Chapter 6 Distribution of phosphorous impurities in particle size fractions of South African phosphogypsum

6.1 Introduction

The particle size distribution of phosphogypsum has a major influence on its technological properties. The particle sizes of phosphogypsum depend on the type of phosphoric acid process applied, the application of crystal modifiers in the process, as well as on the degree of grinding of the raw phosphate rock used.

According to Eipeltauer *et al* (1981) the particle size distribution in a raw slurry determines whether it is necessary to apply further size reduction in order to meet the requirements for a specific purpose. In their investigation, particle size determinations were done on the wet phosphogypsum samples, obtained from the wet phosphoric acid process, after being washed with water. They found that the presence of organic substances resulted in large statistical errors in their determinations.

Krempff (1972) found that the impurities in phosphogypsum are concentrated in the fractions larger than 168 μm and smaller than 25 μm. By washing the fraction recovered between 25 μm and 168 μm, the water-soluble phosphorous was removed completely.

The aim of this chapter is to establish the particle size distribution of dried South African phosphogypsum and to determine the amount of phosphorous impurities contained in each fraction.

6.2 Experimental

6.2.1 Samples

Phosphogypsum samples were obtained from two South-African phosphoric acid producers, Omnia and Kynoch. Batch 2 of both of the Kynoch and Omnia phosphogypsum was used in this study. The samples were dried overnight at 45°C.

6.2.2 Instrumental analysis

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

6.2.3 Sieving

A Fritsch Analysette 3 vibratory sieve shaker was used to sieve the phosphogypsum samples. A set of sieves between 75 and 1700 IS μm were used and 10.0 g of the respective phosphogypsum samples were sieved for 10 minutes.

6.3 Results and discussion

6.3.1 Particle size distribution of the phosphogypsum samples

The particle size distribution of the phosphogypsum samples is presented in Table 6.1. Approximately 85% of the Omnia phosphogypsum and 76 % of the Kynoch phosphogypsum are found in fractions smaller than 150 μm, which indicates that Omnia phosphogypsum is a finer waste product than Kynoch phosphogypsum.

Table 6.1 Particle size distribution of the phosphogypsum samples

Particle size (µm)	Size distribution (mass %)	
	Omnia phosphogypsum	Kynoch phosphogypsum
> 1700	0	4.6
600 - 1700	0	5.4
300 - 600	0.1	3.6
150 - 300	14.1	11.1
75 - 150	48.7	27.7
< 75	37.1	47.5

6.3.2 X-ray fluorescence analysis of the phosphogypsum particle size fractions

Although there are many other impurities contained in the phosphogypsum samples, only phosphorous was studied during this investigation.The phosphorous content of each fraction, determined by XRF analysis, is listed in Table 6.2.

Table 6.2 The total phosphorous content of the particle size fractions of the phosphogypsum samples, as determined by XRF analysis

Particle size (µm)	% P_2O_5	
	Omnia phosphogypsum	Kynoch phosphogypsum
600 - 1700	-	1.09
300 - 600	*	1.08
150 - 300	1.55	1.04
75 - 150	1.29	0.98
< 75	1.29	0.97
Unsieved	1.50	1.00

* Due to the small percentage sample obtained, XRF analysis, was not performed.

The 150 - 300 µm and 300 - 600 µm Omnia phosphogypsum fractions also contained dark particles that can be attributed to unreacted iron oxide and/or magnesium oxide present from the wet phosphoric acid process. The presence of iron oxide was confirmed by the XRF results. From the table, it can also be seen that the amount of phosphorous impurities contained in the Omnia phosphogypsum sample is reduced the finer fractions, when compared to the larger and untreated fractions. However, the amount of phosphorous impurities contained in the different particle size fractions of the Kynoch phosphogypsum did not differ significantly.

6.3.3 Thermal analysis of the phosphogypsum particle size fractions

The thermogravimetrical mass losses obtained for each fraction of the sieves, are given in Table 6.3. The mass losses obtained for Kynoch phosphogypsum are all close to the theoretical mass loss of 20.9%. The mass losses obtained for the Omnia particle size fractions up to 300 µm were also similar to that of the theoretical value. However, the fraction between 300 and 600 µm revealed a mass loss of only 15.2%.

