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Scientific paper

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Abstract

The influence of temperature and added lime on the dissolution of the glassy phase in a binary blend of low-calcium siliceous fly ash and cement. An XRD-based technique is used for quantification of the glassy phase content and the amorphous reaction products in the binary blend. The experimental technique allows for tracking the formation of amorphous reaction products, the availability of lime and the unreacted glassy content. The rate limiting step in the pozzolanic reaction of low calcium fly ash is established to be the dissolution of its glassy phase. Results indicate that increasing the temperature from 25°C to 40°C produces a significant increase in the rate of dissolution of the glassy phase of fly ash and an increase in the rate of formation of reaction products. Addition of quicklime is very effective in producing reactive lime in the solution. The rate of dissolution of the glassy phase of fly ash and the rate of pozzolanic reaction are not significantly influenced by the lime content in the system. The proportion of fly ash which remains unreacted which is indicated by the undissolved glassy phase depends on the availability of lime in the system.

1. Introduction

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 and low early-age strength. This effect is more pronounced in low-calcium fly ashes and as the level of fly ash replacement is increased. In concrete containing low calcium 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 developing an understanding of the influence of process variables on the reactivity of fly ash.

It is generally accepted that contribution of fly ash to the overall cementitious phase is through the pozzolanic reaction, which starts after the breakdown of the amorphous phase identified with its glass phase. Temperature has been shown to improve the fly ash reactivity by enhancing the dissolution of the glassy particles (Ma *et al.*1994; Lokken *et al.*1990; Ma and Brown 1997; Pietersen *et al*. 1990; Luxan *et al.*1989). Unlike cement hydration, temperature has been shown to produce improvements in both early and long term compressive strengths in fly ash cement blended concrete (Maltais and Marchand 1997). It has been suggested that 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; Zhang *et al.* 2000). Recent findings on the glassy phase of fly ash indicate that reactivity of fly ash in a cement system depends on the chemical composition of its glassy phase. The low calcium aluminosilicate glasses, such as those typically found in low calcium, siliceous fly ash have been shown to exhibit low reactivity as indicated by their low rate of dissolution (Durdzinski *et al.* 2015a).

Another factor which determines the rate of reaction in low-calcium fly ash-cement blended system is the sufficient supply of lime that is required to sustain the pozzolanic reaction. External addition of lime in the form of hydrated lime (Ma and Brown 1995, 1997; Shi 1999), slurry (Mira *et al.*2002) and quick lime (Shi 2001; Antiohos *et al.* 2004, 2008) have been evaluated. Quicklime addition has been shown to be the most effective in producing portlandite (CH) in the system and the most efficient way of introducing lime required for pozzolanic reaction (Shi 2001). The addition of quick lime to fly ash-cement system showed positive influence on compressive strength and reaction rate (Antiohos *et al.* 2008). The presence of lime in the system has been shown to accelerate the reaction of fly ash. This effect has been shown to minimal unless curing takes place at a temperature higher than room temperature (Huang and Cheng 1986). The rate of strength gain and the ultimate strength of lime treated fly ash are highly dependent on the curing temperature (Gray and Lin 1972). It has been suggested that solubility of SiO_2 in fly ash increases in the presence of CH in the system

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Table 1 Oxide Composition (% by mass) and some physical properties of cement and fly ash.

Compound	Cement	Fly ash	
		Oxide composition	Reactive oxide composition (Normalized as % of total glass content)
Al_2O_3	3.15	28.31	6.46 (22.76)
SiO_2	15.76	59.31	10.64 (37.49)
CaO	71.33	1.98	1.98 (6.98)
Fe_2O_3	4.99	5.00	3.94 (13.88)
MgO	0.73	0.42	0.42 (1.48)
K_2O	0.72	2.31	2.31 (8.14)
SO_3	2.06	0	0 (0)
P_2O_5	0.31	0.10	0.10 (0.35)
TiO_2	0.52	2.35	2.31 (8.14)
Remaining oxides	0.43	0.22	0.22 (0.78)
Total Glassy content (%)			28.38 (100)
		Physical properties	
Blaine fineness (m^2/kg)	325	320	
Specific gravity	3.15	2.29	
Loss on Ignition	0.8	1.89	

(Lokken *et al.* 1990; Brown 1986); 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). All the studies using hydrated or quick lime for increasing the lime 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 low calcium fly ash at high volume cement replacement is required to produce viable high volume fly ash concrete.

The degree of reaction of fly ash in fly ash cement blended system are determined using methods like the selective acid dissolution (Luke and Glasser 1987, 1998; Sakai *et al.* 2005; Ohsawa *et al.*1985; Suprenant and Papadopoulos 1991; Li *et al.*1985; Fernández-Jiménez *et al.* 2006; Haha *et al.* 2010; Scrivener *et al.* 2015), NMR analysis (Brunet *et al.* 2010), backscattered electron imaging (Deschner *et al.* 2013; Feng *et al.* 2004) SCM with energy dispersive spectroscopy (EDS) (Durdziński *et al.* 2015a) and mass balance (Deschner *et al.* 2012). Among all the methods, selective dissolution is the most widely used method to determine the reaction of fly ash. Recent studies using X-ray diffraction and SEM techniques have shown that portions of clinker and hydrated phases remain in the system after selective dissolution. Inconsistent results have also been reported from the selective dissolution methods which are due to the time required to complete the process and the passing of some undissolved fly ash particles through filter paper (Haha *et al.* 2010). Quick and accurate evaluation of extent of fly ash reaction in a binary blended system has remained a challenge.

The influence of externally added lime and temperature on hydration in blended systems with low-calcium fly ash at very high levels of cement replacement is investigated in this paper. A method for quantitative amorphous phase analysis using X-ray diffraction data, which allows for determining the unreacted glassy phase content and the amorphous reaction product content in the binary cement-fly ash system, is presented. The results reported in this study pertain to low calcium, siliceous fly ash which has a distinct diffuse scattering hump in the XRD spectrum centred on low 2θ angles. Combining information from the quantification method with the data available from strength measurements and Rietveld analysis of the crystalline phases in the XRD diffractogram, the influence of process variables on the reactivity of fly ash is determined.

2. Materials and methods

For evaluating the dissolution characteristics of fly ash, a binary blend with a very high volume cement replacement with fly ash was used. A baseline fly ash (F) 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) and hydrated lime (HL) to the binary fly ash-cement mixture. Reagent grade QL and HL of 95% purity were used.

