

Evaluation of industrial by-products for the control of setting time of cements

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Abstract

This paper is part of an extent research program aiming to investigate alternative calcium sulfate bearing materials, for the partial displacement of natural gypsum, as setting retarders in cements. Three materials of different degrees of purity, found either as natural or as industrial by-products have been examined, either separately or in mixtures with natural gypsum, in order to study the influence of their addition in cement physicommechanical properties. These materials which have been compared with gypsum are: i) natural anhydrite (CaSO_4), ii) phosphogypsum; a by-product of fertilizer industry and iii) the product of flue gas desulfurization, FGD gypsum.

From the results, it is obvious that anhydrite and FGD can displace gypsum with no significant changes either on physical or on mechanical properties. On the contrary cements with phosphogypsum indicated high values of setting time.

Introduction

The majority of cement industries in Greece use natural gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as setting retarder in order to prevent instant hydration of C_3A . This continuous use of

gypsum gradually led to the reduction of its high purity stock. Its partial displacement with anhydrite and industrial by-products, such as phosphogypsum (PG) and gypsum from flue gas desulfurization (FGD), has as basic assumption the examination of a series of parameters, because, as it is nowadays generally known, gypsum not only affects the setting time but also influences grindability, compressive strength and volume stability [1, 2, 3]. It is also known that, immediately after the mixture of cement with the water, the sulfates dissolve and react with aluminate forming ettringite. The ettringite crystals form a covering around the aluminate thereby retarding a subsequent reaction [1]. In order to achieve the best setting behaviour, the availability of sulfate should – by the addition of an appropriate type and quantity of sulfate-bearing substance – be just so controlled that the hydrating portion of the tricalcium aluminate is combined exclusively as ettringite [4]. In the same time, up to a certain point, depending on the composition of clinker, the gypsum content promotes the strength of the cement and avoids shrinkage. Nevertheless, if the gypsum content goes beyond a certain limit, it can give rise to considerable expansion in the concrete. For this reason, the cement standards fix a maximum for the gypsum content (in the form of SO_3) of cement. The need for gypsum in cement increases in accordance with increasing amount of C_3A and alkalis in the clinker and the fineness of the cement [1, 4, 5]. Adjustment of the sulfate-bearing admixture to the reactivity of the tricalcium aluminate is therefore of considerable importance in retarding the setting [4, 6] and improving the strength behaviour of cement.

In certain cases anhydrite can advantageously be used instead of gypsum, and in general, partial replacement of the gypsum with anhydrite is possible in almost the majority of types of clinker. It is appropriate however to use anhydrite for cements with a low aluminate content and for slag cements. The slower dissolution of anhydrite may have adverse effects on the setting of cements with a high alkali or aluminate content [1, 7].

PG is an industrial by-product from phosphoric acid production and fertilizer industry. It consists mainly of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and contains some impurities such as P_2O_5 , F. Some researchers used PG to regulate the setting of ordinary Portland cement (OPC). It was shown that the impurities present in PG retarded the hydration of OPC to large extent [8, 9, 10].

Alternative FGD, a product derived from the desulfurization of residual gases with limestone in thermal plants (flue gas gypsum), may be suitable controller of the setting behaviour [1]. A remarkable research is carried out on this particular subject [11, 12].

For a certain clinker the optimum percentage relating to strength and setting time, of the four materials, either separately or mixtures of them, is investigated. In the same time a comparative study of these four materials focusing on their solubilities is carried out.

Experimental

Four calcium sulfate-bearing materials (CSBM), as are gypsum (as reference material), anhydrite, PG, FGD gypsum, have been interground in different proportions with clinker for an hour. The chemical analysis of these materials, according to ASTM C 471M - 95 [13], as well as their solubility at 25°C are shown in Table 1, while

in Table 2 is shown the chemical analysis of clinker. The % addition of each material in mixtures with clinker and the percentage of SO₃, measured by XRF, is shown in Table 3. The specific surface obtained was in the range of 3700 to 3900 g/cm².

