An Integrated Approach for understanding hydration behavior in Portland Cement Systems containing Silica Fume-A Review

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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.

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].
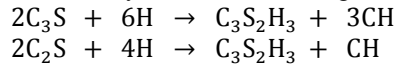
In the 1970s, several studies were carried out to understand the structure and properties of different hydration products such as C-S-H gel and others. Specifically, Feldman and Sereda postulated a layered structure of C-S-H gels, with water bonded between the layers of gels and some water adsorbed on 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.

## 1.2 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:

(i)   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:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad --- (1)$$
$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad --- (2)$$

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.

(ii)   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:

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \qquad --- (3)$$
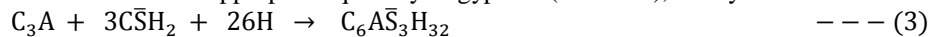
If there are excess quantity of C3A based on aluminate to sulfate ratio (which will be the usual case), the C6AS3H32 converts to C6ASH18 and the reactions are as follows:

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12} \qquad --- (4)$$
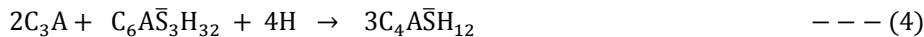
The hydration of C4AF is similar to that of C3A, with the exception that the reactions are much slower with less heat evolution and the products contain alumino-ferrous hydrates instead of mere aluminate hydrates as in the case of C3A.

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.
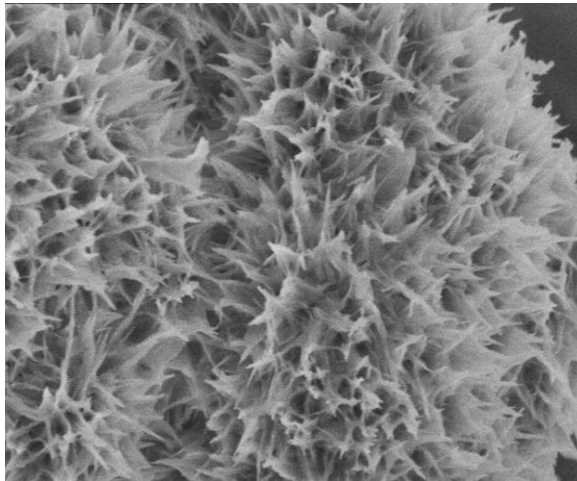

(i) C-S-H gel: constitutes 50-60% of solid volume of solids in hydrated cement paste. It has generally been attributed with a layered chain structure with short-range crystallinity
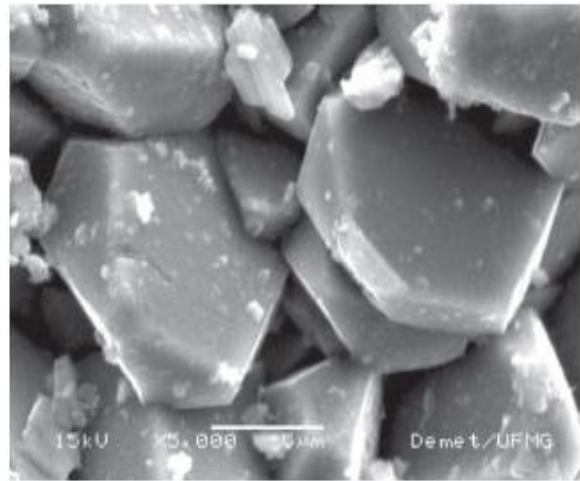
(ii) Calcium hydroxide (CH): constitutes 20-25% of the solid volume in hydrated paste. It forms large crystals with distinctive hexagonal-prism morphology
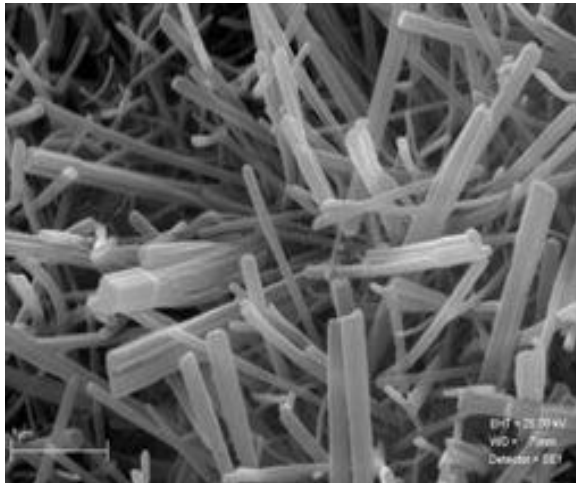
(iii) Ettringite (needle-shaped prismatic crystals)
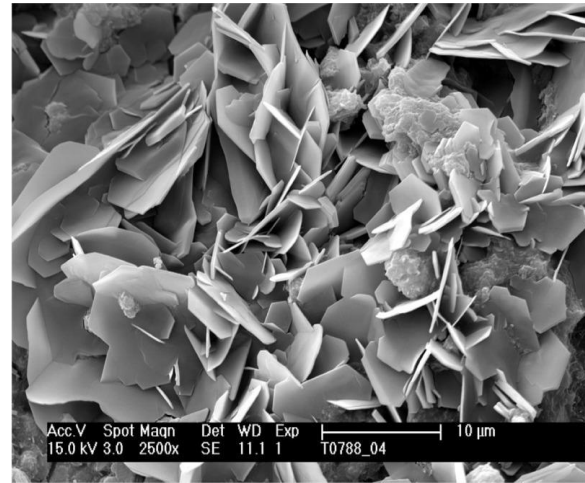
(iv) Monosulfoaluminate (hexagonal-plate crystals)

