Chapter 8 Sulphuric acid treatment of South African phosphogypsum

8.1 Introduction

Jarosiński (1994) described a method in which he first leached the phosphogypsum sample in a 12% (by mass) sulphuric acid solution to recover rare earth elements, followed by a conversion into the β-anhydrite form of calcium sulphate in a 50% sulphuric acid solution. The purpose of this study was to investigate the properties of anhydrite cement by using β-anhydrite obtained from purified phosphogypsum. The procedure he followed to obtain the purified anhydrite is summarised in Table 8.1.

Table 8.1 Experimental conditions followed by Jarosiński (1994) to purify and recrystallize anhydrite phosphogypsum

Parameters	Stage	
	Leaching	Conversion
Temperature (°C)	40	50
Sulphuric acid concentration (% m/m)	12	50
Solid/liquid mass ratio	1 : 2	1 :1
Stirring time (min)	45	120
Standardized mechanical agitation, revolution (min^{-1})	150	150

Jarosiński found this method to be successful in removing the undesirable impurities such as compounds of phosphorous, fluorine and sodium. He claimed that the following equilibrium process takes place in the direction of $CaSO_4$ during the conversion:

$$H_2SO_4\,(aq) + Ca(H_2PO_4)_2\,(s) \rightleftharpoons CaSO_4\,(s) + 2H_3PO_4\,(aq)$$

In this chapter, the application of this method to South African phosphogypsum is discussed. However, the final product to be obtained for use in Portland cement is preferred to be $CaSO_4.2H_2O$ and not the anhydrite form as required by Jarosiński's method.

8.2 Experimental

8.2.1 Samples

Phosphogypsum samples were obtained from two South-African phosphoric acid producers, Omnia and Kynoch. Batch 1 of both the Kynoch and Omnia phosphogypsum was used for the initial small scale treatment, while Batch 2 of both phosphogypsums were used for the large scale treatments and optimization of the method. The samples were dried overnight at 45°C.

8.2.2 Instrumental analysis

Thermal analysis, Infrared analysis and X-ray fluorescence analysis were done as described in Chapter 5.2.

8.2.3 Jarosiński's method applied to South African phosphogypsum

The method followed by Jarosiński was adapted for the Kynoch phosphogypsum and Omnia phosphogypsum samples. Batch 1 of both of the Kynoch and Omnia phosphogypsum was used. A heater stirrer was used to perform the leaching and conversion steps. A solid:liquid mass ratio of 1:2 for the Omnia phosphogypsum formed a paste which could not be stirred by the stirrer. This resulted in using a solid:liquid ratio of 1:4 for the Omnia phosphogypsum and 1:2 for the Kynoch phosphogypsum. The experimental conditions followed, are summarised in Table 8.2.

Table 8.2 Adapted experimental conditions used to purify and recrystallize Omnia and Kynoch phosphogypsum

Parameters	Leaching		Conversion
	Kynoch	Omnia	(Omnia and Kynoch)
Temperature (°C)	40	40	50
Sulphuric acid concentration (% m/m)	12	12	50
Solid:liquid mass ratio	1 : 2	1 : 4	1 :1
Stirring time (min)	45	45	120
Sample mass (g)	15.0 g	15.0 g	-

8.2.4 Sulphuric acid treatment of phosphogypsum at a larger scale

Batch 2 of both of the Kynoch and Omnia phosphogypsum was used in this study. To be able to perform cement tests, the above method had to be repeated on a larger scale so that enough gypsum could be obtained. The method was performed, starting with 300 g of each of the phosphogypsums.

8.2.5 Optimisation of the sulphuric acid method

Batch 2 of both of the Kynoch and Omnia phosphogypsum was used to optimize the sulphuric acid treatment method. Optimisation of the method was performed on the following parameters: temperature, concentration of sulphuric acid, time and solid:liquid ratio. The optimisation was measured in terms of the least amount of phosphorous impurities present in the treated samples, as well as the highest amount of calcium sulphate dihydrate. The aim was also to combine the leaching and conversion stages into one purification step, since this would be more cost-effective and less time consuming. Table 8.3 describes the experimental method followed during optimisation.

Table 8.3 Experimental parameters used for optimisation of the sulphuric acid treatment of phosphogypsum

Order of Optimisation	Temperature (°C)	H_2SO_4 concentration (% m/m)	Time (min)	Solid:liquid ratio
1	23, 27, 40, 51, 60, 69	12	60	1:4
2	23	5, 10, 20, 30, 40, 50	60	1:4
3	23	5 (Omnia) 20 (Kynoch)	15, 30, 45, 60, 90, 120, 180, 360	1:4
4	23	5 (Omnia) 20 (Kynoch)	30	1:1, 1:2, 1:3, 1:4

8.2.6 The optimized sulphuric acid method on a large scale

Batch 2 of both of the Kynoch and Omnia phosphogypsum was used in this study. The untreated phosphogypsum samples were dried overnight at 45°C. Sample masses of 300 g were used. The samples were stirred in sulphuric acid (5% m/m for Omnia phosphogypsum and 20% m/m for the Kynoch phosphogypsum) for 30 minutes at room temperature, at a solid:liquid mass ratio of 1:4. Samples were then filtered and washed with a saturated milk of lime solution and deionised water, and dried overnight at 45°C.

8.2.7 Sulphuric acid treatment combined with thermal treatment

Batch 2 of both of the Kynoch and Omnia phosphogypsum was used in this study. The sulphuric acid treatment was combined with thermal treatment by heating the phosphogypsum samples at 160°C until a constant mass was obtained after approximately 3 hours (i.e. until all the calcium sulphate dihydrate and hemihydrate was converted to the anhydrite). The samples were then treated in sulphuric acid according to the optimum method obtained in the optimisation discussed in Chapter 8.2.5. A solid:liquid mass ratio of 1:4 formed a paste which could not be stirred by the stirrer. It was found that by using a solid:liquid ratio of approximately 1:10, a manageable paste was formed.

Therefore, the samples were thermally treated at 160°C for 3 hours, followed by the acid treatment at a solid:liquid ratio of 1:10 at room temperature for 30 minutes in a 5% (m/m) H_2SO_4 solution for Omnia phosphogypsum and a 20% (m/m) H_2SO_4 solution for the Kynoch phosphogypsum.

8.2.8 Optimisation of the combined thermal and acid treating method

Batch 2 of both of the Kynoch and Omnia phosphogypsum was used to study the effect of sulphuric acid concentration in the combined thermal and acid treating method. Sulphuric acid concentrations used were 1, 5, 10, 20 and 50% m/m. The optimisation was measured in terms of the least amount of phosphorous impurities present in the treated samples, as well as the highest amount of calcium sulphate dihydrate.

8.2.9 The combined thermal and acid treatment of phosphogypsum at a larger scale

Batch 2 of both of the Kynoch and Omnia phosphogypsum was used in this study. To be able to perform cement tests, the above method had to be repeated on a larger scale so that enough gypsum can be obtained.

The method was performed, starting with 300 g of each of the phosphogypsums. To ensure that the samples were completely converted to anhydrite, the samples were thermally treated overnight at 160°C. This was then followed by the acid treatment at a solid:liquid ratio of 1:10 at room temperature for 45 minutes in a 5% (m/m) H_2SO_4 solution for both phosphogypsum samples. The samples were then filtered and repeatedly washed with milk of lime and water, and was then dried overnight at 45°C.

8.2.10 Cement tests

All cement control tests were performed according to standard methods described by the South African Bureau of Standards (SABS EN 196-1). The phosphogypsum samples as well as natural gypsum (used as reference) were interground with Hercules clinker. The SO_3 contents of the clinker and of each gypsum sample was first determined by a wet chemical analysis method as described in Chapter 7.3.4, and each of the gypsum samples was then interground with the clinker to achieve a final SO_3 content of 2.3% in the cement. The sample was then milled to a fineness of approximately 3200 cm^2/g Blaine surface area. The relative density, initial and final setting time and compressive strength of the cement after 2, 7 and 28 days were then determined.

8.3 Results and discussion of the sulphuric acid treatment of South African phosphogypsum

8.3.1 Application of Jarosiński's method to South African phosphogypsum

Results of the XRF analyses of Batch 1 phosphogypsum samples treated by Jarosiński's method are summarised in Table 8.4.

For both phosphogypsum samples, the amount of phosphorous was decreased significantly in the leaching step, and after conversion to the anhydrite in 50% sulphuric acid almost no phosphorous was left in the samples.

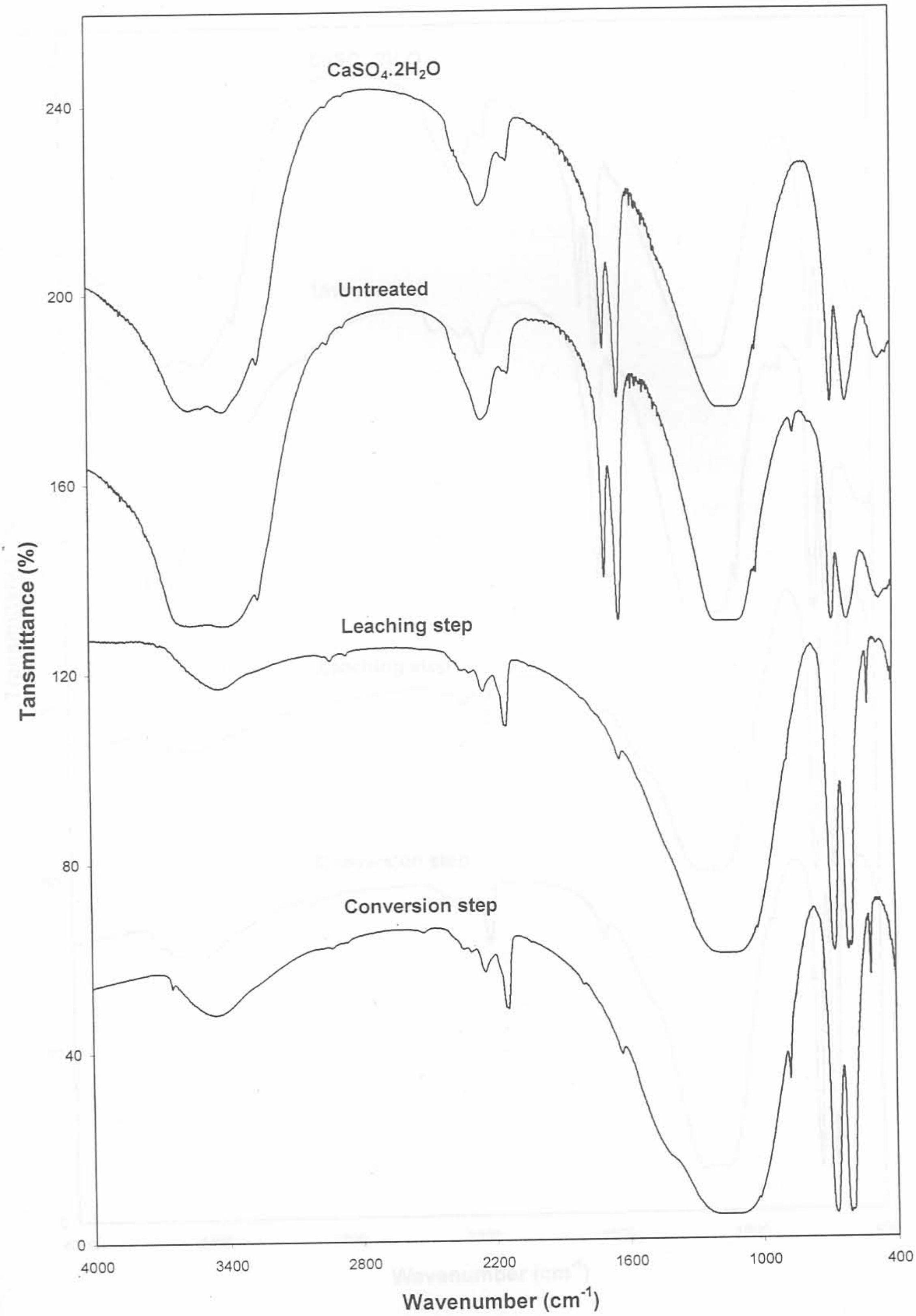
Table 8.4 XRF analysis of Batch 1 phosphogypsum samples treated with H_2SO_4, normalised to a loss free basis

Compounds (%)	Kynoch phosphogypsum			Omnia phosphogypsum		
	Untreated	Leaching	Conversion	Untreated	Leaching	Conversion
Al_2O_3	0.36	0.30	0.58	0.35	0.30	0.30
CaO	38.46	39.73	38.75	38.80	38.31	40.03
Cr_2O_3	0*	0	0	0	0	0.01
Fe_2O_3	0.09	0.07	0.06	0.08	0.04	0.04
K_2O	0	0	0	0	0	0
MgO	0.08	0.10	0.06	0.14	0.07	0.06
MnO	0	0	0	0	0	0
Na_2O	0	0	0	0	0	0
P_2O_5	**0.92**	**0.10**	**0.02**	**1.79**	**0.14**	**0.04**
SiO_2	0.17	0	0	0	0	0
TiO_2	0	0	0	0	0	0
V_2O_5	0	0	0	0	0	0
ZrO_2	0	0	0	0	0	0
Sr	0.29	0.26	0.23	0.33	0.25	0.18
SO_3	59.63	59.45	60.25	58.50	60.89	59.34

*0 means that the compound was present in a quantity below the detection limit

The results of the FT-IR measurements for the different treating steps are presented in Figures 8.1 and 8.2. When the IR spectra of the respective untreated and sulphuric acid treated phosphogypsum samples were compared, it was observed that the small peak at 832 cm^{-1}, due to the presence of phosphate impurities, was only present in the untreated phosphogypsum samples. This confirmed the results obtained by XRF analysis.

