

## Sodium sulfate crystallisation monitoring using IR Thermography

P. Vazquez <sup>\*1</sup>, C. Thomachot-Schneider <sup>1</sup>, K. Mouhoubi <sup>2</sup>, J-L. Bodnar <sup>2</sup>, N. P. Avdelidis <sup>3,4</sup>, D.

Charles <sup>1</sup>, D. Benavente <sup>5</sup>

<sup>\*</sup> Corresponding Author

<sup>1</sup> GEGENAA EA 3795, University of Reims Champagne-Ardenne (URCA), 2 esplanade Roland Garros, 51100 Reims, France

<sup>2</sup> CATHERM, GRESPI EA 4694, University of Reims Champagne-Ardenne (URCA), Moulin de la Housse BP 1039, 51687 Reims, France

<sup>3</sup> Department of Electrical and Computer Engineering, Université Laval, G1V 0A6, Quebec City (Quebec), Canada

<sup>4</sup> Aerospace Integration Research Centre (AIRC), College Road, Cranfield, MK43 0AL, UK

<sup>5</sup> Dpto. Ciencias de la Tierra y del Medio Ambiente, Universidad de Alicante, 03080 Alicante, Spain

### Abstract

In this work, the evaporation of sodium sulfate droplets with different concentrations and at different temperatures were studied using infrared thermography (IRT). IRT allows to detect the evaporation evolution, the crystal growth and for the first time, to observe in vivo the heat release related to sodium sulfate crystallisation. A detailed study revealed that dendritic Thenardite III crystals appeared at the edge of all the crystallised droplets, though they showed a fast increase of temperature related to crystallisation only when a hydrated phase crystallised also from the droplet. The observation of the heat of crystallisation is thus directly related to the supersaturation of the droplet and consequently to temperature. In addition, IRT detection is circumscribed by the location of crystallisation. The heat can be observed and measured only when the crystallisation occurs in the interface solution – air.

**Keywords:** sodium sulfate; infrared thermography, crystallisation, heat release, supersaturation

## 1. Introduction

The crystallisation of sodium sulfate generates a wide interest in different fields. The main issue is the damage produced in porous materials, with special concern in stone buildings of cultural heritage [1]. The crystallisation pressure causes the fracturation of the pores and consequently the deterioration of the stone [2]; [3]; [4]. In addition, the field of energy storage benefits from the heat exchange during the phase transition [5]; [6]. Fundamental researches focus on this salt because of its complexity and the need for a better understanding of its crystallisation [7]; [8].

In nature, sodium sulfate appears commonly in two forms. The first is Thenardite V (anhydrous phase) which crystallises as efflorescence and produces mainly an aesthetic change on stone surface, without strong mechanical damage [9]; [10]; [11]; [12]. The second is mirabilite (decahydrated phase) which crystallises as subflorescence and produces the most severe damage on the stones [13]; [14]; [15]. Thenardite V and mirabilite are the stable phases of the sodium sulfate system, but also two metastable phases are found in determinate conditions. The first is the anhydrous Thenardite III which appears at room conditions, and the sodium sulfate heptahydrate, which is a metastable phase appearing commonly before mirabilite at low temperatures [16]; [17]; [18]; [19]; [20].

In laboratory studies, sodium sulfate materialises through several stable and metastable phases [21]. The temperature, relative humidity and concentration leading to preferential crystallisation of one phase over another. Differences are noticeable if supersaturation is obtained by solution cooling or by evaporation (e.g. [22]; [23]). In addition, factors such as the nature of the substrate,

contact angle, impurities or air currents may play a determinant role in the crystallisation of a given phase in the evaporating droplet experiments [24]. In addition, different phases can coexist within a droplet, elevating the complexity of the process [13]; [25]. This implies that the variability of the results from an evaporating brine droplet is enormous and the repeatability unknown. As mentioned by Genkinger and Putnis (2007) [22], sodium sulfate behaviour is extremely complex, and contemporary research shed light on some questions but gave rise to new ones.

This complexity has led to the use of new and accurate techniques allowing for a deeper understanding of the different processes. Environmental scanning electron microscopy (ESEM) started being used for the assessment of sodium sulfate crystallisation around year 2000 [11]; [26]. This technique threw light on salt hydration and dehydration as well as on the different phases formed. Neutron Magnetic Resonance (NMR) was introduced in recent years for the research of sodium sulfate heptahydrate crystallisation [17]; [18]. This technique allows to observe in-situ crystallisation by controlling temperature and measuring solution concentration. Thus, the supersaturation occurring at the moment of crystallisation can be recovered. Environmental XRD allows to observe in vivo the phase change and coexistence with variations in temperature and humidity [27]. Another analytic technique is Raman spectrometry, this allows to determine which phase corresponds to a fixed crystal with accurate results for sodium sulfate heptahydrate in the case of Hamilton and Menzies 2009 [28] and Linnow et al., (2013) [29]. Even more accurate techniques were utilised to study salt crystallisation, like Synchrotron X-ray tomography to observe salt crystallisation within a porous stone [30] or Rainbow Schlieren deflectometry and liquid crystal thermography [31] providing answers about heat release during crystallisation. Numerous models were introduced in order to simulate the real behaviour of different salts and mixtures, related to crystallisation pressure as well as chemical interaction [7]; [8]; [32], [33].

The use of infrared thermography (IRT) has been widely adopted over the last several years in many areas [34]; [35]. It has proven to be an important non-destructive technique for civil engineering works even for those requiring special attention as in the case of cultural heritage [36]; [37]; [38]; [39]; [40]. One of the last applications of this technique was laboratory detection of salts [41]; [42] and also in real artworks [43].

This non invasive and non destructive technique was recently used for the study of compounds crystallisation as in Parsa et al., (2015) [44] who studied CuO droplet evaporations. Vazquez et al., (2015) [45] presented the study by IRT of sodium chloride from an evaporating droplet, with the differentiation of the different phases in relation to thermosignal variation. Some chemical processes triggered heat exchange reactions such as water evaporation (endothermic reaction) or crystallisation (exothermic reaction). In some cases, this heat was not sufficient to be detected by the IRT camera. However, crystallisation from a droplet entailed a variation in shape and thus in emissivity. This variation in emissivity allowed to observe other phenomena of the crystallisation process as a great evaporation before crystallisation or creeping [45]; [46].

The main aim of this research is to deepen the analysis of sodium sulfate crystallisation by means of IRT. This assessment will be obtained by solving three questions

- What is the thermal response of sodium sulfate resulting from evaporating droplets?
- How repeatable are the results in terms of thermal response, crystal habitus and occurring phases?
- Is there a specific crystal phase associated to a specific thermal response?

## **2. Experimental Setup**

### **2.1 Measurement protocol**

In this study, the thermal effect of the crystallisation of sodium sulfate droplets was assessed by means of a FLIR SC655 long wave infrared thermography camera (7.5 –14  $\mu\text{m}$ ) with a temperature ranging from -40 to 150° C and an accuracy of  $\pm 2\%$  of the reading. The detector is an uncooled array of microbolometers. Image size is 640 x 480 pixels and the noise signal is approximately 40 mK. The recorded signal is called thermosignal (TS). The TS depends on the temperature and emissivity and is expressed in isothermal units (I.U.). All measurements were conducted using the passive IRT mode. Prior tests concluded that the optimal recording speed (frame rate) was 1 image per second throughout the test for the conditions used. The images were treated and analysed with the ThermoCAM Researcher 2.10 and ResearchID software (FLIR).