Table 6.3 The mass losses obtained from the thermogravimetric analysis for the different particle size fractions of the phosphogypsum samples

Particle size (µm)	TG mass loss (%)	
	Omnia phosphogypsum	Kynoch phosphogypsum
600 - 1700	-	21.1
300 - 600	15.2	19.2
150 - 300	20.0	21.7
75 - 150	20.0	19.3
< 75	21.1	19.9
Unsieved	19.8	20.7

Omnia phosphogypsum contains a high percentage phosphorous, and it is possible that in the particle size fraction between 300 and 600 µm, the phosphorous content is higher than in the other fractions. These impurities can cause a slight decrease in the mass loss of the sample, but not to the extent shown here. A more obvious explanation for the decrease in the mass loss percentage for this particle size fraction is that the hemihydrate form of calcium sulphate, which is also contained in the Omnia phosphogypsum sample, mainly accumulates in this fraction.

Figure 6.1 The DSC curves of the particle size fractions and unsieved Omnia phosphogypsum

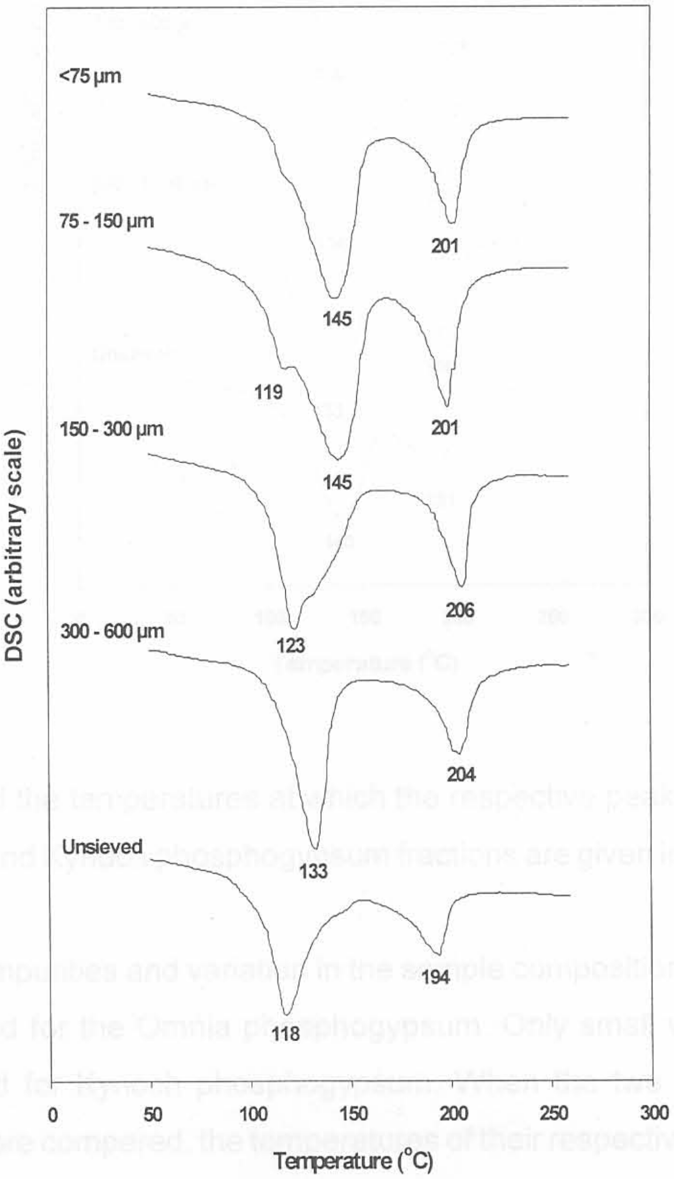
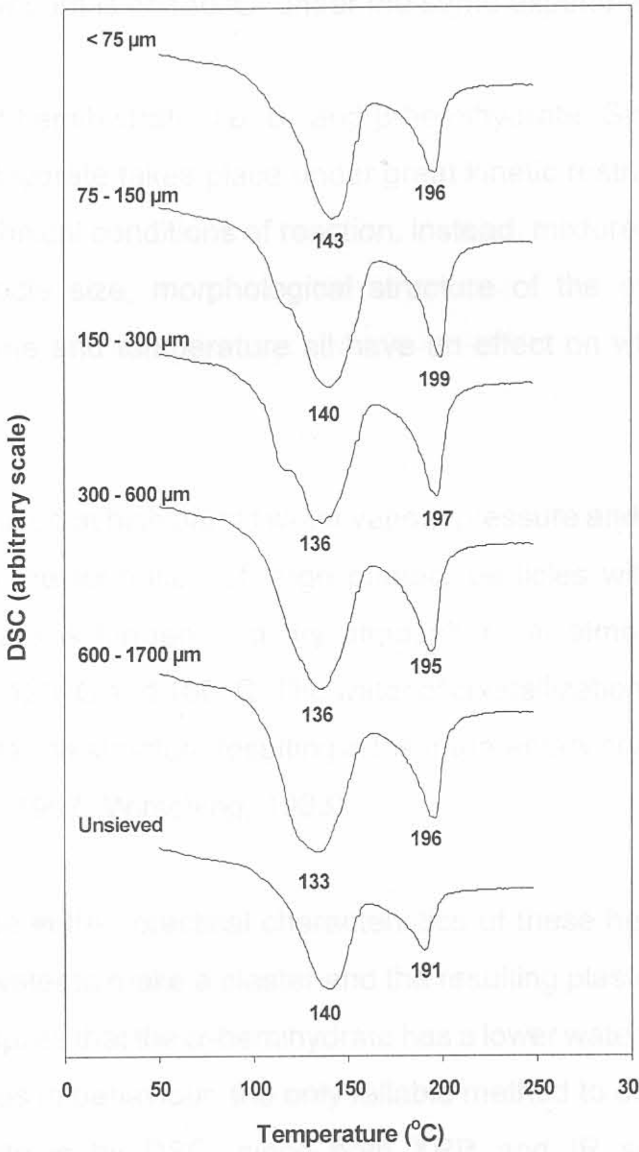


