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Mechanical and durability characteristics of gypsum-free blended cements incorporating sulphate-rich reject fly ash

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Abstract

To accommodate the wide variations among the different types of fly ash and the growing need for its greater utilization in the construction sector, relevant standards have been established that differentiate the appropriate qualities from the unacceptable ones. Unfortunately, potentially reject fly ashes (rFA), which do not comply with standard requirements, comprise a significant part of the total amount produced in coal or lignite burning stations. High-sulphate fly ash (HSFA) is a typical example of reject material, since all relevant standards (both European and ASTM) clearly define that sulphur trioxide should be kept under a certain low limit (approximately 3–5% depending on the standard) or else concrete's durability may be threatened. The aim of this work was to design, produce and monitor the properties of a series of blended cements prepared by mixing clinker with a fly ash of high-sulphate content. No gypsum was added in the mixtures, since it is believed that sulphate ions necessary for the prolongation of the setting process (commonly provided by gypsum) could be provided by fly ash enriched in sulphates. All samples tested exhibited satisfactory initial and final setting times as well as decent compressive strength values when compared to the reference specimen containing only gypsum and no fly ash. Additionally, this paper reports on the performance aspects of blended pastes exposed to chloride binding tests and aggressive (a) 2% H_2SO_4 and (b) simulated marine environment solutions. Results revealed that waste materials not up to relevant standards could still contribute to the production of quality products of energy and economical efficiency.

Keywords: Reject fly ash; Gypsum-free blended cement; Active silica; *k*-value; Gel/space ratio; Chloride binding capacity; Sulphate resistance

1. Introduction

By blending cement with fly ash a significant number of mortar and concrete properties is improved both in the fresh and hardened state. Given the variation among the kinds of fly ashes produced globally, relative standards containing specific requirements for their usage have been issued. Still in many countries, fly ashes with characteristics that do not conform to these specifications are produced. Not being utilized, such ashes are either landfilled, or used in land reclamation applications adjacent to the power stations [1,2]. Practically, apart from the ecological aspect, a large amount of potentially virtuous material is dumped without fully exploring the possibilities for its reuse in advanced applications. The need for the industry to minimize risks when incorporating such highly variable, heterogeneous materials is understandable, but so is the necessity for exploiting the full potential of waste materials with well established assets. This need becomes even more imperative when considering the increasing environmental awareness of the stakeholders and public, as well as the scarcity of dumping sites [2].

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High-sulphate fly ashes (HSFA) are considered potentially reject, since their sulphur percentage (found in the form of anhydrite, gypsum or even ettringite when not properly stored [3]) is higher than the acceptable limit stated in EN 450-1. Such ashes are not used in the cement industry since their incorporation increases the total amount of sulphates in the mix, initiating undesired effects, such as delayed ettringite formation (DEF), expansion and ultimately cracking of the final product [4,5]. In this case, the probability of the significant formation of calcium sulphate and calcium sulfoaluminate hydrated compounds increases markedly. Those hydrates can be dangerous since their final volume may be markedly higher that the volume occupied by the individual compounds before hydration reactions take place. This may lead to the decrease of the compressive strength and gradual degradation of the structure. However, in the past Zhang et al. [6] used a high SO_3 fly ash to produce high performance concrete exhibiting good performance, both in the fresh and hardened states. Excellent concrete performance has also been reported in projects where fly ash exceeded cement by weight in the total binder volume, as well as in projects where coarse fly ashes were utilized [7,8].

In this work, gypsum-free blended cements (GFBC) were prepared by utilizing a non-standardized high-calcium high-sulphate fly ash. Such an ash represents a large part of the Hellenic by-product, since the majority of the 11.5 million tons of local ashes that are annually produced is of high calcium content and contains considerable quantities of free lime and sulphates (mainly in the form of anhydrite) [9]. It has been established that sulphate-bearing phases are mainly located in the exterior part of the ash spheres and are almost instantly dissolved into the pore solution in an alkaline environment such as the one created in the cement–fly ash paste [3,10]. It is believed that sulphate ions abound in this type of fly ashes could be used, instead of natural gypsum, to avoid flash setting during the early stages of cement hydration.

The effort presented herein is considered to have an up-to-date value given the increasing need for preserving natural resources and especially the fact that the natural gypsum deposits steadily decrease with time. Overall, the study investigates the design procedure and feasibility of new gypsum-free blended cements based on the use of HSFA as setting regulator. The setting behaviour and strength development of these materials are closely monitored in the experimental program. The efficiency of the new cements is evaluated via the concept of the *k*-values, which are further used to validate previously reported theoretical expressions correlating active silica of the pozzolan with the mechanical performance of the systems that incorporate it. Additionally, an assessment of the chloride binding capacity and resistance towards external sulphate attack of gypsum-free blended cements is attempted to conclude on the quality of the final products.

