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A comparison of the performance of various synthetic gypsums in plant trials during the manufacturing of OPC clinker

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Abstract

This paper compares the plant performances of various synthetic gypsums used as set regulators in cement. The decision about the suitability of a specific gypsum was based on measurements and comparisons of the specific areas (Blaine), initial setting time (min), final setting time (h), SO_3 content and compressive strength of the OPC clinker mixed with it. The results from the trials run with synthetic gypsum that was wet milled and treated with milk of lime showed no significant difference in compressive strengths at all ages, but a delay of approximately 35% in initial and 50% in final setting times occurred. Gypsum from a Tioxide plant can be successfully used as set retarders for OPC cement if the handling problems can be solved. In this case, no significant difference in either initial or final setting times or the compressive strengths, were observed. The ultrasonically treated phosphogypsum displayed a large variability of 50% or more in final and initial setting times, as well as compressive strengths at all ages, and is unsuccessful in rendering the gypsum usable as a set retarder for OPC cement.

Keywords: Sulphate; Retardation; Portland cement; Compressive strengths; Cement manufacture

1. Introduction

A large quantity of natural gypsum is used by the cement industry as a set retarder for Portland cement. It is added to the clinker at the cement grinding stage, usually at a level of 3–5%, depending on its purity. The use of phosphogypsum and other synthetic gypsums to replace natural gypsum as a set retarder for cement is limited mainly due to varying moisture content and impurities, which can interfere with the workability of the cement.

Natural gypsum deposits in South Africa are located a great distance away from most of the cement production plants. Because of high transport costs, this results in a great increase in the landed price of the gypsum. It would therefore be advantageous if phosphogypsum and other synthetic gypsums produced in proximity to a number of cement plants could be utilised instead of natural gypsum to control the setting time of the cement. Furthermore, it would simultaneously alleviate some waste disposal problems and reduce environmental pollution.

The problems that could be caused in cement hydration due to the impurities present in synthetic gypsum, and in particular phosphogypsum, have been described by a number of investigators [1–10]. It is therefore clear that some treatment of the phosphogypsum will have to be performed before it can be used in the cement production process. Previous reports in the literature [2–11] have mostly concentrated on laboratory evaluations when using various treated phosphogypsums or other synthetic gypsums as set retarders in cement. This investigation differs from previous approaches in not only considering laboratory trials, but also evaluating the use of various treated and untreated synthetic gypsums on full plant scale to arrive at conclusions about their suitability.

Two of the critical factors influencing cement setting time and strength development behaviour are the Blaine specific area and the sulphate content (% SO_3). In order to make meaningful comparisons between the effects of the different gypsum types in the cement, it is therefore extremely important that the surface area and the sulphate

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content of the cement containing phosphogypsum be comparable to that of the normal production cement containing natural gypsum.

2. Experimental procedure

Plant trials were conducted according to the following procedure: At least eight samples of each of the gypsums, clinker and cement produced from it were collected before the introduction of the synthetic gypsum into the mill, during the trial with the synthetic gypsum in the mill and in the aftermath of the trial. Statistical analysis of the results obtained from the various tests and analyses resulted in an objective comparison of the performance of the synthetic gypsum as opposed to that of natural gypsum in cement. It also gave a clear and unbiased indication of the success of the treatment of the synthetic gypsum and the trial itself. A closed-circuit mill was used in all plant trials. The trials conducted concerned in the first instance the production of an ordinary Portland cement (OPC), with treated synthetic gypsum that was wet milled together with a milk of lime solution. The synthetic gypsum was obtained from a fertilizer producer, in this case producer no. 1. A complete description of the treatment process can be found in earlier reports [12–14]. In subsequent trials, phosphogypsum from a second fertiliser producer was used, as well as synthetic gypsum from a Tioxide producer.

Sulphate contents were determined with a Siemens X-ray fluorescence (XRF) spectrometer, whereas strength and setting time tests, as well as Blaine surface area measurements, were conducted in the normal manner as described in the relevant standard specifications [15].

