Chapter 9 Conclusion

Phosphogypsum has to be purified of the harmful phosphorous impurities before it can replace natural gypsum as a set retarder in Portland cement. The amount of impurities contained in phosphogypsum depend upon the purity of the raw materials used in the production of phosphoric acid, the operating conditions of the phosphoric acid process and the age of the disposed phosphogypsum stockpile. These impurities tend in an unpredictable way to delay the setting time, and decrease the mechanical strength development of cement.

The calcium sulphate phase present in the Portland cement mixture will also affect the setting time considerably, due to the difference in solubility of the different phases. The calcium sulphate dihydrate form, $CaSO_4.2H_2O$, is preferred for use in Portland cement.

The different South African phosphogypsum samples used during this study were found to contain a significant amount of phosphorous impurities, substituted in the gypsum crystal lattice. The presence of considerable amounts of calcium sulphate hemihydrate or anhydrite in some of the untreated phosphogypsum samples could also limit the effectiveness of phosphogypsum as a set retarder in Portland cement.

The particle size distribution in the South African phosphogypsum samples plays an important role when the phosphorous impurities are considered, which indicates that sieving can be applied to remove some of the phosphorous impurities. However, this is not effective for the purification of phosphogypsum for use in Portland cement, since the amount of phosphorous impurities, contained in the sieved fractions with fewer phosphorous impurities, was still too large.

In order to remove more of the phosphorous impurities, a combined thermal and washing treatment was performed on the respective phosphogypsum samples. A similar method was described by Ölmez and Yilmaz (1988) as being successful in removing most of the impurities in Turkish phosphogypsum. Application of this method to South African phosphogypsum proved not to remove the phosphorous impurities contained in the phosphogypsum crystal lattice, but was successful in removing some of the water-soluble impurities. The phosphorous impurities contained in South African phosphogypsum seemed to consist mainly of phosphorous combined in the gypsum crystal lattice and not water-soluble compounds.

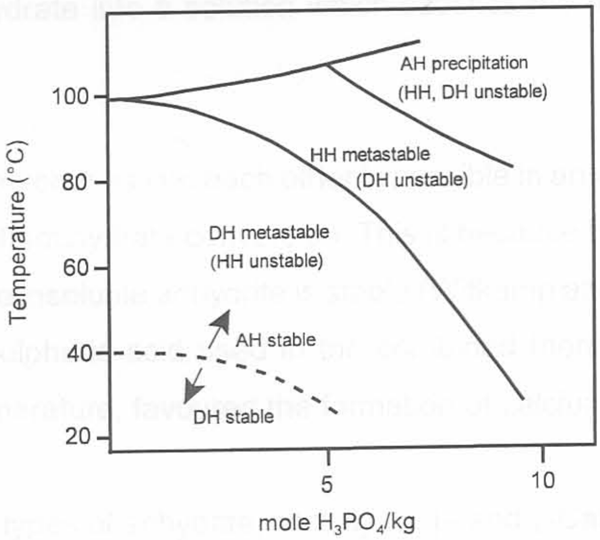
Jarosiński (1994) described a sulphuric acid treatment method for the recovery of rare earths from phosphogypsum. Treatment of the South African phosphogypsum samples by a similar sulphuric acid treatment method removed more phosphorous impurities than the previous washing treatments, and the treated samples contained mainly the dihydrate form of calcium sulphate.

The sulphuric acid treatment method was then combined with thermal treatment, and this method proved to be successful in removing most of the harmful phosphorous impurities from the gypsum crystal lattice. The obtained gypsum products consisted mainly of the required dihydrate form of calcium sulphate. This treatment method proved to be the best for the South African phosphogypsum samples, and a possible explanation for its mechanism will be discussed.

The amount of foreign ions incorporated in the gypsum crystal lattice largely depends on the operating conditions of the phosphoric acid process, given by the H_3PO_4 and H_2SO_4 content of the reaction solution, the temperature, and the supersaturation. The nature of the precipitated calcium sulphate phase also influences the uptake of foreign ions. Depending on the temperature and the H_3PO_4 and H_2SO_4 content of the solution, either calcium sulphate dihydrate, hemihydrate or insoluble anhydrite (β-$CaSO_4$) will be formed, as shown in Figure 9.1 (van der Sluis *et al*, 1986).