The supersaturation needed for sodium sulfate crystallisation was induced by the evaporation of the solvent. The droplets were placed on black adhesive tape (3M), which served as a reference material and was stuck to a glass slide. Its emissivity was determined to be 0.96 in the wavelength analysed by the camera [47]. The 3M tape used as support was cleaned with alcohol before each test to minimise the presence of impurities. Temperature was set constant with a cooling plate Tetech CP-061 that kept it with a precision of 0.01 °C. The droplets were dropped with a micropipette with the same quantity (5  $\mu\text{L}$ ) in each case. During the experimental setup the risks associated to environmental variations were minimised such as control of temperature and humidity of the room with  $20 \pm 2^\circ\text{C}$  and  $40 \pm 5\%$  RH respectively, none artificial or natural light source that could influence the signal and the room temperature and a closed environment with no external interferences. Nevertheless, some variables were introduced due to the manuality of some tasks such as the deposition of the droplets. For example, preliminary tests revealed that for 20 droplets the contact angle could vary between 22 and 40°.

Once the droplets crystallised, the crystal morphology and distribution were assessed by optical microscopy with the aid of an Olympus SZH-ILLB stereomicroscope with a digital Tri-CDD camera (Sony, DXP 930) and image analysis software from Microvision Instruments.

## 2.2 Experimental

Nucleation and growth experiments presented a probabilistic behaviour. Thus, experimental conditions were kept the most identical possible with six droplets tested at the same time in one support so that the differences in the crystallisation process were not due to the environmental conditions. The droplets were placed manually with the most similar spacing among them.

Sodium sulfate solutions were prepared with distilled water at 7, 14, 20 and 28% wt concentrations (purity of >99 %, Sigma Aldrich). These concentrations were chosen because 14% wt is the concentration used in natural stone standards for resistance to salt crystallisation (UNE\_EN 21370) and 28% is the concentration close to saturation at room temperature. The 20% concentration was chosen as the intermediate value and 7% as a weak concentration in order to evaluate the influence of concentration in the crystallisation. Saturation index, SI, describes the saturation degree of mineral phases. It is defined as:

$$SI = \log(IAP/K) \quad (1)$$

where IAP is the ionic product and K is the equilibrium constant. SI is calculated according to the Benavente et al., (2015) [33].

Lower and intermediate concentrations were tested in order to determine the importance of concentration in the thermal response of the evaporating droplets. In all cases, the solutions were mixed at 50°C and stirred for 1 hour to avoid crystal seeds. This temperature kept the solution far from the saturation threshold and thus it avoided the crystallisation during the droplet

deposit. The six droplets of each concentration evaporated at the same time on the cooling plate at 50, 25, 20 and 15°C respectively.

Additionally to image observation, TS was monitored in several points of the droplet. For a better comprehension, data were treated in relation to the 3M tape as follows (2):

$$\Delta TS = TS_{\text{droplet}} - TS_{3M} \quad (2)$$

Negative values corresponded to lower emissivity or/and lower temperature than the black tape. Since the highest emissivity of salt crystals is similar to 3M tape, positive values (higher than  $TS_{3M}$ ) mean only higher temperatures.

### 3. Results

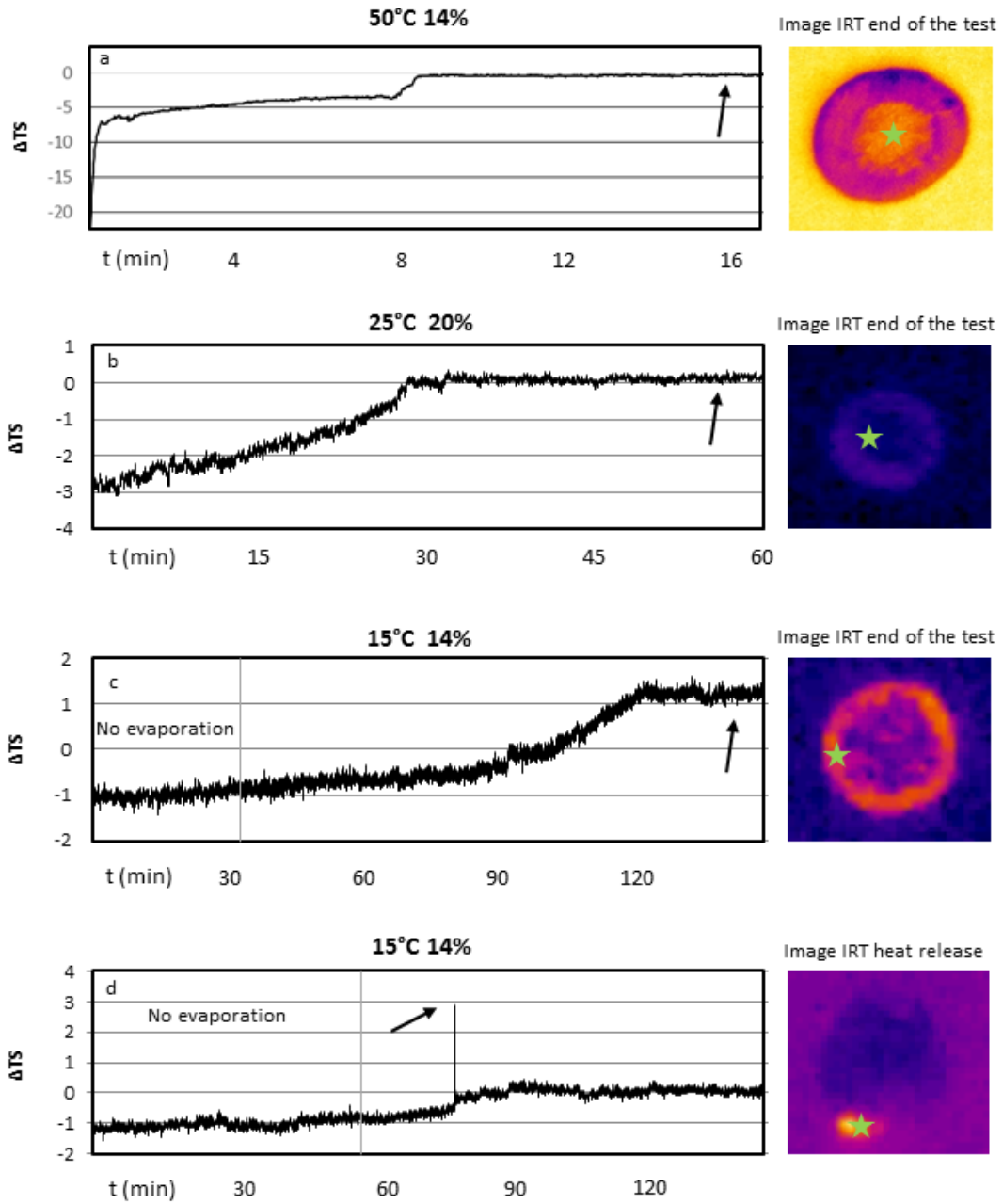
**When a droplet is placed on a substrate, it evaporates through all its surface. Within the droplet, there is a flow that replenished the edge with the liquid from the centre. When the evaporation is enough to create a supersaturation of the saline solution, small crystals appeared. These crystals are usually concentrated on the edge, due to the higher supersaturation in this area and to the flow of small crystals from the centre to the edge.**