3. Results and discussions

3.1. Fertiliser producer no. 1

Initial laboratory tests with this material have been described in a separate report [14] and were sufficiently encouraging to proceed with a full-scale plant trial. The results obtained during the first plant trial manufacturing OPC with treated phosphogypsum are presented in Table 1. It can be concluded that the fineness as well as the sulphate content of the cements before, during and after the first plant trial was, within the error of measurement, the same. The OPC produced with the treated phosphogypsum had an initial setting time that was on average about 30 min longer than that of the OPC containing natural gypsum. The final setting time of the former cement was also at least 30 min longer than that of the latter. The compressive strengths of the cements with the two types of gypsum at different time intervals were practically identical.

Table 1
Summary of setting time and strength development behaviour of an OPC cement produced with natural and treated phosphogypsum

	Specific surface ($cm^2\ g^{-1}$)	Initial setting time (min)	Final setting time (h)	SO_3 cement (%)	Compressive strength (MPa) after		
					2 Days	7 Days	28 Days
Baseline with natural gypsum before the trial							
Average	4105	82	1.90	2.44	31.0	49.2	59.8
S.D.	94	10	0.24	0.39	1.2	1.0	1.3
Cov (%)	2.3	12.2	12.6	16.0	3.9	2.0	2.2
Trial with phosphogypsum							
Average	4285	136	2.93	2.12	29.7	48.6	57.8
S.D.	77	8	0.23	0.62	2.3	1.8	1.9
Cov (%)	1.8	5.9	7.8	29.2	7.7	3.7	3.3
Baseline with natural gypsum after the trial							
Average	4276	96	2.06	2.24	31.5	48.6	57.1
S.D.	118	11	0.08	0.15	0.7	2.4	2.3
Cov (%)	2.8	11.5	3.3	6.7	2.2	4.9	4.0

3.2. Fertiliser producer no. 2

After several laboratory trials, it was decided to conduct plant trials with the phosphogypsum from fertiliser producer no. 2, namely, Omnia. In both these cases, the phosphogypsum was treated with a patented ultrasonic process. It essentially consists of a piece of machinery with two plates about 1 cm apart from each other through which the phosphogypsum moved while an ultrasonic frequency was applied across the plates. According to sonochemistry theory [16], ultrasonic sound waves have the ability to shatter crystals in solid materials and generate local "hot spots" (areas with high pressure and temperature) in liquids. Under such conditions reactions not otherwise possible might now occur. The phosphogypsum was mixed with limestone or lime before the treatment started. The rationale behind this approach was that once the phosphogypsum crystals were shattered by the ultrasonic sound waves, cocrystallised phosphates will be released that can react with the calcium ions released upon cement hydration during mixing of the cement (containing the treated phosphogypsum) with water. This would result in the formation of insoluble tricalcium phosphate that would then eliminate the interference of P_2O_5 on the setting time and strength development of the cement. XRF analysis of material tested in the laboratory once found evidence that CaO had been used in the treatment process, but apparently the materials used in the plant trials were preferentially mixed with limestone and not lime before the treatment process. Limestone is much cheaper than unslaked lime (CaO) (about 40% of the price of unslaked lime) and this will greatly affect the economical operation of the treatment plant. In essence, this is a physical/mechanical treatment method and it does not reduce the phosphate content of the treated material, as can be clearly seen from the results shown in Table 2.

Table 2
Phosphate content (wt.%) of samples treated with an ultrasonic apparatus

Sample No.	Water-soluble P_2O_5	Cocrystalline (acid-soluble) P_2O_5	Total P_2O_5 (calculated)	Total P_2O_5 (by XRF)
1	0.14	0.76	0.90	0.97
2	0.10	0.74	0.84	0.95
3	0.09	0.78	0.87	0.91
4	0.12	0.67	0.79	0.89
5	0.06	0.75	0.81	0.88
6	0.04	0.72	0.76	0.85
7	0.05	0.72	0.77	0.84
8	0.07	0.66	0.73	0.79
9	0.24	0.71	0.95	0.82
10	0.22	0.76	0.98	0.99
11	0.22	0.70	0.92	1.00
12	0.29	0.69	0.98	1.05

Through the course of all the work described in this investigation, it was often noted that the phosphogypsum from fertiliser producer no. 2 had a higher total phosphate content than that from fertiliser producer no. 1.

