

Concrete using Siliceous Fly ash at very High Levels of Cement Replacement: Influence of Lime Content and Temperature

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Abstract

Potential for producing viable binders at very high levels of cement replacement (60% and above) with fly ash is explored. The role of lime content and temperature on the efficiency of fly ash in contributing to strength gain is investigated using quantitative X-ray diffraction (XRD) analysis. Results of fly ash characterization are presented using quantitative X-ray diffraction (XRD) to identify its reactive potential associated with the amorphous silica content. A new method for quantitative phase analysis of the amorphous phase contributions in the XRD spectrum is presented. A strength-based efficiency factor which provides a measure of the contribution of fly ash is introduced. Temperature is shown to increase the efficiency of fly ash by accelerating the dissolution of the reactive amorphous content. Efficiency of fly ash in the binary high volume fly ash-cement blend is limited by the availability of lime. Increasing the lime content in the system provides significant enhancement in strength, but it does not influence the dissolution of fly ash. With the availability of lime, the efficiency is limited by the rate of contribution of reactive Silica from fly ash, which is influenced strongly by temperature. Concrete strengths of 30 MPa and higher were achieved with 65% replacement of cement with fly ash and total cement content of 100 kg/m³. The strength gain in concrete is shown to be related to the depletion of lime in the system, formation of amorphous hydration products and the depletion of Si/Al content from fly ash. An investigation of the underlying mechanisms reveals the potential for further strength enhancement by effectively engaging all the reactive components of fly ash.

Keywords: Fly ash, Quick lime, Rietveld refinement, Efficiency factor, Si/Al dissolution, Amorphous product content.

Introduction

Improvements in specific aspects of concrete performance have been obtained using mineral admixtures or supplementary cementitious materials (SCM) at low levels of cement substitution (ACI report, 2002). Blended cements, which are essentially binary blends of cement and SCMs, are available commercially. The use of fly ash in concrete is particularly attractive for use as a cement

replacement since it allows for beneficial utilization of waste material which is generated in large quantities. Since the demand and consumption of Portland cement are increasing, it is becoming imperative for the cement and concrete industry to start utilizing more fly ash to meet these demands rather than increase Portland cement production.

Fly ash used in moderate quantities as cement replacement can significantly enhance the long-term properties of concrete. However, concrete made with fly ash substitution of cement often displays slow hydration that is accompanied by slow setting, low early age strength. This effect is more pronounced as the level of fly ash replacement is increased. At high levels of replacement there is a reduction even in the final properties. The low reactivity and the lower quantity of reactive components in fly ash is a major hindrance to the development of concrete consisting of large volumes of fly ash. In concrete containing fly ash, a significant proportion of fly ash remains unreacted even after significant time. It is therefore becoming evident that optimal replacement level of fly ash in cement depends on assessing its full reactive potential and allowing the maximum potential of the cementing action provided by fly ash hydration to be harnessed. Effective use of high volume fly ash as cement replacement therefore requires development of an understanding of the reactivity of fly ash.

Hydration in cementitious systems with high volume fly ash as cement replacement involves multiple complex processes. Understanding the underlying processes can lead to production of alternate binders which minimize or totally eliminate the use of cement. Proper understanding of the type and quantity of products formed, the influence of process variables and the link between the products of reaction and the properties of concrete is required. Proper characterization of fly ash is an essential first step. Use of very high volume fly ash in concrete requires very careful consideration, from the characterization of the starting materials, through mixture proportioning and curing options to achieve desired properties, to the in-place early-age and long-term performance of the concrete in its fresh and hardened states.

In this paper results of an experimental study aimed at producing High volume fly ash concrete suitable for warm weather concreting using 100 kg/m³ cement which achieves a target mean strength of 30 MPa at 28 days are presented. Starting with a mix designed for a characteristic strength of 35 MPa, the target strengths are achieved at very high levels of cement replacement with fly ash which is activated using quick lime. The study demonstrates that concretes with acceptable strength can be formulated to meet the original project specifications at 65% replacement of cement with fly ash. An efficiency factor is applied to measure the performance of reactivity of fly ash in concrete compared to cement. An investigation of the underlying reactions reveals the potential for further strength enhancement through activation by effectively engaging all the reactive components of fly ash. A new method based on quantitative XRD is used to determine the quantity of Si/Al cement and the amount of hydrated amorphous product formed in the system.

Background

Fly ash as a cement replacement in concrete is very common and attractive because of its large availability, widespread familiarity with use in construction and the potential for high volume utilization. However, the use of fly ash is also accompanied by increased setting time and decreased early strength. To improve the properties of fly ash researchers have used of the methods like thermal (Maltais and Marchand, 1997; Shi and Day, 1993), mechanical (Bouzoubaa et al., 1997) and chemical (Shi and Day, 1995) activation to achieve enhanced reactivity from fly ash and to compensate the loss of early strength. The efficacy of some of these methods is however debatable since a number of them are too energy demanding, while others fail in simple cost-benefit analysis.

From the different methods to enhance the reactivity of fly ash, such as fine grinding, elevated temperature curing and use of chemical activators it has been found that the efficiency of fly ash is linked to the enhancements of the rate and extent of pozzolanic reactions between fly ash and lime, and hence increase the strength development rate and ultimate strength of hardened concrete containing fly ash. While chemical activation, which consider alternate reaction pathways have been explored, it has been found that the activation of the pozzolanic reactivity of coal fly ashes is the most effective way to improve the performance of the fly ash in concrete.

Pozzolanic reaction starts after the breakdown of glass particles in the fly ash. Fly ash does not react during the first few days of curing, sample cured at 20 deg C and Increasing the temperature from 20 deg C to 40 deg C increases the reactivity of fly ash contributing to improvements in both early and long term the compressive strengths of fly ash cement blended concrete while it reduces the long term compressive strength of the OPC

(Maltais and Marchand, 1997). Temperature increases the pH level of the pore solution increasing the OH⁻ ion concentration in the system, which causes the dissolution of fly ash particles quickly (Fraay et al., 1989). A similar observation was made by (Zhang et al., 2000) and they also reported pH value decreases with increasing amount of fly ash content.

Quick lime as fly ash replacement in cement-fly ash blends has been shown have a positive influence mainly on strength development and has been shown to be an effective way for producing Ca(OH)₂ in the mix (Shi, 1996). The reaction rate of high Calcium fly ash with quick lime has been shown to produce a notable acceleration of the fly ash degree of reaction throughout the curing period (Antiohos et al., 2003&2007). Quick lime addition and its subsequent formation to Ca(OH)₂ result in a higher basicity inside the matrix. It has been suggested that the increase in pH leads to the corrosion of the densified outer layer of fly ash particles leaving more active cores exposed for reacting to form additional hydration products (Ma and Brown, 1997). It must be pointed out that all the studies using hydrated and quick lime for increasing the Ca(OH)₂ content in the mix were limited to lower levels of cement substitution with fly ash. An understanding of the role of temperature and lime content on the reactivity and efficiency of fly ash as high volume cement replacement is required to produce viable high volume fly ash concrete.

