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An investigation into the effect of various chemical and physical treatments of a South African phosphogypsum to render it suitable as a set retarder for cement

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Abstract

The work describes various physical and chemical treatments to eliminate the deleterious effects of impurities in phosphogypsum on the delayed setting time and impaired strength development behaviour of cement to which it was added as a set regulator. The physical treatments included washing, milling, and ultrasonic treatment of the material, while the chemical treatments dealt with acidic and basic additions to the phosphogypsum during the washing stage. It was found that chemical treatment with a milk of lime solution, which is often recommended in literature, was ineffective in reducing set retardation. Treatment with ammonium hydroxide or sulphuric acid was more effective in this regard. Intergrinding phosphogypsum with slaked lime improved its effectiveness in reducing set retardation, but the use of unslaked lime was less effective and also resulted in marked reductions in compressive strengths. A combined treatment of wet milling phosphogypsum with a lime slurry in a ball mall was derived from these experiments and is recommended for full-scale plant applications.

Keywords: Waste management; Cement manufacture; Retardation; Compressive strength; Phosphogypsum

1. Introduction

There are various ways to treat phosphogypsums for utilisation in the cement industry. The treatment methods can roughly be divided into three different types, namely, chemical, physical, and thermal methods of treatment. Sometimes a specific process employs a combination of these different approaches to treat the phosphogypsum and convert it into a suitable product for use in the cement industry.

1.1. Chemical treatments of phosphogypsum

Chemical treatments to render phosphogypsum suitable as a set retarder are fairly simple and easy to employ on a large scale in an economical way. The most common one that has already been referred to in the Introduction and most often recommended [1–6] is washing the phosphogypsum with a milk of lime solution, which is mostly derived from slaking the lime either before or during the process. The purpose with this treatment is to convert the different water-soluble phosphate species to insoluble (or very sparingly soluble) calcium phosphate and thus render it harmless. The major drawback of this and all other similar processes is that the acid-soluble phosphates are not treated and can still influence the setting times and strength development of the cement it is added to. Simple water washing is somewhat effective in removing surface-absorbed impurities, but leaves the bulk of the lattice-incorporated contaminants behind [2,3,6,7].

Other methods of chemical treatment of phosphogypsum include treating it with a mixture of sulphuric acid and silica or hot aqueous ammonium sulphate [5,8]. It was also found [5] that treating phosphogypsum with 10–20% aqueous ammonium hydroxide solution and subsequently washing it with water renders it suitable for use as a set retarder in cement. A method of purification that consists of reprecipitating the phosphogypsum from dilute aqueous phosphoric acid has also been described [6].

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1.2. Physical treatments of phosphogypsum

In the so-called Cerphos process [9] a large part of the impurities in phosphogypsum is removed by sieving. In an investigation of a Moroccan phosphogypsum, it was found that the particle size fractions larger than 170 μm were heavily enriched with fluorine, silicon, and sodium oxide compounds. On the other hand, the particle size fractions smaller than 25 μm were rich in organic substances and in phosphate combined in the crystal lattice. Approximately 75% of the gypsum can be recovered in a clean state by this method.

The purpose of both milling and ultrasonic treatments is to physically break the gypsum crystals up into smaller particles. The rationale of this approach is that impurities will at the same time be released from the crystal lattice and thus to a large extend be removed, similar to the sieving process described above.

In South Africa, major gypsum deposits are located far from cement-producing plants. Increasing transport costs have forced cement companies to seriously consider the replacement of natural gypsum with close by phosphogypsum resources. An investigation was therefore carried out to determine the effect of various treatments of phosphogypsum on the performance of cement made with it. The investigation focused specifically on setting times and strength development of cements containing phosphogypsum instead of natural gypsum.

2. Experimental

2.1. Various chemical treatments of phosphogypsum

A sample of by-product gypsum was split in two equal parts, one-half being dried in an oven at 50 °C. Two kilograms of the other half was stirred for 10 min in 10 l of water, allowed to settle, and the water decanted before also being dried at 50 °C. The first unwashed and second washed parts were subdivided and subsequently given different treatments before being used as set regulators in cement. The different treatments included stirring 2 kg each time for 30 min in a 10-l solution of milk of lime, 5% and 10% ammonium hydroxide, and 1% hydrochloric acid and sulphuric acid. After exposure to these solutions, the gypsum was filtered and washed twice with 10 l of tap water before being dried again at 45 °C. In all cases, the gypsum obtained after various treatments was interground with clinker to obtain a final SO_3 content in the cement of 2.3% and milled to a fineness of approximately 320 $m^2\ kg^{-1}$ Blaine surface area. A summary of the results obtained can be found in Table 1.