Table 1 Chemical analysis and solubility of calcium sulfate-bearings

	Combined							Solubility (g/100g H ₂ O)
	water	SO ₃	SiO ₂	CO ₂	CaO	R ₂ O ₃ *	MgO	
Gypsum	19,30	43,41	0,65	2,51	32,40	0,03	0,92	0,260
Anhydrite	1,81	51,31	27,70	3,44	27,63	0,05	2,14	0,198
PG	19,80	43,79	1,44	1,00	31,80	1,02	0,05	0,234
FGD	18,05	42,19	0,30	1,58	33,40	0,10	0,10	0,273

Table 2 Chemical analysis of clinker

	SO ₃	SiO ₂	CaO	R ₂ O ₃ *	MgO	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Clinker	0,71	22,00	66,15	8,52	1,92	63,87	14,89	6,65	11,23

* R₂O₃: Fe₂O₃ + Al₂O₃

Table 3 % SO₃ of cement mixtures* with different materials vs their % addition

Sample	% addition	% SO ₃	Sample	% addition	% SO ₃
CG1	4,0	2,37	CA1	3,5	2,33
CG2	4,5	2,58	CA2	4,0	2,64
CG3	5,0	2,93	CA3	4,5	2,77
CG4	5,5	3,12	CA4	5,0	3,24
CG5	6,5	3,54	CA5	5,5	3,42
CG6	7,0	3,93	CA6	6,5	3,83
CG7	7,5	4,31	CA7	7,0	4,55
CPG1	2,5	1,66	CF1	4,0	2,46
CPG2	4,0	2,38	CF2	4,5	2,69
CPG3	4,5	2,80	CF3	5,5	3,12
CPG4	5,5	3,25	CF4	6,5	3,47
CPG5	6,5	3,69	CF5	7,0	4,06
			CF6	7,5	4,36

* CG: clinker-gypsum, CPG: clinker-phosphogypsum, CA: clinker-anhydrite, CF: clinker-FGDgypsum

In order to achieve a SO₃ value about to 3.5% which is, as it is derived from Fig. 1, 2, 3 and discussed in the next chapter, the optimum percentage for the addition of the four

calcium sulfate-bearing materials (CSBM), clinker was ground with suitable mixtures of i) gypsum and anhydrite (CGA), ii) gypsum and PG (CGPG) and iii) gypsum and FGD gypsum (CGF). In Table 4 are summarized the ratios of clinker and mixtures of calcium sulfate-bearing materials expressed as gypsum/material [40/60 (1), 50/50 (2), 60/40 (3), 70/30 (4)], as well as the obtained values of SO₃ and the specific surface after their intergrinding for an hour.

Table 4 Admixing ratios for cement mixtures, % SO₃ and specific surface of cements

	CGA1	CGA2	CGA3	CGA4
% Clinker	94,04	93,94	93,83	93,73
% mixture gypsum-anhydrite	5,96	6,06	6,17	6,27
% SO ₃	3,36	3,46	3,45	3,44
Specific surface-Blaine (g/cm ²)	3720	3610	3610	3470
	CGPG1	CGPG2	CGPG3	CGPG4
% Clinker	93,41	93,4	93,40	93,40
% mixture gypsum – PG	6,59	6,6	6,60	6,60
% SO ₃	3,37	3,51	3,42	3,39
Specific surface-Blaine (g/cm ²)	3970	3800	3830	3760
	CGF1	CGF2	CGF3	CGF4
% Clinker	93,26	93,28	93,30	93,32
% mixture gypsum – FGD gypsum	6,74	6,72	6,70	6,68
% SO ₃	3,55	3,58	3,55	3,49
Specific surface-Blaine (g/cm ²)	3760	3830	3590	3600

Results and Discussion

The compressive strengths for 1, 2, 7, 28 days, according to EN 196.2, for the individual CSBM are compared with gypsum in Fig. 1 – 3.