Figure 8.1 **The IR spectra of the untreated and acid treated Batch 1 Kynoch phosphogypsum samples and pure $CaSO_4.2H_2O$**



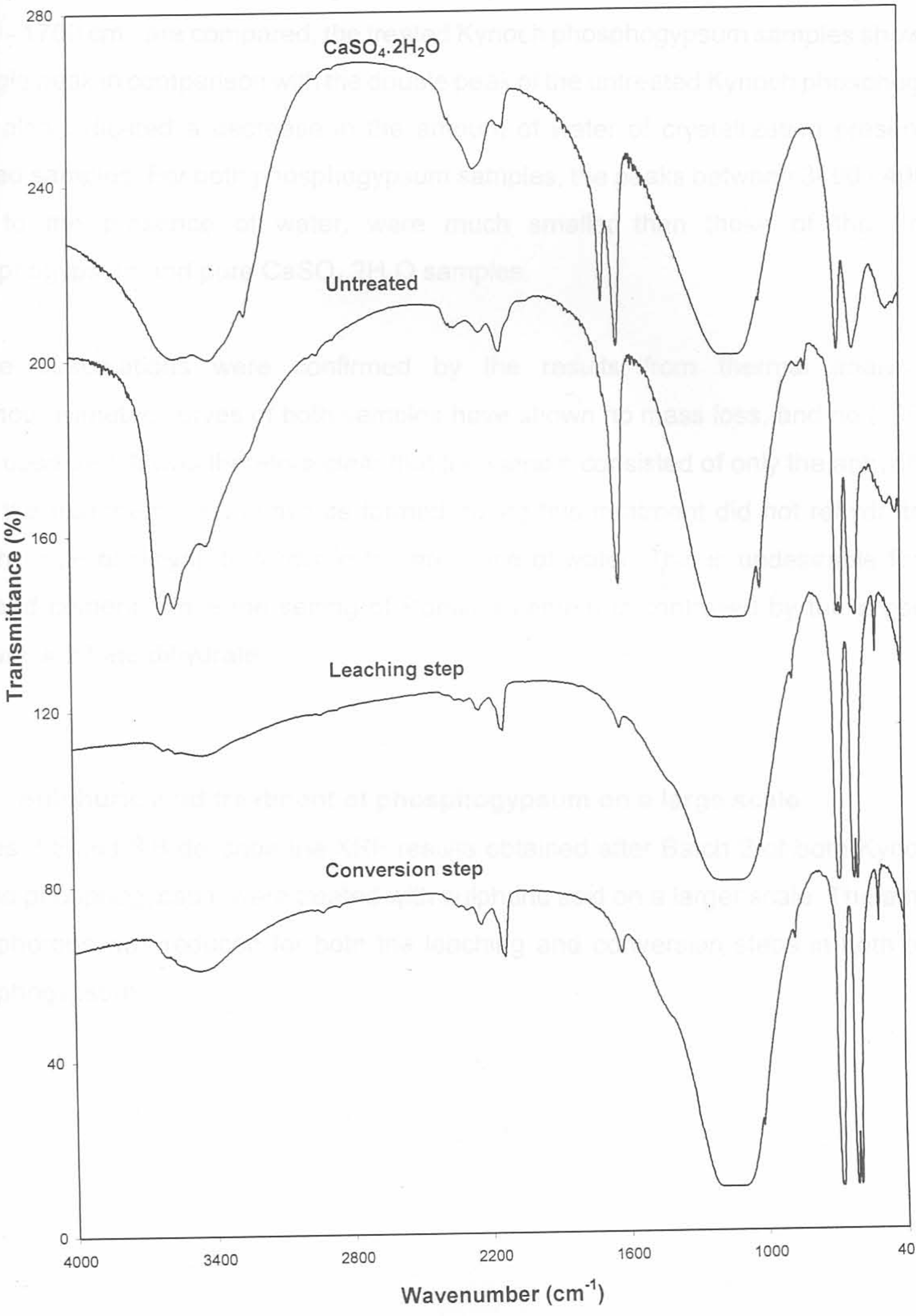


Figure 8.2 **The IR spectra of the untreated and acid treated Batch 1 Omnia phosphogypsum samples and pure $CaSO_4.2H_2O$**

For the treated phosphogypsum samples, a split in the peaks at 600 cm^{-1} and 667 cm^{-1} indicated that the phosphogypsum samples were not in the dihydrate form, but consisted mainly of calcium sulphate hemihydrate or anhydrite. When the peaks in the region between 1600 - 1700 cm^{-1} are compared, the treated Kynoch phosphogypsum samples showed only a single peak in comparison with the double peak of the untreated Kynoch phosphogypsum. This also indicated a decrease in the amount of water of crystallization present in the treated samples. For both phosphogypsum samples, the peaks between 3400 - 4000 cm^{-1}, due to the presence of water, were much smaller than those of the untreated phosphogypsum and pure $CaSO_4.2H_2O$ samples.

These observations were confirmed by the results from thermal analysis. The thermogravimetric curves of both samples have shown no mass loss, and no DSC peaks were observed. It was therefore clear that the sample consisted of only the anhydrite form after the treatment. The anhydrite formed during this treatment did not rehydrate to the hemihydrate or dihydrate forms in the presence of water. This is undesirable for use in Portland cement, since the setting of Portland cement is controlled by the presence of calcium sulphate dihydrate.

8.3.2 Sulphuric acid treatment of phosphogypsum on a large scale

Tables 8.5 and 8.6 describe the XRF results obtained after Batch 2 of both Kynoch and Omnia phosphogypsum were treated with sulphuric acid on a larger scale. The amount of phosphorous was reduced for both the leaching and conversion steps in both types of phosphogypsum.

Table 8.5 XRF analysis of Batch 2 phosphogypsum samples, treated with sulphuric acid on a larger scale

Compounds (%)	**Kynoch phosphogypsum** (Batch2)			**Omnia phosphogypsum** (Batch 2)		
	Untreated	**Leaching**	**Conversion**	**Untreated**	**Leaching**	**Conversion**
Al_2O_3	0.08	0*	0	0	0	0
CaO	33.16	33.44	33.89	33.94	33.46	34.59
Cr_2O_3	0	0	0	0	0.01	0
Fe_2O_3	0.04	0.05	0.05	0.09	0.06	0.08
K_2O	0	0	0	0	0	0
MgO	0.07	0.06	0.08	0.10	0.10	0.06
MnO	0	0	0	0	0	0
Na_2O	0	0	0	0	0	0
$\mathbf{P_2O_5}$	**0.77**	**0.60**	**0.53**	**1.34**	**0.81**	**0.65**
SiO_2	0.03	0	0	0	0	0
TiO_2	0	0	0	0	0	0
V_2O_5	0	0	0	0	0	0
ZrO_2	0	0	0	0	0	0
Sr	0.27	0.26	0.24	0.30	0.29	0.27
SO_3	45.76	44.83	45.90	45.72	44.70	45.76
Loss on ignition	21.29	21.87	20.96	20.02	21.57	19.04
Total	101.47	101.11	101.65	101.51	100.97	100.45

*0 means that the compound was present in a quantity below the detection limit

Table 8.6 XRF analysis of Batch 2 phosphogypsum samples, treated with sulphuric acid on a larger scale, normalised to a loss free basis

Compounds (%)	**Kynoch phosphogypsum** (Batch2)			**Omnia phosphogypsum** (Batch 2)		
	Untreated	**Leaching**	**Conversion**	**Untreated**	**Leaching**	**Conversion**
Al_2O_3	0.10	0*	0	0	0	0
CaO	41.36	42.20	42.00	41.65	42.14	42.68
Cr_2O_3	0	0	0	0	0.01	0
Fe_2O_3	0.05	0.06	0.06	0.11	0.08	0.10
MgO	0.09	0.08	0.10	0.12	0.13	0.07
P_2O_5	**0.96**	**0.76**	**0.66**	**1.64**	**1.02**	**0.80**
SiO_2	0.04	0	0	0	0	0
Sr	0.34	0.33	0.30	0.37	0.37	0.33
SO_3	57.07	56.57	56.88	56.11	56.30	56.46

*0 means that the compound was present in a quantity below the detection limit

The conversion step was then extended to 4 hours, to test the effect of time on the amount of phosphorous. The XRF results are summarised in Tables 8.7 and 8.8. There was not a significant decrease in the amount of phosphorous in any of the phosphogypsum samples after the extended time period.

Table 8.7 XRF analysis of sulphuric acid treatment on large scale with an extended time period of 4 hours for the conversion step

Compounds (%)	**Kynoch phosphogypsum**		**Omnia phosphogypsum**	
	Untreated	**Conversion**	**Untreated**	**Conversion**
Al_2O_3	0.08	0*	0	0
CaO	33.16	35.21	33.94	33.83
Cr_2O_3	0	0.01	0	0.01
Fe_2O_3	0.04	0.04	0.09	0.07
K_2O	0	0	0	0
MgO	0.07	0.06	0.10	0.09
MnO	0	0	0	0
Na_2O	0	0	0	0
P_2O_5	**0.77**	**0.55**	**1.34**	**0.66**
SiO_2	0.03	0	0	0
Sr	0.27	0.26	0.30	0.27
SO_3	45.76	48.40	45.72	47.04
Loss on ignition	21.29	17.22	20.02	20.29
Total	101.47	101.75	101.51	102.26

*0 means that the compound was present in a quantity below the detection limit

Table 8.8 **XRF analysis of sulphuric acid treatment on large scale with an extended time period of 4 hours for the conversion step, normalised to a loss free basis**

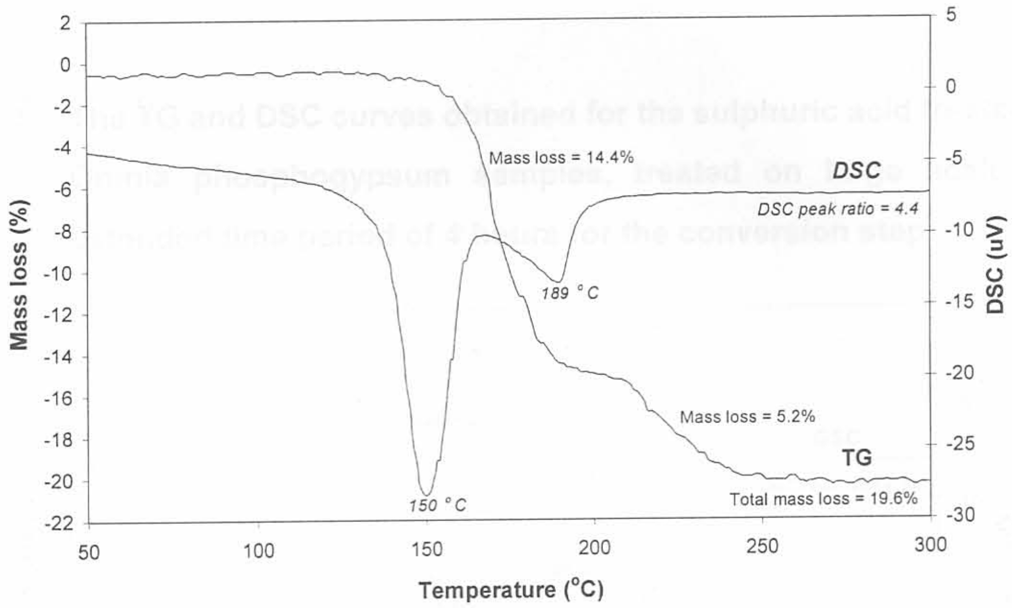
Compounds (%)	**Kynoch phosphogypsum**		**Omnia phosphogypsum**	
	Untreated	**Conversion**	**Untreated**	**Conversion**
Al_2O_3	0.10	0*	0	0
CaO	41.36	41.65	41.65	41.27
Cr_2O_3	0	0.01	0	0.01
Fe_2O_3	0.05	0.05	0.11	0.09
MgO	0.09	0.07	0.12	0.11
P_2O_5	**0.96**	**0.65**	**1.64**	**0.81**
SiO_2	0.04	0	0	0
Sr	0.34	0.31	0.37	0.33
SO_3	57.07	57.26	56.11	57.39

*0 means that the compound was present in a quantity below the detection limit

The inability to remove the phosphorous impurities from these phosphogypsum samples can possibly be ascribed to problems regarding upscaling of the experimental method. The method seemed to be less effective when repeated on a larger scale, due to constraints posed by the laboratory scale apparatus used to conduct these large scale experiments.

When the TG and DSC curves of Figure 8.3 are compared with that of the untreated Batch 2 phosphogypsum samples from Figures 5.6 and 5.7, it can be seen that there was no significant difference in the TG and DSC curves of the treated and untreated Kynoch phosphogypsum samples. The obtained total mass loss of 19.6% is close to the theoretical value of 20.9%, which indicates that the treated phosphogypsum sample contained mainly calcium sulphate dihydrate. The high value obtained for the DSC peak ratio could not be of any use, since the separation of the two dehydration peaks was not satisfactory. Furthermore, the peak for the first dehydration reaction did not return to the baseline before the second dehydration reaction started. The temperatures at which the respective maximums occurred were the same as for the untreated Kynoch phosphogypsum sample.

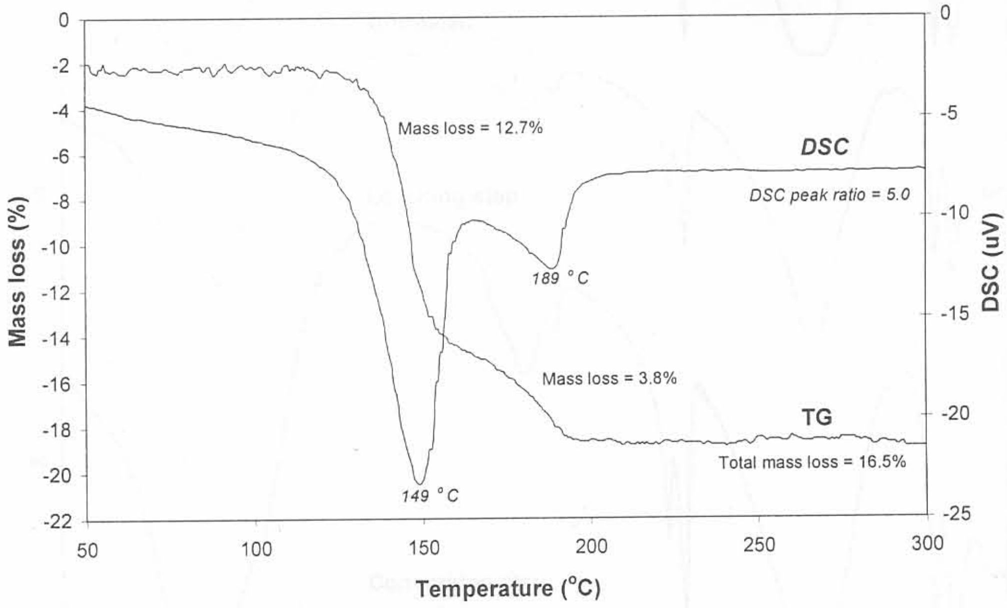
Figure 8.3 The TG and DSC curves obtained for the sulphuric acid treated Batch 2 Kynoch phosphogypsum samples, treated on large scale with an extended time period of 4 hours for the conversion step



When the DSC curves of Figure 8.4 are compared with that of the untreated Omnia phosphogypsum samples, no significant change was observed. However, the TG curve revealed a lower total mass loss of 16.5% when compared to 20.2% for the untreated Omnia phosphogypsum samples (given in Figure 5.5). This indicated that the treated sample contained some calcium sulphate hemihydrate or anhydrite which did not rehydrate during treatment. It seems as if it is the anhydrite form that is present in this samples, due to the small second mass loss of only 3.8%. The presence of calcium sulphate hemihydrate will result in a higher second mass loss due its dehydration. This hemihydrate originates from both dehydrated dihydrate as well as some hemihydrate that was originally present in the sample.

