



# Effect of fly ash on Portland cement systems Part II. High-calcium fly ash

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## Abstract

A high-calcium fly ash (FH, 23% total CaO–5% free CaO), with high SO<sub>3</sub> content (4.3%), was studied as additive in mortar, replacing part of the volume either of Portland cement or aggregate. The development of the strength, porosity, bound water, and calcium hydroxide content was measured. When this fly ash replaces aggregate, significantly higher strengths were observed from the beginning of the hydration, as well as higher water binding and significantly lower porosity. In the case of cement replacement, the strength remained constant. A simplified scheme describing the chemical reactions of the FH in hydrating Portland cement is proposed and applied to develop mathematical expressions for reaction products and porosity estimation. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Concrete; High-calcium fly ash; Modeling; Reaction

## 1. Introduction

High-calcium fly ash (FH) is the combustion residue in electric power plants burning lignite or sub-bituminous coal. It essentially consists of aluminosilicate glass modified by the presence of large amounts of calcium and magnesium. It can be categorized as cementitious material when CaO is greater than 20%, or as cementitious and pozzolanic material when CaO varies between 10% and 20% [1]. A pozzolanic material requires Ca(OH)<sub>2</sub> (CH) in order to form strength-producing products (pozzolanic activity); whereas a cementitious material contains quantities of CaO and can exhibit a self-cementitious (hydraulic) activity. Usually, the CaO content in these materials is not enough to react with all the quantity of the pozzolanic compounds; thus, they also exhibit pozzolanic activity (pozzolanic and cementitious materials). However, these materials are used in combination with Portland cement, which yields on its hydration the CH essential for their activation.

The literature is rich in publications regarding the effect of fly ashes, especially of low-calcium fly ash (FL; CaO less than 10%), on concrete [1–5]. Whereas the use of FL in concrete is a common practice, FH suitability for concrete is still anticipated with skepticism [6]. This is mainly due to problems associated with its chemical composition (high free CaO and sulfur content), which may affect volume stability and concrete durability [7]. In addition, the usual problems associated with any kind of fly ash, such as variation in chemical composition, particle size, water demand, rate of setting, etc., increase the risk of unpredictable performance and low durability. However, the self-cementitious capacity of FH results in early strength development and, with correct proportioning, in economy and concrete quality [6,8].

Whereas experimental results on the effect of supplementary cementing materials abound in the literature, efforts in the direction of theoretical approach of their activity in Portland cement systems are very limited [9,10]. The present author, in two previous publications [11,12] presented a theoretical modeling of silica fume (SF) and FL activity in concrete, in terms of chemical reactions.

In this paper, an experimental investigation of the activity of FH in Portland cement systems is carried out, and a first theoretical approach is presented. The case of FH is more complex than SF and FL due to simultaneous pozzolanic and

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Table 1  
Physical and chemical characteristics of cement and FH<sup>a</sup>

	Cement	Non-pulverized FH	Pulverized FH
<i>Physical properties</i>			
BET specific surface (m <sup>2</sup> /g)	1.3	4.2	6.2
Particle mean diameter (μm)	14.0	22.9	12.6
Density (kg/m <sup>3</sup> )	3130	2428	2660
<i>Chemical analysis (%)</i>			
SiO <sub>2</sub>	20.10	39.50	39.21
Al <sub>2</sub> O <sub>3</sub>	4.25	16.30	16.22
Fe <sub>2</sub> O <sub>3</sub>	3.49	6.67	6.58
CaO	63.20 (1.48 free)	22.77 (4.81 free)	22.78 (5.18 free)
SO <sub>3</sub>	2.88	4.30	4.30
LOI	0.86	1.74	2.10
<i>Mineralogical characteristics</i>			
Insoluble residue (%)	0.14	31.29	30.88
Glass phase content (%)	–	65	50

<sup>a</sup> The BET area (method of Brunauer, Emmett, and Teller) was determined by the N<sub>2</sub> adsorption method, the particle size by the sedimentation technique, and the density by air pycnometry. The methods specified by the European Standards, EN-450, EN-196, and EN-451 were followed for chemical analyses. The insoluble residue was determined by EN-196-2. The glass phase content was determined by optical microscopy.

cementitious activity of this type of fly ash. However, this attempt may be beneficial for the utilization of a rather questionable industrial by-product.