Figure 6.2 The DSC curves of the particle size fractions and unsieved Kynoch phosphogypsum



The DSC curves and the temperatures at which the respective peak maximums occur for the different Omnia and Kynoch phosphogypsum fractions are given in Figures 6.1 and 6.2.

The contribution of impurities and variation in the sample composition are noticeable in the DSC curves obtained for the Omnia phosphogypsum. Only small variations in the DSC curves are observed for Kynoch phosphogypsum. When the two unsieved samples in Figures 6.1 and 6.2 are compared, the temperatures of their respective peak maximums for the dehydration to the hemihydrate differed significantly. The peak temperature for the unsieved Omnia phosphogypsum is 118°C, while the corresponding peak temperature for the Kynoch phosphogypsum is at 140°C, under the same experimental conditions.

There are two types of hemihydrate, i.e. α- and β-hemihydrate. Since the phase change from dihydrate to hemihydrate takes place under great kinetic restraints, pure phases are not obtained under technical conditions of reaction, instead, mixtures of phases are nearly always obtained. Particle size, morphological structure of the gypsum, water vapour pressure, residence time and temperature all have an effect on which calcium sulphate phase will form.

α-Hemihydrate is produced at high partial water vapour pressure and temperatures of 80°C to 180°C, resulting in the formation of large primary particles with an even crystalline structure. β-Hemihydrate is formed in a dry atmosphere at atmospheric pressure and temperatures between 120°C and 180°C. The water of crystallization is driven off as steam, which disrupts the crystalline structure resulting in the fragmentary crystals of β-hemihydrate (Coburn, 1989; Taylor, 1997; Wirsching, 1983).

The principle difference in the practical characteristics of these hemihydrates is that the β-form requires more water to make a plaster and the resulting plaster will set more quickly and be weaker. This implies that the α-hemihydrate has a lower water demand on hydration. Despite their differences in behaviour, the only reliable method to determine the presence of α- or β-hemihydrate is by DSC, since both XRD and IR spectroscopy of these hemihydrates result in traces in which peaks are in identical positions.

