 7 days showed unreacted anhydrite and gypsum in the mixes at 1 and 7 days. In calcium sulfate activated mixes treated at 60^0C for the initial 24 hours showed smaller quantities of unreacted anhydrite and no gypsum after 1 and 7 days curing.
- The addition of sodium sulfate improved compressive strength of the mix treated at 20^0C after 1 day curing by 25% when compared to the un-activated mix. The addition of calcium sulfate and sodium hydroxide provided similar results at 1 day to the un-activated mix but there was less strength gain in these mixes at 3 and 7 days when compared to the sodium sulfate activated mix and the un-activated mix.
- The addition of sodium sulfate and calcium sulfate improved compressive strength of the mixes treated at 60^0C after 1 day curing by 10% and 27% respectively when compared to the un-activated mix. The sodium sulfate and sodium hydroxide activated mixes showed no strength gain at 3 and 7 days. The calcium sulfate activated mix outperformed the un-activated mix at 3 and 7 days also.

Therefore, based on the results presented, the suggestion would be for room temperature curing, sodium sulfate is effective along with SP. For elevated temperature curing at 60^oC, calcium sulfate is effective.

ACKNOWLEDGMENTS

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