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Experimental study and Monte-Carlo simulation of the nucleation and growth processes during the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals

Loïc Favergeon⁽¹⁾, Michèle Pijolat⁽¹⁾, Françoise Valdivieso⁽¹⁾ and Céline Helbert⁽²⁾

⁽¹⁾ LPMG CNRS UMR 5148, Centre SPIN, Ecole Nationale Supérieure des Mines de Saint-Étienne, 42023 Saint-Étienne, France. Fax: 33(0)477499694; Tel: 33(0)477420291; E-mail: favergeon@emse.fr

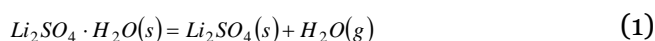
⁽²⁾ 3MI, Ecole Nationale Supérieure des Mines de Saint-Étienne, 42023 Saint-Étienne, France.

ABSTRACT

A kinetic model for the dehydration of lithium sulfate monohydrate is proposed in order to account for experimental data obtained on single crystals by thermogravimetry at 80°C under fixed water vapour pressure, and by optical microscopy. This model is based on the assumptions of Mampel's model, the nucleation takes place randomly at the surface of the solid and is followed by isotropic growth toward the centre of the crystal. Calculated rates $d\alpha/dt$ are obtained by means of Monte-Carlo simulations and compared to the experimental ones, which leads to the determination of two kinetic constants: the areic frequency of nucleation (in number of nuclei. $\text{m}^{-2}.\text{s}^{-1}$) and the areic reactivity of growth (in $\text{mol}.\text{m}^{-2}.\text{s}^{-1}$).

A-INTRODUCTION

The dehydration of lithium sulfate monohydrate corresponds to the equation (1):



The kinetics of this reaction have been extensively studied [1-13]. These works have shown that the isothermal kinetic curves obtained for powders, i.e. fractional conversion α versus time t , are sigmoids and various interpretations have been proposed for the model of transformation.

Some authors [2, 3, 7] have used a contracting-sphere model (R_3) in which the nucleation is assumed to be instantaneous. Galwey *et al.* [6] proposed a R_n model with $n = 2.5$ to describe their kinetic data. Others papers [4, 5, 9, 10, 13] report the choice of an Avrami-Erofeev law (A_n) for the first part of the curve, then a phase boundary reaction law (R_n) for the second one. This means that nucleation would proceed in the bulk of the solid reactant (according to the assumptions used to derive such A_n laws [14]) and then the mechanism would change during the reaction without changing the reaction conditions. A bulk nucleation seems to be impossible for the dehydration of a non-porous solid like lithium sulfate monohydrate since water molecules could not escape from crystal structure. One can also note that the index number n in the kinetic laws (A_n , R_n , D_n , F_n) theoretically represents the degree of symmetry of the reactant solid particles, which means that 1.5 and 3.1 [4] or 1.95 and 2.3 [5] are just mathematical adjustments and have no real physical meaning.

Valdivieso *et al.* [12] have studied the dehydration of commercial $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ powder by means of isothermal thermogravimetry under various water vapour pressures. They proposed a nucleation and anisotropic growth model in order to account for the sigmoid shape of the kinetic curves $\alpha(t)$: the nucleation occurs at the surface of the solid and is followed by a rapid two-dimensional growth (the particles are covered by a thin layer of product as soon as they are nucleated but nuclei do not appear at the same time on all the grains), then the growth proceeds towards the centre of the grains, the rate-limiting step being located at the internal interface. In some experiments on single crystals it was observed a continuously decreasing rate, interpreted by an interface advance model R_n , which is coherent with the model of anisotropic growth proposed for the powder.

In the present work, the dehydration of single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was followed by isothermal and isobaric thermogravimetry. Optical microscopy observations have allowed to ascertain the assumptions of the kinetic model chosen to describe the dehydration behaviour. The kinetic curves $\alpha(t)$ are sigmoids and the observation of the crystals at the beginning of the dehydration has shown that the nucleation is not instantaneous on the surface of the crystals. Consequently, we have proposed to interpret our kinetic data for single crystals with a model involving both nucleation and isotropic growth processes, according to the assumptions of Mampel's model [15]. Due to the particular shape of the crystals, Monte-Carlo simulations were done to calculate the theoretical rates.

