University of Pretoria etd – Van der Merwe E M 2006

Chapter 5 Properties and characterization of South African phosphogypsum

5.1 Introduction

South African phosphogypsum will have to be purified, particularly with respect to phosphorous and fluorine impurities, before it can be used in the building and construction industry. Before this phosphogypsum can be purified, it is important to characterize the impure samples so that the composition of the starting material is known. In this study, the influence of only phosphorous impurities and the hydrated form of calcium sulphate, contained in the South African phosphogypsum samples, on the properties of Portland cement was investigated.

This chapter reports on the results of characterization of different batches of phosphogypsum, obtained from two South African phosphoric acid producers. Two batches of phosphogypsum were obtained from each phosphoric acid producer, in order to study the homogeneity (or inhomogeneity) of samples prepared at different time periods by the same phosphoric acid production method.

5.2 Experimental

5.2.1 Samples

Phosphogypsum samples were obtained from two South-African phosphoric acid producers, Omnia and Kynoch. Two different batches were obtained from each producer. Both batches of Kynoch phosphogypsum were taken from a ten-year-old disposal site at Modderfontein, Johannesburg. The first batch of the Omnia phosphogypsum was taken from an old dumping site at Rustenburg, while the second batch was obtained in the form of a wet filter

University of Pretoria etd – Van der Merwe E M 2006

cake, taken directly from the phosphoric acid plant. All samples were oven-dried overnight at 45 °C.

5.2.2 Thermal analysis

Simultaneous TG and DSC analyses were performed on a NETZSCH STA 409 simultaneous TG/DSC instrument. Open platinum pans as well as crimped hermetic aluminium pans were used. For all analyses a heating rate of 5 °C/min were used in a static air atmosphere, with sample masses between 10 and 15 mg. Temperature and enthalpy calibrations were achieved using the ICTAC recommended DTA standards.

5.2.3 Infrared analysis

A Bruker IFS113v FTIR-spectrometer was used for Infrared spectroscopy analysis. KBr pellets were prepared by mixing 4 mg of sample with 100 mg of dry KBr.

5.2.4 X-ray fluorescence analysis

The X-ray fluorescence analyses were performed on an ARL8429 XRF spectrometer. To determine the loss on ignition, all samples were roasted for 8 hours at 950 °C. Then 1.000 g of the sample was mixed with 6.000 g of $Li_2B_4O_7$ flux, and melted at 1050 °C in a platinum crucible. The samples were cast in a platinum casting, and analyses of the main elements were performed on a pre-calibrated main element program. Three certified standards were analysed with all samples.

University of Pretoria etd – Van der Merwe E M 2006

5.3 Results and discussion

5.3.1 X-ray fluorescence analysis

The XRF analyses of both batches of the respective phosphogypsum samples are given in Table 5.1.

Table 5.1 The XRF results of the different batches of the Omnia and Kynoch phosphogypsum samples

Compounds (%)	Kynoch phosphogypsum		Omnia phosphogypsum	
	Batch 1	Batch 2	Batch 1	Batch 2
Al_2O_3	0.11	0.08	0.04	0
CaO	33.04	33.16	38.38	33.94
Cr_2O_3	0*	0	0	0
Fe_2O_3	0.09	0.04	0.05	0.09
K_2O	0	0	0	0.01
MgO	0.13	0.07	0.16	0.10
MnO	0	0	0	0
Na_2O	0	0	0	0
P_2O_5	**0.71**	**0.77**	**1.68**	**1.34**
SiO_2	0.16	0.03	0	0
TiO_2	0	0	0	0
V_2O_5	0	0	0	0
ZrO_2	0	0	0	0
Sr	0.28	0.27	0.32	0.18
SO_3	44.06	45.76	51.24	47.85
Loss on ignition	22.21	21.29	10.06	20.90
Total	100.79	101.47	101.93	102.64

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

University of Pretoria etd – Van der Merwe E M 2006

For phosphogypsum to be used as a set retarder in cement, the total percentage of P_2O_5 must be lower than 0.5% (PPC report 13/88, Gypsum retarder specifications). From the results in the table, it can be observed that none of the obtained South African phosphogypsum samples satisfied this guideline. The amount of phosphorous impurities in both batches of the Omnia phosphogypsum was significantly higher than for the Kynoch phosphogypsum.