The DSC peak ratio could again not be useful, for the same reason as stated for Kynoch phosphogypsum above. The temperature at which the peak maximum for the first dehydration occur shifted from 118°C for the untreated Omnia phosphogypsum sample, to 149°C for the treated sample. As explained in Chapter 5.3.3, this indicates that the untreated Omnia phosphogypsum forms the α-hemihydrate when dehydrated, while after the sample was treated with sulphuric acid, dehydration results in the formation of the β-hemihydrate.

Figure 8.4 **The TG and DSC curves obtained for the sulphuric acid treated Batch 2 Omnia phosphogypsum samples, treated on large scale with an extended time period of 4 hours for the conversion step**



The respective infrared spectra for the untreated and treated Kynoch and Omnia phosphogypsum samples are given in Figures 8.5 and 8.6. The results obtained from IR measurements confirmed the XRF and TG/DSC results, that indicated that the dihydrate form of calcium sulphate was mainly formed in all instances. The small peak at ~832 cm^{-1} due to phosphorous impurities was still present. No difference in the IR spectra for the leaching and conversion steps was observed for any of the phosphogypsum samples.

Figure 8.5 **The IR spectra of the untreated and acid treated Batch 2 Kynoch phosphogypsum samples, treated on large scale with an extended time period of 4 hours for the conversion step**

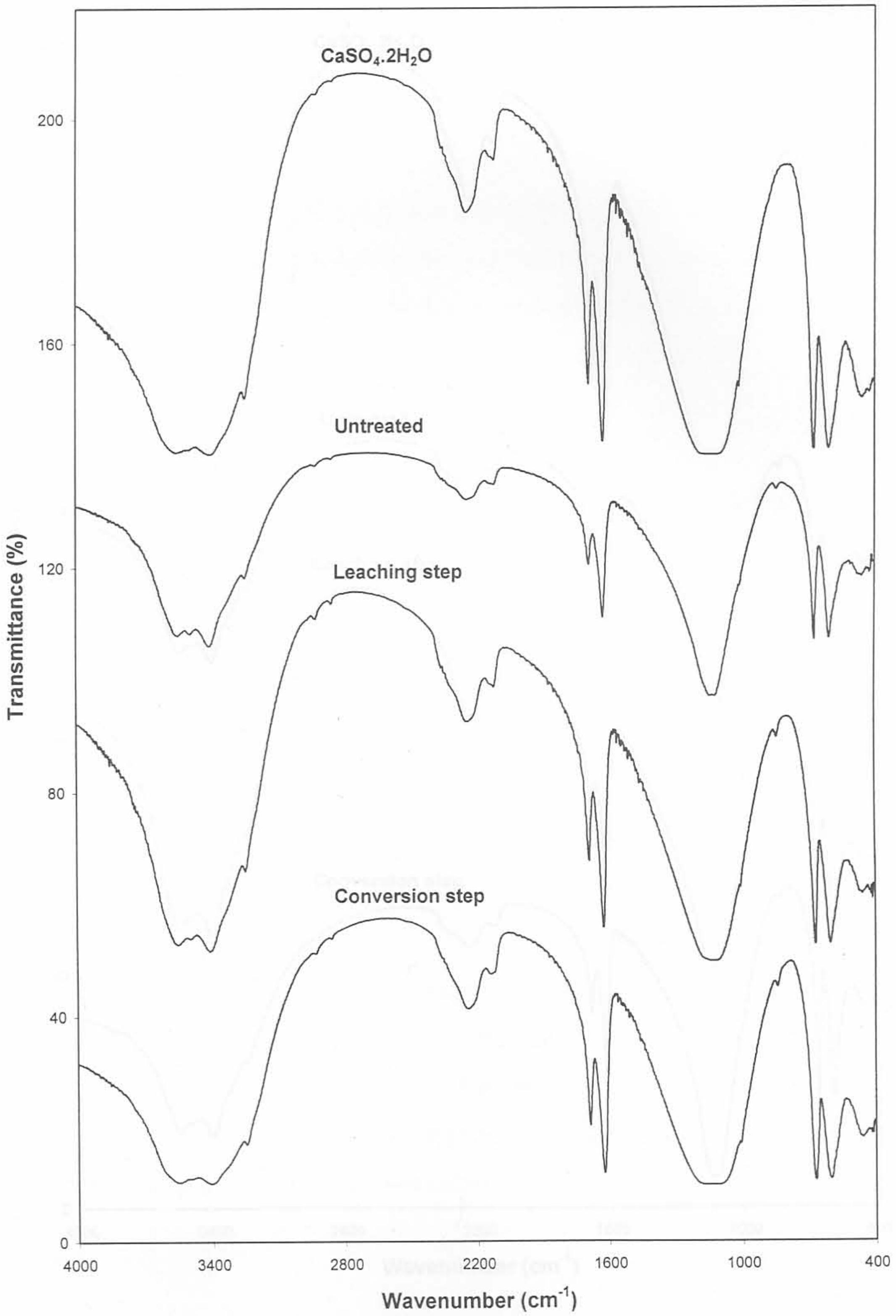
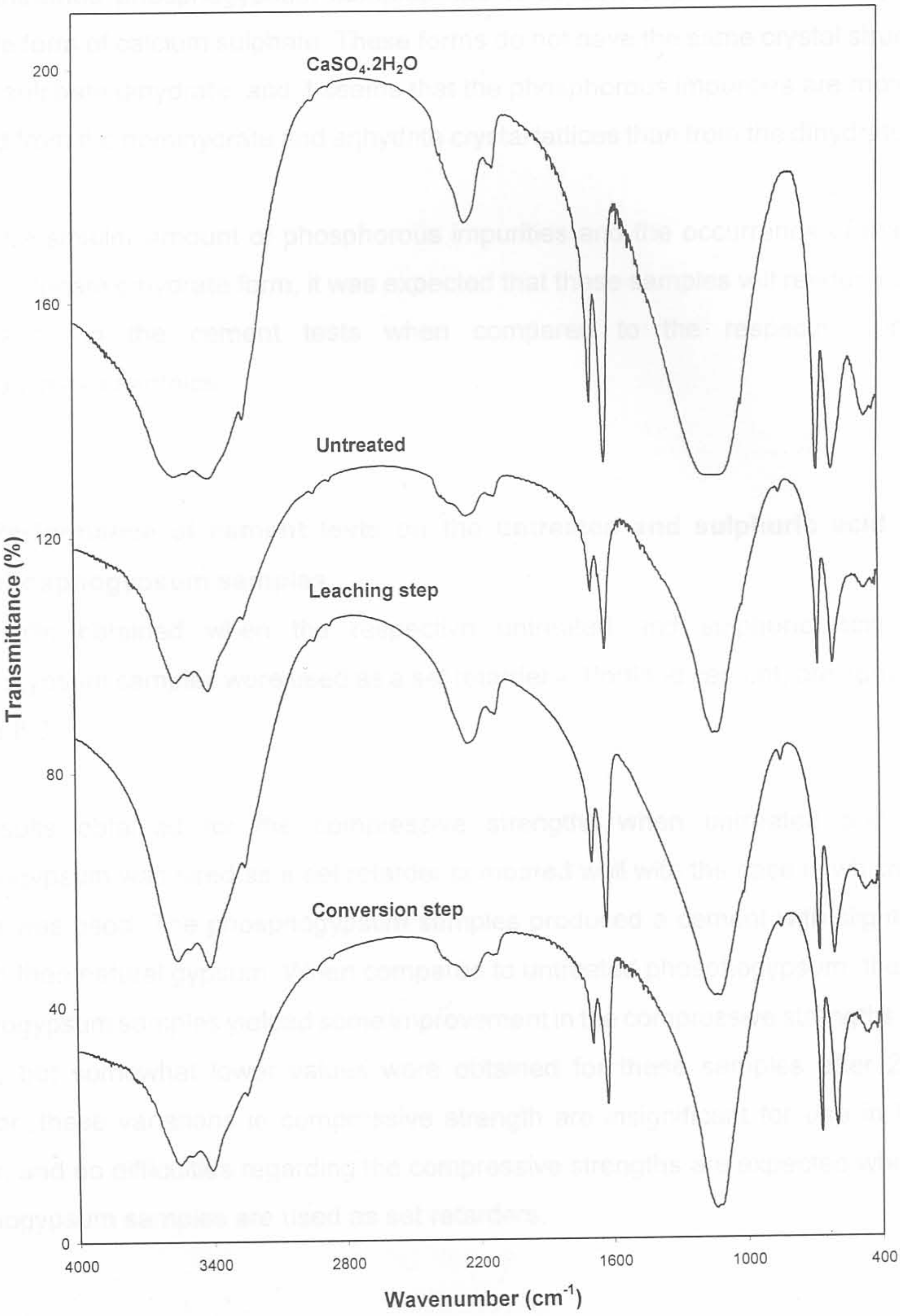


Figure 8.6 **The IR spectra of the untreated and acid treated Batch 2 Omnia phosphogypsum samples, treated on large scale with an extended time period of 4 hours for the conversion step**



The presence of mainly the dihydrate form of calcium sulphate during the course of the treatment was probably the reason for the unsuccessfulness of this method. To be able to remove the phosphorous impurities by reacting it with sulphuric acid, the dihydrate present in the untreated phosphogypsum samples had to be converted to the hemihydrate or anhydrite form of calcium sulphate. These forms do not have the same crystal structure as calcium sulphate dihydrate, and it seems that the phosphorous impurities are more easily removed from the hemihydrate and anhydrite crystal lattices than from the dihydrate lattice.

Due to the smaller amount of phosphorous impurities and the occurrence of mainly the calcium sulphate dihydrate form, it was expected that these samples will render increased performance in the cement tests when compared to the respective untreated phosphogypsum samples.

8.3.3 Performance of cement tests on the untreated and sulphuric acid treated phosphogypsum samples

The results obtained when the respective untreated and sulphuric acid treated phosphogypsum samples were used as a set retarder in Portland cement, are summarised in Table 8.9.

The results obtained for the compressive strengths when untreated and treated phosphogypsum was used as a set retarder compared well with the case in which natural gypsum was used. The phosphogypsum samples produced a cement with slightly lower strength than natural gypsum. When compared to untreated phosphogypsum, the treated phosphogypsum samples yielded some improvement in the compressive strengths at 2 and 7 days, but somewhat lower values were obtained for these samples after 28 days. However, these variations in compressive strength are insignificant for use in Portland cement, and no difficulties regarding the compressive strengths are expected when these phosphogypsum samples are used as set retarders.

Table 8.9 Results of the cement test performed on sulphuric acid treated and untreated Kynoch, Omnia phosphogypsum samples and natural gypsum

Test	O-U[a]	O-ST[b]	K-U[c]	K-ST[d]	N-G[e]
SO_3 content of gypsum (%)	47.24	45.59	46.68	46.96	42.50
Gypsum added to clinker (%)	3.46	3.59	3.50	3.48	3.85
Specific Surface of cement (cm^2/g)	3470	3225	3200	3275	3200
Relative density of cement	3.15	3.10	3.10	3.12	3.10
Initial setting time (min)	243	160	354	184	140
Final setting time (h)	5.11	4.75	6.75	4.25	3.25
2-day Compressive Strength (MPa)	17.12	18.36	17.35	18.89	20.33
7-day Compressive Strength (MPa)	33.91	35.60	34.41	36.97	38.04
28-day Compressive Strength (MPa)	46.07	45.50	47.25	44.01	49.10

[a] Untreated Omnia phosphogypsum

[b] Omnia phosphogypsum treated with H_2SO_4

[c] Untreated Kynoch phosphogypsum

[d] Kynoch phosphogypsum treated with H_2SO_4

[e] Natural Gypsum

The initial and final setting times of cement containing untreated phosphogypsum samples varied significantly from cement containing natural gypsum. By using untreated phosphogypsum instead of natural gypsum as a set retarder, the initial setting time for the cement containing Kynoch phosphogypsum was delayed from 140 minutes to 354 minutes, and that containing Omnia phosphogypsum to 243 minutes. Furthermore, the final setting time of the cement containing untreated Kynoch phosphogypsum, was delayed from 3.25 hours to 6.75 hours, and that for Omnia phosphogypsum to 5.11 hours.

When comparing cement containing treated Kynoch phosphogypsum to the cement containing untreated Kynoch phosphogypsum, the initial setting time improved from 354 minutes to 184 minutes. For the cement containing treated Omnia phosphogypsum, the initial setting time improved from 243 minutes to 160 minutes, when compared to the sample containing untreated Omnia phosphogypsum. This indicates that, when the treated Kynoch and Omnia phosphogypsum samples were used in cement, similar initial setting times were produced, when compared to the initial setting time of 140 minutes obtained when natural gypsum was used.

Similarly, the final setting time for the cement containing treated Kynoch phosphogypsum improved from 6.75 hours to 4.25 hours, and that for the treated Omnia phosphogypsum from 5.11 hours to 4.75 hours. The values obtained when the treated phosphogypsum samples were used, compared better to the final setting time of 3.25 hours obtained for cement containing natural gypsum, than for the cement containing untreated phosphogypsum.

A significant decrease in both the initial and final setting times could be observed when the results of the untreated and treated phosphogypsum samples were compared. These results proved that by decreasing the amount of phosphorous impurities, combined with the presence of mainly calcium sulphate dihydrate in the treated phosphogypsum samples, the performance of phosphogypsum as a set retarder in cement is improved.

8.3.4 Optimisation of the sulphuric acid treatment method

The sulphuric acid treatment method was optimized in terms of the amount of phosphorous removed from the phosphogypsum and the thermogravimetric results which yields the highest amount of calcium sulphate dihydrate. This means that the optimum condition will be when there is the least amount of phosphorous in the gypsum, combined with a TG mass loss of about 20.9% (which is the theoretical amount for pure $CaSO_4.2H_2O$). Because phosphorous was the only impurity of concern in the optimisation, only the values of P_2O_5 from the XRF analyses were considered and reported.

The mass loss percentages and percentage P_2O_5 in the respective untreated phosphogypsum samples differ for the different optimization steps. The amount of phosphogypsum necessary for a specific optimization was taken from the large batch, dried overnight and mixed with a mortar and pestle to homogenise the sample. This sample was then used for the optimization of a specific parameter. Both the mass loss percentage and % P_2O_5 of the homogenised untreated phosphogypsum was determined before optimization. This explains the difference in mass loss percentages and amount of phosphorous impurities for the untreated phosphogypsum samples between the respective optimisation steps.