The solid lines in Figure 9.1 represent equilibrium curves, but since some of the modifications are metastable under the given conditions, these lines merely indicate which phase will initially precipitate. The broken line separates the regions where either dihydrate or anhydrite is stable. The dihydrate and insoluble anhydrite are the only thermodynamically stable forms of calcium sulphate, as the hemihydrate form only exists as a metastable phase. The influence of H_2SO_4 on the position of the curves in Figure 9.1 can be taken into account by assuming 1 mol of H_2SO_4 is equivalent to about 1.5 mol of H_3PO_4 (van der Sluis *et al*, 1986).

Figure 9.1 The precipitated calcium sulphate phase as a function of the H_3PO_4 content and temperature of the solution (van der Sluis *et al*, 1986; Witkamp and van Rosmalen; 1990)



The role of H_2SO_4 and H_3PO_4 in the formation of the different calcium sulphate phases can be explained by the activity of water, as the determining factor in the stability of the three phases (Witkamp and van Rosmalen, 1986). The three phases contain different percentages of water, leading to a dependency of their stability on the activity of water. At higher acid concentrations, the amount of free water, and therefore the activity of water, is lower. This favours the formation of a more dehydrated phase, namely anhydrite or hemihydrate with respect to the dihydrate phase. At higher temperatures, water tends to form looser bonds in the crystal and also in the solution, thus favouring the vapour phase. This makes calcium sulphate forms which contain less water of crystallization stable at high temperatures.

From the diagram it is observed that insoluble anhydrite (β-$CaSO_4$) appears to be stable in the largest part of the diagram, that is above 40°C in pure water, and above lower temperature levels at increasing acid concentrations. Up to high temperatures and acid concentrations, however, metastable dihydrate and hemihydrate can be formed in the stable anhydrite region. This results from the fact that anhydrite growth proceeds very slowly in a large part of the diagram. Eventually, the metastable dihydrate or hemihydrate phases will be transformed into anhydrite, but this only occurs with measurable speed at high temperatures and acid concentrations (Witkamp and van Rosmalen, 1986). It can further be seen that hemihydrate only exists as a metastable phase. Conversion of hemihydrate into dihydrate and vice versa can occur by crossing the dihydrate-hemihydrate equilibrium line, or by bringing dihydrate into a solution which satisfies the metastable hemihydrate conditions.

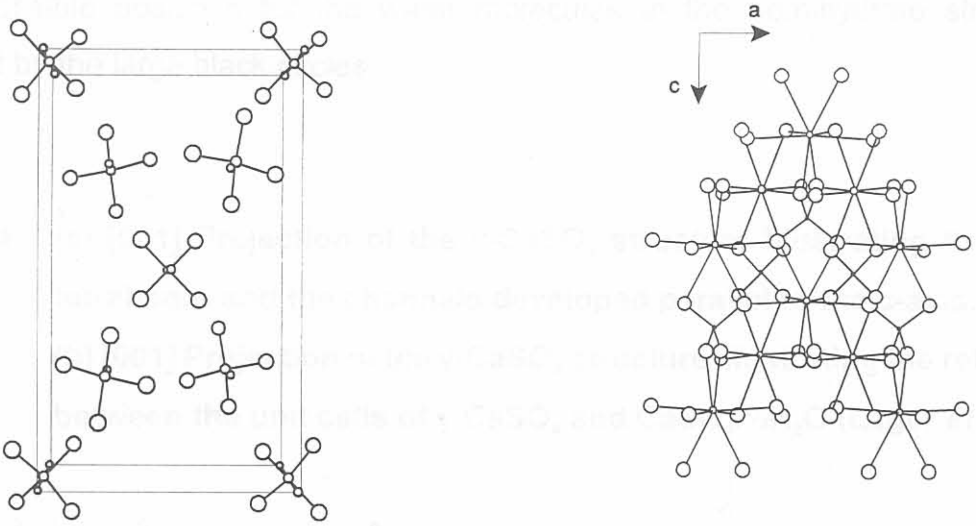
Any transition of the three phases into each other is possible in an acid solution, except the insoluble anhydrite into hemihydrate conversion. This is because hemihydrate can only be formed in a region where insoluble anhydrite is stable (Witkamp and van Rosmalen, 1986). The concentration of sulphuric acid used in the combined thermal and acid treatment, performed at room temperature, favoured the formation of calcium sulphate dihydrate.

