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Microanalysis and optimization-based estimation of C–S–H contents of cementitious systems containing fly ash and silica fume

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ABSTRACT

In this study, a new approach to characterize hardened pastes of pure portland cement as well as those containing cement with supplementary cementitious materials (SCM) was adopted using scanning electron microscopy (SEM) and energy dispersive X-ray spectra (EDS) microanalyses. The volume stoichiometry of the hydration reactions was used to estimate the quantities of the primary and secondary calcium silicate hydrate (C–S–H) and the calcium hydroxide produced by these reactions. The 3D plots of Si/Ca, Al/Ca and S/Ca atom ratios given by the microanalyses were compared with the estimated quantities of C–S–H to successfully determine the Ca/Si ratio of eleven different cementitious systems at four different ages using a constrained nonlinear least squares optimization formulation by General Algebraic Modeling System (GAMS). The estimated mass fraction of calcium hydroxide from the above method agreed well with the calcium hydroxide content determined from the thermogravimetric analyses (TGA).

1. Introduction

High-performance cementitious materials are increasingly used as a major construction material for new construction, repair, and rehabilitations of building and civil infrastructure. The supplementary cementitious materials (SCM) such as fly ash, slag, and silica fume are commonly used for producing high performance cementitious materials to reduce the emission of CO_2 into the atmosphere, construct durable structures, and divert industrial by-products from landfills. The calcium silicate hydrate (C–S–H) is regarded as the principal and most complex component in the cementitious systems. The inclusions of SCM further complicate the matter by forming C–S–H having two different Ca/Si ratios [1,2]. A better understanding of the cement hydration and the formation of C–S–H with different Ca/Si ratios for pastes with or without SCM is extremely important to understand cementitious systems from micro to macro level in order to establish the structure–property relations. Several initial studies by pioneers such as Pommerscheim and Clifton [3], Powers and Brownyard [4], Knudsen [5], and Tennis and Jennings [6]were mostly concerned with portland cement pastes only. Later on, researchers became more interested with the influence of the microstructure of the cementitious pastes containing both portland cement and SCM. The researchers at National Institute of Standards and Technology (NIST) systematically considered cementitious systems containing SCM like fly ash, silica fume, and slag using Virtual Cement and Concrete Testing Laboratory (VCCTL) [7,8] as the numerical modeling software. Also, Maekawa et al. [9,10] studied the behavior of portland cements having various compositions at micro, meso and macro levels. They used the DuCOM software platform to predict the values for the different parameters and compared with the experimental data to validate the model.

The first step towards characterizing a cementitious system containing SCM requires distinguishing between the primary and the secondary C–S–H formed upon hydration of those cementitious pastes. In case of portland cement added with SCM, the hydration of the calcium silicates produces the primary C–S–H. The calcium hydroxide from the original hydration product further reacts with the pozzolanic silica present in the SCM to form secondary C–S–H. In this paper, the primary and secondary C–S–H will be denoted as C–S–H(P) and C–S–H(S), respectively. The two types of C–S–H have different chemical configurations and relative volumes depending on many factors. However, they can be distinguished by their different Ca/Si ratios [1]; although the ratio is variable depending on the types of portland cements and SCM used. In recent times, a popular method of analysis of C–S–H of hydrated portland cement paste involves microanalysis studies by scanning electron microscope (SEM) and energy dispersive X-ray spectra (EDS). Although this approach has been followed by various researchers including the recent works by Wong [11] and Gallucci et al. [12], there is no systematic study to perform the quantitative estimation of

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Table 1
Properties of the materials used.

Materials	Portland cement[*]	Silica fume	Fly ash
Specific gravity	3.15	2.18	2.47
Specific surface (m^2/kg)	320 (Blaine)	21,400 (nitrogen absorption)	490 (Blaine)
Loss on ignition (%)	1.2	1.28	3.00
SiO_2 (%)	20.7	98	49.34
Al_2O_3 (%)	5.5	–	22.73
CaO (%)	63.6	–	3.09
MgO (%)	0.9	–	1.06
SO_3 (%)	2.7	0.15	0.97
$Na_2O + 0.685\ K_2O$ (%)	0.5	0.57	2.75
Fe_2O_3 (%)	3.6	–	16.01
Others (%)	1.3	–	1.05

[*] The initial and final setting times for the portland cement are 90 min and 260 min, respectively.

C–S–H of cementitious pastes containing SCM due to the complexities involved in this method. Also, Beaudoin et al. [13] conducted studies at the nanostructure level to describe C–S–H on the basis of its Ca/Si ratio using adsorption of methylene blue.

This paper undertakes a novel approach to combine the microanalysis results with statistical optimization, to provide fairly accurate quantitative characterization for cementitious systems containing SCM. For our study, microanalysis was carried out on cementitious samples having different proportions of portland cement, fly ash and silica fume, using SEM and EDS. Microanalysis results were plotted on 3D axes based on a concept previously used by Famy et al. [14]. Subsequently, the results obtained from the 3D plots were compared with the theoretical results obtained from a constrained nonlinear optimization model coded using the General Algebraic Modeling System (GAMS).

2. Materials and testing methods

2.1. Materials

A commercially available Type I portland cement conforming to ASTM C 150 (Standard Specification for Portland Cement) was used in this study. The oxide compositions and physical properties are provided in Table 1. The Bogue's composition of portland cement is provided in Table 2. Two types of SCM were used as follows: (1) Class F fly ash conforming to ASTM C 618 (Standard Specification for Coal Fly Ash and Raw Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete) and (2) Silica fume conforming to AASHTO M 307/ASTM C 1240 (Standard Specification for Silica Fume for Use in Hydraulic-Cement Concrete and Mortar). The Class F fly ash was obtained from a local coal power plant and the silica fume used in this study was a commercially available product. The specific gravity, specific surface area and oxide composition of both fly ash and silica fume are listed in Table 1.

2.2. Sample preparations and testing

2.2.1. Mix proportions

The mix proportions were selected so as to compare their influences on the microstructural properties of the cementitious systems for different combinations of portland cement with SCM at different water to cementitious materials ratio (w/cm) as well as at different ages. A total of eleven mixes were produced as follows: (1) Three pure portland cement mixes with w/cm of 0.3, 0.4, and 0.5, respectively; (2) Portland cement mixes with 25% fly ash and 35% fly ash replacement, respectively by weight of portland cement with w/cm of 0.3 and 0.4 for each case; (3) Portland cement with 10% silica fume replacement of portland cement by weight with w/cm of both 0.3 and 0.4; and (4) Portland cement with 25% fly ash and 10% silica fume replacement by weight of portland cement for w/cm of both 0.3 and 0.4. The specimens were studied at ages of 1 day, 7 days, 28 days, and 90 days for all the mixes. The average room temperature was 23 ± 2 °C and the heat transfer conditions were adiabatic. The mixes are shown in Table 3.

Table 2
Bogue's composition of the portland cement.

Compounds	Compound formula	% by mass	% by volume[*]
Tricalcium silicate	C_3S	49.0	50.55
Dicalcium silicate	C_2S	25.0	25.24
Tricalcium aluminate	C_3A	12.0	13.11
Tetracalciumaluminoferrite	C_4AF	8.0	7.10
Gypsum	CSH_2	2.8	3.99
Free lime	CaO	0.8	0.01
Free magnesia	MgO	1.4	0.01
Others	–	2.0	–

[*] Volume fractions were calculated based on density values provided in Table 4.

