Optimum Combinations Of Calcium Sulfate Setting Regulator And Various Superplasticizers For Concrete Production

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ABSTRACT

Previous studies have profoundly investigated the replacement of natural gypsum, by alternative calcium sulfate bearing materials (CSBMs), either natural (anhydrite) or industrial (such as FGD gypsum and phosphogypsum). FGD gypsum, a waste material of the desulphurization process of residual gases with limestone in coal burning power plants, seems to be the most promising one with respect to cement setting. On the other hand the influence of different types of superplasticizers (SPLs), especially those containing sulfuric groups during the early hydration stage, where also setting regulators sulfate ions act to delay the hydration of calcium aluminate phase, is of primal importance for properties of fresh concrete and the compressive strength profile. In this work the compatibility between various SPLs and different cement setting regulators has been investigated. The possible combinations of three SPLs, a polymelamine-sulfonate (PMS) SPL, a polynapthalene-sulfonate (PNS) SPL and a polycarboxylate (PC) SPL and two CSBMs (natural gypsum and FGD gypsum) in concrete mixtures were examined by monitoring concretes' physical and mechanical properties such as slump loss, SPL demand, setting time and compressive strength. Results of this study denote that FGD gypsum exhibits better compatibility than natural gypsum with all SPLs tested; in concrete mixtures containing FGD, slump loss retention and setting times were prolonged, SPL demand was notably reduced and compressive strengths and durability were ameliorated.

INTRODUCTION

The use of superplasticizers in concrete began in the 1960s and was a milestone in concrete technology and the field of construction. In this way the production of concrete of high performance and durability was achieved, because adding, superplasticizers high workability remained at a very low ratio of w/c. The superplasticizers are poly-electrolytes of organic origin, which function like the dispersing chemical media in heterogeneous systems. The first generation of superplasticizers was based on sulfonated naphthalene formaldehyde condensates or sulfonated melamine formaldehyde condensates. These dispersants are polymers based on a single repeating unit, which did not allow for much variation of the molecular architecture. A new generation of superplasticizers, based on polycarboxylate polymers with pendant polyether molecules, was discovered over 20 years ago, but they have been widely used in North America for less than 10 years [4]. Polycarboxylate dispersants are based on two or more structural units that provide for more diversity in possible molecular structures. For example, the relative abundance of anionic units to polyether units can be varied, the molecular weight of the polyether molecule can be varied and the molecular weight of the polycarboxylate main chain can also be adjusted to create polymers with different performance characteristics. These materials are of higher reactivity, they do not contain the sulfonic group and they are totally ionized in alkaline environment [1, 2, 3, 4].

Factors that can influence dispersant performance have been studied, including those situations where dispersant performance is less than expected. Cement chemistry, temperature, soluble alkali sulfates, dispersant chemistry and timing of dispersant addition have been shown by the referenced authors to influence dispersant performance. The influence of different types of superplasticizers (SPLs), especially those containing sulfuric groups during the early hydration stage, where also setting regulators sulfate ions act to delay the hydration of calcium aluminate phase, is of primal importance for properties of fresh concrete and the compressive strength profile [1, 4, 5, 6, 7].

The most common setting regulator in the cement industry is natural gypsum ($C\alpha SO_4 \cdot 2H_2O$) which is added during grinding of Portland cement in order to delay the rapid reaction between C3A and water. However its continuous use has led to the reduction of its high purity stock in some countries. In certain cases anhydrite ($C\alpha SO_4$) has been proved particularly reliable for the partial replacement of natural gypsum [8]. A promising CSBM, which can replace mineral gypsum, seems to be desulphogypsum or FGD gypsum [9, 10]. Recently Tzouvalas et al. [8, 9, 10] attempted to evaluate different CSBMs as setting retarders. The results of the tests on the laboratory and industrially-produced cements with various admixtures were very encouraging. Compared with natural gypsum, anhydrite reduces setting time while FGD prolongs it without having any detrimental effect on the performance of compressive strength. The influence (direct or indirect) of superplasticizers on any process that involves sulfates may therefore be expected to be significant. Since superplasticizers can interfere with reactions which lead to flash or false set (due to the presence of calcium sulfate hydrates), they can potentially create erratic rheological behavior, situations which are commonly referred as cement – SPL incompatibility [1, 2, 3] .

