Effect of fly ash on Portland cement systems
Part I. Low-calcium fly ash

Vagelis G. Papadakis*

Danish Technological Institute, Building Technology Division, Concrete Centre, Taastrup, Denmark

Received 30 September 1998; accepted 28 June 1999

Abstract

A typical low-calcium fly ash was used as additive in mortar, replacing part of the volume either of Portland cement or aggregate. The development of the strength, heat, porosity, bound water, and calcium hydroxide content was measured. In aggregate replacement higher strengths were observed after 14 days, whereas in cement replacement higher strengths were observed after 91 days. The final strength gain was found to be roughly proportional to the content of active silica in the concrete volume. Bound water content and porosity results showed that fly ash reacts with calcium hydroxide, binding small amounts of water. On the basis of the experimental results, a simplified scheme describing the chemical reactions of the low-calcium fly ash in hydrating cement is proposed. Using the reaction stoichiometry, quantitative expressions for the estimation of the chemical and volumetric composition of a fly ash concrete are proposed. The model expressions can be applied in mix design and concrete performance prediction.   © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cement; Fly ash; Modeling; Reaction

1. Introduction

Fly ash is the combustion residue (coal mineral impurities) in coal-burning electric power plants, which flies out with the flue gas stream and is removed by mechanical separators, electrostatic precipitators, or bag filters. It has long been used as a Portland cement additive or as an active addition in concrete [1–3], due to economic and technological benefits.

Two general classes of fly ash can be defined: low-calcium fly ash (FL) produced by burning anthracite or bituminous coal, and high-calcium fly ash (FH) produced by burning lignite or sub-bituminous coal. FL is categorized as a normal pozzolan, a material consisting of silicate glass, modified with aluminum and iron [4]. The CaO content is less than 10%. FL requires $Ca(OH)_2$ to form strength-developing products (pozzolanic activity), and therefore is used in combination with Portland cement, which produces $Ca(OH)_2$ during its hydration.

Contributions of practical or experimental character regarding the effect of FL and other pozzolanic or cementitious additives on concrete properties abound in the literature [1–6]. Despite the wealth of practical information,

efforts to describe the pozzolanic activity by chemical reactions and quantification of products and pore volume are very limited. Papadakis et al. [7] were the first to propose a general simplified scheme describing the pozzolanic activity in terms of chemical reactions, but without an extended experimental verification. This scheme was found to be valid in the case of silica fume activity in concrete [8].

In the present work, an extended experimental investigation of the activity of FL in Portland cement pastes and mortars was carried out, and a quantitative description based on the experimental results is presented. Moreover, the effect of FL addition on main mechanical and durability properties of Portland cement systems as a function of the replacement type (cement or aggregates) is clarified. In a future work, the model will be expanded to include the case of FH.

2. Methods

The same experimental program as described in a previous publication [8] for the case of silica fume was applied. The program included measurements of compressive and flexural strength, $Ca(OH)_2$ (CH), bound H_2O (H), porosity, pore volume distribution (PVD), and heat development, as well as microscopy observations on cement and FL-cement pastes and mortars. It is assumed that comparable conclusions derived from pastes and mortars may be also applicable to concrete.

* Corresponding author. Orfeos 25, Paleo Faliro, GR-175 64, Athens, Greece. Tel.: +30-932-327-323; fax: +30-61-993-255.

E-mail address: takisp@iceht.forth.gr (V.G. Papadakis).

2.1. Materials

FL produced in Denmark (Danaske I/S) was used, as delivered from the producer. A rapid-setting Portland cement was used (400 m^2/kg Blaine's fineness). Normal graded sand (2,670 kg/m^3 density) and a common plasticizer were used for mortar preparation. The physical and chemical characteristics of the materials are given in Table 1. The glass phase content was estimated at about 75% using optical microscopy. This value is consistent with the mean non-crystalline phase content of 76% reported by McCarthy et al. [9]. Representative samples of cement and FL were examined to obtain a general overview of particle shape and surface texture using a scanning electron microscope (SEM, Fig. 1). Cement particles (Fig. 1a) have irregular polygonal shape. FL (Fig. 1b) consists of glassy spheres of various sizes but similar to the cement particle size. Due to the lower proportion of surface deposits consisting of alkali sulfate crystals [2], FL tends to show a cleaner appearance under the microscope.

2.2. Mixture proportions and experimental

A volume unit (1 m^3) of the fresh or hardened mortar was chosen as a common basis. When FL is added to this unit, then an equal volume of another component (either cement or aggregate) was removed in order to keep the same total volume and a common comparison basis.

Mortar specimens were used for mechanical properties and heat measurements. The mixture proportions are summarized in Table 2. In the control specimen the water-cement ratio (W/C) was 0.5 and the aggregate-cement ratio (A/C) was 3. When FL replaces a volume of aggregate, three contents of FL were selected: 10, 20, and 30% addition to the cement weight, giving specimens FLA1, FLA2, and FLA3,

respectively. For cement replacement by FL, the same contents were also selected: 10, 20, and 30% replacement of the control cement weight giving specimens FLC1, FLC2, and FLC3, respectively.

The specimen preparation and the experimental techniques are described in detail elsewhere [8]. The specimens for strength measurements were prisms of 40 × 40 × 160 mm, cured underwater (CH-saturated) at 20℃, and tested after 3, 14, 28, 49, 91, 182, and 364 days. Semiadiabatic calorimetry was used for heat development experiments. FL-cement pastes were also prepared, representing the paste matrix of the mortar specimens, and analyzed for CH content, chemically bound H_2O content (hereafter referred to as H content), and porosity at 3, 7, 14, 28, 49, 112, 182, and 364 days after casting. The paste properties have been reduced to the corresponding mortar specimen volume by multiplying by an appropriate factor (paste volume per mortar volume fraction).

3. Results and discussion

3.1. Strength measurement results

In Fig. 2a, the results (reduced to a common air content, 3.3%) from compressive strength measurements on control and FLA (low-calcium fly ash replaces aggregate) mortars are presented. The compressive strengths of FLA specimens are similar to the controls at 3 and 14 days, but are higher from 28 days and later. This delay is explained as due to the significantly large size of the fly ash particles, which results in low surface area available for reaction, and also as due to the pore solution chemistry [10–13]. The strength increase is due to the higher content of calcium silicate hydrate (CSH; the main carrier of strength in hardened cement) in the FLA specimens due to the reaction of the CH produced from cement hydration with the active silica (S) of the FL. There is a reasonable distribution of the strength increase according to the fly ash content (10, 20, and 30% on the cement weight), but beginning from 91 days it seems that there is no difference among FLA2 and FLA3 specimens. The strength gain for the FLA2 specimen is about 25% after 1 year of hydration.