2.2.2. SEM and EDS microanalysis studies

After adequate hand mixing (portland cement and SCM were always pre-mixed) with small quantity at a time, the samples for the SEM and microanalysis by EDS were cast in cylindrical plastic moulds having 10 mm diameter and 25 mm in height. A cylindrical disc of approximately 3 mm thickness and 10 mm in diameter was then cut out from the central portion of each specimen using a hand-held diamond cutting machine manufactured by Dremel Inc. The samples were then polished using TegraPol-31 polisher with diamond paste and different piano sizes to make it about

Table 3
Details of mix proportions (by weight).

Mixes	w/cm[*]	Cement (%)	Fly ash (%)	Silica fume (%)
100% Portland cement	0.3, 0.4, 0.5	100	–	–
25% Fly ash	0.3, 0.4	75	25	–
35% Fly ash	0.3, 0.4	65	35	–
10% Silica fume	0.3, 0.4	90	–	10
25% Fly ash, 10% silica fume	0.3, 0.4	65	25	10

[*] For 100% portland cement, the w/cm will be w/c (water to cement ratio).

2 mm thick and enough smooth surface for EDS. The samples were stored in 99.8% laboratory grade methanol in air-tight vial until the SEM studies were conducted to stop the continued hydration at respective ages. Before SEM and microanalysis, the specimens were allowed to dry at 50% humidity and 40 °C for 48 h in an environmental chamber to reduce the time of vacuum. Then they were coated with a 15 nm layer of platinum in argon gas atmosphere at a high vacuum of 5.0×10^{-6} Torrs, in order to make them electrically conductive in nature. A state-of-the-art thermal Field Emission Scanning Electron Microscope (FE-SEM), JSM-7600F (accompanied by an EDS analyzer), supplied by JEOL Limited was used for the imaging process. The JSM-7600F incorporates a large specimen chamber which can accommodate specimen stages containing multiple samples at a time. The operating voltage was 15 kV and the current at the surface of the specimen was 65.4–67.0 µA. The images were captured at a vacuum of 9.6×10^{-5} Pa. in two different magnifications of 2200× and 5000×, respectively for each specimen. For each specimen, nine locations were studied for microanalysis. Five points were randomly selected for each location to obtain representative data. This leads to a total of 2 magnifications × 9 locations × 5 points = 90 data for each sample. These 90 data points were analyzed for each of the eleven different mixes at every age (1, 7, 28, and 90 days). The points for microanalysis were chosen randomly to minimize the influence of the microstructural heterogeneity of the cementitious system.

EDS spectra were acquired with the help of the INCA systems software that is used by the Oxford spectrometer. The working distance was maintained at 15 mm and the probe current 8 (65.4–67.0 µA) in order for the EDS analyzer to work properly. As a typical example for a given mix and 2200× magnification, Fig. 1 shows how points on each location are selected for the microanalysis. A similar procedure was followed for the other cases. Fig. 2 furnishes the corresponding EDS of the typical example.

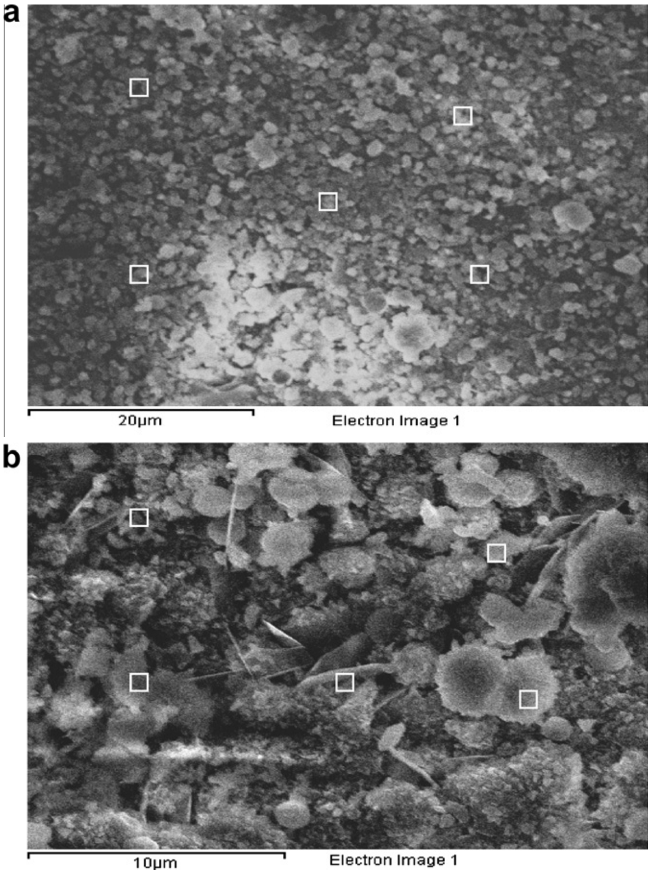


Fig. 1. Typical EDS images of 28-day 100% portland cement specimen with w/c 0.4. (a) 2200× magnification; (b) 5000× magnification. *Note*: For each sample, nine locations were studied for each of the two magnifications. For each location, five points were randomly selected for analysis leading to 9 × 2 × 5 = 90 data points for each sample. The white boxes indicate the points chosen at each location.

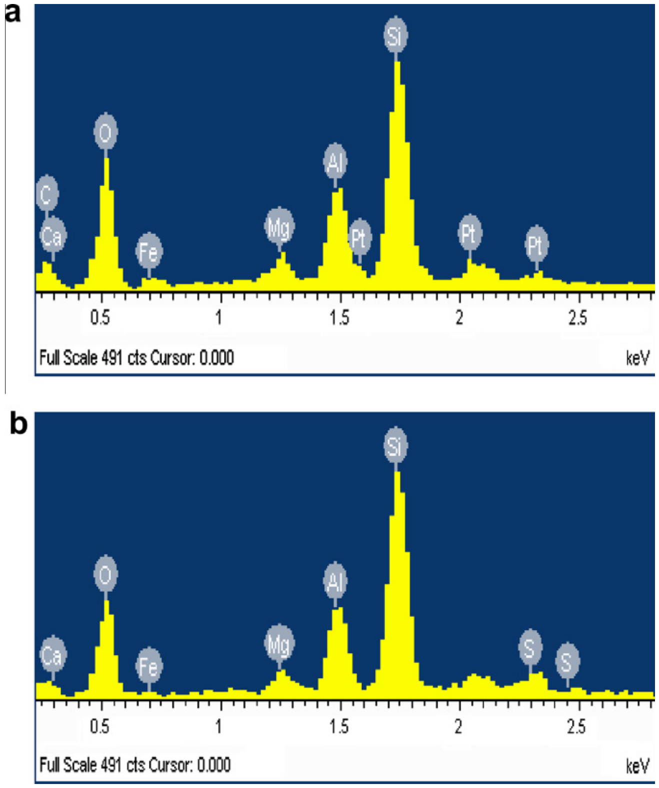


Fig. 2. Typical energy dispersive X-ray spectra (EDS) of 28-day 100% portland cement specimen with w/cm 0.4. (a) 2200×; (b) 5000× magnification. *Note*: For each sample, nine locations were studied for each of the two magnifications. For each location, five points were randomly selected for analysis leading to 9 × 2 × 5 = 90 data points for each sample.

2.2.3. TGA and isothermal calorimetry studies

The thermogravimetric analysis (TGA) tests were conducted using a proximate analyzer called LECO 701 with 180–850 mg of powdered cementitious samples passing through 75 µm sieve. Replicate samples were studied for each specimen at each age. The TGA was carried out between 20 °C and 950 °C in air with the rate of heating at 10 °C per minute to determine the degree of hydration of the hardened paste at a given age and to estimate the mass fraction of calcium hydroxide (CH) in the hardened paste. The calorimetry tests were carried out on eleven cementitious pastes per ASTM C 1679-08 (Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry). The calorimeter used was the TAM-Air model manufactured by TA Instruments. The sealed ampoule arrangement was followed for our studies and the data were collected using the TAM Assistant software. The calorimetry test was conducted to evaluate the rate of hydration.