The hydration behaviour and subsequently the DSC traces of autoclaved α- and calcined β-hemihydrates are different. However, there has been substantial disagreement about how these differences arise and whether or not any other subhydrate species exists. In particular, it has been suggested that there are whole series of subhydrates of the form $CaSO_4.nH_2O$, where n varies from 0 to 2/3 or even between 0 and 1. Alternatively, it has been suggested that there is only one other subhydrate apart from hemihydrate, but there is disagreement over the amount of water in the structure as $CaSO_4.3/5H_2O$, $CaSO_4.2/3H_2O$, or even $CaSO_4.4/5H_2O$ have all been suggested as the chemical formula of the additional subhydrate. Some authors have claimed that the higher subhydrate ($CaSO_4.2/3H_2O$) actually is the referred to hemihydrate. On the whole, it seems likely that at high water partial pressure another subhydrate exists (Hand, 1997).

It is therefore most probable that the Kynoch and Omnia phosphogypsum samples produced these different types of hemihydrates. The α-hemihydrate is formed at a lower temperature, and it seemed to be the form that was produced from the dehydration of unsieved Omnia phosphogypsum. If this was the case, then β-hemihydrate was formed when the Kynoch phosphogypsum was dehydrated. In the DSC curves of the sieved phosphogypsum samples, the existence of a shoulder and occasionally a second peak was observed in the region of the first dehydration reaction. This suggested that these two types of hemihydrates were produced simultaneously.

For the Kynoch phosphogypsum, the β-hemihydrate was formed predominantly in all size fractions. From Figure 6.1 it can be seen that the temperature of the first dehydration peak is higher for the two smaller particle size fractions than for the particle size fractions larger than 150 μm. This indicates that the Omnia phosphogypsum formed mainly β-hemihydrate in the dehydration of the smaller particle size fractions and α-hemihydrate for the larger fractions.

6.3.4 Infrared spectroscopy analysis of the phosphogypsum particle size fractions

The results of the FT-IR analyses of the different size fractions are given in Figures 6.3 and 6.4. In all spectra, small bands at 832 cm^{-1} can be observed, indicating the presence of phosphorous impurities.

Figure 6.3 The IR spectra of the particle size fractions and unsieved Kynoch phosphogypsum