Table 1
Physical and chemical characteristics of cement and low-calcium fly ash

	Cement	FL
Physical properties		
BET specific surface (m^2/g; N_2 adsorption)	1.3	1.2
Particle mean diameter (μm; sedimentation technique)	14.0	13.9
Density (kg/m^3; air pycnometry)	3,130	2,250
Chemical analysis (%)[a]		
SiO_2	20.10	53.50
Al_2O_3	4.25	20.40
Fe_2O_3	3.49	8.66
CaO	63.20 (1.48 free)	3.38 (0.36 free)
SO_3	2.88	0.60
L.O.I.	0.86	2.20
Mineralogical characteristics		
Insoluble residue (%)	0.14	78.4
Glass phase content (%)	–	75

[a] The methods specified by the European Standards, EN-450, EN-196, and EN-451 were followed. The insoluble residue was determined by EN-196-2. The glass phase content was determined by optical microscopy.

Table 2
Absolute and relative mixture proportions for mortar specimens[a]

Specimen	C	W	P	A	W/C	P/C	A/C
Control	514.6	257.4	0.0	1543.8	0.50	0.00	3.00
FLA1	514.6	257.4	51.5	1482.7	0.50	0.10	2.88
FLA2	514.6	257.4	102.9	1421.7	0.50	0.20	2.76
FLA3	514.6	257.4	154.4	1360.6	0.50	0.30	2.64
FLC1	463.1	257.4	51.5	1526.6	0.556	0.111	3.30
FLC2	411.7	257.4	102.9	1509.4	0.625	0.250	3.67
FLC3	360.2	257.4	154.4	1492.3	0.715	0.429	4.14

[a] C, W, P, A: kg of cement, water, FL, and aggregate, respectively, per m^3 of total mortar volume; W/C, P/C, A/C: the water-cement, FL-cement, and aggregate-cement ratio (by weight), respectively.
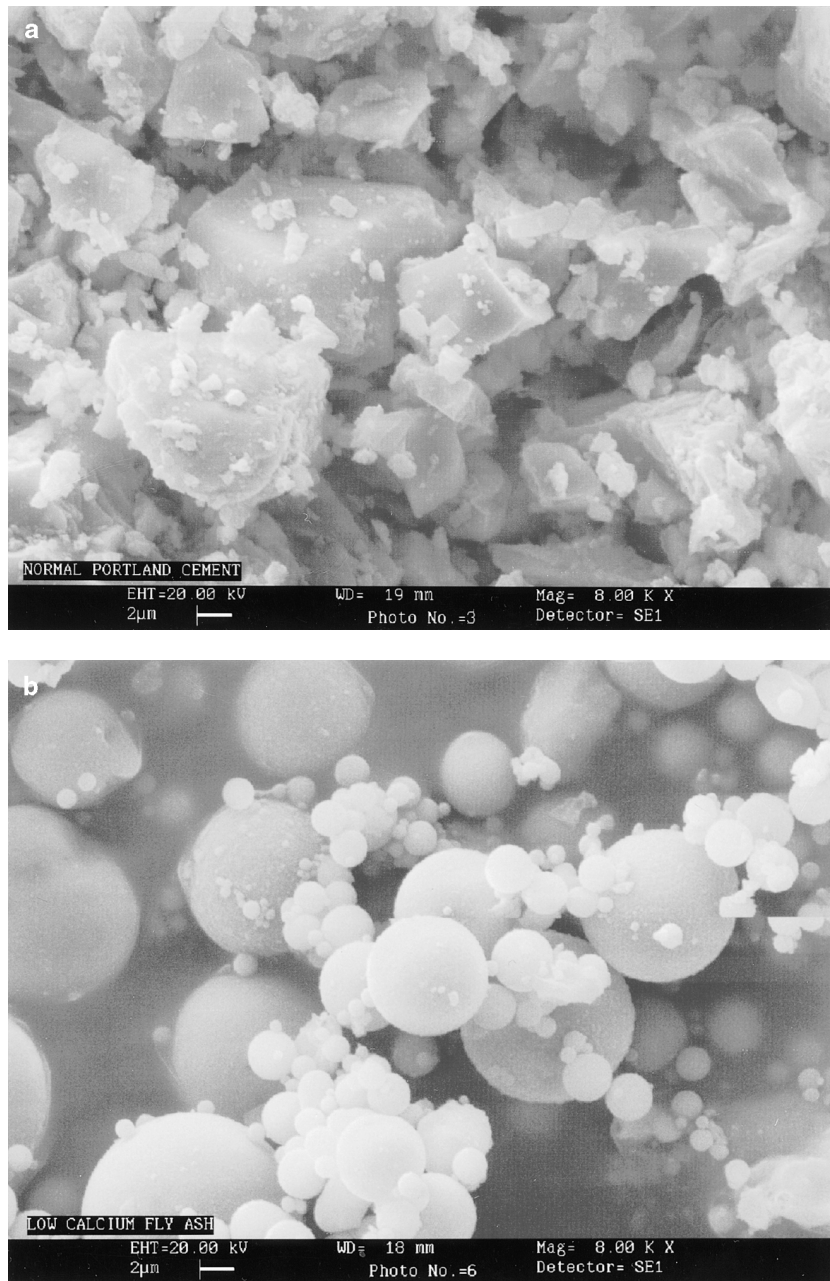
Fig. 1. SEM micrographs (8,000×) of Portland cement (a) and low-calcium fly ash (b).

When fly ash replaces cement (Fig. 2b) the strength is reduced, at first due to lower activity of the large fly ash particles, but as time proceeds this gap is gradually eliminated. The reduction is proportional to the fly ash content. After 6 months for FLC1 and FLC2 specimens and after 1 year for the FLC3 specimen, the strength becomes higher than that of the control. Moreover, the FLC2 specimen presents the highest strength. This ultimate improvement is due to the higher active silica content (40%) of low-calcium fly ash in comparison with the cement (20%).

The results of flexural strength measurements are similar to those of compressive strength, but due to their higher scattering will not be discussed further.

3.2. Heat development results

The heat development curves of control and FLA2 specimens are almost identical for the first few days, presenting after 1 week some differences that finally lead to higher values of liberated heat for the FLA2 mixture (Fig. 3). This increase seems to be smooth and may be correlated with a diffusion-controlling mechanism of the pozzolanic reaction.
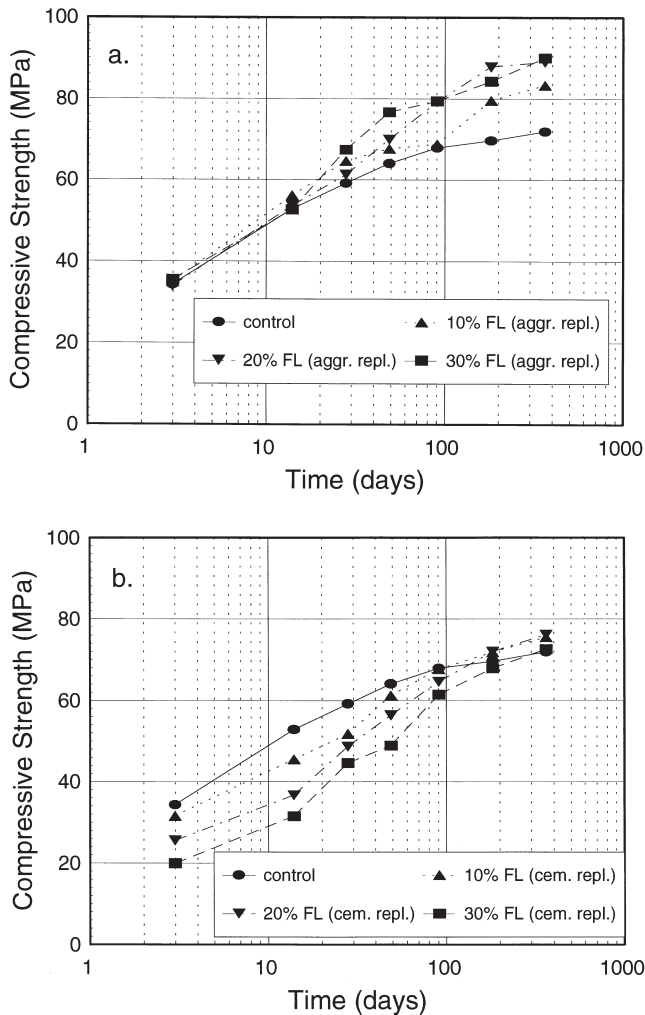
Fig. 2. Compressive strength development of mortars when FL replaces (a) aggregate (10, 20, and 30% addition to the cement weight) and (b) cement (10, 20, and 30% cement replacement).