#### 3.1 Thermal responses of droplet evaporation

The thermal response of salt solution evaporating from a droplet observed with IRT consists of three phases [45]: (I) homogeneous evaporation, (II) crystal growth driven by evaporation and (III) crystal growth fed by solution creeping. Phases I and II always appear whereas the type of salt and the environmental conditions will condition the occurrence of phase III. These three

phases were defined for NaCl droplets and they may not fit in exactly with the behaviour of other salt types.

Figure 1 shows the TS of the whole process of crystallisation of sodium sulfate at different temperatures, from the deposit of the droplet down to the stabilisation of the signal after crystallisation. The droplet evaporation (Phase I) was measured as a linear increase in  $\Delta TS$ , i.e. the  $TS_{\text{droplet}}$  (negative) approaches the  $TS_{3M}$  (zero). Sometimes a rapid slope appeared, i.e. the  $\Delta TS$  reduced drastically (Fig 1, a) that indicated the total evaporation at this point. At 50°C and 25°C evaporation started instantaneously with the deposit of the droplet on the plate. When the temperature was set at 20°C and 15°C, the evaporation did not start until several minutes later and even hours in extreme cases. After a determinate time, there was an inflexion point in which TS started increasing linearly at the same rate approximately as that at 25°C (Fig 1c, d). During this Phase I, crystals could grow within the solution, nevertheless they were not observed by the IRT due to the low crystallisation energy and the heat dissipation into the droplet. The detection limit of the IRT camera was not high enough to register these temperature variations.



200

201

## Figure 1

Fig 1: Examples of  $\Delta TS$  evolution with time of the droplet during crystallisation on the point indicated by a star. The image of the droplet corresponds to the  $\Delta TS$  indicated by an arrow on the graph. a) Droplet evaporation with no crystal formation in the measuring point; b) Similar process than in a) with different substrate temperature; c) A crystal appeared at the measuring point with positive TS at the end of the crystallisation; d) Heat release due to crystallisation (“flash”) observed as a peak of TS increase.

Phase II was characterised by a crystal growth on the edge and in the centre of the droplet. This phase starts at the inflexion point after the homogeneous increasing slope of phase I. At the end of evaporation (Fig 1 a, b c), crystals showed a slightly different TS from the reference black tape due to a low emissivity produced by the shape effect and a difference of temperature between the substrate and the environment (observed also in [45]). The environment temperature was fixed at 22°C so that if the temperature of the support was higher than that of the environment (22°C), the crystals would show colder TS and if temperature of the support was colder than the environment, crystals would appear hotter.

In some points (Fig 1 d), the heat release due to crystallisation was high enough for the observation of some early crystal formation leading to a sudden peak of TS (due to a temperature increase). This peak was called “flash” since it was observed as a photographic flash with the IRT.

Weak creeping was observed in a few cases (Phase III) [45]. As explained in Vazquez et al., (2015) [45], after Phase II, when no solution was visible with the IRT, a series of intermittent decreases of the TS around and on the previously formed crystals were observed. This indicated that evaporation was not yet complete and that stepped crystal growth or dehydration processes

were still occurring. The IRT signal recorded intermittent decrease in the TS and only when this intermittent variation stopped, was crystallisation considered to be completed.

### 3.2 Types of exothermal reactions

During a sodium sulfate droplet evaporation, in some cases an increase of temperature was recorded with IRT, corresponding to the exothermal reaction linked to crystallisation. This phenomenon called “flash” could reach a few degrees and last for a few seconds. After that, TS returned to the same or slightly higher values. The flash phenomenon started at a single point and moved with a wicking effect through the droplet. Regarding the wick movement, the flash could be divided out into three forms (Fig 2):

- **Single Ring** (Fig 2 top, Figure 3 - Video 1): it could appear before any crystal was visible in the droplet or with several crystallisations in the centre and edge of the droplet. In both cases, the solution was still visible by IRT. In this case, a starting point showed a higher TS than the rest and it started moving through the droplet edge in one direction. This direction could be clockwise or contrarily, without any priority. Once the high TS had completed part of the droplet perimeter, the temperature dropped to that of the solution and evaporation accelerated.
- **Double Ring** (Fig 2 middle): similarly to the first case, a point of the droplet edge increased its temperature. From this point, the heat propagated clockwise or in counter-clockwise directions through the droplet edge until confluence and recovery of solution temperature. The droplet continued evaporating after this process. Sometimes, the movement of the high TS was not continuous but intermittent and the whole loop could be divided into two or three steps.

- **Scanning** (Fig 2 bottom): from the first heating point, the high thermosignal spread linearly across the whole droplet like a scan. Solution remained in some parts of the droplet that continued evaporating.

