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The thermal dehydration of synthetic gypsum[☆]

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Abstract

Mass losses vary between 13.7 and 16.5% and heat of dehydration values between 377 and 420 J g⁻¹ for the dehydration of ground and mixed inhomogeneous gypsum samples. As for the dehydration of CaSO₄·2H₂O, the dehydration of synthetic gypsum proceeds via multi-step reactions. Using a heating rate of 5°C min⁻¹, the very slow dehydration of CaSO₄·2H₂O and impurities in the gypsum samples start at temperatures lower than 95°C. The main dehydration of the calcium sulphate dehydrate part of synthetic gypsum occurs between 95 and 170°C (heating rate 5°C min⁻¹) and seems to proceed via a process with an activation energy of 392 ± 100 kJ mol⁻¹ for α -values between 0 and 0.1. For α -values between 0.1 and 0.7, the reaction can be described by a first-order process with autocatalysis with an activation energy value of 100.5 ± 1.2 kJ mol⁻¹. The third part of the reaction (0.7 < α < 1), up to temperatures of 180°C, gives an activation energy value of 96 ± 15 kJ mol⁻¹. Even at temperatures above 250°C, some CaSO₄·0.15H₂O was still observed. The dehydration of calcium hemihydrate seems to proceed via the formation of CaSO₄·0.15H₂O.

Keywords: Dehydration; Synthetic gypsum

1. Introduction

Gypsum (mainly calcium sulphate hydrate) is used extensively in many industries, e.g. the fertilizer and cement production industries. The cement manufacturers add between 3% and 6% gypsum to avoid flash (immediate) setting of the cement [1, 2]. Gypsum, which acts as a retarder during the setting reaction of cement, also affects

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strength development and volume stability in the cement [3]. Gypsum is a mixture of mainly calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and calcium sulphate anhydrite (CaSO_4). A high hemihydrate content results in false setting of the cement, thus a maximum percentage of the hemihydrate is required in gypsum samples [3].

It is shown in the literature that the decomposition of calcium sulphate dihydrate proceeds via two reactions [4, 5]



Molony and Ridge [4] suggested that the dehydration is a diffusion-controlled process where the reaction begins at nuclei on the surface of small single crystals. Ball and Norwood [5] found the activation energy to be 96.2 kJ mol^{-1} and suggested that at lower temperatures nucleation was the rate-controlling process. They found that at temperatures above 110°C , the dehydration follows the parabolic law, $\alpha^2 = kt$. They also found that calcium β -hemihydrate has some micropores which makes the outward diffusion of water molecules relatively easy at low partial pressures of water, thus implying a low activation energy for the dehydration of the hemihydrate [6].

McAdie [7] found that the dehydration could be described by the rate law, $\alpha = kt$, and that the activation energy at 760 mmHg was $201.7 \text{ kJ mol}^{-1}$. Heide [8] suggested that the dehydration reaction follows the Avrami–Erofe'ev nuclei growth mechanism with an activation energy of $130.5 \text{ kJ mol}^{-1}$. Murrat and Commal [9] presented three stages, with different mechanisms that dominate during the various stages of dehydration. The activation energy values obtained were $251\text{--}502 \text{ kJ mol}^{-1}$ for the nucleation formation stage, $104\text{--}251 \text{ kJ mol}^{-1}$ for the nuclei growth stage, and $58\text{--}62 \text{ kJ mol}^{-1}$ corresponding to a stage in which the diffusion of water molecules determines the rate of the reaction. Various other investigations suggested activation energy values differing from 110 to 378 kJ mol^{-1} for the overall reaction [10–12].

The kinetics of the dehydration of gypsum is dependent on the origin of the gypsum and on the impurities in the gypsum samples. It was thus decided to investigate the dehydration reactions of synthetic and natural Southern African gypsum samples (unpure) and to compare the results to the dehydration of pure calcium sulphate dihydrate, which is a well-investigated subject. This paper on the dehydration of a synthetic Southern African Gypsum, forms the first part of this investigation. Since particle size may also influence the kinetics of the dehydration reactions, it was decided to do this investigation on ground, mixed and sifted powdered samples of gypsum with diameters between 45 and $106 \mu\text{m}$.

2. Experimental

2.1. Synthesis of gypsum

Synthetic gypsum is prepared via the reaction of limestone with sulphuric acid as described in the literature [13]. For the purpose of this study, synthetic gypsum was

obtained from the PPC plant in Cleveland, Johannesburg. Samples were ground to a fine powder and thoroughly mixed to obtain an almost homogeneous sample with as constant a composition as possible.

