

# The Use of Nephelometric Measurements in Crystallization Operations

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In this work the use of a nephelometric probe for the investigation on crystallization kinetics is reported. The nephelometric signal was proven to be directly proportional to the overall surface of the suspended solid. An experimental investigation on the nucleation of potassium sulphate crystals from aqueous solution was carried out by applying both polythermal and isothermal methods. The nephelometer allowed to properly detect the nucleation point both in polythermal and isothermal runs. The recorded signal during the first period of time after nucleation was related to the growth of the crystal mass by means of a simplified model. The nephelometric signal was proven to well represent the overall crystal surface evolution at the starting of the crystallization operation.

## 1. Introduction

Turbidimetric techniques have been used since long time for the characterization of the particles in a suspension. Turbidimeters, based on the detection of on-axis light attenuation, are generally adopted for the characterization of moderately concentrated solution, while nephelometers, based on the detection of angled scattered light, are more suitable for the characterization of very diluted suspensions (Richardson, 1943): this is the case of the detection of nucleation point.

The control of nucleation is crucial in industrial crystallization operations, since it affects the possibility to obtain a crystal product of the required quantity, purity and size distribution. For this reason both in the past decades (Nývlt et al., 1985) and in more recent years there has been a great interest on the experimental investigation on nucleation kinetics (Wantha and Flood, 2012) and on its theoretical modelling (Vekilov, 2010).

In this work the usefulness of nephelometric techniques for monitoring crystallization operations is investigated: the adopted instrument is a nephelometer supplied by OptSensor s.r.l. (2013). In a previous work (Parisi and Chianese, 2012) the nucleation of potassium sulphate from water solution was investigated. Both isothermal and polythermal methods (Nývlt et al., 1985) were adopted. The appearance and disappearance of crystals throughout both kinds of runs, leading to the detection of induction time and metastable zone width, respectively, are very well detected by the nephelometer. Moreover, the instrument gives a clear recording of the intensity light signal along the time after the occurring of nucleation, allowing the distinction of different regimes, ranging from the pure nucleation to the crystallites growing. An attempt to derive the nucleation and growth rate kinetics from the light intensity evolution was carried out by means of a simplified model.

## 2. Experimental apparatus and methods

### 2.1 Experimental apparatus

The experimental apparatus, described in details elsewhere (Parisi and Chianese, 2012) is shown in Figure 1: it consists of a thermostated stirred vessel, where a nephelometric probe is inserted. The probe is connected to an acquisition data system and allows the recording of the nephelometric signal and of the temperature with an accuracy of 0.1 °C.

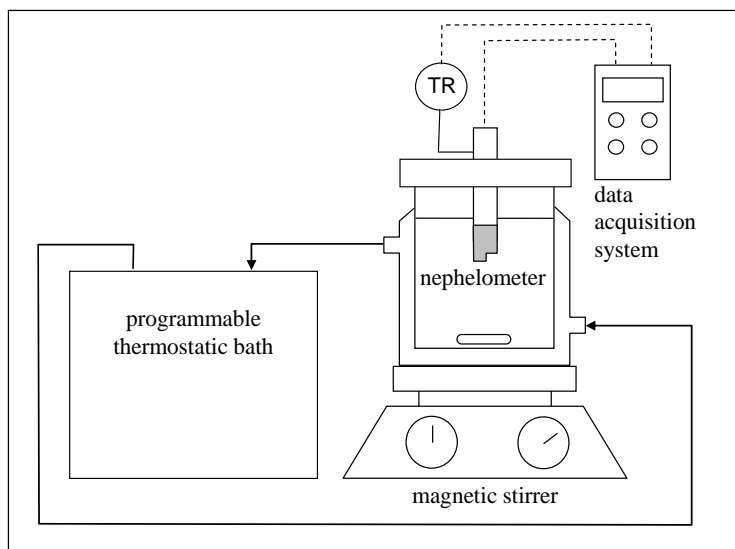


Figure 1: The experimental apparatus.

Figure 2 shows how the nephelometric probe works: a laser beam is emitted and passes through the solution perpendicularly to a detector with the aid of a mirror. When the solution is clear, the beam crosses the solution without any scattering and no signal is detected (Figure 2A). On the contrary, when crystals are suspended, the beam is scattered and the light reaches the detector (Figure 2B), where the light intensity is converted into a frequency signal: below a threshold of 12,000 Hz, the detected signal is proportional to the suspension turbidity (OptSensor, 2013).