Table 1
Setting times and compressive strengths of cements containing various chemically treated phosphogypsums

Treatment	Gypsum type	ISO Strengths (in MPa)			Setting time	
		2 days	7 days	28 days	Initial	Final
Milk of lime	washed	14.9	28.2	43.3	315	360
	unwashed	14.9	27.8	38.5	330	405
1% HCl wash	washed	14.4	30.5	42.5	315	360
	unwashed	13.3	27.7	40.5	215	340
1% H_2SO_4 wash	washed	13.6	25.9	41.1	165	210
5% NH_4OH wash	washed	15.0	29.5	41.0	360	450
	unwashed	14.5	28.2	40.4	360	450
10% NH_4OH	unwashed	15.0	29.5	39.6	215	315
No treatment	washed	14.5	26.5	36.2	315	435
	unwashed	13.0	25.0	37.2	285	415
	natural	10.3	24.6	39.4	115	210

Table 2
Treatment specifications of phosphogypsum

Sample number	Mass of lime (g)	Mass of gypsum (g)	% Lime in gypsum	Milling time (min)
1	20	2000	1.00	15
2	25	2000	1.25	15
3	25	2000	1.25	30
4	30	2000	1.50	15
5	35	2000	1.75	15
6	25	2000	1.25	15
7	30	2000	1.50	15
8	35	2000	1.75	15
9	40	2000	2.00	15
10	40	2000	2.00	30
11	blank	2000	0.00	15
12	blank	2000	0.00	30

CaO (1–5)
$Ca(OH)_2$ (6–10)
Blank (untreated phosphogypsum)

2.2. Physical treatments of milling phosphogypsum

In the second instance, different amounts of unslaked and slaked lime were milled together with phosphogypsum containing about 1.1% total P_2O_5. The milling times were 15 min and in some cases 30 min. The amounts of unslaked and slaked lime milled together with 2 kg of phosphogypsum are summarised in Table 2. The reference samples were prepared with natural gypsum. The material was also slurried in tap water and subjected to ultrasonic vibration for 15–30 min. These treated gypsums were then mixed with clinker to yield cement with a SO_3 content of 2.3% and milled to a Blaine surface area of approximately 320 $m^2\ kg^{-1}$. A summary of the results can be found on Table 3.

All setting times were measured with Vicat needles, while compressive strengths at various time intervals were measured with EN 196-1 prisms. These measurements were performed according to the standard EN 196 specification methodology [10]. An in-house manufactured ball mill was used for the milling of all materials. A laboratory ultrasonic

Table 3
Setting times and compressive strengths of cements containing phosphogypsum treated by physical methods

% Lime in gypsum	Treatment time (min)	Initial set (min)	Final set (min)	Strength (MPa) after		
				2 days	7 days	28 days
1.00	15 (milled)	255	365	17.0	30.6	42.5
1.25	15 (milled)	285	365	5.5	11.5	20.8
1.25	30 (milled)	350	410	3.8	7.6	16.8
1.50	15 (milled)	310	355	4.0	8.8	14.9
1.75	15 (milled)	345	410	4.2	9.6	16.9
1.25 (slaked)	15 (milled)	210	295	17.6	31.3	44.2
1.50 (slaked)	15 (milled)	250	330	16.6	31.1	41.2
1.75 (slaked)	15 (milled)	255	305	16.0	30.6	44.2
2.00 (slaked)	15 (milled)	255	330	15.0	28.1	41.2
2.00 (slaked)	30 (milled)	340	435	7.7	17.2	34.2
0.00	30 (U/s washed)	395	450	15.5	29.5	39.6
0.00	30 (U/s)	285	415	15.2	30.6	39.5
0.00	15 (U/s)	235	345	14.9	30.0	40.2
0.00	15 (milled)	390	465	8.0	17.1	34.2
0.00	30 (milled)	290	440	8.5	17.6	33.6
0.00	natural	115	210	10.3	24.6	39.4

bath was used to subject the phosphogypsum slurries to ultrasonic treatment.