Experimental program and methodology

For evaluating very high volume cement replacement with fly ash, a baseline fly ash concrete mixture with the 70% of the cementitious binder consisting of fly ash was considered. The role of lime content was evaluated by adding quick lime (QL) to the binary fly ash-cement mixture. Reagent grade QL of 95% purity was used. When QL was added, equal weight of fly ash was replaced with QL. The total mass of the binder phase consisting of cement fly ash and QL was kept constant in all concrete mixtures. 5% and 10% of fly ash was replaced with QL (by equal weight) keeping the content of cement at 30% by mass of the total binder phase. To investigate the influence of temperature, two different curing temperatures were used. The role of temperature and lime content on fly ash reaction were evaluated using quantitative XRD analyses performed on paste samples with identical water to binder content as the concrete mixtures.

Commercially available ordinary Portland cement conforming to Grade 53 of the Indian Standard, IS 12269 and Siliceous fly ash conforming to the requirements of IS 3812 and IS 1727 were used for all concrete mixtures. The oxide composition of the cement and fly ash used in this study were determined using X-ray fluorescence spectroscopy (XRF). The chemical and physical properties of cement and fly ash are given in Table 1.

Table 1. Chemical composition (% by mass) and physical properties of cement and fly ash		
Compound Name	Cement (% mass)	Fly ash (% mass)
Al ₂ O ₃	3.10	28.83
SiO ₂	15.76	57.35
CaO	71.33	1.92
Fe ₂ O ₃	5.53	5.97
MgO	0.72	0.50
K ₂ O	0.72	1.93
SO ₃	2.06	0
Cl	0.23	0.25
Na ₂ O	0	0
TiO ₂	0.52	2.24
Loss of Ignition	0.8	1.89
Blaine Fineness (m ² /kg)	325	320
Specific gravity	3.15	2.29

The particle size distributions of all the components of the binder phase were determined using Microtrac S3500 Particle Size Analyzer. Isopropanol was used as the medium for dispersion to arrest the agglomeration between particles. The particle size distributions of all the materials of the binder phase are shown in Figure 1. It can be seen that while the cement and fly ash have comparable size distributions, QL is finer.

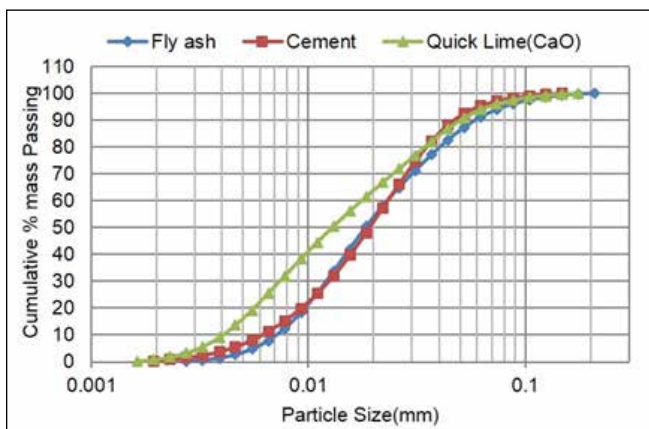


Fig. 1: Particle size distributions of the components of the binder phase

Concrete mix design was for a target mean strength of 43 MPa, and the water/cementitious ratio was taken equal to 0.43. The cement content for the control mixture was fixed at 340 kg/m³. In the concrete mixture fine aggregate were taken as 40% of the total aggregate volume fraction. The batch weights for the control mixture, which contained no fly ash and the baseline fly ash mixture prepared with 70% by mass replacement of cement with fly ash are shown in Table 2. Concrete mixtures were prepared with quick lime activator dosages of 5 and 10% by weight of the cementitious binder material. The weight of the quicklime activator was included in the weight of the cementitious

binder. In concrete mixtures containing lime activators, the equivalent weight of fly ash was reduced to keep the total weight of the cementitious binder equal to 340 kg/m³. The batch weights of the lime activated mixtures are also shown in Table 2.

Standard 150 mm cubes were casted from each mixture to evaluate compressive strength gain. A slump in the range of 60-100 mm was obtained for all concrete mixtures. No other admixtures were used or added to the concrete mix. Immediately after casting, all specimens were covered with plastic covers to minimize moisture loss and transferred to a temperature chamber, which was maintained temperature 25 deg C and 40 deg C with the humidity range 80-85%. Specimens were demolded after 24 hours and kept in same temperature chambers till the day of testing. For each mix, compressive strength was measured at 1, 3, 7, 14, 28, 56 and 90 days of age. A 5000 kN Compressive testing machine was used for testing. A loading rate of 5.25 kN/sec was prescribed during the compressive test.

Table 2. Batch weights in kg/m ³ for concrete mixtures (water to cementitious ratio 0.43)				
Mix Designation/ Materials(kg/m ³)	Control	Baseline Fly Ash	5% Quicklime	10% Quicklime
OPC 53 grade cement	340	100	100	100
Fly ash	0	240	221	204
20 mm aggregates	573	573	573	573
10mm aggregates	573	573	573	573
Fine aggregates	767	767	767	767
Water	146	146	146	146
Quick lime	--	--	19	36
Label	C	F	5QL	10QL

The paste samples were prepared using a paddle mixer, rotated at 275 rpm for 3 minutes. Immediately after mixing, the paste was cast into 2 ml air tight vials and placed in a temperature controlled chamber which was maintained at a constant temperature. All vials were kept at the constant curing temperature until tested. At the designated age, the paste specimens were crushed inside the vials and ground to a finer size using a mortar and a pestle. Particles passing through a 0.5 mm sieve were collected, immersed in methanol for one hour and oven dried at 40 deg C to evaporate the methanol, before collecting XRD data.

Laboratory X-ray diffraction measurements were in vertical Bragg-Brentano (θ/θ) geometry between 10° and 70° at 0.02° steps using a D2 PHASER (Bruker) automated diffractometer with Cu- α radiation (1.5418 Å). X-ray tube was operated at 30 kV and 10 mA and the samples were rotated at 15 rpm during acquisition to improve powder averaging and α -Al₂O₃ was used as an external standard. A first-order Chebyshev polynomial combined with 1/2 θ term was used to fit the background intensity

before performing phase analysis. Rietveld refinement was performed on the powder patterns, using TOPAS 4.2 software. The crystal structures used to interpret the powder patterns were taken from the inorganic crystal structure database (ICSD). The quantification of the crystalline phases was performed using the external standard method with the refined Rietveld scale factors.