5.3.2 Infrared analysis

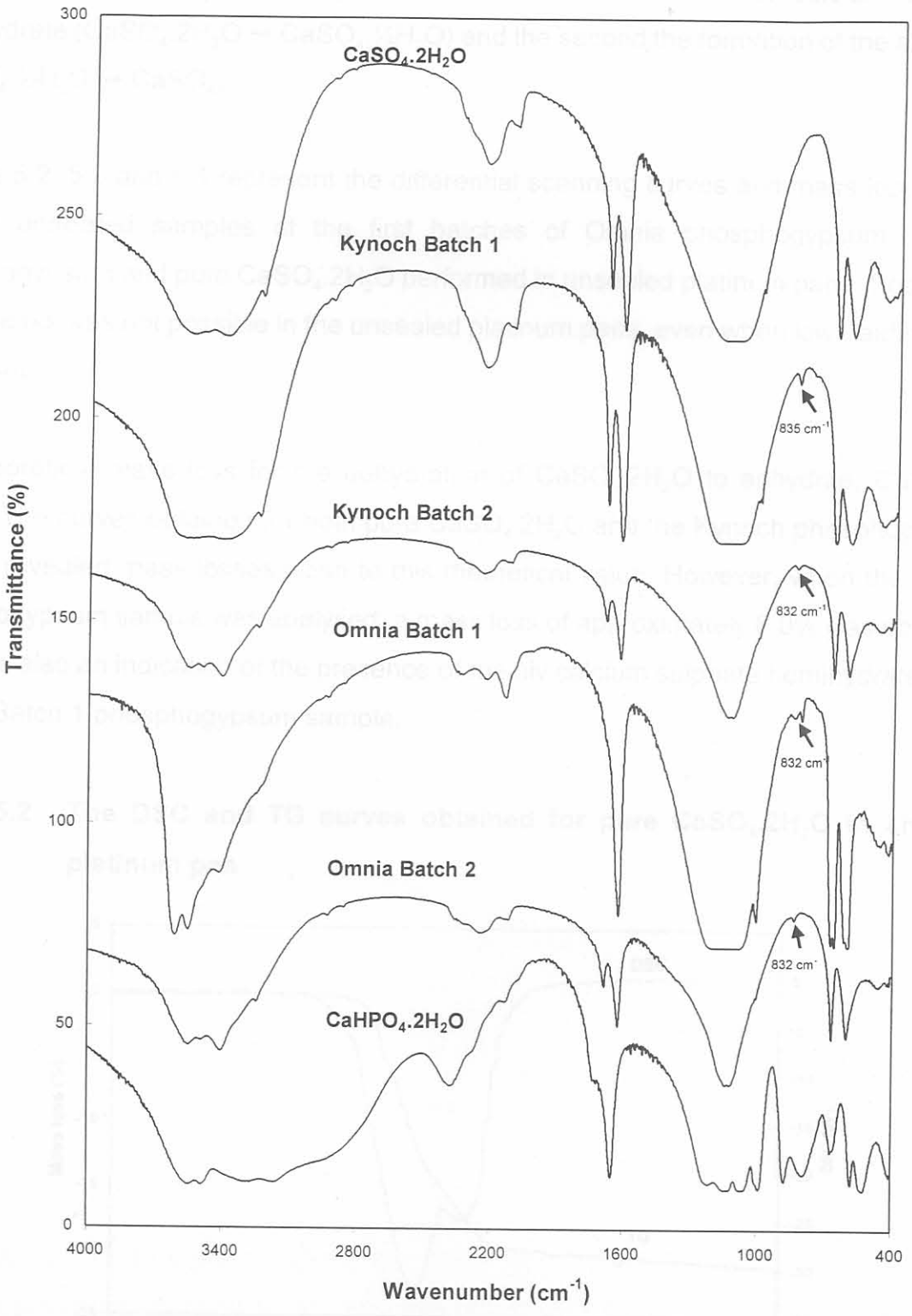
Murakami (1968) showed that phosphogypsum produces weak absorptions at about 1015 cm^{-1} and 837 cm^{-1} in the related characteristic absorption bands of HPO_4^{2-}. These displacements can be ascribed to the formation of the solid solution of gypsum with dicalcium phosphate equivalent to the amount of phosphorous impurities in the crystal lattice of phosphogypsum. Ölmez and Yilmaz (1988) have also successfully identified the phosphorous impurities contained in phosphogypsum by using infrared analysis.