In this work the compatibility between various SPLs and different cement setting regulators has been investigated. The possible combinations of three SPLs, a polymelamine-sulfonate (PMS) SPL, a polynapthalene-sulfonate (PNS) SPL and a polycarboxylate (PC) SPL and two CSBMs (natural gypsum and FGD gypsum) in concrete mixtures were examined by monitoring physical and mechanical properties of concrete such as slump loss, SPL demand, setting time and compressive strength.

EXPERIMENTAL

Clinker produced from Titan S.A. cement plant (Kamari) was ground with natural gypsum (G) and FGD gypsum (F) in a lab ball mill in order to produce cement type I (CEM I, Blaine: 3800cm2/g). CSBMs addition was 5% aiming at the optimum SO3 content in cement which has been found from previous studies to be 3,5% [8, 9]. These cements with two types of aggregates crushed fine and coarse limestone and sand at total cement to aggregate ratios of 1:0.38, 1:2.62, and 1:3.26 respectively were used to prepare concrete mixes of category C20/25 according to EN 206-1.

Two concrete mixes (one with gypsum and the other with FGD as cement setting regulator) without SPL addition were produced aiming at slump 9cm (reference samples). The w/c ratio was determined to 0.67.

Six concrete mixtures (each CSBM was combined with all three SPLs) with a 12% reduction of w/c ratio (0.55), according to EN 934.2, and the appropriate addition of each SPL in order to achieve a slump 9cm, a usual slump value when concrete is casted in site. All three SPLs complied with ASTM C 494. PNS spl had a 40% solid content; PMS spl appeared with a 37% solid content, while that of PC spl was 35%.

Six concrete mixtures (each CSBM was combined with all three SPLs) with a w/c ratio 0.55 and the demanded addition of each SPL in order to achieve a slump 14cm, a usual slump value when concrete has to be transferred before casted.

Slump was firstly measured in the aforementioned concretes. Then the slump loss during the first hour (0, 20, 40 and 60 minutes) was determined.

Twelve cubic mortars of 15cm for the compressive strength of 2, 7, 28 and 90 days, two cubic mortars of 10cm for the sulftate attack and two cubic mortars of 10cm for the capillary absorption measurement were prepared for each concrete mix. The mortars were poured into the molds that were vibrated on a vibrating table to remove the entrapped air. After casting and finishing the molds were kept for 24 hours under laboratory conditions and then demolded and cured at temperature of 20^0C and relative humidity 100% till the measurements. Compressive strength measurements were carried out according to Greek standards.

In order to have a strong and precise indication for the setting time the measurement of workable life of fresh mortar took place according to EN 1015-9. The concrete mortars should have, after the addition of SPL, an expansion target value of 17±1cm and then the workable life of the fresh mortar was measured by the time in minutes at which it reached a defined limit of resistance to penetration of a standard rod forced into it.

The sulfate attack was measured according the following steps: after 28 days of curing (20^0C, RH 100%) the two specimens were weighted and the one was immersed in a saturated solution of $C\alpha(OH)_2$ and the other in a solution of H_2SO_4 3% for 50 days. After the exposure mass loss and compressive strength were measured.

For the capillary absorption, the method named: Determination of the capillary absorption of water of hardened concrete (Materials and Structures, Vol. 32, April 1999) was followed. The two cubic mortars of 10cm were dried to 60^oC up to constant weight. In order to avoid a moisture exchange of the test specimen with the ambient air during the absorption experiment, the free surfaces were sealed against the penetration of water vapour with an approximately 1mm thick epoxy coating and then dried again. The specimens were cooled to room temperature. The top surface of the specimens were covered with an impermeable but flexible plastic hood to avoid pore pressure from building up and then weighted. The moulded bottom side of the specimen was immersed in water up to a depth of 3-5mm. The uptake of water by capillary absorption was measured through the weight of the specimens at time intervals of 10 minutes, 1, 4 and 24 hours.

RESULTS AND DISCUSSION

The compressive strengths of 1, 7 and 28 days for concrete mixes with each SPL are shown in Figures 1-3. As expected, the addition of SPL increased the compressive strength in a range of 10 to 40% compared with the two reference concrete (R) which had no SPL.