Results

The X-ray diffractogram of the unhydrated fly ash is shown in Figure 2. The crystalline phases associated with Quartz and Mullite are readily identified in the diffractogram. The diffuse scattering produced by the amorphous phase present in fly ash appears as a broad hump on the diffractogram (shown in the inset for angles between 15 and 35 degrees). The amorphous phase of fly ash is indicative of the reactive component of fly ash. It is mainly associated with the amorphous forms of Silica and Alumina and is referred to as amorphous Si/Al in the rest of the paper. The absolute weight fraction, w_α of a crystalline phase, α was determined as

$$w_\alpha = \left[\left(\frac{(ZMV)_\alpha}{(ZMV)_s} \right) \left(\frac{S_\alpha}{S_s} \right) \left(\frac{\mu_{sample}}{\mu_s} \right) \right] w_s \dots\dots\dots(1)$$

where $(ZMV)_\alpha$ and $(ZMV)_s$ are the phase constants of the phase α and the standard, respectively, S_α is the scale factor of the phase, S_s is the scale factor of the standard, μ_{sample} and μ_s are the mass absorption coefficient of the sample and standard, respectively and w_s is weight fraction of the standard. The phase constant (ZMV) of a crystalline phase can be calculated from the crystal structure obtained

from the refinement. The mass absorption coefficients of samples were calculated considering the composition using the International tables of crystallography for $CuK\alpha$ radiation. The amorphous content was determined as the residue of the weight fractions of determined crystalline phases. The total amorphous content and the weight fractions of Mullite and Quartz in the fly ash determined from X-ray analysis, are listed in Table 3. The results suggest a significant percentage of the Silica and Alumina are available in the non-reactive crystalline forms associated with Quartz and Mullite.

Reactive SiO ₂ ^a	Amorphous Si/Al ^b	Total SiO ₂ and Al ₂ O ₃ ^c	Quartz ^d	Mullite ^d
20.19	34.90	86.18	25.64	30.07

- ^a Value determined as specified in Indian Standard (IS 3812-part 1).
- ^b Value determined from quantitative phase analysis after Rietveld refinement.
- ^c Al₂O₃ and SiO₂ content obtained from XRF
- ^d Quartz and Mullite determined by Rietveld-based external standard method

The reactive silica content of the fly ash determined using the acid dissolution method given in IS 3812 is listed in Table 3. The reactive Silica is indicative of its potential for use as replacement of cement. For the fly ash used in this study, only 20.2% of the total 57.4% Silica content available in the reactive form. The results of the study indicate that the reactive components of fly ash cannot

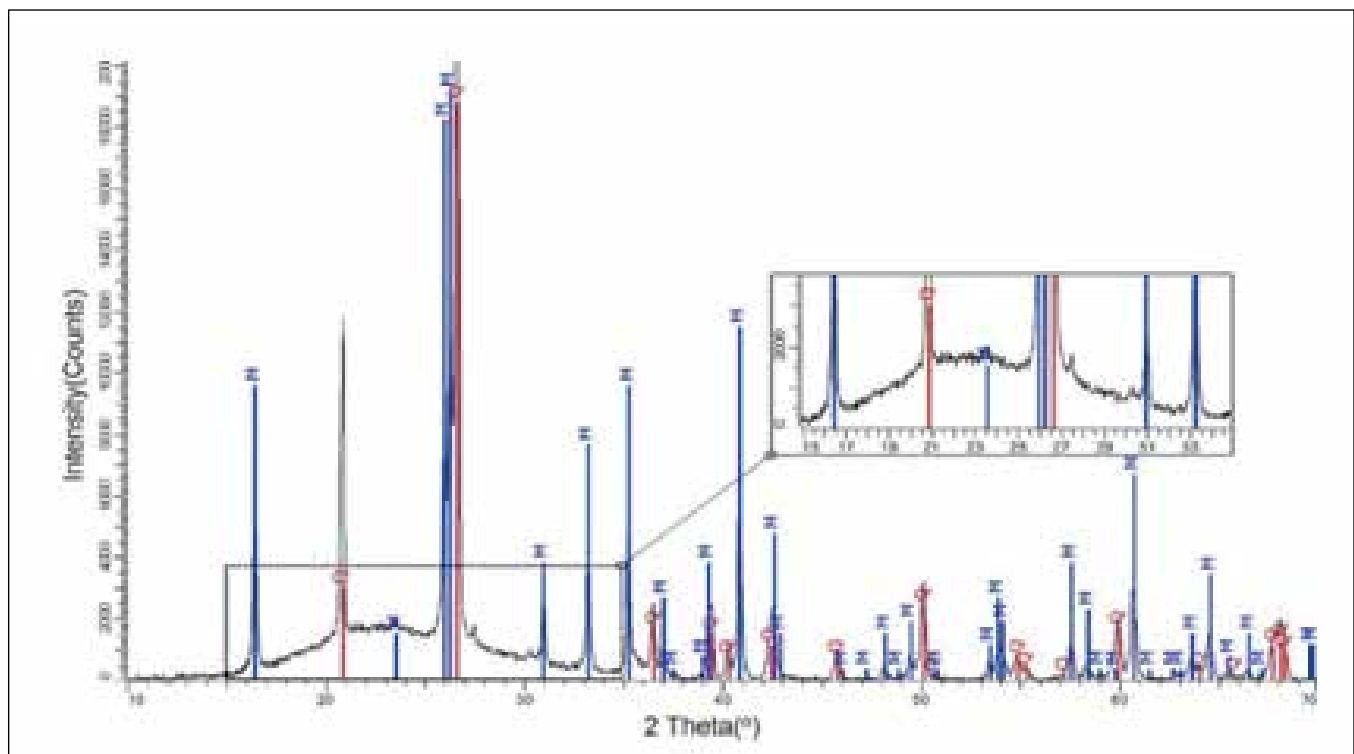


Fig. 2: X-ray diffractogram of fly ash. (Q-quartz, M-mullite)