B-EXPERIMENTAL RESULTS

B.1-EXPERIMENTAL

Lithium sulfate monohydrate single crystals were grown through slow evaporation of a saturated aqueous solution (using powdered materials (Aldrich 99%) and pure water) at room temperature. Single crystals thus obtained have the typical shape of hexagonal plates which can be represented by a rectangle (length L and width w) and two isosceles triangles (base w and height h) with a constant thickness e (figure 1).

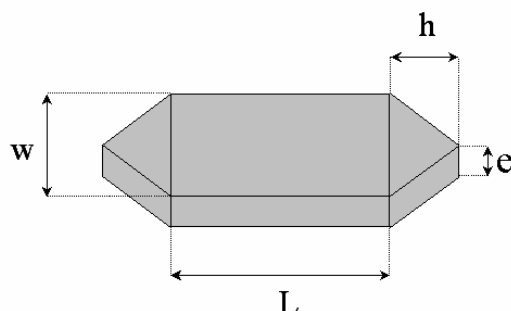


Figure 1: Scheme of a recrystallized single crystal of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

The mean dimensions for a single crystal are about 2200 μm for L , 1500 μm for w , 530 μm for h and 650 μm for e .

The kinetic curves (fractional conversion α versus time t) were obtained by means of isothermal thermogravimetry at 80°C, in a water vapour atmosphere ($P_{(\text{H}_2\text{O})}=2.6$ hPa). A symmetrical thermobalance was used in static conditions (Sétaram MTB 10-8) as follows : after introduction of the sample (approximate mass 2-7 mg) at room temperature and evacuation up to a vacuum of 0.001 hPa, a pressure of water vapour equal to 123 hPa was established (this value being higher than the dehydration equilibrium pressure at 80°C (equal to 93 hPa), in order to prevent the sample from dehydration during the heating up to 80°C). When the temperature was stabilized at 80°C, the water pressure was then rapidly decreased to the pressure chosen for the experiment by a short pumping, and then maintained constant during each experiment due to a thermoregulated bath, the total pressure being that of water vapour.

Optical observations were carried out with a microscope Zeiss Axioskop. Single crystals were observed without any preparation, the sample being placed on a glass slide.

In order to observe the bulk of the crystals, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals were coated with an epoxy resin (Buehler) under vacuum. Samples thus obtained were polished using a polishing machine Lam Plan MM8027A (individual pressure) and different polishing cloths (successively P600, P1200, P2500, P4000 then diamond stick on woven fabrics disc) under a pressure of 1.4 hPa at 150 RPM. Observations were done with an inverted metallurgical microscope Olympus PME3.

B.2 KINETIC CURVES

For each single crystal, kinetic curves $\alpha(t)$ were sigmoids as shown in figure 2, thus the rate of reaction $d\alpha/dt$ exhibited a maximum versus time, the corresponding fractional conversion α being approximately 0.4.

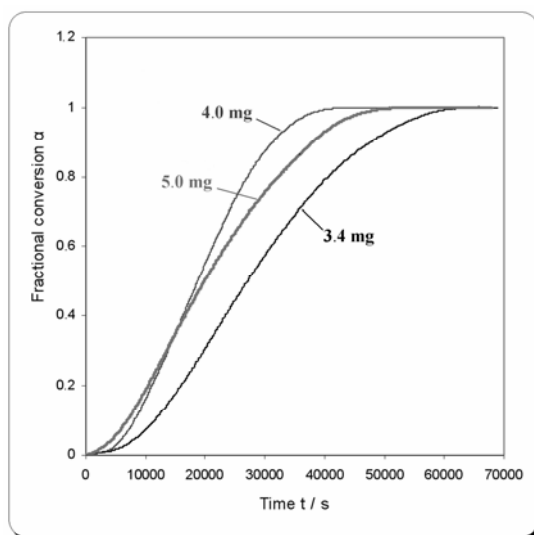


Figure 2: Kinetic curves obtained for the dehydration of three different $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals ($T=80^\circ\text{C}$, $P(\text{H}_2\text{O})=2.6 \text{ hPa}$). Initial mass of each crystal is indicated.