Fly ash with very low calcium content meeting the requirements of siliceous fly ash as per IS 3812 - 2003 and Class F fly ash as per ASTM C 618 was used. Commercially available ordinary Portland cement conforming to the 53 grade as per IS 12269 - 2013 were used in the study. The oxide composition and some physical properties of the cementitious materials are listed in **Table 1**. The oxide composition of raw materials were determined using X-Ray Fluorescence spectroscopy (XRF). The physical properties were determined as per IS 4031 (part-2) -1999 and IS 1727 - 2003. The reactive components of fly ash determined using the procedure described by the authors (Bhagath Singh and Subramaniam 2016a) are also listed in the same Table. The fly ash used in this study is typically available siliceous fly ash in India which has very low lime and glassy content. An experimental program involving binary blends with three different low calcium siliceous fly ashes blended with cement was studied and reported in Bhagath Singh and Subramaniam (2016c). Different

Table 2 Mix designation of samples tested (% by weight of cementitious material content).

Label/ Mix	Cement (%)	Fly ash (%)	Quick Lime (%)	Curing Temperature (^{o}C)
F-25	30	70	0	25
F-40				40
5QL-25	30	65	5	25
5QL-40				40
10QL-25	30	60	10	25
10QL-40				40
10HL-25	30	60	10	25
10HL-40				40

low calcium fly ashes were collected from different sources and had different glassy contents. It was shown that the low calcium fly ashes have identical type of glass as indicated by the XRD signature. The fly ashes collected from the different sources showed almost similar behaviour in the binary system even through the collected source and the glassy contents were different. In this study, one of those fly ashes is used to investigate the influence of temperature and added lime on the pozzolanic reaction.

The particle size distributions of 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 **Fig. 1**. It can be seen that while the cement and fly ash have comparable size distributions, QL and HL are finer.

Paste samples of cement-fly ash blends were prepared by substituting cement with equal mass of fly ash and lime. The baseline mix, identified by the letter F, consisted of the binary blend where the mass proportion of fly ash to cement was taken as 7:3. When QL or HL were added, equal weight of fly ash was replaced. Two different replacement levels of fly ash with QL, at 5% and 10% of the mass of fly ash identified as 5QL and 10QL, respectively were evaluated. A mixture with 10% replacement of fly ash with HL identified as 10HL was also prepared. In all mixes, the total cementitious material was identified with cement, fly ash and QL. The total cement content was kept constant equal to 30% of

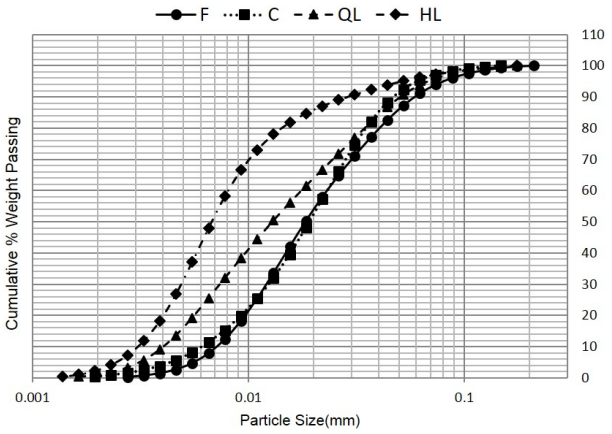

Fig. 1 Particle size distributions of raw materials (F- fly ash; C – cement; QL – quick lime; HL - hydrated lime).

the total mass of the cementitious material. The water-to-cementitious material ratio by mass was kept constant, equal to 0.43 in all mixes. Two different curing temperatures corresponding to 25^{o}C and 40^{o}C were used. Samples of pure cement paste identified as control specimens were also prepared and cured for one year at 25^{o}C. The baseline, QL and HL paste designations and the curing temperatures are summarized in **Table 2**.

The paste samples were prepared in a paddle mixer, rotated at 275 rpm for 3 minutes. Immediately after mixing, the paste samples were kept in 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 vails and ground to a finer size using a mortar and a pestle. Particles passing through a 60 microns sieve were collected. To stop the further hydration, samples were immersed in isopropanol and during this period solvent was exchanged several times. The sample were then dried at 40^{o}C to remove the isopropanol and stored in a sealed condition over silica gel in a Nitrogen atmosphere till the day of testing.

Concrete cubes of 150 mm size were prepared and cured in a sealed condition in the same environment used for curing cement paste samples. The cementitious content of the concrete mixtures was fixed at 340 kg/m^3. The coarse and fine aggregates were taken in the mass proportion equal 60% and 40%, respectively of the total aggregate volume fraction. The weights of fine and coarse aggregate were 767 kg and 1146 kg/m^3 of concrete. The compression tests were performed on the cubes at age of 1, 3, 7, 14, 28, 56 and 90 days to determine the strength gain.

X-ray diffraction measurements were performed on raw materials and hydrated pastes samples using the D2 PHASER (Bruker) bench-top automated diffractometer with Cu-Kα-radiation equipped with Lynxeye super speed position sensitive detector. Specimens for XRD were prepared using the back loading technique to minimize preferred orientation. Incident beam with Soller 2.5^{o} and 0.6 mm slit width and diffracted beam with Soller 4^{o} and 8mm anti scatter slit width was used. An air scatter screen module positioned 2 mm above the sample was used to reduce the air scattering. The readings were taken in vertical Bragg-Brentano (θ-θ) geometry between 10^{o} and 70^{o} at 0.02^{o} step size at 0.6 step per second, resulting in a total measurement time about

30 minutes per scan. In order to improve powder averaging and obtain accurate intensities, the samples were rotated at 15 rpm during acquisition. The X-ray tube generator was operated at 30 kV and 10 mA. All measurements were carried out three times to check for repeatability. Rietveld-based quantitative phase analysis was performed using TOPAS 4.2 Software (Bruker 2009). Crystal structure of known phases were taken from Inorganic Crystal Structure Database (ICSD 2013). A first order Chebyshev polynomial combined with a 1/2θ term was used to fit the background intensity before performing phase analysis

Phase quantification was done using the external standard method with NIST SRM 676a α-Al_2O_3 as the external standard. In the external standard method, the absolute weight fractions of known phases, $w_{\square}$ are determined using the refined Rietveld scale factors of the phases and of an external standard (Madsen and Scarlett 2011; Scarlett and Madsen 2006; O'Connor and Raven 1988).

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

where Z represents the number of formula units in the unit cell, M is the mass of unit cell, V is the volume of the unit cell, $(ZMV)_\alpha$ and $(ZMV)_s$ are the phase constants of the phase 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 the standard, respectively. The mass absorption coefficients (MAC) of fly ash samples were calculated from the composition using the International tables of crystallography for CuKα radiation (Creagh and Hubbell 2006). To calculate the mass absorption coefficients of the hydrated pastes the water content of the paste was included as the bound water content determined by the weight loss of samples heated to 600 °C for 1 hour. The amorphous content is calculated by subtracting the sum of the weight fractions of crystalline phases from unity.