## 2. Experimental

### 2.1. Materials

An FH, produced in Greece (Public Power, Ptolemais), was used. This specific FH contains high content of calcium (23% CaO) and sulfates (4.3% SO<sub>3</sub>). The free lime content is almost one fourth of the total CaO content (5.2%). Prior to use, FH was pulverized to meet the cement mean particle size. A rapid setting Portland cement was used (400 m<sup>2</sup>/kg Blaine's fineness). Normal graded sand (2670 kg/m<sup>3</sup> density) and a common plasticizer were used for mortar preparation. The physical and chemical characteristics of the materials are given in Table 1. Cement particles as examined by SEM have irregular

polygonal shape (Fig. 1). Many of the FH particles, before grinding, were plerospheres containing numerous smaller particles. Grinding of FH reduced the particle size, broke up cenospheres, and released smaller particles contained in plerospheres. These should be the reasons for glass phase decrease from 65% to 50% following grinding. The particle shape in the latter case became similar to that of the cement particles (Fig. 1).

### 2.2. Mixture proportions and experimental program

An experimental program similar to that applied for the case of SF [11] was developed. The program included measurements of compressive strength, CH, bound H<sub>2</sub>O (H), porosity, pore volume distribution (PVD), and microscopy observations. A volume unit (1 m<sup>3</sup>) of the fresh or hardened mortar was used as a common comparison basis.

The mixture proportions are given 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. Two

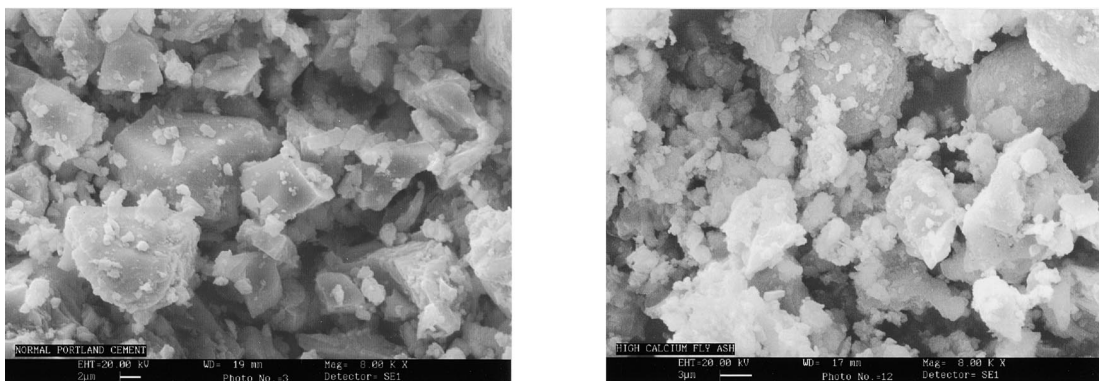


Fig. 1. SEM micrographs (8000×) of Portland cement (left) and pulverized FH (right).

Table 2  
Absolute and relative mixture proportions for mortar specimens<sup>a</sup>

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
FHA1	514.6	257.4	51.5	1492.1	0.50	0.10	2.90
FHA2	514.6	257.4	102.9	1440.5	0.50	0.20	2.80
FHA3	514.6	257.4	154.4	1388.8	0.50	0.30	2.70
FHC	411.7	257.4	102.9	1528.3	0.625	0.250	3.71

<sup>a</sup> C, W, P, A: kg of cement, water, FH and aggregate, respectively, per cubic meter of total mortar volume; W/C, P/C, A/C: the water–cement, FH–cement and aggregate–cement ratio (by weight), respectively.

different cases were studied: FH to replace either equal volume of aggregate or cement. In the former case, three contents of FH were selected: 10%, 20%, and 30% addition to the cement weight giving specimens FHA1, FHA2, and FHA3, respectively. In the latter case, a 20% replacement of the control cement weight, giving specimen FHC, was selected.

The specimen preparation and the experimental techniques are described in detail elsewhere [11]. The specimens for strength measurements were prisms of  $40 \times 40 \times 160$  mm, cured under lime-saturated water at 20°C, and tested after 3, 14, 28, 49, 91, 182, and 364 days. FH–cement pastes were also prepared, representing the paste matrix of the mortar specimens, and analyzed for CH content, chemically bound water content (denoted 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 multiplying by the appropriate paste/mortar volume fraction. The paste properties may not be necessarily proportional to mortar properties. The experiments are more precise when performed in pastes rather than mortars.