From these Fig. is derived that the optimum percentage of SO₃ relating to the compressive strength, changes from 3,5% for cements with gypsum (Fig. 1, 2, 3), anhydrite (Fig. 1) and FGD gypsum (Fig. 3) to 3,0% for cements with PG (Fig. 2). The highest compressive strength for the optimum percentage of all cements are in the same order, the cement with anhydrite showing a slightly higher value (61,7N/mm²) compared with the cement with PG (59,9N/mm²) and the cement with FGD gypsum (60,0N/mm²).

In more details each material showed the following behaviour compared to gypsum: From Fig. 1, is shown that the compressive strength of cements with anhydrite are slightly higher for all range of SO₃ addition.

From Fig. 2, is evident that cements containing PG have considerably lower compressive strength at the 1st and 2nd day. This deviation is reduced for the ages of 7 and 28 days.

From Fig. 3, is shown that the results of compressive strength of cements with FGD are in the same order. This is more clear for SO₃ percentages around the optimum addition of 3,5%.

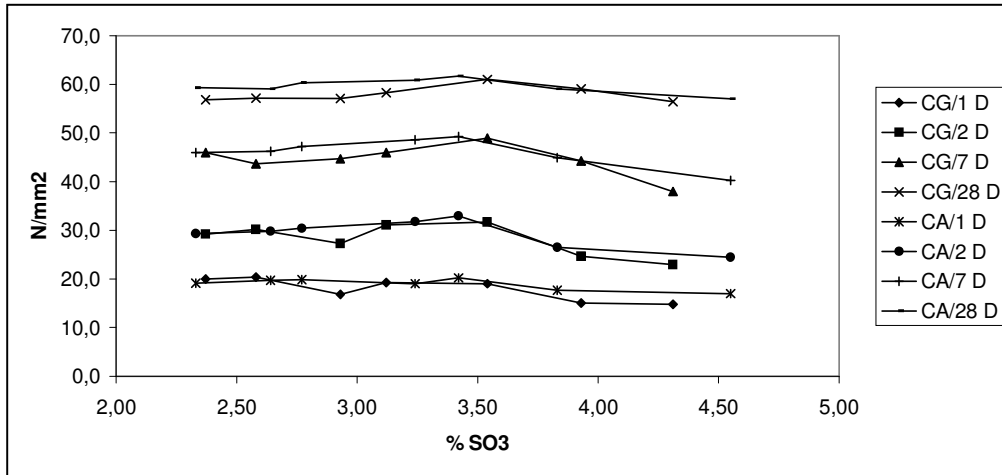


Fig. 1: Comparison of compressive strengths of CG and CA cements vs % SO₃

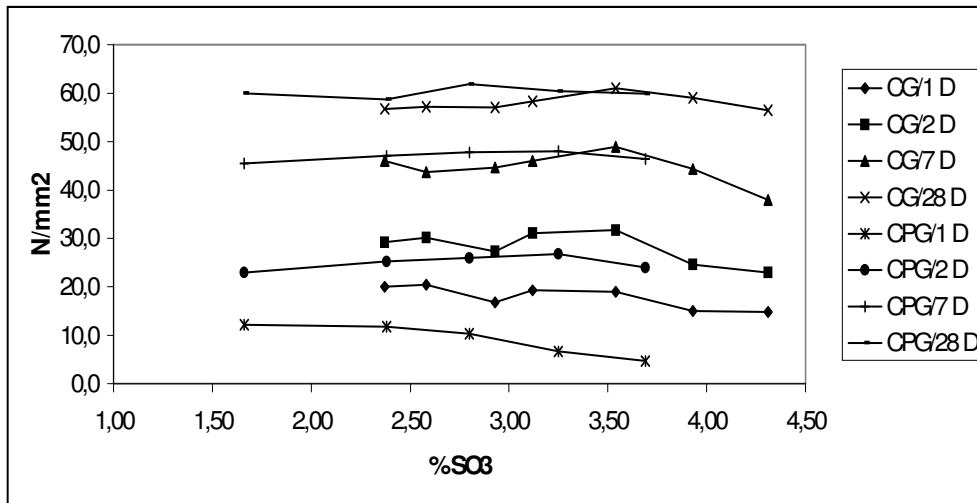


Fig. 2: Comparison of compressive strengths of CG and CPG cements vs % SO₃

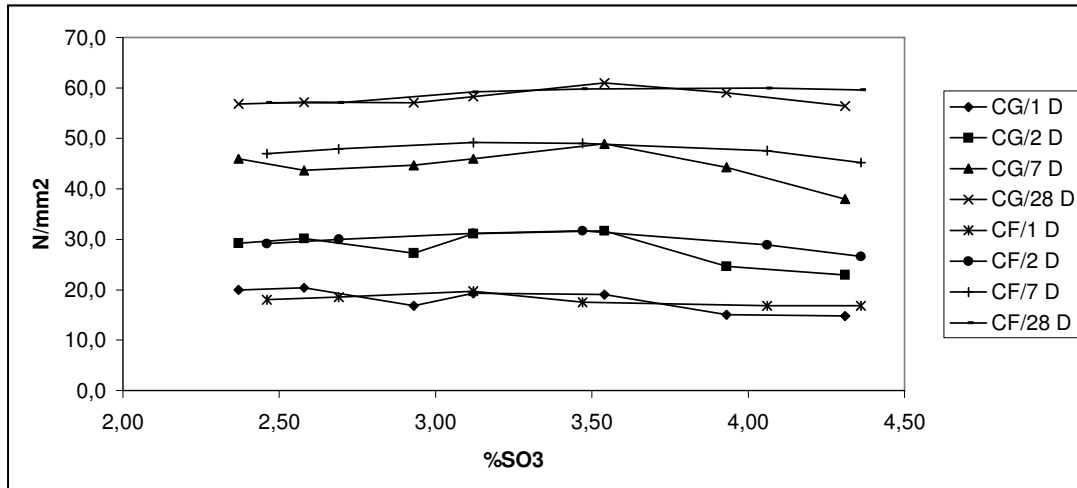


Fig. 3: Comparison of compressive strengths of CG and CF cements vs % SO₃

For setting time (EN. 196.3) it must be mentioned that PG sets much slower comparing to the other three materials (Fig. 4). This must be attributed to its impurities such as F⁻, PO₄³⁻ [8, 10].

As it is also shown in Fig. 4, cements with anhydrite set faster than those with gypsum and FGD gypsum, which showed relatively higher setting times. Faster setting of anhydrite must be attributed to its lower solubility, as well as FGD gypsum showed the higher solubility and consequently the higher setting times. It must be also pointed out that FGD gypsum contains a small percentage of CaSO₃·0.5H₂O, which may retard the setting furthermore.