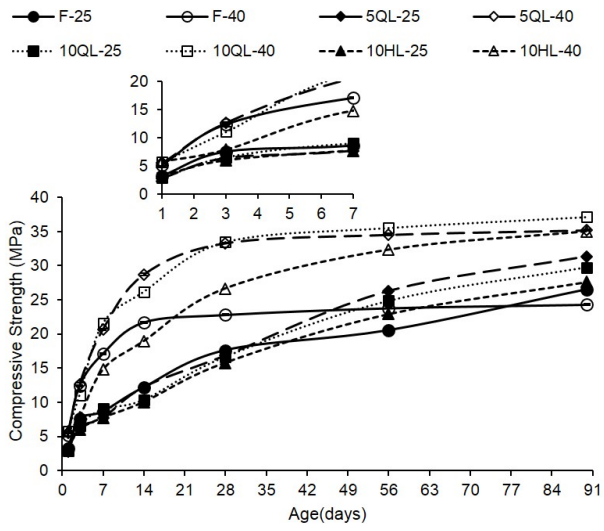

Fig. 2 Compressive strength of base line (F), Quick lime (QL) and Hydrated Lime (HL) activated fly ash cement mixes cured at 25°C and 40°C with age.

3. Experimental results

The compressive strength obtained from the baseline (F mix), the quick lime-fly ash (QL) and hydrated lime-fly ash (HL) mixtures cured at 25°C and 40°C with age are shown in **Fig. 2**. The F mix exhibits a significantly accelerated strength gain at 40°C, while similar long-term strengths are obtained at both the curing temperatures. For samples cured at 40°C, there is a more rapid strength gain in the early ages and no significant change after 28 days. At 25°C, there is a continued linear increase in strength after 28 days. The results of QL and HL addition indicate a clear improvement in strength compared to the F mix at the corresponding curing temperature. The observed difference in strength between the F and the mixes containing added lime is much higher in samples cured at 40°C. At 25°C, the compressive strength increase in the QL and HL mixes is visible only after 28 days. At 40°C, the QL mixes showed a clear enhancement in the rate of early strength gain and an improvement in the strength at lateral ages when compared with the F mix cured at 40°C. The 10HL mix shows improvements in compressive strength over the base line mix after 21 days and reaches the same ultimate strength as the QL mixes. At both curing temperatures, the 5QL and the 10QL mixes showed little difference in compressive strength.

Typical X-ray diffractograms of the 28 day hydrated samples of the F mix and the QL mixes cured at 25° and 40°C are shown in **Fig. 3**. The calculated patterns for the individual crystalline phases after Rietveld refinement for the 5QL mix cured at 25°C are also shown in the figure. The unreactive phases like Quartz, Mullite, Magnetite, Hematite and Rutile essentially remain un-

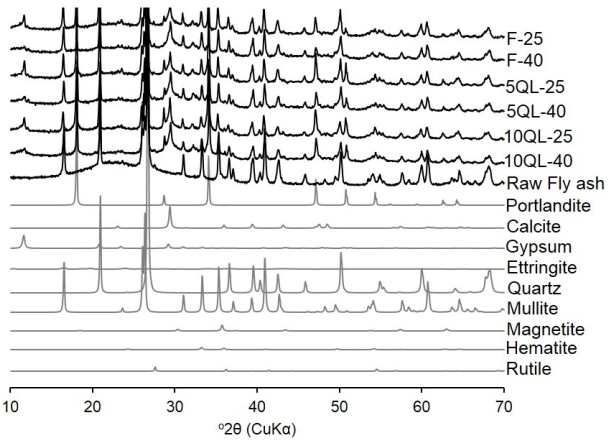

Fig. 3 Base line mix (F) and QL activated mixes cured at 25°C and 40°C at the age of 28 days. The individual crystalline phases shown in light grey colour. Raw fly ash also shown in the figure.

changed with curing temperature. The Calcium sulfoaluminate peaks have a very low intensity, and hence do not show in the entire spectrum. The crystalline phases shown in the figure indicate that in all fly ash cement paste samples there is a higher gypsum consumption in samples cured at 40°C than at 25°C. The presence of portlandite (CH) in the diffractogram is due to the contribution of cement hydration and the addition of QL, and its depletion is indicative of the pozzolanic reaction. In all the QL mixes, there is an increase in the CH content in the system; addition of QL results in a significant increase in the portlandite peak than the corresponding F mix. The portlandite peak in F-40 is significantly smaller than in F-25 at both levels of QL addition. For a given level of QL addition, increased temperature produces a decrease in the portlandite peak.

A broad hump between 2θ angles equal to 15° and 30° is identified in the diffraction signature of fly ash. In the blended systems, a broad hump in the diffractogram is observed between 2θ angles equal to 15° and 38°. The broad amorphous hump is the combination of the glassy phase of fly ash and the amorphous reaction products in the fly ash-cement blended system. The depression in the amorphous hump at lower 2θ angles and a rightward shift of the entire hump in the diffraction pattern of the blended system, indicates a decrease in the glassy content of fly ash (centered on lower 2θ angles) and the formation of amorphous reaction products (centered on higher 2θ angles).

The CH content as a percentage of the cementitious binder obtained from Rietveld refinement analysis for samples cured at 25°C and 40°C is shown in **Fig. 4**. A notable increase in the CH content can be observed at one day in the QL and HL mixes, and higher dosage of QL results in a larger CH content. QL is more efficient in producing CH in the system; The CH content at 1 day in the 5QL system is comparable to the 10HL system. The CH content of the lime added mixes is consistently higher than the base line mix at any age. Results indicate that at 25°C, CH depletion is initiated at 7 days of age and there is a steady almost linear decrease in the CH content after 14 days. At 40°C, in all mixes the CH depletion starts earlier at the age of 3 days and rate of depletion is very rapid up to 14 days of age. After 14 days of age there is a steady linear decrease in the CH content up to 90 days. At any temperature, the trends in the production and depletion of CH content in the F, the QL and the HL systems are effectively similar, which indicates that the production of CH from cement hydration and the subsequent consumption are not influenced by the CH content of the system. There is however an accelerated consumption of CH at 40°C, when compared with 25°C. In the F mix cured at 25°C, the CH is reduced to a very small quantity by 90 days. In the QL mixes cured at 25°C, a supply of lime is available and the trend indicates is a continued consumption of lime at a decreasing rate, which is essentially equal in the QL and HL systems. In the F mix cured at 40°C, the CH content is almost completely depleted at the age of 28 days. In the QL and HL mixes cured at 40°C, while a supply of lime is available there is little change in the CH content after 28 days.