XRF analysis of synthetic gypsum was performed on a Siemens MRS 400 MP wavelength-dispersive XRF spectrometer. Results are summarized in Table 1. All samples were sifted and only gypsum particles with diameters between 45 and 106 μm were used. The surface area of the sifted samples was determined on a Micromeritics FlowSorb II 2300 BET surface area analyser and was found to be $0.7 \text{ m}^2 \text{ g}^{-1}$. This relatively small surface area could be due to the fact that the particles tend to adhere to each other, thereby decreasing the surface area.

2.2. Thermogravimetric and calorimetric analysis

A Netzsch STA 409 simultaneous TG/DSC instrument was used to collect thermogravimetric and calorimetric data. Nitrogen was employed as a dynamic atmosphere (flow rate $\approx 5 \text{ cm}^3 \text{ min}^{-1}$) as platinum sample pans were used. Temperature and enthalpy calibration were achieved using the ICTAC recommended DTA standards. Sample masses varied between 5 and 15 mg. The software module for the kinetic analysis of thermal measurements by means of multivariant non-linear regression developed by Netzsch was used to investigate the kinetic behaviour of the dehydration of gypsum.

2.3. XRD analysis

X-ray powder diffraction analyses were performed on a Siemens D500 XRD spectrometer using $\text{Cu K}\alpha$ radiation. The British Cement Association's database for cement-related compounds was used to analyse the data.

Table 1
XRF results of synthetic gypsum

Compound	Percentage
SiO_2	4.9
Al_2O_3	0.4
Fe_2O_3	0.8
Mn_2O_3	0.1
TiO_2	0.1
CaO	33.2
MgO	0.6
P_2O_5	0.02
SO_3	45.4
Cl	0
K_2O	0.04
Na_2O	0
Loss on ignition	23.7

3. Results and discussion

Using a heating rate of approximately $5^{\circ}\text{C min}^{-1}$, synthetic gypsum shows firstly a very low mass loss ($\pm 1\%$) from ambient temperature to 95°C , as presented in Fig. 1. The DSC curve suggested two small reactions between 53 and 63°C , and between 63.5 and 84°C . For the first reaction, an enthalpy value of between 1.9 and 3.0 J g^{-1} gypsum sample was obtained, and for the second process it was found to be between 6.7 and 7.2 J g^{-1} . These two processes were observed on all the DSC curves and could be the result of the dehydration reactions of some of the other impurities in the gypsum samples. Since it proved impossible to obtain 100% homogeneous gypsum samples, the percentage mass loss and the enthalpy values were found to differ slightly for the various samples.

XRD results indicated that the starting compound consists of the dihydrate and the anhydrite. No hemihydrate was observed. At 60°C , a very small amount of the hemihydrate is observed, indicating the very slow dehydration of the dihydrate at temperatures below 95°C (using a heating rate of $5^{\circ}\text{C min}^{-1}$).

The greatest mass loss (between 13.7 and 16.5% for different samples) occurs between 95 and 170°C using a heating rate of $\pm 5^{\circ}\text{C min}^{-1}$ (Fig. 1). Enthalpy change values for this total reaction vary between 377 and 420 J g^{-1} of the gypsum sample. XRD results show that the main product at 165°C is CaSO_4 , anhydrite, but that some $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is still present. At 172°C , no hemihydrate could be observed, but some $\text{CaSO}_4 \cdot 0.15\text{H}_2\text{O}$ and minute amounts of CaSO_3 were measured. At 250°C the reaction mixture consists of $\text{CaSO}_4 \cdot 0.15\text{H}_2\text{O}$, calcium sulphite, $\gamma\text{-CaSO}_4$ and possibly some bassinite, $\text{Ca}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. Even at temperatures as high as 450°C some $\text{CaSO}_4 \cdot 0.15\text{H}_2\text{O}$ and $\text{Ca}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ are observed together with the anhydrous compounds, CaSO_3 , $\gamma\text{-CaSO}_4$ and possibly some $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4$.