Fig. 3. Comparative heat development results for control and fly ash (FLA2) mixtures.

These results strengthen the above conclusions for the initiation of the pozzolanic reactions, which in the case of FL takes place some time after the initiation of cement hydration (1–3 weeks).

3.3. H, CH, and porosity measurement results

The H content (kg H_2O/m^3 mortar) of the control and FLA specimens is shown in Fig. 4a. An important observation is that the control specimen as well as all FLA specimens have almost the same H content, at least for the first 3 months of hydration. This is in agreement with a previous publication's result regarding silica fume (SF) activity in concrete [8]. It was shown that the pozzolanic reaction of SF (essentially the reaction of the S of SF with the CH of the hydrating cement) does not include any additional water. However, a lower bound water content was observed at intermediate ages. This behavior was explained as due to the selective reaction of the CH with the SF instead of its re-
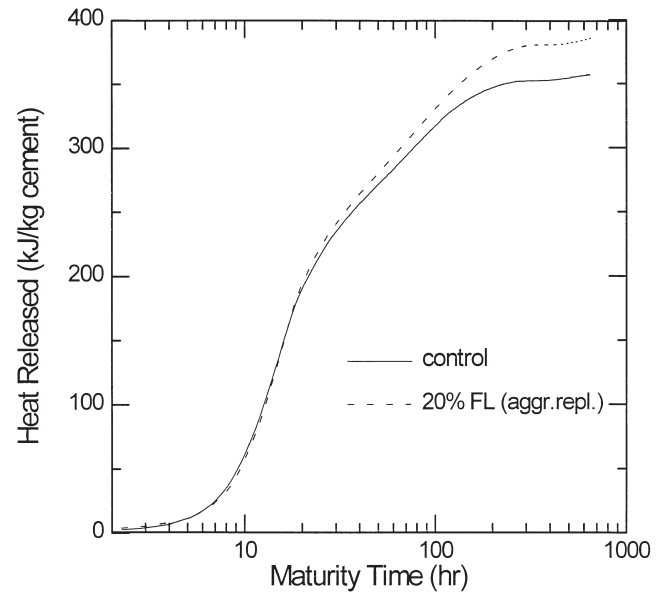
action with the C_3A and C_4AF phases of cement, which contribute significantly to water binding. In the case of FL, due to its significant content in the aluminate phase, such decrease in H content is not observed. A selective reaction of CH with fly ash may also take place, but the high content of aluminate in fly ash counterbalances the H content loss.

After 3 months, the H content values for FLA specimens exceeded those of the controls. It seems that during this late period the remaining amounts of the C_3A and C_4AF phases of cement have reacted, binding additional water. Because water binding is the cause of the pore volume reduction, the porosity ε (m^3 of pores/m^3 mortar) should be expected to follow the H content development results, as was indeed found (Fig. 4b). When FL replaces cement, a decrease in the H content and an increase in the total porosity was observed.

The CH content (kg CH/m^3 mortar) for the control and FLA specimens is shown in Fig. 5. It can be seen that the CH content of the control specimen increases with time until a steady state is attained. The CH content of FLA specimens follows the CH content of the control, but after 14 days is consumed at a slow rate. By 28 days and later, CH consumption and therefore pozzolanic reactions proceed at higher rates.

3.4. Microscopy analysis and PVD results

In Fig. 6 typical SEM images of the FLA2 paste specimen are shown at different ages of hydration. It is interesting that FL particles are used as sites where cement hydration products (CH, ettringite) are grown the first 3 days (Fig. 6a). This is because of their acidic character and thus they have great affinity for lime and alkalis. In the early hy-
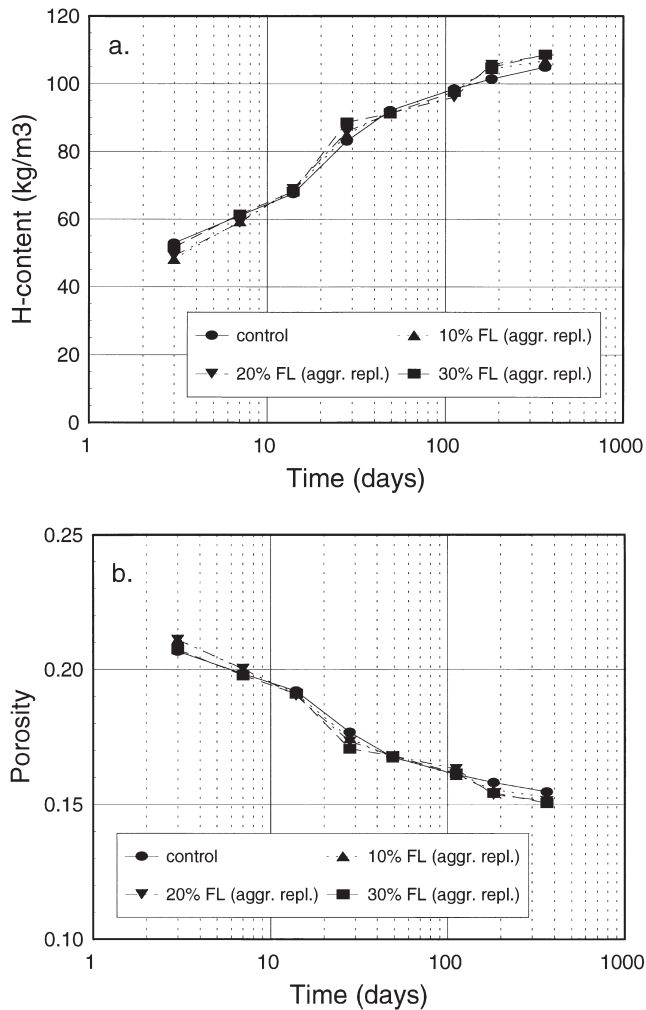
Fig. 4. (a) Chemically bound water content and (b) porosity of mortars with low-calcium fly ash to replace aggregate (0, 10, 20, and 30% addition to the cement weight) as a function of time.
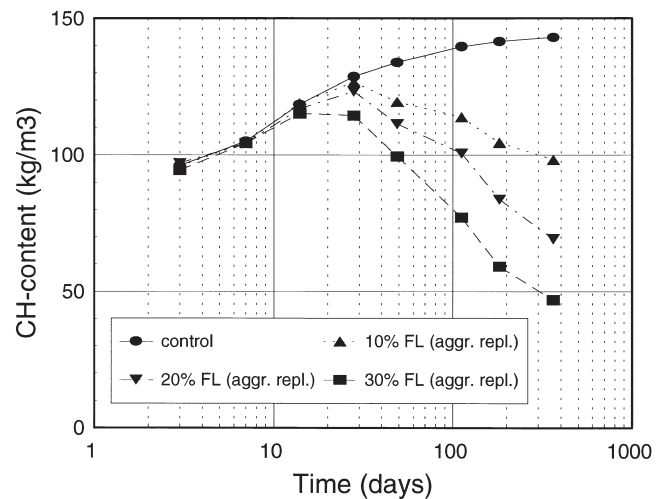