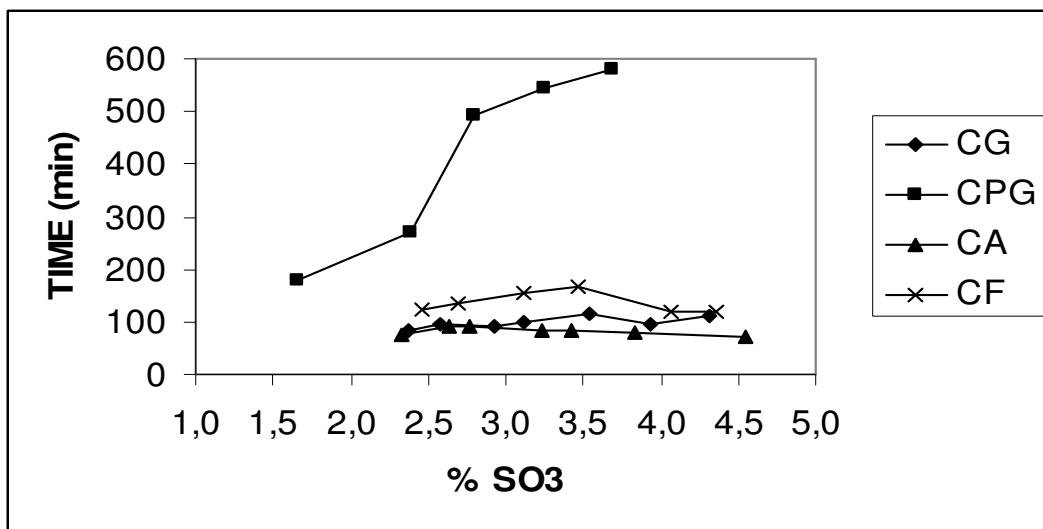


Fig.4: Setting times of CG, CA, CPG, CF cements

Relating to the behaviour of cement with mixtures of the sulfate-bearing materials, we must point out that, as it is shown from Fig. 5, 7, no significant differences are observed concerning the compressive strength of mixtures. The compressive strengths of CGA cements as well as those of CGF cements showed the same values for all examined ratios.

This figure also occurs for the CGPG cements for the ages of 7, 28 days (Fig. 6). For compressive strength of the 1st day there is a linear increase relating to the percentage of gypsum, while in the 2nd day strength, a percentage of gypsum of 40% is able to help the compressive strength to reach the relative value of gypsum.