### 3. Results and discussion

#### 3.1. Strength results

In Fig. 2, the compressive strength results from all tested mortars are presented. It should be noted that all results have been reduced to a common air content (3.3%). In the case of aggregate replacement by FH, significantly higher strength values are observed compared to controls. This strength enhancement is proportional to the FH content (10%, 20%, or 30% relative to cement). The FH activity seems to start from the beginning of the hydration. It must also be emphasized that the fly ash has been pulverized and, therefore, its pozzolanic–cementitious activity accelerated. The strength gain for the FHA2 specimen is about 31% in the first 3 days of hydration and 26% after 1 year. This high early strength should be correlated not only to the grinding process but also to the self-cementitious activity of FH. The free lime content seems to contribute to early strengths, because a reduction of these is observed by a partial hydration of FH before mixing [6].

The total strength enhancement is due to FH activity products, mainly to calcium silicate hydrate (C-S-H), as a relatively high SiO<sub>2</sub> content is observed (about 40%). Even in the case when 50% of this amount is active (glass content), such a content is still considerable, especially when it can be used from the beginning of hydration. Calcium aluminate or sulfo-aluminate products also participate in this enhancement due to their filling properties [8].

When FH replaces cement (20%), the strength is slightly reduced in the first days. As time proceeds, FHC strengths are closer to the control's, and are almost identical after 49 days. This behavior strengthens the above conclusions regarding the initiation and the development of the FH activity.

#### 3.2. Physicochemical results

The H content (kg H/m<sup>3</sup> mortar) and the total porosity  $\epsilon$  (m<sup>3</sup> of pores/m<sup>3</sup> mortar) of the control and FHA specimens are presented in Fig. 3. A higher H content and a lower porosity is observed for all FHA specimens compared to the corresponding control values, from the initiation of the cement hydration. This increase in H values or the similar decrease in porosity values is almost

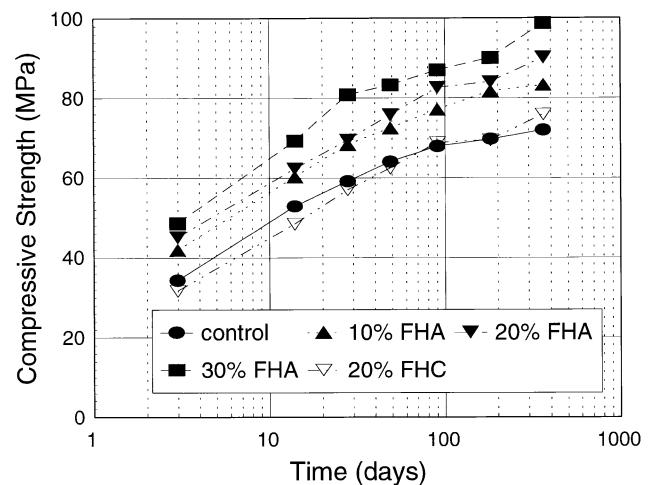


Fig. 2. Compressive strength development of mortars when FH replaces aggregate (FHA: 10%, 20%, and 30% addition to the cement weight) or cement (FHC: 20% cement replacement).

proportional to the fly ash content in the specimen. This behavior can be partly explained as due to the presence of free CaO in the FH, which reacts rapidly with water to give calcium hydroxide, almost doubling its volume. Also significant is the contribution of the hydration of the tricalcium aluminate present in FH. Moreover, the presence of other compounds, except silica [11], leads to further increase of H content and decrease of porosity with time. The early formation of water-rich and pore-filling ettringite and its subsequent transformation to other hydrates contribute significantly to the increased hydration and decreased porosity.

