An Integrated Approach for Understanding Hydration Behavior in Portland cement Systems Containing Silica Fume

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Abstract— One of the key behaviours that predict the performance of portand cement system containing silica fume is hydration. Hydration affects the microstructure of concrete, which in turn alters its engineering properties such as strength, elastic moduli, toughness and other durability related properties like porosity and permeability. Therefore in order to predict such properties, fundamental study of the hydration process of portland cement system containing silica fume is very important. The main aim of the present investigation is to gain insight on the effects of silica fume addition on the hydration process and microstructural development of cement paste. This was done by adopting an integrated approach involving combination of theoretical models and experimental investigation, and developing mathematical equations to predict hydration behavior of the system. Quantitative studies on cement hydration is conducted using thermo-gravimetric analysis and other techniques, and qualitative studies is done using X-ray diffraction techniques. The non-evaporable water content and the calcium hydroxide content of paste obtained from experiments coupled with the use of suitable theoretical models is used to determine the degree of hydration, degree of pozzolanic reaction and calculated porosity for paste containing silica fume at different dosages of silica fume. (0%, 4%, 8% and 12%). Attempts were made to further understand the trends obtained using curve-fitting techniques and other theoretical models. Results from the study indicated that the addition of silica fume at all replacement levels depletes Ca (OH) 2 produced from cement hydration and forms C-S-H gel and this reaction starts at early curing periods. In addition, the non-evaporable water content and the fraction of silica fume that completely reacted decreases, with increase in its replacement level and helped in determining the degree of cement hydration and pozzolanic reaction of silica fume particles. A significant portion of unreacted silica fume remains in the paste and is involved in the pore filling process. The porosity values for paste containing silica fume decreased with increase in its replacement levels due to both its pozzolanic reactivity and pore-filling ability. The compressive strength data showed that mortars containing 4% and 8% replacement level of silica fume have higher strength than the control mortar. However, SF-12% mortars registered lower strength than the control. The trends obtained are reasoned to be due to variations in the amounts of primary and secondary C-S-H gel. Further, mathematical equations are developed through curve-fitting of experimental data, and analysis of these equations revealed that the effect of variation observable with control and SF-4% paste, and SF-8% and SF-12% are merely due to the dosage of silica fume while the effect of variation observable with SF-4% and SF-8% is due to the dosage of silica fume and other mechanisms associated with its dosage.

Keywords: Portland Cement Systems, Silica Fume, Hydration Process

I. INTRODUCTION

The invention of Portland cement by Joseph Aspdin in 1824 laid the foundation for today's cement industry and other related construction activity. Although he obtained a patent for producing hydraulic cement by heating a mixture of finely ground limestone and clay in laboratory, high reactivity and strong cementing properties were not achieved due to the use of low temperature as compared to the current-day cement. A few years later, in 1845, Isaac Johnson made the first modern Portland cement by firing a mixture of chalk and clay at a much higher temperature (14000C-15000C), similar to those used today. The cement formed at this high temperature was much more reactive and had stronger cementing property. Since then till the present day we use the same raw materials as Johnson had used but significant developments have been made in the manufacturing process like the development of rotary kilns, addition of gypsum to control setting, use of ball mills to grind clinker and raw materials, etc. While Portland cement has been an integral part in the construction industry during the period from its invention until about the start of the twentieth century (1824-1918), concrete structures were designed primarily based on strength and the concrete mixture proportions were chosen merely based on trial studies, without much information about the effect of w/c and knowledge about the hydration kinetics.

In 1918, Duff Abram performed a detailed investigation to study the effect of w/c on the strength development in concrete and proposed an inverse relationship popularly known as 'Abrams' law, which is the basis in many standard methods of concrete mixture design even today[1].

Kolmogorov in 1937, Johnson and Mehl in 1939 and Avarami in 1940 tried to explain the mechanism involved in cement hydration as a growth and nucleation process [2,3,4]. They proposed that initially stable nuclei of hydration products are formed at random locations in the volume of cement paste and as the reaction makes progress, these nuclei grow isotropically in a homogeneous manner to form spherical particles that impinge against each other due to the limitation of capillary space. In 1947, Powers and Brownyard started their systematic investigation on the hydration of cement and structure of hydrated cement paste [5]. In their study, cement microstructure was presented as a collection of spherical hydrate product gel formed around unreacted cement particles, leaving empty spaces called as capillary pores. In their model, unreacted water, cement, hydration product gel and porosity (gel and capillary) were distinguished and equations relating the volume fraction of these different components with the degree of hydration (α) and w/c were proposed. In 1955, electron microscopy

technique was first introduced by Grudemo to study the microstructure of hydrated cement paste and, the shape and morphology of hydrated compounds were identified to be ribbon-like fibers [6]. In 1968, Kondo and Udea classified the cement hydration product into two parts, inner and outer product. As hydration proceeds, they proposed that cement particle shrinks and will be replaced by a dense inner hydration product which grows inward from the original layer and a porous outer hydration product which grows outward into capillary pores [7].

