

## **KINETICS OF GYPSUM DEHYDRATION**

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### **Abstract**

The kinetics of gypsum dehydration in non-isothermal conditions with constant heating rate as well in quasi-isotherm, quasi-isobar regime, was investigated. The latter ones of these methods allowed putting in evidence the autocatalytic character of the dehydration, as well as the change of the activation energy with the conversion.

The activation energy change was explained by the crystal growth and sample compaction observed by optical microscopy.

Microscopic observations show that at higher conversions a compaction occur. This process is probably favoured by the accumulation of the water vapour from the dehydration (autogenerated atmosphere). These are the reason for step III characterised by higher activation.

**Keywords:** gypsum dehydration, non-isothermal kinetic, thermal analysis

### **Introduction**

The thermal behaviour of gypsum was frequently investigated due to its use as construction material. The thermal decomposition of gypsum depends on the experimental conditions. Among them the heating rate and the atmosphere of the thermal treatment are particularly important. Thus a slow rate of heating as well as a low water vapour partial pressure determine the formation of a product with high specific area called  $\beta$ -CaSO<sub>4</sub> III. The subsequent heating loose material leads to compact  $\alpha$ -CaSO<sub>4</sub> IV.

The influence of the water vapour partial pressure on the gypsum dehydration was evidenced using the method of quasi-isotherm, quasi-isobar thermal analysis [1–3].

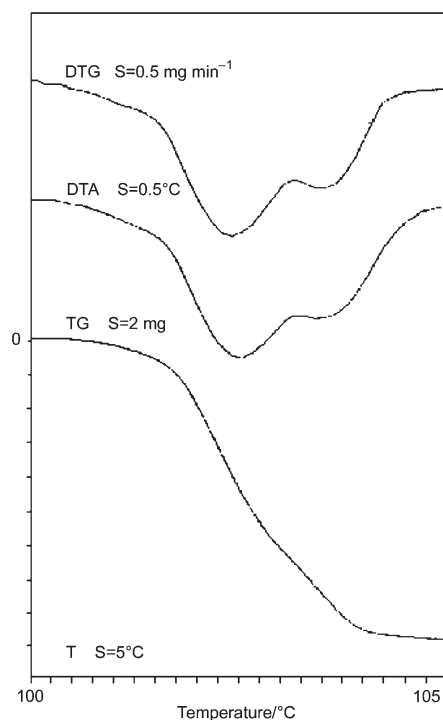
### **Experimental**

Powders of CaSO<sub>4</sub>·2H<sub>2</sub>O was chemical purity/analytical grade, provided by REACTIVUL, Romania, exempt of wastes, were used. The heating curves were recorded by help of a C-Derivatograph type Paulik–Paulik. The microscopic investigations were performed by help of IOR microscope.

## Results and discussions

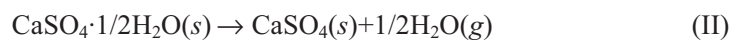
In order to obtain new information on the gypsum dehydration, in this paper we report some problems concerning non-isothermal kinetic of the dehydration.

Thermal analysis curves corresponding to dehydration of a 81 mg sample in a platinum crucible, at 5 K min<sup>-1</sup> are shown in Fig. 1.



**Fig. 1** Dehydration curves of CaSO<sub>4</sub>·2H<sub>2</sub>O

According to the thermal curves, the gypsum dehydration comports two steps described by the following equations:



At a heating rate of 2 K min<sup>-1</sup> the two steps are satisfactorily separated. Using a low heating rate (2 K min<sup>-1</sup>), the temperature and mass gradients are lower, so the consecutive decomposition stages are better separated. For the kinetic analysis of step (I) 'reaction order *n*' conversion function was considered, i. e.

$$f(\alpha) = (1 - \alpha)^n \quad (1)$$

where  $\alpha$  is the degree of conversion.

This function proved to be reliable for many thermal decompositions [4] and in comparison to the Avrami–Erofeev equation [5, 6] is more sensitive to mechanism change and from a mathematical stand point is more simple.