If the FT-IR spectra of pure $CaSO_4.2H_2O$, pure $CaHPO_4.2H_2O$, and the different batches of Kynoch and Omnia phosphogypsum samples in Figure 5.1 are compared, the small band characteristics (indicated in the figure) at 837 cm^{-1} and 1015 cm^{-1} can be attributed to the water-insoluble phosphorous impurities in phosphogypsum.

According to Todorovsky *et al* (1997), the presence of $CaSO_4.½H_2O$ can be confirmed in an IR spectrum when a split in each of the peaks at 600 cm^{-1} and 667 cm^{-1} is observed. Only the Omnia Batch 1 phosphogypsum sample has shown this characteristic, and was also the only sample that produced a single peak in the region between 1600-1700 cm^{-1}. The peaks between 3400 - 4000 cm^{-1} were narrower than those of the other gypsum samples. This serves as a further indication of the presence of mainly calcium sulphate hemihydrate.

University of Pretoria etd – Van der Merwe E M 2006

Figure 5.1 The FT-IR spectra of pure $CaSO_4.2H_2O$, pure $CaHPO_4.2H_2O$ and the different batches of the Kynoch and Omnia phosphogypsum samples



University of Pretoria etd – Van der Merwe E M 2006

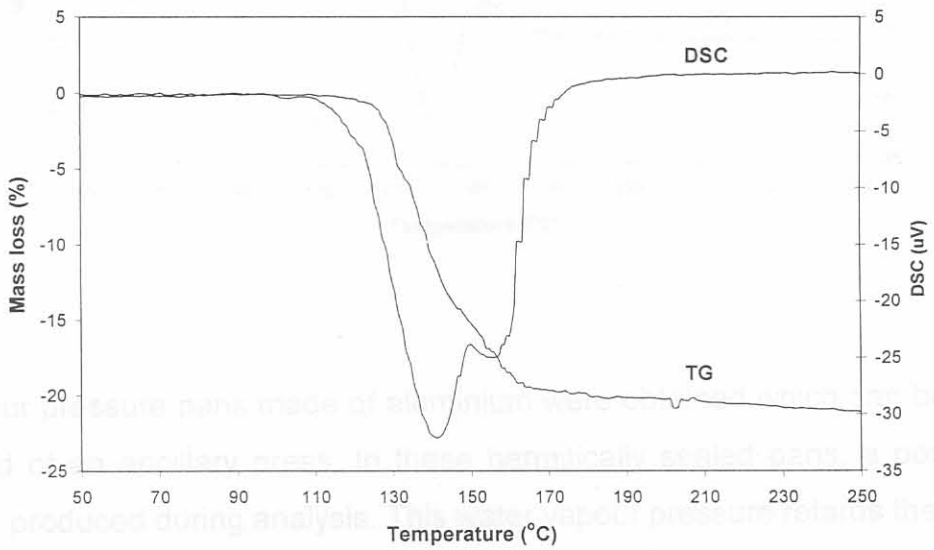
5.3.3 Thermal analysis

The DSC curve obtained for pure calcium sulphate dihydrate gives a two-step dehydration process. The first endothermic peak represents the formation of calcium sulphate hemihydrate ($CaSO_4.2H_2O \rightarrow CaSO_4.½H_2O$) and the second the formation of the anhydrite ($CaSO_4.½H_2O \rightarrow CaSO_4$).