In the 1970s, several studies were carried out to understand the structure and properties of different hydration products such as C-S-H gel and others. Specifically, Feldman and Sereda postulated a layered structure of C-S-H gels, with water bonded between the layers of gels and some water adsorbed on their surface layers popularly known as gel water [8]. In 1972, Hadley observed the presence of hollow shells of hydrates around cement grains and the growth of needle-like crystals inside these shells popularly known as "Hadley Grains"[9]. Scrivener, in 1984, explained the formation of these hollow shells using a combination of different electron microscopy techniques [10]. He proposed that at the onset of hydration, ettringite needles are formed around cement grains. But when at a later stage C-S-H gel is formed, it gets deposited on these needles at a distance from the cement particles thereby forming hollow shells.

In the 1980s, investigations were carried out on pure cement compounds and the hydration mechanism of silicates and aluminates were studied separately. The reaction mechanism and kinetics of calcium silicate compounds were studied by Barret et al 1983, Jennings et al 1986, Damidot et al 1994[11,12,13]. They divided the alite hydration into three stages and proposed different hypotheses to explain these stages. The reaction of aluminate compounds were studied by Breval 1976 and Scrivener et al 1984[14, 15]. They proposed various theories to explain the interconversion of ettringite and monosulfoaluminate phases and systematically investigated the role of gypsum in retarding the hydration of aluminates. Since then, more advancement has been made in cement science and many microstructural models have been proposed to represent the structure of different hydration products and many attempts has been made to understand the reaction kinetics and model them theoretically.

A. Hydration of compounds in Portland cement

The important compounds present in Portland cement are tri-calcium silicate (C3S), di-calcium silicate (C2S), tri-calcium aluminate (C3A), and tetra-calcium alumino-ferrite (C4AF), in addition to gypsum and other minor impurities. When Portland cement is mixed with water, these compounds react and the solid volume in cement paste increases, converting cement into a stiff mass or solid. The reaction products (hydrates) give cement its binding properties and are responsible for its strength development. The hydration of different cement compounds is briefly discussed below:

1) Calcium silicates: The hydration of the two calcium silicates, C3S and C2S are stoichiometrically similar, differing only in the amount of hydration products [C-S-H gel and calcium hydroxide (CH)] formed. The hydration of silicates is shown below:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (1)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad (2)$$

In the above reactions, C3S is highly reactive at early periods and is responsible for the initial strength development of Portland cement system. C2S is reactive at later periods and contributes to the later strength development of the system.

2) Calcium aluminates and alumino-ferrites(C3A and C4AF): The hydration of C3A can result in one or more of the products such as ettringite (C6AS3H32), monosulphoaluminate (C6ASH18), calcium aluminate hydrate (C3AH6 or C4AH19) and hydrogarnet (C2AH8), depending upon the quantity of gypsum ($3C\bar{S}H_2$) present in cement. With appropriate quantity of gypsum (~4%-5%), the hydration of C3A is as follows:

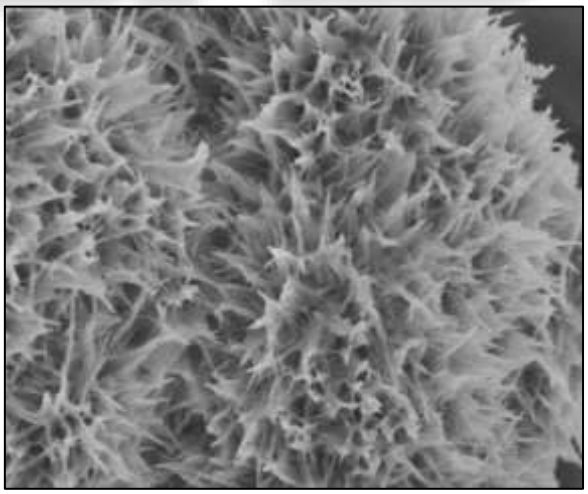
$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \quad (3)$$