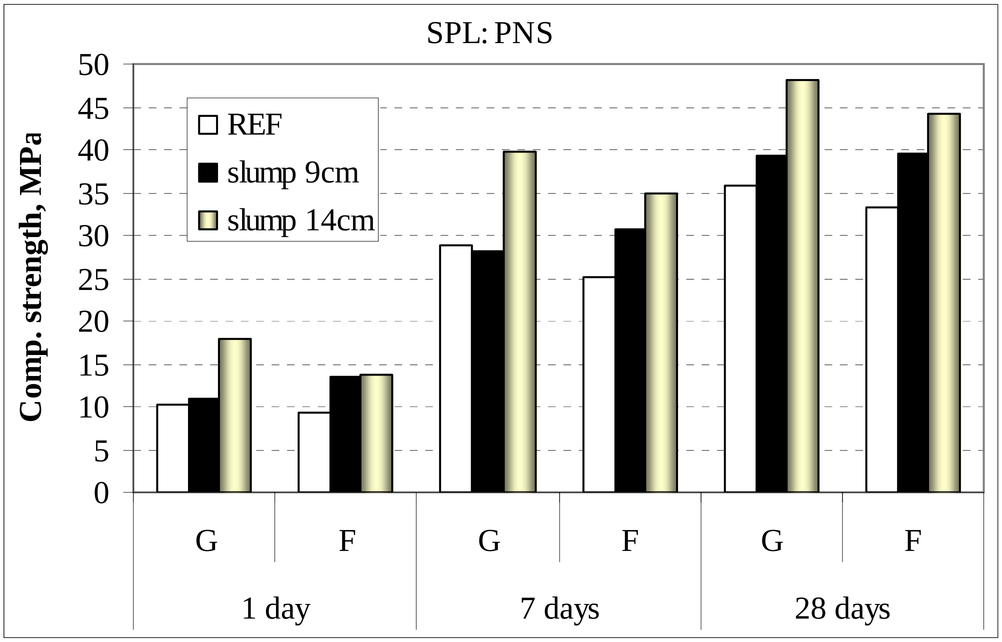

Figure 1 Compressive strengths of concrete with PNS superplasticizer.

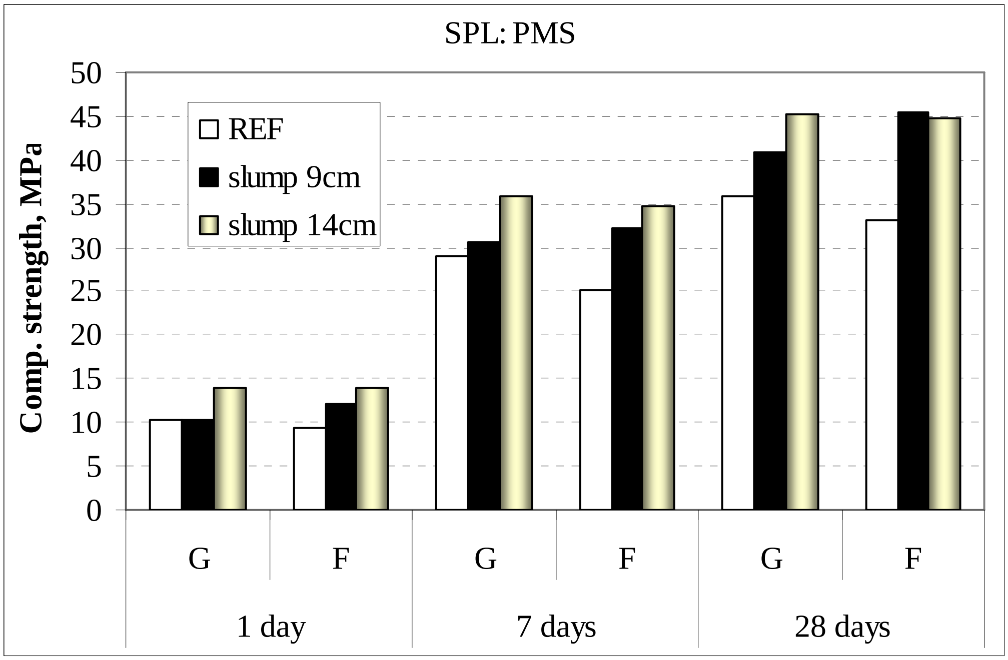

Figure 2 Compressive strengths of concrete with PMS superplasticizer.