There are three distinct types of anhydrite, namely α-, β- and γ-$CaSO_4$. The first, α-$CaSO_4$ only exists at temperatures above 1180°C, and is therefore not relevant to this discussion. The γ-$CaSO_4$ form, also called soluble anhydrite readily absorbs vapour or liquid water to convert to the hemihydrate form. Instead, β-$CaSO_4$ or insoluble anhydrite, converts to the dihydrate form through a solution process (i.e. recrystallization). The rate of conversion of insoluble anhydrite to gypsum is relatively slow and depends on the particle size and temperature at which it was formed as well as the temperature, composition and pH of the hydrated solution.

During the combined thermal and sulphuric acid treatment method, phosphogypsum in the dihydrate form is first changed, in a laboratory oven at 160°C, into the soluble anhydrite (γ-$CaSO_4$) form. When this soluble anhydrite is added to the sulphuric acid solution, immediate uptake of water in the crystal lattice of the γ-$CaSO_4$, to form calcium sulphate hemihydrate takes place. The calcium sulphate hemihydrate formed has a similar crystal structure as γ-$CaSO_4$, with the main difference the presence of water of crystallization in the hemihydrate structure, which causes the unit cell volume of the hemihydrate to be twice that of γ-$CaSO_4$, due to elongation of the c-axis (Bezou *et al*, 1995).

The crystal structures of γ-$CaSO_4$ and $CaSO_4.½H_2O$ are given in Figures 9.2 and 9.3 respectively. The basic structural unit of both these crystal structures is a chain of edge-sharing sulphate tetrahedra and CaO_8 polyhedra (Lager *et al*, 1984). In γ-$CaSO_4$ these chains are related by a six-fold screw axis to form one-dimensional channels. These channels make the uptake of water into the anhydrite structure possible, resulting in its hydration to the hemihydrate form.

Figure 9.2 Crystal structure of γ-$CaSO_4$ (Bezou *et al*, 1995; Lager *et al*, 1984)



[001] projection of the γ-$CaSO_4$ structure. The b-axis is along the page.

[010] projection of the γ-$CaSO_4$ structure illustrating the chains of sulphate tetrahedra and CaO_8 polyhedra parallel to the c-axis.

Figure 9.3 Projection of the crystal structure of $CaSO_4.½H_2O$ along [001]. The b-axis is along the page (Bezou *et al*, 1995)

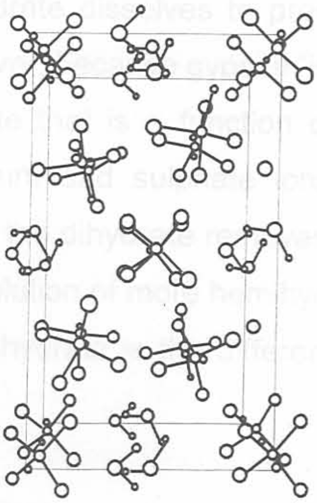
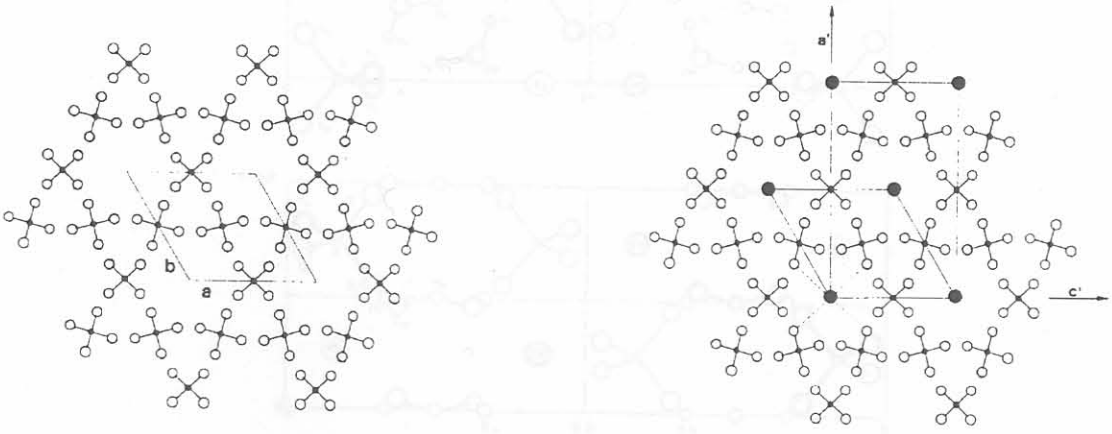


Figure 9.4 illustrates the sulphate tetrahedra and the channels developed parallel to the c-axis. Possible positions for the water molecules in the hemihydrate structure are presented by the large black circles.