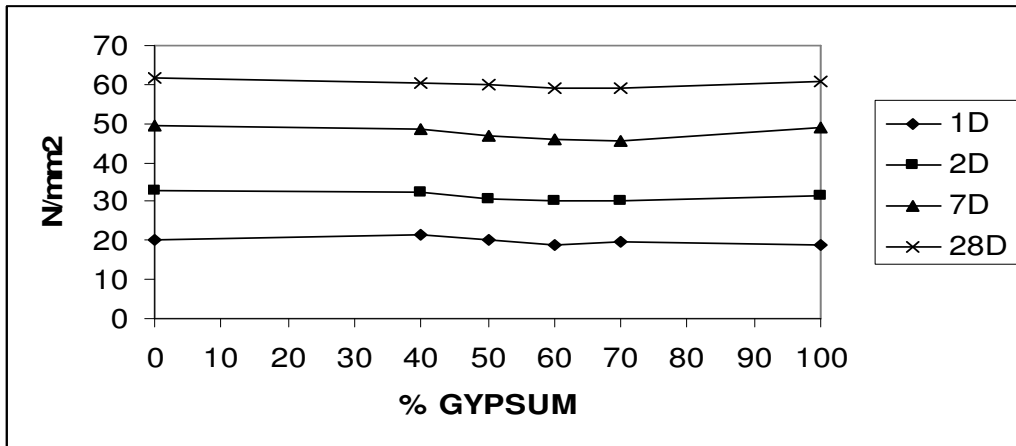


Fig. 5: Compressive strengths of CGA cements vs the ratio of CSBM

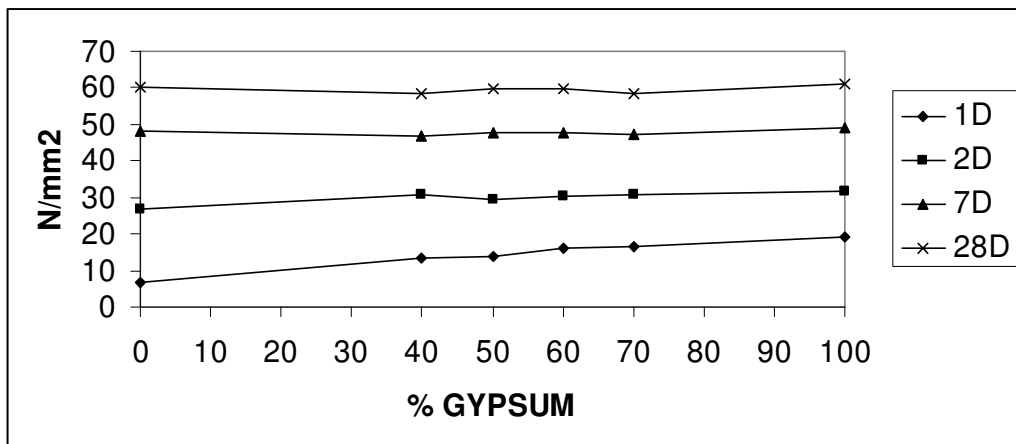


Fig. 6: Compressive strengths of CGPG cements vs the ratio of CSBM

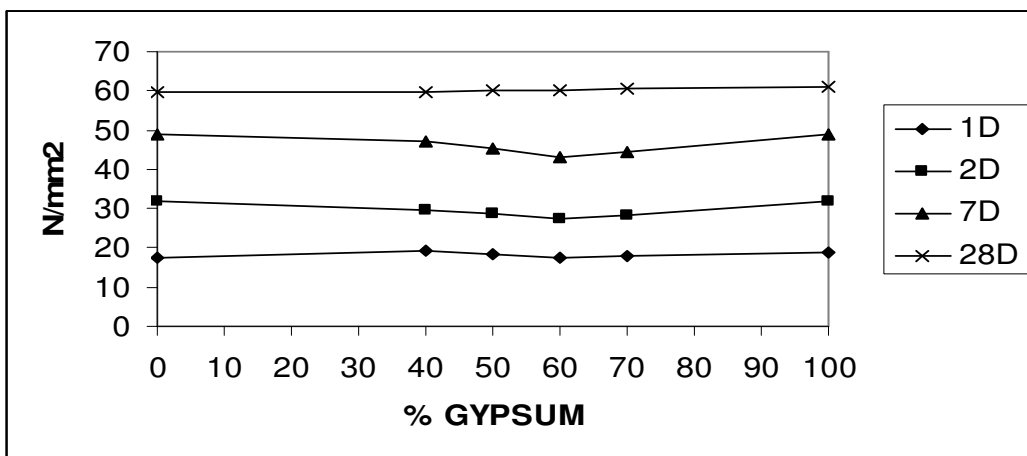


Fig. 7: Compressive strengths of CGF cements vs the ratio of CSBM

Finally, in Fig. 8 are plotted the setting times of all mixtures. It is evident that the addition of PG leads to significantly higher setting times, while the addition of FGD gypsum leads to slightly higher setting times. On the other hand, the addition of anhydrite accelerates the setting of cement. This comment is of major importance, as it gives the possibility to regulate the setting time to desired values. It is also extracted that PG is the better controller of setting comparing to other materials, as it can give, in mixtures with gypsum, a large range of setting time (150 - 230 min).