The first plant trial conducted with the ultrasonically produced material was conducted in the same cement plant and on the same mill as those described previously for the treated material from fertiliser producer no. 1. First, a 4-h baseline test was performed, using the natural gypsum that is normally added in the cement milling process. This was followed by the production trial using the ultrasonically treated phosphogypsum, which lasted for a total of 17 h. The baseline test proceeded without any serious problems and the various samples of interest were collected every 30 min.

Upon introduction of the treated gypsum through the mill feed chute, the process was given about 30 min to stabilise before the performance trials commenced. The treated gypsum had a darker cream colour and was much finer than the natural material. From visual observations, it seemed as though the treated gypsum had higher moisture content than the natural material. This caused the treated gypsum to build up at the mill feed chute, and the material had to be constantly cleared and pushed into the mill. The mill feed chute also did not have the correct inclination angle for the treated gypsum to flow easily, and this contributed to the buildup experienced. All these effects would have resulted in an uneven addition of gypsum to the cement and therefore effect the quality of the final product. To solve the feed problems experienced, one or more of the following options can be considered:

(a) The material should be dry so that it can flow more easily.
(b) The feed system can be changed to eliminate buildups.
(c) The treated material can be blended with the natural gypsum to decrease the overall moisture content before feeding the composite material into the mill.
(d) The treated material can be blended with clinker and then fed into the mill.

Unfortunately, the product elevator broke a bucket during the trial and this caused the system to trip. Repairs had to be done before the trial could proceed again. This resulted in the trial being done in two parts. Samples of the relevant materials were collected every hour during the trial. The results obtained are summarised in Table 3.

Analysis of the results showed that there were considerable differences between the setting times (initial and final), the SO_3 content and the compressive strength at 28 days between the cements produced with natural gypsum and those produced with the ultrasonically treated phosphogypsum. Because only three samples were taken after the plant trial for a baseline test, not too much attention should be paid to the values summarised in the table for the final baseline. Concentrating on the initial baseline test values and those obtained during the trial with the treated material, one can conclude that only the specific surface areas were, within experimental error, the same.

The treated phosphogypsum setting times showed a huge variability in the results, where the average for the initial setting time was 255 min and the range was 190 to 325 min. In comparison with the baseline samples, the initial set average was 137 min, with a range of 115 to 155 min. The same variation was found in the final setting times, with the treated phosphogypsum ranging from 4.25 to 6.00 h with an average of 5.38 h in comparison with the baseline samples that ranged from 2.75 to 3.75 h with an average of 3.03 h. The results indicated that the cement with treated phosphogypsum performed in a much poorer manner than the cement containing natural gypsum. Because of the problems experienced during the trial (as described above) and also because some contamination of the treated phosphogypsum was suspected, it was decided to perform another plant trial with this material.

Table 3
Summary of the setting time and strength development behaviour of OPC cement produced with natural and ultrasonically treated phosphogypsum in the first plant trial

	Specific surface ($cm^2\ g^{-1}$)	Initial setting time (min)	Final setting time (h)	SO_3 cement (%)	Compressive strength (MPa) after		
					2 Days	7 Days	28 Days
Baseline with natural gypsum before the trial							
Average	3514	137	3.03	2.07	20.9	42.3	56.5
S.D.	107	13	0.45	0.10	1.4	2.3	1.9
Cov (%)	3.0	9.5	14.8	4.8	6.7	5.4	3.4
Trial with phosphogypsum							
Average	3413	255	5.38	1.86	17.3	37.8	49.7
S.D.	218	39	0.58	0.22	3.3	3.1	3.5
Cov (%)	6.4	15.3	10.8	11.8	19.1	8.2	7.0
Baseline with natural gypsum after the trial							
Average	4267	73.3	2.42	2.99	25.9	42.2	53.2
S.D.	306	20.3	0.5	0.41	1.2	1.6	1.7
Cov (%)	7.2	27.7	20.7	13.7	4.6	3.8	3.2

Table 4
Summary of setting time and strength development behaviour of OPC produced with natural and ultrasonically treated phosphogypsum during the second plant trial