3. Analysis of test data using volume stoichiometry and statistical optimization

3.1. Volume stoichiometry to estimate C–S–H(P), C–S–H(S) and CH

The concept of the portland cement hydration model, originally developed in two dimensions by the researchers at NIST and later extended to three dimensions, is used as the basis of the equations here to estimate the quantities of the hydration products. They used a value of 1.7 [2] for the atomic ratio (which is also the molar ratio) of calcium to silicon (Ca/Si) present in C–S–H(P), which was accurate enough for the portland cement they used. As the portland cement used in this study was from a different source, a Ca/Si ratio with unknown value of '*n*' was assumed. Statistical optimization techniques were implemented on the microanalysis results and the estimated quantities of hydrated products to determine '*n*'. Since this approach to analyze the volume stoichiometry results through statistical optimization was not attempted in the past, the present study thus deals with a new approach on how to use the stoichiometry equations and obtain optimized results for the volumes of the products of hydration of cementitious pastes.

3.1.1. Hydration reactions for pure portland cement

The hydration process of the pure portland cement is composed of two steps-(a) silicate hydration and (b) aluminate and ferrite hydrations. The reactions involved are:

Silicate reactions:

$$C_3S + (7-n)H \rightarrow C_nSH_4 + (3-n)CH \tag{1}$$

$$C_2S + (6-n)H \rightarrow C_nSH_4 + (2-n)CH \tag{2}$$

Aluminate and ferrite reactions:

$$C_3A + 6H \rightarrow C_3AH_6\ \text{(hydrogarnet formation)} \tag{3}$$

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_32\ \text{(AFt phase)} \tag{4}$$

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4(A\bar{S}H_{12}\ \text{(AFm phase)} \tag{5}$$

$$C_4AF + 3C\bar{S}H_2 + 30H \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \tag{6}$$

$$2C_4AF + C_6A\bar{S}_3H_{32} + 12H \rightarrow 3C_4A\bar{S}H_{12} + 2CH + 2FH_3 \tag{7}$$

$$C_4AF + 10F \rightarrow C_3AH_6 + CH + FH_3 \tag{8}$$

The set of equations furnished above shows the formation of the products of portland cement hydration.

3.1.2. Hydration of portland cement blended with fly ash and silica fume

The silica present in the SCM (fly ash or silica fume) reacts with the CH produced from the hydration of the pure portland cement to form C–S–H(S), at a reaction rate different from that of primary hydration. The Ca/Si ratio in C–S–H(S) is assumed to be n'. Then, the balanced chemical equation for the hydration of the portland cement with SCM can be written as:

$$n'CH + SiO_2 + (3.9 - n')H = C_{n'}SH_{3.9} \tag{9}$$

The chemical formula for C–S–H(S) is modified from the one proposed by the researchers at NIST. This is due to the fact that the Si/Ca atomic ratio varies in portland cements when the source is changed.

The volume stoichiometries for the hydration reactions for both pure portland cement and portland cements with SCM have been provided by the researchers at NIST [2]. These are based on the molar stoichiometries of the compounds. These molar volumes were used for all our calculations. A 100 mL basis was assumed for the portland cement paste and the volumes of all the hydrated paste. Each individual hydrated product and the total paste volume at any instant of time was calculated as a function of 'n' and the degree of hydration, α.

3.2. Estimation of quantities of C–S–H(P), C–S–H(S) and CH

3.2.1. Estimation of C–S–H(P) for pure portland cement

Using Eq. (1) and the specific gravity values given in Table 4 [2], it is found that 1 volume of C_3S produces 1.521 volume of C–S–H(P) upon full hydration. From Table 2, the100 mL of pure portland cement used in this study contains 50.6 mL of C_3S. So, 50.6 mL of C_3S contributes:

Table 4
Densities and molar volumes of cementitious materials [2].

Compounds	Compound formula	Density ($g\ cm^{-3}$)	Molar volume ($cm^3\ mol^{-1}$)
Tricalcium silicate	C_3S	3.21	71
Dicalcium silicate	C_2S	3.28	52.4
Tricalcium aluminate	C_3A	3.03	89.1
Tetracalciumaluminoferrite	C_4AF	3.73	128
Gypsum	CSH_2	2.32	74.2
Calcium silicate hydrate	C_nSH_4	1.85	124
Pozzolanic C–S–H	$C_{n'}SH_{3.9}$	1.69	81
Calcium hydroxide	CH	2.24	33.1
Ettringite	$C_6AS_3H_{32}$	1.75	715
Monosulfate	C_4ASH_{12}	1.99	313
Hydrogarnet	C_3AH_6	2.52	150
Iron hydroxide	FH_3	2.2	95.2
Pozzolanic silica	S	2.2	27

$$50.6 \times \frac{(56.08n + 132.14)/1.85}{228/3.21} \tag{10}$$

mL of C–S–H(P) per 100 mL of the unreacted portland cement.

So, at any instant of time, *t* or any degree of hydration, α, the total volume of C–S–H(P) due to C_3S and C_2S hydration, $V_{C-S-H(P)}$ is given by:

$$V_{C-S-H(P)} = \propto \times (21.6n + 50.9) \tag{11}$$

mL per 100 mL of the unreacted portland cement.

From the heat evolution vs. time plot obtained from isothermal calorimetric study, it is evident that the peaks of mixes with low w/cm appeared later and they had lower magnitude compared to the higher w/cm mixes (the figures are not shown here for brevity). Therefore, for low w/cm, the rate of hydration, $d\alpha/dt$, has been reduced by a factor, *f*(w/cm) to account for the slow progress of the reaction. From the works of Parrot and Killoh [15] the following relationship is obtained:

$$f(\text{w/cm}) = [1 + 4.444(\text{w/c}) - 3.333\alpha]^4 \tag{12}$$

The degree of hydration, α' for the low w/cm cases is subsequently expressed as

$$\alpha_1 = A^* t^* [1 + 4.444(\text{w/cm}) - 3.333\alpha]^4 \tag{13}$$

where *t* denotes the age of the hydrated paste (in days) and $A = 286.51\alpha^3 - 352.82\alpha^2 + 142.38\alpha - 18.604$.

So, the resulting volume of C–S–H becomes:

$$V_{C-S-H(P)} = \alpha_1 \times (21.6n + 50.9). \tag{14}$$

The volumes of the other hydrated products were calculated in a similar manner and are provided in Table 5.

The total volume of the hydrated paste at any degree of hydration is given by:

$$V_{hcp} = \propto \times (153.2 + 45.998\gamma_{AF} - 17.8n) \tag{15a}$$

mL per 100 mL of the unreacted portland cement.

Table 5
Volume of hydrated phases at full hydration (per 100 mL of hydrating cementitious paste).

Compounds	Compound formula	Volume (in mL)
Calcium silicate hydrate	C_nSH_4	$21.6n + 50.9$
Calcium hydroxide	CH	$102.3 - 39.4n + 1.753\gamma_{AF}$
Ettringite	$C_6AS_3H_{32}$	$12.12\gamma_{AF}$
Monosulfate	C_4ASH_{12}	$16.88\gamma_{AF}$
Hydrogarnet	C_3AH_6	23.69
Iron hydroxide	FH_3	3.68

For the low w/cm cases, the expression is modified and written as:

$$V_{hcp} = \alpha_1 \times (153.2 + 45.998\gamma_{AF} - 17.8n) \tag{15b}$$

mL per 100 mL of the unreacted portland cement.