Fig. 5. Calcium hydroxide content in mortars with low-calcium fly ash to replace aggregate (0, 10, 20, and 30% addition by cement weight) as a function of time.

dration period of 0–21 days no traces of reaction among FL particles can be detected, at least for the FL particle size that can be observed (Fig. 6b). After 28 days, the ash particles are extensively etched and surrounded by hydration products, while they retain their spherical shape (Fig. 6c). When pozzolanic reaction has significantly proceeded (6 months), FL particles are difficult to identify because they are covered by the reaction products (Fig. 6d). Few entirely round particles are still distinguished (nonreacted).

The volume of micropores (pores with diameter less than 20 nm) of well-hydrated pastes (6 months) was measured using N_2 adsorption. This quantity (cm^3/g) was converted to content of micropores in the total pore volume. The micropore content of the FLA2 specimen (10%) was found to be significantly higher than that of the control (6%). Thus, although control and FLA2 specimens have almost the same total porosity, the latter presents significant pore refinement.

4. Theoretical approach of FL activity in Portland cement systems

4.1. Determination of products and reaction stoichiometry

Fly ash is a complex material consisting of a wide range of glass and crystalline compounds. Although these compounds, as well as their hydration products in the presence of CH, are generally nonstoichiometric, simplifying assumptions are made herein for modeling purposes.

As given in the materials section, FL is primarily composed of SiO_2 (S, 53.5%), Al_2O_3 (A, 20.4%), and Fe_2O_3 (F, 8.7%). It also contains a small amount of CaO (3.4%) and very small amounts of other compounds.

In the case of this fly ash, in reactive form there is aluminosilicate (A-S) glass with a high content of S. One should expect the hydration product of an aluminosilicate glass/hydrated lime mixture to be a C-S-H gel incorporating significant amounts of A. As a first approximation, the S of A-S glass is proposed to react with CH without additional water binding and to form a calcium silicate hydrate described by the simplified formula of $C_3S_2H_3$, as was shown elsewhere using almost pure vitreous silica (silica fume [8]). The main difference is in the reaction rate; a lower rate is observed in the case of FL due to higher particle size. The S present as quartz or in crystalline aluminosilicate phases is inert [1,2].

Similarly, reactive alumina is found only in the aluminosilicate glass, whereas the alumina part in the crystalline phases is not reactive [1,2]. Thermodynamic study of the $CaO-Al_2O_3-SiO_2-SO_3-H_2O$ system [1] confirms that phases that originate after reaction of fly ash with lime can be:

- hydrated calcium silicate C-S-H, which appears as ill-crystallized gel
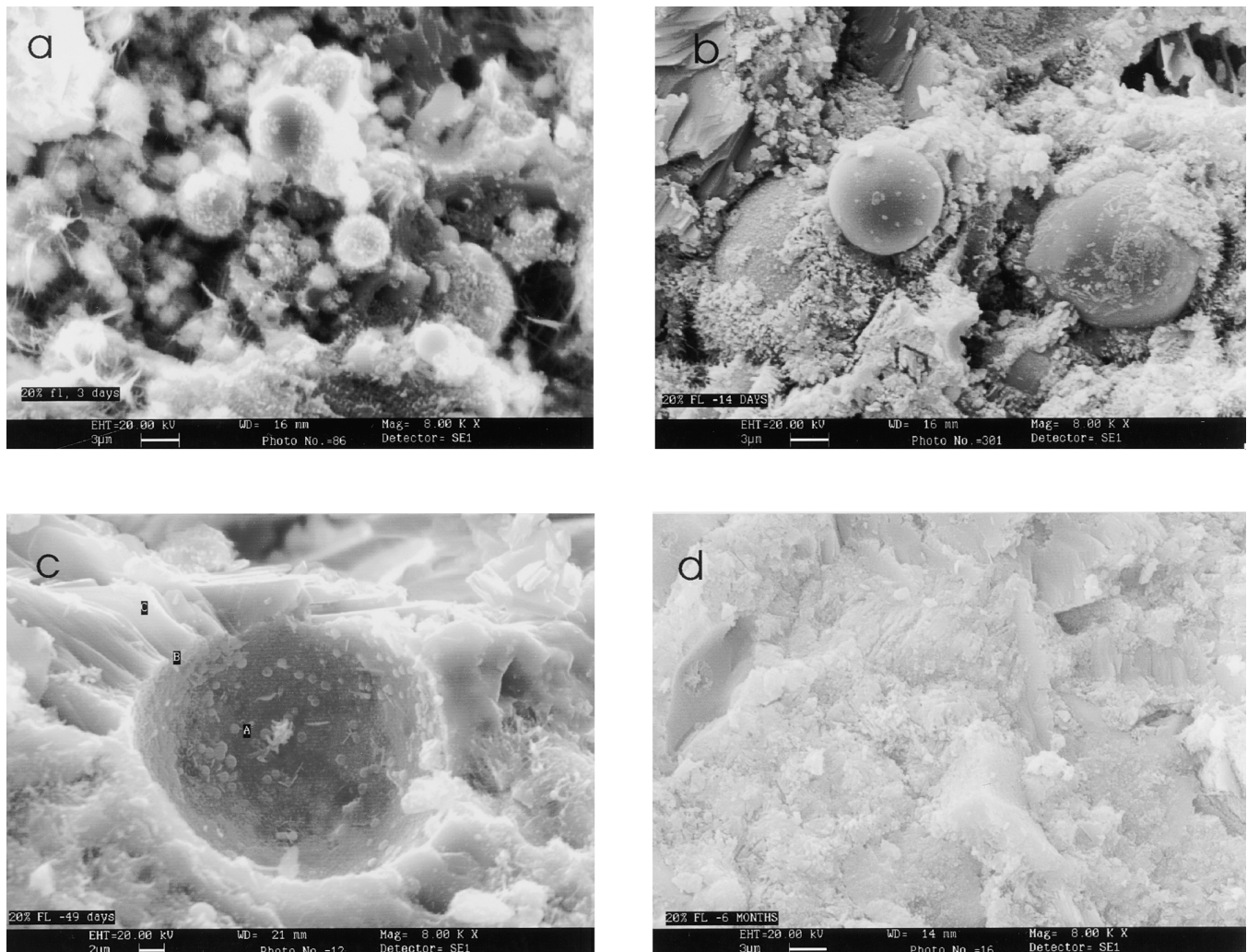- hexagonal tetracalcium aluminate hydrate C_4AH_{13}
- hydrated gehlenite C_2ASH_8

Fig. 6. Scanning electron micrographs (8,000×) of 20% FL-cement paste after (a) 3, (b) 14, (c) 49, and (d) 182 days of hydration.