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

II.   LITERATURE REVIEW

Pommersheim et al. 1982 proposed a mathematical equation to model cement hydration using many of the features of the Kondo's single particle model [23]. The cement hydration kinetics

$$\frac{d\alpha}{dt} = \frac{C_o D_i / a R^2 \rho}{y^2 \left[\left(\frac{D_i}{kRy^2} + \frac{1}{y} - 1 \right) + \frac{D_i x}{D_x R} + \frac{D_i}{D_0} \left(1 - \frac{R}{r_0} \right) \right]}$$

where α is the degree of hydration, ρ is the density of cement, C_0 is the concentration of water, 'a' is a stoichiometric coefficient, k is the reaction rate constant, x is the thickness of metastable layer, y is the ratio of the radius of unhydrated cement grain (r_0) at any given time to the original radius of cement grain (R), D_i, D_o and D_x are the diffusivities for the inner, outer and metastable layer, respectively.

The advantage of this model is that it explicitly accounts for the growing inner and outer hydration products and considers diffusion across all three layers (inner, outer and metastable). Two limitations of Pommersheim model are that it does

was approximated to a time-dependent diffusion equation in spherical coordinates, solved for pseudo-steady-state conditions applying appropriate boundary conditions and is shown below.

$$- - - (8)$$

not account for particle-particle interaction or space filling considerations of the cement paste, and neglects the wide range of particle size of cement.

Tomosawa 1997 proposed a modified version of the earlier proposed single-particle model in which adjustments to account for global microstructural properties such as particle fineness and w/c was made [33]. The model is expressed as a single equation composed of four rate determining coefficients, which determine the rate of formation and destruction of initial impermeable layer. The activated chemical reaction process and the following relent diffusion controlled process are shown below.

$$\frac{d\alpha}{dt} = \frac{C_w \rho_w / (w/c) \rho_c \, r_t^2}{\left[\frac{1}{k_d r_t^2} + \frac{1/r_t - 1/R_t}{D_e} + \frac{1}{k_r r_t^2} \right]} \qquad - - - (9)$$

where r_t is the radius of an unhydrated cement particle, R_t is the total radius of cement particle including the gel layer, D_e is the effective diffusion coefficient of water in the cement gel, k_r is the coefficient of reaction rate per unit area at reaction front, k_d is the coefficient of resistance by protective layer at dormant period, ρ_c and ρ_w is the density of cement and water, respectively, and C_w is

the volumetric density of water in cement paste matrix.

Although, Tomosawa's model provides excellent predictions of degree of hydration, it has limited sphere of applicability due to its empirical nature.