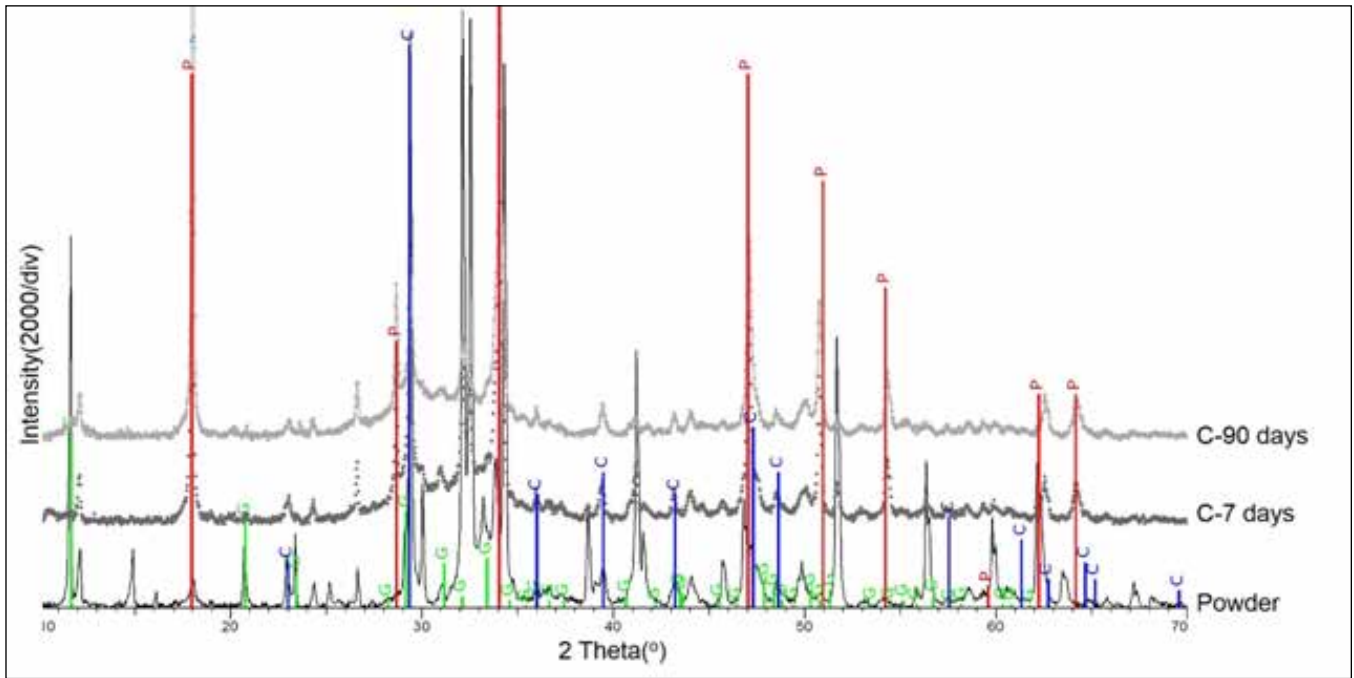


Fig. 3: X-ray diffractograms of Cement and hydrated cement samples. (P-portlandite (CH), C-calcite, G-gypsum)

directly be assessed from an oxide content evaluation as is traditionally done, but require a careful evaluation of the phases of Silica and Alumina present in the ash.

The X-ray diffraction patterns of a hydrated cement sample is shown in Figure 3. Hydration transforms the cement into an X-ray amorphous calcium silicate hydrate that appears as a broad hump (between 25 and 40 degrees) on the diffractogram of the hydrated cement sample. The hump associated with amorphous calcium silicate hydrates. New crystalline phase can be identified with the formation of Calcium Hydroxide. The hydration of cement leads to a total consumption of Gypsum. Additionally, Ettringite was found to form within the first day.

The compressive strength obtained from base line (F mix) and quick lime (QL) activated fly ash mixtures cured at 25 deg C and 40 deg C are shown in Figures 4(a) and 4(b), respectively. 30% scaled values obtained of the control mix are also plotted in the figures for comparison. Results indicate that at both the curing temperatures QL activated mixes showed improvement in compressive strength when compared with the base line mix. At 25 deg C, the compressive strength increase in the QL mixes is visible only after 28 days and it is very nominal when compared to the base line mix. At 40 deg C, the base line (F mix) and QL activated mixes show higher strength than the 30% control mix at all ages. QL activation indicate a clear enhancement in the rate of early strength gain and improvement in the strength at lateral ages when compared with the baseline fly ash mixture. At both curing temperatures 5% and 10% QL activated mixed showed very little difference in compressive strength. The increase in compressive strength of base line fly ash mix above the 30% scaled value

obtained from the control mix is indicative of pozzolanic reaction involving fly ash. The QL activated fly ash mix showed further enhancement in strength compared with the base line mix (F mix), which is indicative of further enhancement of the pozzolanic reaction in the presence of extra CH supplied by QL addition. The test results indicate that QL is effective in increasing the rate of strength gain at a higher temperature.

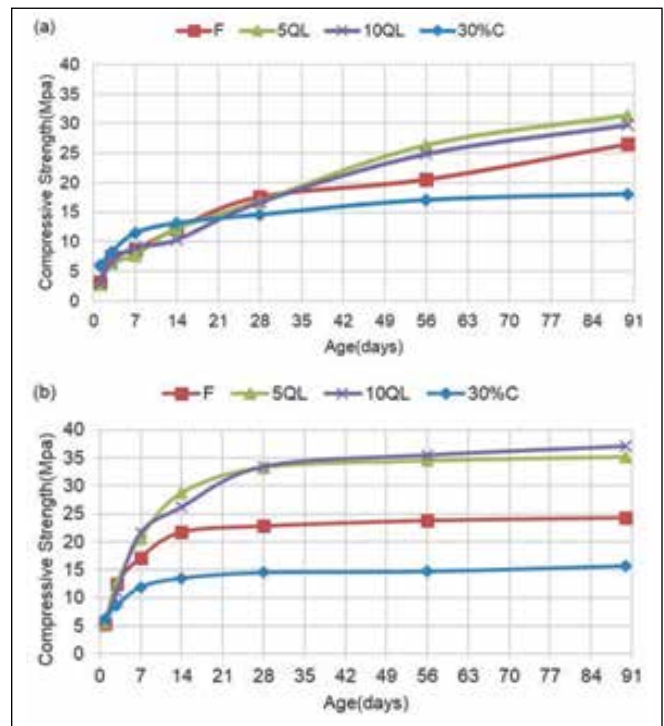


Fig. 4: Compressive strength gain in quick lime activated fly ash concrete mixtures cured at (a) 25 deg C and (b) 40 deg C with age.