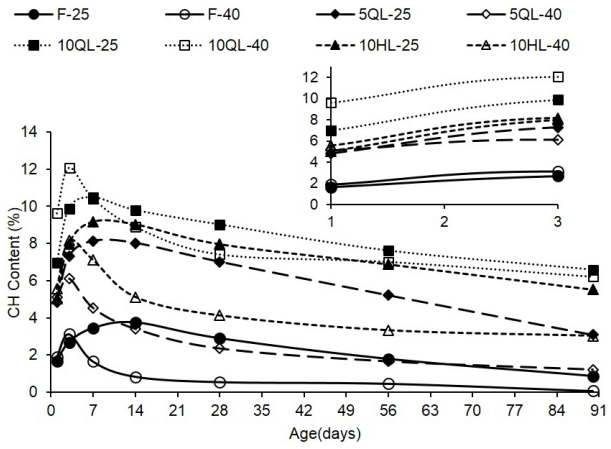

Fig. 4 CH content of base line (F), Quick lime (QL) and Hydrated lime (HL) activated fly ash-cement mixes cured at 25°C and 40°C with age.

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. The complete depletion of lime in the baseline mix suggests that the pozzolanic reaction is limited by lime availability from the cement in the F mixes. The observed rate of depletion agrees well with the strength gain in the different mixes. The steady linear decrease of lime in the mixes cured at 25°C matches with the linear increase in strength with age at later ages. The constant values of CH in QL mixes cured at 40°C after 28 days suggests that the reaction is limited by reactive potential of fly ash. The changes in the CH contents measured in the different mixtures indicate that the presence of lime in the system does not influence the rate of depletion of CH in the mixtures. The rate of CH depletion is primarily influenced by the temperature.

4. Quantitative analysis of glassy phase

The experimentally observed XRD intensity patterns from the hydrating fly ash-cement blended system contain contributions from both amorphous and crystalline phases. The intensity profiles associated with the total amorphous phase and the crystalline phases in the experimental intensity profile were obtained using the Pawley intensity refinement method (Pawley 1981). In the Pawley intensity refinement method, individual intensity peaks in the pattern are modelled using the same factors as those used in the Rietveld method. The intensity refinement, however does not require a knowledge of the crystal structure. The crystalline and the amorphous components were refined using space groups as *hkl* phases. For the Pawley refinement, space groups were selected from Powder Diffraction File (ICSD 2013) to fit the total crystalline and amorphous phase. A

Pseudo Voigt (PV) profile shape was used for the XRD pattern associated with the total amorphous phase and the crystalline phases. The unit cell parameters and the individual peak intensities were refined. A 2-step refinement process was followed in which an initial refinement was performed in the 2θ range of 10°-40°. Refinement was then performed over the entire 2θ range. Quality of a fit was judged using the weighted profile R-factor and by viewing the observed and calculated patterns graphically to ensure that the refined model gives a good fit (Toby 2006). The intensity profiles for the amorphous phase and the total crystalline components obtained from the Pawley method for the cement powder, the fly ash powder and the control sample (the one year hydrated cement sample) are shown in **Fig. 5.** A broad X-Ray amorphous hump located between the 2θ angles of 15° and 30° associated with the glassy phase of fly ash is identified in the diffraction signature of fly ash powder as shown in **Fig. 5(a).** In low calcium siliceous fly ash, the peak position of the glassy phase has a distinct center, which occurs at the lower 2θ angle. The peak position of the glassy phase has been shown to vary with the composition of the glassy phase. In glass with high calcium content, the peak in the XRD spectrum has been shown to occur at higher 2θ angles (Durdziński *et al.* 2015 (b)). In this case, the peaks of the amorphous reaction product may overlap significantly with the peak of the glassy phase. The broad hump in the diffraction signature of the one year hydrated cement sample is found between 2θ angle equal to 25° and 38° as shown in **Fig. 5(b)**.

A peak fit algorithm, which uses unconstrained non-linear optimization, was used to decompose the X-ray diffraction pattern of the amorphous phase. Iterative least squares fit of unconstrained PV peak functions to the diffraction pattern of the total amorphous phase was performed. The center (2θ angle), height (modal frequency) and the FWHM were varied to achieve the best fit indicated by the regression coefficients. The regression coefficient (r^2) varied between 0.999 and 0.995 using PV fit. A single pseudo Voigt peak was fitted to the XRD pattern associated with the glassy phase of fly ash and the hydrated cement is shown in light grey in **Fig. 5 (a) and (b)**. The center of the fitted PV peak of the glassy phase of fly ash is centered on 2θ angle equal to 22.6° and the center of the amorphous reaction products in the one year old hydrated cement is near 2θ angle equal to 30°.

Typical X-ray diffractograms of the 28-day hydrated F and the 10 QL mixes cured at 25°C are shown in **Fig. 6**. The measured intensity patterns for the total amorphous phase and the total crystalline phases obtained from the Pawley method are also shown in the figure.

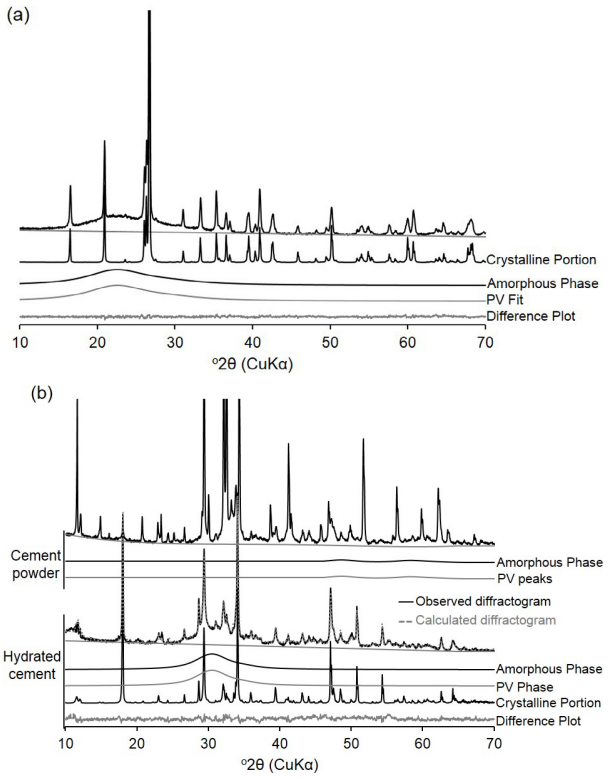

Fig. 5 The XRD patterns of (a) Fly ash; (b) cement powder and control sample obtained from one year old hydrated cement paste cured at 25°C. The decomposed patterns for the amorphous and crystalline phases obtained from the Pawley method are shown in black. The fitted pseudo-Voigt function for the amorphous phase is shown in grey.