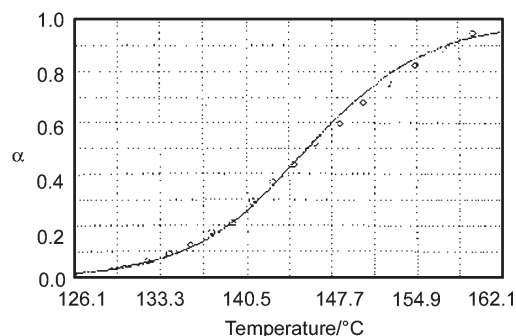
In order to evaluate the kinetic parameters the integral methods Coats–Redfern [7], Flynn–Wall [8] and Coats–Redfern modified [9] were used as less sensitive to the experimental errors with respect to the differential ones.

The values of the activation energy  $E$ , pre-exponential factor  $A$ , reaction order  $n$  and correlation coefficient  $r$  of the linear equations are listed in Table 1.

**Table 1** The values of the kinetic parameters of reaction (I)

Method	Coats–Redfern	Flynn–Wall	Coats–Redfern modified
$E/\text{kJ mol}^{-1}$	290.62	285.49	282.15
$A/\text{s}^{-1}$	$7.9 \cdot 10^{33}$	$1.6 \cdot 10^{34}$	$2.7 \cdot 10^{33}$
Reaction order	2.10	2.11	1.90
Correlation coefficient	-0.9963	-0.9965	-0.9957

As seen from Table 1 the three applied methods lead to values of the kinetic parameters in good agreement with each other. One has to notice the values close to unity of the correlation coefficient.

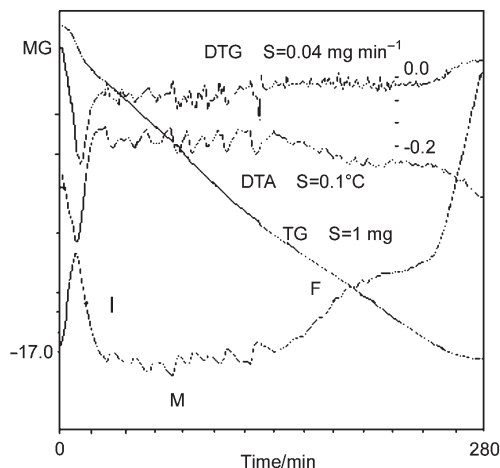


**Fig. 2** Simulated curve and experimental points for reaction (I)

Figure 2 shows the experimental points for the first dehydration step as well as the simulated curve based on the average values of the kinetic parameters as given by the three applied methods.

Although the experimental points lie practically on the simulated curve, it is not sure that the conversion function (1) corresponds to the reaction mechanism. On the other hand, the values of the pre-exponential factor are too high for some associated physical meanings. These are the reason why we applied the isokinetic method [10], which allows to evaluate the activation energy independently of the form of conversion function, at the constant dehydration rate.

The quasi-isothermal curves for the first dehydration step of the gypsum with the rate of 0.05 mg are given in Fig. 3.



**Fig. 3** Curves of quasi-isothermal analysis curves corresponding to reaction (I) S-step on the curve scale

Actually, the isokinetic method used by us is a variant of the constant rate thermal analysis (CRTA). The lower curve (IMF), corresponding to the change of temperature in the time shows a minimum. As shown in a previous work [10], such curves correspond to the autocatalytic processes. The system keeps the dehydration rate constant in the neighbourhood of the point M. The oscillations are due to the regulation system which switches on and off the heating for lower and higher values of the dehydration rate with respect of the programmed one ( $0.04 \text{ mg min}^{-1}$ ).