- ettringite $C_3A.3C\bar{S}.H_{32}$
- monosulfate $C_4A\bar{S}H_{12}$

These reactions proceed with additional binding of water, as H content and porosity results show. It must be emphasized that ettringite is converted to monosulfate soon after the gypsum is consumed. Hydrated gehlenite is formed in a high-lime system and in the presence of gypsum gradually decreases and eventually disappears after 60 days [5]. The same hydration products of fly ash in the presence of CH have been reported by numerous researchers [10,11,14–20].

It seems also that in both fly ashes (low- and high-calcium) the ferrous phase is found mostly in crystalline form, as hematite (Fe_2O_3) or magnetite (Fe_3O_4), and thus does not participate in the pozzolanic reactions [2,14,18].

Assuming for the modeling purposes that all F content belongs to nonglass content, the remaining constituents would have a glass content of $75/(100 - 8.7) = 82\%$. Therefore, it can be assumed, as a rough approximation, that this particular FL contains $0.82 \times 53.5 = 44\%$ active SiO_2,

$0.82 \times 20.4 = 17\%$ active Al_2O_3, and the rest (39%) is inert.

According to the above analysis, the following simplified equations may describe the pozzolanic activity of the low-calcium fly ash [see Eq. (1), Eq. (2), and Eq. (3)]:

$$2S + 3CH \rightarrow C_3S_2H_3 \tag{1}$$

$$A + C\bar{S}H_2 + 3CH + 7H \rightarrow C_4A\bar{S}H_{12} \tag{2}$$

$$A + 4CH + 9H \rightarrow C_4AH_{13} \tag{3}$$

The reaction shown in Eq. (2), which dominates in the high-gypsum system [21], takes place through several intermediate steps including the reaction seen in Eq. (3), ettringite formation, and ettringite conversion to monosulfate. Thus, in an excess of gypsum the total pozzolanic reaction of the active alumina is described by Eq. (2). The reliability of the above equations can be verified through the CH and H content results compared with their theoretical predictions, based on the above reactions.

4.2. Quantification of the final products

A common reference base is used in these calculations: 1 m³ of concrete (or mortar), which contains C, W, A, and P kg of Portland cement, water, aggregate and pozzolan (FL), respectively. When a blended cement is used, the pozzolan must be separated and included in the P content.

The Portland cement and the FL can be analyzed in terms of oxides: total CaO (C), free CaO (Cf), SiO₂ (S), Al₂O₃ (A), Fe₂O₃ (F), SO₃ ($\bar{S}$), and other oxides or impurities denoted by R. Let us denote as $f_{i,c}$ and $f_{i,p}$ the weight fractions of the constituent i (i = C, Cf, S, A, F, $\bar{S}$, and R) in the cement and pozzolan, respectively. As mentioned above, not all of the total mass of the oxide i in a pozzolan is active (only the glass phase, with the exception of FH where some crystalline phases are also active). Let us denote by γ_i the weight fraction of the oxide i in the pozzolan that contributes to the pozzolanic reactions ("active" ratio). In the case of FL, the weight fractions of S and A in fly ash, $f_{S,p}$ and $f_{A,p}$, and their active (glass) part, γ_S and γ_A respectively, are required for the quantitative calculations. If, however, active ferrous phases are included [9], then a γ_F term should be included in the model.

In the Appendix, the Portland cement hydration reactions, the molar weights of the reactants and products, and a quantification of the final products in a Portland cement concrete are given. When low-calcium fly ash is present in concrete, in addition to the Portland cement hydration reactions, the pozzolanic reactions seen in Eq. (1) through Eq. (3) take place. Two different cases can be distinguished according to the level of total gypsum present. If the gypsum content is *higher* than that required for full hydration of the cement and complete pozzolanic reaction of fly ash alumina, Eq. (2); i.e [see Eq. (4)]:

$$C\bar{S}H_2 > (1.689 f_{A,c} - 1.078 f_{F,c})C + 1.689 \gamma_A f_{A,p} P \quad \text{or}$$
$$f_{\bar{S},c} > 0.785 f_{A,c} - 0.501 f_{F,c} + 0.785 \gamma_A f_{A,p}(P/C) \quad (4)$$

then, Eq. (3) does not take place (these factors have been calculated using the stoichiometry of Portland cement and fly ash hydration reactions, and the molar weights given in Appendix; Table A1). Thus, the S and A of the fly ash consume the CH produced during Portland cement hydration according to the reactions seen in Eqs. (1) and (2), respectively. Taking into account the stoichiometry of these reactions and the Portland cement hydration as well and using the molar weights of reactants and products, the amounts of the "finally" produced compounds can be determined (after the completion of the hydration and pozzolanic activity). These amounts of CH, C₃S₂H₃ (CSH), C₄A$\bar{S}$H₁₂ (CA$\bar{S}$H), C₆AFH₁₂ (CAFH), remaining constituents (R), and bound water (H) are given as follows, in kg/m³ of concrete [see Eqs. (5) through (10)]:

$$CH = \{1.321(f_{C,c} - 0.7 f_{\bar{S},c})$$
$$- (1.851 f_{S,c} + 2.182 f_{A,c} + 1.392 f_{F,c})\}C$$
$$- (1.851 \gamma_S f_{S,p} + 2.182 \gamma_A f_{A,p})P \quad (5)$$

$$CSH = 2.85(f_{S,c}C + \gamma_S f_{S,p}P) \quad (6)$$

$$CA\bar{S}H = (6.106 f_{A,c} - 3.898 f_{F,c})C + 6.106 \gamma_A f_{A,p}P \quad (7)$$

$$CAFH = 5.099 f_{F,c}C \quad (8)$$

$$R = (f_{R,c} + 1.7 f_{\bar{S},c} - 1.689 f_{A,c} + 1.078 f_{F,c})C$$
$$+ (1 - \gamma_S f_{S,p} - 2.689 \gamma_A f_{A,p})P \quad (9)$$

$$H = \{0.321(f_{C,c} - 0.7 f_{\bar{S},c})$$
$$+ 1.236 f_{A,c} - 0.113 f_{F,c}\}C + 1.236 \gamma_A f_{A,p}P \quad (10)$$

For the completion of the pozzolanic activity, the left-hand side of Eq. (5) must be positive. Otherwise, there will not be enough lime solution to react with the entire quantity of the active S and A of the FL. If CH = 0 in Eq. (5), the maximum pozzolan content that can react with all lime produced during cement hydration, P_{max}, can be obtained [see Eq. (11)]:

$$P_{max} = \{1.321(f_{C,c} - 0.7 f_{\bar{S},c})$$
$$- (1.851 f_{S,c} + 2.182 f_{A,c} + 1.392 f_{F,c})\}C/$$
$$(1.851 \gamma_S f_{S,p} + 2.182 \gamma_A f_{A,p}) \quad (11)$$

In this case, P_{max} is used in calculations and the rest (P − P_{max}) is added to the R content.

