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The thermal dehydration of natural gypsum and pure calcium sulphate dihydrate (gypsum)¹

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Abstract

A kinetic study has been undertaken of the thermal decomposition of naturally-occurring gypsum and pure calcium sulphate dihydrate. The reaction proceeds without any evidence of detectable melting. From X-ray diffraction analysis, it appears, that the decomposition reaction of both the natural gypsum and pure calcium sulphate dihydrate proceeds via the hemihydrate and $\text{CaSO}_4 \cdot 0.15\text{H}_2\text{O}$ to form anhydrite. Kinetic data for natural gypsum show that the reaction appears to proceed via the following:

For the α -range $0 < \alpha < 0.2$, Jander's three-dimensional diffusion equation is followed and an average activation energy of $88 \pm 18 \text{ kJ mol}^{-1}$ is found. For the α -range, $0.2 < \alpha < 0.5$, it is the first order with autocatalytic activation (the average activation energy is $97.9 \pm 4.3 \text{ kJ mol}^{-1}$). In the α -range, $0.5 < \alpha < 0.7$, the d -dimensional Avrami–Erofe'ev equation fits (the average activation energy is $97.2 \pm 20.4 \text{ kJ mol}^{-1}$) and in the $0.7 < \alpha < 1$ range, the two-dimensional Avrami–Erofe'ev equation (the average activation energy is $93.6 \pm 1.4 \text{ kJ mol}^{-1}$).

Kinetic data for pure calcium sulphate dihydrate show that the reaction seems to proceed via the following:

For the α -range $0 < \alpha < 0.1$, Jander's three-dimensional equation is followed and an average activation energy of $137.2 \pm 24.5 \text{ kJ mol}^{-1}$ is found. In the α -range, $0.1 < \alpha < 0.8$, the d -dimensional Avrami–Erofe'ev equation (average activation energy is $107.3 \pm 2.4 \text{ kJ mol}^{-1}$) fits and for $0.8 < \alpha < 1$, the first order kinetic model is used (average activation energy is $106.9 \pm 1.5 \text{ kJ mol}^{-1}$).

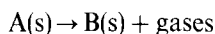
Keywords: Calcium sulphate dihydrate, Dehydration, Kinetics, Natural gypsum

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¹ Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

1. Introduction

The uses of gypsum (mainly calcium sulphate dihydrate) are well-known; the dehydration of the material has been discussed extensively in the literature [1–3] and can be described by the general reaction



In the literature much confusion exists about which kinetic model best describes the reaction (Table 1).

The results published on synthetic gypsum [14] compared well with results obtained by Murrat and Commal for calcium sulphate dihydrate [10]. The study on synthetic gypsum also showed three distinct stages: for reaction fraction values less than 0.1, the activation energy value found was $392 \pm 100 \text{ kJ mol}^{-1}$. For $0.1 < \alpha < 0.7$, the activation energy value was $100.5 \pm 1.2 \text{ kJ mol}^{-1}$ and for $\alpha > 0.7$, it was found to be $96 \pm 15 \text{ kJ mol}^{-1}$.

This paper is a continuation of the investigation into the dependence of the kinetics of dehydration of gypsum on the origin of the material.

2. Experimental

2.1. Natural gypsum

Natural gypsum was obtained from PPC Technical Services in Cleveland, Johannesburg. The material is mined in the Eastern Cape and is used by PPC, Port Elizabeth. The samples were ground to a fine powder and thoroughly mixed in order to obtain a homogeneous sample.

2.2. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ used in this present work was obtained from PAL Chemicals as an analytically pure reagent.

Natural gypsum and pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ samples were ground, mixed and sifted with diameters between 45 and 106 μm .

2.3. Thermogravimetric and Calorimetric Analysis

Dynamic kinetic measurements for the dehydration of gypsum were performed with a Netzsch STA 409 simultaneous TG–DSC instrument and analysed by means of a multivariant non-linear regression developed by Netzsch. Thermogravimetric and calorimetric data were collected in a dynamic nitrogen atmosphere (flow rate $\approx \text{cm}^3 \text{ min}^{-1}$). Platinum sample pans were used. Sample masses used varied between 8.5 and 10.5 mg. ICTA-recommended standards were used for temperature and enthalpy calibration.