To evaluate the activation energy one more curve for the rate of  $0.1 \text{ mg min}^{-1}$  was recorded. As the experimental curves  $T$  vs.  $\alpha$ , exhibit a minimum, shows that the process possesses an initial accelerating period. The kinetic of such processes are described by the following equation rate:

$$\frac{d\alpha}{dt} = A e^{-E/RT} \alpha^m (1-\alpha)^n \quad (2)$$

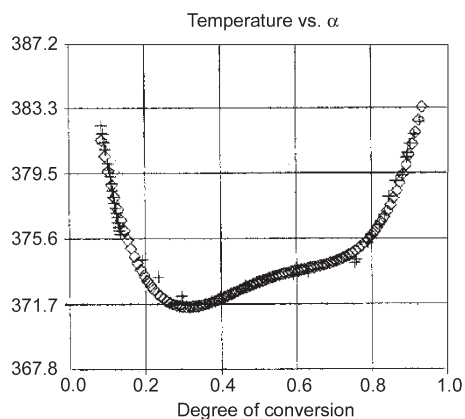
Here  $\alpha$  is the degree of conversion,  $t$  – the time,  $A$  – the pre-exponential factor,  $E$  – the activation energy,  $R$  – the gas constant,  $T$  – the absolute temperature,  $m$  and  $n$  are constants which depend on the reaction mechanism.

After processing the experimental data by the algorithm and program presented in the papers [11] and [12] the following values of the kinetic parameters were obtained:

**Table 2** Average values of the kinetic parameters concerning the process (III)

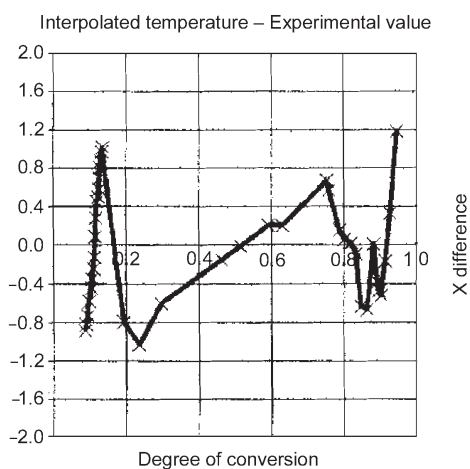
$E/\text{kJ mol}^{-1}$	$m$	$n$	$A/\text{s}^{-1}$
202	1.0	2.2	$6.3 \cdot 10^{24}$

A good agreement between the experimental points and there calculated by the help of the VERSATILE programme are to be noticed (Fig. 4).



**Fig. 4** The agreement between the experimental points (+)  $T$ ,  $\alpha$ , and there generated ( $\diamond$ ) by the programme

In order to put in evidence the distribution of the deviation with the degree of conversion, Fig. 5 shows the temperature between the calculated and experimental ones.



**Fig. 5** The agreement between the calculated temperature ( $\diamond$ ) and experimental one (+) vs. the degree of conversion

The highest deviations are recorded at the extreme values of the degree of conversion and the lowest ones correspond to  $0.2 < \alpha < 0.9$ . The explanation consists in the fact that for the last range of  $\alpha$  the dehydration rate is quasi-constant.

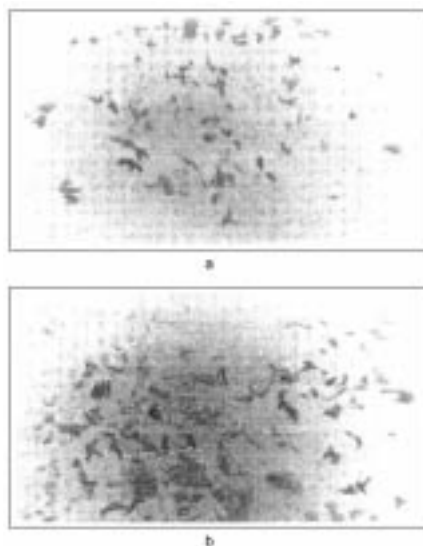
As shown in Table 3, for the investigated system, the activation energy changes with the degree of conversion.

**Table 3** Average value of the activation energy of gypsum dehydration for the steps, which can be seen in Fig. 4

$E/\text{kJ mol}^{-1}$	216	184	238	117
$\alpha$ step	0.08–0.24	0.24–0.51	0.52–0.72	0.72–0.92
Step number	I	II	III	IV

The first step, in the range of the low values of  $\alpha$  is characterised by relatively high values of the activation energy and can be assigned to the growth of low sizes nuclei. The second step in the range  $0.24 < \alpha < 0.51$  corresponds to the growth without interaction of bigger nuclei. This whenever requires a lower activation energy.