Figures 5.2, 5.3 and 5.4 represent the differential scanning curves and mass loss curves for the untreated samples of the first batches of Omnia phosphogypsum, Kynoch phosphogypsum and pure $CaSO_4.2H_2O$ performed in unsealed platinum pans. Separation of the peaks was not possible in the unsealed platinum pans, even when low heating rates were used.

The theoretical mass loss for the dehydration of $CaSO_4.2H_2O$ to anhydrite, $CaSO_4$, is 20.9%. The curves obtained for both pure $CaSO_4.2H_2O$ and the Kynoch phosphogypsum sample revealed mass losses close to this theoretical value. However, when the Omnia phosphogypsum sample was analysed, a mass loss of approximately 8.0% was obtained. This was also an indication of the presence of mainly calcium sulphate hemihydrate in the Omnia Batch 1 phosphogypsum sample.

Figure 5.2 The DSC and TG curves obtained for pure $CaSO_4.2H_2O$ in an open platinum pan



University of Pretoria etd – Van der Merwe E M 2006

Figure 5.3 The DSC and TG curves obtained for Omnia phosphogypsum (Batch 1) in an open platinum pan

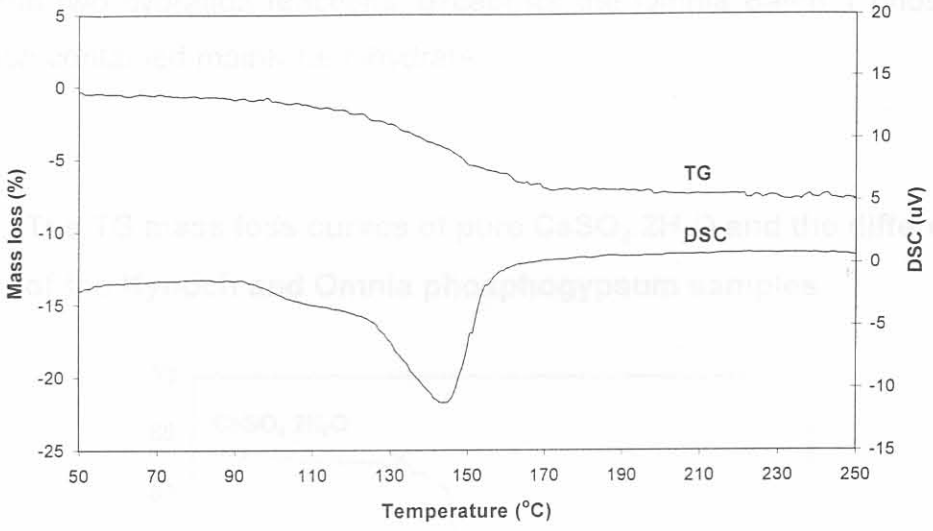
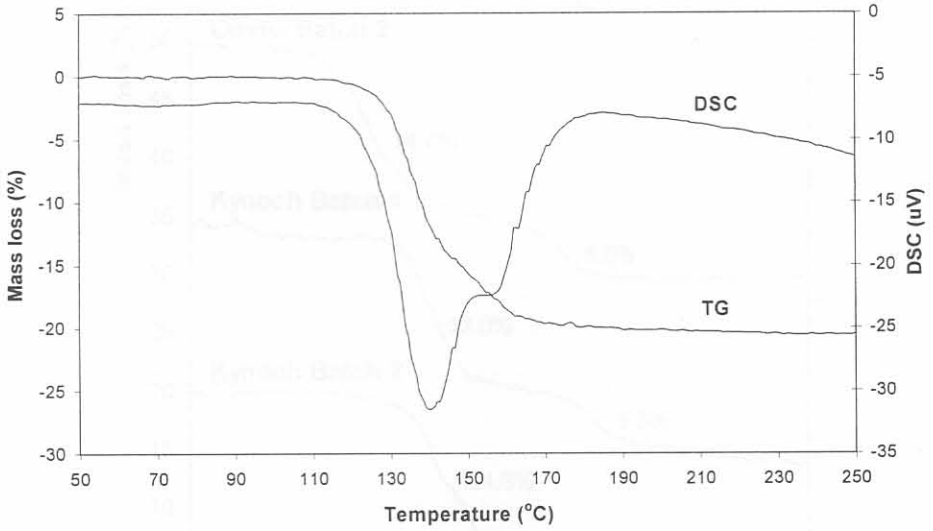