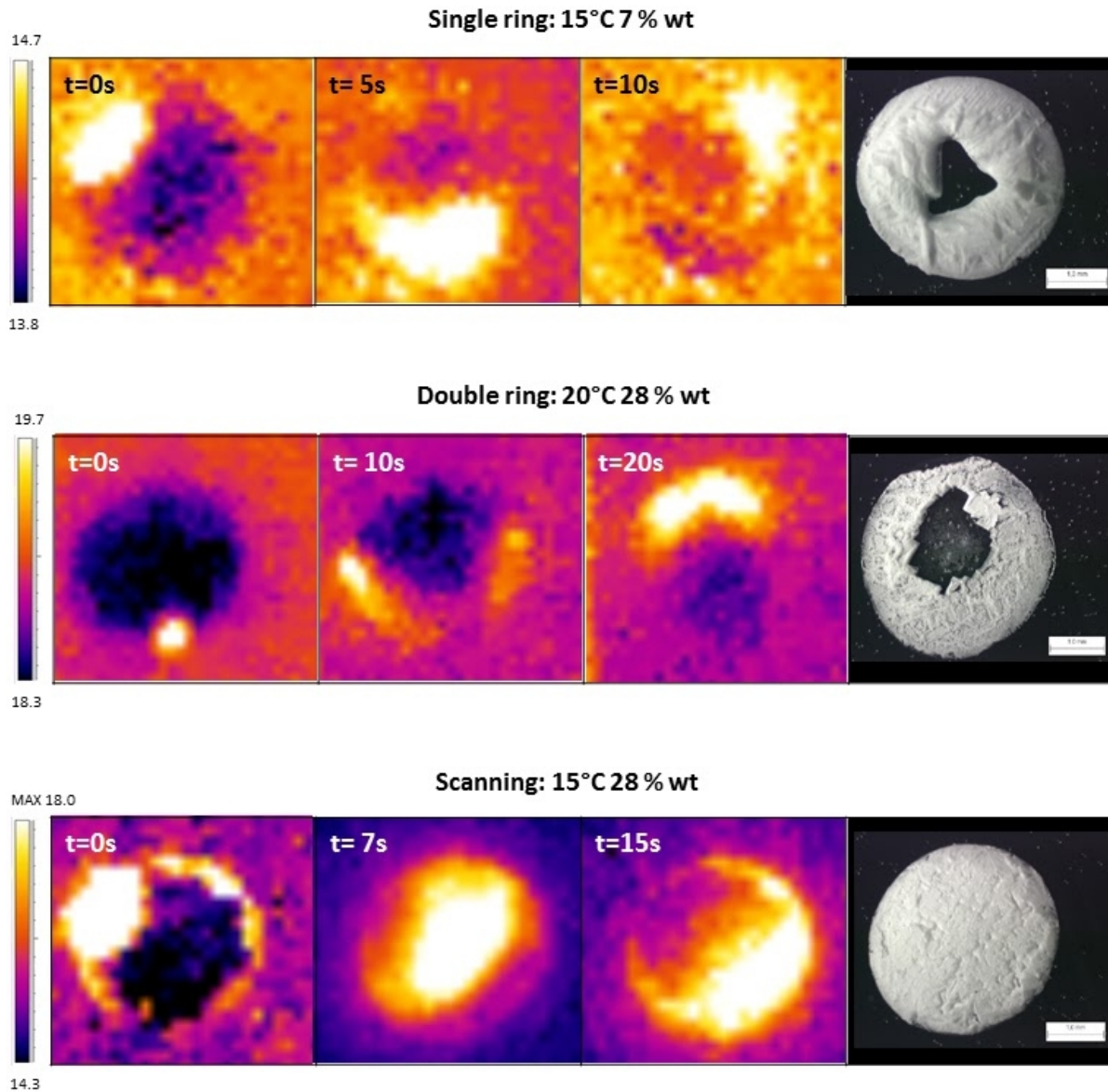


Fig 2: Different steps of flash phenomena and the corresponding crystallised droplet at the end of the evaporation viewed under magnification eye. Top: single ring; Middle: double ring; Bottom:

scanning. The crystallised droplet with white and powdery aspect corresponded to thenardite as product of dehydration of a previous hydrated phase.

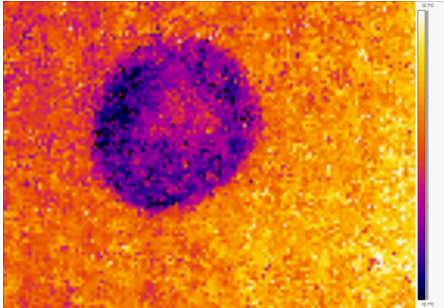


Figure 3 - Video 1: Flash with ring shape recorded in a droplet with 14% concentration at 15°C.

### 3.3 Relation between thermal response, temperature and saline concentration

For the four different temperatures (50°, 25°, 20°, and 15°C) and the four different concentrations (7, 14, 20, and 28% wt), the results of the thermal response are shown in Table 1.

Table 1: For each temperature and concentration, number of flashes over the 6 droplets tested (sudden TS increases), minimal and maximal  $\Delta TS$  measured and flash type description.

|      |                            | 7%      | 14%     | 20%     | 28%     |
|------|----------------------------|---------|---------|---------|---------|
| 50°C | N° Flash                   | 0       | 0       | 0       | 0       |
|      | Min-Max $\Delta TS$ (I.U.) |         |         |         |         |
|      | Shape                      |         |         |         |         |
| 25°C | N° Flash                   | 0       | 0       | 0       | 0       |
|      | Min-Max $\Delta TS$ (I.U.) |         |         |         |         |
|      | Shape                      |         |         |         |         |
| 20°C | N° Flash                   | 1       | 1       | 1       | 4       |
|      | Min-Max $\Delta TS$ (I.U.) | 2       | 2.2     | 2.4     | 2.2-3.6 |
|      | Shape                      | sr      | dr      | dr      | dr, sc  |
| 15°C | N° Flash                   | 4       | 2       | 2       | 3       |
|      | Min-Max $\Delta TS$ (I.U.) | 2.2-3.6 | 3.2-3.6 | 2.0-2.2 | 1.2-6.8 |

| Shape                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | dr, sc | sr | dr | sc, sr |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|----|----|--------|
| sr: single ring; dr: double ring; sc: scanning.                                                                                                                                                                                                                                                                                                                                                                                                                                            |        |    |    |        |
| At 50°C and 25°C no increase in TS was observed for any concentration. Droplets evaporated showing low TS in the whole droplet.                                                                                                                                                                                                                                                                                                                                                            |        |    |    |        |
| When temperature was set at 20°C, only one of the six droplets tested at the same time exhibited a flash phenomenon. The increment of TS was comparable for all concentrations. Values were found around 2 I.U. The most common type of flash was the ring, single in low concentrations and double in high concentrations.                                                                                                                                                                |        |    |    |        |
| At 15°C, the flash phenomena became more frequent. For all the concentrations, the number of flashes per droplet was between 2 and 4. In general, values of $\Delta TS$ were higher than those at 20°C, reaching even almost 7 I.U. for 28% concentration. The type of flash was variable, with single and double ring, and also scanning at high concentrations (Fig 1, 2).                                                                                                               |        |    |    |        |
| <b>3.3 Relation between thermal response and crystal shape</b>                                                                                                                                                                                                                                                                                                                                                                                                                             |        |    |    |        |
| The observation with naked eye revealed a difference in the type of crystals in the droplets that exhibited flash or not.                                                                                                                                                                                                                                                                                                                                                                  |        |    |    |        |
| - Droplets that did not show a flash phenomenon showed transparent and elongated crystals.                                                                                                                                                                                                                                                                                                                                                                                                 |        |    |    |        |
| Two elongated crystal shapes were found in these droplets i) transparent crystals forming aggregates in fan-shape that corresponded to Thernadite (V) [11]; [13] and ii) transparent crystals with dendritic shape that corresponded toThernardite (III). The latter owes its whitish color to small prismatic crystals (Thernadite V) that appeared on the thenardite (III) during the last evaporation process [11]; [13]; [25]; [29]; [30]. Both types of elongated crystals (fan-shape |        |    |    |        |

and dendritic) grew from the edge to the centre. Thenardite (V) is the stable anhydrous phase  
 and Thenardite (III) the metastable anhydrous phase of sodium sulfate. The thickness of this  
 ring-like crystal varied in relation to temperature and concentration. Figure 4 shows that the  
 thickness was lower at low concentrations and low temperatures, increasing linearly with  
 concentration.