Table 1
Summary of published results of the dehydration mechanisms and activation energy values of gypsum

Author	Experimental method	Kinetic model	Activation energy (kJ mol ⁻¹)
McAdie [4] 1964	Isothermal gravimetry	Rate law ($\alpha = kt$)	201.7
Pi�e [5] 1965–1970	Thermogravimetry	Diffusion of water molecules	$71 \leq E_a \leq 163.15$
Molony and Ridge [6] 1968	X-ray diffraction	Boundary control	–
Ball and Norwood [7, 8] 1969	Isothermal gravimetry	< 110°C Avrami–Erofe'ev nucleation + boundary control > 110°C parabolic law ($\alpha^2 = kt$)	$246 \geq E_a \geq 144.7$ $92.9-96.6$ $36 \leq E_a \leq 51$
Heide [9] 1969	Micro thermogravimetry	Avrami–Erofe'ev nuclei growth	130.5
Murrat and Commol [10] 1970	Micro and macro DTA	Nuclei formation	351–502
		Nuclei growth	104–251
		Diffusion of water molecules	58–62
Other authors [11–13]	–	–	110–378

2.4. XRD analysis

X-ray powder diffraction analyses were performed on an automated Siemens D 501 XRD spectrometer with a 40-position sample changer and monochromated CuK_α radiation. The results were analysed with the use of the International Centre Diffraction Data for PDS database sets 1–44.

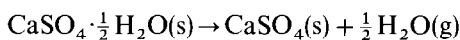
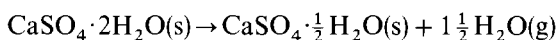
2.5. Other analyses

XRF analyses were performed on a Siemens MRS 400 MP wavelength dispersive XRF spectrometer. The results are summarised in Table 2.

Surface areas of the sifted samples were determined on a Micromeritics Flow Sorb II 2300 BET surface analyser. The surface areas of natural gypsum and calcium sulphate dihydrate are ≈ 11.0 and $\approx 0.8 \text{ m}^2 \text{ g}^{-1}$, respectively.

3. Results and discussion

The decomposition of calcium sulphate dihydrate proceeds via two reactions [6, 7]:



XRD results indicated that the unheated natural gypsum consists of the dihydrate and silicon dioxide. The calcium sulphate dihydrate consists mainly of the dihydrate

Table 2
XRF results from natural gypsum and pure calcium sulphate dihydrate

Components	Amount in natural gypsum/%	Amount in calcium sulphate dihydrate/%
SiO_2	33.3	6.7
Al_2O_3	8.3	3.3
Fe_2O_3	4.6	0.0
Mn_2O_3	0.0	0.0
TiO_2	0.3	0.3
CaO	13.8	33.6
MgO	1.5	1.3
P_2O_5	0.2	0.1
SO_3	18.8	34.4
Cl	0.0	0.0
K_2O	1.9	0.2
Na_2O	0.3	0.0
Loss on ignition	16.5	20.0
Total	99.5	99.9

but there is some anhydrite present. At $\approx 60^\circ\text{C}$, it is observed that natural gypsum and calcium sulphate dihydrate appear to have a very small amount of hemihydrate present. The calcium sulphate dihydrate also shows the presence of more anhydrite than was initially present. At $\approx 170^\circ\text{C}$ (heating rate 5°C min^{-1}), there is an increase in the hemihydrate and anhydrite content of natural and pure gypsum and possibly $\text{CaSO}_4 \cdot 0.62 \text{H}_2\text{O}$ could also be present. In these samples there also appears to be some $\text{CaSO}_4 \cdot 0.15 \text{H}_2\text{O}$ present. When the temperature reaches $\approx 240^\circ\text{C}$, there appears to be more $\text{CaSO}_4 \cdot 0.15 \text{H}_2\text{O}$ than hemihydrate present in the natural gypsum with a growing anhydrite content but approximately equal quantities of hemihydrate and $\text{CaSO}_4 \cdot 0.15 \text{H}_2\text{O}$ in the pure dihydrate sample. At 450°C , only anhydrite is present in the calcium sulphate dihydrate but also possibly hemihydrate in the natural gypsum.

The XRD results from synthetic gypsum in Ref. [14] show that at $\approx 60^\circ\text{C}$ very little hemihydrate is present. At 165°C , the main product is anhydrite but there is still some hemihydrate present. 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, $\text{Ca}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. It was also found that even at temperature of 450°C , there was some $\text{CaSO}_4 \cdot 0.15 \text{H}_2\text{O}$ and $\text{Ca}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ as well as CaSO_3 , $\gamma\text{-CaSO}_4$ and possibly even $\text{Ca}_3(\text{SO}_3)_2 \cdot \text{SO}_4$.