The sigmoid shape of the kinetic curves for the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals means that the reaction of dehydration involves simultaneous nucleation and growth processes.

Two kinds of models are available to describe the variations of the fractional conversion with time: first, those in which the nucleation rate is very high (or very low) compared to the growth rate. If the rate of reaction is governed by the progression of the interface, it is continuously decreasing with time (as for example with R_n or D_n kinetic models).

The second kind of models are those in which the nucleation and growth rates are of the same order of magnitude: the competition between the two processes leads to sigmoid curves. In these models, it is possible to distinguish two alternatives for the growth process : either the growth is isotropic, as for example in the Mampel's model [15], or it is anisotropic as for example in the Valdivieso et al.'s [12] or Jacobs and Tompkins's [16,17] models. In our experiments, the kinetic rate corresponds to the dehydration of a unique crystal, which means that only the first case (isotropic) is expected, since the second one should only be encountered with powders. The microscopic observations of the surface and the bulk of partially dehydrated single crystals may thus indicate if the reaction proceeds according to the assumptions of Mampel's model, typically a random surface nucleation and an isotropic growth.

B.3 OPTICAL MICROSCOPY OBSERVATIONS

Observations have been carried out with an optical microscope in order to determine the evolution of the new phase during the dehydration. In this aim, single crystals at various fractional conversions have been observed (figures 3 and 4).

For each single crystal, it could be observed that the new phase (i.e. anhydrous Li_2SO_4) appears randomly and grows isotropically at the surface of the crystal.

In order to see the evolution of the new phase in the bulk, partially dehydrated crystals were coated with epoxy resin then polished up to the bulk. Figure 5 shows the bulk of a partially dehydrated $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal at $\alpha = 0.079$.

These micrographs show that nucleation takes place at the surface of the crystal and that the new phase grows isotropically towards the centre of the crystal.

Finally, these observations clearly indicate that a random nucleation occurs at the surface of the crystal and is followed by isotropic growth of the nuclei towards the centre of the crystal. In consequence Mampel's model was used to represent the kinetic behaviour of the dehydration of each single crystal.

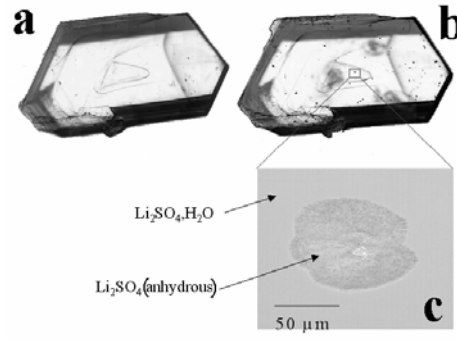


Figure 3: Micrograph of a partially dehydrated $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ single crystal :
a) before dehydration, b) at $\alpha=0.00187$ and c) magnification of b)

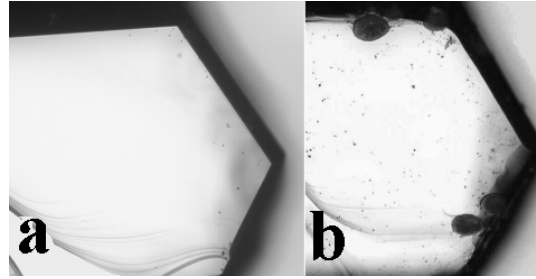


Figure 4: Micrograph of a partially dehydrated $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ single crystal
a) before dehydration and b) at $\alpha=0.0095$