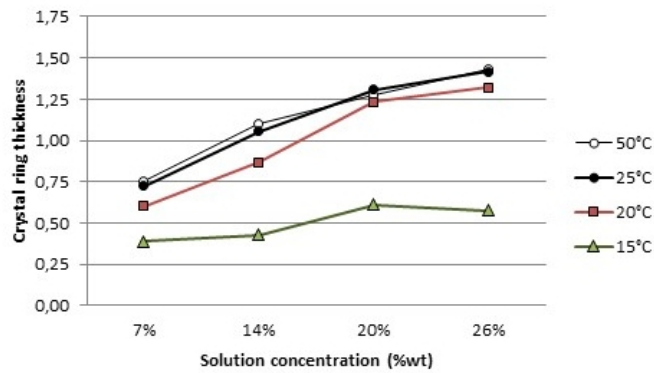
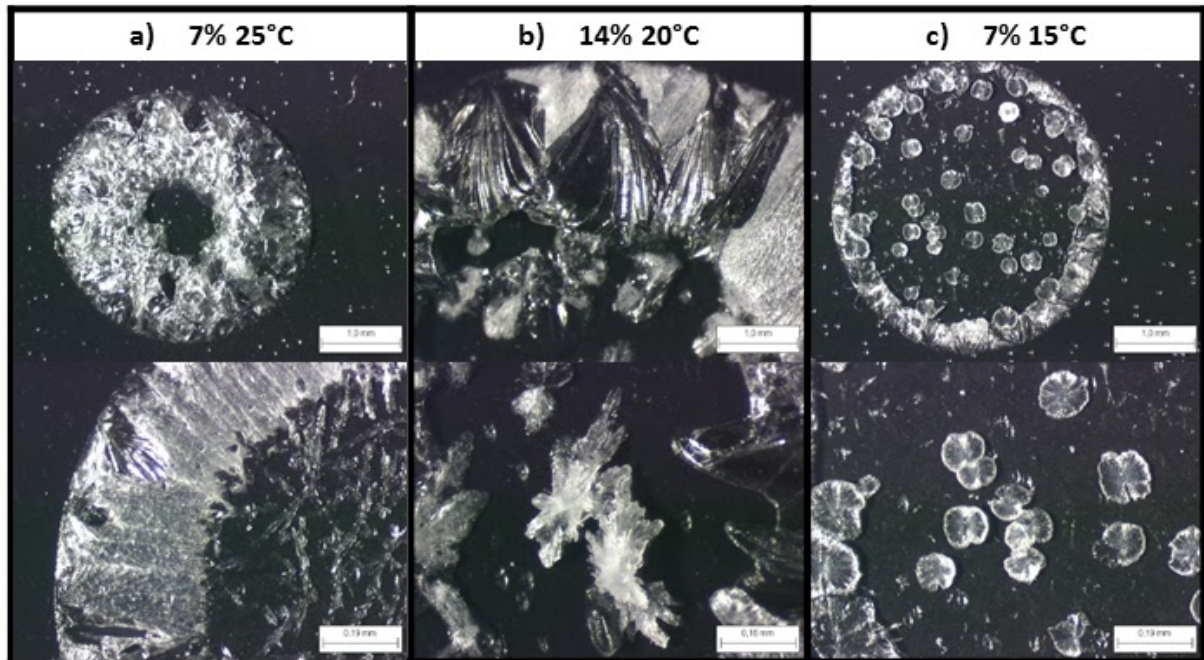


*Fig 4: Ring thickness with temperature and concentration.*



312 Fig 5: Crystal shape of droplets evaporating without flash phenomenon. Thenardite V and  
313 Thenardite III are visible in each droplet.

314

315 At 20°C, droplets that did not show a flash, appeared similar to those at 50 and 25°C, with  
316 Thenardite V transparent, with radial elongated crystals and Thenardite III from the edge to the  
317 droplet centre and, in this case, bigger crystals of Thenardite III in the centre. At 15°C, the  
318 droplets that did not experiment a flash showed lot of dogteeth on the edge (Thenardite V) and  
319 small radial crystals on the edge and in the droplet centre (Thenardite III).

320 In the case of 7 and 14% concentrations and for all temperatures, all the crystals were ordinated  
321 figuring a radial geometry towards the centre of the droplet (Fig 5). These crystals were longer  
322 with a 14% concentration and they occupied more than half of the droplet. With 20 and 26%  
323 concentrations these crystals were more chaotic in the centre, masking the radial structure  
324 converging from the edge. In the centre of the ring, small dendritic crystals appeared dispersed.

325

326 - Crystallised droplets that showed flash phenomena (ring or scanning) were white and  
327 powdery which corresponded to a dehydrated phase formed from a previous hydrated phase  
328 (Fig. 4).

329 During the tests carried out at 20°C and 15°C, transparent crystals appeared in first place (phase  
330 not recognised during the monitoring). However, after total crystallisation the crystals become  
331 white and with a powdery aspect, sometimes with geometrical remnants of transparent crystal  
332 shapes (Fig 2). This kind of white crystals are typical of stable Thenardite V as a product of  
333 dehydration indicating the existence of a previous hydrated phase. The ring flashes (simple and  
334 double) originated on the droplet edge and they moved only through the border [25]. Closer  
335 observation with the binocular microscope, focusing on the edge crystals where flash flashes  
336 originated, showed a different type of crystals from the rest of the droplet. Dendritic transparent

of Thenardite III grew among hydrated phases and remained transparent after dehydration, indicating the absence of overgrowth Thenardite V.

## **4. Discussion**

### **4.1 Droplet evaporation**

Droplets with four concentrations were evaporated at different temperatures ranging from 15°C to 50°C in laboratory conditions (22°C and 33% RH). The water evaporation enthalpy is around 40 kJ/mol and the evaporation heat around 2250 kJ/Kg. As evaporation is an endothermal process, the IRT TS is lower in the evaporating area. However, as observed in Vazquez et al., (2015) [45], the low TS of this process is not related only to the evaporation process. Droplet emissivity depends on the observation angle. For observation angles of 45 or more, the emissivity was found to decrease [48]. As evaporation proceeds, the contact angle is reduced and the droplet surface becomes flatter. This produces a homogeneous increase of the measured emissivity (Fig 2). In addition, during this study the evaporation process showed slight random variations on TS. These fluctuations were too weak and they were measured as TS noise. However, since temperature remains constant, these variations may correspond to the likely convective movements due to concentration gradients at the evaporating surface [22]; [31]; [49].

The differences of temperature between the substrate and the environment may create various crystallisation patterns due to Marangoni effects. After comparing the results obtained by Parsa et al., (2015) [44] and the results of this research, it can be stated that the differences due to Marangoni effect related to differences in temperature can be neglected. There were more variations between droplets tested at the same time in the same conditions than with droplets tested at different temperatures.

363

## 364 **4.2 Thermal response of sodium sulfate**

### 365 4.2.1 Influence of the crystal location and temperature for the detection of the exothermal 366 reaction

367

368 During phase change (liquid to solid), the temperature of the crystal remains constant.  
369 Nevertheless, this process involves a heat exchange with the surroundings that can be  
370 sometimes measured by IRT. Two options must be considered: i) the crystallisation occurs inside  
371 the droplet as in the case of faceted crystals or ii) the crystallisation occurs at the air-solution  
372 interface as in the case of the edge dendritic crystals.