	Specific Surface (cm^2 g^{-1})	Initial setting time (min)	Final setting time (h)	SO_3 cement (%)	Compressive strength (MPa) after		
					2 Days	7 Days	28 Days
Baseline with natural gypsum before the trial							
Average	4080	143	3.05	2.85	23.9	40.1	53.5
S.D.	76	16	0.21	0.11	2.6	2.5	2.2
Cov (%)	1.9	11.2	6.9	3.9	10.9	6.2	4.1
Trial with phosphogypsum							
Average	3779	323	4.21	1.86	16.8	34.4	46.7
S.D.	99	69	1.22	0.12	2.7	5.3	5.0
Cov (%)	2.6	21.4	29.0	6.5	16.1	15.4	5.0
Baseline with natural gypsum after the trial							
Average	3881	162	3.41	2.80	23.0	41.1	55.5
S.D.	110	28	0.4	0.12	2.0	3.1	2.6
Cov (%)	2.8	17.3	11.7	4.3	8.7	7.5	4.7

In this instance the initial baseline test lasted only 2 h before the actual trial run commenced. The trial with treated phosphogypsum being milled with the clinker lasted a total of 9 h, after which a second baseline test with natural gypsum was run for 5 h. Sample intervals were similar to that of the previous plant trial. The first baseline trial differed from the final one, because rapid hardening cement with a higher surface area was produced. During the trial and the second baseline test, OPC with a lower surface area was produced. One should therefore compare the results obtained during these latter two parts to arrive at fair conclusions about the performance of the manufactured cements. The results obtained on this occasion are given in Table 4.

Despite a repeat of the plant trial, the results still indicated significant differences between the baseline material produced with natural gypsum and those cements made with the treated phosphogypsum. The phosphogypsum-containing cement had longer initial and final setting times than the baseline cement (initial set more than 70 min and final set more than 0.8 h longer). The standard deviation in both initial and final setting time values for the cement with treated phosphogypsum is higher than that of the baseline material.

Furthermore, the cement containing treated phosphogypsum had lower compressive strengths at 28 days than the baseline material (on average about 8.8 MPa), and its standard deviation was again substantially higher than in the case of the baseline material. Both the specific surface (100 cm^2 g^{-1}) as well as the SO_3 content of the material produced with the treated phosphogypsum were lower than the corresponding values of the cement containing natural gypsum, which could partially explain the slower setting times and lower final strengths observed.

Table 5
Characteristics of the synthetic gypsum received from a Tioxide producer

Parameter	Amount (%)
$CaSO_4 \cdot 2H_2O$	85–90
$CaCO_3$	4.0
Acid insolubles (SiO_2)	4.0
Free moisture	11–13
Iron (Fe)	3.0
Manganese (Mn)	0.08

Table 6
Comparison of the performance of OPC containing natural and a synthetic gypsum

Parameter	OPC–natural gypsum	OPC–synthetic gypsum
Surface area (m^2/kg)	308.5	384.3
Standard consistency (mm)	24.3	25.1
Initial setting time (min)	150	160
Final setting time (min)	205	190
Compressive strength (MPa)		
2 Days	18	22
7 Days	32	43
28 Days	46	57

3.3. Tioxide producer

The decision to evaluate this material stemmed from the fact that one of the cement plants in South Africa is currently using it as a set retarder in their plant. A visit paid to Natal Portland Cement (NPC) revealed that the handling equipment on the plant was specially reengineered to handle this material without hassles. Due to the high moisture content of the synthetic gypsum, container bins and feeders were lined with Teflon and fitted with mechanical vibrators to ensure a good flow of the material under plant conditions. As was previously the case, the experimental work comprised both a laboratory and plant phase. In the first phase, the synthetic gypsum was evaluated on a laboratory scale. The characteristics of the synthetic gypsum are summarised in Table 5.