2. Experimental procedures

2.1. Initial materials characteristics and setting measurements

The chemical properties and main physical characteristics of the clinker and fly ash used are provided in Table 1. Fly ash (designated here as F_{HS}) was selected among a series of specimens from Ptolemais area, and is considered to be of low quality since it contains low levels of reactive silica and large amounts of sulphur and free-lime contents. F_{HS} was ground – before use – in a lab-ball mill to increase its specific surface and promote its pozzolanic activity. Since incorporating fly ash into cementitious systems is known to have an effect on setting time, the authors' first concern was to examine whether the ash utilized (and the fact that no gypsum was introduced in the mix) would have any influence on the setting behaviour of the gypsum-free specimens. This was accomplished by preparing a series of samples containing up to 50% F_{HS} (by weight of clinker) and measuring their initial and final setting times using the Vicat-needle apparatus. Comparisons were made with a reference specimen prepared by intergrinding the same clinker with 5% natural gypsum to similar Blaine fineness.

2.2. Compression test

To monitor the compressive strength development of the GFB cements, mortar specimens were prepared by adopting a cementitious materials-to-sand ratio of 1:3 and water-to-cementitious materials ratio of 0.5 following a

Table 1
Chemical composition (% by mass) and main physical characteristics of raw materials

	Clinker	F_{HS}
CaO	65.54	35.22
CaO-free	0.74	7.59
CaO_{re}[a]	n.a.[c]	29.13
SiO_2	21.51	33.43
SiO_{2re}[a]	n.a.	23.96
Al_2O_3	4.88	12.56
Fe_2O_3	3.79	5.96
MgO	2.23	3.31
SO_3	1.36	6.57
R_2O	0.48	1.15
LOI	2.31	3.36
Y_s[d]	n.a.	71.67
IR (%)[a]	0.18	14.66
Glass content S[b] (%)	n.a.	85.34
Blaine fineness (cm^2/g)	4.120	5.230
Specific gravity	3.13	2.83

[a] The method specified in the European Standard EN 450-1 was followed for the estimation of the reactive silica and calcium oxide contents and the insoluble residue (IR) of the fly ashes.

[b] The method specified in the RILEM Recommendations (TC FAB-67 Use of Fly Ash in Building) was followed for calculating the content of the LOI-free fly ash constituents soluble in hydrochloric acid and potassium hydroxide ($S = 100 - IR$).

[c] n.a: not available.

[d] Y_s: active ratio (ratio of active: total silica).

strict procedure described in previous works [9,11]. In the work presented herein a 20% and 30% replacement of clinker by F_{HS} was adopted (no gypsum was added) during the preparation of pozzolanic specimens. Strength tests were conducted at 2, 7, 28 and 90 days after mixing and values were used to calculate the efficiency factors (k-values) in each case. For each age, three specimens of every mixture were tested, and the mean value is reported.

2.3. Evaluation of hydration process

For evaluating the hydration process, paste specimens were prepared following a similar procedure with the one described in Section 2.2. Paste samples were cast in plastic vials after intensive shaking to remove any air content. At the same ages that compression testing took place, hydration was stopped with the addition of organic solvents and overnight drying in a vacuum pump. Fragments from the core of each dried sample were taken and were further pulverized to assure that they all run through the 125-μm sieve. The pulverized material was then kept sealed into plastic bags and stored hermetically into dryers until testing. For monitoring the hydration process, the non-evaporable water contents, and gel/space ratios of the new cements were determined. Comparisons were made in all cases with the reference (no fly ash) specimen.

To determine the non-evaporable water content (W_n) of the hydrated samples, 1 g of the hydrated sample was first dried at 70 °C overnight (dried weight of paste) and was afterwards ignited at 950 °C in an electric furnace for 1 h (ignited weight of paste). Then the W_n content of the samples was calculated by using Eq. (1) proposed by Zhang et al. [12] after subtracting the amount of calcium carbonate present in all blended cements (as this was estimated from the data derived from the thermogravimetric analysis and the weight loss observed in the temperature area between 750 and 800 °C). Thermogravimetric analyses were performed in a Mettler STARe 851/LF/1600 TG/SDTA in a N_2-atmosphere (50 ml min^{-1}) at a heating rate of 10 °C/min.

$$W_n = \frac{W_1 - W_2}{W_2} - \frac{r_{fc}}{1 - r_{fc}}, \quad (1)$$

where W_n is the non-evaporable water content, W_1 and W_2 are the weight of specimens before and after ignition, respectively, and r_{fc} is a coefficient taking into account the loss on ignition and weights of the cement and fly ash used in each blend. The latter is calculated as follows:

$$r_{fc} = p_f r_f + p_c r_c, \quad (2)$$

where p_f and p_c are the weight percentages of fly ash and clinker and r_f and r_c are the loss on ignition of fly ash and clinker respectively.