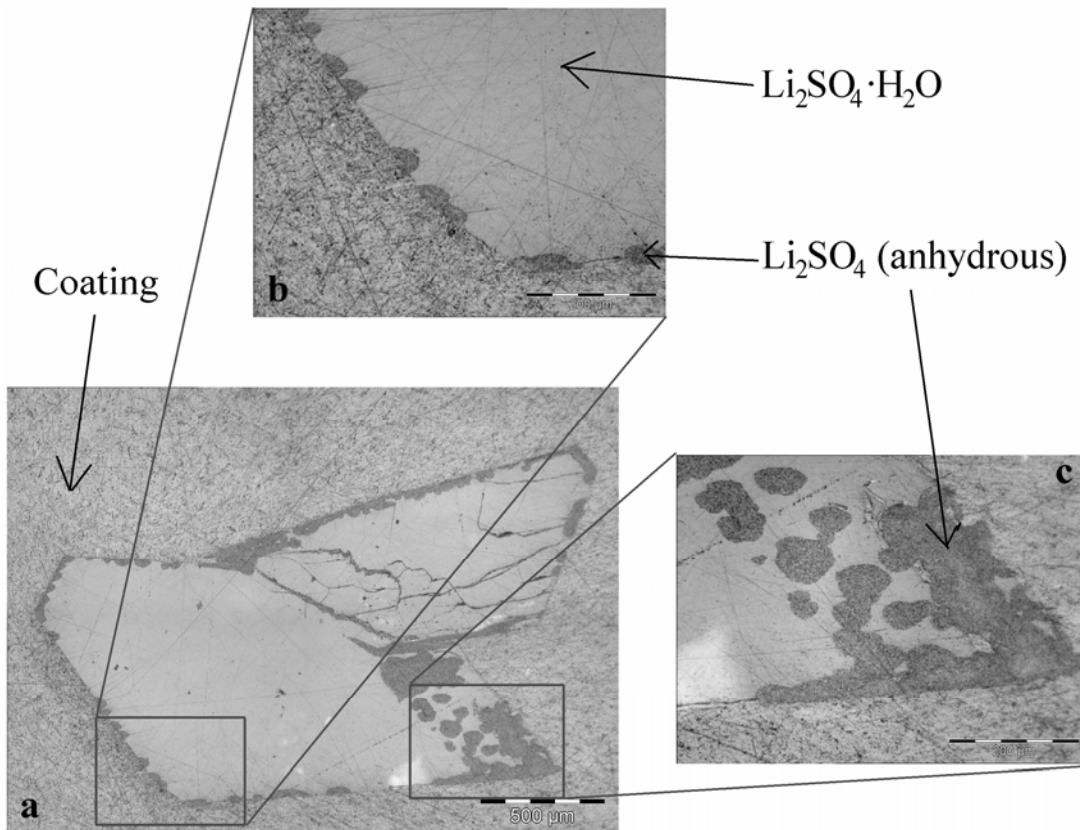


Figure 5: Bulk micrograph of a partially dehydrated $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ single crystal at $\alpha=0.079$ a) the whole crystal, b) and c) magnification of a).

C. DESCRIPTION OF THE MODEL

First described by W.A. Johnson and R.F. Mehl [18], this model was allocated to K.L. Mampel [15] and related in detail by B. Delmon [19]. In our laboratory, we have already used calculations based

on Mampel's mathematical analysis to describe sigmoid curves obtained in the case of several transformations with powders : CeOHCO_3 into CeO_2 in oxygen [20], CaCO_3 decomposition [21], transformation of $\text{HGdP}_2\text{O}_7 \cdot 1.5\text{H}_2\text{O}$ into $\text{HGdP}_2\text{O}_7 \cdot 1.5\text{H}_2\text{O}$ [22]. In the present study, it has been necessary to adapt the assumptions to the case of each unique crystal with its own geometric shape, as described in the following sections.

C.1. ASSUMPTIONS OF MAMPEL'S MODEL

The assumptions of Mampel's model are a random nucleation occurring at the surface of the crystal, followed by an isotropic growth towards the centre of the crystal. The rate-limiting step is located at the internal interface (reactant/product).