If there are excess quantity of C3A based on aluminate to sulfate ratio (which will be the usual case), the C6AS3H32 converts to C6ASH18 and the reactions are as follows:

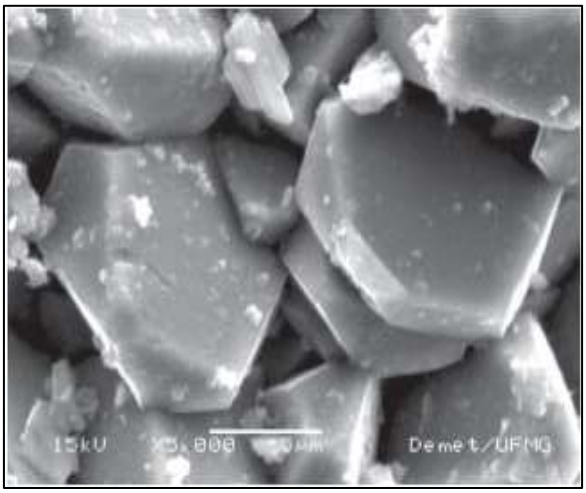
$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12} \quad (4)$$

The hydration of C4AF is similar to that of C3A, with the exception that the reactions are much slower with less heat evolution and the products contain alumino-ferrous hydrates instead of mere aluminate hydrates as in the case of C3A.

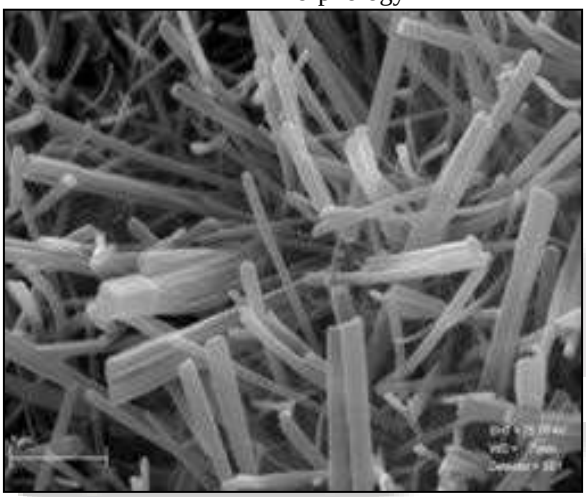
The hydration of cement particles is associated with microstructural changes that have been observed using electron microscopy technique. Scanning electron microscopy (SEM) is one versatile technique for investigating the microstructure of materials and has been extensively used as qualitative tool to the microstructural evolution of hydration products. Four principle solid phases in hydrated products namely, C-S-H gel, Ca(OH)2,ettringite and monosulphoaluminates are observed as shown in Figure 1.



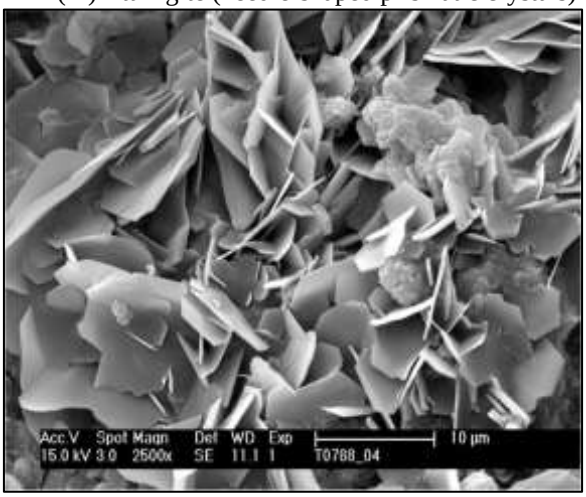
(i) C-S-H gel: constitutes 50-60% of solid volume of solids in hydrated cement paste. It has generally been attributed with a layered chain structure with short-range crystallinity



(ii) Calcium hydroxide (CH): constitutes 20-25% of the solid volume in hydrated paste. It forms large crystals with distinctive hexagonal-prism morphology



(iii) Ettringite (needle-shaped prismatic crystals)



(iv) Monosulfoaluminate (hexagonal-plate crystals)

Note: (iii) and (iv) together constitute 15-20% of the solid volume in hydrated paste

Fig. 1: Microstucture of hydration products [16].

II. RESULTS

In this Chapter, the experiment results obtained from different tests are reported and discussed. In addition, mathematical equations are developed for predicting the experimental test results and the hydration behavior of Portland cement systems containing silica fume.