2.4. Chloride binding capacity

For obtaining an indication of the chloride resistance of the new cements, the chloride binding capacity (CBC) of the constructed pastes was measured using a slightly modified method initially implemented by Delagrave et al. [13]. According to that, granulated pastes are immersed into a chloride solution (i.e. 0.10 molar NaCl solution in 0.2 molar KOH) for a period of 5 and 14 days and then chloride content is determined using potentiometric titration. The difference accounts for the chloride bound by each paste. In this study, pastes whose hydration was terminated after short (7 days) and longer (90 days) curing periods were examined so as to look into the effect of the pozzolanic action on the examined parameter.

2.5. Immersion tests

Accelerated immersion tests were conducted in gypsum-free cement pastes containing 30% fly ash to assess their resistance towards aggressive media. For this purpose, clinker was thoroughly mixed (no further grinding was performed) with 30% F_{HS} and water was added (a W/C of 0.4 was adopted). Pastes were moulded into 50-mm cubes. The moulds were vibrated for 2 min to remove any air bubbles and voids. Immediately after moulding, the samples were cured under moisture conditions (wet burlap was used) for 24 h. After one day, the specimens were demoulded and cured under de-ionized water for 14 days at 23 ± 2 °C. After water curing, a first group of specimens that were used as reference remained under water, while a second group of specimens were weighed on dry basis and then transferred in the aggressive 2% H_2SO_4 solution at 23 ± 2 °C, where they remained stored for 90 days. A third group of specimens was immersed in a solution simulating a marine environment (NaCl + Na_2SO_4 of equivalent concentration to that of the seawater; that is 0.03 and 0.045 M for sulphate and chloride respectively [14]), also at 23 ± 2 °C. These concentrations are according to Mehta [15] within the range of concentrations that can cause a severe attack.

The solutions were rejuvenated every 30 days. Even though non-standardized, such accelerated immersion tests have been extensively used by several researchers to assess the resistance of plain and blended cements [14,16]. Compressive strength was determined for all samples after 105 days of total curing (15 days in water and 90 days in the aggressive solution). Mass change was recorded after 20, 40, 60 and 90 days exposure to the aggressive solution. The reported values for both factors measured (strength and weight change) are the average of two samples.

3. Results and discussion

3.1. Setting time

Experimental results of setting time are given in Table 2 along with data concerning the water demand of each sample tested and equivalent amount of So_3 content in each pozzolanic mixture. As was more or less expected, addition of high-calcium fly ash increased the water demand up to

Table 2
Setting behaviour of gypsum-free blended cements with fly ash percentage

Binder composition	SO_3 (%)[a]	WD (mL)	Initial ST (min)	Final ST (min)
95%C + 5%gypsum	–	114	105	130
80%C + 20%F_{HS}	2.32	131	105	140
70%C + 30%F_{HS}	2.85	137	135	155
60%C + 40%F_{HS}	3.38	148	155	180
50%C + 50%F_{HS}	3.92	148	155	205

[a] Equivalent amount of sulphur trioxide content in the mixture.

30% (for a 40% and 50% fly ash addition). With regards to setting times measured, it can be observed that the mixture utilizing 20% F_{HS} (and no gypsum) attains similar initial and final setting times with the reference sample, indicating that such an addition can compensate for the absence of gypsum in the mix. With increasing F_{HS} addition, setting times are normally delayed, but even in the cases of high volume replacements (i.e. 40% and 50% by clinker weight), setting started with less than an hour delay, indicating that decent early-age strengths could be achieved in cases of such a significant clinker replacement.

In a previous effort, high volumes (50% and more by weight of Portland cement) of a high-calcium ash with high-sulphur content were used in the production of HPC [6]. Contrary to what is observed here, pastes prepared with the specific ash exhibited significant setting delay (for the case of 70% ash addition, a delay of approximately 12 h was observed). According to Zhang et al. [6], this was the result of the strong presence of ettringite (amplified by the sulphur ions supplied from the dissolution of the ash particles) formed in all FC pastes. When comparing the results of the aforementioned work with those shown in Table 2, it appears that the introduction of a large amount of a fly ash rich in SO_3 in a matrix already containing gypsum, may lead to an excess of SO_3^- in the hydrating system and subsequently to an undesired retardation of the setting process. Since setting can designate, to a large extent, the ability of a cementitious system to achieve desirable early strengths, results presented in this section indicate that high-calcium high-sulphate fly ashes should be introduced into cement and concrete systems, preferably when little or no gypsum is included.