Figure 9.4 (a) [001] Projection of the γ-$CaSO_4$ structure illustrating the sulphate tetrahedra and the channels developed parallel to the c-axis, and (b) [001] Projection of the γ-$CaSO_4$ structure illustrating the relation ship between the unit cells of γ-$CaSO_4$ and $CaSO_4.½H_2O$ (Lager *et al*, 1984)



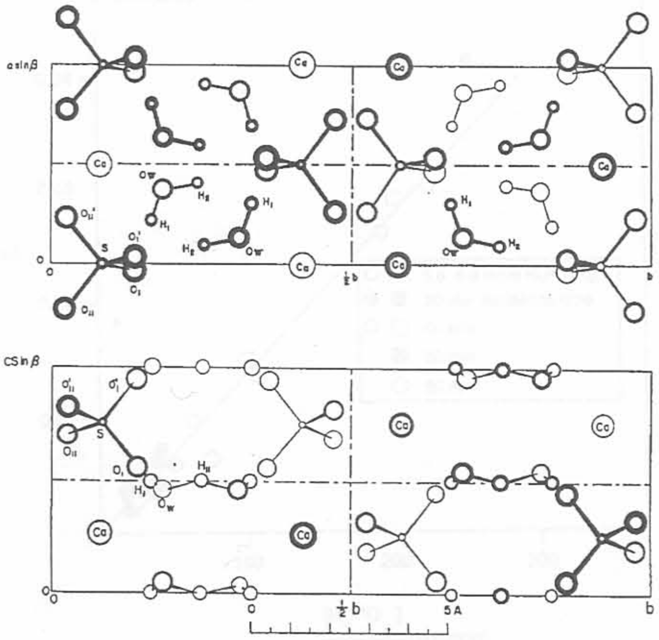
(a)

(b)

The next step will be the rehydration of calcium sulphate hemihydrate to the dihydrate, a process which is relatively rapid and occurs through a recrystallization process. Upon dispersion in water, the hemihydrate dissolves to produce a liquid phase saturated in calcium and sulphate ions. However, because gypsum is less soluble than hemihydrate, it immediately precipitates at a rate that is a function of slurry conditions, the solubility product, the availability of calcium and sulphate ions and the available surface for precipitation. The precipitation of the dihydrate removes calcium and sulphate ions from solution which promotes the dissolution of more hemihydrate. Therefore, the driving force of the hydration reaction of hemihydrate is the difference in solubility product between hemihydrate and dihydrate.

The crystal structure of $CaSO_4.2H_2O$ is given in Figure 9.5. In the structure of gypsum, pairs of adjacent layers which contain Ca^{2+} and SO_4^{2-} ions exist. Between successive pairs of layers the water molecules are located in such a way that they are hydrogen bonded to the oxygen atoms of the sulphate groups. Each Ca^{2+} ion is coordinated by six oxygen atoms of SO_4^{2-} groups and by two water molecules.

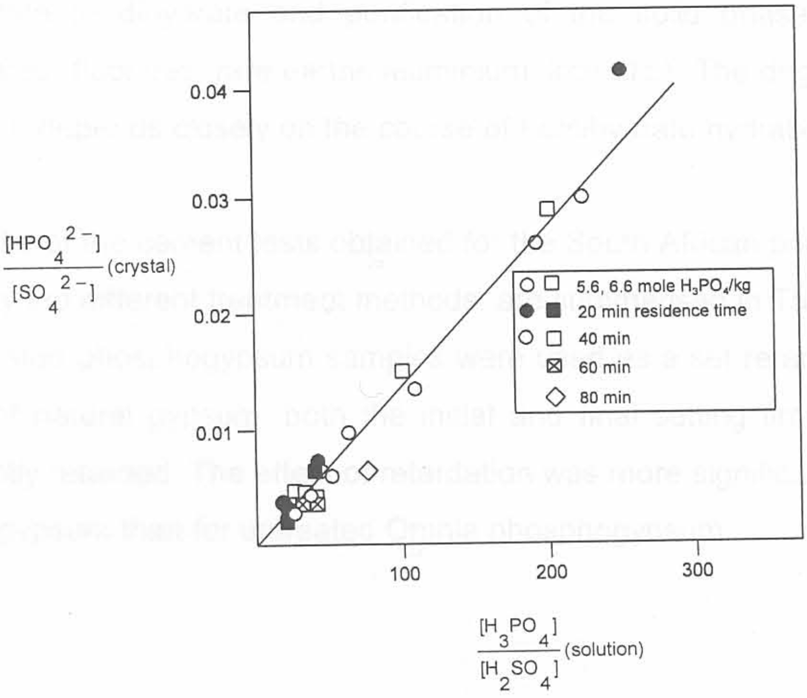
Figure 9.5 The crystal structure of gypsum (Atoji and Rundle, 1958)