The results of the effect of reaction temperature are summarised in Table 8.10. The XRF results were normalised to a loss free basis.

Table 8.10 **XRF and thermogravimetric results for the optimisation of temperature for the sulphuric acid method**

Temperature (°C)	Kynoch phosphogypsum		Omnia phosphogypsum	
	P_2O_5 (%)	Mass loss (%)	P_2O_5 (%)	Mass loss (%)
Untreated	1.09	19.5	2.15	14.3
23	0.77	19.9	0.73	18.7
27	0.75	19.1	0.79	18.7
40	0.78	19.0	0.72	19.5
51	0.72	19.5	0.68	17.4
60	0.73	19.9	0.73	18.8
69	0.80	21.4	0.64	18.8

From the results in Table 8.10, it was clear that by using a sulphuric acid concentration of 12%, the effect of temperature on the amount of phosphorous contained in the treated samples, was insignificant for both the Kynoch and Omnia phosphogypsum. Except for the Omnia phosphogypsum treated at 51°C, all other samples contained mainly dihydrate. Based on these results, it was decided to use room temperature (20 - 25°C) for the following optimization steps.

The effect of acid concentration on the amount of phosphorous impurities and dihydrate at constant room temperature of 23°C is given in Table 8.11. The XRF results were normalised to a loss free basis.

Table 8.11 **XRF and thermogravimetric results for the optimisation of concentration H_2SO_4 for the sulphuric acid method**

Concentration H_2SO_4 (% m/m)	Kynoch phosphogypsum		Omnia phosphogypsum	
	P_2O_5 (%)	Mass loss (%)	P_2O_5 (%)	Mass loss (%)
Untreated	0.99	19.5	1.97	14.3
5	0.63	13.7	0.49	19.0
10	0.83	17.2	0.43	18.3
20	0.54	18.7	0.43	19.0
30	0.56	15.5	1.04	17.1
40	0.57	17.7	0.95	19.1
50	0.58	16.0	1.09	20.7

For the Kynoch phosphogypsum, the amount of dihydrate in the treated samples was reduced for all sulphuric acid concentrations. The highest amount of phosphorous impurities was removed when the Kynoch phosphogypsum was treated in H_2SO_4 solutions with concentrations of more than 20% by mass. The highest mass loss, and therefore the most dihydrate, was obtained by stirring in a 20% H_2SO_4 solution. Consequently, the optimum H_2SO_4 concentration for treating Kynoch phosphogypsum was chosen as 20%.

For the Omnia phosphogypsum, the amount of dihydrate increased when the samples were treated with sulphuric acid. Treatment of Omnia phosphogypsum in 5%, 10% or 20% H_2SO_4 solutions removed the highest amount of phosphorous impurities, while more dihydrate was obtained by treatment in a 50% H_2SO_4 solution. However, treatment in a 50% H_2SO_4 solution removed far less impurities than the other concentrations, while treatment in the 5%

and 20% H_2SO_4 solutions produced mainly dihydrate. It was therefore decided to use a sulphuric acid concentration of 5% in further optimization steps, due to economical aspects.

The phosphogypsum samples were then treated at room temperature in a 20% H_2SO_4 solution for the Kynoch phosphogypsum, and 5% for Omnia phosphogypsum. The effect of different stirring times at constant room temperature is shown in Table 8.12. The XRF results were normalised to a loss free basis.

Table 8.12 XRF and thermogravimetric results for the optimisation of reaction time for the sulphuric acid method

Time (min)	Kynoch phosphogypsum		Omnia phosphogypsum	
	P_2O_5 (%)	Mass loss (%)	P_2O_5 (%)	Mass loss (%)
Untreated	1.04	19.5	2.25	14.3
15	0.82	19.0	1.05	19.3
30	0.77	18.9	0.77	19.5
45	0.77	18.0	1.04	18.6
60	0.78	20.8	1.02	18.0
90	0.81	18.5	0.72	19.2
120	0.76	17.8	0.70	19.4
180	0.71	16.2	1.10	19.6
360	0.74	18.9	1.06	17.5

The effect of reaction time was not significant for the treatment of Kynoch phosphogypsum. The same quantity of impurities was removed, regardless of the reaction time. The samples treated for 180 minutes revealed a lower mass loss than the other treated samples, which can possibly be ascribed to experimental error.

For the treated Omnia phosphogypsum samples, fewer phosphorous impurities were present in the samples treated for 30, 90 and 120 minutes. For all Omnia samples, an improvement in the amount of dihydrate was observed due to the higher mass losses. It was decided to choose the optimum time for both Omnia and Kynoch phosphogypsum as 30 minutes.

The phosphogypsum samples were then treated for 30 minutes at room temperature in a 20% H_2SO_4 solution for the Kynoch phosphogypsum, and 5% for Omnia phosphogypsum. The effect of varying the solid:liquid ratio is shown in Table 8.13. The XRF results were normalised to a loss free basis.

Table 8.13 XRF and thermogravimetric results for the optimisation of the solid : liquid ratio for the sulphuric acid method

Ratio (s:ℓ)	Kynoch phosphogypsum		Omnia phosphogypsum	
	P_2O_5 (%)	Mass loss (%)	P_2O_5 (%)	Mass loss (%)
Untreated	0.95	17.2	2.08	15.1
1:1	0.82	18.8	0.85	20.0
1:2	0.76	20.1	0.83	20.6
1:3	0.77	18.7	0.82	19.2
1:4	0.77	19.4	0.75	20.2

Contrary to what was observed for the Batch 1 Omnia phosphogypsum sample, the Batch 2 samples of both the Kynoch and Omnia phosphogypsum formed a manageable paste when a solid:liquid ratio of 1:1 was used. It was therefore decided to vary the solid:liquid ratio between 1:1 and 1:4.

For both Kynoch and Omnia phosphogypsum, the treated samples showed an improvement in the amount of calcium sulphate dihydrate, when compared to the untreated samples. The treated samples contained mainly calcium sulphate dihydrate. The difference in the amount of phosphorous impurities between the different treated samples was insignificant. A solid:liquid ratio of 1:4 was chosen as the optimum, because this produced a paste that could be stirred more easily.

When all optimisation steps were combined, the phosphogypsum samples were treated for 30 minutes at room temperature at a solid:liquid ratio of 1:4 in a 20% H_2SO_4 solution for the Kynoch phosphogypsum, and 5% for Omnia phosphogypsum.

8.3.5 The optimum sulphuric acid treatment of phosphogypsum on a large scale for performance of cement tests

The Kynoch and Omnia phosphogypsum samples were treated on a large scale for use in the performance of cement tests, according the optimum sulphuric acid method as discussed above. The results of the XRF analyses are summarised in Tables 8.14 and 8.15. For both types of phosphogypsum, the amount of phosphorous impurities was reduced by the optimum sulphuric acid treatment.

Table 8.14 **XRF analysis of Batch 2 phosphogypsum samples, treated on a large scale for the performance of cement tests by the optimum sulphuric acid treatment method**

Compounds (%)	Kynoch phosphogypsum		Omnia phosphogypsum	
	Untreated	Optimum acid treatment	Untreated	Optimum acid treatment
SiO_2	0.22	0.11	0.14	0.05
Al_2O_3	0.11	0.01	0.01	0
Fe_2O_3	0*	0	0	0
MnO	0	0	0	0
MgO	0	0	0	0
CaO	32.75	32.88	32.21	33.68
Cr_2O_3	0	0	0	0
K_2O	0	0	0	0
Na_2O	0	0	0	0
P_2O_5	**0.81**	**0.57**	**1.21**	**0.64**
SO_3	42.85	44.80	45.75	44.68
LOI	21.38	20.55	20.35	20.68
TOTAL	98.12	98.92	99.67	99.73

*0 means that the compound was present in a quantity below the detection limit

Table 8.15 XRF analysis of Batch 2 phosphogypsum samples, treated on a large scale for the performance of cement tests by the optimum sulphuric acid treatment method, normalised to a loss free basis

Compounds (%)	Kynoch phosphogypsum		Omnia phosphogypsum	
	Untreated	Optimum acid treatment	Untreated	Optimum acid treatment
SiO_2	0.29	0.14	0.18	0.06
Al_2O_3	0.14	0.01	0.01	0*
CaO	42.68	41.95	40.59	42.61
P_2O_5	**1.06**	**0.73**	**1.53**	**0.81**
SO_3	55.84	57.16	57.67	56.52

*0 means that the compound was present in a quantity below the detection limit

The thermogravimetric curves for the optimum sulphuric acid treated phosphogypsum samples are presented in Figures 8.7 and 8.8.

Figure 8.7 The TG and DSC curves obtained for the optimum sulphuric acid treated Batch 2 Kynoch phosphogypsum samples, treated on a large scale for the performance of cement tests

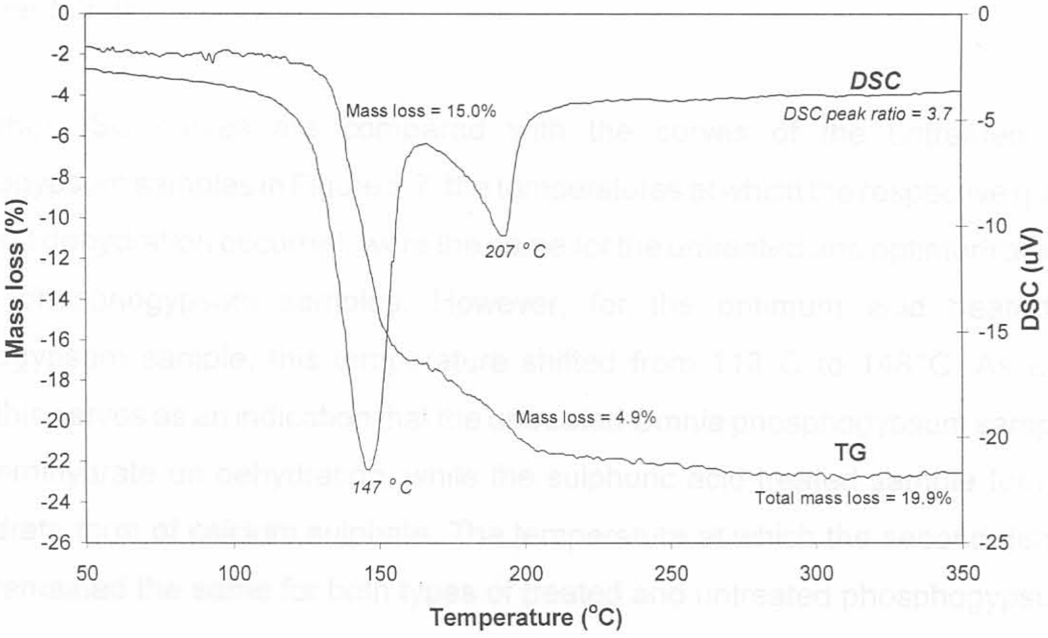
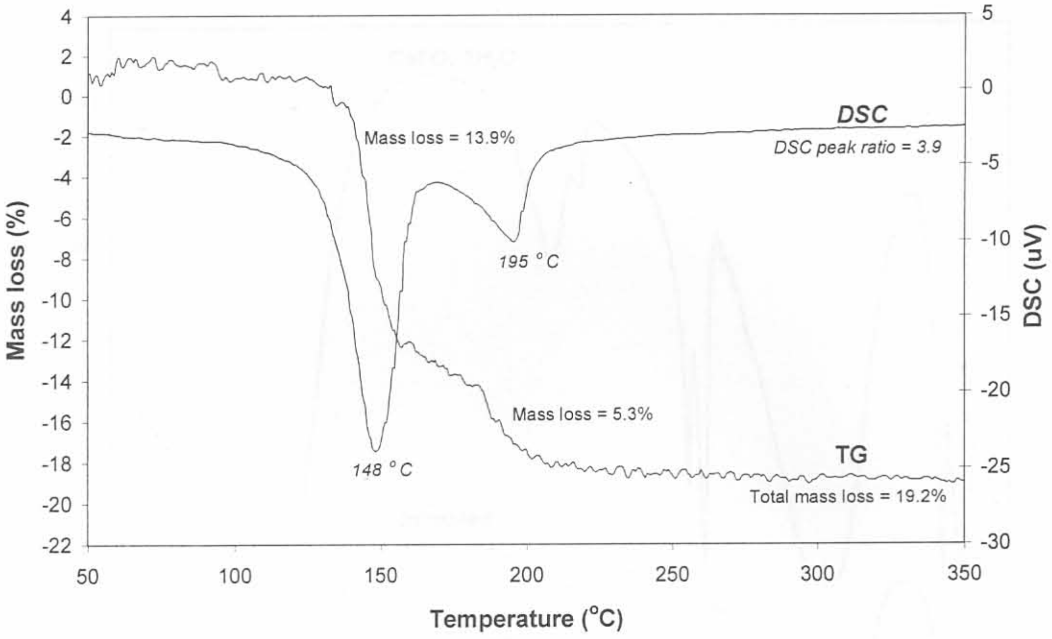


Figure 8.8 The TG and DSC curves obtained for the optimum sulphuric acid treated Batch 2 Omnia phosphogypsum samples, treated on a large scale for the performance of cement tests



Both the Kynoch and Omnia phosphogypsum samples contained mainly the dihydrate form of calcium sulphate after the optimum treatment, as can be seen from the total mass losses which are in both cases close to the theoretical value of 20.9%. This is confirmed by the values of the DSC peak ratios, which are close to the theoretical value of 3.3 (as discussed in Chapter 5.3.3).

When the DSC curves are compared with the curves of the untreated Batch 2 phosphogypsum samples in Figure 5.7, the temperatures at which the respective maximums for the first dehydration occurred, were the same for the untreated and optimum acid treated Kynoch phosphogypsum samples. However, for the optimum acid treated Omnia phosphogypsum sample, this temperature shifted from 118°C to 148°C. As explained before, this serves as an indication that the untreated Omnia phosphogypsum sample forms the α-hemihydrate on dehydration, while the sulphuric acid treated sample forms the β-hemihydrate form of calcium sulphate. The temperature at which the second dehydration occurs remained the same for both types of treated and untreated phosphogypsum.