If the gypsum content is *lower* than that required for cement hydration and for complete pozzolanic reaction of the active part of fly ash alumina [i.e., see Eq. (12)]:

$$C\bar{S}H_2 < (1.689 f_{A,c} - 1.078 f_{F,c})C + 1.689 \gamma_A f_{A,p}P \quad \text{or}$$
$$f_{\bar{S},c} < 0.785 f_{A,c} - 0.501 f_{F,c} + 0.785 \gamma_A f_{A,p}(P/C) \quad (12)$$

then, it is assumed that Eq. (2) takes place until all gypsum is consumed, and the remaining active A reacts only with CH according to the reaction in Eq. (3) giving C₄AH₁₃ (CAH). The remaining gypsum that reacts with A according to Eq. (2) is $(2.15 f_{\bar{S},c} - 1.689 f_{A,c} + 1.078 f_{F,c})C$. In this case, the following "final" contents are calculated as seen in Eqs. (13) through (19):

$$CH = (1.321 f_{C,c} - 1.851 f_{S,c} - 2.907 f_{A,c} - 0.928 f_{F,c})C$$
$$- (1.851 \gamma_S f_{S,p} + 2.907 \gamma_A f_{A,p})P \quad (13)$$

$$CSH = 2.85(f_{S,c}C + \gamma_S f_{S,p}P) \quad (14)$$

$$CA\bar{S}H = 7.774 f_{\bar{S},c}C \quad (15)$$

$$CAH = (5.497 f_{A,c} - 3.509 f_{F,c} - 7.0 f_{\bar{S},c})C$$
$$+ 5.497 \gamma_A f_{A,p}P \quad (16)$$

$$CAFH = 5.099 f_{F,c}C \quad (17)$$

$$R = (f_{R,c} - 0.45 f_{\bar{S},c})C + (1 - \gamma_S f_{S,p} - \gamma_A f_{A,p})P \quad (18)$$

$$H = (0.321 f_{C,c} - 0.675 f_{\bar{S},c} + 1.590 f_{A,c}$$
$$- 0.339 f_{F,c})C + 1.590 \gamma_A f_{A,p}P \quad (19)$$

For this case, P_{max} is [see Eq. (20)]:

$$P_{max} = \frac{(1.321 f_{C,c} - 1.851 f_{S,c} - 2.907 f_{A,c} - 0.928 f_{F,c})C}{(1.851 \gamma_S f_{S,p} + 2.182 \gamma_A f_{A,p})}$$
(20)

As can be observed from the above equations, the CSH content increases with FL addition, regardless of whether FL replaces aggregates or cement, because $\gamma_S f_{S,p}$ is usually higher than $f_{S,c}$. In the latter case, however, there is an upper limit in P content, higher than P_{max} [see Eq. (21)]:

$$2.85\{f_{S,c}(C - P) + \gamma_S f_{S,p}P_{max}) > 2.85 f_{S,c}C \rightarrow$$
$$P < (\gamma_S f_{S,p}/f_{S,c})P_{max}$$
(21)

The H content, when FL replaces aggregates (C constant), increases due to the active alumina content of the FL. Obviously, the following equation must be satisfied [see Eq. (22)]:

$$CH + CSH + CA\bar{S}H + CAH + CAFH + R = C + P + H$$
(22)

4.3. Estimation of final pore volume

The concrete porosity ε, is given by Eq. (23):

$$\varepsilon = \varepsilon_{air} + W/\rho_w - \Delta\varepsilon_h - \Delta\varepsilon_p - \Delta\varepsilon_c$$
(23)

where ε_{air} is the volume fraction of entrapped or entrained air in concrete, ρ_w the water density (1000 kg/m^3), and $\Delta\varepsilon_h$, $\Delta\varepsilon_p$, $\Delta\varepsilon_c$ are the porosity reductions due to hydration of Portland cement, pozzolanic activity, and carbonation, respectively. The term $\Delta\varepsilon_h$ was calculated and presented in a previous publication [8]. In the same publication, the porosity reduction due to the pozzolanic reaction of S, Eq. (1), was found equal to zero. The porosity reduction, because of the pozzolanic reaction of FL, is due to the reaction of A [Eqs. (2) and (3)].

If the gypsum content is *higher* than the maximum required [i.e., when Eq. (4) holds], then the term $\Delta\varepsilon_p$ is calculated only from the reaction in Eq. (2) [see Eq. (24)]:

$$\Delta\varepsilon_p = (\gamma_A f_{A,p}P)\Delta\bar{V}_{A,\bar{S}}$$
(24)

where $\Delta\bar{V}_{A,\bar{S}}$ is the molar volume difference for the reaction in Eq. (2), in m^3/kg. It can be calculated knowing the stoichiometry of the reactions and the molar volumes of the solid reactants and products (see the Appendix and [22–24]): $\Delta\bar{V}_{A,\bar{S}} = (319.24 \times 10^{-6}$ m^3/gmol C$_4$A$\bar{S}$H$_{12}$ − 25.49 × 10^{-6} m^3/gmol A − 74.21 × 10^{-6} m^3/gmol C$\bar{S}$H$_2$ − 3 × 33.08 × 10^{-6} m^3/gmol CH)/(101.96 × 10^{-3} kgA/gmolA) = 1.18 × 10^{-3} m^3/kg A. By substituting $\Delta\varepsilon_h$ and $\Delta\varepsilon_p$ terms in Eq. (23), the final value of the porosity of a noncarbonated FL concrete is given by Eq. (25):

$$\varepsilon = \varepsilon_{air} + W/\rho_w - \{0.249(f_{C,c} - 0.7f_{\bar{S},c})$$
$$+ 0.191 f_{S,c} + 1.118 f_{A,c} - 0.357 f_{F,c}\}(C/1000)$$
$$- (1.18\gamma_A f_{A,p})(P/1000)$$
(25)

If the gypsum content is *lower* than that required for cement hydration and for complete pozzolanic reaction [i.e., when Eq. (12) holds], then the term $\Delta\varepsilon_p$ is calculated from both Eq. (2) and Eq. (3) [see Eq. (26)]:

$$\Delta\varepsilon_p = (C\bar{S}H_2)_{rem}\Delta\bar{V}_{A,\bar{S}}$$
$$+ \{\gamma_A f_{A,p}P - 0.5922(C\bar{S}H_2)_{rem}\}\Delta\bar{V}_A$$
(26)