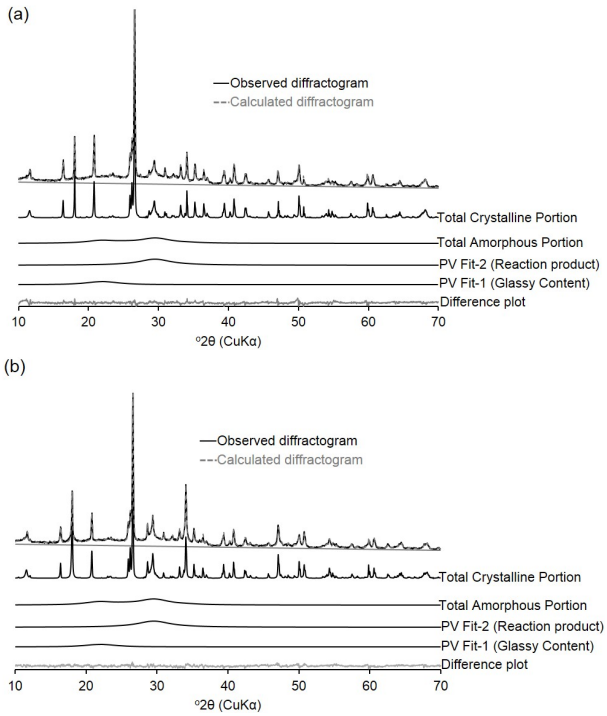

Fig. 6 The decomposed total crystalline and total amorphous portion in hydrated mixes cured at 25°C at 28 days: (a) fly ash cement mix, (b) 10%QL activated to fly ash cement mix. PV fit-1 for unreacted glassy phase of fly ash and PV fit-2 for amorphous reaction products are shown in light grey colour.

Two distinct humps can be identified in the intensity pattern of the total amorphous phase in the binary blends (both F and QL mixes). The diffuse scattering hump from the total amorphous phase contains contributions from the unreacted glassy phase in fly ash and amorphous reaction products.

The Degree of Crystallinity method is a whole pattern method, based on the area contribution of the amorphous phase in the total intensity pattern (Riello 2004). The quantification of any phase by this method requires an accurate intensity profile of the phase. The Degree of Crystallinity method was extended to quantify the contents of individual amorphous phases in binary blends of cement and fly ash (Bhagath Singh and Subramaniam 2016b). Later this method was extended to quantify the glassy phase dissolution and amorphous reaction product formation in hydrating binary blends with different low calcium siliceous fly ashes (Bhagath Singh and Subramaniam 2016c). In the direct decomposition method, the intensity pattern of total amorphous phase is decomposed into component pseudo Voigt (PV) peaks, to determine the contributions from the individual components.

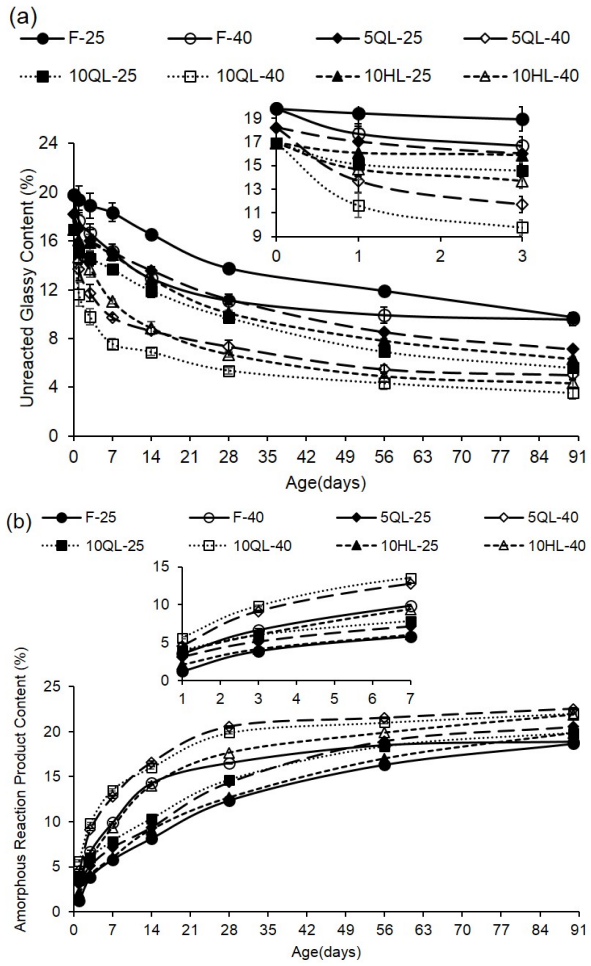

Fig. 7 (a) Unreacted glassy content and (b) amorphous reaction product content in hydrated mixes cured at 25°C and 40°C with age. (Avg of 5 replicates).

The intensity contributions of individual amorphous components to the intensity pattern of the total amorphous phase is obtained by decomposition of the total intensity signature as a sum of fundamental underlying PV peak shapes using the unconstrained non-linear peak fit algorithm. The intensity patterns associated with the glassy phase of fly ash and the amorphous reaction products obtained from the decomposition of intensity pattern of the total amorphous phase for the F and QL mixes are shown in **Fig. 6**. Results of decomposition of the total amorphous phase into component PV peaks clearly indicate two distinct peaks; a peak at lower 2θ angle identified as PV fit-1 and the second peak at higher 2θ angles identified as PV fit-2. The use of additional peaks did not result in any improvement to the overall fit. The peak position of the base line mix and QL activated mixes in hydrating pastes, PV fit-1 is centered on 2θ angle between 22.5 and 22.7° and PV fit-2 is centered on 2θ angle near 30°. The centers of the PV peak fits obtained from the decomposition remain unchanged with hydration and the centers obtained from the decomposition compare very well with the centers obtained from the raw fly ash and one year hydrated cement sample (Bhagath Singh and Subramaniam 2016c). It is established that the unreacted glassy content of siliceous fly ash and the amorphous reaction product are each associated with distinct peaks with well-defined centers; PV fit-1 and PV fit-2 are associated with unreacted glassy content of fly ash and amorphous reaction products, respectively.