3.2. Strength development and efficiency factors

Compressive strength data of the mortars prepared are given in Table 3 in relation to hydration age. During the first week, the strength values of the fly ash specimens decreased since at this age F_{HS} is inert and cannot compensate for the loss of clinker strength carriers (mainly C_3S). At this stage and up to the first month of curing, strength decrease is proportional to the amount of clinker replaced. Only after the first two days of curing the mixture with 30% ash performs better than the one with less ash inclusion, possibly due to the drastic effect of reactive lime contained in the utilized pozzolan [11,17]. As curing continues, given

Table 3
Compressive strength development of reference and fly ash mortars

Blend type	Compressive strength (MPa)			
	Age (days)			
	2	7	28	90
Reference	27.0	41.7	55.8	61.1
$20F_{HS}$	18.8	30.9	48.3	59.3
$30F_{HS}$	20.2	30.6	47.5	60.2

the high glass content of F_{HS} (see GC factor at Table 1) and the progress of pozzolanic reactions, fly ash cements develop strength at a faster rate than the reference mixture achieving similar strength after 3 months. The noticeable strength gain of pozzolanic specimens during this period (28–90 days) along with the fact that dissolution of active silica is expected to continue after the end of the testing period [18,19] creates room to estimate that fly ash samples will overcome the reference mixture with continuous hydration. However, this increase is not expected to be significant since active silica content of F_{HS} is considered to be low (in fact is less than 25% which is the minimum requirement stated in the European Standard EN 450-1 [20] for ashes that could be used in concrete).

It has been well established [9,11,16] that in the case of mortars and concrete that incorporate supplementary cementing materials (SCM), the k-value can be derived from the following expression for the measured compressive strength (f_c):

$$f_c = K\left(\frac{1}{W/(C+kP)} - a\right), \tag{3}$$

where K is a parameter depending on the cement type (here 38,8 MPa), C and P are the cement and fly ash contents, respectively, in the mortar (kg/m^3), W is the water content (Kg/m^3) kept constant in all the mixes and a, a parameter depending mainly on time and curing. Based on the above expression and strength values in Table 3, the k-values of the F_{HS} blends were calculated (and presented in Table 4) to validate previous remarks on satisfactory later-age strengths and the inability of F_{HS} to contribute to early-age strength development, respectively.

In recent work [21] the authors reported, for the first time, analytical expression that related active silica of artificial pozzolans with k-values of their respective cementitious systems aiming to enable a first approximation of

Table 4
Efficiency factors of fly ash mortars with respect to hydration age

Blend type	k-Values			
	Age (days)			
	2	7	28	90
$20F_{HS}$	0.46	0.30	51.8	0.88
$20F_{HS\text{-theor}}$[a]	n.a.	n.a.	n.a.	0.88
$30F_{HS}$	0.71	0.52	0.64	0.96

[a] Calculated based on the theoretical equation (4).

their performance only by knowing the amount of amorphous silica. The authors concluded that for a SCM-system, k-value can be expressed as follows:

$$k = (Y_S f_{S,P}/f_{S,C})(1 - aW/C), \quad (4)$$

where Y_S is the weight fraction of the oxide SiO_2 in the SCM (given in Table 1), which contributes to the pozzolanic reactions (i.e. the ratio of active silica to the total silica in the SCM) and $f_{S,P}$ and $f_{S,C}$ are the weight fraction of silica in the SCM and cement respectively. By applying the above equation in the case of $20F_{HS}$ blended cement at 90 days (a stage where active silica is known to hold a critical role) an identical k-value (with the experimental one) of 0.88 was calculated. The latter observation demonstrates the credibility and predictive power of the abovementioned expression even in cases where fly ash is used in the production of non-standardized blended cements. It should be noted that the same theoretical expression has been tested successfully also in the case of blends of different types of fly ashes [17] and potentially reject coarse fly ash–cement systems [22].

3.3. Non-evaporable water contents (W_n) and gel/space ratios

It is widely anticipated that due to the complexity of the pozzolanic reactions, the amount of water bound in the reaction products of fly ashes is uncertain. Therefore direct determination of the degree of hydration from the non-evaporable water data cannot be accomplished [12]. However, in the frame of this work, the amount of W_n was determined to obtain an image on the hydration evolution of gypsum-free cements and the effect of fly ash added. The data of the combined water contents of all specimens as a function of curing time are presented in Fig. 1. For all hardened pastes W_n contents increase gradually with time as a result of the continuing accumulation of hydration products. Fly ash presence diminishes the W_n contents during the first week of hydration, a decrease that is proportional to the amount of clinker that was replaced. Obviously, the inability of fly ash to act drastically during this stage accounts for the limited amount of water combined. As hydration progresses though, first the 20% F_{HS} sample (at 28 days) and then the 30% F_{HS} (after 3 months) are producing more water-binding phases as a result of the development of the pozzolanic reactions. These reactions result in the superiority of the fly ash specimens at the end of the curing period (they both exceed the reference specimen) in terms of non-evaporable water contents, a fact that is well associated with the strength development of the corresponding mortars discussed earlier.

Gel/space ratio is defined as the ratio of the volume occupied by hydrated cement to the sum of the volumes occupied by hydrated cement and by capillary pores that are present in the matrix. Given that for a Portland cement paste, each ml of hydrated cement occupies 2.06 ml, the gel/space ratio (X_c) can be calculated according to the following equation proposed by Neville [23]:

$$X_c = \frac{2.06 v_c a_c}{v_c a_c + \frac{W}{C}}, \quad (5)$$

where v_c is the specific volume of anhydrous cement, α_c is the degree of cement hydration at a given curing stage, and W/C is the water-to-cement ratio used for preparing the paste.