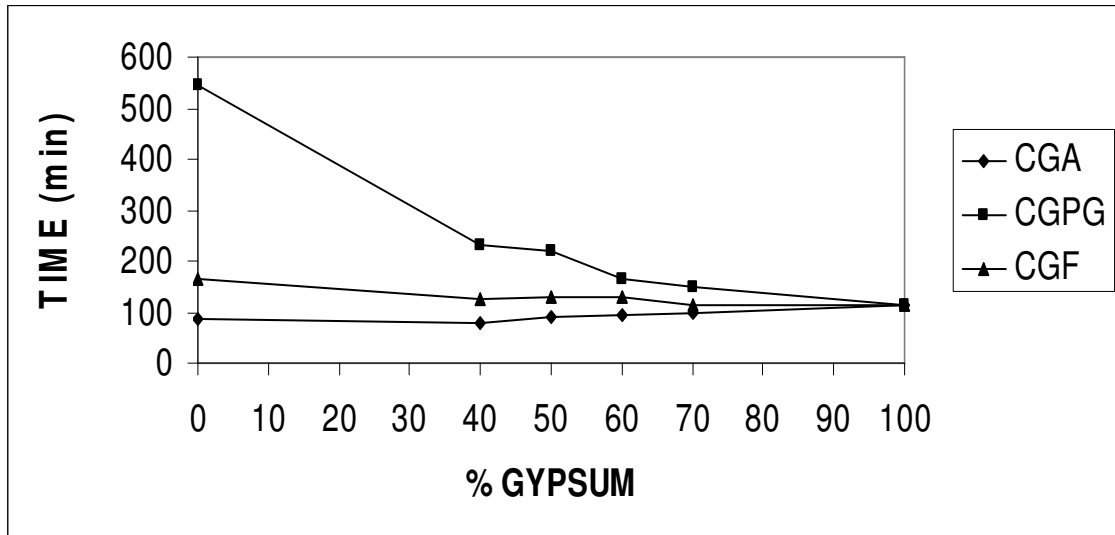


Fig. 8: Setting times of CGA, CGPG, CGF cements vs the ratio of CSBM

Conclusions

From the present work it is extracted that:

Phosphogypsum differs from the other two sulfate bearing materials either in setting time or in the initial strengths. This behaviour discourages us to propose PG as a unique common retarder material. On the other hand, for constructions which demand higher setting time, phosphogypsum probably will serve as a good controller in mixtures with natural gypsum.

Anhydrite and FGD gypsum show similar to gypsum behaviour in compressive strength development, especially in the range of the optimum SO_3 addition (about to 3,5%). They also indicate small deviations on setting time characteristics, with anhydrite accelerating the hydration reactions and FGD gypsum relatively retarding them.

The use of mixtures of sulfate bearing materials with gypsum seems to be advantageous for the precise control of setting time.

References

1. Holderbank, Gypsum during cement grinding, Seminar on Grinding, pp. 14-25.

2. Locher F. G., Richartz W., Sprung S. 1976, Setting of cement – Reaction and development of structure, ZKG, vol. 10, pp. 436-460.
3. Theisen K., 1983, Relationship between gypsum dehydration and strength development in Portland Cement, ZKG, vol. 10, pp. 571-577.
4. Locher F. G., Richartz W., Sprung S., 1980, Setting of cement – Effect of adding calcium sulfate, ZKG, vol. 6, pp. 271-277.
5. Bensted J., 1982, Effects of the clinker-gypsum grinding temperature upon early hydration of Portland Cement, Cement and Concrete Research, vol. 12, pp. 341-348.
6. Taylor H.F.W., 1992, Cement Chemistry, Academic Press Limited, Second printing, pp. 199-241.
7. Samet B., Sarkar S., 1997, The influence of calcium sulfate form on the initial hydration of clinkers containing different alkali combinations, Cement and Concrete Research, vol. 27, No 3, pp. 369-380.
8. Erdem E., Olmez H., 1993, The mechanical properties of supersulfated cement containing phosphogypsum, Cement and Concrete Research, vol. 23, pp. 115-121.
9. Demirbas Ayhan, 1996, Optimizing the physical and technological properties of cement additives in concrete mixtures, Cement and Concrete Research, vol. 26, No 11, pp 1737-1744.
10. Roy A., Kalvakaalava R., Seals R., 1998, Microstructural and phase characteristics of phosphogypsum-cement mixtures, Journal of materials in civil engineering, pp. 11-18.
11. Hamm H., 1994, Coping with FGD gypsum, ZKG, Nr 8, pp. 443-450.
12. Wirsching F., Huller R., Olejnik R., 1994, Gypsum from flue gas desulphurisation plants, ZKG, Nr2, pp. 65-71.
13. ASTM C 471M – 95, Standard test methods for chemical analysis of gypsum and gypsum products".