A. Calcium hydroxide content of pastes

The $Ca(OH)_2$content of pastes containing silica fume at different replacement levels with period of curing is shown in Figure 15.

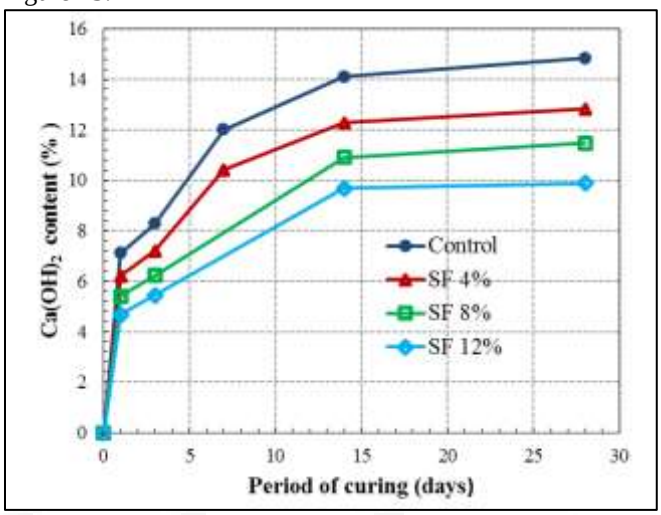
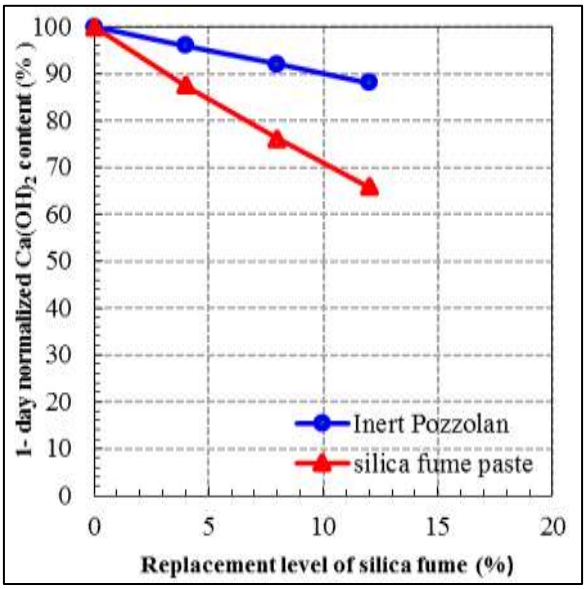


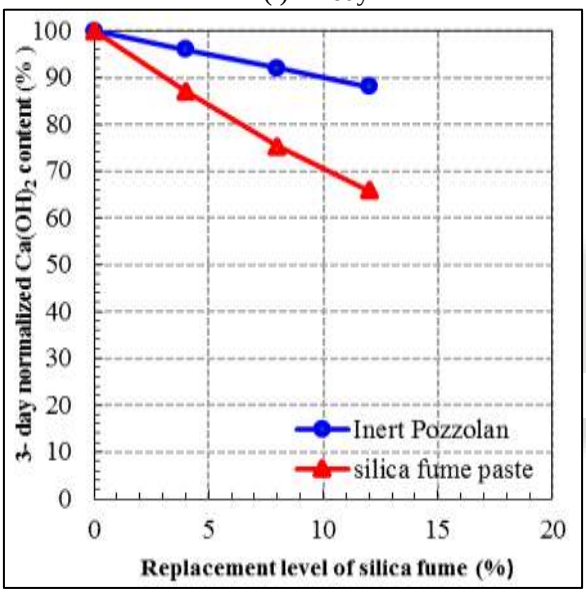
Fig. 15: $Ca(OH)_2$content of pastes containing silica fume at different replacement levels

As the figure shows, the $Ca(OH)_2$ content of all pastes increases with increase in the period of curing until ~14 days, beyond which the value levels-off. This increasing trend is an indication of the combined progress of cement hydration and pozzolanic reaction, and the level-off trend is an indication of the slow progress of these reactions. In addition, the $Ca(OH)_2$ content of pastes containing silica fume is lower than that of the control paste and decreases with increase in the replacement level of silica fume. This decreasing trend may be attributed to the lower cement content of silica fume pastes arising due to its partial replacement for cement at appropriate dosage levels (dilution effect), and the depletion of $Ca(OH)_2$ by the silica fume particles (pozzolanic effect).