In the laboratory stage of the investigation, the performance of natural and the synthetic gypsum were compared

Table 7
Summary of setting time and strength development behaviour of OPC produced with natural and a synthetic gypsum

	Specific Surface (cm^2 g^{-1})	Initial setting time (min)	Final setting time (h)	SO_3 cement (%)	Compressive strength (MPa) after		
					2 Days	7 Days	28 Days
Trial with phosphogypsum							
Average	3200	229	4.61	2.25	14.6	28.9	51.5
S.D.	120	15	0.23	0.28	1.0	1.2	1.9
Cov (%)	3.8	6.6	5.1	12.4	6.9	4.2	3.7
Baseline with natural gypsum after the trial							
Average	3260	222	4.48	3.08	11.3	26.2	47.4
S.D.	80	12	0.17	0.14	0.7	1.6	1.3
Cov (%)	2.5	5.4	3.7	4.5	6.2	6.1	2.7

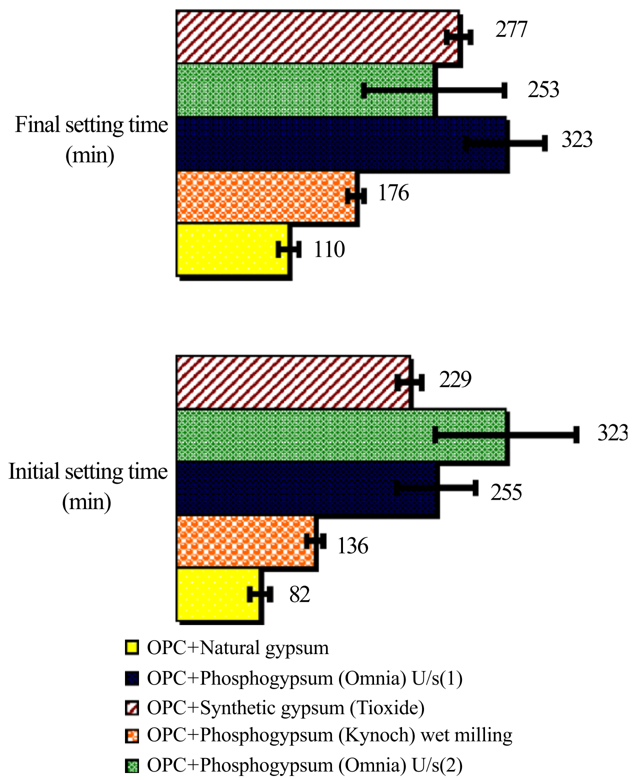

Fig. 1. Schematic comparison of the initial and final setting times of all the OPCs produced in the various plant trials with different treated and synthetic gypsums.

in terms of their effect on the setting time and strength development of an OPC produced with both. The results obtained are given in Table 6.

The results indicate that the sample containing synthetic gypsum compared well to the baseline one with natural gypsum. There was, however, a significant difference in the surface area measurements of the two samples, which will impact favourably on the strength development of the sample containing synthetic gypsum. The results were sufficiently encouraging to embark on a plant trial.

A plant trial was subsequently conducted to evaluate the material's handling aspects in the existing plant, the compatibility with the process and its effects on the cement quality produced. From the onset, problems were experienced due to the fine nature and high moisture content of the material. At the start of the tests, the synthetic gypsum was fed into the gypsum feed bin with a grab crane. The material bridged up in the bin and would not flow under normal plant operation. The material had to be trickle fed from the grab crane and a team of three persons was required to ease the material through the chute onto the gypsum-weighing belt. This could potentially result in inconsistent feed of the gypsum and, subsequently, problems with the cement quality. The trial with the synthetic gypsum ran for 7.6 h before there was a switchover to natural gypsum to complete a baseline test. The baseline test after the trial with synthetic gypsum lasted for 5.5 h. During the trial, samples of the gypsum, clinker and final cement were taken hourly, and