3. Results and discussion

3.1. Various chemical treatments of phosphogypsum

The setting time and EN 196-1 prism strength values obtained for the various chemical treatments of the phosphogypsum are summarised in Table 1. From the results summarised, it appears that the initial and final setting times of the cements containing the unwashed gypsum are shorter than those containing washed gypsum, regardless of other treatments the gypsum might have had. The only exception in this case is the unwashed gypsum treated with 1% HCl. This might be due to different amounts of chloride being retained in the phosphogypsum that could influence the setting times to a significant effect. In most cases ,the strength of the cements containing unwashed gypsum are marginally lower than those of the cements containing washed gypsum. Subject to further treatment with milk of lime and dilute hydrochloric and sulphuric acid washes, there are no significant differences in all strengths obtained between the different treatments of the gypsums added to the clinker. All the different treatments did, however, seem to increase the final strength of the cement compared to the cement containing just the washed and unwashed phosphogypsum. Compared to cement containing natural gypsum, all cements containing phosphogypsum showed much longer initial and final setting times. The most encouraging result in terms of setting time reduction was obtained with sulphuric acid. One of the authors pursued this treatment further and described the results recently [11]. The further treatments of washed and unwashed gypsum resulted in cements having comparable final strengths to the one containing natural gypsum.

3.2. Physical treatments of phosphogypsum

The cement samples containing phosphogypsum milled together with unslaked lime showed longer initial and final setting times compared with the material containing natural gypsum, as the results in Table 3 and Figs. 1 and 2 show.

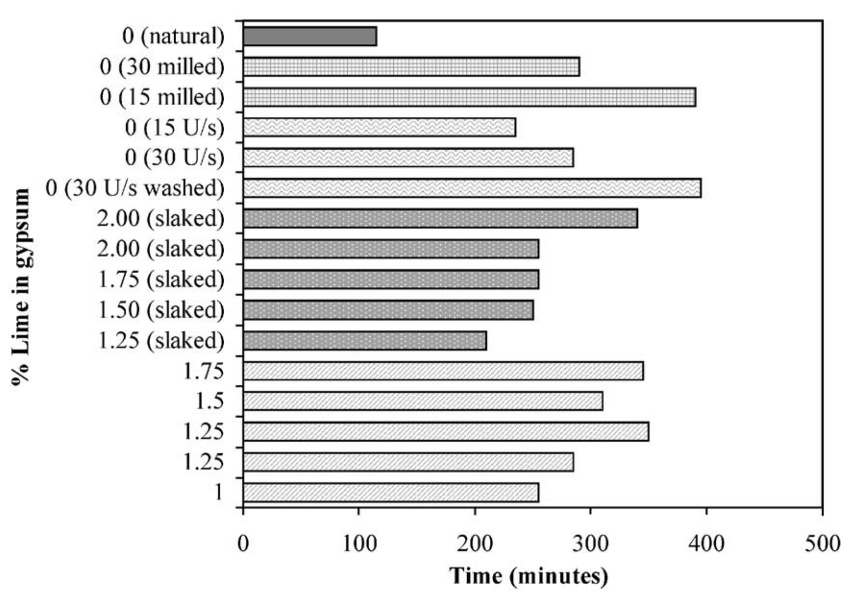

Fig. 1. Comparison of initial setting times with different treatments.

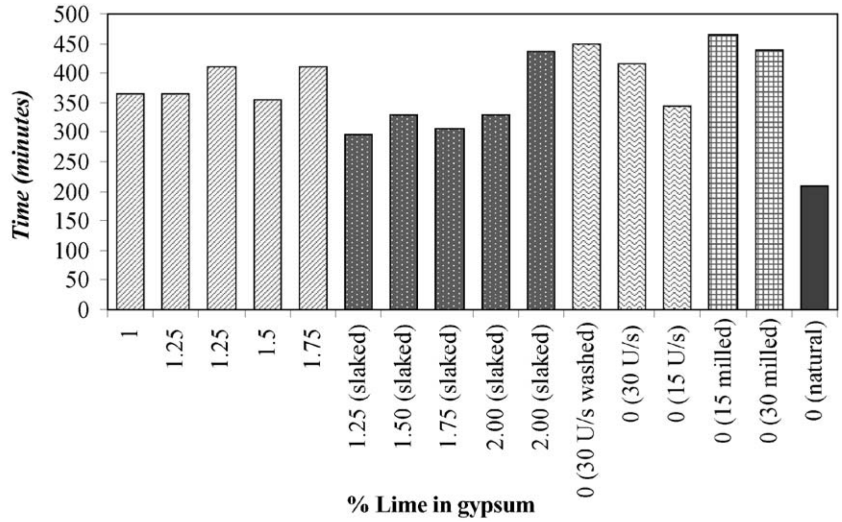

Fig. 2. Comparison of final setting times and different treatments.