Even though the application of the above equation in the case of blended cement and concrete is debatable and with regard to the use of fly ash (since the exact volume stoichiometry of the pozzolanic reactions has not been established yet) the situation seems even scantier, Lam et al. [24] and Heikal [25] are some of the researchers that applied the above equation to pozzolanic specimens. For

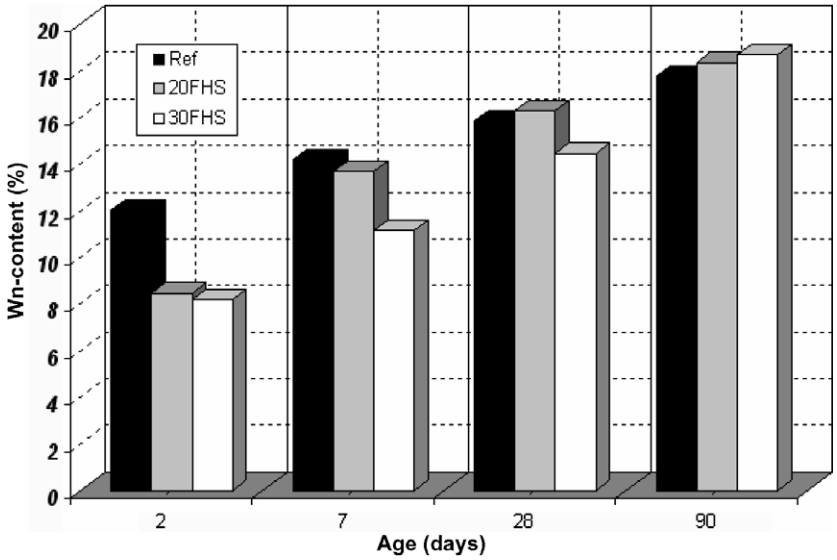

Fig. 1. W_n contents of reference and gypsum-free blended cement pastes with curing age.

estimating the hydration degree of the examined systems they used the non-evaporable water contents, taking into account that a fully hydrated cement paste is assumed to have a W_n content of approximately 23%. Based on the above assumption, the measured density of cement (3.19 g/cm^2 corresponding to a value of $v_c = 1/3.19 =$ 0,313) and the W/C_M 0.5 ratio applied in all pastes, gel/space ratios were calculated and presented in Table 5 in relation to curing time. The results demonstrate once again the efficiency of the fly ash cements, especially at later ages, a stage that secondary gel supplements the one produced due to clinker hydration to fill the pores in the matrix. Superiority of the GFB cements when compared to the gel/space ratio of the reference specimen creates optimism regarding the durability properties of the same cements since these are governed to a large extent by the pore size distribution of the paste (a factor directly associated with gel/space ratio).

3.4. Chloride binding capacity

Chloride binding capacity results are given in Table 6 as a function of curing and abidance time inside the aggressive solution. For the one week-cured samples, it can be observed that the amount of bound chlorides (C_b) increases with abidance time. At both stages examined, the reference mixture binds more chlorides than the pozzolanic specimens, possibly due to the greater production of C–S–H whose ability to bind chloride ions is well known [13]. Specimens with fly ash inclusion, perform satisfactory in terms of chloride binding, as early as 7 days. In fact the more clinker remains in the blended system, the greater is their efficiency in binding chlorides.

Table 5
Gel/space ratios of reference and gypsum-free blended cements with curing age

Blend type	Gel/space ratios			
	Age (days)			
	2	7	28	90
Reference	0.598	0.670	0.722	0.775
$20F_{HS}$	0.460	0.654	0.734	0.792
$30F_{HS}$	0.449	0.566	0.679	0.801

Table 6
Chloride binding capacities of reference and GFB cements with respect to days of water curing and exposure period

Specimen	Days of curing	Bound chloride (mg Cl^{minus}/g paste)	
		Days inside the solution	
		5	14
Reference	7	4.74	5.96
$20F_{HS}$	7	4.68	5.68
$30F_{HS}$	7	4.28	4.691
Reference	90	3.86	3.83
$20F_{HS}$	90	4.93	4.60
$20F_{HS}$	90	4.95	4.81

On the other hand, GFB cements cured for 90 days, exhibit a notable increase in the amount of chlorides they bind possibly due to the respective increase of the C–S–H created by the co-production of secondary gel from the pozzolanic reactions. In fact, both cements (with 20% and 30% F_{HS}) outperform the reference specimen, regardless of the period they were kept inside the solution. The same samples however, present an erratic behaviour since they bind more chlorides after spending 5 days in the solution than they do after 2 weeks stay. It is believed that during the second week of their stay inside the aggressive medium, a part of the bound chlorides, initially present in the interlayer spaces, is again liberated into the solution, an observation that was also confirmed in earlier works by Beaudoin et al. [26] who worked on synthetic systems that had been first cured and then immersed in chloride solutions.