Figure 8.9 **The IR spectra of the untreated and optimum sulphuric acid treated Batch 2 Kynoch phosphogypsum samples, used for the performance of cement tests**

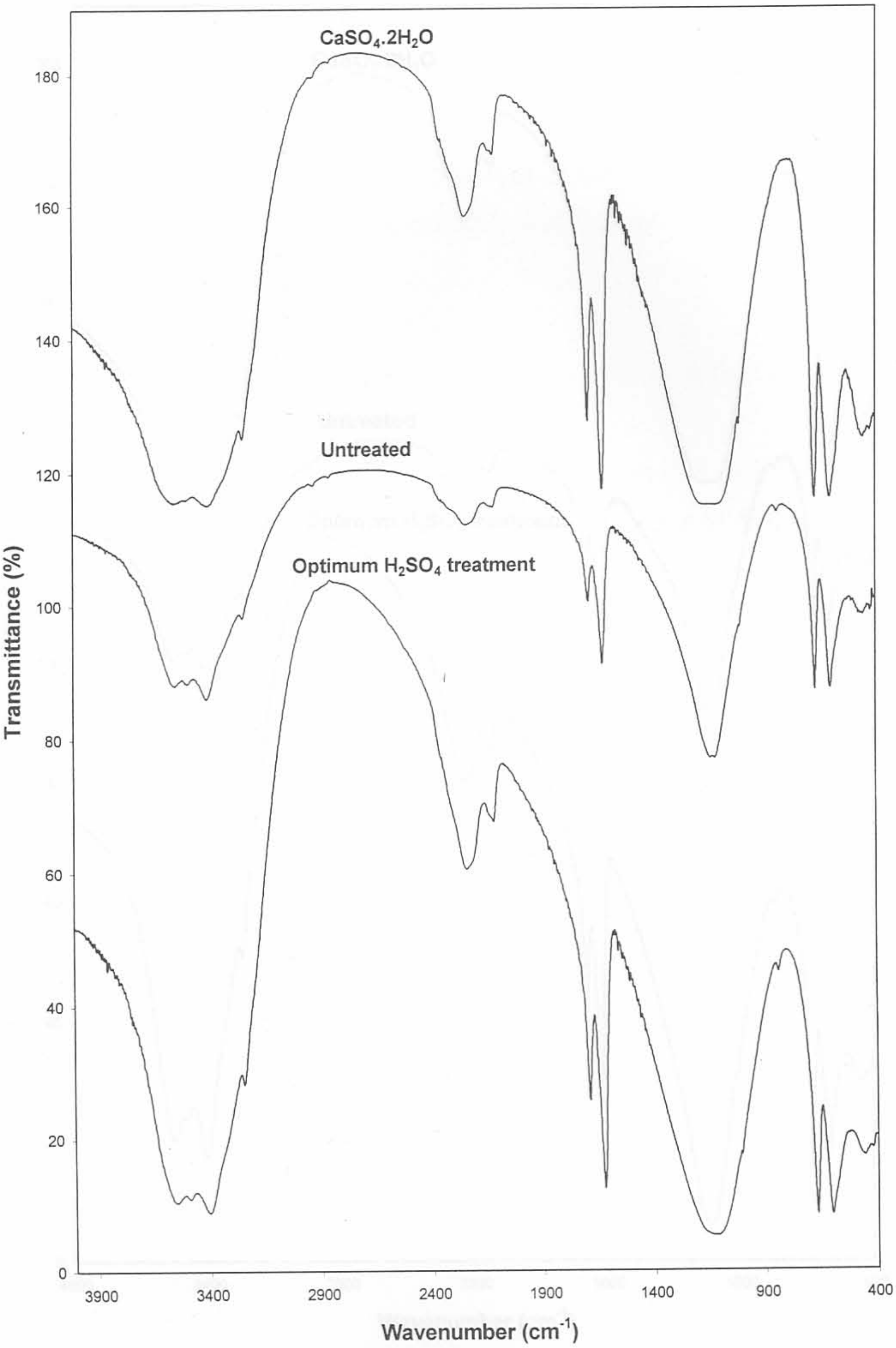
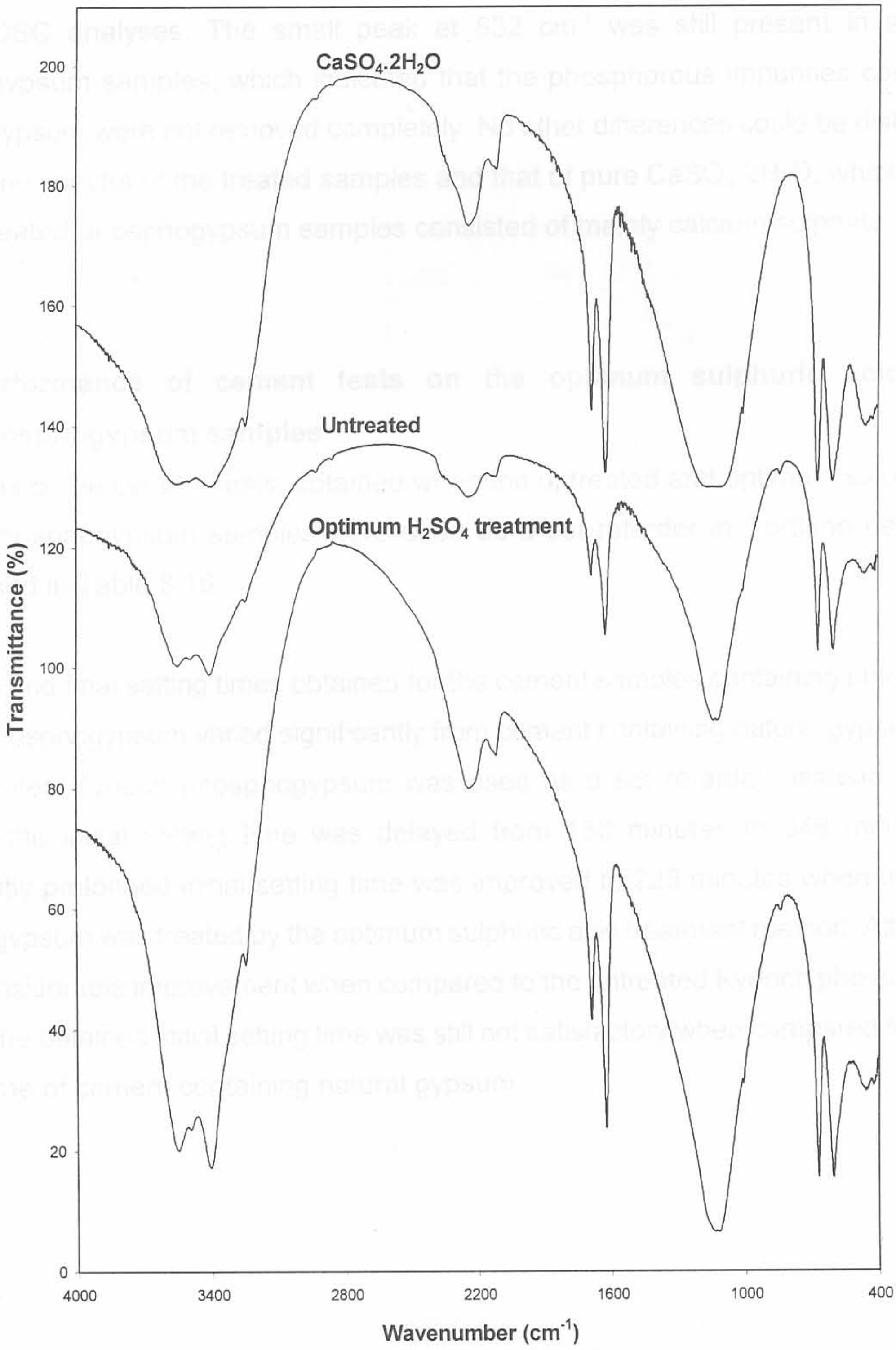


Figure 8.10 The IR spectra of the untreated and optimum sulphuric acid treated Batch 2 Omnia phosphogypsum samples, used for the performance of cement tests



The results of the FT-IR analyses of the untreated and optimum sulphuric acid treated phosphogypsum samples are given in Figures 8.9 and 8.10.

The results obtained from the IR analyses supported the conclusions made from the XRF and TG/DSC analyses. The small peak at 832 cm^{-1} was still present in all treated phosphogypsum samples, which indicated that the phosphorous impurities contained in phosphogypsum were not removed completely. No other differences could be distinguished between the spectra of the treated samples and that of pure $CaSO_4.2H_2O$, which confirms that the treated phosphogypsum samples consisted of mainly calcium sulphate dihydrate.

8.3.6 Performance of cement tests on the optimum sulphuric acid treated phosphogypsum samples

The results of the cement tests, obtained when the untreated and optimum sulphuric acid treated phosphogypsum samples were used as a set retarder in Portland cement, are summarised in Table 8.16.

The initial and final setting times obtained for the cement samples containing untreated and treated phosphogypsum varied significantly from cement containing natural gypsum. When the untreated Kynoch phosphogypsum was used as a set retarder instead of natural gypsum, the initial setting time was delayed from 130 minutes to 348 minutes. This significantly prolonged initial setting time was improved to 228 minutes when the Kynoch phosphogypsum was treated by the optimum sulphuric acid treatment method. Although this was a considerable improvement when compared to the untreated Kynoch phosphogypsum sample, the obtained initial setting time was still not satisfactory when compared to the initial setting time of cement containing natural gypsum.

Table 8.16 Results of the cement test performed when untreated and optimum sulphuric acid treated Kynoch and Omnia phosphogypsum samples, and natural gypsum was used as a set retarder in Portland cement

Test	O-U[a]	O-OST[b]	K-U[c]	K-OST[d]	N-G[e]
SO_3 content of gypsum (%)	47.06	45.98	45.76	45.78	42.50
Gypsum added to clinker (%)	3.47	3.56	3.57	3.57	3.85
Specific Surface of cement (cm^2/g)	3159	3457	3180	3258	3314
Relative density of cement	3.15	3.15	3.14	3.14	3.14
Initial setting time (min)	265	189	348	228	130
Final setting time (h)	5.8	4.2	7.2	4.9	3.0
2-day Compressive Strength (MPa)	14.17	17.35	14.67	15.07	19.27
7-day Compressive Strength (MPa)	31.17	33.47	34.40	33.13	32.37
28-day Compressive Strength (MPa)	38.28	45.47	41.43	39.10	47.90

[a] Untreated Omnia phosphogypsum

[b] Omnia phosphogypsum treated by the optimum H_2SO_4 treatment method

[c] Untreated Kynoch phosphogypsum

[d] Kynoch phosphogypsum treated by the optimum H_2SO_4 treatment method

[e] Natural Gypsum

The initial setting time of cement containing untreated Omnia phosphogypsum was delayed from 130 minutes to 265 minutes, when compared to cement containing natural gypsum. The retardation effect was smaller than in the case of untreated Kynoch phosphogypsum. When the Omnia phosphogypsum was treated by the optimum sulphuric acid treatment method, the initial setting time was improved to 189 minutes. Although this was still not comparable to the initial setting time of 130 minutes obtained for the cement samples containing natural gypsum, the Omnia phosphogypsum sample treated by the optimum sulphuric acid treatment method yielded an initial setting time closest to the desired value. This indicates that the optimum sulphuric acid treatment method has been successful in improving the initial setting times of cement containing phosphogypsum as a set retarder.

The final setting time of cement containing untreated Kynoch phosphogypsum was significantly impeded from 3.0 hours to 7.2 hours, but was improved to 4.9 hours when the Kynoch phosphogypsum sample was treated by the optimum sulphuric acid treatment method. Similarly, the final setting time of cement containing untreated Omnia phosphogypsum was delayed from 3.0 hours to 5.8 hours, with an improvement to 4.2 hours when the treated Omnia phosphogypsum was used.

The prolonged setting times of cement containing phosphogypsum can again be ascribed to the fact that all the treated and untreated phosphogypsum samples still contained a considerable amount of phosphorous impurities.

The 2-day compressive strength was in all instances lower when treated and untreated Kynoch phosphogypsum samples were used as a set retarder instead of natural gypsum. However, some improvement was observed in the 2-day compressive strength of the cement sample containing the optimum sulphuric acid treated Omnia phosphogypsum sample. The cement samples containing both the treated and untreated phosphogypsum have shown similar performance in the 7-day compressive strengths when compared to the cement sample containing natural gypsum.

For both Kynoch and Omnia phosphogypsum, the 28-day compressive strengths of cement containing the untreated phosphogypsum samples were lower than that of the cement sample containing natural gypsum. Treatment of these samples by the optimized sulphuric acid treatment method improved the performance of the cement sample containing the treated Omnia phosphogypsum, but had no significant effect on the 28-day compressive strength of cement containing treated Kynoch phosphogypsum.

8.4 Results and discussion of the combined thermal and sulphuric acid treatment method, applied to South African phosphogypsum

A new method was developed in which the South African phosphogypsum samples were subjected to thermal treatment, followed by treatment in sulphuric acid. The aim of this method was to change the hydrated form of calcium sulphate contained in phosphogypsum, and subsequently study the effect of a change in the amount of water of crystallization on the purification of phosphogypsum.

8.4.1 The combined thermal and sulphuric acid treatment method

Tables 8.17 and 8.18 describe the XRF results obtained after Batch 2 of both Kynoch and Omnia phosphogypsum were treated by the combined thermal and sulphuric acid method. The treated samples contained almost no P_2O_5, which implies that this method was successful in removing the harmful phosphorous impurities from the phosphogypsum samples.

Table 8.17 XRF analysis of Batch 2 phosphogypsum samples, treated by the combined thermal and sulphuric acid treatment method

Compounds (%)	Kynoch phosphogypsum		Omnia phosphogypsum	
	Untreated	Treated	Untreated	Treated
SiO_2	0.23	0.12	0.05	0
Al_2O_3	0.12	0	0	0
Fe_2O_3	0*	0	0	0
MgO	0	0	0.07	0
CaO	32.58	33.07	33.79	33.45
P_2O_5	**0.76**	**0.03**	**1.69**	**0.07**
SO_3	46.22	48.86	45.35	48.83
LOI	21.31	19.25	18.78	18.79
TOTAL	101.64	101.33	99.73	101.14

*0 means that the compound was present in a quantity below the detection limit

Table 8.18 XRF analysis of Batch 2 phosphogypsum samples, treated by the combined thermal and sulphuric acid treatment method, normalised to a loss free basis

Compounds (%)	**Kynoch phosphogypsum**		**Omnia phosphogypsum**	
	Untreated	**Treated**	**Untreated**	**Treated**
SiO_2	0.29	0.15	0.06	0*
Al_2O_3	0.15	0	0	0
MgO	0	0	0.09	0
CaO	40.46	40.29	41.74	40.56
P_2O_5	**0.95**	**0.04**	**2.09**	**0.09**
SO_3	57.54	59.53	56.02	59.30

*0 means that the compound was present in a quantity below the detection limit

The results obtained from the thermogravimetric analyses of the phosphogypsum samples, treated by the combined thermal and sulphuric acid method, are given in Figures 8.11 and 8.12.