In order to minimize the noise on the nephelometric signal due to the external light, the vessel was covered with a black cover. Nevertheless some reflected light reached the detector even in a clear solution: thus for each run it was necessary to record a baseline signal corresponding to the signal detected in absence of suspended solids.

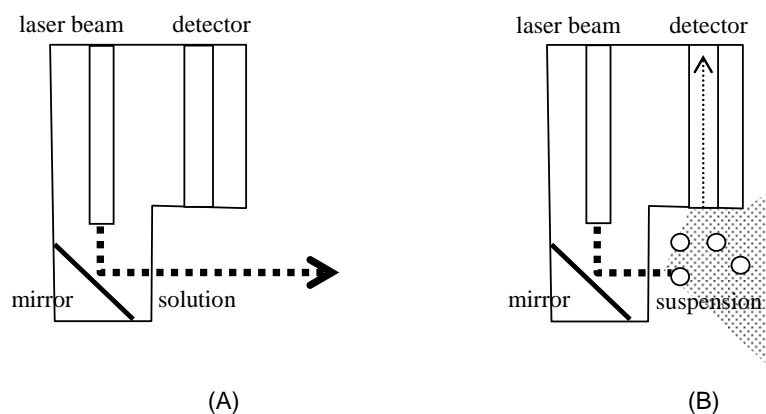


Figure 2: The nephelometric probe.

## 2.2 Experimental procedures

Both the polythermal and isothermal runs started from a saturated solution. The required amount of demineralised water and potassium sulphate were poured in the vessel and heated up to 5 °C above the expected equilibrium temperature in order to completely dissolve the salt and possibly disrupt any molecular cluster of the solute. The solution was then filtered and cooled down to the saturation temperature. Once the saturation temperature is attained, for the polythermal runs the temperature was lowered at constant cooling rate, whereas for the isothermal runs a sudden step temperature change was performed to reach the fixed operating constant temperature. In this latter case, in order to get the required temperature as fast as possible, the saturated solution was poured into an empty vessel, whose

thermostatic jacket was at the fixed final temperature, and the run started. For both the kinds of runs, nucleation was detected when the nephelometric signal showed a sharp increase.

In order to estimate the average size of the new born crystals and the slurry magma density, in some of the polythermal runs a slurry sample was withdrawn just after the nucleation detection and the crystal size distribution was measured by means of a Malvern Particle Sizer 3600 E type.

### 3. Experimental results

#### 3.1 Polythermal runs

The obtained results are summarized in Table 1. As expected, the measured metastable zone width,  $\Delta T_{\text{met}}$ , enlarges as the cooling rate increases.

Table 1: Results of the series of polythermal run:  $c = 134 \text{ kg}_{\text{K}_2\text{SO}_4}/\text{m}^3$ .  $T_{\text{eq}} = 37.8 \text{ }^\circ\text{C}$ .

ID run	b $^\circ\text{C}/\text{h}$	$T_{\text{nucl}}$ $^\circ\text{C}$	$\Delta T_{\text{met}}$ $^\circ\text{C}$
P1	5.0	27.7	10.1
P2	9.7	26.9	10.9
P3	10.8	26.2	11.6
P4	11.0	26.2	11.6

For the runs P1 and P2, a sample of the slurry was withdrawn about 5 min after nucleation, that is as soon as the volume concentration of the crystals was high enough to be detected by the Malvern Particle Sizer. By this instrument the CSD and the magma density of the slurry were measured. In both runs the mean size of the produced crystal was around  $20 \mu\text{m}$  and the measured overall distributions were very similar. The size distribution for run P1 is shown in Figure 3 the slurry sample was withdrawn and the measured volume concentration of crystals was 58 ppm.

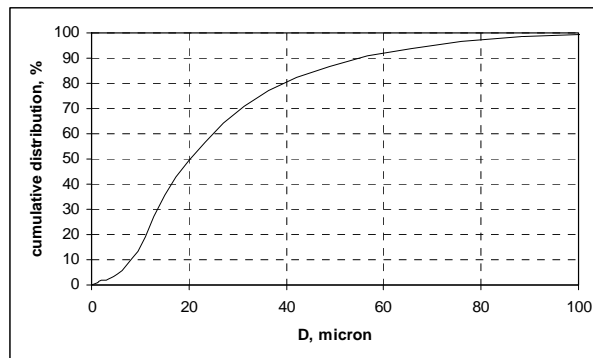


Figure 3: CSD 5 min after nucleation for run P1.