3.5. Resistance in aggressive environment

The compressive strength values of the pastes immersed in sulphuric acid are presented in Table 7 in comparison to the respective samples cured under water. The strength deterioration factors (SDF) are also given for each case of exposure. The latter denotes the reduction of compressive strength for a cementitious system that is exposed in contaminated environments. It is defined as

$$\mathrm{SDF} = (1 - \sigma_R/\sigma) \cdot 100, \quad (6)$$

where σ_R is the average compressive strength (in MPa) of concrete specimens after exposure to sulphuric acid for a period of t days and σ is the average compressive strength (MPa) of concrete specimens cured in water after time t, where t is the curing period in days.

Data in Table 7 reveal that the pastes stored in the sulphuric acid solution, presented a significant strength decrease during their 90-day exposure, whereas the same samples exhibited an almost negligible strength decrease under the simulated marine environment solution. In both cases, the reference specimen (containing gypsum and no fly ash) shows greater resistance under attack as denoted by the respective SDF values with respect to the pozzolanic specimen. However, the gypsum-free fly ash cements perform satisfactory especially when considering that the ash used in this work is of low reactivity. Its relatively better resistance behaviour during the exposure to the marine-environment solution could be attributed not only to the

Table 7
Compressive strength for reference and gypsum-free blended cement under aggressive solutions

Sample	Compressive strength (MPa)				
	Water	2% H_2SO_4	SDF_{SULF}	$Nacl + Na_2SO_4$	SDF_{MARI}
Reference	108.8	35.8	67.1	104.0	4.6
$30F_{HS}$	106.2	22.4	78.9	97.3	8.4

restrained aggressiveness of the medium but also to the fact that sulphate and chloride can facilitate the pozzolanic reaction of fly ash even when their source is external, with a mechanism similar to that dominating when they are added during mixing [27].

The results of mass change in relation to exposure time for the sulphuric acid solution are plotted in Fig. 2. A continuous mass increase up to the first 40 days of exposure can be observed both for the reference and the pozzolanic specimen, followed by a mass decrease thereafter. The greater mass increase was found in the sample containing F_{HS} fly ash. This could be attributed to the accumulation of more hydration products, not only from the hydration of clinker constituents but additional due to the reaction of the active centers of the ash with the lime liberated from clinker hydration towards the formation of secondary C–S–H gel. It is therefore possible that if the compression test was performed at that age (and not after 50 days more) the fly ash samples might exhibited improved resistance to sulphuric acid attack compared to the reference specimen.

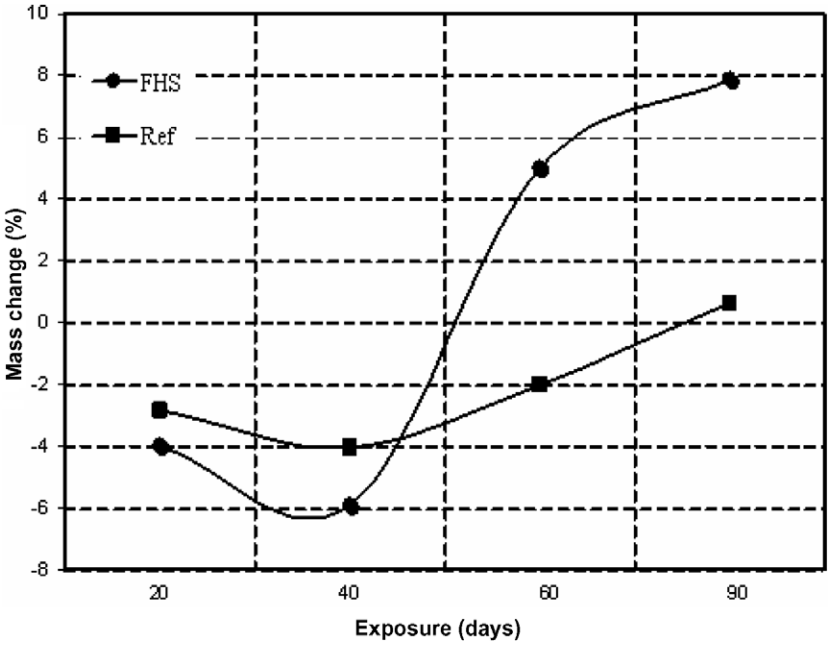

Fig. 2. Percentage mass change in relation to exposure time in 2% H_2SO_4 solution.