The thermogravimetric analysis of natural gypsum and pure calcium sulphate dihydrate (Figs. 1 and 2) shows a very low mass loss ($\pm 1\%$) from ambient temperature to 95°C , as was seen with synthetic gypsum [14].

The mean weight loss for natural gypsum was $7.39 \pm 0.91\%$ of the original reactant weight. On calculation it would appear that only $\sim 35\%$ of the sample is calcium sulphate dihydrate. The DSC curve for the dehydration of calcium sulphate dihydrate shows a double peak which was not present in the DSC curve for the dehydration of natural gypsum. The mean weight loss for calcium sulphate dihydrate was $19.2 \pm 0.89\%$ (which corresponds to the loss of 1.79 water molecules from the reactant) but is somewhat less than the 21% calculated for the formation of the anhydrite. It was calculated that $\sim 92\%$ of the pure sample was calcium sulphate dihydrate.

The heat of dehydration was obtained from the DSC curve and was found to be $147\text{--}205 \text{J g}^{-1}$ for natural gypsum and $394\text{--}500 \text{J g}^{-1}$ for pure calcium sulphate dihydrate.

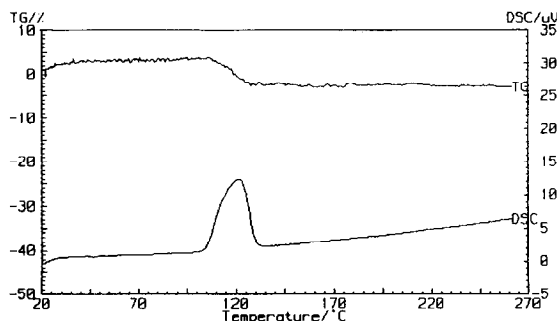


Fig. 1. The mass loss and DSC curves for the dehydration of natural gypsum at 5°C min^{-1} in an inert atmosphere.

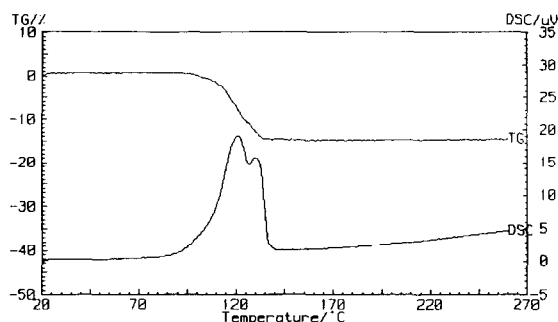


Fig. 2. The mass loss and DSC curves for the dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 5°C min^{-1} in an inert atmosphere.

The thermogravimetric data was used to calculate the activation energy at different α -values, using the iso-conversion method described by Ozawa [15] and Flynn and Wall [16]. The activation energy values obtained are plotted against α (reaction fraction decomposed) for different heating rates ($0.5^\circ\text{C min}^{-1} < \beta < 5^\circ\text{C min}^{-1}$). Figs. 3 and 4 (plots of activation energy E vs α for natural gypsum and calcium sulphate dihydrate, respectively) are obtained for the dehydration reactions up to 180°C . It is clear from the figure that the dehydration reactions do not occur in single steps. There are at least four stages for natural gypsum and three stages for pure calcium sulphate dihydrate. From Fig. 3 for natural gypsum it can be seen that the activation energy increases from an α -value of 0 to 0.2, where it remains constant at a value of $\approx 94 \text{ kJ mol}^{-1}$ until $\alpha = 0.5$. The $\ln A$ value is ± 10 for this part. There is a sharply decreasing activation energy value for $0.5 < \alpha < 0.7$. From Fig. 4 for calcium sulphate dihydrate, the activation energy also increases from 0 to 0.1, where it remains constant at a value of $\approx 109 \text{ kJ mol}^{-1}$ until $\alpha = 0.8$. The $\ln A$ value is ± 6 . From $0.8 < \alpha < 1$, there is also a sharply decreasing activation energy value.

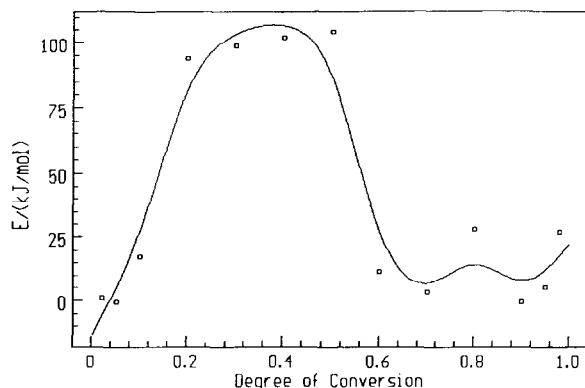


Fig. 3. Plot of activation energy E vs α for natural gypsum.