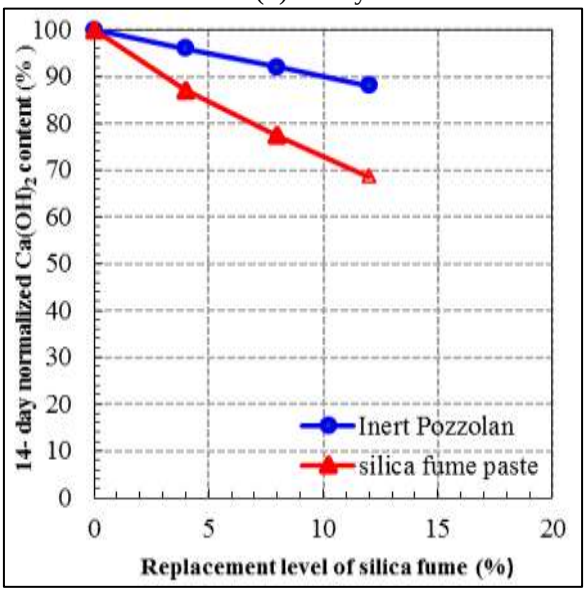
In order to further understand the effect of addition of silica fume on $Ca(OH)_2$ content, the value for the control paste is first considered as reference (i.e., 100) and other values are normalized to this value. Then, the dilution and pozzolanic effect are isolated by comparing the normalized value obtained for silica fume paste with the value obtained for an inert pozzolan (i.e., one which remains inert and do not participate in the pozzolan reaction), at same replacement levels. The effect of silica fume addition on the normalized $Ca(OH)_2$ content for different curing periods, separating the dilution and pozzolanic effect is shown in Figure 16 (i) through 16 (iv).



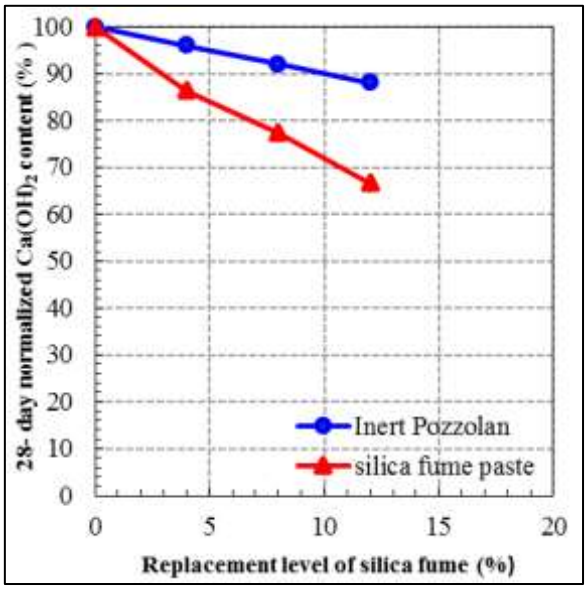
(i) 1 day



(ii) 3 Days



(iii) 7 Days



(iv) 28 Days

Fig. 16: Effect of addition of silica fume on the normalized $Ca(OH)_2$ content for different curing periods

As the figures show, the normalized value for paste containing silica fume is significantly lower than for the inert pozzolan, clearly indicating that silica fume can be reactive at early as well as later curing periods. In addition, the normalized $Ca(OH)_2$ depletion due to pozzolanic reaction only (i.e., difference between the values for inert pozzolan and paste containing silica fume in the figures) is higher at early curing periods (i.e., 1-day and 3-day) than at later curing periods (i.e., 7-day and 28-day).

Another representation of the effect of silica fume on cement hydration and pozzolanic reaction is shown in Figure 17. In this figure, the $Ca(OH)_2$ content of pastes are normalized to that of the control paste at respective curing periods and the values for control paste is considered as 1 (denoted as dotted line in the figure). Accordingly, a value greater or lower or equal to 1 is obtained for any paste for the same amount of cement used. In all pastes investigated, the normalized $Ca(OH)_2$ content is lower than 1, indicating that enhancement in cement hydration takes place with pozzolanic reaction as reported in other literatures [58,59] although other effects, which may affect the enhancement in cement hydration, are investigated at a later stage.