In the crystal structure of phosphogypsum, small amounts of HPO_4^{2-} ions replace SO_4^{2-} ions. The HPO_4^{2-} ion can easily substitute a sulphate ion, since these two ions are similar in size and share the same affinity towards calcium ions. The similarity of these anions is also reflected by the existence of two comparable salts: $CaHPO_4.2H_2O$ and $CaSO_4.2H_2O$, which are both sparingly soluble in water and have the same molar volume (van der Sluis *et al*, 1986).

In Figure 9.6 the HPO_4^{2-} incorporation in hemihydrate crystals, expressed as the molar concentration of HPO_4^{2-} over SO_4^{2-} ratio in the crystals, is given versus the molar concentration of H_3PO_4 over H_2SO_4 ratio in the solution (van der Sluis *et al*, 1986). The phosphate ion uptake decreases with increasing concentration of H_2SO_4 and a linear dependence between the molar phosphate concentration over sulphate concentration ratios in the crystals and in the solution appears to exist. This linearity points to a competition between the two anions for the available adsorption sites at the crystal surface.

Figure 9.6 **The phosphate incorporation in $CaSO_4.½H_2O$ crystals, expressed as the molar phosphate over sulphate concentration ratio in the crystals, as a function of the same ratio in the solution for various residence times (van der Sluis *et al*, 1986)**



Similar results were obtained for the uptake of phosphate in calcium sulphate dihydrate (Witkamp and van Rosmalen, 1990). The phosphate uptake in dihydrate and anhydrite is lower at higher H_2SO_4 concentrations and temperatures. The H_3PO_4 concentration in the solution plays a less important role in the uptake of phosphate impurities with relation to the concentration of H_2SO_4 (Witkamp and van Rosmalen, 1986).

Therefore, it seems that during rehydration of the calcium sulphate hemihydrate to dihydrate through recrystallization, the uptake of HPO_4^{2-} ions are suppressed by the relatively high concentration of SO_4^{2-} ions. This process produces a gypsum with a very low percentage of phosphorous impurities contained in the gypsum crystal lattice.

H_2SO_4 has not only an effect as an acid, like phosphoric acid, in affecting the solubility of the calcium sulphate, but also as a constituent ion of the calcium sulphate, influencing the molar Ca^{2+}/SO_4^{2-} ratio in the solution. The presence of sulphate ions, even at concentrations as low as a few weight percentage, generally enhances the conversion rate of any of the calcium sulphate phase transitions.

Jarosiński *et al* (1993) confirmed that in the process of hemihydrate phosphogypsum leaching with sulphuric acid, two simultaneous processes occur; i.e. the conversion of hemihydrate to dihydrate and purification of the solid phase from initial impurities (phosphates, fluorides, rare earths aluminium, iron etc.). The degree of phosphogypsum purification depends closely on the course of hemihydrate hydration.

The results of the cement tests obtained for the South African phosphogypsum samples, treated by the different treatment methods, are summarised in Tables 9.1 and 9.2. When the untreated phosphogypsum samples were used as a set retarder in Portland cement instead of natural gypsum, both the initial and final setting times of the cement were significantly retarded. The effect of retardation was more significant for untreated Kynoch phosphogypsum than for untreated Omnia phosphogypsum.

Table 9.1 **Combination of the results of the cement test performed on Kynoch phosphogypsum, treated by the respective treatment methods. The amount of phosphorous impurities contained in the samples is also included in the table**