The percentage of unreacted glassy content of fly ash in hydrated blended samples is determined as the proportion of the area under the intensity profile obtained from PV fit-1 to the area under the total intensity profile. The unreacted glassy content in the F mix, the QL and the HL mixes cured at 25°C and 40°C obtained from direct decomposition of the intensity pattern are shown in **Fig. 7(a)**. The unreacted glassy content obtained from the intensity profile is referred to the total weight of the reacting system. The influence of temperature in reducing the unreacted glassy content is evident from the results of F mix. In the F mix cured at 25°C, there is little early reactivity in the first 7 days, which is followed by a steady linear decrease in the reacted glassy content with the age. In the F mix, cured at 40°C, there is a noticeable decrease in the unreacted glassy content at the age of 1 day and it decreases rapidly up to 14 days. After 14 days, there is a decrease in the rate of reaction, and the unreacted glassy content decreases steadily at a very slow rate up to 90 days. Comparing the F mixes cured at 25°C and 40°C, the influence of temperature is clearly identified with an increase in the early dissolution. The total level of dissolution achieved at 90 days is however identical for both curing temperatures.

The HL and QL mixes exhibit a lower initial unreacted glassy content than the base line mix and the reduction in the glass content decreases with increasing substitution of fly ash with HL or QL. There is a

reduction in the glassy content contributed by fly ash due to a decrease in fly ash content to 65% and 60%, respectively in the 5QL and 10 QL (or 10HL) mixes. The results indicate that the addition of QL enhances the early dissolution of glassy phase in fly ash, which is observed in the first few day. However, this is not observed in the 10HL system. The trends in the decrease in the unreacted glassy content in the lime added mixes (HL and QL mixes) and the corresponding F mixes are nominally similar after 28 days.

The amorphous reaction product content is determined from the proportion of the area under the intensity profile obtained from PV fit-2 to the area under the total intensity profile, and is plotted in **Fig. 7(b)**. The amorphous reaction product content includes the amorphous reaction products formed due to cement hydration and the products of the pozzolanic reaction, as a proportion of the total mass of the reacting system. At an early age, there is a larger amorphous reaction product content at 40°C than in sample cured at 25°C. The QL mixes show a higher amorphous reaction product content than the F mix at both the curing temperatures. Results indicate that there is very rapid increase in the reaction product formation at 40°C up to 14 days of age and the QL mixes showed much higher reaction product content at 1 day age than the F mix. At 25°C, there is a steady linear continued increase up to 90 days of age. The total amorphous reaction product content obtained for 25 and 40°C is comparable at 90 days of age in the F mix. The 5QL and the 10QL mixes showed almost identical reaction product content throughout the age.

In all the results presented in **Figs. 7(a)** and **(b)**, the mean of five measurements are plotted with error bars indicating the range of scatter. The repeatability error varied between the 0.5-1%. The error is nearly 1% in the early ages and with increasing age the error decreased to 0.5%. Additionally, there is a small residual error at 10° 2θ angle, which potentially effects the quantitative value of the amorphous products. In all the analysis, the magnitude of the error was found to be less than 0.5%. The direct decomposition method of the X-ray diffraction pattern provides a fast way for studying the reaction kinetics and for assessing the influence of process variables in hydrating binary blends of cement and low calcium siliceous fly ash. The direct decomposition method offers the advantage of not requiring any calibration profiles.

5. 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. Considering the similar sizes of cement and fly ash, the observed acceleration in fly ash concrete cannot be attributed to the fine particle effect due to enhanced packing density (Maltais and Marchand 1997). A correlation between the reaction product content and the compressive strength for all the mixes is shown in **Fig. 8**. The available data indicates that the strength gain in concrete is directly proportional to the reaction product content in the system, which is controlled by the dissolution of glassy phase in fly ash. The compressive strength is directly related to the amorphous reaction product content; higher reaction product content and lower the unreacted glassy content resulted in higher compressive strength. In the lime added systems (HL and QL systems), there is an increase in the reaction product content, which contributes to higher strength.

The strength gain data indicates that there is no further increase in the F mix cured at 40°C after 28 days. The long-term strength attained by the F mix cured at 25°C is identical to the strength obtained at 40°C. Higher long-term strengths are obtained in QL mixes cured at 40°C. This suggests that while reactive species are present in the F mixes, the reaction is limited by the availability of CH. This is in agreement with the CH measurements obtained from Rietveld analysis. CH measurements indicate that at the age of 90 days, CH is almost completely depleted in the F mixes. The strength and CH measurements can also be reconciled with the unreacted glassy content and the reaction product content obtained from quantitative phase analysis. The unreacted glassy content and the reaction product content in the F mixes cured at 25°C and 40°C are identical at 90 days. This suggests that the glass dissolution in the F mix is limited by the availability of CH in the system.

Temperature influences the early rate of dissolution of glassy content from fly ash. There is an additive effect of QL and temperature on the glassy phase dissoluion (decrease in unreacted glassy content), which is evident within the first few days. The enhancement in the early dissolution of the glassy phase in fly ash observed in the QL mixes, which is not seen in the HL mix indictes that the dissolution is not influenced by the CH content in the system; the CH contents produced in the 5QL and 10HL mixes are comparable. The percentage of QL addition does not influence the dissolution of fly ash evidenced by comparing the results of 5QL and 10QL mixes at both curing temperatures. Thus, the QL content in the system, does not appear to influence the reacted

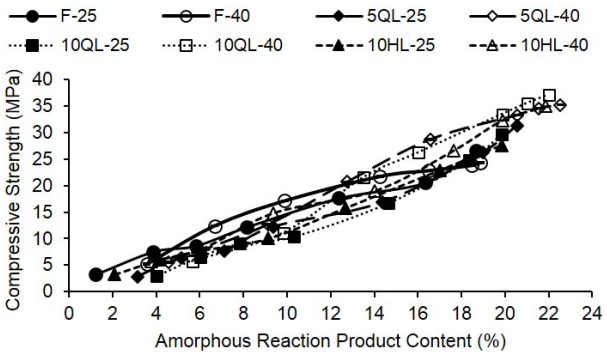

Fig. 8 Correlation between the amorphous reaction product content and compressive strength.

glassy content after the early increase in reactivity observed in the first few days. There is an exothermic reaction of hydration of in water QL and the associated temperature change increases the reacted glassy phase content of fly ash content in QL mixes. The additive influence of the exothermic heat release and temperature for the QL samples produces an enhanced early dissolution in samples cured at 40°C.