The treated Kynoch phosphogypsum revealed a total mass loss of 19.5%, which is close to the theoretical value of 20.9%. This indicates that the sample consisted mainly of calcium sulphate dihydrate. However, the treated Omnia phosphogypsum sample showed a total mass loss of only 15.4%, which means that this sample contained a mixture of calcium sulphate dihydrate and one or both of the hemihydrate and anhydrite forms. The DSC peak ratio obtained for the treated Omnia phosphogypsum could not be of any help to solve this, since the first dehydration peak did not return to the baseline before the second peak started, which makes the value of the peak ratio unusable.

Figure 8.11 TG and DSC curves obtained for the Batch 2 Kynoch phosphogypsum sample, treated by the combined thermal and H_2SO_4 treatment method

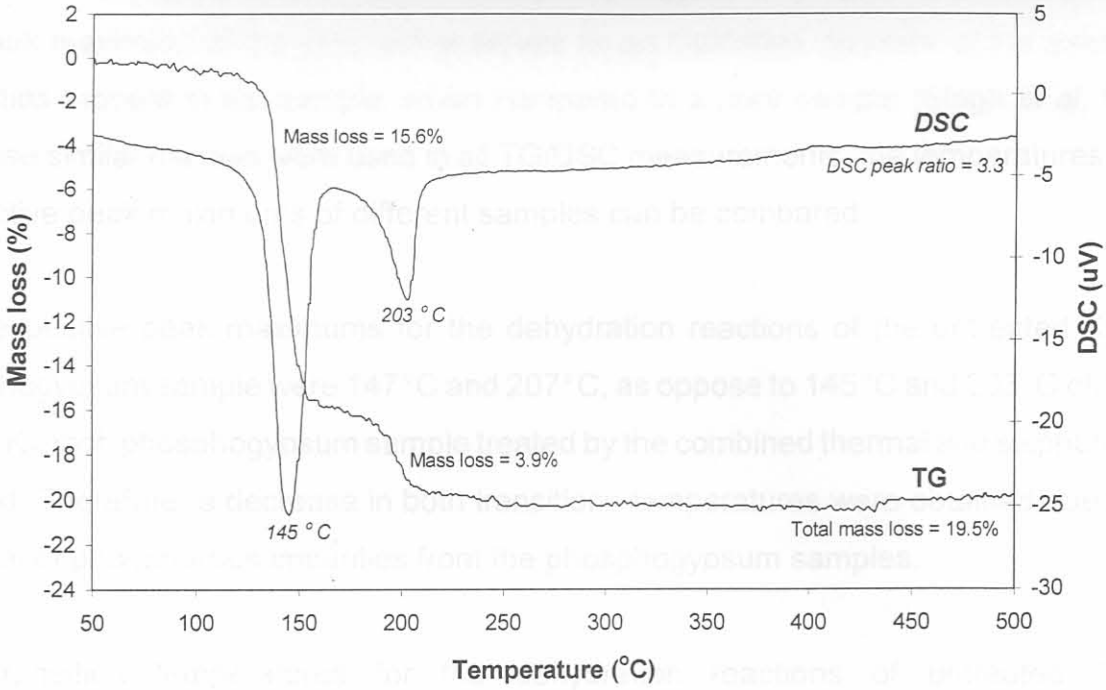
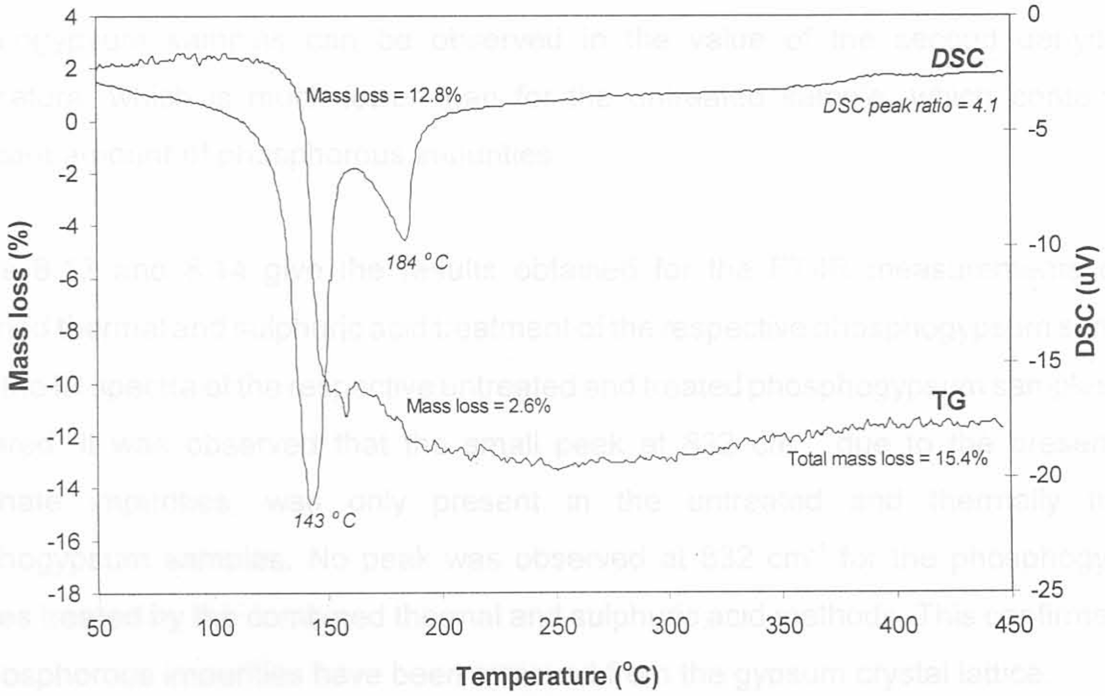


Figure 8.12 TG and DSC curves obtained for the Batch 2 Omnia phosphogypsum sample, treated by the combined thermal and H_2SO_4 treatment method



When the DSC curves are compared with the curves of the untreated Batch 2 phosphogypsum samples in Figure 5.7, the maximum temperatures for both dehydration reactions were slightly lower for the treated phosphogypsum samples. The temperature at the peak maximum of the DSC curve serves as an indicative measure of the amount of impurities present in the sample, when compared to a pure sample (Singh *et al*, 1996). Because similar masses were used in all TG/DSC measurements, the temperatures of the respective peak maximums of different samples can be compared.

The respective peak maximums for the dehydration reactions of the untreated Kynoch phosphogypsum sample were 147 °C and 207 °C, as oppose to 145 °C and 203 °C obtained for the Kynoch phosphogypsum sample treated by the combined thermal and sulphuric acid method. Therefore, a decrease in both transitions temperatures were obtained due to the removal of phosphorous impurities from the phosphogypsum samples.

The transition temperatures for the dehydration reactions of untreated Omnia phosphogypsum were 118 °C and 194 °C, compared to 143 °C and 184 °C for the combined thermal and sulphuric acid treated samples. The much lower value of the first transition can again be explained by the formation of the α-hemihydrate on dehydration of the untreated Omnia phosphogypsum, while the treated Omnia phosphogypsum samples formed the β-hemihydrate. The effect of the removal of phosphorous impurities from the treated Omnia phosphogypsum samples can be observed in the value of the second dehydration temperature, which is much lower than for the untreated sample, which contained a significant amount of phosphorous impurities.

Figures 8.13 and 8.14 give the results obtained for the FT-IR measurements of the combined thermal and sulphuric acid treatment of the respective phosphogypsum samples. When the IR spectra of the respective untreated and treated phosphogypsum samples were compared, it was observed that the small peak at 832 cm^{-1}, due to the presence of phosphate impurities, was only present in the untreated and thermally treated phosphogypsum samples. No peak was observed at 832 cm^{-1} for the phosphogypsum samples treated by the combined thermal and sulphuric acid methods. This confirmed that the phosphorous impurities have been removed from the gypsum crystal lattice.

Figure 8.13 **The IR spectra of $CaSO_4.2H_2O$, the untreated and treated Batch 2 Kynoch phosphogypsum samples, treated by the combined thermal and H_2SO_4 treatment method**

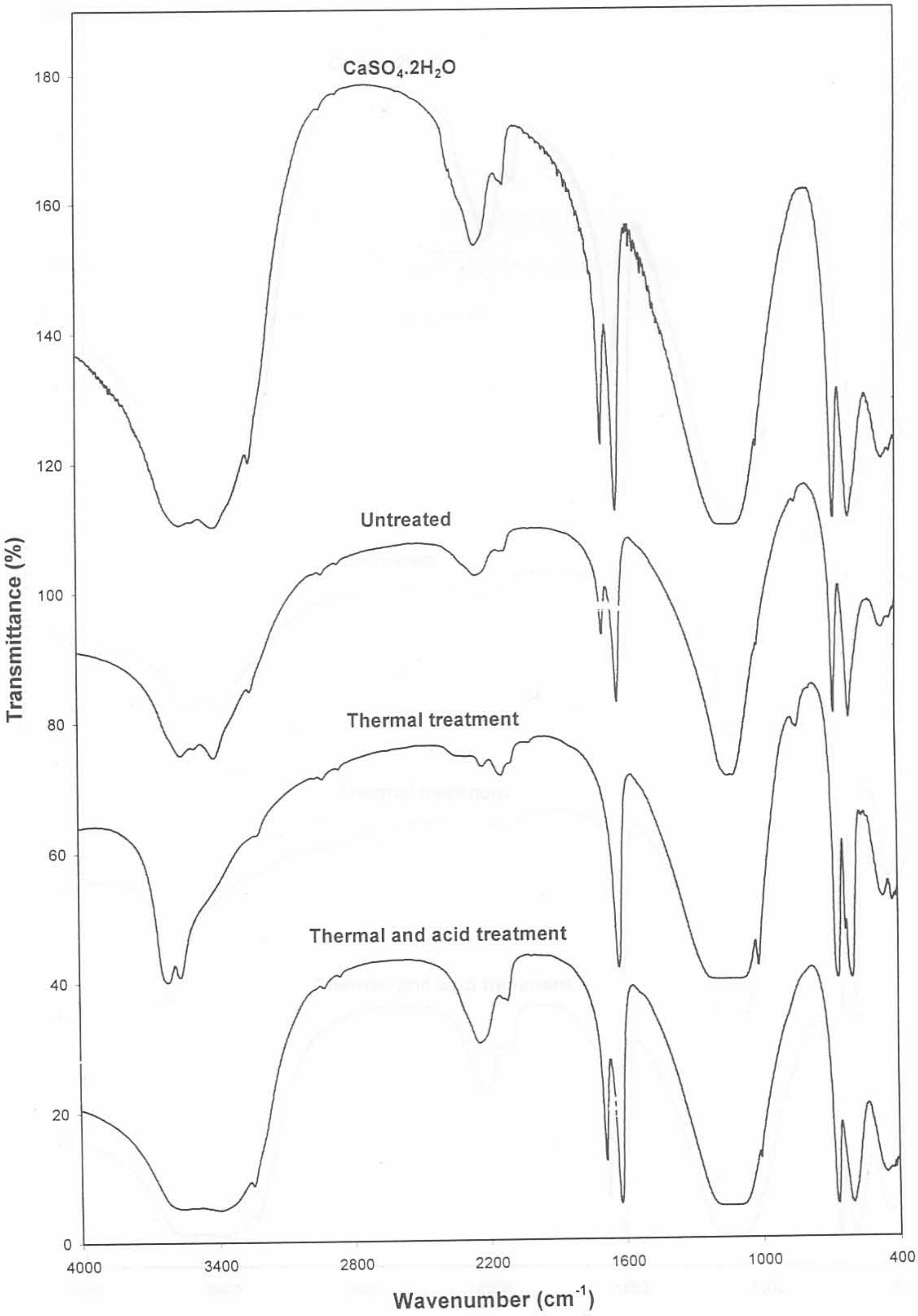
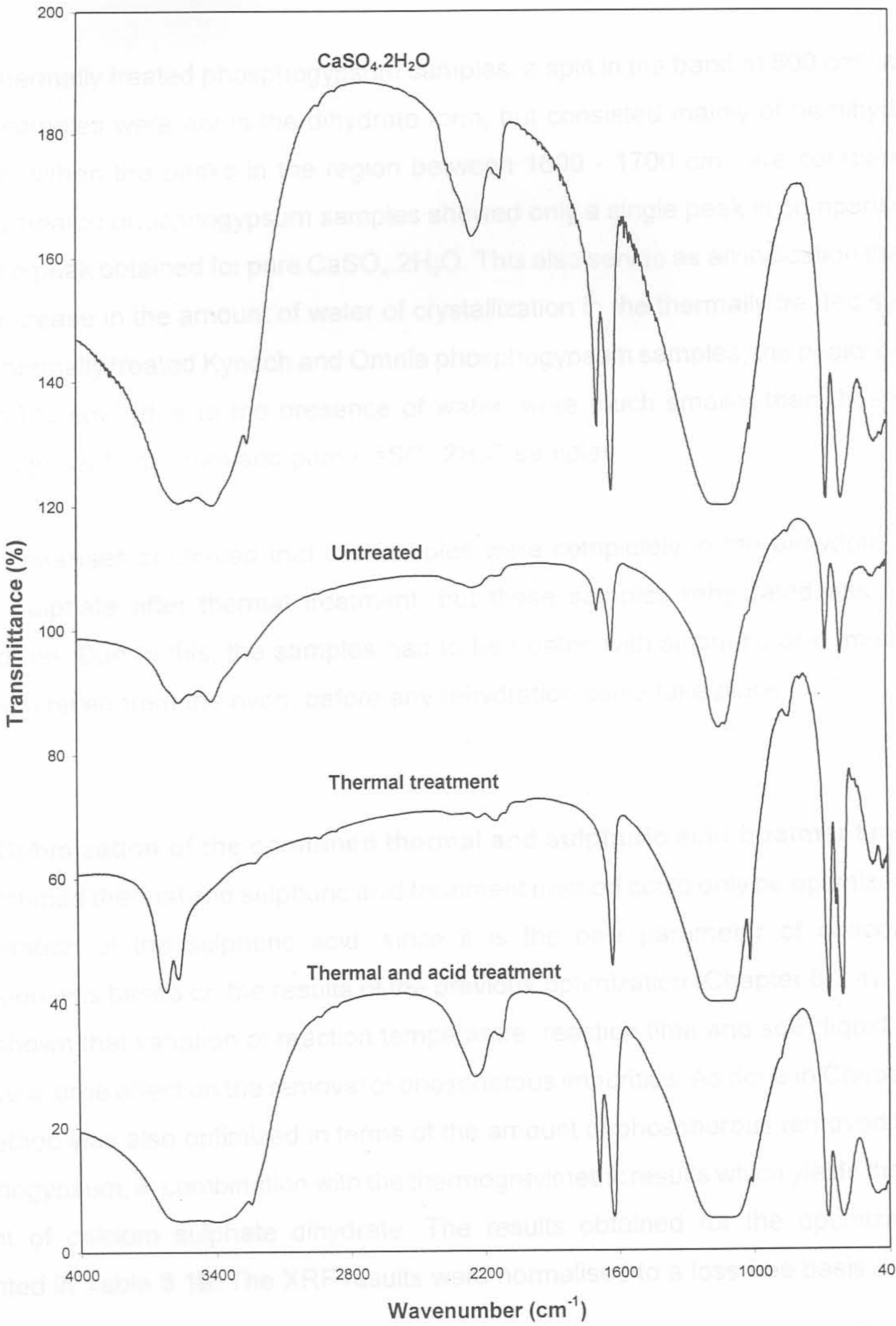


Figure 8.14 The IR spectra of $CaSO_4.2H_2O$, the untreated and treated Batch 2 Omnia phosphogypsum samples, treated by the combined thermal and H_2SO_4 treatment method



The IR spectra of the phosphogypsum samples treated by the combined thermal and sulphuric acid method was the same as that obtained for pure $CaSO_4.2H_2O$, which also confirms the TG/DSC results in that the samples consisted of the dihydrate form of calcium sulphate.