Figure 5.4 The DSC and TG curves obtained for Kynoch phosphogypsum (Batch 1) in an open platinum pan

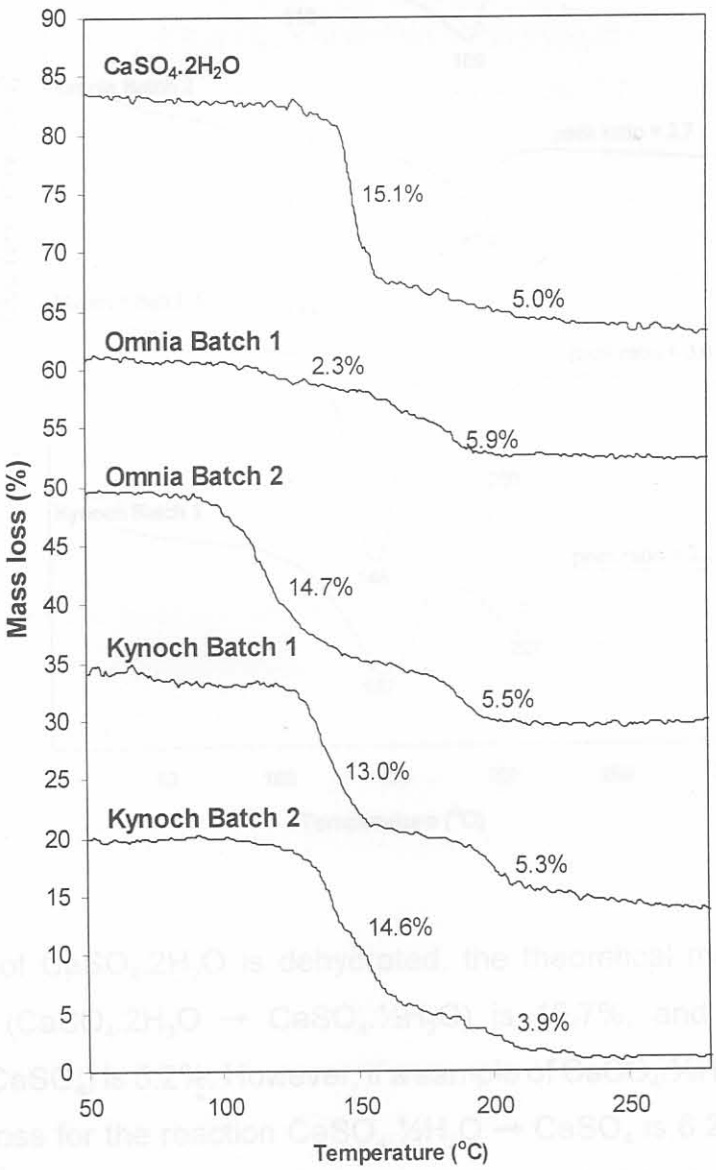


Small vapour pressure pans made of aluminium were obtained which can be tightly shut with the aid of an ancillary press. In these hermitically sealed pans, a positive vapour pressure is produced during analysis. This water vapour pressure retards the onset of the second dehydration reaction, resulting in better separation in the TG curve and DSC peaks.

