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Utilization of citro- and desulphogypsum as set retarders in Portland cement

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Abstract

The utilization of citro- and desulphogypsum in the cement industry as set retarders was tested and compared with natural gypsum. Chemical gypsums were used in two different forms, powder and agglomerated under pressure. Setting times and volume stability of cement pastes, as well as compressive and flexural strengths of cement mortars were evaluated. A Student's *t* statistic was applied to test the equality of strength results at the ages of 3, 7, and 28 days. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the cement industry, gypsum is added into the clinker in order to delay the rapid reaction between C_3A ($3CaO{\cdot}Al_2O_3$) and water. Conventionally, natural gypsum is used as a retarder, however, in some countries, because of the lack of gypsum deposits or ecological necessities, new sources of gypsum, i.e. by-product gypsum is utilized in cement production. Various by-product gypsums, such as phospho-, fluoro-, boro-, citro-, titano-, tartaro-, and desulphogypsum have the same chemical composition as the natural one.

Most of the research has focused on phosphogypsum, which contains some impurities that may affect the setting properties of cement, but does not change strength development [1]. In a number of researches [2,3], attempts were made to remove or stabilize the impurities in chemical gypsums of phospho- or boro- types. It was also proposed to add phosphogypsum directly into the raw mix of cement before clinkering, and as a result, lower temperature for clinker formation, as well as a retarding effect, were reported [4].

Desulphogypsum, a waste material of the desulphurization process in coal burning power plants, to convert flue gases into gypsum, is another important source of chemical gypsum [5]. Early hydration behavior of Portland cement containing various chemical gypsums, including citro-, by-product of citric acid production, and desulphogypsum were investigated [6]. It was found that more ettringite was formed upon hydration with these gypsums and compressive strength development was satisfactory.

After drying the by-product gypsums, a finely divided material is usually obtained. However, the cement industry got used to the natural gypsum in dry and lumpy form, and for this reason, the powder form of by-product gypsum may cause problems with handling or with storage. Agglomeration of gypsum was proposed to overcome these problems by one of the following processes:

(a) agglomeration by pelletizing;
(b) agglomeration by extrusion; and
(c) agglomeration by compacting.

It was reported [7] that technically and economically, the latter process was found to be the best for the agglomeration of desulphogypsum; besides, the original gypsum crystal had intergrown into a rocklike body after compacting.

In this study, the utilization of two types of chemical gypsum, citro- and desulpho-, was investigated as a set retarding additive to the Portland cement clinker, and in addition, the effect of agglomeration by compacting on the physical and mechanical properties of cement was analyzed.

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2. Experimental

Desulphogypsum was obtained from Cayirhan Powerplant, near Ankara (Turkey) and citro- was a waste material of citric acid factory in Izmit (Turkey). Both gypsums were in moist form and were dried in an oven at 40°C before using. The chemical compositions of both gypsums and the natural one used in the experiments were given in Table 1. A Portland cement clinker of PC 42.5 (Turkish Standard, TS19), with the chemical composition given in Table 1, was used in the experiments.

Both chemical gypsums in the dry state were agglomerated by compacting under pressure in steel moulds to have an apparent density of 2.1 g/cm^3, which is comparable with that of natural gypsum, i.e. 2.3 g/cm^3.

Clinker was interground together with the chemical gypsums at 4% of mixing ratio each, to the same level of fineness (315 m^2/kg) and the following mixes were obtained:

- cement with natural gypsum;
- cement with citrogypsum;

Table 1
Chemical composition of clinker and gypsums

Composition	Clinker (wt.%)	Natural gypsum (wt.%)	Citrogypsum (wt.%)	Desulphogypsum (wt.%)
SiO_2	22.42	0.61	0.44	2.03
Al_2O_3	3.89	0.11	0.11	0.52
Fe_2O_3	4.42	0.11	0.06	0.21
CaO	67.15	36.23	32.42	31.91
MgO	1.15	1.48	0.07	0.42
SO_3	0.26	34.05	45.81	43.13
LOI	0.30	26.86	21.30	20.88
Free CaO	1.37	–	–	–