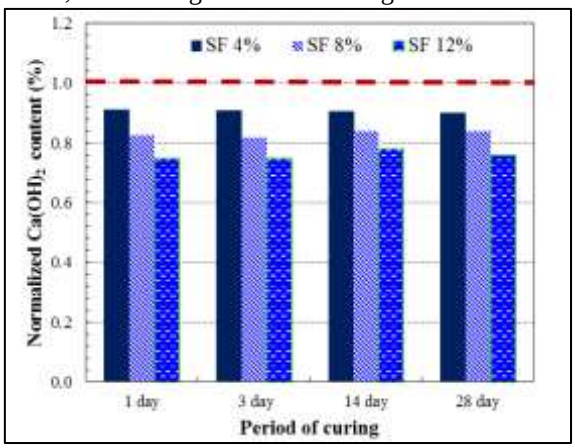


Fig. 17: Normalized $Ca(OH)_2$content of pastes containing silica fume at different curing period

B. Non-Evaporable Water Content of Pastes

The non-evaporable water content of pastes containing silica fume at different replacement levels with period of curing is shown in Figure 18.

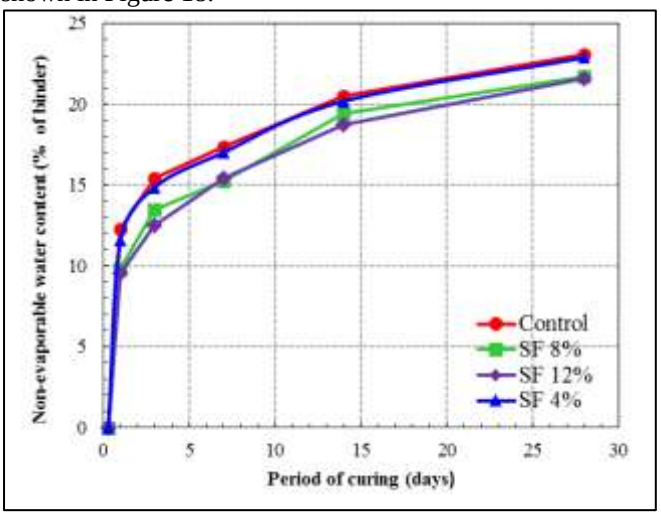


Fig. 18: Non-evaporable water content of pastes at different replacement levels of silica fume

As the figure shows, the non-evaporable water content (w_n) of all pastes increases with increase in the period of curing until ~14 days, beyond which the value slowly starts leveling-off. This trend is similar to the trend observed with the $Ca(OH)_2$ content discussed previously except that the leveling-off is relatively slower here. The trend indicates a quantitative measure of the progress of reactions in the paste based primarily on the formation of hydration products such as C-S-H gel and $Ca(OH)_2$ combined together with time, in addition to few aluminates. Similarly, the w_n of pastes containing silica fume (SF-4%, SF-8% and SF-12%) is slightly or substantially lower than that of the control paste, which may be due to two reasons: (i) the reduction in the quantities of hydration products due to reduced cement content (i.e., 'dilution effect'), and (ii) the variation in the amount of water present in secondary C-S-H gel formed due to silica fume addition. The effect of silica fume addition on the non-evaporable water content of paste is difficult to understand as the values for the pastes are too close to each other. Hence, better representation can be obtained if water associated with $Ca(OH)_2$(obtained from the TGA curve) is deducted from w_n values to obtain hydrate water content, which is a measure of water associated with primary and secondary C-S-H gel.

The hydrate water content (w_h) of pastes containing silica fume at different replacement levels with period of curing is shown in Figure 19. As the figure shows, an increasing trend in the hydrate water content of pastes is observed with increasing the period of curing. The hydrate water content for the control paste is initially higher than for others until ~14 days. While the cement hydration produces primary C-S-H gel in the control paste that increases its w_h content initially, pastes containing silica fume has lower w_h content (dilution effect) despite producing primary and secondary C-S-H gel as evidenced in Figure 16. However at 14 days and then after, the values for the control paste is lower than for the SF-4% but higher than for the SF-8% and SF-12%.

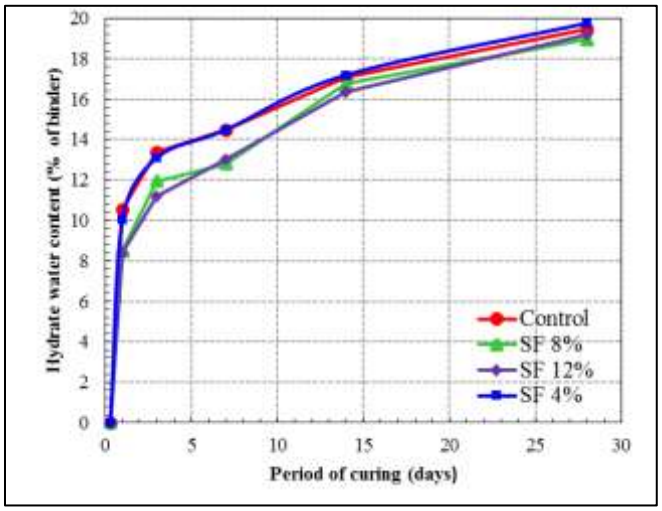


Fig. 19: Hydrate water content of pastes at different replacement levels of silica fume