A correlation between the unreacted glassy content and the CH content for all the mixes is shown in **Fig. 9**. Considering the samples cured at 25°C, the Rietveld analysis indicates that there is a significant difference in the CH content between the 5QL and 10QL mixes at all ages. Following the initial increase in the dissolved glassy content in the 10QL mix, due to the early temperature rise, there is no noticeable difference in the reacted glassy content of fly ash in the 5QL and 10QL samples cured at 25°C. The CH contents of the 10HL and 5QL systems are comparable. This suggests that the CH content does not influence the rate of dissolution of the fly ash glassy phase. The influence of CH is to raise the pH of the solution. It is known that the minimum solubility of CH at 25°C is limited to 1.2gm of CaO per liter of water. Increasing the QL content from 5% to 10% limits the CH content in the solution to the saturation limit. There is hence no difference in the pH of the working solution on increasing the QL content from 5% to 10% and hence no improvement in the dissolution of the glassy phase. The pH of saturated CH is known to decrease with temperature. Thus the enhanced early dissolution at 40°C is produced by temperature. The results of the experimental program indcate that the dissolution of the glassy phase in fly ash is significantly enhanced by temperature. While the CH content in the system does not produce an increase in the dissolution, complete consumption of CH results in and the associated decrease in pH limits the dissolution of the glassy phase.

6. Conclusions

The rate controlling step in the reactivity of fly ash is the dissolution of its reactive components, primarily silica. Temperature increases the dissolution of the glassy phase from fly ash which contributes the reactive silica to the pozzolanic reaction. However, to sustain the reaction, sufficient portlandite should be available in the solution. Initially, the lime provided by cement hydration is sufficient to support the pozzolanic reaction. The total quantity of portlandite made available from the cement may not be sufficient for reacting with the available silica at high volumes of cement replacement. Addition of quick lime or hydrated lime resulted in an increase in the portlandite content in the system which allows the pozzolanic reaction to continue. The excess portlandite available in the quicklime systems does not appear to influence the rate of pozzolanic reaction as indicated by the similar quantity of amorphous products formed. Therefore, the rate limiting step in the fly ash reaction is the dissolution of fly ash.

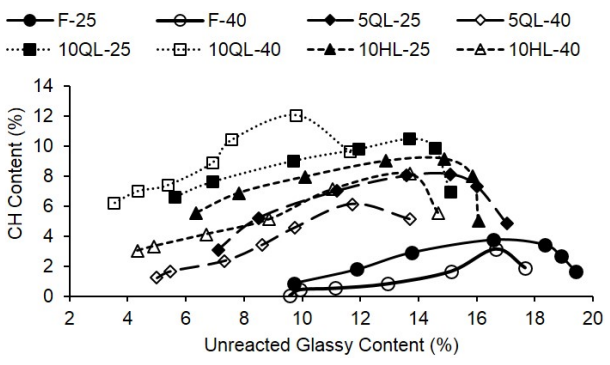

Fig. 9 Correlation between the CH content and the unreacted glassy phase content.

References

Antiohos, S. K., Papageorgiou, A., Papadakis, V. G. and Tsimas, S., (2008). "Influence of quicklime addition on the mechanical properties and hydration degree of blended cements containing different fly ashes." *Constr. Build. Mater.*, 22, 1191-1200.

Antiohos, S. K. and Tsimas, S., (2004). "Activation of fly ash cementitious systems in the presence of quick lime (part-1) Compressive strength and pozzolanic reaction rate." *Cem. Concr. Res.,* 34, 769-779.

ASTM, (2015). "*Standard C 618: Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete*."

Bhagath Singh, G. V. P. and Subramaniam, K. V. L., (2016a). "Quantitative XRD analysis of binary blends of siliceous fly ash and hydrated cement." *J. Mater. Civ. Eng*., 28(8), 04016042 (1-7).

Bhagath Singh, G. V. P. and Subramaniam, K. V. L., (2016b) "Direct decomposition X-ray diffraction method for amorphous phase quantification and glassy phase determination in binary blends of siliceous fly ash and hydrated cement." *Journal of Sustainable Cement-Based Materials*, http://dx.doi.org/10.1080/21650373.2016.1177478.

Bhagath Singh, G. V. P. and Subramaniam, K. V. L., (2016c). "Method for Direct Determination of Glassy Phase Dissolution in Hydrating Fly ash-Cement System Using X-ray Diffraction" *Journal of American Ceramic Society*, doi:10.1111/jace.14486.

Brown, P. W., (1986). "The system Na_2O-CaO-SiO_2-H_2O." *J. Am. Ceram. Soc*., 73, 3457-63.

Bruker AXS, (2009). TOPAS V4.2: General Profile and Structure Analysis Software for Powder Diffraction Data, B. A. Karlsruhe.

Brunet, F., Charpentier, T., Chao, C. N., Peycelon, H. and Nonat, A., (2010). "Characterization by solid-state NMR and selective dissolution techniques of anhydrous and hydrated CEM V cement pastes." *Cem. Concr. Res*., 40(2), 208-19.

Bureau of Indian Standards, (1999). "*Methods of physical tests for hydraulic cement*." IS 4031(part-2),

New Delhi, India.

Bureau of Indian Standards, (2003a). "*Methods of test for pozzolanic materials*." IS 1727, New Delhi, India.

Bureau of Indian Standards, (2003b). "*Pulverized fuel ash-specification*." IS 3812-part 1, New Delhi, India.

Bureau of Indian Standards, (2013). "*Ordinary Portland cement, 53 Grade-Specifications*." IS 12269, New Delhi, India.

Creagh, D. C. and Hubbell, J. H., (2006). "X-ray absorption (or attenuation) coefficients." In: E. Prince (Ed.), Int. Tables Crystallogr. Vol. C Math. Phys. Chem. Tables, 6th ed., International Union of Crystallography, 220-229.

Deschner, F., Unch, B. M., Winnefeld, F. and Lothenbach, B., (2013). "Quantification of fly ash in hydrated, blended Portland cement pastes by backscattered electron imaging." *J. Microsc.*, 251(2), 188-204.

Deschner, F., Winnefeld, B., Lothenbach, S., Seufert, P., Schwesig, S., Dittrich, F., Neunhoeffer, G. and Neubauer, J., (2012). "Hydration of a portland cement with high replacement by siliceous fly ash." *Cem Concr Res*., 42(10), 1389-1400.

Durdziński, P. T., Dunant, C. F., Haha, M. B. and Scrivener, K. L., (2015a). "A new quantification method based on SEM-EDS to assess fly ash composition and study the reaction of its individual components in hydrating cement paste." *Cem. Concr. Res*., 73 111-22.