Table 2
Physical properties of cements

Gypsum type	Consistency of water (%)	Setting times: Initial	Setting times: Final	Total volume expansion (mm)
Citro-	26	2 h 5 min	4 h 30 min	3
Agg. citro-	26	2 h 50 min	5 h 20 min	4
Desulpho-	26	4 h	5 h 45 min	3.5
Agg. desulpho-	26	3 h 20 min	5 h 35 min	2
Natural	26	3 h 40 min	4 h 40 min	3

Table 3

(A) Mechanical testing results of cement mortars at 3 days age

Test number	Gypsum type	Compressive strength (MPa): Sample size	Mean	Standard deviation	Flexural strength (MPa): Sample size	Mean	Standard deviation
1	Citro-	6	21.3	0.8	3	4.4	0.3
2	Agg. Citro-	6	24.1	3.1	3	5.2	0.1
3	Desulpho-	6	19.8	0.5	3	4.5	0.3
4	Agg. Desulpho-	6	21.2	0.6	3	4.7	0.4
5	Natural	6	23.8	0.7	3	5.2	0.2

(B) Student's t statistics for one- and two-tailed testing of equality of two means

Comparison	Compressive strength tests: Degrees of freedom	Calculated	Tabular: Two-tailed	Tabular: One-tailed	Flexural strength tests: Degrees of freedom	Calculated	Tabular (two-tailed)
1–5	10	−5.76	−3.17	−2.76	4	−4.13	−4.60
3–5	10	−11.40	−3.17	−2.76	4	−4.16	−4.60
1–2	10	−2.14	−3.17	−2.76	4	−4.56	−4.60
3–4	10	−4.39	−3.17	−2.76	4	−0.73	−4.60
2–5	10	0.23	3.17	2.76	4	0	4.60
4–5	10	−6.91	−3.17	−2.76	4	−2.03	−4.60

- cement with desulphogypsum;
- cement with agglomerated citrogypsum; and
- cement with agglomerated desulphogypsum.

Setting times were measured on cement pastes with a Vicat needle in accordance with TS24. Mortars were prepared at sand/cement ratio of 3:1 and water/cement ratio of 0.5 in accordance with TS24 and RILEM recommendations for measuring mechanical properties at 3, 7, and 28 days.

3. Results and discussion

The addition of citrogypsum reduced the initial setting times for both in powder and in agglomerated forms with respect to the mix with a natural gypsum as shown in Table 2. A retarding effect of about 1 h was experienced for the chemical gypsums tested except for the citro- in the powder form. However, all the results are in accord with the standard (TS19).

Almost similar results were obtained in the Le Chatelier tests of volume stability, as given in Table 2, which remained within the limits of the corresponding standards.

Flexural and compressive test results of mixes at the ages of 3, 7, and 28 days were given in Tables 3–5, respectively. A statistical evaluation was applied to compare the results because the difference between some of them are slight. Mean and standard deviations were calculated in the usual manner and the Student's t statistic was used to test the equality of strength results at a significance level of 1%, which corresponds to a 99% confidence level. For a two-tailed test, when the calculated t statistic is smaller than the tabular one for the positive values or when the former is greater than the latter for the negative ones, the hypothesis cannot be rejected, i.e. the two means are not significantly different [8]. Similarly, for the comparison of two means, whether the first one is significantly greater or smaller than the second one, a one-tailed test is applied and the calculated statistic should be greater than the tabular one for the former, and it should be smaller than the negative of the tabular one for the latter case, respectively.

Tables 3–5 indicate that the flexural strengths of all mixes tested at three different ages are not significantly different at the 1% level. The same conclusion can be made for the compressive strengths of citrogypsum-added mixes including the agglomerated form except the one at 3 days of the former mix when compared with the results of natural gypsum. However, the one-tailed statistic shows that the compressive strength of the mix with citrogypsum in powder form at 3 days is 12% smaller than that of the natural one at the same significance level. It can also be added that the agglomeration process did not change the compressive strengths of these mixes significantly.