University of Pretoria etd – Van der Merwe E M 2006

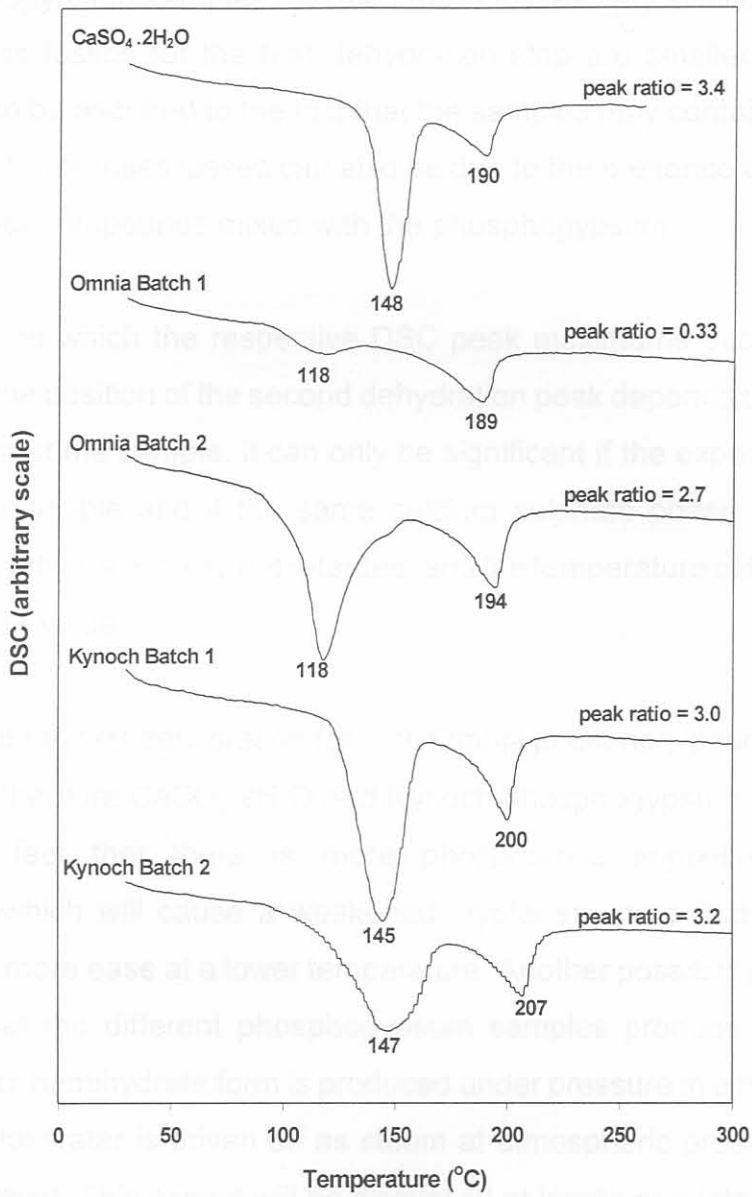
The TG and DSC curves given in Figures 5.5 and 5.6 were obtained by encapsulating the samples in aluminium hermetic pans. This method proved to resolve the two peaks, thus separating the two hydration reactions, except for the Omnia Batch 1 phosphogypsum sample, which contained mainly hemihydrate.