Microscopic observations show that a compaction occur at higher conversions (Figs 6a and 6b).

**Fig. 6** The microphotograms of the gypsum powder for various conversions: a –  $\alpha=0.36$ , b –  $\alpha=0.62$ 

This process is probably favoured by the accumulation of the water vapour from the dehydration (autogenerate atmosphere). These are the reasons for step III characterised by higher activation energy, which can be associated with the interaction of the nuclei with the generation of a compact texture. The last step with the lowest value of activation energy can be assigned to the loss of water from the pores previously generated.

The initial accelerating period is due to the fact that the slow period of nucleation and growth of the small nuclei are followed by the fast growth of nuclei with sizes over the critical value. The shape of the temperature – time curve from Fig. 3 can be explained also taking into account that the nucleation and the growth of small nuclei require higher values of activation energy than the growth of the stable nuclei.

Thus at the beginning of the experiment, when the decomposition rate is zero, the temperature programme orders the heating to a temperature high enough in order to start the nucleation.

After the stable nuclei are formed, they grow at high rate as they require lower value of activation energy. In such conditions the decomposition rate ( $v_d$ ) surpasses the programmed value ( $v_p$ ). For this reason the temperature programmer cuts the heating. Consequently, the sample cools itself until  $v_d < v_p$ . Under such conditions the heating programme starts again until  $v_d < v_p$ . It turned out that the value of the parameter  $v_d$  oscillates close to  $v_p$ . The oscillations can be observed on the curves  $T$  and DTA.

When the reaction is almost finished the amount of the reactant is lower and even lowers. The decrease of the reaction rate is avoided by the increase of the temperature. In such a way the temperature curve with oscillations and minimum is generated.

## Conclusions

The investigation of gypsum dehydration at constant heating rate allows to put in evidence two reaction steps. The evaluation of the apparent kinetic parameters does not offer information concerning the mechanism.

The use of a variant of the CRTA method showed the auto-catalytic character of step (I).

Using an algorithm and a programme of data processing worked out by us the values of the kinetic parameters corresponding to an auto-catalytic conversion function were evaluated.

A significant change of activation energy with the conversion, showing various mechanism of dehydration was put in evidence:

1. Nucleation and growth of low sizes nuclei.
2. Relatively fast growth of stable nuclei.
3. Agglomeration of the crystals.
4. The final loss of water from the pores.

The algorithm as well as the programme developed by us allows the use of the curves recorded in quasi-isothermal conditions not only in analytical purposes but also in kinetic studies.

## References

- 1 L. Erdey, F. Paulik and J. Paulik, Hungarian Patent No. 152197, 1962.
- 2 F. Paulik, 'Special trends in thermal analysis' John Wiley & Sons, Chichester, New York 1995, p. 177.
- 3 J. Rouquerol, *Thermochim. Acta*, 144 (1980) 31.
- 4 E. Segal and D. Fatu, 'Introduction to Non-isothermal Kinetics', Ed. Academiei Romane, Bucharest 1983, p. 64.
- 5 M. Avrami, *J. Chem. Phys.*, 7 (1939) 1103; 8 (1940) 212.
- 6 B. V. Erofeev, *Dokl. Akad. Nauk, SSSR*, 52 (1946) 511.

- 7 A. W. Coats and P. J. Redfern, *Nature*, 21 (1964) 68.
- 8 J. H. Flynn and L. A. Wall, *Polym. Lett.*, 4 (1966) 323.
- 9 E. Urbanovici and E. Segal, *Thermochim. Acta*, 80 (1984) 379.
- 10 D. Fatu and E. Segal, *Thermochim. Acta*, 61 (1983) 215.
- 11 D. Fatu and N. Dragoe, *The 11<sup>th</sup> International Congress on Thermal Analysis and Calorimetry, Philadelphia, USA 1996, Program Book*, p. 218.
- 12 N. Dragoe, D. Fatu and E. Segal, *J. Therm. Anal. Cal.*, 56 (1999) 793.