The factor γ_{AF} accounts for the hydration of the aluminates and the aluminoferrites which occur at a rate that is different from the rate of the silicate hydration. This difference in hydration rates has a significant influence on the total volume of hydrated paste that is produced at any stage of the hydration of the cementitious paste. The magnitude of γ_{AF} is computed by solving a set of simultaneous equations using optimization, as explained in Section 4, Eq. (34).

The corresponding unhydrated fraction of portland cement paste is given by $100^*(1 - \alpha')$ mL per unit volume of the unreacted portland cement.

Thus, the volume of C–S–H(P) expressed as a fraction of the total portland cement paste volume at any degree of hydration α is given by:

$$v_{\mathrm{C-S-H(P)}} = V_{\mathrm{C-S-H(P)}}/[V_{hcp} + 100(1 - \alpha)] \text{ for normal w/cm} \tag{16a}$$

and

$$v_{\mathrm{C-S-H(P)}} = V_{\mathrm{C-S-H(P)}}/[V_{hcp} + 100(1 - \alpha_1)] \text{ for low w/cm cases} \tag{16b}$$

3.2.2. Estimation of C–S–H(P) and C–S–H(S) for portland cement with SCM

3.2.2.1. P% portland cement containing Q% fly ash or silica fume as SCM. Using the previous approach, the volume of C–S–H(P) produced by the blend containing *P*% of portland cement is:

$$V'_{\mathrm{C-S-H(P)}} = \frac{P}{100} \times V_{\mathrm{C-S-H(P)}} \tag{17}$$

mL per 100 mL of the unreacted portland cement with SCM.

Using Eq. (9) and the specific gravity values given in Table 4 [2], it is found that the volume of C–S–H(S) is given by:

$$V_{\mathrm{C-S-H(S)}} = \frac{sQ\alpha'}{100} \times (1.215n' + 2.821)/2.2 \tag{18}$$

mL per 100 mL of the unreacted portland cement containing *Q*% of fly ash or silica fume as SCM.

Here, α' denotes the degree of reaction of the pozzolanic SiO_2 with the CH from the portland cement hydration. Here, s_f and s_s denotes the silica content of the SCM or pozzolan used. The list of values for the degree of reaction of the pozzolanic materials at different ages has been given in Table 6 [16].

The total volume of the hydrated paste in case of the portland cement with SCM can be computed similarly to those computed for pure portland cement. This leads to:

$$V'_{hcp} = \left[\frac{P\alpha}{100} \times (153.2 + 45.998\gamma_{AF} - 17.8n) + \frac{sQ\alpha'}{220} \times (0.005n' + 2.821)\right] \tag{19}$$

mL per 100 mL of the unreacted portland cement with SCM.

Table 6
Degree of reaction of fly ash and silica fume [16].

Cement type	Age 1 day	7 days	28 days	180 days
Fly ash cement	0.01–0.02	0.02–0.05	0.05–0.10	0.15–0.20
Silica fume cement	0.35–0.60	0.80–0.90	>0.90	≈0.98

The volume of the unhydrated paste in case of portland cement with SCM at any instant of time is given by:

$$V'_{\mathrm{unhyd}} = P^*(1 - \alpha) + Q^*(1 - \alpha') \tag{20}$$

mL per 100 mL of the unreacted portland cement with SCM.

The total volume of the paste for portland cement with SCM at any instant of time is given by:

$$V_{\text{paste with SCM}} = V'_{hcp} + V'_{\mathrm{unhyd}} \tag{21}$$

Thus, the volume of C–S–H(S) expressed as a fraction of the total portland cement paste volume at any degree of hydration α is given by:

$$v_{\mathrm{C-S-H(S)}} = V_{\mathrm{C-S-H(S)}}/V_{\text{paste with SCM}} \tag{22}$$

In all the above cases, the degree of hydration, α for pure portland cement must be replaced by α' for the low w/cm cases.

3.2.2.2. P% portland cement containing Q% fly ash and R% silica fume as SCM. Similarly, the volume of C–S–H(P) produced by the blend containing *P*% of portland cement is given by:

$$V'_{\mathrm{C-S-H(P)}} = \frac{P}{100} \times V_{\mathrm{C-S-H(P)}} \tag{23}$$

mL per 100 mL of the unreacted portland cement with SCM.

Let us consider unit weight of fly ash and silica fume to contain 's_f%' and 's_s%' by weight of SiO_2 respectively. Then, the volume of C–S–H(S) is:

$$V_{\mathrm{C-S-H(S)}} = \frac{(s_f Q\alpha' + s_s R\alpha'')}{100} \times (1.215n' + 2.821)/2.2 \tag{24}$$

mL per 100 mL of the unreacted portland cement containing *Q*% of fly ash or silica fume as SCM.

Here, α' and α'' denote the degrees of reaction of the pozzolanic SiO_2 present in fly ash and silica fume respectively, with the CH from the portland cement hydration. Here, s_f and s_s denote the silica content of the fly ash and the silica fume, respectively. The list of values for the degree of reaction of the pozzolanic materials at different ages has been given in Table 6 [16].

The total volume of the hydrated paste in case of the portland cement with SCM can be computed similarly as performed in case of pure portland cement. The equation is furnished as follows:

$$V'_{hcp} = \left[\frac{P\alpha}{100} \times (153.2 + 45.998\gamma_{AF} - 17.8n) + \frac{(s_f Q\alpha' + s_s R\alpha'')}{220} \times (0.005n' + 2.821)\right] \tag{25}$$

mL per 100 mL of the unreacted portland cement with SCM.

The volume of the unhydrated paste for portland cement with SCM at any instant of time is given by $V'_{\mathrm{unhyd}} = P^*(1 - \alpha) + Q^*(1 - \alpha') + R^*(1 - \alpha'')$ mL per 100 mL of the unreacted portland cement with SCM.

The total volume of the paste for portland cement with SCM at any instant of time is given by:

$$V_{\text{paste with SCM}} = V'_{hcp} + V'_{\mathrm{unhyd}} \tag{26}$$

Thus, the volume of C–S–H(S) expressed as a fraction of the total portland cement paste volume at any degree of hydration α is given by:

$$v_{\mathrm{C-S-H(S)}} = V_{\mathrm{C-S-H(S)}}/V_{\text{paste with SCM}} \tag{27}$$

Again, α must be replaced by α_1 for all the low w/cm cases.

3.2.3. Estimation of CH for pure portland cement

The volume of CH present in the portland cement paste at any instant of time is composed of the CH produced by the hydration of the silicates as well as those from the aluminoferrites. A similar technique is followed to the one that applied during the estimation of the quantity of C–S–H(P).

At full hydration, 1 volume of C_3S produces [(74*(3 − n)/2.24)/(228/3.21)] volumes of CH (using Eq. (1) and Table 5). At the same time, 1 volume of C_2S produces [(74*(2 − n)/2.24)/(172/3.28)] volumes of CH. Thus at a degree of hydration of α, the total CH produced by silicate hydration from the portland cement will be:

$$V_{\text{CH, silicate}} = \alpha^*(102.3 - 39.4n)\text{mL of CH per100mL of the unreacted portland cement paste} \tag{28}$$

Following the similar methodology, the aluminoferrites were found to produce 1.753 mL of CH per 100 mL of the unreacted paste upon full hydration.

Thus, the total volume of CH produced at any degree of hydration, α is given as:

$$V_{\text{CH}} = (104.053 - 39.4n + 1.753\gamma_{\text{AF}})^*\alpha \tag{29}$$

mL per 100 mL of the unreacted portland cement paste

The expression must incorporate the α_1 values instead of α for the low w/cm cases.