Figure 5.5 The TG mass loss curves of pure $CaSO_4.2H_2O$ and the different batches of the Kynoch and Omnia phosphogypsum samples



University of Pretoria etd – Van der Merwe E M 2006

Figure 5.6 The DSC curves of pure $CaSO_4.2H_2O$ and the different batches of the Kynoch and Omnia phosphogypsum samples



If a pure sample of $CaSO_4.2H_2O$ is dehydrated, the theoretical mass loss for the first dehydration step ($CaSO_4.2H_2O \rightarrow CaSO_4.½H_2O$) is 15.7%, and that of the second ($CaSO_4.½H_2O \rightarrow CaSO_4$) is 5.2%. However, if a sample of $CaSO_4.½H_2O$ is dehydrated, the theoretical mass loss for the reaction $CaSO_4.½H_2O \rightarrow CaSO_4$ is 6.2%. This explains the higher second mass loss of 5.9% for the Omnia Batch 1 phosphogypsum sample. As confirmed by the IR results, this sample contained more hemihydrate than dihydrate, resulting in a very low mass loss for the first dehydration step, followed by a higher mass

University of Pretoria etd – Van der Merwe E M 2006

loss for the second step.

The other phosphogypsum samples revealed mass losses very similar to that of the pure gypsum. The mass losses for the first dehydration step are smaller than that for pure gypsum, which can be ascribed to the fact that the samples may contain small amounts of hemihydrate. The lower mass losses can also be due to the presence of small amounts of impurities and other compounds mixed with the phosphogypsum.

The temperatures at which the respective DSC peak maximums occur are indicated in Figure 5.6. Since the position of the second dehydration peak depends on the water vapour pressure produced at the sample, it can only be significant if the experimental conditions were exactly reproducible and if the same calcium sulphate phase was present in all samples. The first dehydration was not retarded, and the temperature of this peak maximum can be of significant value.

The temperature of the first dehydration for both Omnia phosphogypsum samples is much lower than that of the pure $CaSO_4.2H_2O$ and Kynoch phosphogypsum. This can partly be ascribed to the fact that there is more phosphorous impurities in the Omnia phosphogypsum, which will cause a weakened crystal structure that will lose water of crystallization with more ease at a lower temperature. Another possibility that needs further investigation is that the different phosphogypsum samples produce different forms of hemihydrate. The α-hemihydrate form is produced under pressure in a humid atmosphere, but when the crystal water is driven off as steam at atmospheric pressure, crystals of β-hemihydrate is formed. This aspect will be discussed at length at a later stage.

The peak ratios of the DSC peaks of the different gypsum samples are also indicated in Figure 5.6. Dunn *et al* (1987) reported the DSC peak ratio for the two stage dehydration of pure gypsum as 3.3. This is in agreement with the DSC peak ratio of 3.4 obtained experimentally for pure $CaSO_4.2H_2O$. The DSC curves also confirmed the presence of mainly hemihydrate for the Omnia Batch 1 phosphogypsum sample, which revealed a peak ratio of only 0.33. All other phosphogypsum samples produced DSC curves with peak ratios similar to that of pure $CaSO_4.2H_2O$.

University of Pretoria etd – Van der Merwe E M 2006

5.4 Conclusion

FT-IR analysis can be used to identify the phosphorous impurities contained in phosphogypsum, and can also indicate the presence of calcium sulphate hemihydrate. TG and DSC analyses can serve as useful tools in determining more comprehensively which form of the calcium sulphate phases are present in the phosphogypsum samples.

By using the abovementioned techniques, most of the phosphogypsum samples have shown characteristics close to that of pure gypsum in terms of the calcium sulphate phase. Only the Omnia Batch 1 phosphogypsum sample contained mainly the hemihydrate form, while the other samples contained predominantly calcium sulphate dihydrate.

The different South African phosphogypsum samples were analysed and found to contain a significant amount of phosphorous impurities. In addition to this high phosphorous content, the presence of a relevant amount of hemihydrate underpins its unsuccessful utilization as a set retarder in cement. Therefore, the harmful phosphorous impurities contained in the phosphogypsum must be removed or neutralized, and the hemihydrate must be rehydrated to dihydrate. These two aspects will be dealt with in the following chapters.