373

374 i) If the crystallisation occurred inside the droplet, the heat released that could be measured by  
375 the camera corresponded to the indirect signal of the solution heating.

$$376 \quad TS \Leftrightarrow \xi_s S_d \sigma (T_s^4 - T_{env}^4) + \tau_s \xi_c S_c \sigma (T_c^4 - T_{env}^4) \quad (3)$$

377

378 Where,

379  $\xi_s S_d \sigma (T_s^4 - T_{env}^4)$  is the indirect emission

380  $\tau_s \xi_c S_c \sigma (T_c^4 - T_{env}^4)$  is the direct emission

381 TS= IRT thermosignal

382  $\xi_s$  = emissivity of the solution

383  $\xi_c$  = emissivity of the salt crystal

384 Sd: projected droplet surface

385 Sc= projected crystal surface

386  $\sigma$  = Stephan Boltzmann constant

387  $\tau_s$  = solution transmissivity

388  $T_s$  = temperature of the solution  
389  $T_c$  = temperature of the crystal  
390  $T_{env}$  = temperature of the environment

391

392 Taking into account the ratio volume crystal/volume droplet, this heating can be considered  
393 negligible. The direct transmission from the droplet to the air can also be considered insignificant  
394 because of the low transmissivity of the water. During this test, the growth of hydrated or anhydre  
395 crystals in the centre of the droplet was observed due to emissivity variations when the solution  
396 formed a film around the crystals. However, according to the above mentioned, the heat of  
397 crystallisation of crystals in the centre of the droplet was not observed by IRT.

398

399 ii) If the crystallisation occurred at the liquid-air interface, two parameters were responsible for  
400 the received signal. The heat was released in the droplet edge producing an increase of  
401 temperature of the surrounding solution. In this case, the affected volume was much lesser that  
402 in case i) and thus this area of the droplet heats up high enough to be detected by the IRT  
403 camera. Besides, there is a direct transmission from the crystal to the air that can also be added  
404 to the droplet signal.

$$405 TS \Leftrightarrow \xi_s S_d \sigma (T_s^4 - T_{env}^4) + \tau_a \xi_c S_c \sigma (T_c^4 - T_{env}^4) \quad (4)$$

406

407 Where

408  $\tau_a$  is the air transmissivity

409

#### 410 4.2.2. Supersaturation and maximum increase of temperature

411

Most of the studies of sodium sulfate thermodynamics were carried out with solutions in closed systems. In these cases, supersaturation leading to crystallisation is obtained by decreasing the temperature. During crystallisation, the heat is released and diffuses through the solution, being measured as an increase of temperature [20]; [23]; [31]; [50]. This temperature increase during crystallisation is directly related to the solution supersaturation. Espinosa et al., (2008) [23] observed an increase of temperature of 0.1°C for a supersaturation ratio of a salt in the solution of 1.8, whereas a supersaturation ratio of 7.5 implicated an increase of 11°C. Vavouraki and Koutsoukos (2012) [50] measured a maximum increase of T of 3.5°C with a relative supersaturation of 0.54 (or a saturation index (SI) of 0.19). Since there is not heat loss into the atmosphere, temperature values in a closed system were expected to be higher than in open system evaporating droplets. Nevertheless, the increase of temperature could be comparable with the results of this IRT study even if a big variation (1.6 -6.8 I.U.) was measured.

According to the observations with IRT, the highest increase of temperature appeared mainly at the beginning of the crystallisation. This agrees with other studies in closed systems that did not register other signs of heat release even with further crystallisation and its consequent increase of supersaturation [23] or that measured different heat peaks but which corresponded to different crystallisation phases [20].

In this study, more than one increase of temperature (flash) in different parts of one droplet and separated in time were observed in isolated cases. These increases were mostly in the form of ring flashes. Egan et al., (2014) [31] found a more important temperature increase during nucleation but also during dendritic crystal growth, which could explain the various flash phenomena observed.

The duration of the heat release went from several minutes [50] to more than one hour in closed systems [20]; [23], while the flashes observed in this study with IRT lasted only a few seconds.

4.2.3. Thermal behaviour and crystallisation patterns in relation to T:

Figure 6 shows the initial concentrations and temperatures and the increasing concentration pathways during evaporation.

At 50°C, all the solutions were undersaturated, with a saturation index of -1.53 for 7% to -0.73 for 28%, and the increase in concentration due to evaporation should lead to Thenardite crystallisation (Fig 6). Observation of the formed crystals showed that they are solid and transparent to quasi transparent with different shapes but all similar to Thenardite III and Thenardite V [11]; [13]; [25]; [51]. At 50°C temperature, the crystallisation enthalpy is positive for all the solution concentrations even supersaturated [52], explaining the lack of temperature increase during crystallisation. Temperature decrease was neither observed.

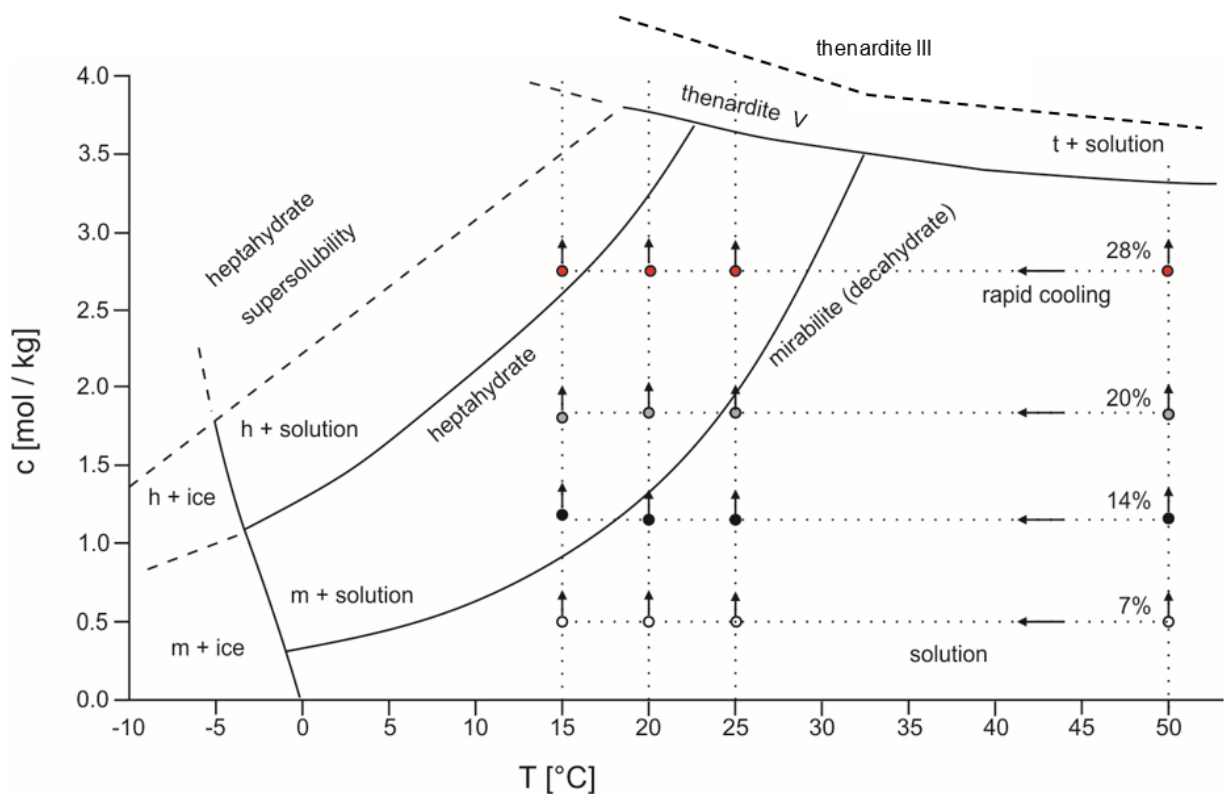


Fig. 6: Initial concentrations and temperatures of the tested droplets. The arrows indicate the fast cooling from the solution at 50°C to the temperature of the test, and the increasing concentration pathways during evaporation.