The CH content (kg CH/m<sup>3</sup> mortar) for the control and FHA specimens is given in Fig. 4. 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 FHA specimens presents a rather complicated picture due to the simultaneous CH production from the CaO hydration and CH consumption from other phases of the FH. In the first

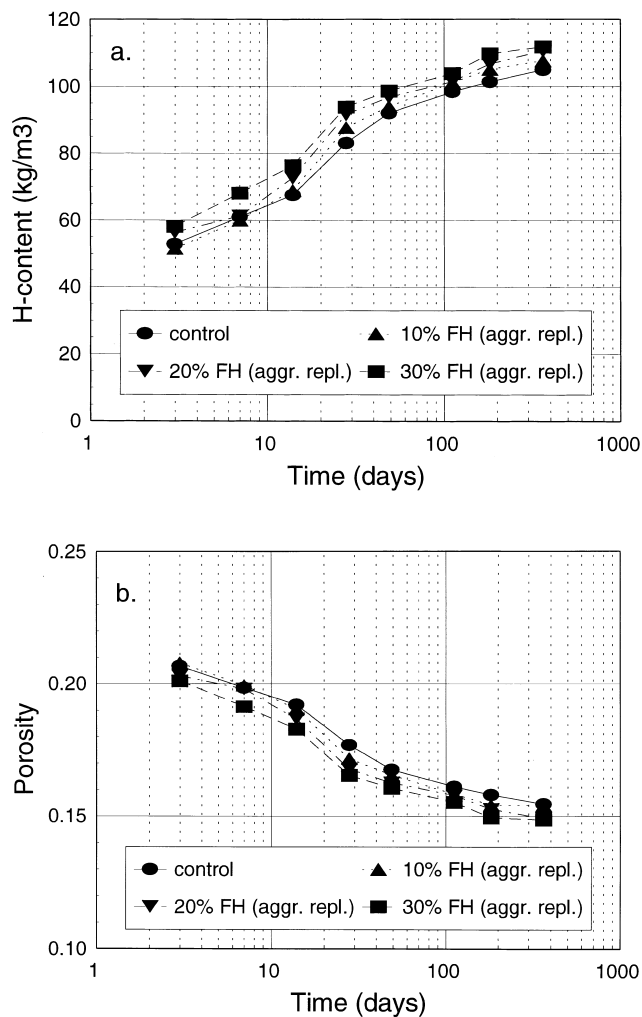


Fig. 3. Development of bound (a) water content and (b) porosity in mortars with FH to replace aggregate (0%, 10%, 20%, and 30% addition to the cement weight).

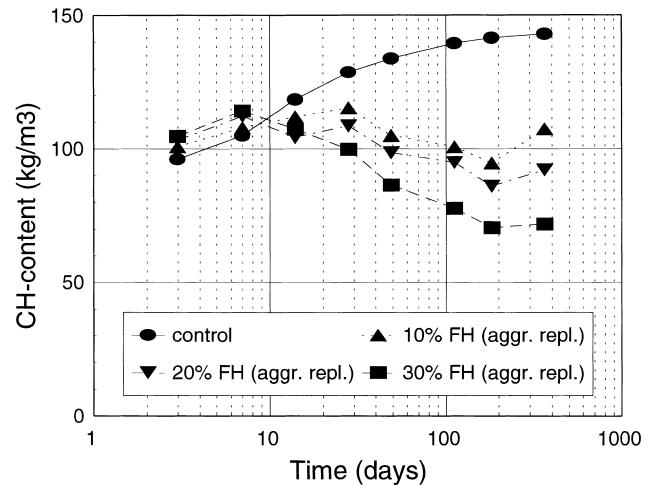


Fig. 4. Development of calcium hydroxide content in mortars with FH to replace aggregate (0%, 10%, 20%, and 30% addition to the cement weight).

week, CH contents are higher in fly ash specimens, due to the rapid free CaO hydration. These CH contents pass through a maximum, due to higher CH production, but afterwards decrease, as the FH–CH reaction proceeds at higher rates.

In Fig. 5, typical SEM images of 20% FH–cement paste at different times of hydration are presented. From the beginning (3 days), reaction products are observed on the surface of the FH particles. However, after 2–3 weeks, FH particles are difficult to identify in the created microstructure. After a longer time (6 months), a dense structure has formed.

The volume of micropores (pores with diameter less than 200 Å) of well-hydrated pastes (6 months) was measured using N<sub>2</sub> adsorption. This quantity (cm<sup>3</sup>/g) was converted to content of micropores in the total pore volume. FHA2 specimen was found to have higher micropore content (9%) comparing to the control (6%), and taking into account its lower total porosity, it is established as a denser and finer microstructure.