The remaining gypsum, $(C\bar{S}H_2)_{rem}$, which reacts with A according to Eq. (2) is $(2.15 f_{\bar{S},c} - 1.689 f_{A,c} + 1.078 f_{F,c})C$. According to the reactions' stoichiometry and using the molar volumes of the solid reactants and products (see the Appendix and [22–24]), the molar volume difference for the reaction in Eq. (2) is: $\Delta\bar{V}_{A,\bar{S}} = 0.6987 \times 10^{-3}$ m^3/kg C$\bar{S}$H$_2$, and for the reaction in Eq. (3) is: $\Delta\bar{V}_A = (272.07 \times 10^{-6}$ m^3/gmol C$_4$AH$_{13}$ − 25.49 × 10^{-6} m^3/gmol A − 4 × 33.08 × 10^{-6} m^3/gmol CH)/(101.96 × 10^{-3} kgA/gmolA) = 1.1206 × 10^{-3} m^3/kg A. Thus, the final value of the porosity of the FL concrete, when Eq. (12) is satisfied, is given by Eq. (27):

$$\varepsilon = \varepsilon_{air} + W/\rho_w - (0.249 f_{C,c} - 0.1 f_{\bar{S},c}$$
$$+ 0.191 f_{S,c} + 1.059 f_{A,c} - 0.319 f_{F,c})$$
$$\times (C/1000) - (1.121\gamma_A f_{A,p})(P/1000)$$
(27)

According to Eq. (25) or (27), the porosity always decreases when FL replaces aggregates (C: constant). On the other hand, when FL replaces cement the porosity increases proportionally with the amount replaced.

4.4. Application

The model equations will be applied for the specimens of the present work (C, P, and W contents are given in Table 2). For cement: $f_{C,c} = 0.632$, $f_{S,c} = 0.201$, $f_{A,c} = 0.0425$, $f_{F,c} = 0.0349$, $f_{\bar{S},p} = 0.0288$, and $f_{R,c} = 0.0608$. For FL: $f_{S,p} = 0.535$, $f_{A,p} = 0.204$, and $\gamma_S = \gamma_A = 0.82$.

In almost all specimens (except FLA1), the gypsum content is lower than that required for complete reaction with A of cement and fly ash. Thus, the Eqs. (13) through (19) are mainly used. P_{max}/C is calculated as 0.24 kg FL/kg cement. By applying the above equations, the "final" composition of the FL specimens is given in Table 3. The calculated values of CH and H cannot completely be compared with the experimental values of 1-year hydration due to the relatively lower degree of pozzolanic reaction. However, the experimental values show a trend toward the theoretical values. For example, the experimentally determined CH content (98 kg/m^3) for the FLA1 specimen is close to the estimated one (91 kg/m^3). A higher deviation is observed for FLA2 and FLA3 specimens, where the fly ash content is higher. The only qualitative indication derived from the calculated H contents is that they follow the experimental trend presenting higher values than the control.

As was mentioned, if $P < (\gamma_S f_{S,p}/f_{S,c})P_{max}$ and for all cases of replacement, CSH content is higher than that of the control specimen. When FL replaces aggregates by 10, 20, and 30% (by weight of cement) then CSH increase is 22, 44, and 52%, respectively. When FL replaces cement by 10, 20, and 30%, then CSH increase is 12, 21, and 6%, respectively (it passes through a maximum, as the experimental results

Table 3
Final chemical (in kg/m^3) and volume composition of FL specimens

	Control (0% FL)	FLA1 (10% FL, aggr repl)	FLA2 (20% FL, aggr repl)	FLA3 (30% FL, aggr repl)	FLC1 (10% FL, cem repl)	FLC2 (20% FL, cem repl)	FLC3 (30% FL, cem repl)
CH	152	91	24	0	75	0	0
CSH	295	359	423	447	330	357	313
CA$\bar{\text{S}}$H	64	116	115	115	104	92	81
CAH	0	0	48	65	5	52	46
CAFH	92	92	92	92	82	73	64
R	39	45	65	105	42	64	120
H	126	137	150	155	124	124	109
ε (m^3/m^3)	0.141	0.131	0.121	0.118	0.143	0.146	0.160

aggr repl: aggregate replacement; cem repl: cement replacement.

also showed). These increases are roughly proportional to the strength results.

By applying Eq. (25), in the case of FLA1, and Eq. (27) in the other cases and for $\varepsilon_{air} = 0$, the "final" porosity of the FL specimens is given in Table 3. When FL replaces aggregates by 10, 20, and 30% (by weight of cement) then the porosity decreases by 7, 14, and 16%, respectively. When FL replaces cement by 10, 20, and 30%, then the porosity increases by 1, 3, and 13%, respectively.

5. Conclusions

1. When aggregates or cement are replaced by low-calcium fly ash (up to a certain level, P_{max}) higher strengths are observed. In the former case the strength enhancement is significantly higher and obvious 2–3 weeks after the mixing, whereas in the latter case the enhancement is much lower and obvious after 3 months. The final strength gain is roughly proportional to the content of active silica in the concrete volume.
2. FL reacts with the CH, binding small amounts of water and thus, in the case of aggregate replacement, gives higher bound water content and lower total porosity than the control specimen.
3. Using the experimental results and information from the literature, a first approximation of the reactions and products of FL in Portland cement systems was proposed.
4. Based on this reaction scheme, a theoretical model predicting the behavior of concrete containing FL was developed. This model comprises quantitative expressions for the estimation of the final chemical and volumetric composition of FL concrete. The experimental results referred to 1 year of hydration show a trend toward the theoretical values referred to infinite time.
5. Knowing these characteristics (CSH, CH, H content, and porosity), the concrete strength and durability can be determined indirectly. Intermediate values can be obtained using the presented experimental results. Thus, the model expressions can be applied in mix de-

sign and performance prediction of fly ash/Portland cement systems giving a first quantitative approximation.

Appendix

The weight fractions of the various phases (C$_3$S, C$_2$S, C$_3$A, C$_4$AF, C$\bar{\text{S}}$H$_2$) in Portland cement can be determined from the oxide analysis using Bogue's formulas [22; see Eqs. (A1) through (A5)]:

$$C_3S = 4.071(f_{C,c} - f_{Cf,c} - 0.7f_{\bar{S},c}) \\ - (7.60f_{S,c} + 6.72f_{A,c} + 1.43f_{F,c}) \tag{A1}$$

$$C_2S = 2.867f_{S,c} - 0.754(C_3S) \tag{A2}$$

$$C_3A = 2.65f_{A,c} - 1.692f_{F,c} \tag{A3}$$

$$C_4AF = 3.043f_{F,c} \tag{A4}$$

$$C\bar{S}H_2 = 2.15f_{\bar{S},c} \tag{A5}$$

Although the chemical reactions of hydration of these phases are complex and do not proceed to completion, a simplified view may be presented as follows [21,22; see Eqs. (A6) through (A9)]:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{A6}$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \tag{A7}$$