Since an analytical solution for the Mampel model is very difficult to obtain except for spheres, cylinders and infinite plates, we have developed a stochastic approach of this model, based on Monte-Carlo simulations. One advantage of this approach is that it is adaptable to any crystal geometry. In order to describe our experimental data, this Monte-Carlo simulation was adapted to the hexagonal plate shape with four geometrical parameters (length L and width w of the rectangle, height h of the isosceles triangles and thickness e of the plate). One dimensionless parameter is necessary for calculations : A_{MC} which involves the ratio γ/ϕ between two kinetic constants linked to the nucleation and growth rates, defined as follows :

$$A_{MC} = \frac{4\pi\gamma}{V_m\phi} \quad (2)$$

The calculation is facilitated by the use of a variable θ_{MC} defined as :

$$\theta_{MC} = \phi V_m t \quad (3)$$

where γ is the areic frequency of nucleation ($\text{nuclei.m}^{-2}.\text{s}^{-1}$) and ϕ is the areic reactivity of growth ($\text{mol.m}^{-2}.\text{s}^{-1}$) [see also 11,19-21]. In general, when experiments are conducted in isothermal and isobaric conditions, γ and ϕ are assumed to be independent of time. These two parameters are quite different from the parameters A and θ previously defined by Mampel [14,18].

In equations 2 and 3, V_m corresponds to the molar volume of lithium sulfate monohydrate ($V_m = 6.34 \cdot 10^{-5} \text{ m}^3.\text{mol}^{-1}$).

Geometrical parameters (L , w , h and e) are determined using optical microscopy observations and the model parameter A_{MC} is adjusted in order to obtain the best fit between the theoretical and experimental curves, as explained further.

C.2. MONTE CARLO SIMULATIONS

The fractional conversion $\alpha(t)$ for a single crystal at time t is calculated using the ratio of points X_i reached by the new phase over n points uniformly distributed in the bulk of the crystal.

The point X_i is reached by the new phase if there is at least one nucleus which covers it.

Nuclei are characterized by :

- ✓ - their number,
- ✓ - their birth date,
- ✓ - their localization.

On all the surfaces and at time t , the number of nuclei is random and follows a Poisson law whose intensity is equal to $S\gamma t$. Nuclei birth dates τ_j are uniformly distributed from 0 to t . The sites of nucleation σ_j are uniformly distributed on the entire surface S .

At time t , the point X_i is reached by a nucleus born in σ_j (on the surface S) at time τ_j (τ_j being include between 0 and t) if the distance between X_i and σ_j is lower than the nucleus radius $r = \phi V_{mA}(t - \tau_j)$:

$$\|\sigma_j - X_i\| \leq \phi V_{mA}(t - \tau_j) \quad (4)$$

More details about Monte-Carlo simulation of Mampel's model can be found in [23].

C.3. IMPACT OF PARAMETER A_{MC}

In order to compare experimental and simulated curves of the rate $d\alpha/dt$ vs. α , we have defined two reduced rates which are the ratios of these rates to the value of the rate for α equal to 0.5, which leads to the following expressions of the experimental and reduced rates, denoted respectively $\omega_{\text{exp}}(\alpha)$ and $\omega_{\text{mod}}(\alpha)$:

$$\omega_{\text{exp}}(\alpha) = \frac{\left(\frac{d\alpha}{dt}\right)_{\alpha}}{\left(\frac{d\alpha}{dt}\right)_{\alpha=0,5}} \quad (5)$$

$$\omega_{\text{mod}}(\alpha) = \frac{\left(\frac{d\alpha}{d\theta}\right)_{\alpha}}{\left(\frac{d\alpha}{d\theta}\right)_{\alpha=0,5}} \quad (6)$$

For the comparison of the experimental curves to the calculated one, one can see that these two ratios should be equal ($\omega_{\text{mod}}(\alpha) = \omega_{\text{exp}}(\alpha)$) since

$$\frac{d\alpha}{dt} = \frac{d\alpha}{d\theta} \times \frac{d\theta}{dt} \quad (7)$$

the term

$$\frac{d\theta}{dt} = \phi V_m \quad (8)$$

(derived from equation 3) being eliminated in the ratio.

Figure 6 shows the influence of the model parameter A_{MC} on the Monte-Carlo simulations for a given geometrical dimensions of the crystal ($L=1630 \mu\text{m}$, $w=1420 \mu\text{m}$, $h=510 \mu\text{m}$, $e=850 \mu\text{m}$).