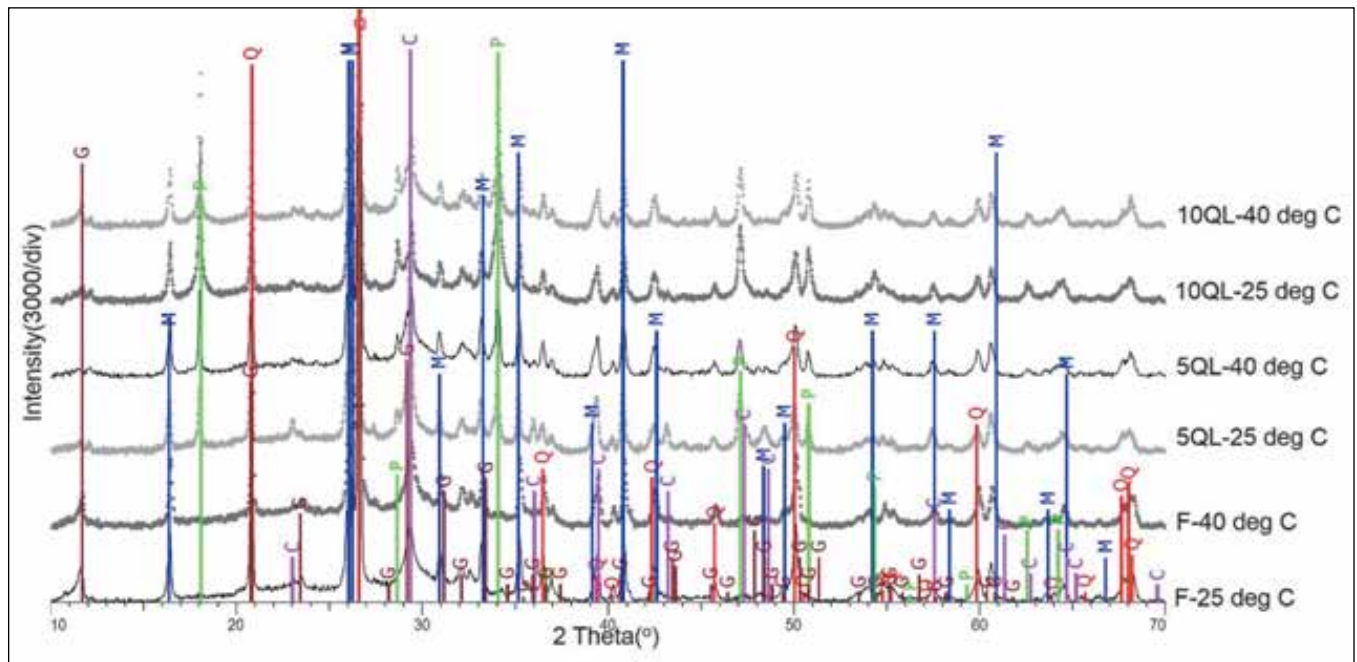


Fig. 5: X-ray diffractograms of base line (F) mix and QL activated fly ash paste sample cured at 25 deg C and 40 deg C at the age 90 days. (Q-quartz, M-mullite, P-portlandite(CH), C-calcite, G-gypsum)

The X-ray diffractograms of the baseline (F) mix and QL activated fly ash mixes cured at 25 deg C and 40 deg C at the age of 90 days are shown in Figure 5. The crystalline phases quartz and mullite are readily identified in all the mixes and are observed to remain unchanged with age. A broad amorphous hump is observed in all the mixes between 15° and 38° 2-theta angles. A depression in the amorphous hump at lower theta angles and a rightward shift of the entire hump is observed with age. The diffuse scattering produced by the amorphous phase of fly ash is associated with lower 2-theta angles, in the range 15 to 30 degrees. The amorphous products of hydration contribute to diffuse scattering pattern at higher 2-theta angles in the range 25 to 40 degrees. In the base line (F) mix, the Portlandite peak is almost absent at 90 days of age indicating a complete depletion of lime in the system. In the QL activated mixes, the Portlandite peaks are decreased yet visible at the age of 90 days indicating availability of lime in the system. In all mixes tested the reduction of the hump associated with amorphous phases of fly ash (at lower theta angles) and the rightward shift associated with the formation of amorphous silicate hydrates is accompanied by a reduction in Portlandite. In all hydrated mixes the quantities of crystalline phases like gypsum, portlandite and calcite are observed to change with age. The depletion of Gypsum coincides with the formation of ettringite in all mixes and gypsum is totally depleted by 90 days in all mixes.

The $\text{Ca}(\text{OH})_2$ (CH) content with age as a percentage of the cementitious binder cured at 25 deg C and 40 deg C obtained from Rietveld refinement is shown in Figure 6(a) and 6(b). The 30% scaled values of the control mixture

are also plotted in the figures for comparison. It can be seen that for the control mixture, the hydraulic activity of cement results in continuous increase in the CH content. QL activated mixes showed higher CH content than the base line mix (F mix) and higher dosage of QL producing higher CH content in the system. The results indicate that the QL addition immediately contributes to CH content in the system and would therefore be available for reaction.

At 25 deg C, CH depletion is initiated between 7 and 14 days of age and there is a steady decrease in the CH content after 14 days. The rate of CH depletion is same in baseline and QL activated mixes. At 40 deg C, CH depletion initiated at the age of 3 days and rate of depletion is very rapid up to 7 days of age. After 14 days of age there is a steady linear decrease in the CH content up to 28 days. There is a small change in the CH content after 28 days and up to 90 days of age. Considering the pozzolanic reaction to be the only source of lime consumption, the depletion of CH can be related to the rate and extent of pozzolanic reaction.

CH content is almost completely depleted in base line mix (F mix) while there is CH content left over in the QL activated mixes at the age of 90 days. The complete depletion of lime in the the baseline mix suggests that level of cement replacement is limited by lime availability from the cement. The 10% QL activated mixes showed more CH content than the 5QL at the age of 90 days. The rate and pace of CH depletion in the system correlates very well with strength development. At 40 deg C the rapid initial consumption of CH in the first 7 days matches well with the observed higher rate of strength gain. At 25 deg C, the rapid uptake of CH after 14 days coincides with the observed increase in the rate of strength gain after 14

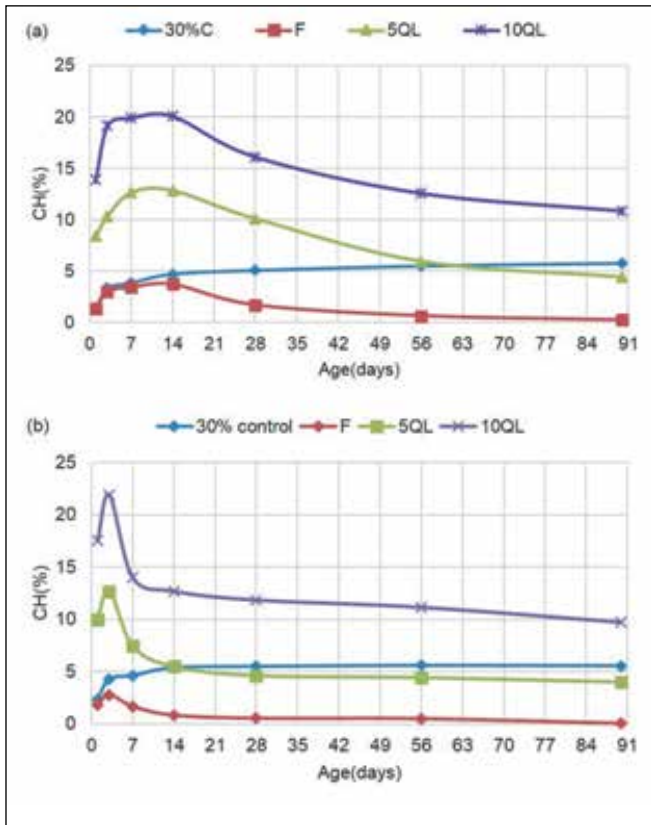


Fig. 6: Calcium hydroxide content of quick lime activated fly ash mix cured at (a) 25 deg C and (b) 40 deg C with age.

days. There is a larger residual CH in the 10% quicklime system at any age which does not appear to influence the strength gain.