#### 4. Theoretical approach of the FH activity in Portland cement systems

##### 4.1. Reactions and products

FH has a composition closer to the Portland cement than FL or SF. Although the FH constituents are generally non-stoichiometric, as well as their hydration products in the presence of CH, simplifying assumptions are made herein for modeling purposes. As given in Section 2.1, an oxide analysis of this FH is: SiO<sub>2</sub> (S), 39.2%; Al<sub>2</sub>O<sub>3</sub> (A), 16.2%; Fe<sub>2</sub>O<sub>3</sub> (F), 6.6%; CaO (C), 22.8%; and SO<sub>3</sub> (S), 4.3%. About one-fourth of the total CaO is free CaO (5.2%). The glass phase content was found to be 50%.

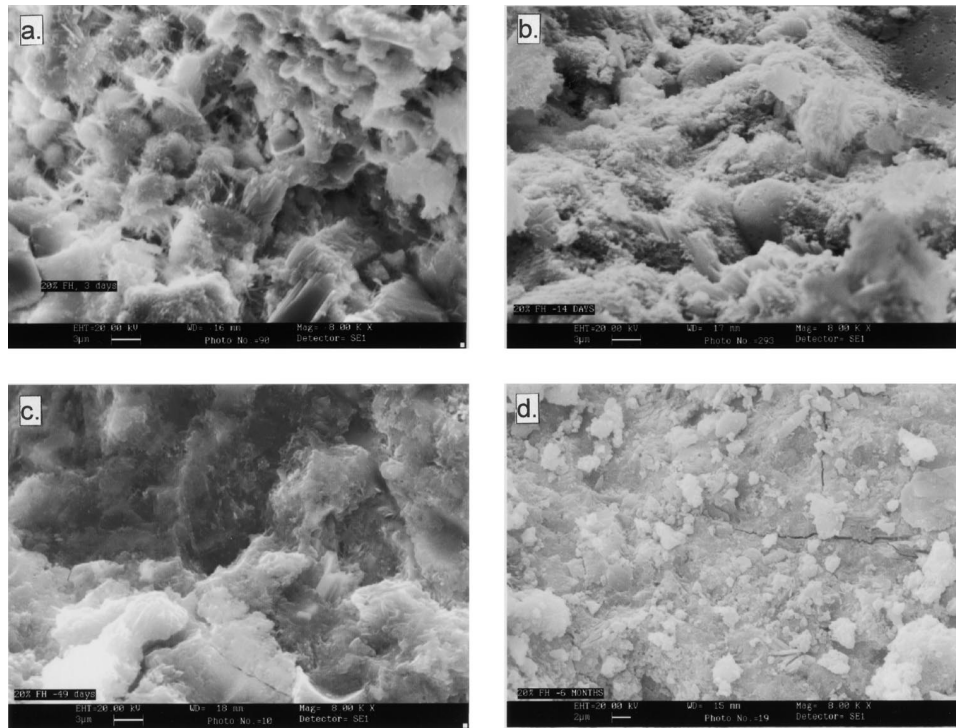


Fig. 5. Scanning electron micrographs (8000 ×) of 20% FH–cement paste after (a) 3, (b) 14, (c) 49, and (d) 182 days of hydration.

With all of these constituents present, FH hydration together with Portland cement is more complicated than SF or FL due to simultaneous pozzolanic and cementitious reactions. An attentive examination of the principal phases in FH and their hydrates, through literature survey [1,2,6,13–16], will contribute in the proposal of a quantitative reaction scheme.

The majority of the reactive part of silica in FH is present in aluminosilicate (A-S) and calcium aluminosilicate (C-A-S) glass. Small amounts of dicalcium silicate ( $C_2S$ ) have also been reported. The non-reactive part of silica is present in quartz or in crystalline A-S phases. Calcium silicate hydrate (C-S-H) is formed from the pozzolanic action of the reactive silica of FH, which, as was found earlier [11] using almost pure SF, can be described as a first approximation as follows:

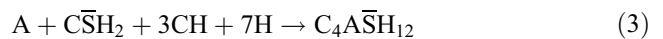


Part of alumina, found as tricalcium aluminate ( $C_3A$ ) and monocalcium aluminosulfate ( $C_4A_3\bar{S}$ ), reacts with water, CH, and/or gypsum, as in cement hydration, showing these high early strengths. This reaction in an excess of sulfate ions (as applies in this case) can be described, totally, as follows [17]:



The crystalline part of alumina found in corundum and  $A_3S_2$  will not react. The rest of the alumina present in A-S

and C-A-S glass is expected to react according to the following equations found to apply in the case of FL [12]:



The above conclusions are supported by the fact that the non-carbonated products of FH–CH reactions relating with alumina are found to be mainly  $C_4AH_{13}$ ,  $C_4A\bar{S}H_{12}$ ,  $C_3A \cdot 3C\bar{S} \cdot H_{32}$ , and  $C_3AH_6$  [1,6,13–16]. From these products, ettringite and tricalcium aluminate hydrate formed initially, and as time proceeds, converted into the most stable Ca-monosulfoaluminate and tetracalcium aluminate hydrates. These products contain additional quantities of water and, thus, the higher H contents and the lower porosity found in this case can be explained.

Regarding calcium, the majority is present in crystalline and reactive constituents, such as  $C_3A$ ,  $C_4A_3\bar{S}$ ,  $C\bar{S}$ , free CaO, and C-A-S glass. The free CaO is hydrated rapidly to CH, i.e.:



the gypsum ( $C\bar{S}$ ) participates in reactions with alumina and the remaining phases are hydrated as described above. As referred [1,13], most of the iron is in crystalline phases hematite and/or magnetite, and does not participate in the reactions.

According to the above analysis, the most possible simplified equations that can describe the pozzolanic acti-

vity of the FH are given by Eqs. (1)–(5). Especially, for this particular FH of high  $\bar{S}$  content, glass A will react (totally) according to Eq. (3). The extremely high H content observed must be correlated not only to the free CaO hydration, but also to the high ettringite formation. Afterwards, this ettringite is expected to convert gradually to monosulfate as additional Al is liberated from FH glass.

#### 4.2. Determination of chemical and volumetric composition

One common reference basis is used in these calculations: 1 m<sup>3</sup> of concrete (or mortar), which contains: C, W, A, and P kg of Portland cement, water, aggregate, and pozzolan (FH), respectively. In the case when a blended cement is used, the part of the pozzolan must be considered in the P content.

The Portland cement and FH can be analyzed in terms of oxides: total CaO (C), SiO<sub>2</sub> (S), Al<sub>2</sub>O<sub>3</sub> (A), Fe<sub>2</sub>O<sub>3</sub> (F), SO<sub>3</sub> ( $\bar{S}$ ), and other oxides or impurities denoted by R. Let us denote by  $f_{i,c}$  and  $f_{i,p}$  the weight fractions of the constituent  $i$  ( $i=C, S, A, F, \bar{S}, R$ ) in the cement and FH, respectively. As was referred, not all of the total mass of the oxide  $i$  in a pozzolan is active, only the glass phase; with the exception of calcium constituents where crystalline phases are also active (C<sub>3</sub>A, free CaO, etc.). Let us denote by  $\gamma_i$  the weight fraction of the oxide  $i$  in the pozzolan, which contributes to the pozzolanic reactions (“activity” ratio). In the case of FH, the weight fractions of S, A, and C in fly ash,  $f_{S,p}$ ,  $f_{A,p}$ , and  $f_{C,p}$  and their active part,  $\gamma_S$ ,  $\gamma_A$ , and  $\gamma_C$ , respectively, are required for quantitative calculations. As was discussed above, the ratio  $\gamma_C$  can be considered equal unity in good approximation. Finally, the weight fraction of sulfates in fly ash,  $f_{\bar{S},p}$ , is considered in the calculations.

In previous publications [11,12], the cement hydration reactions and a quantification of the final products in a Portland cement concrete were presented in detail. When FH is used, in addition to Portland cement hydration reactions, pozzolanic reactions (Eqs. (1)–(5)) take place. For an FH of high  $\bar{S}$  content, the gypsum content is higher than that required for complete hydration of the cement and complete pozzolanic reaction, and thus the reaction given by Eq. (4) does not take place. Taking into account the stoichiometry of the pozzolanic 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 completion of the hydration and pozzolanic activity). These amounts of CH, C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> (CSH), C<sub>4</sub>A $\bar{S}$ H<sub>12</sub> (CASH), C<sub>6</sub>AFH<sub>12</sub> (CAFH), rest constituents (R), and bound water (H) are given in Eqs. (6)–(11) (in kg/m<sup>3</sup> of concrete):