The strengths at 2, 7, and 28 days were all lower than that of cement with natural gypsum except for the material milled with 1% unslaked lime, as illustrated in Fig. 3. An increase in the milling time for the same unslaked and slaked lime content in a specific sample resulted in longer initial and final setting times, as well as a lowering in all the strengths measured. Milling the phosphogypsum with hydrated lime seemed very beneficial and improved the strengths at all ages compared to cement made with natural gypsum. Provided that a setting time retardation of approximately an hour and a half can be tolerated in practical applications and is acceptable to customers, milling the phosphogysum with 1.25% of slaked lime before adding it to cement seems to be a viable treatment option.

Ultrasonic treatment of the phosphogypsum before mixing it with the clinker gave similar setting times and strength developments behaviour in the final cements as was observed with the materials prepared with the phosphogypsum milled with hydrated lime. Both unwashed phosphogypsum samples treated ultrasonically had shorter initial and

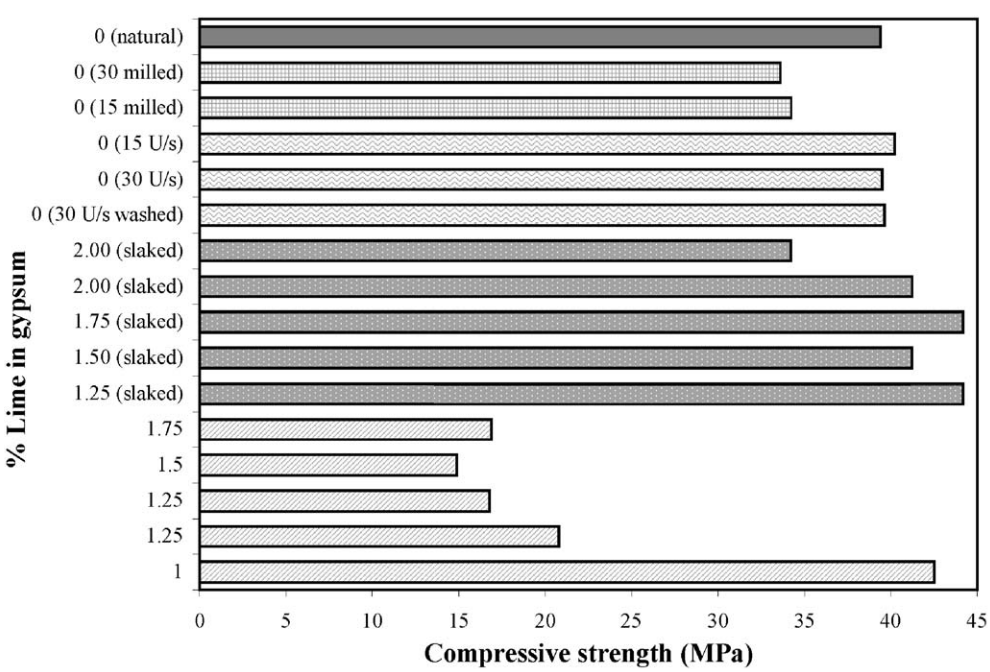

Fig. 3. Comparison of compressive strength (MPa) after 28 days with different treatments.

final setting times than the sample containing the washed material. It also seems as if a shorter ultrasonic treatment period of 15 instead of 30 min is more beneficial, as can be deduced from the data in Table 3.

4. Conclusions

Provided that the longer initial and final setting times can be tolerated, these results indicate that phosphogypsum can be rendered suitable for use as a set retarder by subjecting it to washing with dilute acid solutions or dilute basic solutions. The milling of phosphogypsum with small quantities of hydrated lime definitely seem to have beneficial effects on the strength development of the final cement. It is surprising that the most common method of washing with a milk of lime solution that is often recommended did not yield promising results in terms of reducing the setting time retardation. From this observation, as well as the results obtained when milling the phosphogypsum with 1.25% of slaked lime, one can conclude that the phosphate responsible for the setting time retardation is most probably present mainly in the coprecipitated form that is incorporated in the crystal structure of the gypsum rather than in the water-soluble form. Therefore, a treatment consisting of combined milling with a slurry of slaked lime is recommended to render phosphogypsum suitable as a substitute for natural gypsum as a set retarder in cement. Follow-up work in this regard has been reported in a subsequent communication [12].

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