3.2.3.1. Estimation of CH for portland cement with SCM.

3.2.3.1.1. P% portland cement blended with Q% fly ash or silica fume. Following the same approach as performed above the volume of CH due to the pure portland cement is given by:

$$V'_{\text{CH}} = \frac{P}{100} \times V_{\text{CH}} \tag{30}$$

As the reaction with pozzolanic SiO_2 proceeds, the CH remaining in the cementitious system decreases.

The resultant volume of CH is then expressed as:

$$V'_{\text{CH}} = V_{\text{CH}} - sQn'\alpha'/220 \tag{31}$$

where α' denotes the degree of reaction and s stands for the silica content.

3.2.3.1.2. P% portland cement blended with Q% fly ash and R% silica fume. The volume of CH due to the pure portland cement is given by:

$$V'_{\text{CH}} = \frac{P}{100} \times V_{\text{CH}} \tag{32}$$

After the reaction with the pozzolanicSiO_2, the volume of CH remaining in the cementitious systems is given by:

$$V'_{\text{CH}} = V_{\text{CH}} - (sfQ\alpha' + s_sR\alpha'')n'/220 \tag{33}$$

In all the low w/cm cases, the values of α must be replaced by α_1.

4. Interpretation of microanalysis data using statistical optimization

4.1. Significance of microanalysis and optimization

As mentioned earlier, the cementitious pastes were observed under the SEM at two different magnifications-2200× and 5000×. EDS microanalysis was carried out on a total of 90 data points for each cementitious sample. The results obtained from the microanalysis were in terms of the atomic percentages of the different elements present in the cementitious system. The relative percentages of the aluminum, silicon and sulfur were computed with respect to the corresponding calcium atom for each of the 90 data points. They were plotted on 3D axes using Origin Pro 8.1 software (Figs. 3 and 6). The concept of 3D plot was used by Famy et al. [14] to characterize the C–S–H and its phase compositions in case of portland cement mortars through the solution of simultaneous algebraic equations. The results of the works done by previous researchers showed that for all pure portland cement pastes, the Si/Ca atom ratio lies in the range of 0.48–0.61 for the C–S–H [1]. The total number of points, for each sample, composed of Si/Ca ratio in the given range and Al/Ca and S/Ca ratios less than 0.1 were counted as representing the C–S–H component of the total paste volume. As mentioned earlier in Section 2.2.2, the SEM/EDS microanalyses were carried out at randomly chosen points to account for the heterogeneity of the microstructure of the portland cement paste. Each of the scanned areas was approximately 120 μm by 120 μm square. The C–S–H was detected from SEM morphology and features, both at early stage and later. They were present as common fibrous to irregular grains forming reticular network, depending on the age. The ratio of the number of points representing C–S–H to the total number of data points for each sample was taken as the representative volume fraction of C–S–H for each sample. This approach was somewhat similar to the point-count procedure as proposed by Feng et al. [17]. The volume fraction from SEM was compared with the results from the proposed algebraic equation and the square of the errors was minimized using optimization technique with the help of GAMS software. The optimization was done for the Ca/Si atomic ratio for each specimen in the range of 1.57–2.1. The Ca/Si ratios remain more or less consistent, irrespective of the age of the specimen, for both the inner product as well as the outer product C–S–H [1,18]. Thus, a unique ‘*n*’ value was obtained which most nearly represents the Ca/Si atomic ratio of each specimen.

Similar approach was followed to find the volume fraction of C–S–H(S) in case of portland cements with SCM. The range of Ca/Si atom ratio in C–S–H(S) in case of fly ash cements is about 1.5 to 1.6 [1]. For silica fume cements, it is about 1.1–1.4 [1,19]. Thus, from the 3D plots of the microanalysis data, the number of points at which the Si/Ca ratio lies in the range of C–S–H(S) were counted and expressed as a fraction of the total number of data points. The volume fraction of C–S–H(P) from the theoretical approach was computed using the ‘*n*’ value derived from the optimization technique. This was compared with the experimental values in case of the pastes with SCM and they showed very good agreement. The details are discussed in Section 4.2.

4.2. Optimization using GAMS

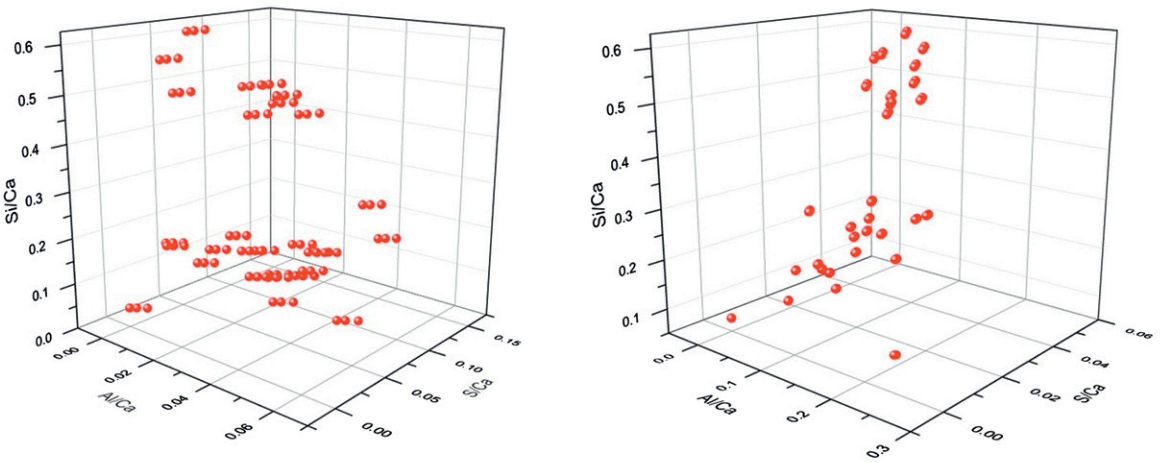
The parameters were obtained by comparing experimental values with theoretical predictions using a constrained nonlinear least squares approach. Let t denote an index for time. Note that t can take values 1,2,3 and 4 corresponding to 1 day, 7 days, 28 days and 90 days respectively. Let $v^{\text{exp},t}_{\text{C–S–H}}$ denote the experimentally determined volume fraction of C–S–H at time t, and $v^{\text{pred},t}_{\text{C–S–H}}$ denote the predicted volume fraction of C–S–H at time, t. For pure portland cement, the values of n and γ_{AF} can be determined by solving the nonlinear constrained optimization problem for the high w/cm case.

$$\min \sum_{t=1}^{4} \left(v^{\text{exp},t}_{\text{C–S–H}} - v^{\text{pred},t}_{\text{C–S–H}} \right)^2 \tag{34}$$