For the thermally treated phosphogypsum samples, a split in the band at 600 cm^{-1} showed that the samples were not in the dihydrate form, but consisted mainly of hemihydrate or anhydrite. When the peaks in the region between 1600 - 1700 cm^{-1} are compared, the thermally treated phosphogypsum samples showed only a single peak in comparison with the double peak obtained for pure $CaSO_4.2H_2O$. This also serves as an indication that there was a decrease in the amount of water of crystallization in the thermally treated samples. For the thermally treated Kynoch and Omnia phosphogypsum samples, the peaks between 3400 - 4000 cm^{-1}, due to the presence of water, were much smaller than those of the untreated phosphogypsum and pure $CaSO_4.2H_2O$ samples.

TG/DSC analyses confirmed that the samples were completely in the anhydrite form of calcium sulphate after thermal treatment, but these samples rehydrated easily to the hemihydrate. Due to this, the samples had to be treated with sulphuric acid immediately after being taken from the oven, before any rehydration could take place.

8.4.2 Optimization of the combined thermal and sulphuric acid treatment method

The combined thermal and sulphuric acid treatment method could only be optimized for the concentration of the sulphuric acid, since it is the only parameter of concern. This conclusion was based on the results of the previous optimization (Chapter 8.3.4), in which it was shown that variation of reaction temperature, reaction time and solid:liquid ratio did not have a large effect on the removal of phosphorous impurities. As done in Chapter 8.3.4, this method was also optimized in terms of the amount of phosphorous removed from the phosphogypsum, in combination with the thermogravimetric results which yields the highest amount of calcium sulphate dihydrate. The results obtained for the optimization are presented in Table 8.19. The XRF results were normalised to a loss free basis.

Table 8.19 XRF and TG results for the optimization of the concentration of sulphuric acid for the combined thermal and acid treatment method

Concentration H_2SO_4 (% m/m)	**Kynoch phosphogypsum**		**Omnia phosphogypsum**	
	P_2O_5 (%)	**Mass loss (%)**	**P_2O_5 (%)**	**Mass loss (%)**
Untreated	1.05	17.2	1.86	15.1
1	0.14	19.1	0.20	18.1
5	0.08	18.4	0.09	19.9
10	0.06	16.8	0.06	19.1
20	0.05	20.4	0.06	19.9
50	0.04	19.5	0.63	15.8

For the Kynoch phosphogypsum sample treated in a 1% H_2SO_4 solution there were still some phosphorous impurities present. All other samples contained almost no phosphorous impurities, and produced mainly calcium sulphate dihydrate, as can be observed from the high mass losses. The sample treated in a 10% H_2SO_4 solution yielded a lower amount of calcium sulphate dihydrate than the other samples.

The phosphorous impurities contained in Omnia phosphogypsum were removed in the samples treated in 5%, 10% and 20% H_2SO_4. Fewer phosphorous impurities were removed when the Omnia phosphogypsum samples were treated in a 50% H_2SO_4 solution, and the percentage mass loss for this sample was smaller than that of the other treated Omnia phosphogypsum samples. This indicates that treatment of the Omnia phosphogypsum in a 50% H_2SO_4 solution resulted in the formation of a smaller amount of the dihydrate form of calcium sulphate when compared to the other samples.

Based on the abovementioned remarks, a sulphuric acid concentration of 5% (by mass) was chosen as the optimum concentration. Although other concentrations produced similar results, it is more economical for industrial purposes, to use an acid concentration as low as possible.

8.4.3 The combined thermal and sulphuric acid treatment on a large scale for the performance of cement tests

After optimization of the concentration of sulphuric acid, the combined thermal and acid treatment method was used to treat the Kynoch and Omnia phosphogypsum samples on a large scale for use in cement tests. The results of the XRF analyses are summarised in Tables 8.20 and 8.21. For both types of phosphogypsum, the phosphorous impurities were almost completely removed, which means that the samples consisted of mainly pure calcium sulphate.

Table 8.20 XRF analysis of Batch 2 phosphogypsum samples, treated on a large scale by the combined thermal and H_2SO_4 method, for the performance of cement tests

Compounds (%)	Kynoch phosphogypsum		Omnia phosphogypsum	
	Untreated	Thermal and acid treatment	Untreated	Thermal and acid treatment
SiO_2	0.22	0.15	0.14	0.07
Al_2O_3	0.11	0*	0.01	0
Fe_2O_3	0	0	0	0
MnO	0	0	0	0
MgO	0	0	0	0
CaO	32.75	32.56	32.21	33.24
Cr_2O_3	0	0	0	0
K_2O	0	0	0	0
Na_2O	0	0	0	0
P_2O_5	**0.81**	**0.03**	**1.21**	**0.05**
SO_3	42.85	46.34	45.75	45.79
LOI	21.38	21.01	20.35	20.90
TOTAL	98.12	100.13	99.67	100.05

*0 means that the compound was present in a quantity below the detection limit

Table 8.21 XRF analysis of Batch 2 phosphogypsum samples, treated on a large scale by the combined thermal and H_2SO_4 method, for the performance of cement tests

Compounds (%)	Kynoch phosphogypsum		Omnia phosphogypsum	
	Untreated	Thermal and acid treatment	Untreated	Thermal and acid treatment
SiO_2	0.29	0.19	0.18	0.09
Al_2O_3	0.14	0*	0.01	0
CaO	42.68	41.15	40.61	42.00
P_2O_5	**1.06**	**0.04**	**1.53**	**0.06**
SO_3	55.84	58.57	57.68	57.85

*0 means that the compound was present in a quantity below the detection limit

The results obtained from the thermogravimetric analysis of these samples are summarised in Figures 8.15 and 8.16.

Figure 8.15 The TG and DSC curves obtained for the untreated and treated Batch 2 Kynoch phosphogypsum samples, treated on a large scale by the combined thermal and H_2SO_4 method, for the performance of cement tests

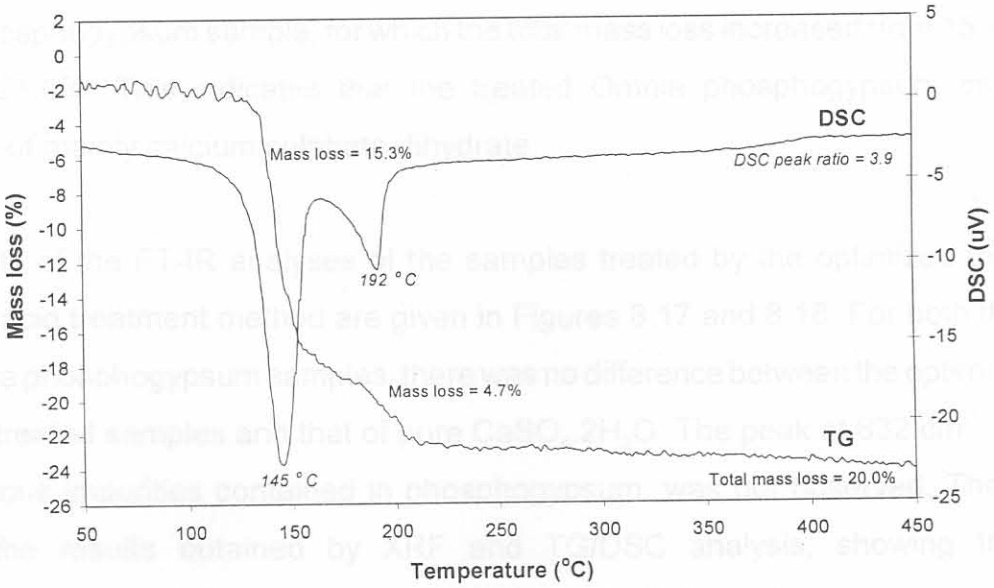
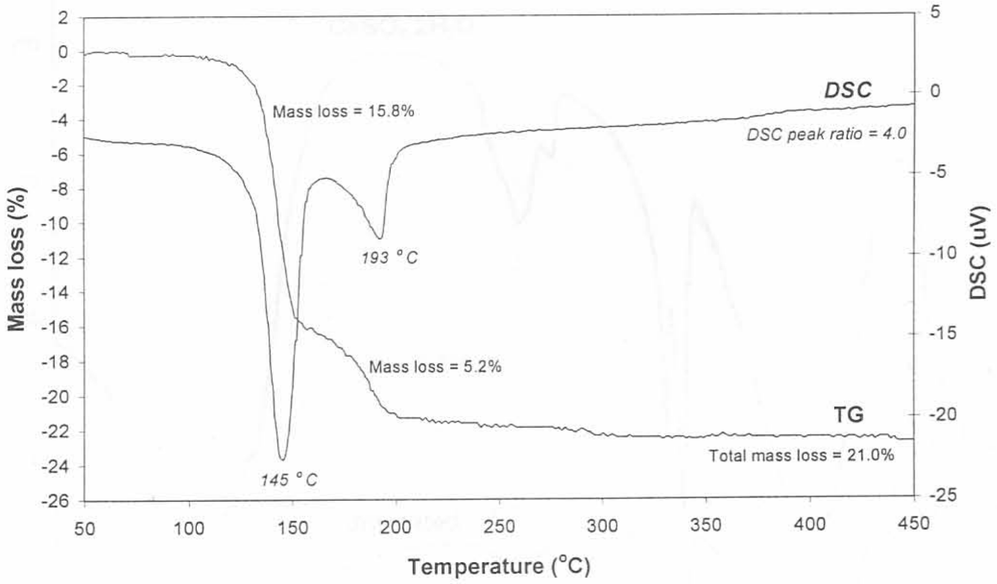


Figure 8.16 **The TG and DSC curves obtained for the untreated and treated Batch 2 Omnia phosphogypsum samples, treated on a large scale by the combined thermal and H_2SO_4 method, for the performance of cement tests**



The DSC curves are similar to the results obtained when the phosphogypsum samples were treated by this method on a small scale, as discussed in Chapter 8.3.7. After optimization of the concentration of H_2SO_4, the TG curve obtained for Kynoch shows that the treated Kynoch phosphogypsum sample, which revealed a total mass loss of 20.0%, was still in the preferred dihydrate form. The optimization had a significant effect on the treatment of the Omnia phosphogypsum sample, for which the total mass loss increased from 15.4% (Figure 8.12) to 21.0%. This indicates that the treated Omnia phosphogypsum sample also consisted of mainly calcium sulphate dihydrate.

The results of the FT-IR analyses of the samples treated by the optimized thermal and sulphuric acid treatment method are given in Figures 8.17 and 8.18. For both the Kynoch and Omnia phosphogypsum samples, there was no difference between the optimum thermal and acid treated samples and that of pure $CaSO_4.2H_2O$. The peak at 832 cm^{-1}, due to the phosphorous impurities contained in phosphogypsum, was not observed. These results confirm the results obtained by XRF and TG/DSC analysis, showing the treated phosphogypsum samples consisted mainly of pure $CaSO_4.2H_2O$.