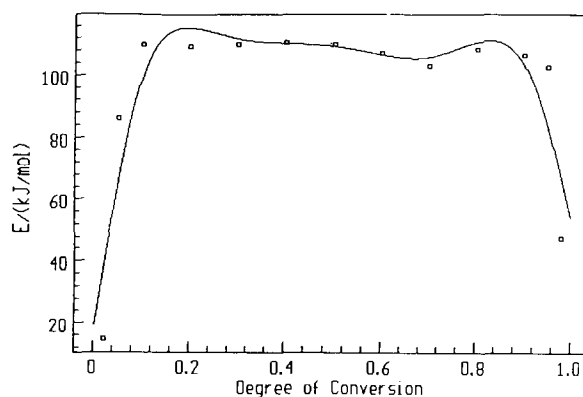


Fig. 4. Plot of activation energy E vs α for calcium sulphate dihydrate.

From these activation energy versus alpha graphs and the Netzsch Thermokinetic Analysis Program [17], the different solid state decomposition kinetic models [18] were fitted to the experimental data in the observed fraction reaction ranges.

For natural gypsum, and α -values in the range of 0 and 0.2, the 3-dimensional diffusion equation of Jander

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

appears to fit the data best; the correlation coefficient value is only 0.726 and the equation gives an average activation value of $88 \pm 18 \text{ kJ mol}^{-1}$ and an average $\ln A$ value of 7.7 ± 2.7 . This is a non-conclusive fit as the Durbin–Watson value is 0.306, and the activation energy values differ with α .

For α -values between 0.2 and 0.5, the first order with autocatalytic activation is obtained. A much better fit of the equation is found; the correlation coefficient is 0.974. The average activation energy value of $97.9 \pm 4.3 \text{ kJ mol}^{-1}$ and $\ln A$ of 10.1 ± 2.1 correlates very well with the $\sim 94 \text{ kJ mol}^{-1}$ and $\ln A$ of 10 obtained using the isoconversional method. From Fig. 5 it can be seen that the fit is good between 0.2 and 0.5 but that at the start and end of the dehydration process other mechanisms could be dominating.

For $0.5 < \alpha < 0.7$, quite a few models appear to fit the data well, namely the d -dimensional Avrami–Erofe'ev equation, or the second order equation, or the first order with autocatalytic activation or even the first order or two-dimensional phase boundary model. The best fit however, was the d -dimensional Avrami–Erofe'ev equation with a correlation coefficient of 0.989 and Durbin–Watson value of 0.049. An average activation energy value of $97.2 \pm 20.4 \text{ kJ mol}^{-1}$ was obtained and a $\ln A$ value of 10.6 ± 2.6 .

The two-dimensional Avrami–Erofe'ev equation appears to fit the data the best for $0.7 < \alpha < 1$ with a correlation coefficient of 0.982 and Durbin–Watson value of 0.248. An average activation energy value of $93.6 \pm 1.4 \text{ kJ mol}^{-1}$ was obtained and $\ln A$ of 10.1 ± 0.1 . The second order, first order with autocatalytic activation and even first

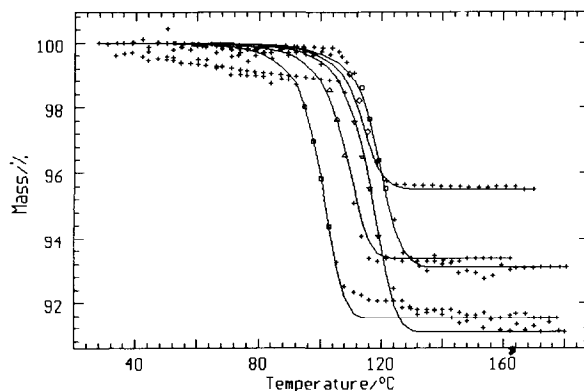


Fig. 5. Fitting of experimental data of natural gypsum with theoretical data for $0.2 < \alpha < 0.5$.

order kinetic models were also found to be reasonable descriptions of the dehydration in this stage of the dehydration reaction.

Calcium sulphate dihydrate also appears to dehydrate according to the three-dimensional diffusion equation of Jander for $0 < \alpha < 0.1$. The correlation coefficient was only 0.634 but the Durbin–Watson value was 0.082. The average activation energy recorded was $137.2 \pm 24.5 \text{ kJ mol}^{-1}$.