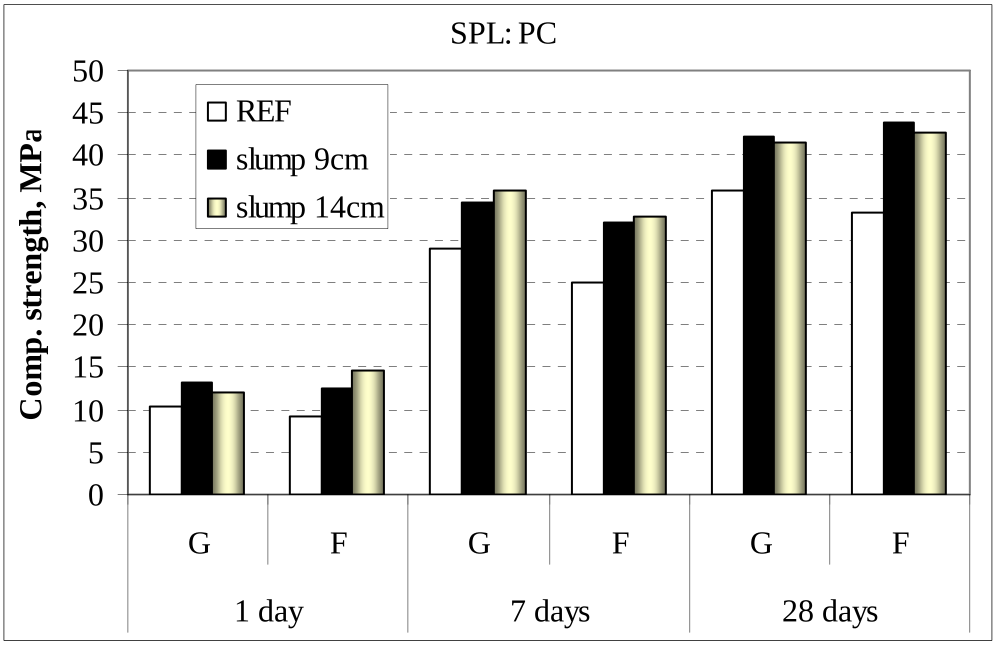

Figure 3 Compressive strengths of concrete with PC superplasticizer.

The reference concrete mix with gypsum as cement setting regulator showed a slightly higher strength than the one with FGD. This happened because FGD had a slightly higher SO_3 content than gypsum (48% vs

43%) and consequently the cement with FGD (3.7% SO_3) had exceeded the optimum SO_3 content of 3,5%. Nevertheless, when SPL was added the concrete mixes with FGD reversed this handicap and developed higher or at least equal strengths compared with concrete mixes with natural gypsum for both ranges of slump. The only exception is the concrete mixes with PNS of slump value 14cm. At the low slump value (9cm) the PNS SPL, compared with the other two SPLs, appeared to be less effective to the performance of compressive strengths with both natural gypsum and FGD used as calcium sulfate bearing material, while at higher slump (14cm) concrete with PC as SPL showed slightly lower compressive strengths.

In Figure 4 the duration of workable life is plotted. It is obvious that concrete mixes containing FGD showed a more prolonged workability compared with natural gypsum. Polycarboxylate (PC) SPL seemed to be more reactive compared with PNS and PMS SPL, as for the same setting regulator, concrete mixes with PC SPL addition showed the most prolonged time of workability. It must be also mentioned that concrete mixes containing FGD achieved the target value of expansion (17cm) with less quantity of SPL compared with natural gypsum, as it derived from Table 1.

From both compressive strength and workable life performance, it is extracted that FGD has a more profound and positive effect than natural gypsum to physicomechanical properties of concrete with SPL admixture.