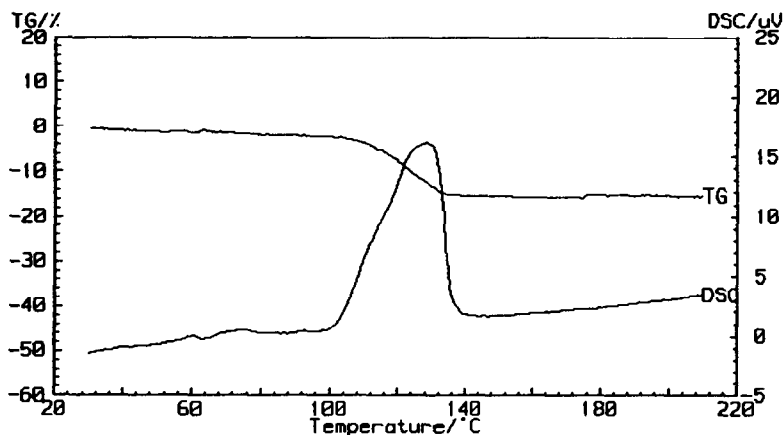


Fig. 1. The mass loss and DSC curves of the dehydration of synthetic gypsum using a heating rate of $5^{\circ}\text{C min}^{-1}$.

Samples with masses varying from 5 to 15 mg were heated using heating rates between 1 and 5°C min⁻¹ to obtain the mass loss curves. The data were used to calculate the activation energy values at different fraction reaction (α) values, using the isoconversion method described by Ozawa [14] and Flynn and Wall [15]. The following equation is used to determine the activation energy values (E) and the pre-exponential factor values at different α -values without knowledge of the reaction model that describes the reaction [16]

$$\ln \beta = \ln(AE/R) - \ln g(\alpha) - 5.3305 + 1.052E/RT$$

The method forms part of the kinetic analysis program described in the experimental part of this paper. Using the temperature values at different α -values for different heating rates ($0.5^\circ\text{C min}^{-1} < \beta < 5^\circ\text{C min}^{-1}$), Fig. 2 (activation energy E vs. α) is obtained for the dehydration reactions of gypsum up to 180°C. From the figure it is clear that the dehydration reactions do not occur in single steps. At least three stages in the dehydration can be observed. The activation energy increases between an α -value of 0 and 0.1, from where it stays more or less constant at a value of ± 100 kJ mol⁻¹ until $\alpha=0.7$. For this part of the reaction, the $\ln A$ value is ± 10 . A sharply decreasing activation energy value with fraction reaction is observed for the last part of the dehydration reaction ($0.7 < \alpha < 1$).

Using Fig. 2 and the Netzsch Thermokinetic Analysis Program [16], the different solid state decomposition kinetic models [17] were fitted to the experimental data in the observed fraction reaction ranges. For α -values between 0 and 0.1, the 3-dimen-

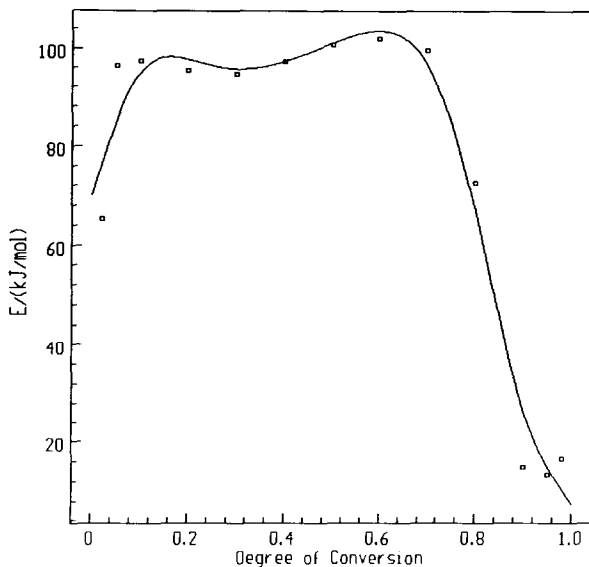


Fig. 2. Activation energy values (E) at different degrees of conversion (fraction reaction values (α)) for the dehydration of gypsum.

sional diffusion equation of Jander

$$f(\alpha) = [1 - (1 - \alpha)^{1/3}]^2 = kt$$

fits the data best (although only with a correlation coefficient value of 0.6421) and gives an activation energy value of $392 \pm 100 \text{ kJ mol}^{-1}$ and a $\ln A$ value of 49 ± 14 . The Durbin–Watson value of 0.123 for the fit of the experimental data to the model also indicates a non-conclusive fit.

Between α -values of 0.1 and 0.7, a much better fit of the equation describing a first-order reaction with autocatalytic activation is obtained [16]. Fitting of the model to experimental data gives a correlation coefficient value of 0.989 and a Durbin–Watson value of 0.047, both implying a good correlation between the experimental and theoretical data for this model. The activation energy value of $100.5 \pm 1.2 \text{ kJ mol}^{-1}$ and $\ln A$ of 10.6 ± 0.4 also fit very well to the values obtained using the isoconversional method.