C. Total Apparent Degree of Hydration of Paste

In this section, mass balance equations as explained by Neithalath et al. 2009 are used to determine the degree of hydration of paste containing silica fume [45]. Accordingly, the enhancement or retardation in cement hydration due to the addition of silica fume is first determined, which is equal to the difference between the w_n of silica fume paste and that of the control paste $(\Delta w_n)_r$. The difference is shown below and the plot is shown in Figure 20.

$$(\Delta w_n)_r = (w_n)_c\, m_c - w_n \qquad (16)$$

where

$(w_n)_c$ is the non-evaporable water content of plain cement paste (control)

m_c is the mass fraction of cement present in the paste and

Δw_n can be determined from equation (1) as w_n , $(w_n)_c$ and m_c are already obtained

w_n is the non-evaporable water in paste

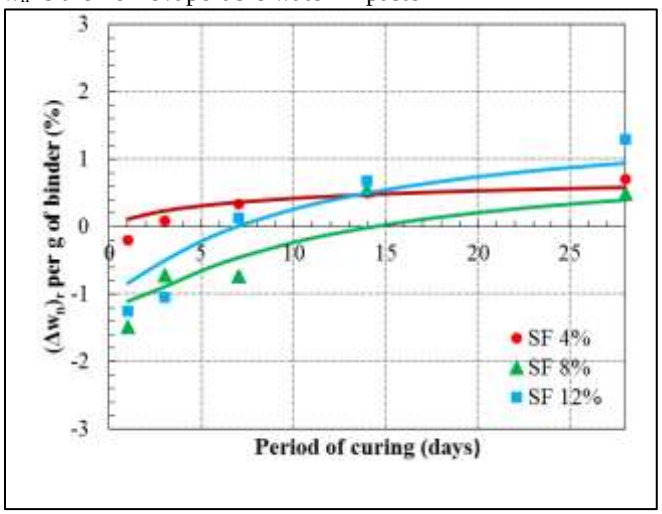


Fig. 20: Change in non-evaporable water content due to presence of silica fume

As the figure shows, the silica fume addition plays a significant role in the retardation or enhancement in cement hydration. At 4% replacement level (i.e., for the SF-4% paste), a slight retardation in the cement hydration was observed during until ~2 days. Such a behavior may be because some relatively large-sized silica fume particles may

not disperse effectively in solution and does not quickly produce nucleation sites for the grown of hydration products, thereby negatively affecting the cement hydration. Beyond this period, a definite enhancement was observed until 28 days, with enhancement rate slowly reducing with increase in curing period. This may be because the pozzolonic reaction is much slower at later curing periods and does not bind much water as cement hydration [45, 55, 56]. In addition, the silica fume particles may be available for the precipitation of hydration products after their surfaces gets exposed. Similar behavior has been reported by other investigators also [48, 60]. At higher replacement level (i.e., for the SF-8% and SF-12% paste), the retardation in cement hydration is observed for a longer period of 10-11 days and 6-7 days, respectively, beyond which the enhancement in cement hydration starts. This retardation period is shorter for the SF-12% paste than for the SF-8% paste perhaps because the former has more fine particles that react faster and help in enhancement in cement hydration at an earlier curing period.

The enhancement in cement hydration, i.e., $(\Delta w_n)_r$ values obtained previously is due to the presence of silica fume and additional water associated with the pozzolanic reaction of silica fume, and to proceed further, the former is assumed to be negligible as suggested by other studies [44, 45, 56]. Due to the above mentioned reason, the $(\Delta w_n)_r$ values actually represent the apparent enhancement or retardation in cement hydration and hence, the term 'total apparent degree of hydration' $[(\boldsymbol{\alpha_T})_{\boldsymbol{app}}]$ is used from now on instead of just 'total degree of hydration' [45].

$$(\alpha_T)_{app} = \frac{(w_n)_c}{(w_n)_{c-\infty}} m_c + \frac{(\Delta w_n)_r}{(w_n)_{c-\infty}} \quad (17)$$

where $(w_n)_c$ is the non-evaporable water content of the plain paste, m_c is the mass fraction of cement present in paste and $(w_n)_{c-\infty}$ is the ultimate non-evaporable water content of cement. $(w_n)_{c-\infty}$ is determined from the Bogues composition of cement (See Table 3) using Powers formula as shown below.

$$(w_n)_{c-\infty} = 0.23\,(C_3S) + 0.32\,(C_2S) + 0.317\,(C_3A) + 0.368(C_4AF) \quad (18)$$

where the factors inside parenthesis indicate the quantity of Bogues compound in cement.