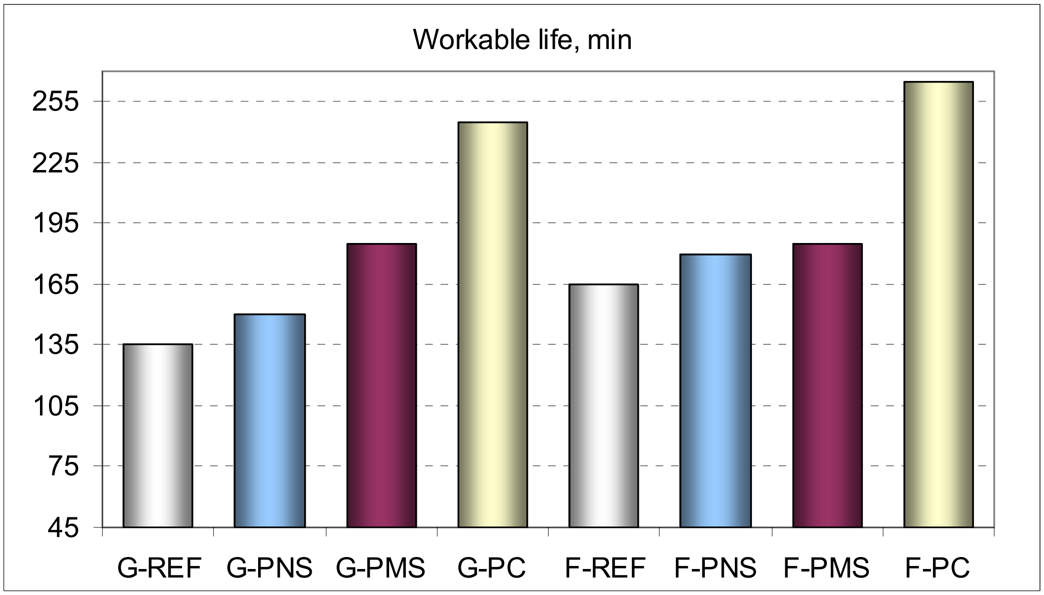

Figure 4 Workable life of fresh concrete mixtures with PC superplasticizer.

Table 1 SPL demand for fresh concrete with an expansion target value of 17cm.

	SPL, ml	SPL / cement, %
G-PNS	**3,4**	0,76
G-PMS	**5,5**	1,22
G-PC	**3,14**	0,70
F-PNS	**3,3**	0,73
F-PMS	**5**	1,11
F-PC	**2,5**	0,56

The slump loss rate for the addition of each SPL admixture in concrete mixes is plotted in Figures 5-7. In the same time the tread line of slump loss for each concrete, which is very well determined by a linear equation, is proposed. In all extracted equations the coefficient of time variable (slope of the linear tread line) when FGD was used was lower than in the case of natural gypsum. It is denoted from these results that in concrete mixtures containing FGD, slump loss retention was prolonged. Moreover it must be noted that concrete with PNS admixture exhibited the faster slump loss rate, while concrete with PC admixture showed the most delayed slump loss.

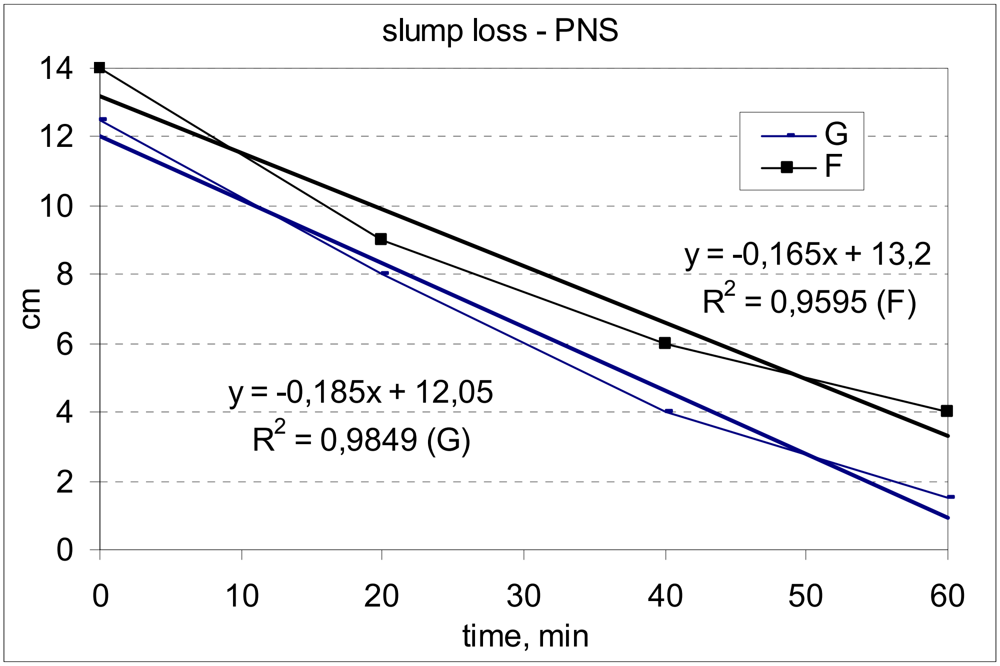

Figure 5 Slump loss of concrete with PNS superplasticizer.