Figure 8.17 The IR spectra of the untreated and treated Batch 2 Kynoch phosphogypsum samples, treated on a large scale by the combined thermal and sulphuric acid method, for the performance of cement tests

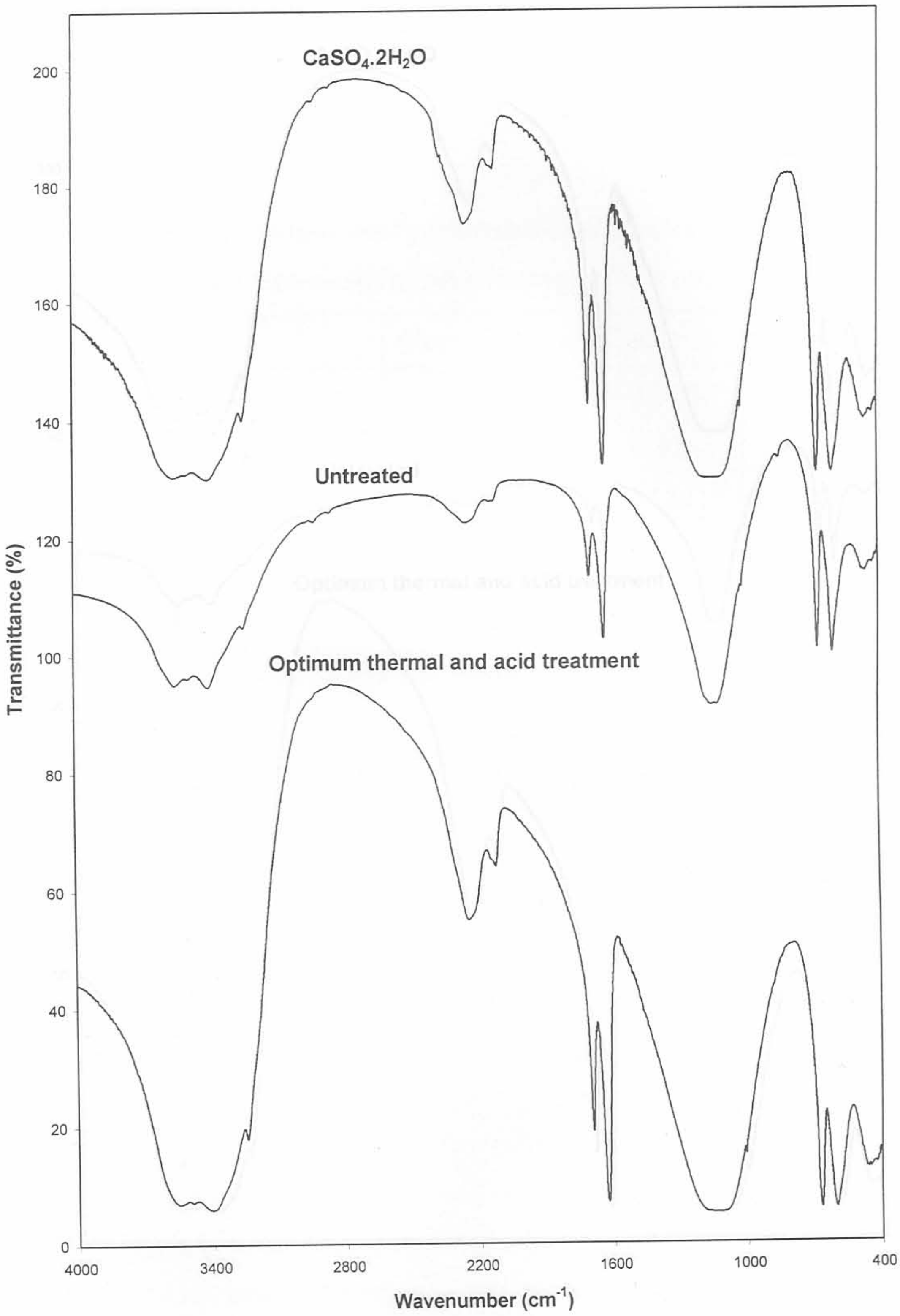
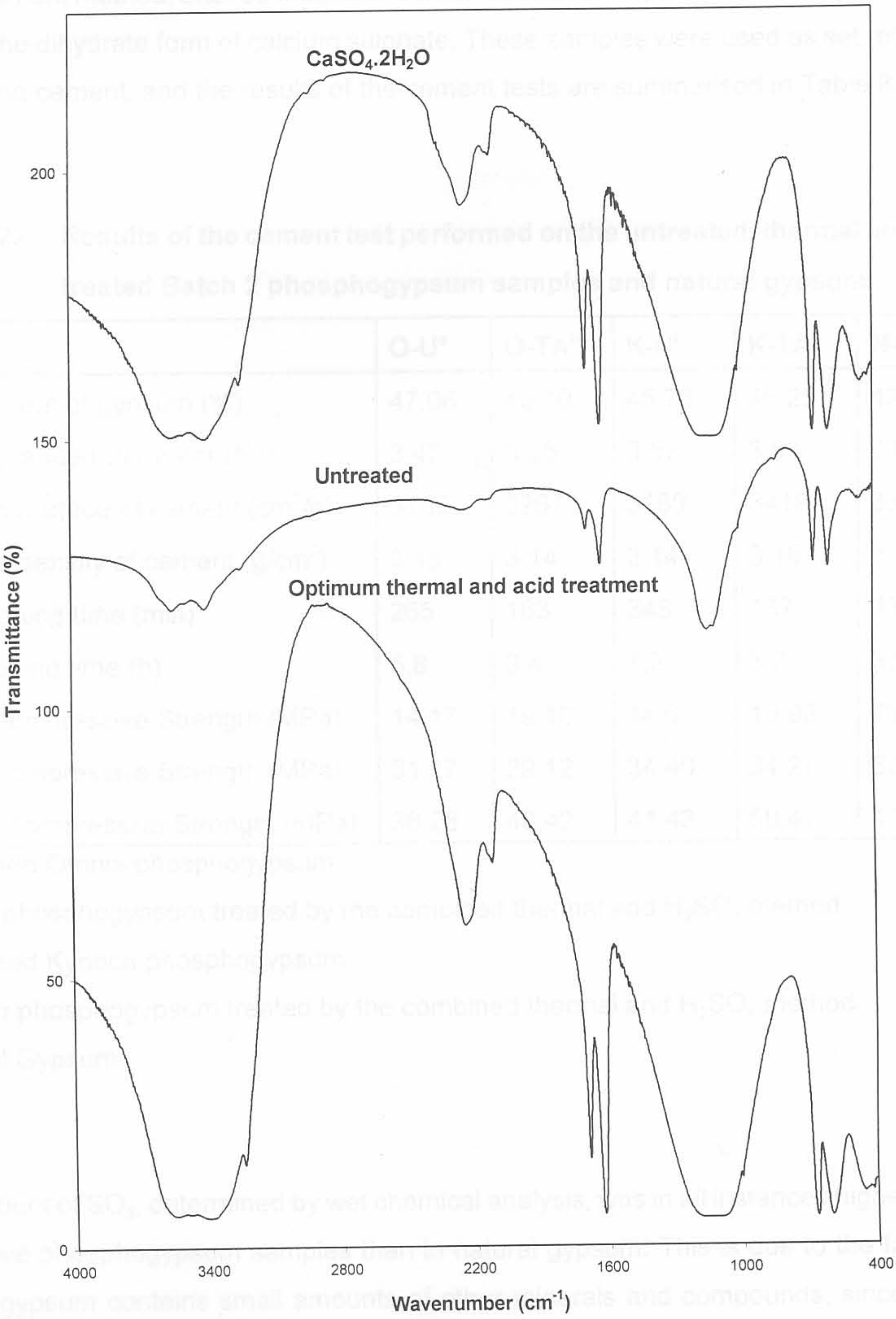


Figure 8.18 **The IR spectra of the untreated and treated Batch 2 Omnia phosphogypsum samples, treated on a large scale by the combined thermal and sulphuric acid method, for the performance of cement tests**



8.4.4 Performance of cement tests on the combined thermal and sulphuric acid treated phosphogypsum samples

The treated phosphogypsum samples obtained from the combined thermal and sulphuric acid treatment method, after optimization, contained almost no phosphorous impurities and were in the dihydrate form of calcium sulphate. These samples were used as set retarders in Portland cement, and the results of the cement tests are summarised in Table 8.22.

Table 8.22 Results of the cement test performed on the untreated, thermal and acid treated Batch 2 phosphogypsum samples and natural gypsum

Test	O-U[a]	O-TA[b]	K-U[c]	K-TA[d]	N-G[e]
SO_3 content of gypsum (%)	47.06	46.10	45.76	46.25	42.50
Gypsum added to clinker (%)	3.47	3.55	3.57	3.53	3.85
Specific Surface of cement (cm^2/g)	3159	3267	3180	3419	3314
Relative density of cement (g/cm^3)	3.15	3.14	3.14	3.16	3.14
Initial setting time (min)	265	163	348	137	130
Final setting time (h)	5.8	3.4	7.2	3.2	3.0
2-day Compressive Strength (MPa)	14.17	19.10	14.67	19.93	19.27
7-day Compressive Strength (MPa)	31.17	29.12	34.40	34.27	32.37
28-day Compressive Strength (MPa)	38.28	46.42	41.43	50.47	47.90

[a] Untreated Omnia phosphogypsum

[b] Omnia phosphogypsum treated by the combined thermal and H_2SO_4 method

[c] Untreated Kynoch phosphogypsum

[d] Kynoch phosphogypsum treated by the combined thermal and H_2SO_4 method

[e] Natural Gypsum

The amount of SO_3, determined by wet chemical analysis, was in all instances higher in the respective phosphogypsum samples than in natural gypsum. This is due to the fact that natural gypsum contains small amounts of other minerals and compounds, since it is a naturally mined product. The specific surface area and relative density of the cement containing the respective treated and untreated phosphogypsum samples was similar to that containing natural gypsum.

The 2-day compressive strength of the cement containing untreated Kynoch and Omnia phosphogypsum was lower than cement containing natural gypsum, However, after the phosphogypsum samples were treated by the combined thermal and sulphuric acid treatment method, the respective 2-day strengths were improved to values similar to that obtained for the cement sample containing natural gypsum. The 7-day compressive strengths of cement samples containing the untreated and treated Kynoch and Omnia phosphogypsum compared well to the compressive strength value obtained for the cement sample containing natural gypsum.

The 28-day compressive strength of cement containing untreated Kynoch and Omnia phosphogypsum was lower than that of cement containing natural gypsum. After treatment of the respective phosphogypsum samples by the combined thermal and sulphuric acid treatment method, the 28-day compressive strength of cement containing the treated phosphogypsum samples improved to values similar to that for cement containing natural gypsum.

The initial setting time of the cement containing untreated Omnia phosphogypsum sample was delayed from 130 minutes to 265 minutes, when compared to the sample containing natural gypsum. This was improved to 163 minutes after the Omnia phosphogypsum was treated by the combined thermal and sulphuric acid treatment method. This sample contained 0.06% P_2O_5, and was mainly in the dihydrate form of calcium sulphate.

For the untreated Kynoch phosphogypsum, an initial setting time of 348 minutes was obtained when used as a set retarder in cement. The initial setting time for cement containing Kynoch phosphogypsum treated by the combined thermal and sulphuric acid treatment method, was considerably improved to 137 minutes, which compares well to the value of 130 minutes obtained for cement containing natural gypsum. The treated Kynoch phosphogypsum sample contained 0.04% P_2O_5, and was also mainly in the dihydrate form of calcium sulphate.

The final setting time of cement containing untreated Omnia phosphogypsum was 5.8 hours, and 7.2 hours for cement containing untreated Kynoch phosphogypsum. These samples produced final setting times that were significantly longer than the value of 3.0 hours obtained when natural gypsum was used as a set retarder. After treatment of the phosphogypsum samples by the combined thermal and sulphuric acid treatment method, the final setting time of cement containing treated Omnia phosphogypsum, was improved to 3.4 hours, and that for Kynoch phosphogypsum to 3.2 hours. These values correspond well to the value obtained when natural gypsum is used as a set retarder.

According to Jackson (Hewlett, 1998b), the retarding action of phosphorous impurities can only be eliminated if the water-soluble content of P_2O_5 is reduced to below 0.02%. The effect of the amount of phosphorous impurities has been demonstrated clearly in this study, and the total amount of phosphorous impurities contained in phosphogypsum should preferably be kept below 0.06%.

8.5 Conclusion

When Jarosiński's method was applied to Batch 1 of both types of South African phosphogypsum, the phosphorous impurities were removed completely. However, the final products consisted of only calcium sulphate anhydrite. Although these treated samples were free of phosphorous impurities, they could not be applied as a set retarder in Portland cement, because the dihydrate form of calcium sulphate is required. Rehydration of these samples was not possible since the insoluble anhydrite, which shows no reaction with water, was formed.

This method was repeated on new batches of both types of phosphogypsum. Fewer phosphorous impurities were removed, when compared to the first batches, but the obtained products contained mainly calcium sulphate dihydrate. Treatment of Batch 2 phosphogypsum samples removed about 32% of the phosphorous impurities contained in Kynoch phosphogypsum, and 51% from the Omnia phosphogypsum. The respective total mass losses obtained by TG analysis were 19.6% for the Kynoch phosphogypsum sample and 16.5% for the Omnia phosphogypsum. This indicated that the treated Omnia phosphogypsum sample contained some calcium sulphate hemihydrate and/or anhydrite. After optimization of this method, the total mass loss for the Omnia phosphogypsum sample increased to 19.2%, which means that this sample also contained mainly calcium sulphate dihydrate.

A possible explanation for the difference in behaviour of these different batches of phosphogypsum can be found from the FT-IR analyses. These analyses have shown that, after the leaching step, the respective Batch 1 phosphogypsum samples were in the anhydrite form, while the corresponding samples for the Batch 2 phosphogypsum were in the dihydrate form. This shows that the phosphorous impurities are more easily removed from the anhydrite crystal lattice than from the dihydrate lattice. The Batch 1 phosphogypsum samples possibly formed the anhydrite due to different physical properties of these samples, or due to the fact that this treatment was done on a smaller scale than treatment of the Batch 2 phosphogypsum samples.

The results obtained for the cement tests when sulphuric acid treated phosphogypsum samples were used instead of natural gypsum as a set retarder in Portland cement have shown that the compression strengths of cement containing untreated and treated phosphogypsum compared well with the case in which natural gypsum was used.

When compared to the cement containing untreated phosphogypsum, the initial and final setting times of the cement samples containing the sulphuric acid treated phosphogypsum samples improved significantly. However, this improvement was not satisfactory when compared to the performance of the cement tests when natural gypsum is used as a set retarder in Portland cement.

Treating the respective Batch 2 phosphogypsum samples by the combined thermal and sulphuric acid treatment method removed 96% of the phosphorous impurities for both the Kynoch and Omnia phosphogypsum. A total mass loss of 19.5% was obtained for the dehydration reaction of the treated Kynoch phosphogypsum sample, while a mass loss of 15.4% was obtained for the Omnia phosphogypsum sample. After optimization of the concentration of sulphuric acid, the total mass loss obtained for Omnia phosphogypsum was increased to 21.0%.

The combined thermal and sulphuric acid treatment method was successful in removing the harmful phosphorous impurities from the gypsum crystal lattice, and the obtained products consisted of the required dihydrate form of calcium sulphate. These samples produced FT-IR curves that were the same as that of pure $CaSO_4.2H_2O$.

The initial setting time of the cement containing Omnia phosphogypsum treated by the combined thermal and sulphuric acid treatment method improved to from 265 minutes to 163 minutes. This sample contained 0.06% P_2O_5, and was mainly in the dihydrate form of calcium sulphate. The initial setting time for cement containing Kynoch phosphogypsum treated by the same treatment method was considerably improved from 348 minutes to 137 minutes, which compares well to the value of 130 minutes obtained for cement containing natural gypsum. The treated Kynoch phosphogypsum sample contained 0.04% P_2O_5, and was also mainly in the dihydrate form of calcium sulphate.

After treatment of the phosphogypsum samples by the combined thermal and sulphuric acid treatment method, the final setting time of cement containing treated Omnia phosphogypsum was improved to 3.4 hours, and that for Kynoch phosphogypsum to 3.2 hours. These values correspond well to the value obtained when natural gypsum is used as a set retarder.

These results have proved that the combined thermal and sulphuric acid treatment method was successful in removing most of the phosphorous impurities from the phosphogypsum crystal lattice, as well as in converting the samples to the dihydrate form of calcium sulphate. Portland cement containing phosphogypsum samples treated by the combined thermal and sulphuric acid treatment method revealed setting times and compressive strength values similar to values obtained when natural gypsum was used as a set retarder.