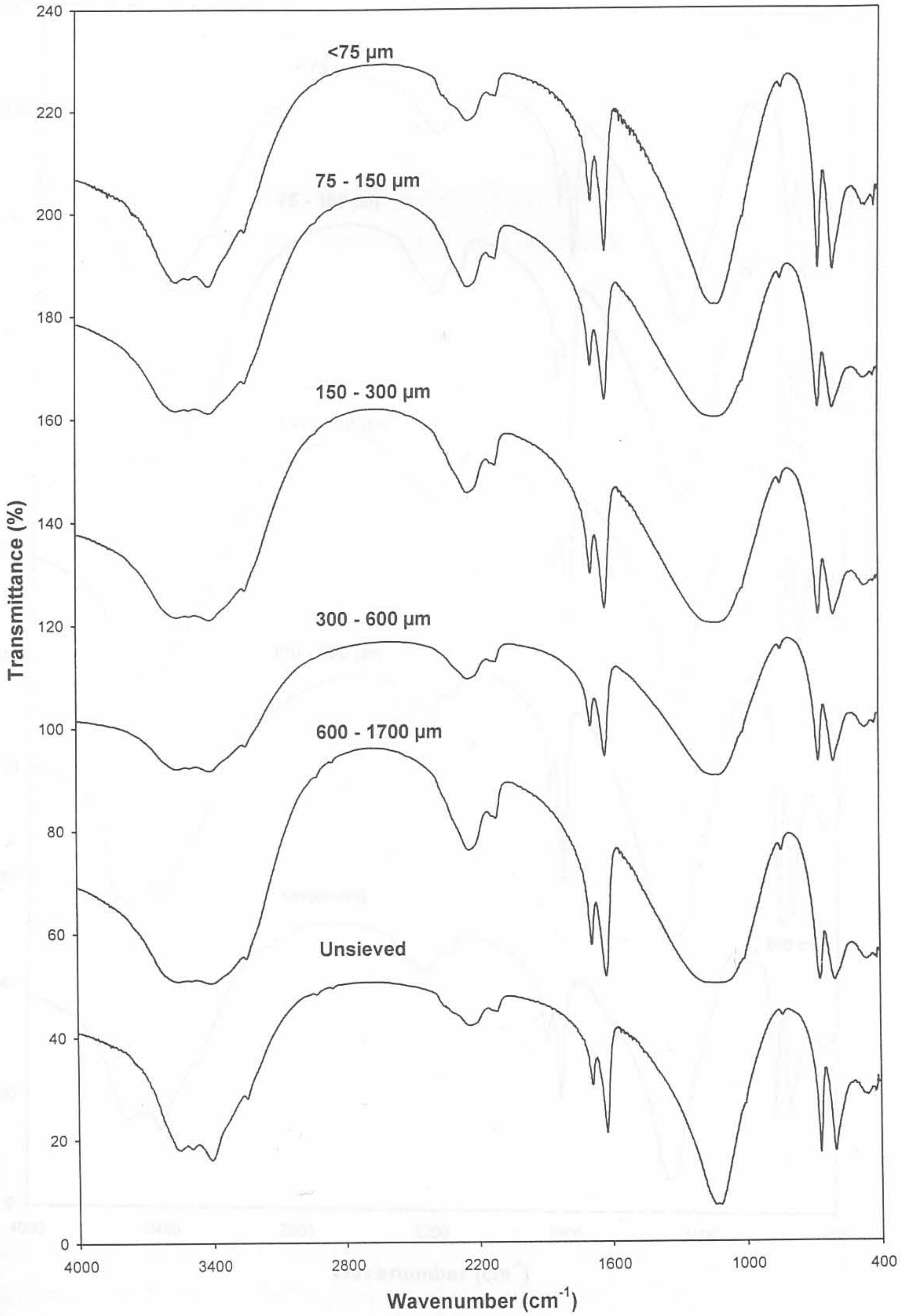
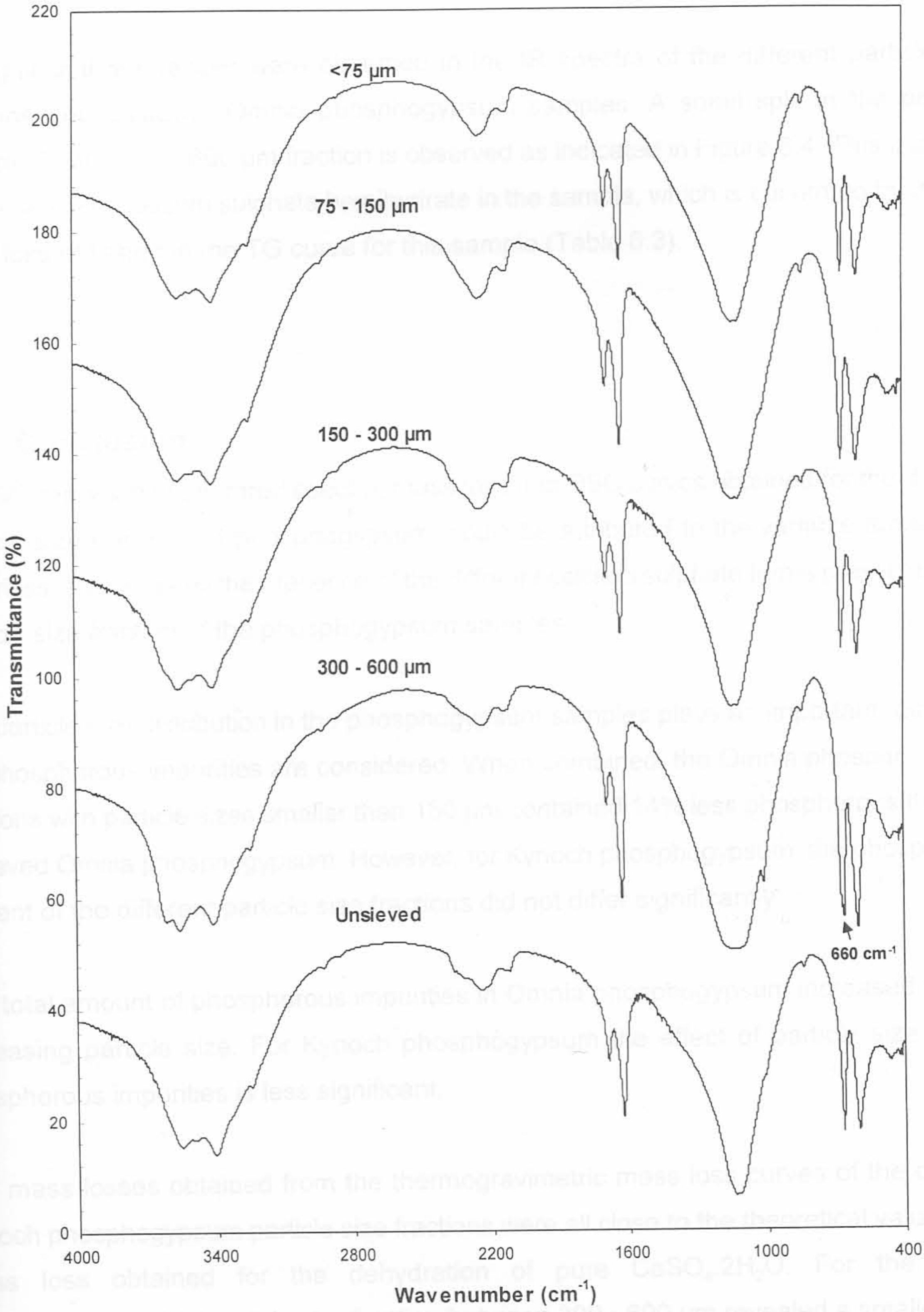