At 25°C, the solutions with 7, 14 and 20% concentrations were undersaturated in relation to mirabilite crystallisation (SI are -0.82, -0.32 and -0.03 respectively) meanwhile during the cooling of the 28% concentration the threshold of mirabilite saturation was crossed (SI= 0.17). In spite of these differences, all the droplets crystallised similarly to those at 50°C, with the ring-like shape of acicular Thenardite V and the dendritic crystals of Thenardite III on the droplet edge and isolated dendritic crystals in the centre. During evaporation at 25°C, saturation of the solution aimed at forming mirabilite. However, supersaturation aimed at producing the mirabilite nucleation was not high enough and so it was Thenardite that crystallised [7]. At this

466 temperature, no heat release was recorded with the IRT in spite of having negative enthalpies  
467 (exothermal reactions) for supersaturated concentrations. The solubility limit of Thenardite  
468 crystals is 35% [25] and due to this fact, the heat released is too weak to be detected by the  
469 camera.

470

471 At 20°C the 7 and 14% solutions remained under the mirabilite saturation threshold (-0.6 and -  
472 0.1 respectively) whereas the 20 and 28% solutions rapidly cooled down to the solubility  
473 boundaries between mirabilite and heptahydrate and then started evaporating. In this case, five  
474 of the six droplets followed the same behaviour as the ones at 50°C and 25°C with Thenardite  
475 as the predominant crystallisation phase (Phase III and Phase V). However, one of the six  
476 droplets for each concentration performed differently. These droplets showed an increase of  
477 temperature on the edge during crystallisation, with a single ring flash at 7%, a scanning flash  
478 at 14% and a double ring flash at higher concentrations. The crystallisation enthalpy was  
479 negative and with a heat release superior than at 25°C [52]. This fact could explain the detection  
480 with the IRT camera, although the high supersaturation reached in the nucleation spot, the higher  
481 energy released by metastable phases, together with a difference in the crystallised volume  
482 could enhance the recorded signal. After the test, these crystals were white and powdery,  
483 characteristic of Thenardite V formed by dehydration of hydrated phases [13]. The dehydration  
484 is produced by evaporation pulses, observed as dark intermittent signal with IRT [13]; [45]. The  
485 hydrated phase that corresponds to these crystals is however not clear. On one hand, some  
486 authors crystallised or found mirabilite at temperatures around 20°C. According to Telkes, 1952  
487 [5], at 20°C mirabilite precipitated in an spontaneous way if concentration was 3.7m, Vavourakis  
488 and Koutsoukos (2012) [50] found mirabilite after introducing mirabilite seeds at 20°C and 18°C  
489 and Donkers et al., (2015) [6] crystallised mirabilite at 22°C. On the other hand, in a 7% droplet,  
490 a truncated pyramid of four sides appeared within the rest of the crystals, reminding of  
491 heptahydrate habit found in Hamilton et al., (2008) [17] (Fig 8) . Even if most of the researches

showed the appearance of heptahydrate at low temperatures [17]; [18]; [19]; [20] others found the heptahydrate at higher temperatures (22°C) [27]; [53]. Higher temperatures allow higher concentrations that can be set for heptahydrate to crystallise [18]. All these data cast doubts about the identification or not of the crystal shown in Fig 7 as heptahydrate at 20°C.



Fig 7: Crystal showing a heptahydrate shape (according to Hamilton et al., 2008).

At 15°C the 7% solution started evaporating in undersaturated conditions meanwhile the 14 and 20% crossed the solubility limit of mirabilite (SI are 0.13 and 0.4 respectively) and the 28% crossed the heptahydrate threshold (SI=0.06). In this case, for every concentration, half of the droplets showed crystals with similar acicular and dendritic habits to those recognised as Thenardite V and III. The main difference is that in hotter conditions, crystals grow from the edge to the centre of the droplet with a fan-like shape, and at 15°C most of them grow with a circle-radial shape. This means that even at 15°C and with supersaturated conditions in mirabilite and even heptahydrate, Thenardite has 50% possibilities of crystallising. The other half of the droplets showed flash phenomena, in which the ring flash was more frequent than the scanning. The differences in temperatures measured during the flash (Table 1) revealed that in general the increase was higher at 15°C than at 20°C according to the higher exothermal enthalpy [52] and the increase of supersaturation leading to crystallisation with lower temperatures [53]. The

final crystals were also white and powdery with no well-defined shape. One case was the exception. Fig 8 shows three droplets evaporating at 15°C and with the same 14% concentration. All the three are white and powdery crystals and were produced by dehydration of a hydrated phase. However, Fig 8c shows the crystallised droplet without any flash phenomena. In the two cases in which a ring flash was observed with IRT, the droplets keep their circle shape with a very thin crystal layer (Fig 8 a and b). The flash (sudden increase of temperature) corresponds to the crystallisation of crystals at the edge following a “wicking effect” [54]. However, in the only case of dehydrated crystals that did not show a flash, the crystals grew in the centre of the droplet and nothing remained in the droplet edge. This indicates that the growth of big hydrated crystals is not related to temperature increase.

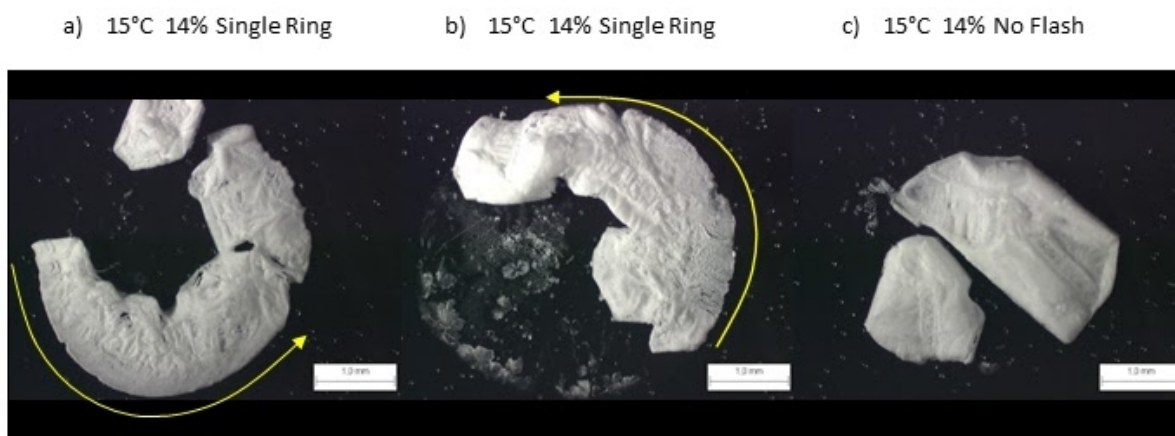


Fig 8: a, b) sodium sulfate crystals that showed ring flash phenomena and the direction of the flash during their crystallisation. c) sodium sulfate crystals of droplets that did not show any flash phenomenon.