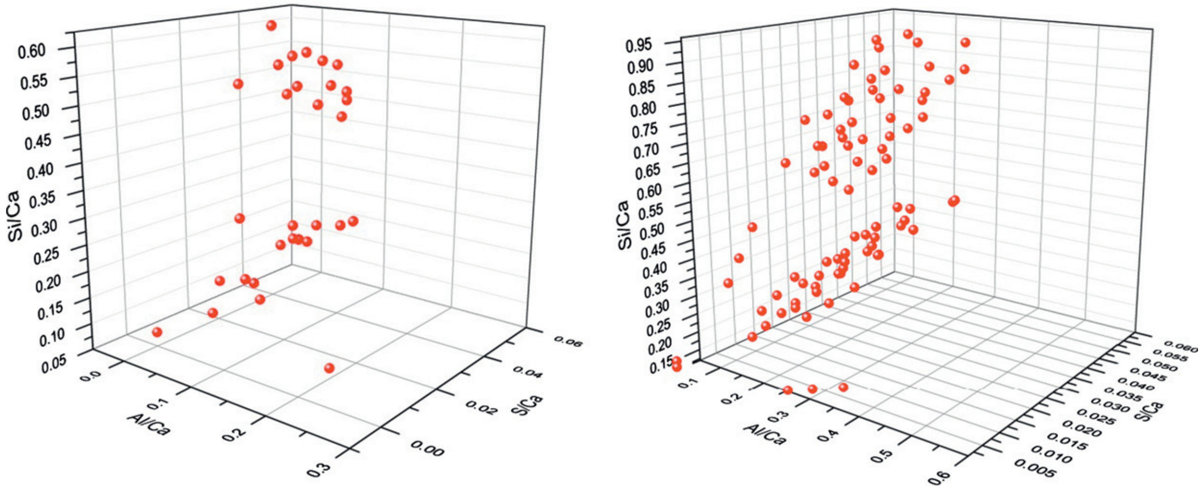
$$1.57 \le n \le 2.1$$

$$0.4 \le \gamma_{AF} \le 0.5$$

For portland cement with fly ash as SCM, knowing the value of n, the volume of C–S–H(P) at time t, $v^{t}_{\text{C–S–H(P)}}$ can be determined using the formula provided in Eq. (17). The values of n' and $\alpha'^{,t}$



a 1-day **b** 7-day



c 28-day **d** 90-day

Fig. 3. (a–d) 3D plots of atomic ratios of silicon, aluminum and sulfur with respect to calcium for 100% portland cement paste (w/cm of 0.4) at four different ages.

can be determined by minimizing the sum of square differences between $v^{\mathrm{exp},t}_{\mathrm{C-S-H(S)}}$ and $v^{\mathrm{pred},t}_{\mathrm{C-S-H(S)}}$ as shown below.

$$\min \sum_{t=1}^{4} \left(v^{\mathrm{exp},t}_{\mathrm{C-S-H(S)}} - v^{\mathrm{pred},t}_{\mathrm{C-S-H(S)}} \right)^2 \tag{35}$$

$1.5 \leqslant n' \leqslant 1.6$

$0.01 \leqslant \alpha'^{,1} \leqslant 0.02$

$0.02 \leqslant \alpha'^{,2} \leqslant 0.05$

$0.05 \leqslant \alpha'^{,3} \leqslant 0.1$

$0.15 \leqslant \alpha'^{,4} \leqslant 0.2$

Similarly, for portland cement with silica fume as SCM, the values of n' and $\alpha''^{,t}$ can be determined by minimizing the sum of square differences between $v^{\mathrm{exp},t}_{\mathrm{C-S-H(S)}}$ and $v^{\mathrm{pred},t}_{\mathrm{C-S-H(S)}}$ as shown below.

$$\min \sum_{t=1}^{4} \left(v^{\mathrm{exp},t}_{\mathrm{C-S-H(S)}} - v^{\mathrm{pred},t}_{\mathrm{C-S-H(S)}} \right)^2 \tag{36}$$

$1.1 \leqslant n' \leqslant 1.4$

$0.35 \leqslant \alpha''^{,1} \leqslant 0.6$

$0.8 \leqslant \alpha''^{,2} \leqslant 0.9$

$0.9 \leqslant \alpha''^{,3} \leqslant 0.95$

$0.95 \leqslant \alpha''^{,4} \leqslant 0.99$

Similarly, for portland cement containing both silica fume and fly ash as SCM, the values of n', $\alpha'^{,t}$ and $\alpha''^{,t}$ can be determined by solving the following nonlinear optimization problem.

$$\min \sum_{t=1}^{4} \left(v^{\mathrm{exp},t}_{\mathrm{C-S-H(S)}} - v^{\mathrm{pred},t}_{\mathrm{C-S-H(S)}} \right)^2 \tag{37}$$

$1.1 \leqslant n' \leqslant 1.2$

$0.35 \leqslant \alpha''^{,1} \leqslant 0.6$

$0.8 \leqslant \alpha''^{,2} \leqslant 0.9$

$0.9 \leqslant \alpha''^{,3} \leqslant 0.95$

$0.95 \leqslant \alpha''^{,4} \leqslant 0.99$

$0.01 \leqslant \alpha'^{,1} \leqslant 0.02$

$$0.02 \leqslant \alpha'^{,2} \leqslant 0.05$$

$$0.05 \leqslant \alpha''^{,3} \leqslant 0.1$$

$$0.15 \leqslant \alpha'^{,4} \leqslant 0.2$$

Table 7
The n and n' values for all the mix proportions.

Mix proportions	w/cm	n	n'
100% Cement	0.3	1.753	–
100% Cement	0.4	1.753	–
100% Cement	0.5	1.753	–
25% Fly ash	0.3	1.753	1.5
25% Fly ash	0.4	1.753	1.5
35% Fly ash	0.3	1.753	1.6
35% Fly ash	0.4	1.753	1.6
10% Silica fume	0.3	1.753	1.1
10% Silica fume	0.4	1.753	1.1
25% Fly ash, 10% silica fume	0.3	1.753	1.1
25% Fly ash, 10% silica fume	0.4	1.753	1.1

Note: The C–S–H(P) is contributed by the portland cement part of the mix. So, the values of 'n' remain constant for all mixes [1]. The n' values vary with the varying proportions of the SCM, but remain constant for all w/cm for each mix.

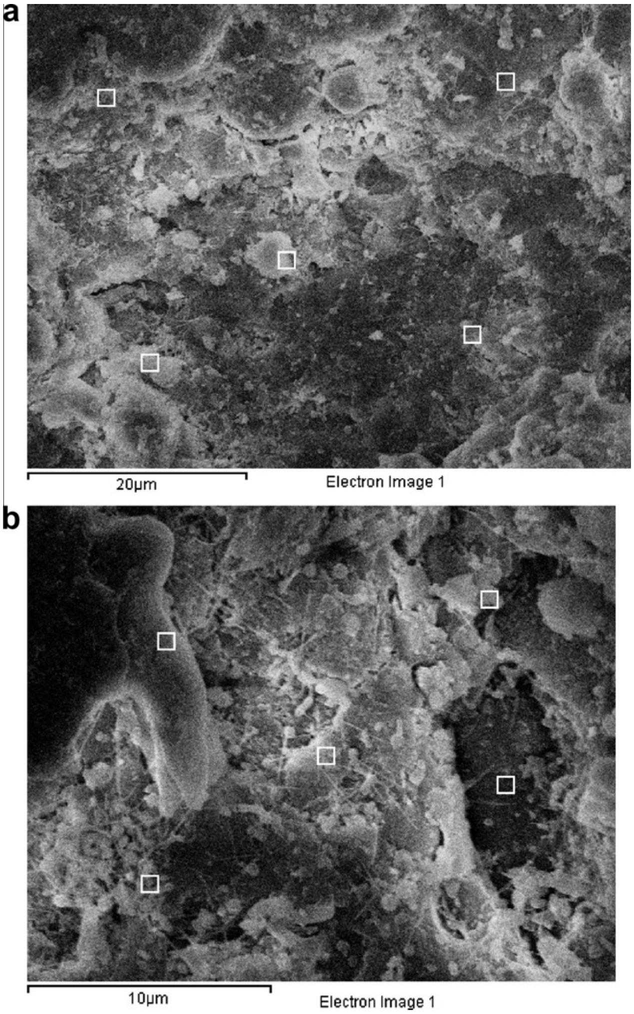


Fig. 4. Typical EDS images of 28-day cement with SCM specimen containing 65% portland cement, 25% fly ash and 10% silica fume with w/cm ratio 0.4 (a) 2200×; (b) 5000× magnification. *Note*: For each sample, nine locations were studied for each of the two magnifications. For each location, five points were randomly selected for analysis leading to 9 × 2 × 5 = 90 data points for each sample. The white boxes indicate the points chosen at each location.