Test	Untreated (1)	Untreated (2)	$Ca(OH)_2$ treatment	H_2SO_4 treatment before optimization	H_2SO_4 treatment after optimization	Combined thermal and sulphuric acid treatment	Natural gypsum (1)	Natural gypsum (2)
Phosphorous impurities in gypsum (% P_2O_5)	0.99	1.06	0.98	0.65	0.73	0.04	-	-
SO_3 content of gypsum (%)	46.68	45.76	45.70	46.96	45.78	46.25	42.50	42.50
Gypsum added to clinker (%)	3.50	3.57	3.58	3.48	3.57	3.53	3.85	3.85
Specific surface of cement (cm^2/g)	3200	3180	3250	3275	3258	3419	3200	3314
Relative density of cement (g/cm^3)	3.10	3.14	3.12	3.12	3.14	3.16	3.10	3.14
Initial setting time (min)	354	348	274	184	228	137	140	130
Final setting time (h)	6.8	7.2	5.8	4.3	4.9	3.2	3.3	3.0
2-day Compressive strength (MPa)	17.35	14.67	16.96	18.89	15.07	19.93	20.33	19.27
7-day Compressive strength (MPa)	34.41	34.40	35.36	36.97	33.13	34.27	38.04	32.37
28-day Compressive strength (MPa)	47.25	41.43	44.83	44.01	39.10	50.47	49.10	47.90

Table 9.2 **Combination of the results of the cement test performed on Omnia phosphogypsum, treated by the respective treatment methods. The amount of phosphorous impurities contained in the samples is also included in the table**

Test	Untreated (1)	Untreated (2)	Washed with distilled H_2O	H_2SO_4 treatment before optimization	H_2SO_4 treatment after optimization	Combined thermal and sulphuric acid treatment	Natural gypsum (1)	Natural gypsum (2)
Phosphorous impurities in gypsum (% P_2O_5)	2.15	1.53	1.08	0.81	0.81	0.06	-	-
SO_3 content of gypsum (%)	47.24	47.06	46.39	45.59	45.98	46.10	42.50	42.50
Gypsum added to clinker (%)	3.46	3.47	3.52	3.59	3.56	3.55	3.85	3.85
Specific surface of cement (cm^2/g)	3470	3159	3175	3225	3457	3267	3200	3314
Relative density of cement (g/cm^3)	3.15	3.15	3.10	3.10	3.15	3.14	3.10	3.14
Initial setting time (min)	243	265	257	160	189	163	140	130
Final setting time (h)	5.1	5.8	5.3	4.8	4.2	3.4	3.3	3.0
2-day Compressive strength (MPa)	17.12	14.17	17.74	18.36	17.35	19.10	20.33	19.27
7-day Compressive strength (MPa)	33.91	31.17	34.15	35.60	33.47	29.12	38.04	32.37
28-day Compressive strength (MPa)	46.07	38.28	48.01	45.50	45.47	46.42	49.10	47.90

After treatment of the Kynoch phosphogypsum samples by the respective treatment methods, the best results for both the initial and final setting times were obtained for the Kynoch phosphogypsum sample treated by the combined thermal and sulphuric acid treatment method. The setting times, obtained when this sample was used as a set retarder, were in the same range as the values obtained when natural gypsum was used.

For the Omnia phosphogypsum sample, similar results were obtained for the initial setting times of cement, containing phosphogypsum treated by the combined thermal and sulphuric acid treatment method, and the sample treated by the sulphuric acid treatment method before optimization. However, an improved result, in terms of the comparison with natural gypsum, was obtained for the final setting time when the phosphogypsum sample was treated by the combined thermal and sulphuric acid treatment method. Therefore, the combined thermal and sulphuric acid treatment method also proved to be the best for the Omnia phosphogypsum.

The compressive strength of the cement containing the respective phosphogypsum samples treated by the combined thermal and sulphuric acid treatment method was in the same range as the compressive strengths obtained for the cement samples containing natural gypsum.

It seemed as if the optimization of the sulphuric acid treatment method was not successful in improving the results of the setting times of the cement obtained before optimization. For both Kynoch and Omnia phosphogypsum, the initial setting times increased after optimization of the method. Only the cement containing optimum treated Omnia phosphogypsum has shown some improvement in its final setting time.

These results show that the impurities contained in South African phosphogypsum as well as the occurrence of the anhydrite and hemihydrate forms of calcium sulphate have a greater influence on the setting times of Portland cement than on its strength development. However, treatment of the phosphogypsum samples by the combined thermal and sulphuric acid treatment method removes most of the phosphorous impurities contained in the phosphogypsum samples, and convert the sample to mainly the dihydrate form of calcium sulphate. These samples have proved to yield results similar to that of natural gypsum when used as a set retarder in Portland cement.

On a worldwide basis phosphogypsum is produced as a by-product form the wet phosphoric acid process, and its rate of utilization remains low. Consequently there is a strong need to widen the field of application of this by-product. The purified South African phosphogypsum was found suitable for use in Portland cement manufacture, and the cement produced revealed compressive strength and setting time characteristics similar to cement produced using mineral gypsum.