For $0.1 < \alpha < 0.8$, the dehydration reaction could be described by the first order, the n -th order or the d -dimensional Avrami–Erofe'ev. The d -dimensional Avrami–Erofe'ev equation does appear, however, to give the best fit with a correlation coefficient of 0.992 and an average activation energy of $107.3 \pm 2.4 \text{ kJ mol}^{-1}$ and $\ln A$ of 11.9. The activation energy value corresponds very well with that of $\approx 109 \text{ kJ mol}^{-1}$ obtained using the isoconversional method. Fig. 6 is the d -dimensional Avrami–Erofe'ev fit; there is also a poor fit at the start and end of the dehydration process but a good fit for $0.1 < \alpha < 0.8$.

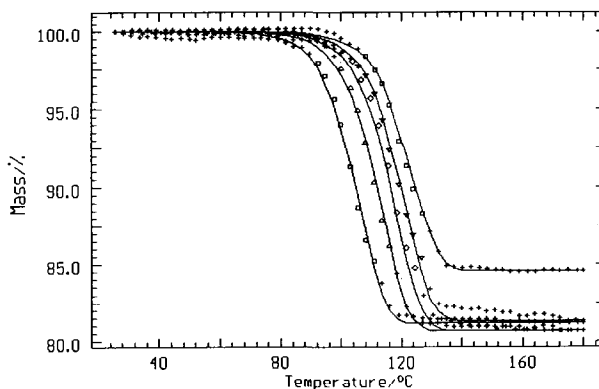


Fig. 6. The fit of experimental mass loss data to the kinetic model for a d -dimensional Avrami–Erofe'ev decomposition reaction.

The last stage of dehydration for $0.8 < \alpha < 1$ appears to be best described by the first order decomposition reaction

$$1 - \alpha = e^{-kt}$$

with a correlation coefficient of 0.982 and $\ln A$ of 11.9 ± 0.2 , and an average activation energy value of $106.9 \pm 1.5 \text{ kJ mol}^{-1}$. Again this is a non-conclusive fit as the activation energy values differ with α -values indicating a complex reaction.

From the electron micrographs no evidence of melting was found since no rounded textures (attributed to control by surface tension) were found in the decomposed material. Dehydration of natural gypsum resulted in minor changes to the surface texture. Partial decomposition ($\alpha < 0.1$) ($\sim 60^\circ\text{C}$) resulted in no marked textural change. For $\alpha > 0.1$ –1.0, the texture appears to be more spongy and the reaction interface appears to grow three-dimensionally.

Calcium sulphate dihydrate electron micrographs show that the decomposition of the dihydrate to the anhydrite proceeds via nuclei formation and the growth of the nuclei. This confirms the kinetic model proposed for this decomposition reaction namely d -dimensional Avrami–Erofe'ev rate equation.

4. Conclusion

The influence of the dehydration of impurities appears to have a marked effect on the mass loss curve; thus makes the kinetic investigation difficult. The change in activation energy for the various gypsums for $0 < \alpha < 0.2$ indicates a complex reaction mechanism and thus it is also difficult to fit a reaction model. Natural gypsum shows a much smaller mass loss due to the removal of water than does calcium sulphate dihydrate; calculation shows that natural gypsum contains only approximately 35% calcium sulphate dihydrate. The heat of dehydration of calcium sulphate is 394 – 500 J g^{-1} and for natural gypsum 147 – 205 J g^{-1} . However only $\sim 35\%$ of natural gypsum is calcium sulphate dihydrate. Thus on calculating, 35% of the heat of dehydration of the calcium sulphate dihydrate value gives a heat of dehydration of the calcium sulphate dihydrate in natural gypsum of ~ 140 – 175 J g^{-1} . The activation energy values were very similar for the reaction fraction of $\approx 0.2 < \alpha < 0.5$ and $0.2 < \alpha < 0.7$ namely $97.9 \pm 4.3 \text{ kJ mol}^{-1}$ and $107.3 \pm 2.4 \text{ kJ mol}^{-1}$ for natural gypsum and pure calcium sulphate, respectively.

It would thus appear that natural gypsum and calcium sulphate dihydrate seem to dehydrate via the hemihydrate and $\text{CaSO}_4 \cdot 0.15 \text{ H}_2\text{O}$ to form anhydrite, as was found with synthetic gypsum [14].

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