Figure 6.4 **The IR spectra of the particle size fractions and unsieved Omnia phosphogypsum**



In the IR spectra obtained for the Kynoch phosphogypsum samples, the < 75 and 75 -150 µm fractions, and also the sample of unsieved Kynoch phosphogypsum, contained higher amounts of dihydrate, resulting in a broadening of the 3000 - 4000 cm^{-1} band.

No significant differences were observed in the IR spectra of the different particle size fractions and unsieved Omnia phosphogypsum samples. A small split in the peak at 660 cm^{-1} for the 300 - 600 µm fraction is observed as indicated in Figure 6.4. This indicates the presence of calcium sulphate hemihydrate in the sample, which is confirmed by the low mass loss obtained in the TG curve for this sample (Table 6.3).

6.4 Conclusion

The differences in the infrared spectra, mass loss and DSC curves obtained for the different particle size fractions of phosphogypsum, could be attributed to the variable amounts of impurities, as well as by the presence of the different calcium sulphate forms present in each particle size fraction of the phosphogypsum samples.

The particle size distribution in the phosphogypsum samples plays an important role when the phosphorous impurities are considered. When combined, the Omnia phosphogypsum fractions with particle sizes smaller than 150 µm contained 14% less phosphorous than the unsieved Omnia phosphogypsum. However, for Kynoch phosphogypsum, the phosphorous content of the different particle size fractions did not differ significantly.

The total amount of phosphorous impurities in Omnia phosphogypsum increased with an increasing particle size. For Kynoch phosphogypsum the effect of particle size on the phosphorous impurities is less significant.

The mass losses obtained from the thermogravimetric mass loss curves of the different Kynoch phosphogypsum particle size fractions were all close to the theoretical value of the mass loss obtained for the dehydration of pure $CaSO_4.2H_2O$. For the Omnia phosphogypsum, the particle size fraction between 300 - 600 µm revealed a smaller mass loss, which indicated the presence of calcium sulphate hemihydrate. All other Omnia particle size fractions contained mainly the dihydrate form of calcium sulphate. These results were confirmed by the FT-IR analyses of the respective particle size fractions for both Kynoch and Omnia phosphogypsum.

It seemed as if the Kynoch and Omnia phosphogypsum samples formed different types of calcium sulphate hemihydrate on dehydration. These results were obtained from the DSC curves of the respective phosphogypsum particle size fractions. Mainly the α-Hemihydrate was obtained, as measured in a lower temperature from the dehydration of unsieved Omnia phosphogypsum; while the β-hemihydrate was primarily formed as observed in the higher dehydration temperatures for the unsieved Kynoch phosphogypsum. In the sieved particle size fractions of both Kynoch and Omnia phosphogypsum, both types of hemihydrates were produced.

The temperature at the peak maximum of the DSC curve serves as an indicative measure of the amount of impurities present in the fraction (Singh *et al*, 1996). There was no significant change in the amount of phosphorous impurities contained in the different particle size fractions of Kynoch phosphogypsum, and therefore the DSC peak maximums for the different particle size fractions could not be compared in this regard. The results obtained for Omnia phosphogypsum were difficult to analyse due to the unpredictable formation of the different hemihydrate species.