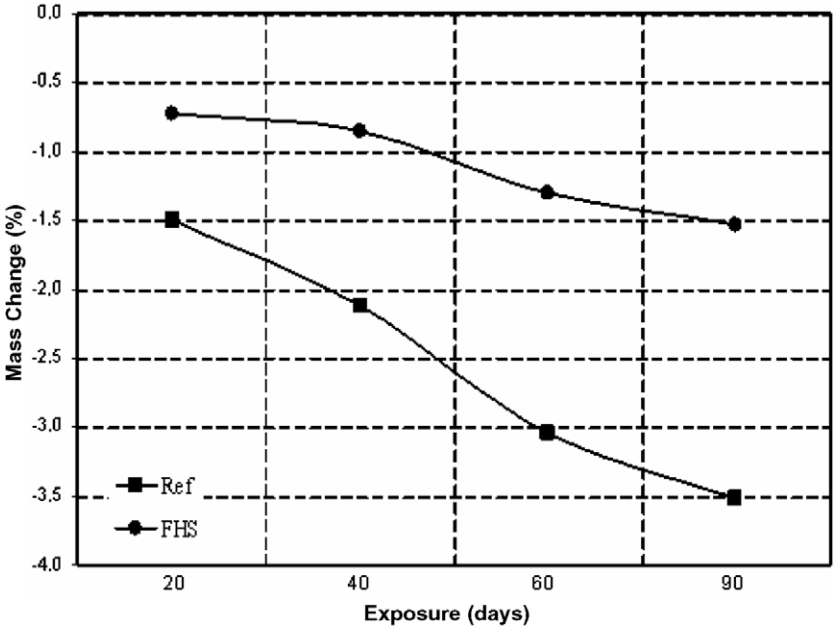

Fig. 3. Percentage mass change in relation to exposure time in simulated marine environment.

As exposure continues, the reference pastes deteriorate less than the gypsum-free cement pastes, a fact that is in accordance with strength results presented earlier. However, given the low-quality of the ash used herein and the rather significant substitution ratio (i.e. 30% by weight of clinker) the performance of the GFBC pastes could be described as satisfactory.

Mass change data in the case of the marine-environment solution are depicted in Fig. 3. Despite remaining for 3 months under aggressive environment, the mass of the GFBC pastes did not decrease at all. On the contrary the samples gained weight throughout the exposure period at a rate very similar to that of the reference specimen. The fact that the examined specimens continuously gain weight until the end of the exposure period while their compressive strength slightly decreases (as testified by the respective SDF values in Table 5) could be attributed to the nature of the reactions formed, principally gypsum and ettringite, or even Friedel's salt which increase the total mass of the specimens, but they ultimately lead to a decrease of their compressive strength. Evidence of these compounds was verified by means of XRD examination in the pastes tested at the end of the exposure time and is going to be published shortly.

4. Conclusions

In this work, a potentially reject high-calcium fly ash of high sulphur content was exploited towards the production of gypsum-free blended cements. Besides its use as a supplementary cementing material, the ash examined was additionally used as a setting regulator. Research continues with expansion tests (extreme cautiousness is paid in mixtures with high total SO_3 percentage) and solubility experiments to investigate further on the dissolution rate of the sulphur ions from the fly ash during setting period. The production and partial evaluation of the novel type of cements investigated herein led to the following major conclusions:

1. Cement pastes incorporating up to 50% of high sulphate fly ash exhibited normal setting behaviour, almost similar to that of a typical Portland cement. The mixture utilizing 20% fly ash attains similar initial and final setting times with the reference sample, whilst for maximum ash addition (i.e. 50%), setting started with less than an hour delay.
2. Gypsum-free fly ash blended mortars exhibited low early-age and improved later-age compressive strengths. A previously reported expression, correlating active silica of artificial pozzolans with k-value, was validated. Using such an expression can lead to a relatively good approximation of the future mechanical performance of the final product.
3. W_n contents and gel/space ratios results confirmed the efficiency of the GFB cements, especially at later ages, a stage where pozzolanic gel supplements the production of additional water-binding phases in the hydrating matrix. GFBC pastes bind a great amount of chlorides (C_b) similar to that bound by the reference mixture. When inserted in the chloride solution after being cured for 90 days, the same samples outperformed the sample containing gypsum as a result of the continuous production of a secondary C–S–H gel and the chloride binding action of the aluminate phase of the ash.
4. GFBC pastes exposed to a 2% sulphuric acid solution, showed a significant strength decrease during their 90-day exposure, whereas the same samples exhibited an almost negligible strength decrease under the simulated marine environment solution. In both cases of exposure, the reference specimen (containing gypsum and no fly ash) show greater resistance under attack with respect to the pozzolanic specimen. Given the low-quality of the ash used herein and the significant substitution ratio (i.e. 30% by weight of clinker) applied, the performance of the GFBC pastes could be described as satisfactory and their use viable especially for marine structures.