$$\begin{aligned} \text{CH} = & \{1.321(f_{C,c} - 0.7f_{\bar{S},c}) - (1.851f_{S,c} + 2.182f_{A,c} \\ & + 1.392f_{F,c})\}C + \{1.321(f_{C,p} - 0.7f_{\bar{S},p}) \\ & - (1.851\gamma_S f_{S,p} + 2.182\gamma_A f_{A,p})\}P \end{aligned} \quad (6)$$

$$\text{CSH} = 2.85(f_{S,c}C + \gamma_S f_{S,p}P) \quad (7)$$

$$\text{CASH} = (6.106f_{A,c} - 3.898f_{F,c})C + 6.106\gamma_A f_{A,p}P \quad (8)$$

$$\text{CAFH} = 5.099f_{F,c}C \quad (9)$$

$$\begin{aligned} R = & (f_{R,c} + 1.7f_{\bar{S},c} - 1.689f_{A,c} + 1.078f_{F,c})C \\ & + (1 - \gamma_S f_{S,p} - 2.689\gamma_A f_{A,p} - f_{C,p} + 0.7f_{\bar{S},p})P \end{aligned} \quad (10)$$

$$\begin{aligned} H = & \{0.321(f_{C,c} - 0.7f_{\bar{S},c}) + 1.236f_{A,c} - 0.113f_{F,c}\}C \\ & + \{0.321(f_{C,p} - 0.7f_{\bar{S},p}) + 1.236\gamma_A f_{A,p}\}P \end{aligned} \quad (11)$$

For the completion of the pozzolanic activity, the left-hand side of Eq. (6) 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. (6), the maximum pozzolan content, which can react with all lime produced during cement hydration,  $P_{\max}$ , can be obtained using Eq. (12):

$$\begin{aligned} P_{\max} = & \{1.321(f_{C,c} - 0.7f_{\bar{S},c}) - (1.851f_{S,c} + 2.182f_{A,c} \\ & + 1.392f_{F,c})\}C / \{1.321(f_{C,p} - 0.7f_{\bar{S},p}) \\ & - (1.851\gamma_S f_{S,p} + 2.182\gamma_A f_{A,p})\} \end{aligned} \quad (12)$$

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

As can be observed from the above equations, the CSH content increases with FH addition, always when FH replaces aggregates, and only if  $\gamma_S f_{S,p}$  is higher than  $f_{S,c}$  when FH replaces cement. The H content when FH replaces aggregates (C: constant) increases significantly, primarily due to the calcium content of the FH and secondly due its active alumina content. Obviously, Eq. (13) must be satisfied:

$$\text{CH} + \text{CSH} + \text{CASH} + \text{CAFH} + R = C + P + H \quad (13)$$

The concrete porosity,  $\varepsilon$ , can be estimated by Eq. (14):

$$\varepsilon = \varepsilon_{\text{air}} + W/\rho_w - \Delta\varepsilon_h - \Delta\varepsilon_p - \Delta\varepsilon_c \quad (14)$$

where  $\varepsilon_{\text{air}}$  is the volume fraction of entrapped or entrained air in concrete,  $\rho_w$  the water density (1000 kg/m<sup>3</sup>) 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 [11]. In the same publication, the porosity reduction due to the pozzolanic reaction of S, Eq. (1), was found to be equal to zero. The porosity reduction because of the pozzolanic reaction of FH is attributed to the reactions in Eqs. (2)–(5). If the gypsum content is higher than the maximum required, then the term  $\Delta\varepsilon_p$  can be calculated using Eq. (15):

$$\Delta\varepsilon_p = (\gamma_A f_{A,p}P)\Delta\bar{V}_{A,\bar{S}} + (f_{C,p} - 0.7f_{\bar{S},p})\Delta\bar{V}_C \quad (15)$$

where  $\Delta\bar{V}_{A,\bar{S}}$  and  $\Delta\bar{V}_C$  are the molar volume differences for the reactions in Eqs. (3) and (5), respectively (equal to  $1.18 \times 10^{-3}$  and  $0.289 \times 10^{-3}$  m<sup>3</sup>/kg, respectively [12]). By substituting the  $\Delta\varepsilon_h$  and  $\Delta\varepsilon_p$  terms in Eq. (14), the final

Table 3  
Final chemical (in kg/m<sup>3</sup>) and volume composition of FH specimens