$$C_3A + C\bar{S}H_2 + 10H \rightarrow C_4A\bar{S}H_{12} \tag{A8}$$

$$C_4AF + 2CH + 10H \rightarrow C_6AFH_{12} \tag{A9}$$

These reactions are valid in an excess of gypsum [i.e., when $C\bar{S}H_2 > 0.637C_3A$ or, equivalently, $f_{\bar{S},C} > (0.786f_{A,C} - 0.501f_{F,C})$; as applies in typical Portland cements]. Using the stoichiometry of these reactions and the molar weights of the reactants and products (given in Table A1), the amounts of the finally produced compounds can be estimated. Eqs. (A1) through (A5) can be used to express these amounts as a function of the oxide contents in cement. Thus, the amounts of CH, $C_3S_2H_3$ (CSH), $C_4A\bar{S}H_{12}$ (CA$\bar{S}$H), C_6AFH_{12} (CAFH), remaining constituents (R), and chemically bound water (H) are given as follows, in kg/m³ of concrete [see Eqs. (A10) through (A15)]:

$$CH = \{1.321(f_{C,c} - 0.7f_{\bar{S},c}) \\ - (1.851f_{S,c} + 2.182f_{A,c} + 1.392f_{F,c})\}C \quad (A10)$$

$$CSH = 2.85f_{S,c}C \quad (A11)$$

$$CA\bar{S}H = (6.106f_{A,c} - 3.898f_{F,c})C \quad (A12)$$

$$CAFH = 5.099f_{F,c}C \quad (A13)$$

$$R = (f_{R,c} + 1.7f_{\bar{S},c} - 1.689f_{A,c} + 1.078f_{F,c})C \quad (A14)$$

$$H = \{0.321(f_{C,c} - 0.7f_{\bar{S},c}) \\ + 1.236f_{A,c} - 0.113f_{F,c}\}C \quad (A15)$$

In the above equations, free CaO was assumed to be completely converted to CH, whereas the remaining oxides (MgO, Na_2O, K_2O) was assumed not to participate in the reactions.

Table A1
Molar weights and volumes of the main compounds found in Portland cement and Portland cement-based binders[a]

Compound	Molar weight $\times$ 10^3 (kg/gmol)	Density $\times$ 10^{-3} (kg/m³)	Molar volume $\times$ 10^6 (m³/gmol)
C_3S	228.30	3.20	71.34
C_2S	172.22	3.30	52.19
C_3A	270.18	3.03	89.17
C_4AF	485.96	3.77	128.90
$C\bar{S}H_2$	172.17	2.32	74.21
H	18.02	1.00	18.02
CH	74.10	2.24	33.08
$C_3S_2H_3$	342.41	$\approx$2.28	$\approx$150
$C_4A\bar{S}H_{12}$	622.51	1.95	319.24
C_4AH_{13}	560.47	2.06	272.07
$C_3A \cdot 3C\bar{S} \cdot H_{32}$	1255.13	1.78	705.13
C_6AFH_{12}	814.31	2.65	307.87
$C_8AF\bar{S}_2H_{24}$	1302.44	$\approx$2.3	$\approx$560
C_8AFH_{26}	1178.29	$\approx$2.3	$\approx$500
$C\bar{C}$	100.09	2.71	36.93
C	56.08	3.32	16.89
S	60.08	2.20	27.28
A	101.96	4.00	25.49
F	159.69	5.24	30.48
$\bar{S}$	80.07	–	–

[a] Values taken from refs. [22–24].

References

[1] R. Sersale, Aspects of the chemistry of additions, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, New York, 1983, p. 537.

[2] P.K. Mehta, Pozzolanic and cementitious by-products in concrete—Another look, in: Proceedings of the 3d International Conference on the Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, ACI SP-114, Trondheim, 1989, p. 1.

[3] ACI Committee 226, Use of fly-ash in concrete, ACI Mater J 84 (1987) 381.

[4] RILEM 73-SBC Committee, Siliceous by-products for use in concrete, Mater and Struct Jan. (1988) 69.

[5] F. Massazza, Pozzolanic cements, Cem Concr Comp 15 (1993) 185.

[6] A.M. Neville, Properties of concrete, Longman, Essex, 1995.

[7] V.G. Papadakis, M.N. Fardis, C.G. Vayenas, Hydration and carbonation of pozzolanic cements, ACI Mater J 89 (1992) 119.

[8] V.G. Papadakis, Experimental investigation and theoretical modeling of silica fume activity in concrete, Cem Concr Res 29 (1999) 79.

[9] G.J. McCarthy, J.K. Solem, O.E. Manz, D.J. Hasset, Use of a database of chemical, mineralogical and physical properties of North American fly ash to study the nature of fly ash and its utilization as a mineral admixture in concrete, Mat Res Soc Symp 178 (1990) 3.

[10] S. Urhan, Alkali silica and pozzolanic reactions in concrete. Part 1: Interpretation of published results and a hypothesis concerning the mechanism, Cem Concr Res 17 (1987) 141.

[11] A.L.A. Fraay, J.M. Bijen, Y.M. de Haan, The reaction of fly ash in concrete. A critical examination. Cem Concr Res 19 (1989) 235.

[12] Y. Maltais, J. Marchand, Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars, Cem Concr Res 27 (1997) 1009.

[13] A. Katz, Microscopic study of alkali-activated fly ash, Cem Concr Res 28 (1998) 197.

[14] G.J. McCarthy, K.D. Swanson, L.P. Keller, W.C. Blatter, Mineralogy of western fly ash, Cem Concr Res 14 (1984) 471.

[15] P.C. Aitcin, F. Autefage, A. Carles-Gibergues, A. Vaquier, Comparative study of the cementitious properties of different fly ashes, in: Proceedings of the 2d International Conference on the Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, ACI SP-91, Madrid, 1986, p. 91.

[16] M. Atkins, D.E. Macphee, F.P. Glasser, Chemical modeling in blended cement systems, in: Proceedings of the 3d International Conference on the Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, ACI SP-114, Trondheim, 1989, p. 73.

[17] D.M. Roy, Fly ash and silica fume chemistry and hydration, in: Proceedings of the 3d International Conference on the Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, ACI SP-114, Trondheim, 1989, p. 117.

[18] E.E. Berry, R.T. Hemmings, W.S. Langley, G.G. Carette, Beneficiated fly ash: Hydration, microstructure, and strength development in Portland cement systems, in: Proceedings of the 3d International Conference on the Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, ACI SP-114, Trondheim, 1989, p. 241.

[19] M.P. Luxan, M.I. Sanchez de Rojas, M. Frias, Investigations on the fly ash: Calcium hydroxide reactions, Cem Concr Res 19 (1989) 69.

[20] C. He, B. Osbaeck, E. Makovicky, Pozzolanic reactions of six principal clay minerals: Activation, reactivity assessments and technological effects, Cem Concr Res 25 (1995) 1691.

[21] J. Bensted, Hydration of Portland cement, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, New York, 1983, p. 307.

[22] F.M. Lea, The Chemistry of Cement and Concrete, Edward Arnold Ltd., London, 1970.

[23] H.M. Jennings, The developing microstructure in Portland cement, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, New York, 1983, p. 537.

[24] R.H. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, McGraw-Hill, New York, 1984.