Analysis of Results

Efficiency factor of the base line fly ash mix (F mix) and quick lime activated mixes with age was evaluated considering the basic relationship for strength gain in a concrete mixture (given as a proportion of strength at a given age t , S and strength at infinity, S_∞) is given as

$$\frac{S}{S_\infty} = K_f \left[\frac{t}{1 + K_f t} \right] \dots\dots\dots(2)$$

where, K_f is a factor which depends on the cement type and temperature [Carino, 2004]. An expression for efficiency factor, C_{eff} , obtained from strength gain was derived as

$$C_{eff} = \frac{S}{S_\infty} \left[\frac{1}{K_f t} + 1 \right] \dots\dots\dots(3)$$

C_{eff} provides a measure of efficiency of fly ash in contributing to compressive strength when compared with concrete with equal weight of pure cement. The efficiency factor for cement with no replacement is 1.0 and it provides a basis for assessing the efficiency of other supplementary cementitious materials at different replacement levels.

Efficiency Factor of all the mixes as a function of age cured at 25 deg C and 40 deg C is shown in Figure 7(a) and 7(b). The efficiency of cement fly ash blended system clearly

depends on the age and temperature. At 25 deg C the efficiency factor Improved after 14 days .Intially, in the first 7 days the fly ash acts as an inert material. The resulting decrease inefficiency in this period can be associated with the dilution effect considering cement hydration as the only contributor to strength in the system. Base line mix (F mix) shows only 50% efficiency when compared with QL activated fly ash system. This may be related to the complete depletion of lime and leading to non-availability of lime to support the pozzolanic reaction. However the small increase in efficiency in the QL systems suggests at later ages indicates the possibility of additional factors which influence the strength gain.

At 40 deg C, the QL activated mixes achieve higher efficiency, close to 70%. The efficiency factor clearly demonstrates the efficiency of QL increases with increasing temperature. The improved efficiency in the QL systems correlates well with the depletion of CH content. The differences in the efficiency factors obtained for baseline and QL activated blends after 3 days coincides with the initiation of CH consumption. However, the limiting efficiency of 70% in QL systems suggests other limiting factors which control strength gain despite availability of CH in the system.

A quantitative phase analysis of the amorphous phase was performed using the available XRD data. A whole pattern based method which relies on determining the total intensity contribution from the different components from the total areas associated with each is used. The method

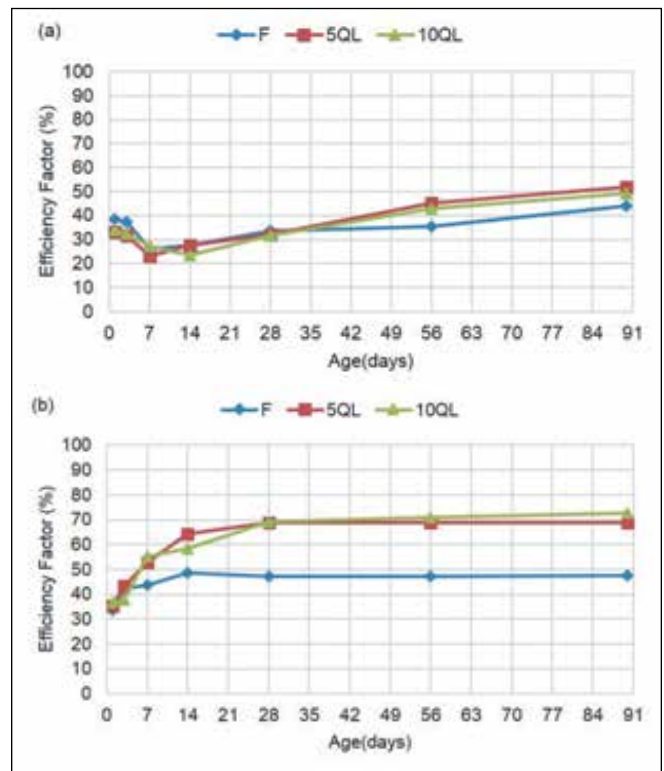


Fig. 7: Efficiency Factor of base line mix and QL activated fly ash mixes cured at (a) 25 deg C and (b) 40 deg C with age.

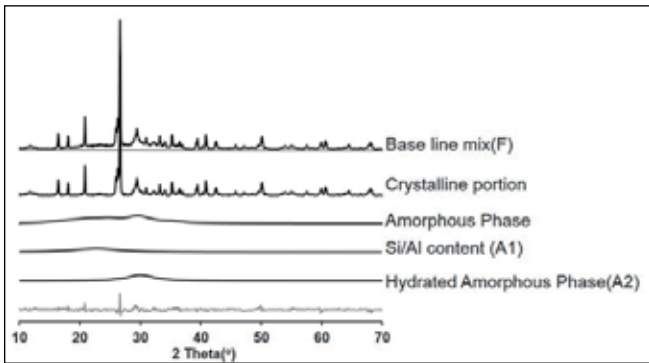


Fig. 8: Pawley fit and Deconvolution of the hydrated base line mix (F mix) paste cured at 25 deg C at the age of 90 days.

for quantitative phase determination using this approach was developed for determining the the degree of crystallinity by (Riello ,2004). This method is extended for amorphous phase quantification in hydrating fly ash-cement system where the amorphous phases in both fly ash and products of hydration contribute to diffuse scattering. The quantification of the amorphous phases requires an accurate intensity profile of the total amorphous phase, which is then decomposed to determine the individual contribution from the two components.

The experimentally observed intensities for the amorphous and crystalline phases were determined using the Pawley method. The Pawley method models each individual intensity peak of the pattern using the same factors of the Rietveld method. The intensities are refined without the crystal structure. For the Pawley intensity refinement, known crystalline components were defined using space groups as hkl phases. Arbitrary space group and lattice parameters were selected for the broad hump, which were refined in the analysis for best fit. The decomposed intensity profiles for the amorphous and crystalline components from the Pawley fit for the hydrating baseline fly ash-cement sample at 90 days of age is shown in Figure 8.

The decomposition of the intensity pattern of the entire amorphous phase, deconvoluted using pseudo Voigt (PV) peaks. A peak fit algorithm, which uses unconstrained, non-linear optimization, was used to decompose the broad amorphous intensity pattern obtained from the Pawley refinement in the 2θ region 15°-38° into its component pseudo voigt functions. Typical deconvolution of the amorphous hump of the base line fly ash cement paste sample at the age of 90 days is shown in Figure 8. The PV peak (A₁) at the smaller 2θ corresponds to the amorphous Si/Al content in fly ash and the PV peak at the larger 2θ(A₂) corresponds to the products of hydration. The center of the first PV peak was consistently found between 2θ angle of 22-22.5 and the other one was centered around 2-theta angles ranging between 29.5 to 30 degrees. The 2-theta of the centers and the full width half maximum (FWHM) values of the PV peaks for A₁ and A₂ for the base line mixes

cured at 25 deg C and 40 deg C with different ages are shown in Table 4. It can be seen that the centers of the 2 peaks and the FWHM values are relatively invariant with time and the values are consistent at the both curing temperatures. A₁ and A₂ however continuously change with age due to the relative decrease the amorphous Si/Al in fly ash and the relative increase in the content of amorphous products of hydration.