#### 4.2.4 Determination of the phase that corresponds to the highest heat release

The droplets were observed with higher magnification in order to determinate which sodium sulfate phase was producing the flash. Strikingly, at first sight, dendritic crystals of Thenardite III were responsible of either behaviours, heat release (flash) and no heat release (no flash). In Fig

8c these dendritic crystals are not present. Fig 9 shows in detail the dendritic crystals observed in hydrated and dehydrated crystallisations.

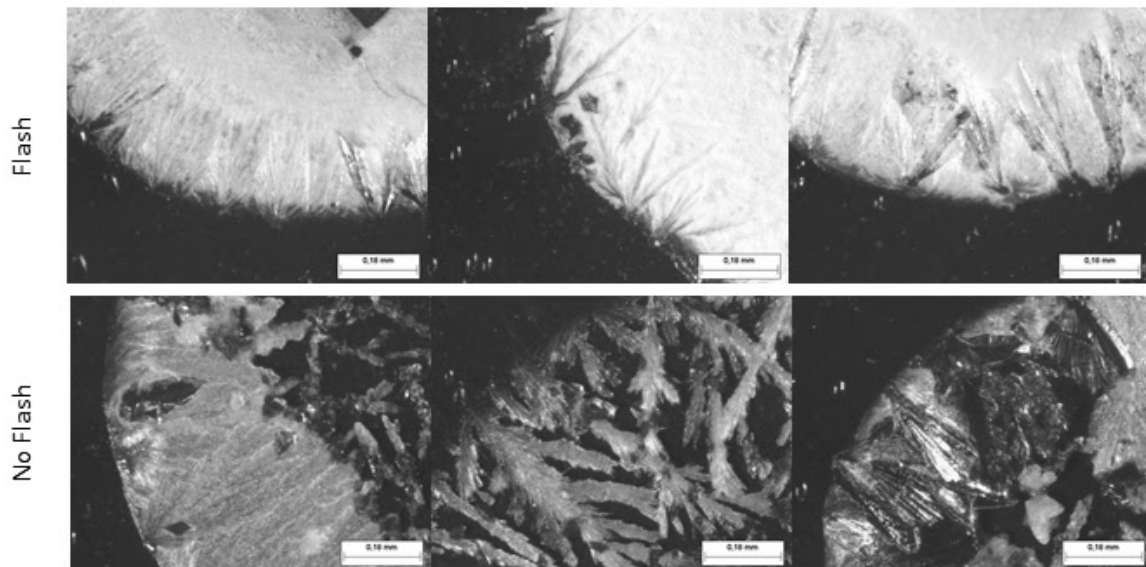


Fig 9: Detail of crystals that initiated the flash compared to those that did not flash (15°C, 14% concentration).

The crystallisation of dendritic crystals corresponding to metastable Thenardite III (paragraph 3.1) is common in environmental conditions [5]; [16]. Egan et al., (2014) [31] precipitated sodium sulfate at low temperatures and they observed an increase of temperature during nucleation but also during the growth of dendritic crystals. After the dendritic growth, they observed another more faceted phase that grew slowly.

Füredi Milhofer et al., (1990) [55] reported that in supersaturated conditions, the solutions with lower supersaturation led to dendrite precipitation while hydrated and compact crystals resulted from higher supersaturations. This explains that at higher temperatures, supersaturations only entailed the crystallisation of Phase III which needed less concentration to nucleate.

In addition, with the decrease of temperature, the nucleation threshold decreases as supersaturation increases. In both cases there is an exothermal reaction, but at 15°C the energy released is higher [52] and thus it is within the detection range of the IRT camera. This explains that for the same crystallisation phase (dendrites of phase III) high supersaturations involve a heat release higher than low supersaturations. In high supersaturations, even with the initial precipitation of phase III, hydrated crystals continued precipitating, confirming the high supersaturation needed for a hydrate to crystallise instead of the anhydrous phase.

## **5. Conclusions and perspectives**

IRT is a promising tool for salt crystallisation studies, which allows differentiating some processes that cannot be distinguished with visual methods. IRT has been successfully applied to the sodium sulfate system and has permitted to characterise the heat released of both stable and metastable phases. In this study, IRT allowed to observe in vivo the heat released during crystallisation and its relation to temperature and supersaturation.

The main purposes of this research were to determine the thermal response of sodium sulfate resulting from evaporating droplets, and if there is a specific crystal phase associated to a specific thermal response. The main findings were:

- During droplet evaporation, the first crystals that appear are the dendritic Thenardite crystals, which is the metastable phase that arises with the lowest supersaturation degrees. A heat release is produced by these dendritic crystals (Thenardite III) growing on the edge of the droplets that involved an increase of temperature in a precise small spot on the droplet edge that propagates following a wicking effect through this contact.
- At the end of the crystallisation process, a hydrated phase was observed in droplets showing flash (even if the flashes are produced by Thenardite). Due to the fact that crystals are

571 already present, and if saturation is on the threshold of the mirabilite - heptahydrate, this  
572 phase should be to crystallise.

- 573 • At lower temperatures, the mineral saturation at the moment of the first crystallisation  
574 (dendrites) and crystallisation enthalpy is higher and so is the heat released by this process.
- 575 • Thermosignal can only be observed mainly when the crystallisation takes place in the  
576 interface droplet air. However, some phenomena such as scanning did not find any  
577 explanation.

578  
579 Other of the goals of this research was to determine the flash phenomena repeatability in terms  
580 of thermal response, crystal habitus and occurring phases. Regarding the results from six  
581 droplets, further analysis will be needed to state a behaviour and a probabilistic result.  
582 Additionally, further clarification is needed regarding some questions that resulted during these  
583 research studies e.g. it is necessary to understand why heat release takes the form of scanning;  
584 to determine the statistical repeatability of one or the other phases of flash phenomena at  
585 temperatures below 20°C; and test the feasibility of IRT in other conditions, at lower  
586 temperatures to detect heptahydrate or during hydration/dehydration processes.

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**Conflict of interest**

The authors declare that there is no conflict of interest with this work.



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## **Sodium sulfate crystallisation monitoring using IR Thermography**

**Vazquez, P.; Thomachot-Schneider, C.; Mouhoubi, K.; Bodnar, J-L.; Avdelidis, Nicolas Peter ...**

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