The total apparent degree of hydration $(\boldsymbol{\alpha_T})_{\boldsymbol{app}}$ for pastes containing silica fume at different replacement levels with the period of curing is shown in Figure 21.

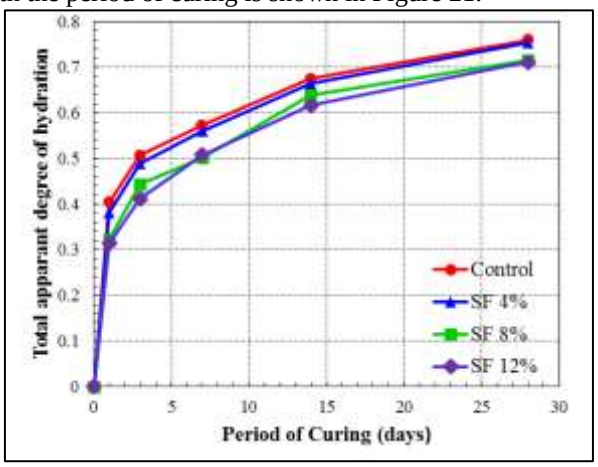


Fig. 21: Degree of hydration of pastes containing silica fume at different replacement levels

As the figure shows, the $(\boldsymbol{\alpha_T})_{\boldsymbol{app}}$ for the control paste is the highest and decreases with increase in the replacement level of silica fume. Such a behavior is observed at all curing periods and is also reported in other literatures [44, 45].

III. Conclusion

From the experimental results and the development of mathematical equations for understanding the hydration behavior of Portland cement systems containing silica fume, the following conclusions are drawn.

1) The addition of silica fume at all replacement levels depletes the $Ca(OH)_2$ produced from cement hydration and forms C-S-H gel (pozzolanic reaction) and this reaction starts as early as 1 day. The replacement of silica fume for cement results in dilution effect (due to reduction of cement content) and pozzolanic effect (due to pozzolanic reaction). The extent of $Ca(OH)_2$ depletion is higher at early-curing periods than at later-curing periods, excluding the dilution effect.
2) The non-evaporable water content of pastes decreases with increase in replacement level of silica fume at all curing periods, with the reduction being more prominent for the 8% and 12%replacement levels than for the 4% replacement level. The hydration behavior of pastes was better explained from hydrate water content data.
3) The addition of silica fume initially retards the retards the cement hydration for some period, beyond which a definite enhancement in cement hydration was observed. The retardation in cement hydration is higher at higher replacement levels of silica fume
4) The total apparent degree of hydration is the highest for plain cement paste and decreases with increase in the replacement level of silica fume.
5) The degree of pozzolanic reaction decreases with increase in the replacement level of silica fume. The quantity of silica fume that has fully reacted is about 3.92% to 5.4% of the total added and its reminder remains in the system and takes part in pore filling process.
6) The calculated porosity of pastes containing silica fume show lower porosity than for the control paste at equal degrees of hydration and the porosity values decrease with increase in the replacement level of silica fume
7) The strength of mortars containing 4% and 8% replacement level of silica fume showed higher strength than the control mortars. However, SF-12% mortars registered lower strength than the control mortars due to lower amounts of primary C-S-H gel in the former and limited quantity of silica fume particles to actively participate in pozzolanic reaction
8) Crystalline products such as $Ca(OH)_2$,ettringite,alite,belite, C_4AF, quartz and gypsum, with some traces of monosulfates were observed in both control and silica fume pastes. The progress of hydration is indicated indirectly by the diminishing of alite and belite slowly from the pastes at later curing periods.

9) The effect of variation observable with the combinations - control and SF-4% paste, and SF-8% and SF-12% are merely due to the dosage of silica fume.
10) A significant variation in different hydration parameters were observed for the combination - SF-4% and SF-8% .Therefore, the effect of this variation are not only due to the replacement level of silica fume but also because of different mechanisms associated with these replacement levels.

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