All the above formulations were coded in the General Algebraic Modeling System (GAMS) [20] and solved using the in-built CONOPT solver [21] – a popular solver for nonlinear optimization problems [22].

The optimization technique discussed above gives the representative value of the Ca/Si atomic ratio, n as 1.753 for the pure portland cement. For the pure portland cement, the EDS data were used to calculate the atomic ratios of silicon, aluminum and sulfur with respect to calcium. Fig. 1 shows the typical EDS images of 28-day 100% portland cement specimen with w/cm 0.4. In this figure, one representative location is shown for each of: (a) 2200×; and, (b) 5000× magnification in which five points were chosen randomly at each location, leading to 90 data points for each sample. The relevant 3D atom-ratio plots at different ages, such as at 1-day, 7-day, 28-day and 90-day are shown in the Fig. 3.

The portland cement mixes with SCM were optimized individually. The n value was used as 1.753 for each of them. Since the n value (Ca/Si ratio of C–S–H(P)) was governed by the portland cement component only, it remained constant for all the mixes. Similar observation was made by Taylor [1]. However, the n' values varied with the varying proportions of the SCMs due to different mechanisms of reactions by various pozzolanic materials. But for each mix they remained constant for both w/cm of 0.4 and 0.3. Based on this, a unique n' was computed for each mix of varying SCM. The n' values for each cementitious material combinations is furnished in Table 7. The mixes containing 65% portland cement, 25% fly ash, 10% silica fume and w/cm ratio of 0.4 are used as an example. The various analyses carried out on a 28-day old specimen of this mix proportion are shown in the Figs. 4–6 as typical examples. The comparison between the experimentally obtained

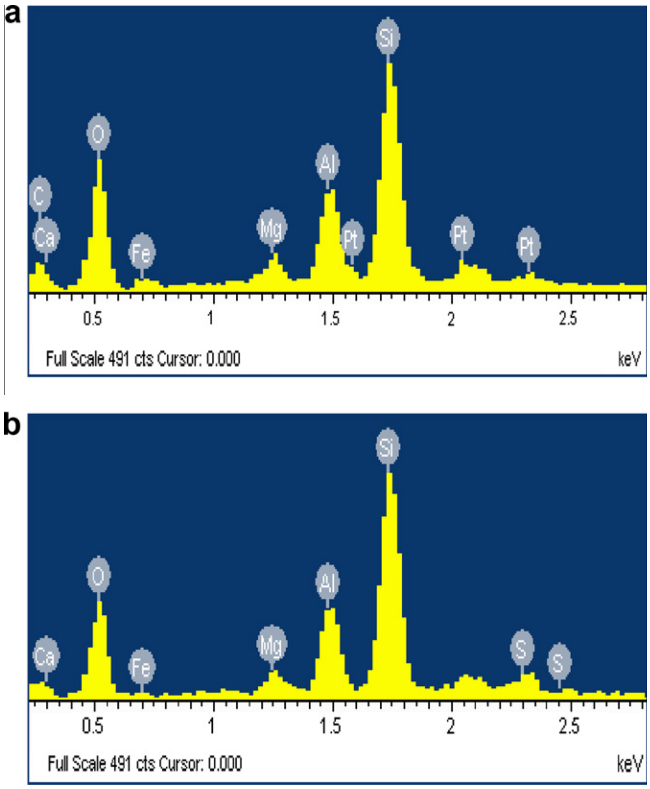
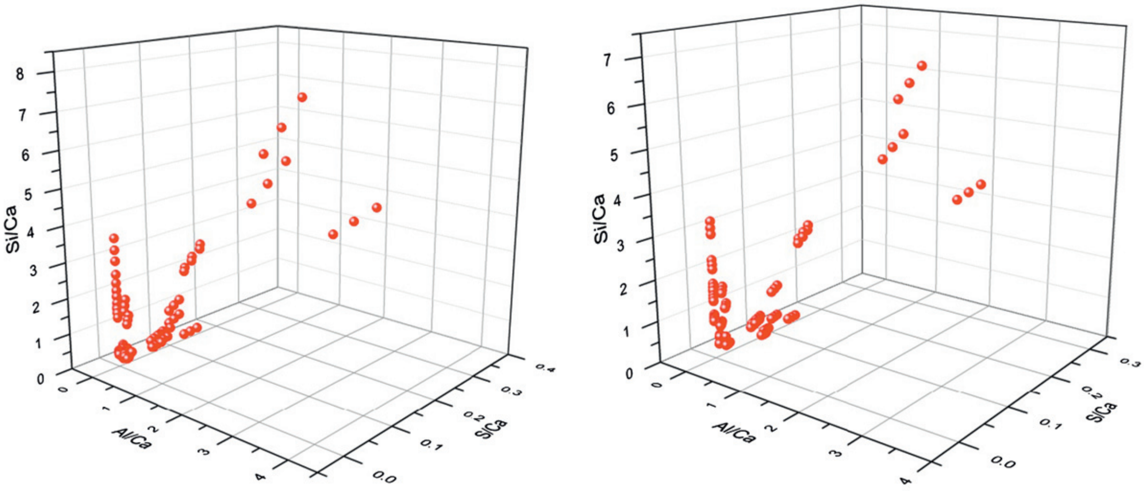
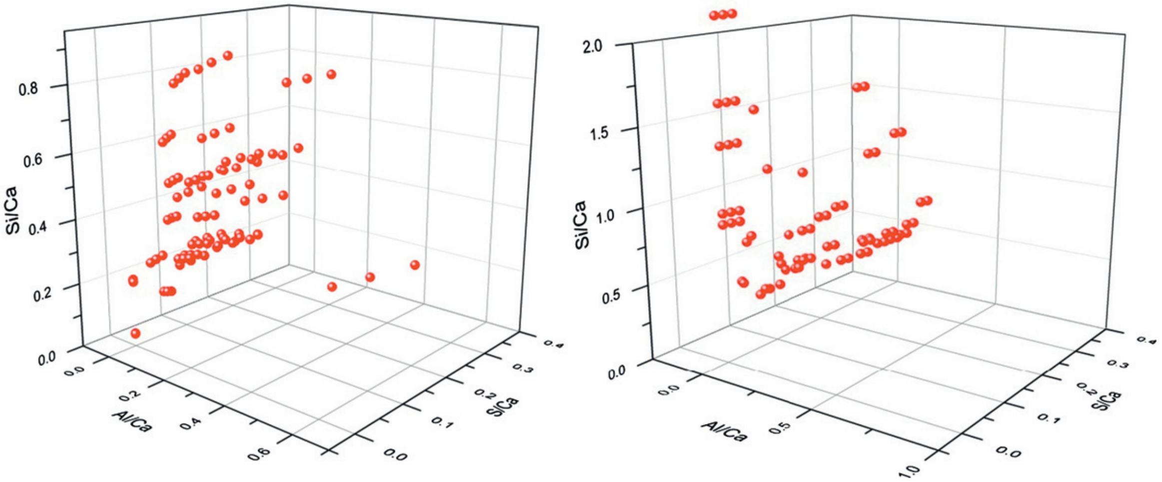


Fig. 5. Typical EDS images of 28-day cement specimen with SCM containing 25% fly ash and 10% silica fume with w/cm ratio 0.4. (a) 2200×; (b) 5000× magnification. *Note*: For each sample, nine locations were studied for each of the two magnifications. For each location, five points were randomly selected for analysis leading to 9 × 2 × 5 = 90 data points for each sample.



a 1-day

b 7-day



c 28-day

d 90-day

Fig. 6. (a–d) 3D plots of atomic ratios of silicon, aluminum, and sulfur with respect to calcium for paste containing 65% portland cement, 25% fly ash, and 10% silica fume (w/cm of 0.4) at four different ages.

volume fractions from SEM-EDS and those obtained using the optimization technique for C–S–H(P) of all mixes at 28 days is shown in Table 8.