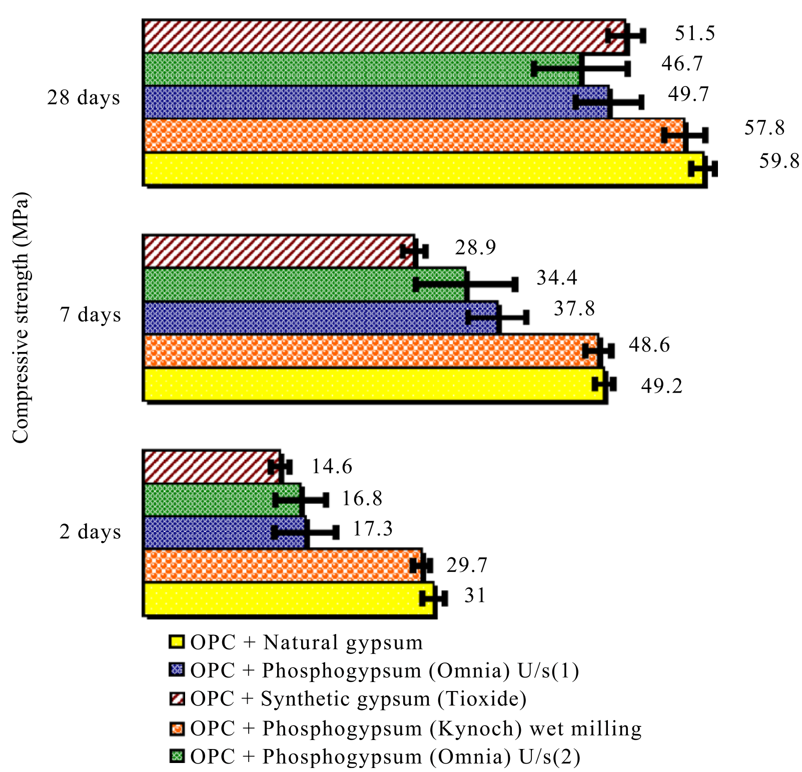

Fig. 2. Schematic comparison of the 2-, 7-, and 28-day compressive strengths of all the OPCs produced in the various plant trials with different treated and synthetic gypsums.

during the baseline test materials were sampled every half an hour.

The results obtained are summarised in Table 7. From the averages of the data, as presented in Table 7, it can be concluded that the fineness of the cements during and after the plant trial was, within the error of measurement, the same. There was a significant difference in the SO_3 contents of the cement produced with synthetic gypsum, compared to the one produced with natural gypsum. The lower concentration and large coefficient of variance in the SO_3 content of the cement produced with synthetic gypsum bear witness to the handling problems experienced with this material during plant operation. However, despite this, the initial and final setting times of the cements were, within experimental error, the same. The compressive strength of the cement made with synthetic gypsum was initially marginally higher after 2 days than that of the cement produced with natural gypsum, but at later ages the strength of the cements with the two types of gypsum were, for all intents and purposes, the same.

Figs. 1 and 2 give a comparison of the average performances of OPCs produced during the four plant trials, both in terms of the performance in relation to one another, as well as to OPC containing natural gypsum.

The following can be very clearly deduced from these two figures:

(i) All the synthetic gypsums, except the treated AECI/Kynoch one, significantly retard the initial and final setting times of OPC containing them, when compared to natural gypsum.
(ii) There is an additional lowering of the early-age strengths of all the OPCs containing synthetic gypsums, with the exception of the AECI/Kynoch treated gypsum.
(iii) The OPC with the treated AECI/Kynoch phosphogypsums showed the least amount of variance in performance among all the OPCs containing synthetic gypsums.
(iv) The OPC with the treated AECI/Kynoch phosphogypsum showed the closest resemblance in performance to the OPC containing natural gypsum.
(v) The gypsum treated by wet milling it with a milk of lime slurry can be substituted for natural gypsum in OPC without compromising the performance of the product.

4. Conclusions

In summary, the plant trials indicate that both the treated gypsum from fertiliser producer no. 1, which has been wet milled with milk of lime, as well as the synthetic gypsum from the Tioxide producer can be used successfully as set retarders for cement and can act as replacements for natural gypsum without compromising the performance of cement. However, from a logistical point of view, the synthetic gypsum from the Tioxide producer is a nightmare to handle without suitable reengineering of parts of the plant. This will necessarily result in increased initial costs before any potential savings of replacing natural gypsum can be realised. On the other hand, the gypsum wet milled with milk of lime would also require a dedicated plant to produce this material, which entails an additional capital outlay. However, once it is produced, it can be handled with normal existing plant equipment without modifications. From the point of view of the quality and performance of the cement, the ultrasonically treated phosphogypsum displays the most variability and least consistency when replacing natural gypsum in cement. There are of course other issues that have not been addressed in this study, for example, the effect of organic admixtures like superplasticisers and set retarders on cements containing synthetic gypsums.

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