The Sestak–Berggren equation [16] gives the best description (correlation coefficient = 0.954, Durbin–Watson value = 0.116) of the dehydration during the last stage of the dehydration reactions of gypsum (up to a maximum temperature of 180°C). An activation energy of $96 \pm 15 \text{ kJ mol}^{-1}$ and $\ln A$ of 10 ± 3 is calculated using this model.

Fig. 3 gives the fitting of the experimental data ($0 < \alpha < 1$) to the first-order with autocatalysis reaction model. It is clear that for α -values between 0.1 and 0.8 a good correlation is obtained, but that during the beginning and end of the reactions other mechanisms must be dominating.

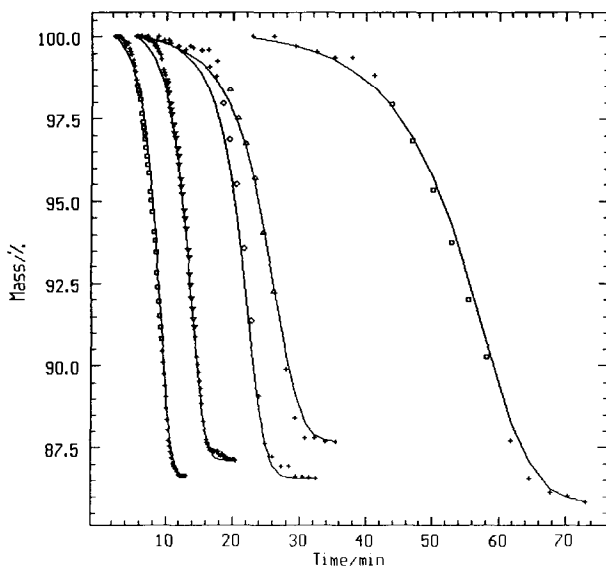


Fig. 3. Fitting of experimental mass loss data to the kinetic model for a first-order decomposition reaction with autocatalytic activation.

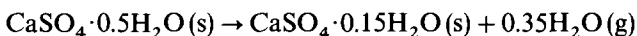
4. Conclusions

The results of this study compare very well to the results obtained by Murrat and Commal for calcium sulphate dihydrate [9]. They also found three distinct stages during the dehydration reaction which they divided into a first stage of nucleation formation with activation energy values between 251 and 502 kJ mol⁻¹. In this study, an activation energy value of 392 ± 100 kJ mol⁻¹ was calculated for reaction fraction values less than 0.1. Their activation energy value of 104–251 kJ mol⁻¹ for the growth stage of the dehydration compares very well to the value of 100.5 ± 1.2 kJ mol⁻¹ found in this study. And their value of 58–62 kJ mol⁻¹ for the last stage which they described as controlled by the diffusion of water molecules compares well to the value of 96 ± 15 kJ mol⁻¹ for α -values greater than 0.7 in this study. This last stage of the dehydration reaction can also be attributed to the second of the dehydration reactions, which thus seems to be diffusion-controlled.

It can be expected that, during the first part of the dehydration of gypsum (at temperatures less than 95°C, using a heating rate of 5°C min⁻¹), the influence of the dehydration of impurities will have a marked effect on the mass loss curve. This will also make the kinetic investigation of a single reaction in this range impossible. As soon as the dehydration percentage of the CaSO₄·2H₂O part of gypsum reaches a considerably higher value than the dehydration percentage of the other impurities, the first reaction can be studied. This seems to occur at an α -value of approximately 0.1. Good results are obtained between α -values of 0.1 and 0.7. XRD results also indicated that the first dehydration reaction is the same as that reported in the literature [4, 5]



The second dehydration reaction seems to start during the end of the first dehydration reaction. It appears to be the result of consecutive reactions with a small overlapping range where they occur together ($\pm 0.7 < \alpha < \pm 0.8$). However, since XRD results indicated the formation of a calcium sulphate compound with 0.15 water molecules attached to it, the second reaction could be



The nature of the calcium sulphate–water bonds is still under investigation, but they seem to be relatively strong as the compound can still be observed at temperatures up to 450°C. The possibility of parallel dehydration reactions after the first reactions will also be investigated, i.e. the dehydration of the hemihydrate directly to the anhydrous compound and the dehydration to the compound containing 0.15 moles of water.

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