Mix-Temp-Age	Si/Al content Area (A ₁)		Hydrated Amorphous Area (A ₂)	
	Center Position-1	FWHM	Position-2	FWHM
F-25-1	22.524	7.703	30.010	6.503
F-25-3	22.445	7.303	29.961	6.803
F-25-7	22.277	7.508	29.956	6.608
F-25-14	22.288	7.561	29.919	6.561
F-25-28	22.280	7.559	29.969	6.559
F-25-56	22.433	7.492	29.921	6.452
F-25-90	22.309	7.680	29.782	6.680
F-40-1	22.402	7.317	29.895	6.517
F-40-3	22.439	7.401	30.086	6.601
F-40-7	22.418	7.576	29.855	6.562
F-40-14	22.353	7.510	29.764	6.510
F-40-28	22.316	7.540	29.941	6.540
F-40-56	22.334	7.585	29.874	6.485
F-40-90	22.222	7.684	29.940	6.584

The amorphous Si/Al content (A₁) of the total area under the diffractogram as a function of age for samples cured at 25 deg C and 40 deg C are shown in Figures 9(a) and 9(b). Results indicate that initial amorphous Si/Al content depends on the replacement level of fly ash with QL. In QL systems, fly ash was substituted by an equal mass of QL. Therefore the reduction of fly ash content in QL systems decreases the initial amorphous Si/Al content. The results clearly indicate the differences in the rate of reduction of amorphous Si/Al in fly ash produced by dissolution. The rate of depletion is significantly higher at 40 deg C, particularly in the early ages. At 25 deg C, after some early decrease in the amorphous Si/Al content, Si/Al dissolution starts after 7 days of age and it steadily decreases up to 90 days. At 40 deg C dissolution starts at 1 day and it steadily decrease till 28 days following which the rate of decrease is very slow. The total extent of fly ash dissolution at both 25 deg C and 40 deg C appears to be similar at 90 days of age. The trend in the dissolution of Silica and Alumina from fly ash is not influenced by the QL dosage. The results of the quantitative XRD indicate that the dissolution of fly ash is strongly influenced by temperature although the final extent of dissolution is not dependent on the temperature.

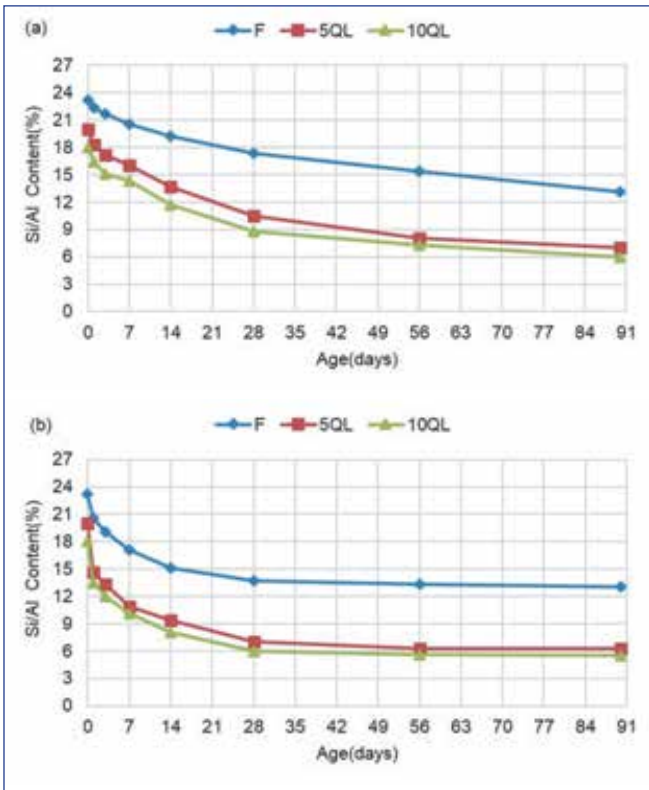


Fig. 9: Si/Al content of QL activated fly ash mix cured at (a) 25 deg C and (b) 40 deg C with age.

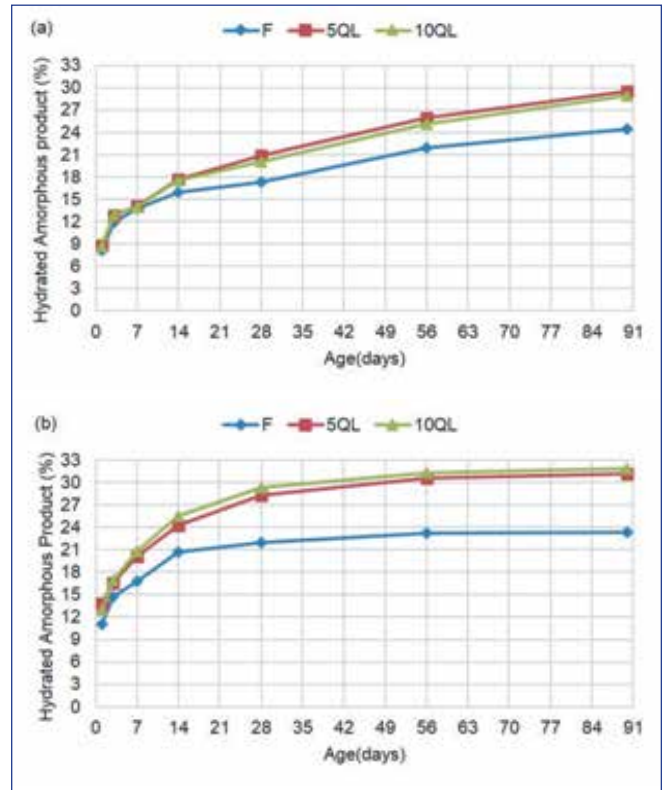


Fig. 10: Hydrated amorphous product in base line (F mix) and QL activated pastes cured at (a) 25 deg C and (b) 40 deg C with age.

The lime content in the system does not appear to influence the dissolution of fly ash. Further, at both temperatures, there is still residual amorphous Si/Al in the fly ash, which is not completely dissolved.