When we compare the mixes prepared with desulphogypsum, the situation is somewhat different; the compressive strengths remained below those with the natural gypsum; about 20% and 28% reductions in strength were obtained at 3 and 7 days ages, respectively. It seems that desulphogypsum has a delaying effect at the early ages as was reported in Ref. [9]. However, the agglomeration process increased the strengths at all ages, hence, the mix with agglomerated

Table 4

(A) Mechanical testing results of cement mortars at 7 days age

		Compressive strength (MPa)			Flexural strength (MPa)		
Test number	Gypsum type	Sample size	Mean	Standard deviation	Sample size	Mean	Standard deviation
1	Citro-	6	35.1	1.3	3	6.8	0.6
2	Agg. Citro-	6	32.9	4.0	3	6.3	0.8
3	Desulpho-	6	28.8	1.4	3	6.1	0.3
4	Agg. Desulpho-	6	36.3	0.9	3	6.7	0.4
5	Natural	6	36.8	1.6	3	6.3	0.1

(B) Student's t statistics for one- and two-tailed testing of equality of two means

	Compressive strength tests				Flexural strength tests		
			Tabular				
Comparison	Degrees of freedom	Calculated	Two-tailed	One-tailed	Degrees of freedom	Calculated	Tabular (two-tailed)
1–5	10	– 2.02	– 3.17	– 2.76	4	1.42	4.60
3–5	10	– 9.22	– 3.17	– 2.76	4	– 1.10	– 4.60
1–2	10	1.28	3.17	2.76	4	0.90	4.60
3–4	10	– 11.04	– 3.17	– 2.76	4	– 2.08	– 4.60
2–5	10	– 2.22	– 3.17	– 2.76	4	0	4.60
4–5	10	– 0.67	– 3.17	– 2.76	4	1.68	4.60

Table 5

(A) Mechanical testing results of cement mortars at 28 days age

		Compressive strength (MPa)			Flexural strength (MPa)		
Test number	Gypsum type	Sample size	Mean	Standard deviation	Sample size	Mean	Standard deviation
1	Citro-	6	50.6	2.4	3	7.8	0.3
2	Agg. Citro-	6	52.1	2.9	3	7.7	1.5
3	Desulpho-	6	47.4	0.5	3	7.4	0.8
4	Agg. Desulpho-	6	53.4	1.9	3	7.8	0.2
5	Natural	6	48.9	1.6	3	7.1	0.2

(B) Student's t statistics for one- and two-tailed testing of equality of two means

	Compressive strength tests				Flexural strength tests		
			Tabular				
Comparison	Degrees of freedom	Calculated	Two-tailed	One-tailed	Degrees of freedom	Calculated	Tabular (two-tailed)
1–5	10	1.44	3.17	2.76	4	3.36	4.60
3–5	10	− 2.19	− 3.17	− 2.76	4	1.26	4.60
1–2	10	− 0.98	− 3.17	− 2.76	4	0.11	4.60
3–4	10	− 7.48	− 3.17	− 2.76	4	− 0.84	− 4.60
2–5	10	2.37	3.17	2.76	4	0.69	4.60
4–5	10	4.44	3.17	2.76	4	4.28	4.60

desulphogypsum reached the strength level with the natural gypsum at 7 days age, and even exceeded the strength of the latter beyond 28 days. This might be attributed to the new structure of crystals formed after compacting [7].

4. Conclusions

The setting times of cements prepared by the addition of citro- and desulphogypsum in both powder and agglomerated forms remained within the limits of the standards. However, the mix with citrogypsum exhibited some reduction in initial time while that with desulphogypsum showed about 1 h delay in its final setting time with respect to those of the mix with natural gypsum.

Although the addition of chemical gypsum did not change the flexural strengths of cements significantly at all ages, as compared with the reference mix of natural gypsum, desulphogypsum caused some reduction in compressive strength at early ages. However, agglomeration increased the strength of later cement to the level of the reference mix. On the other hand, citrogypsum gave similar results to natural gypsum at all ages except the one in powder form at the age of 3 days, which exhibited a smaller compressive strength than that of the reference. It can be concluded that the strength development of mixes prepared by chemical gypsums tested in this study gave satisfactory results.

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