Durdziński, P. T., Snellings, R., Dunant, C. F., Haha, M. B. and Scrivener, K. L., (2015b). "Fly ash as an assemblage of model Ca–Mg–Na-aluminosilicate glasses," *Cem. Concr. Res*., 78 [part-B], 263-72.

Feng, X., Garboczi, E. J., Bentz, D. P., Stutzman, P. E. and Mason, T. O., (2004). "Estimation of the degree of hydration of blended cement pastes by a scanning electron microscope point-counting procedure." *Cem. Concr. Res*., 34(10), 1787-93.

Fernández-Jiménez, A., de la Torre, A. G., Palomo, A., López-Olmo, G., Alonso, M. M. and Aranda, M. A. G., (2006). "Quantitative determination of phases in the alkaline activation of fly ash. Part II: degree of reaction." *Fuel*, 85(15), 1960-69.

Fraay, A. L. A., Bijen, J. M. and de Haan, Y. M., (1989). "The reaction of fly ash in concrete a critical examination." *Cem. Concr. Res*., 19 (2), 235-246.

Gray, D. H. and Lin, Y. K., (1972). "Engineering properties of compacted fly ash." *J. Soil Mech. Found. Div*., 98(4), 361- 380.

Haha, M. B., Weerdt, K. D. and Lothenbach, B., (2010), "Quantification of the degree of reaction of fly ash." *Cem. Concr. Res*., 40(11), 1620-1629.

Huang, S. and Cheng, J., (1986). "Kinetic of reaction in the system fly ash- $Ca(OH)_2$-H_2O." *J. Chin. Ceram. Soc*., 14 (1), 191- 197.

ICSD, (2013). "Inorganic crystal structure database." Fachinformationszentrum: Karlsruhe, Germany.

Powder Diffraction File-2, "International Centre for Diffraction Data," edited by Frank McClune, 12 Campus Boulevard, Newtown Square, PA, 19073-3272, 2013.

Li, S., Roy, D. M. and Amitabha, K., (1985). "Quantitative determination of pozzolanas in hydrated sstems of cement or $Ca(OH)_2$ with fly ash or silica fume." *Cem. Concr. Res*., 15(6). 1079-86.

Lokken, R. O., Shade, J. W. and Martin, P. F. C., (1990). "Effect of curing temperature on the properties of cementitious waste forms." *Mater. Res. Soc. Symp. Proc*., 176, 23- 29.

Luke, K. and Glasser, F. P., (1987). "Selective dissolution of hydrated blast furnace slag cements." *Cem. Concr. Res*., 17(2), 273-82.

Luke, K. and Glasser, F. P., (1988). "Internal chemical evolution of the constitution of blended cements." *Cem. Concr. Res*., 18(4), 495-502.

Luxan, M. P., Sanchez de Rojas, M. I. and Frias, M., (1989). "Investigations on the fly ash-calcium hydroxide reactions." *Cem. Concr. Res*., 19, 69-80.

Ma, W. and Brown, P. W., (1997). "Hydrothermal reactions of fly ash with $Ca(OH)_2$ and $CaSO_4$-$2H_2O$." *Cem. Concr. Res*., 27(8), 1237-1248.

Ma, W., Liu, C., Brown, P. W. and Komarneni, S., (1995). "Pore structures of fly ashes activated by $Ca(OH)_2$ and $CaSO_4$-$2H_2O$." *Cem. Concr. Res*., 25(2), 417- 425.

Ma, W., Sample, D., Martin, R. and Brown, P. W., (1994). "Calorimetric study of cement blends containing fly ash, silica fume and slag at elevated temperature." *Cem. Concr. Aggr*., 16, 93-99

Madsen, I. C., Scarlett, N. V. Y. and Kern, A., (2011). "Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction." *Z. Kristallogr*., 226(12), 944-55.

Maltais, Y. and Marchand, J., (1997), "Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars." *Cem. Concr. Res*., 27(7), 1009-1020.

Mira, P., Papadakis, V. G. and Tsimas, S., (2002). "Effect of lime putty addition on structural and durability properties of concrete." *Cem. Concr. Res*., 32 (5), 683- 689.

O'Connor, B. H. and Raven, M. D., (1988). "Application of the Rietveld refinement procedure in assaying powdered mixtures." *Powder Diffr*., 3(1), 2-6.

Ohsawa, S., Asaga, K., Goto, S. and Daimon, M., (1985). "Quantitative determination of fly ash in the hydrated fly ash -$CaSO_4$·$2H_2O$-$Ca(OH)_2$ system." *Cem. Concr. Res*., 15(2), 357-366.

Pawley, G. S., (1981). "Unit-cell refinement from powder diffraction scans." *J. Appl. Crystallogr*., 14 (6), 357-61.

Pietersen, H. S., Fraay, A. L. A. and Bijen, J. M., (1990). "Reactivity of fly ash at high pH." *Mat. Res. Soc. Symp. Proc*., 178, 139-157.

Riello, P., (2004). "Quantitative analysis of amorphous fraction in the study of the microstructure of semi-

crystalline materials." In: E. J. Mittemeijer and P. Scardi Eds., *Diffraction Analysis of the Microstructure of Materials*, Berlin Heidelberg: Springer Verlag.

Sakai, E., Miyahara, S., Ohsawa, S., Lee, S. H. and Daimon, M., (2005). "Hydration of fly ash cement." *Cem. Concr. Res*., 35(6), 1135-1140.

Scarlett, N. V. Y. and Madsen, I. C., (2006). "Quantification of phases with partial or no known crystal structures." *Powder Diffr*., 21(4), 278-84.

Scrivener, K. L., Lothenbach, B., Belie, N. D., Gruyaert, E., Skibsted, J., Snellings, R. and Vollpracht, A., (2015). "TC 238-SCM: hydration and microstructure of concrete with SCMs." *Mater. Struct*. 48(4), 835-62.

Shi, C., (2001). "Studies on several factors affecting hydration and properties of lime-pozzolan cements." *J. Mat Civ. Eng*. 13(6), 441-445.

Shi, C., (1999). "Studies on several factors affecting hydration and properties of lime- pozzolan cements." *J. Mater. Civ. Eng*. 29(4), 467-472.

Suprenant, B. A. and Papadopoulo, G., (1991). "Selective dissolution of Portland-fly ash cements." *J. Mater Civ Eng*., 3(1), 48-59.

Toby, B. H., (2006), "R factors in Rietveld analysis: How good is good enough." *Powder Diffr.*, 21(1), 67-70.

Zhang, Y. M., Sun, W. and Yan, H. D., (2000). "Hydration of high-volume fly ash cement pastes." *Cem. Concr. Comp*., 22, 445-452.