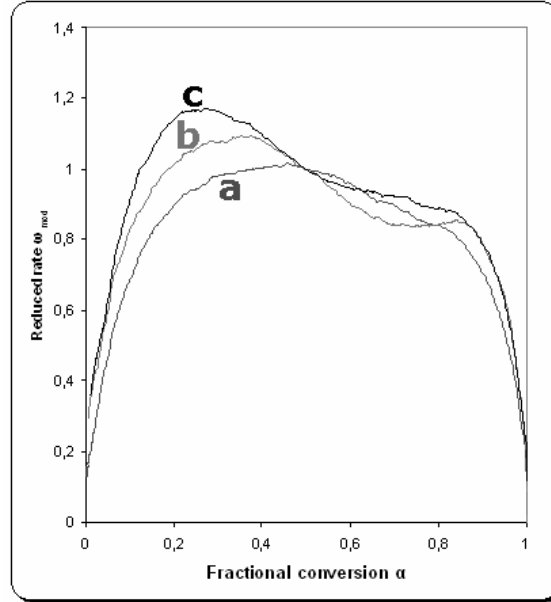


Figure 6: Influence of the parameter A_{MC} on Monte-Carlo simulation (with the same geometrical parameters) : a) $A_{MC}=15 \cdot 10^{11}$, b) $A_{MC}=35 \cdot 10^{11}$ and c) $A_{MC}=45 \cdot 10^{11}$.

C.4. COMPARISON BETWEEN EXPERIMENT AND SIMULATION

Results for two $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals are presented in this section. The mass and the geometrical dimensions of each single crystal are given in table 1.

Single crystal	Mass (mg)	L (μm)	w (μm)	h (μm)	e (μm)
A	4.7	2166	1560	575	550
B	3.3	2401	1322	396	550

Table 1: Mass and geometrical dimensions for two $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals.

Figure 7 shows the comparison between experimental and calculated curves for both single crystals. The curves are in a good agreement for $\alpha \geq 0.12$ (single crystal A) and $\alpha \geq 0.20$ (single crystal B).

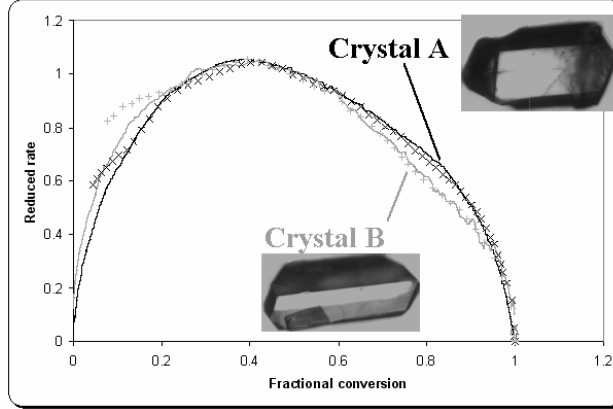


Figure 7: Comparison between experimental and calculated kinetic curves for two single crystals A and B (full line : experimental data, dashed line : calculated data).

The error on the parameter A_{MC} can be estimated using a visual criterion : lower and upper values of A_{MC} are found when calculated curves are no longer in good agreement with experimental ones.

The areic reactivity of growth ϕ can be determined using eq. 3 : the plot of θ_{MC} as a function of experimental time t (figures 8 and 9) should give a straight line with a slope equal to the product ϕV_m . For each crystal, linear relationships are given on these figures.

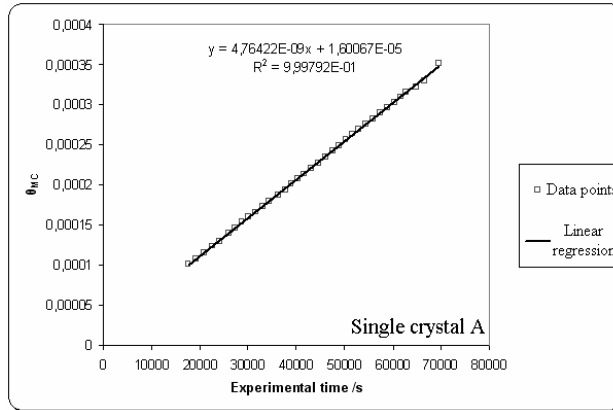


Figure 8: Plot of θ_{MC} as a function of experimental time t for single crystal A.