Garrault and Nonat 2001 proposed a modified nucleation and growth model in which the

growth of nuclei in both perpendicular and parallel directions to the surface of cement grain is considered [34]. Experimental data closely fitted for cases where the perpendicular growth rate is assumed to be higher than for the parallel growth rate case. The drawback of this model is that the effect of inter-particle interaction is not considered when considering the growth of nuclei explicitly.

Li et al. 1996 reported that cement hydration is enhanced by silica fume addition at w/c above 0.30 due to filler effect, i.e., silica fume particles bridge the gap between cement grains and do not allow excess water to bleed out from the fresh paste, which increases the effective water available for cement hydration [35].Some particles also suspend in capillary water and act as nucleation sites for hydration products to grow and fill capillary voids, causing further enhancement of cement hydration.

Greenberg 1961andTakemoto and Uchikawa 1980 proposed a mechanism involving physiochemical process for the pozzolanic reaction between silica fume and $Ca(OH)_2$ [36, 37]. Accordingly, $Ca(OH)_2$ produced by cement hydration at early periods gets adsorbed on the surface of silica fume and leads to an increase in the coordination number of Si atom, thereby weakening the oxygen bonds of the underlying silicon atoms. This increases the pH of the solution, creates more Si atoms to go into solution as silicate ions and explains the high degree of pozzolanic reaction observed at early ages. In addition, the dissolution of silica depends on the size of silica fume particles and of solution. As pozzolanic reaction progresses, more particles react with $Ca(OH)_2$to form C-S-H gel, reducing the pH of solution and dissolution of silica at later ages. Further, the C-S-H gel produced encloses the silica fume particles preventing it from further dissolution. Thus, $Ca(OH)_2$depletion drastically reduces at later curing periods and pozzolanic reaction becomes diffusion-controlled. In another study, Wild et al.1995 has also observed pozzolanic reaction becoming 'diffusion-controlled 'and found that this reaction rate decreases with time in a parabolic manner. Such a trend was probably due to the development of a diffusion-inhibiting layer of reaction products around silica fume particles.

In some studies, significant improvement in mortar strength was observed with increase in silica fume dosage levels. For example, Li et al. 1996 observed that strength enhancement obtained for silica fume mixtures was more prominent at w/c above 0.30 and at early curing periods [35]. In addition, silica fume mixtures registered lower compressive strength compared to control at all curing periods for w/cm <0.24. In another study, Qing et al. 2005 proposed that nano-silica should be used in the place of silica fume to attain higher compressive strengths at w/c < 0.22 [38]. For the same dosage levels, the study also showed better bond strengths of paste-aggregate interface and higher pozzolanic reactivity for the nano-silica modified mortars than for the silica fume modified mortars.

Several studies were performed to comprehend the hydration of cement systems containing fly ash [39, 40, 41, 42, 43]. Some important inferences are as follows: (i) The presence of fly ash particles in cement system augments hydration due to the replacement of cement by fly ash, which increases the w/c significantly and the fly ash particles act as lubricating agents, thus providing precipitation sites for hydration products. (ii) The pozzolanic reactivity of fly ash is influenced by the glass content and its chemical composition. While some research has reported that fly ash starts reacting just after 3 days of curing of the cementitous paste, some others have found that fly ash starts reacting only after 7 or 14 days. Unlike silica fume, fly ash shows wide variation in chemical composition based on its source and has low reactivity due to higher amounts of crystalline compounds. Its addition lowers the heat of hydration of cement substantially.

Some other studies were conducted to compare the effects of adding silica fume and other pozzolans in cement systems. For example, Pane and Hansen 2003 compared hydration process of systems containing fly ash, slag and silica fume [44]. At early curing periods, the degree of pozzolanic reaction was highest for silica fume followed by slag and fly ash. However at later curing periods, the degree of pozzolanic reaction showed similar values for all pozzolans. Similarly, the degree of hydration of cement was lowest for slag, followed by silica fume and then fly ash. In another study performed by Neithalath et al. 2009, the hydration behavior in cementitious systems containing silica fume and vitreous calcium aluminosilicate (VCAS) was studied [45]. Silica fume showed higher reactivity as compared to VCAS but the degree of hydration of silica fume modified pastes was lower than that of VCAS modified pastes at later curing periods.

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