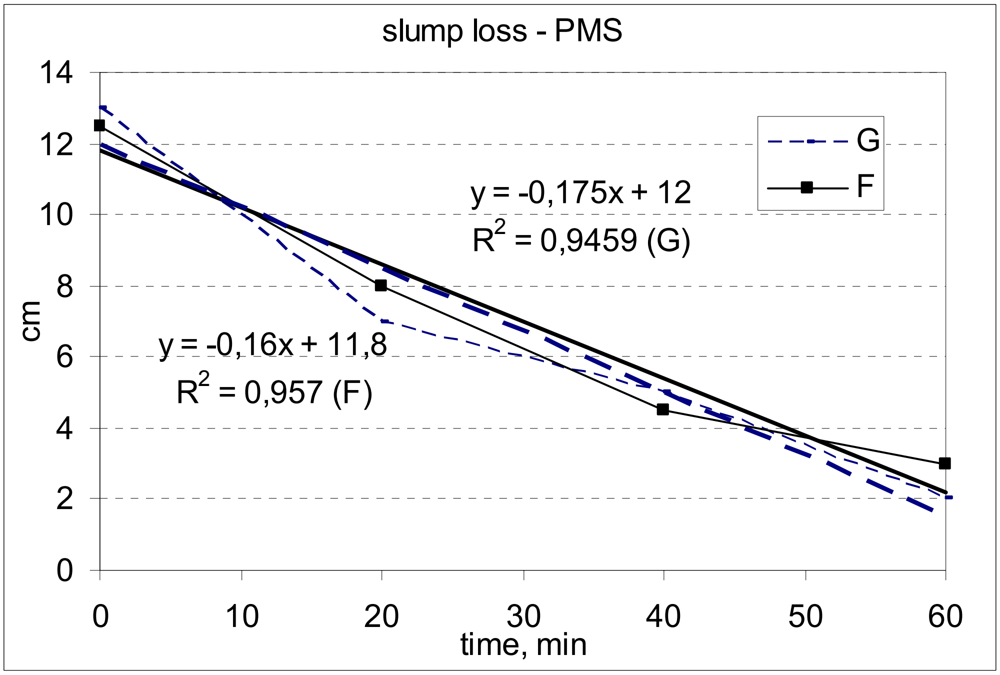

Figure 6 Slump loss of concrete with PMS superplasticizer.

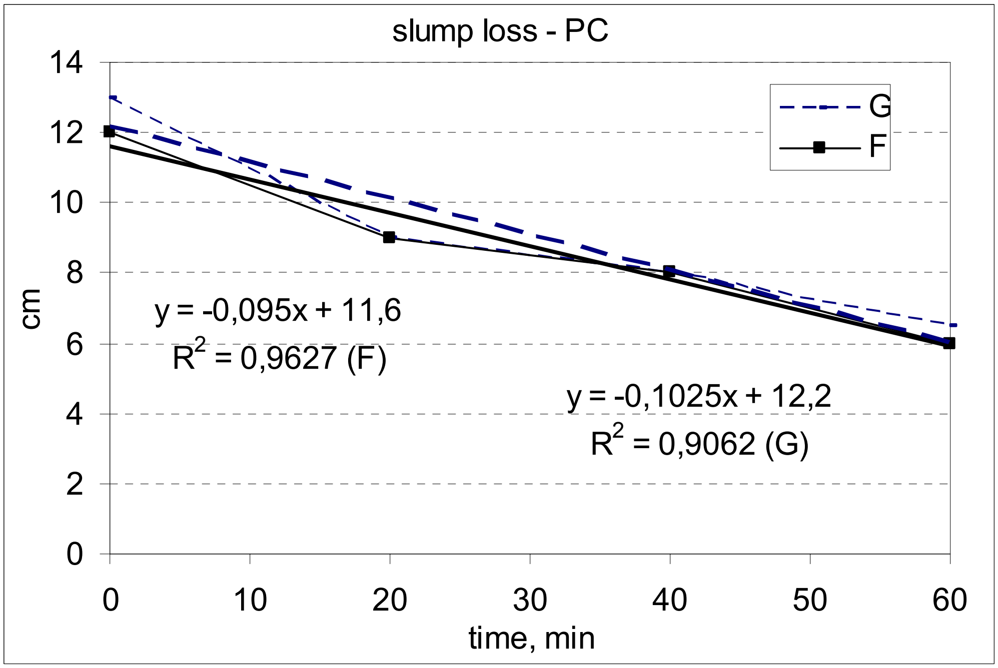

Figure 7 Slump loss of concrete with PC superplasticizer.