	Control (0% FH)	FHA1 (10% agg)	FHA2 (20% agg)	FHA3 (30% agg)	FHC1 (10% cem)	FHC2 (20% cem)	FHC3 (30% cem)
CH	152	126	100	74	111	70	29
CSH	295	335	376	417	306	317	328
CAŠH	64	100	136	172	93	130	153
CAFH	92	92	92	92	82	73	64
R	39	50	61	72	46	53	61
H	126	137	147	158	124	122	120
$\varepsilon$ (m <sup>3</sup> /m <sup>3</sup> )	0.141	0.128	0.115	0.102	0.140	0.138	0.137

agg: aggregate replacement; cem: cement replacement.

value of the porosity of a non-carbonated FH concrete is given by:

$$\varepsilon = \varepsilon_{\text{air}} + W/\rho_w - 0.249(f_{C,c} - 0.7f_{S,c}) + 0.191f_{S,c} \quad (16)$$

$$+ 1.118f_{A,c} - 0.357f_{F,c} \} (C/1000)$$

$$- \left\{ 0.289(f_{C,p} - 0.7f_{S,p}) + 1.18\gamma_A f_{A,p} \right\} (P/1000)$$

According to Eq. (16), porosity always decreases when FH replaces aggregates. When FH replaces cement the porosity will rather remain the same as the following application show.

#### 4.3. Application

The mixtures of the present work are used (C, P and W contents are given in Table 2). For cement:  $f_{C,c} = 0.632$ ,  $f_{S,c} = 0.201$ ,  $f_{A,c} = 0.0425$ ,  $f_{F,c} = 0.0349$ ,  $f_{S,c} = 0.0288$ , and  $f_{R,c} = 0.0608$ . For FH:  $f_{S,p} = 0.3921$ ,  $f_{A,p} = 0.1622$ ,  $f_{C,p} = 0.2278$ , and  $f_{S,p} = 0.043$ . Because the F content of FH is assumed to be crystalline and assuming that all calcium constituents belong to non-glass content, the remaining constituents will have a glass content of  $50/(100 - 6.58 - 22.78) = 70.8\%$ . Therefore, it can be supposed, as a rough approximation, that  $\gamma_S = \gamma_A = 0.71$ .

$P_{\text{max}}/C$  is calculated as 0.5 kg FH/kg cement. By applying the above equations, the “final” composition of the FH specimens is given in Table 3. The calculated values of CH and H are not highly correlated with the experimental values for 1-year hydration, due to the relatively lower degree of pozzolanic reaction. However, they show a trend towards the theoretical values. Moreover, H contents for FHA specimens are always much higher than the controls.

When FH replaces aggregates by 10%, 20%, and 30% (by weight of cement) then the model predicts CSH increases of 13.8%, 27.6%, and 41.4%, respectively. When FH replaces cement by 10%, 20%, and 30%, then CSH increases are 3.8%, 7.6%, and 11.4%, respectively. These increases are proportional with the increases in strength results.

By applying Eq. (16) and for  $\varepsilon_{\text{air}} = 0$ , the “final” porosity of the FH specimens is given in Table 3. When FH replaces aggregates by 10%, 20%, and 30% (by weight

of cement) then the porosity decreases by 9.3%, 18.6%, and 27.8%, respectively. When FH replaces cement by 10%, 20%, and 30%, then the porosity decreases by 1.1%, 2.1%, and 3.1%, respectively.

## 5. Conclusions

(1) In the case when aggregates are replaced by FH (up to a certain level, about 50% of the cement weight), higher strengths are observed. The strength enhancement is obvious almost directly after the mixing (for pulverized fly ash). The final strength gain is roughly proportional to the content of active silica in the mortar volume.

(2) In the case where Portland cement is replaced by FH, the final strength will exceed that of the control only if the content of active silica in the fly ash is higher than that in the cement. In this case of tested fly ash, similar strengths are observed due to almost equal active silica content.

(3) The reaction of FH in hydrating cement is followed from high water binding and, thus, lower porosity is created. This behavior is due to the high content of reactive calcium-bearing phases in fly ash.

(4) Using the experimental results and information from the literature, a first approximation of the reactions and products of FH in Portland cement systems was proposed. Based on this reaction scheme, theoretical expressions predicting the chemical and volumetric composition of FH concrete were proposed.

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