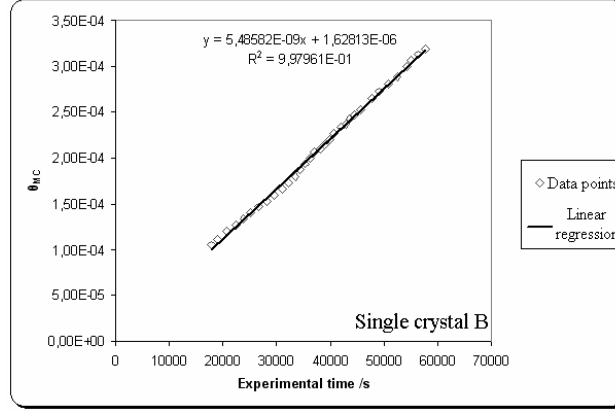


Figure 9: Plot of θ_{MC} as a function of experimental time t for single crystal B.

Then equation 2 allows to calculate the value of the areic frequency of nucleation γ knowing A_{MC} and ϕ .

The uncertainties on ϕ and γ are estimated using the limit-values of A_{MC} .

The values of γ and ϕ obtained for each single crystal are reported in table 2.

Single crystal	A_{MC}	ϕ (mol.m ⁻² .s ⁻¹)	γ (nuclei.m ⁻² .s ⁻¹)
A	(37±1)10 ¹¹	(7.36±0.17)10 ⁻⁵	1374±69
B	(66.0±0.5)10 ¹¹	(8.93±0.21)10 ⁻⁵	2975±107

Table 2: Values of A_{MC} , ϕ and γ for each single crystal.

On the one hand, the values of the areic reactivity of growth ϕ are in the same order of magnitude for both single crystals. On the other hand, the areic frequency of nucleation γ changes by a factor of more than 2 from one single crystal to the other.

Previous work about decompositions of powders (especially V. Bouineau [24] and S. Perrin [25]) have already highlighted that the nucleation process is more difficult to quantify than the growth process. In particular a very large uncertainty in γ values (deduced from the model) appears for powders.

If the values obtained for ϕ seem to be very dependent on temperature and pressure as predicted, γ appears to be also dependent on the crystal. However the good agreement between the Monte-Carlo simulations and the experimental rates indicates that the areic frequency of nucleation γ should remain constant during the complete transformation of each single crystals. This suggests that the surface properties of the two crystals should differ significantly since the nucleation process seems to be very dependent on the defects present at the crystal surfaces.

With the Monte-Carlo simulations, it thus will be possible to show if some fluctuations of the nucleation frequency γ exist over a large number of single crystals transformed in the same experimental conditions : this would explain the behaviour of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ powder in which the nucleation occurs successively at different times on the grains (cf “nucleation and anisotropic growth” model described in [12]). Monte Carlo simulations offer also the possibility to investigate the variations of γ with the temperature and the water vapour pressure and thus to better understand the mechanism of nucleation which is still not well described.

D. CONCLUSION

The kinetic curves for the dehydration of single crystals of lithium sulfate monohydrate have been described with a model involving nucleation at the surface of the crystals, followed by an isotropic growth towards the centre of the crystals. This model was chosen in agreement with both thermogravimetric experiments and observations by optical microscopy. The experimental curves are confronted to the results of Monte-Carlo simulations based on the assumptions of Mampel's model, and adapted to the real geometrical shape and dimensions of the crystals. From the best agreement between the experiments and the model, we can get information on the rates of the nucleation and growth processes through the values of the areic frequency of nucleation γ and the areic reactivity of growth ϕ . As predicted, ϕ is fully determined by the water pressure and the temperature conditions. On the contrary, γ seems to vary from one crystal to another, and further work is necessary to confirm and understand this result.

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