Capillary sorptivity is a serious indication for the durability of concrete with different CSBM as setting retarders and SPL as water reducers, since water presence is an obligatory requirement for any chemical external attack to mass concrete. It is obvious from Table 2 that the addition of SPL eliminated water sorptivity in all concrete mixes. Synthetic CSBM showed lower proportions of absorption compared with the natural one for both slump ranges and with all water reducer agents. The only exception was in the case of PNS SPL at the slump of 14cm. This fact has to be investigated furthermore perhaps with the repetition of the trial as it must be mentioned that two batches for each concrete mix were prepared. It is also impressive that the absorption values after 24 hours of concrete mortars with FGD and SPL were lying in a much more narrow range than those with natural gypsum (1.20-1.48 vs. 1.04-1.80). This is a strong indication that FGD controls and regulates more effectively than gypsum the physicomechanical properties of concrete in the presence of superplasticizers.

Table 2 Capillary sorptivity of concrete mixtures.

	Capillary sorptivity, %								
		10 min		60 min		240 min		24 h	
SLUMP, cm	SPL	G	FGD	G	FGD	G	FGD	G	FGD
9	**REF.**	**0,27**	**0,20**	**0,62**	**0,59**	**1,14**	**1,12**	**2,07**	**2,21**
	PNS	0,18	0,15	0,45	0,33	0,85	0,60	1,64	1,20
	PMS	0,20	0,15	0,49	0,38	0,87	0,71	1,66	1,36
	PC	0,20	0,15	0,42	0,36	0,87	0,67	1,80	1,24
14	PNS	0,19	0,15	0,35	0,41	0,58	0,75	1,04	1,48
	PMS	0,24	0,14	0,48	0,34	0,81	0,65	1,47	1,28
	PC	0,21	0,15	0,43	0,31	0,83	0,62	1,66	1,20

The results of the resistance of concrete with different CSBMs as cement setting regulators and SPLs to sulfate attack are presented in Table 3. In general the addition of SPL seemed to improve the resistance of concrete to sulfate attack. Concrete with FGD gypsum and PNS and PC SPL showed a more vigorous resistance compared with natural gypsum. On the contrary, when natural gypsum and PMS were combined, the strength loss was reduced compared with the concrete mixes containing FGD. The range of compressive strength of concrete mortars with FGD which were imposed to sulfate attack was obviously less extended (FGD: 33,2-28,5=4,7 vs. Gypsum: 31,1-23,7=7,4). This also proves the the strong regulating action of FGD on the control of concrete properties in the presence of SPLs.

Table 3 Strength loss of concrete mixtures due to sulfate attack.

		Compressive strength, MPa		**Compressive strength, MPa**		**% strength loss**	
		Curing method: 1% $Ca(OH)_2$		Curing method: 3% H_2SO_4			
SLUMP, cm	SPL	G	FGD	G	FGD	G	FGD
9	REF	35,06	33,31	23,01	22,61	34,4	32,1
	PNS	36.2	36,0	26,6	31,4	26,4	12,6
	PMS	35.2	44,3	24,3	28,5	30,9	35,7
	PC	35.3	43,3	22,3	31,1	36,8	28,3
14	PNS	44,3	39,3	26,0	33,2	41,4	15,5
	PMS	42,5	42,7	31,1	30,0	26,8	29,8
	PC	36,2	45,1	23,7	32,6	34,5	27,7

CONCLUSIONS

From the laboratory production of concrete with different calcium sulfate bearing materials as cement setting retarders and different superplasticizers as water reducer agents the following conclusions are extracted:

The addition of SPL admixture in the concrete ameliorates the compressive strength performance, increases the workable life of fresh concrete and enhances the durability of hardened concrete.

FGD gypsum exhibits better compatibility than natural gypsum with all SPLs tested. This must be attributed to the higher solubility of FGD gypsum compared with natural gypsum. When FGD gypsum is added in the mixture, more soluble SO_3 ions in the hydrated cement are available and hydration rate is delayed. That's why in concrete mixtures containing FGD, slump loss retention and setting times were prolonged, SPL demand was reduced and compressive strengths were ameliorated. This is a strong indication that FGD controls and regulates more effectively than gypsum the physicomechanical properties of concrete in the presence of superplasticizers.

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