The fraction of the amorphous hydration product content (A_2) of the total area under the diffractogram as a function of age for cured at 25 deg C and 40 deg C are shown in Figures 10(a) and 10(b). Results clearly indicate the QL activated mixes at 40 deg C showed a significant high early increase in the amorphous hydration product content than the corresponding mixes cured at 25 deg C. After 3 days of age, there are also noticeable difference in the amorphous product formation in the QL mixes cured at 40 deg C when compared with the baseline mix. There are differences in the base line mix at early and lateral ages. At 25 deg C, differences between the baseline and QL mixes are noticeable after 7 days of age. At 25 deg C the amorphous hydration product content increases steadily up to 90 days and the final contents in the baseline and QL mixes are nominally similar to the values in the corresponding mixes at 40 deg C. At 40 deg C, the amorphous product content increases very rapidly in the first 28 days following which it starts approaching an asymptotic value. The 5% and 10% QL mixes showing very little difference in quantity of product at both temperatures. The amorphous product content of all the mixes very well compares with strength data.

Discussion

The information from the different experimental techniques can now be combined to arrive at an understanding of reactions in binary mix of cement with high level of fly ash replacement. The dissolution of Si/Al from fly ash in the early ages is not influenced by the lime content of the mix. Initially, the lime provided by cement hydration is sufficient to support the pozzolanic reaction. The excess lime available in the QL systems does not appear to influence the pozzolanic reaction as indicated by the similar quantity of amorphous products formed. This is also supported by the identical efficiency factors up to 3 days for fly ash mixtures with and without QL.

The strength-based efficiency factor of fly ash relates directly with the decrease in amorphous Si/Al content from fly ash resulting from dissolution. In baseline systems, the early increase in the efficiency of fly ash correlates with a larger decrease in amorphous Si/Al content of fly ash. To sustain the pozzolanic reaction, sufficient lime should be available in the system. The lime made available from the cement may not be sufficient for reacting with the available silica at high level of cement replacement with fly ash. Considering the cement and fly ash used in this study, cement contributed 15.76% Silica while fly ash contains 20.2% reactive Silica. Therefore cement replacement with fly ash results in larger silica content in system. However, since the fly ash contains very little lime, the replacement of cement by fly ash results in a decrease

in the lime available to support the pozzolanic reaction. At 70% replacement of cement, the lime produced by cement hydration is clearly insufficient to react with the available reactive silica.

Addition of QL resulted in an increase in the CH content in the system which allows the pozzolanic reaction to continue, while it does not influence the dissolution of fly ash. In the presence of excess CH, the increase in efficiency factor is directly related to the decrease in amorphous Si/Al in fly ash. Higher level of dissolution at 40 deg C results in enhanced efficiency factor. The reduction in the efficiency factor at any age for 25 deg C compared with 40 deg C is related to the lower level of fly ash dissolution. In the lime rich system, the dissolution of fly ash which contributes reactive Silica to the pozzolanic reaction is the rate controlling step.

There is an enhancement in the quantity of amorphous hydrated reaction products in the QL systems, which is very evident after 7 days of age. This also corresponds with the increase in the efficiency factor in the QL systems after 7 days of age. However, increasing the quick lime dosage to 10% did not produce further improvement compared to 5% quick lime dosage in both amorphous product and efficiency factor. From the results of quantitative XRD analysis, it is evident that there is excess CH in the both QL systems at 90 days of age. There is however little change in the Si/Al content after 28 days of age, indicating no additional reactive Silica is available for reaction

In fly ash cement blended system, the reactive silica content depend on the level of replacement of cement with fly ash. At 5% and 10% quicklime additions, there is a reduction in the silica contributed by fly ash due to a decrease in fly ash content to 65% and 60%, respectively. This suggests that at 10% quicklime addition, the reduction in reactive silica contributed by the fly ash results in an overall excess unreacted $\text{Ca}(\text{OH})_2$ in the system. At 5% QL addition, while there is a reduction in the silica content compared to the cement fly ash mixture, the available lime is sufficient to support the pozzolanic reaction.

The highest efficiency factor achieved in the fly ash mix was 70%. The availability of amorphous Si/Al indicated by the presence of the amorphous hump in the XRD spectrum suggests that a portion of amorphous Si/Al is still undissolved in fly ash. Further improvement in efficiency factor is possible if all the reactive components of fly ash utilized. Further, at 90 days, the dissolution percentages and amorphous hydration product contents are nominally similar in QL systems at both temperatures, while the the efficiency factor is higher for curing at 40 deg C. This suggests that the differences in the strength are related to the influence of temperature on the long-term strength in concrete with cement as the binder. Concrete made with cement has been shown to produce higher long-term strength when cured at lower temperature. The results from this study suggest that temperature is

less detrimental on the long-term strength produced by fly ash. This has also been observed previously [Maltais and Marchand,1997].

The strength-based efficiency factor is a good indicator of the reactive potential of fly ash in the blended system and it compares very well with the amorphous hydration product and the reduction of the amorphous Si/Al content in fly ash. The level of cement replacement to achieve required strength depends on the efficiency factor. There appears to be an optimal replacement level of fly ash for cement considering silica replacement, lime availability and the silica available from fly ash dissolution. The optimal quantity of quicklime can be established based on the available silica to maximize the use of reactive silica.

Findings and Conclusions

The findings of this investigation pertaining to very high levels of fly ash replacement, 60% by mass of cement and higher, can be summarized as below.

1. The primary indication is that the strength gain is associated with the formation of an amorphous hydrate product and is linked with the rate of depletion of CH in the system.
2. The rate of strength gain is directly influenced by the consumption of CH, which depends on the reactive silica in the system. Increasing the CH content in the mix does not appear to influence the release of silica into the mix at the levels of replacement, 60% by mass of cement and higher.

The findings presented here indicate the possibility of producing high volume fly ash concrete with a target strength using quick lime activation. Commercial products can be developed, where the quick lime required is optimized for a given fly ash. The results presented were conducted using a specific portland cement and a specific fly ash. The degree to which the concrete mixture will require modification, or whether the specified properties can be achieved at all, will depend upon the specific characteristics of the fly ash being employed. Following points require careful consideration

1. The requirement of quick lime is currently based on the formation of calcium silicate hydrate as the primary product of hydration. Fly ash also contains reactive Alumina in addition to reactive Silica. Enhancing the potential of fly ash requires utilizing the reactive Alumina as well. Further strength gains can be achieved if the Alumina in the fly ash is activated in generating additional reaction products.
2. Cement used in this study contained 15.76% Silica while fly ash contained 20.2% reactive Silica. There is a higher contribution of Silica when cement is replaced with fly ash. Therefore if sufficient lime is available, more calcium silicate hydrate should be formed. However, even with lime available in the system, the

strengths of fly ash concrete are lower than pure cement system. This suggests efficiency of fly ash is related significantly with the dissolution of fly ash and the silica made available by the fly ash.

3. Considering the lower density of fly ash relative to cement, for a replacement of cement by mass, fly ash occupies a larger volume than the cement it replaces. The effective cement content in a unit volume of binder is lower than the cement content obtained from mass proportions. Mix design procedures which consider the efficiency of fly ash are required. Volumetric-based replacements and proportioning instead of the conventional mass-based approaches may lead to better mix designs considering the large difference in specific gravity between cement fly ashes.

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