Table 8
Comparison between the experimentally obtained volume fractions from SEM/EDS and those obtained by the optimization technique for C–S–H(P) at 28-day age of pastes.

Mix proportions	w/cm	Experimental C–S–H(P)	Predicted C–S–H(P)
100% Cement	0.3	0.400	0.415
100% Cement	0.4*	–	–
100% Cement	0.5	0.700	0.702
25% Fly ash	0.3	0.367	0.387
25% Fly ash	0.4	0.433	0.461
35% Fly ash	0.3	0.300	0.335
35% Fly ash	0.4	0.400	0.399
10% Silica fume	0.3	0.400	0.464
10% Silica fume	0.4	0.533	0.554
25% Fly ash, 10% silica fume	0.3	0.333	0.335
25% Fly ash, 10% silica fume	0.4	0.400	0.399

* The values for 100% portland cement with a w/cm of 0.4 are not shown here, because they were used as the datum (control) for the optimization.

4.3. Estimation of CH volume from optimization and validation through TGA

The values of n and n' obtained by the optimization technique were used as input into Eqs. (29)–(33) to estimate the volume fractions of CH produced by pure portland cement and the portland cement with SCM pastes. The volume fractions were then converted to the corresponding mass fractions using the specific gravity values as provided in Table 4. The expressions for the volumes of CH produced by the hydration of the different cementitious pastes were obtained from Eqs. (29)–(33). By multiplying them with the specific gravity of CH, the volumes were converted to the corresponding mass quantities. For the different cementitious pastes, the volumes of the various products of the aluminate and aluminoferrite hydration were obtained using Eqs. (3)–(8). They were subsequently converted to the corresponding masses and the total mass of the pastes were determined by adding the mass of the hydration products with the mass of the unhydrated residues for each specimen. For the cementitious specimens with w/cm of both 0.4 and 0.3, the mass of CH was divided by the total mass to get the CH mass fraction of the paste.

The mass fractions of CH thus obtained using stoichiometry and statistical optimization was then compared with the corresponding

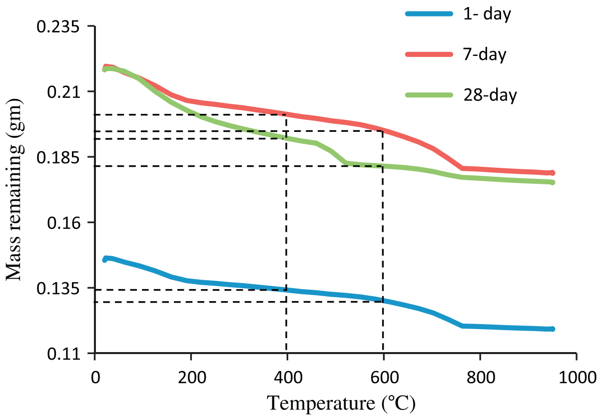


Fig. 7. TGA results for 100% portland cement paste (w/cm of 0.4) at 1-day, 7-day, and 28-day age.

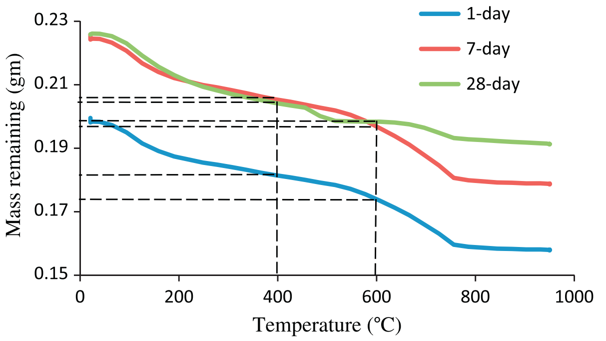


Fig. 8. TGA results for 1-day, 7-days and 28-days old cementitious specimen containing 65% portland cement, 25% fly ash and 10% silica fume with w/cm ratio of 0.4.

mass fractions obtained from the TGA results. The TGA results of 28-day pure portland cement paste (w/cm = 0.4) and cement + SCM containing 25% fly ash and 10% silica fume (w/cm = 0.4) are furnished in Figs 7 and 8, respectively as typical examples. The TGA results were expressed as the mass remaining in the crucible (in gm) with the increasing temperature. The concept suggested by Mounganga et al. [23] was used for this purpose. The water of crystallization of CH is released in the temperature range of 400–600 °C. The loss of water in this range of temperature can be directly used to estimate the mass of CH that was lost due to heating, which is equal to the CH content in the cementitious paste and is expressed as:

$$M_{CH} = [(74.09/18.01)/(M_{400} - M_{600})/M_C] \quad \text{gm per gm of the hydrating cementitious paste.} \tag{38}$$

where M_{CH} is the mass fraction of CH in the cementitious paste; M_{400} is the mass of the paste specimen at 400 °C; M_{600} is the mass of the paste specimen at 600 °C; M_C is the initial mass of the specimen.

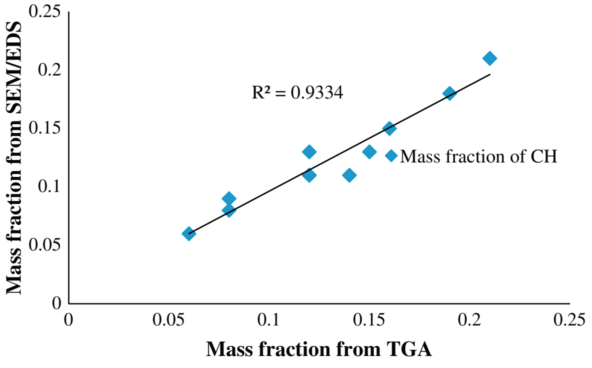


Fig. 9. Comparison between the mass fraction of calcium hydroxide from TGA and SEM/EDS microanalysis results at 28-day age.

The TGA results were plotted in terms of mass of the specimen remaining at any instant of time with respect to temperature of the crucible. The comparison of the 28-day data is shown for all the mixes in Fig. 9. Linear regression shows a correlation coefficient of 0.93, which indicates good agreement between the experimental and analytical data.

5. Conclusions

Estimation of the quantity of C–S–H is difficult in hydrated pure portland cement due to the uncertainty in obtaining the accurate Ca/Si ratio. The partial replacement of pure portland cement with SCM further complicates the estimation process due to the formation of a secondary C–S–H with a different Ca/Si ratio. The above study considered both EDS microanalysis and nonlinear optimization tool to accurately define the Ca/Si ratio for the following pastes: (1) hydrated pure portland cement; (2) portland cement replaced with fly ash; (3) portland cement replaced with silica fume; and (4) portland cement replaced with fly ash and silica fume. Based on the Ca/Si ratios, the volumes of primary and secondary C–S–H were estimated. The values of volume fractions of the primary gel predicted by the optimization technique and those obtained by experimental methods (using SEM/EDS microanalysis) were very close for all mix proportions. The estimated mass fractions of calcium hydroxide from the above method and those obtained from the thermogravimetric analyses (TGA) correlated well with regression coefficient of 0.93, justifying the acceptability of the technique adopted in this study.

This method may further be utilized to estimate the quantity of C–S–H for cement pastes containing other types of SCM such as slag and metakaolin, but for those cases the modified stoichiometric equations and optimizations will be required. Finally, these estimated C–S–H values may be used as a parameter to predict the chemical shrinkage of cementitious systems containing different combinations of portland cement and SCM.

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