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References

[1] Cheerarot R, Jaturapitakkul C. A study of disposed fly ash from landfill to replace Portland cement. Waste Manage 2004;24(7):701–9.
[2] Roth L, Eklund M. Framework for environmental assessment of using industrial by-products and used building materials, In: Vasquez E, Hendriks ChF, Janssen GMT, editors. Proceedings of the international RILEM conference on the use of recycled materials in buildings and structures, vol. 1, p. 255–64.
[3] Tishmack JK, Olek J, Diamond S. Characterization of high-calcium fly ashes and their potential influence on ettringite formation in cementitious systems. Cem Concr Aggr 1999;21(1):82–92.
[4] Kuzel HJ. Initial hydration reactions and mechanisms of delayed ettringite formation in Portland cement. Cem Concr Comp 1996;18(3):195–203.
[5] Schlorholtz S, Bergesson KL. Evaluation of the chemical durability of Iowa fly ash concrete, final report, Iowa Department of Transportation, project HR-327, ERI Project 3295 (1993), ISU-ERI Ames 93–411.
[6] Zhang Y, Sun W, Shang L. Mechanical properties of high performance concrete made with high calcium high sulfate fly ash. Cem Concr Res 1997;27(7):1093–8.
[7] Bouzoubaâ N, Zhang MH, Malhotra VM. Mechanical properties and durability of concrete made with high-volume fly ash blended cements using a coarse fly ash. Cem Concr Res 2001;31(10):1393–402.
[8] Jiang LH, Liu ZQ, Ye YQ. Durability of concrete incorporating large volumes of low-quality fly ash. Cem Concr Res 2004;34(8):1467–9.
[9] Papadakis VG, Tsimas S. Supplementary cementing materials for sustainable building-sector growth, European Commission DGXII, Marie Curie Fellowship, Final Report, Project No HPMF-CT-1999-00370, NTU of Athens, Greece, 2001, p. 74.
[10] Ghosh SN, Sarkar LS. Mineral admixtures in cement and concrete. In: Ghosh SN, editor. Progress in cement and concrete. New Delhi, India: ABI Books; 1993.

[11] Antiohos S, Tsimas S. Activation of fly ash cementitious systems in the presence of quicklime. Part I. Compressive strength and pozzolanic reaction rate. Cem Concr Res 2004;34(5):769–79.
[12] Zhang YM, Sun W, Yan HD. Hydration of high-volume fly ash cement pastes. Cem Concr Res 2000;22(6):445–52.
[13] Delagrave A, Marchand J, Ollivier J-P, Julien S, Hazrati K. Chloride binding capacity of various hydrated cement paste systems. Adv Cem Bas Mater 1997;6(1):28–35.
[14] Lorenzo MP, Goni S, Guerrero A. Role of aluminous component of fly ash on the durability of Portland cement–fly ash pastes in marine environment. Waste Manage 2003;23(8):785–92.
[15] Mehta PK. Concrete: Structure, properties and materials. 2nd ed. Englewood Cliffs, New Jersey: Prentice-Hall; 1992.
[16] Kumar P. Influence of water quality on the strength of plain and blended cement concretes in marine environments. Cem Concr Res 2000;30(3):345–50.
[17] Antiohos S, Maganari K, Tsimas S. Evaluation of blends of high and low calcium fly ashes for use as supplementary cementing materials. Cem Concr Comp 2005;27(4):349–56.
[18] Antiohos S, Tsimas S. Chloride resistance of concrete incorporating two types of fly ashes and their intermixtures. The effect of the active silica content. In: Malhotra VM, editor. Proceedings of the 6th CANMET/ACI international conference on the durability of concrete (Supplementary Papers). Thessaloniki, 2003, p. 115.
[19] Antiohos S, Tsimas S. Investigating the role of reactive silica in the hydration mechanisms of high-calcium fly ash/cement systems. Cem Concr Comp 2005;27(2):171–81.
[20] European Committee for Standardization, European Standard EN 450-1, Fly Ash for Concrete – Part 1: Definitions, specifications and conformity criteria, CEN, Brussels, 2002.
[21] Papadakis VG, Antiohos S, Tsimas S. Supplementary cementing materials in concrete – Part II: A fundamental estimation of the efficiency factor. Cem Concr Res 2002;32(10):1533–8.
[22] Antiohos SK, Tsimas S. A Novel way to upgrade the coarse part of a high-calcium fly ash for reuse into cement systems. Waste Manage 2006;27(5):675–83.
[23] Neville AM. Properties of concrete. Fourth and Final ed. Longman; 1995.
[24] Lam L, Wong YL, Poon CS. Degree of hydration and gel/space ratio of high-volume fly ash/cement systems. Cem Concr Res 2000;30(5):747–56.
[25] Heikal M. Effect of calcium formate as an accelerator on the physicochemical and mechanical properties of pozzolanic cement pastes. Cem Concr Res 2004;34(6):1051–6.
[26] Beaudoin JJ, Ramachadran VS, Feldman RF. Interaction of chloride and C–S–H. Cem Concr Res 1990;20(6):875–83.
[27] Shi C, Day RL. Pozzolanic reaction in the presence of chemical activators. Part I. Reaction kinetics. Cem Concr Res 2000;30(1):51–8.