#### 3.2 Isothermal runs

The obtained results are summarized in Table 2.

Table 2: Results of the series of isothermal run:  $c = 134 \text{ kg}_{\text{K}_2\text{SO}_4}/\text{m}^3$ .

ID run	T $^\circ\text{C}$	$\sigma$	$t_{\text{ind}}$ s	$dI/dt$ Hz/s
I1	28	0.11	600	1.26
I2		0.11	750	1.42
I3		0.11	950	2.81
I4		0.09	1,200	0.42
I5	30	0.09	1,280	0.75
I6		0.09	1,390	1.33
I7		0.06	1,510	0.53
I8	32	0.06	1,650	0.18

From Table 2 it appears evident that induction time measurements do not have a good reproducibility, as expected when considering the stochastic nature of primary nucleation (Izmailov et al., 1999). Despite the great scattering of the experimental results, we may observe that the induction time decreases as the supersaturation increases, while the light intensity slope increases with the supersaturation. Both these results are as expected: in fact the detected light intensity slope is related to both the nucleation and the growth rates occurring in the first period of time after nucleation.

#### 4. The simulation model

Many models on potassium sulphate crystallization can be found in the literature: Parisi and Chianese (2003) proposed a semiempirical model for batch crystallization based on three equations representing the unsteady state heat, mass and population balances. When the crystallizer's temperature is controlled, the heat balance can be substituted by the temperature profile:

$$T = T_0 - b \cdot t \quad (1)$$

Where T is the temperature in the crystallizer, t is the time, b is the adopted constant cooling rate and the subscript 0 refers to the initial conditions.

When the slurry magma density is quite low, the solute mass balance can be expressed by the following equation:

$$M_{T0} + c_0 = M_T(t) + c(t) \quad (2)$$

where  $M_T(t)$  is the magma density, expressed in kg of solid per  $m^3$  of suspension, and  $c(t)$  is the solute concentration, expressed in kg of solute per  $m^3$  of solution.

From Eq(1) and Eq(2) and the solubility curve  $c_{eq}(T)$ , the relative supersaturation profile,  $\sigma(t)$ , can be calculated:

$$\sigma(t) = \frac{c(t) - c_{eq}(t)}{c_{eq}(t)} \quad (3)$$

The population mass balance, according to Randolph and Larson (1988), can be expressed by the equation:

$$\frac{\delta n}{\delta t} = -\frac{\delta(Gn)}{\delta L} + b(L) - d_a(L) \quad (4)$$

Where L is a characteristic dimension of the crystals, G is the linear growth rate, equal to  $dL/dt$ ,  $n(L)$  is the population density function and  $b(L)$  and  $d_a(L)$  are the birth and death density functions, respectively. For  $L > 0$  both the birth and the death density functions depend on collision mechanisms, which are negligible for very small crystals, as in the present case: as a consequence, Eq(4) can be simplified as follows:

$$\frac{\delta n}{\delta t} = -\frac{\delta(Gn)}{\delta L} \quad (5)$$

Eq(5) can be integrated with the initial condition at  $t = 0$ :

$$n(L)_0 = 0 \quad (6)$$

and the boundary condition for  $L = 0$ :

$$n(0) = \frac{B}{G} \quad (7)$$

where B is the nucleation rate. When no seeds are added, B is determined by the primary heterogeneous nucleation, that occurs when the undercooling overcomes the threshold value  $\Delta T_{met}$ , that depends on the cooling rate. Thus before nucleation B is equal to zero, while after nucleation B is a function of the supersaturation and so is G.

The magma density,  $M_T$ , is a function of the 3<sup>th</sup> moment of the population density function (Mullin, 2001): if the volume shape factor  $k_v$  does not depends on the crystal dimension, it holds:

$$M_T = k_v \cdot \rho_{cryst} \cdot \int_0^{L_{max}} n(L) \cdot L^3 dL = k_v \cdot \rho_{cryst} \cdot M_3 \quad (8)$$

Where  $\rho_{\text{cryst}}$  is the crystal density and  $M_3$  the 3<sup>rd</sup> moment of the population density function.

The proposed model was applied to represent a very short period of time after nucleation, that is 5 min. During this short period of time the changes of both temperature and concentration may be neglected, supersaturation can be considered constant and both B and G as well.

The recorded nephelometric signal is proportional to the overall surface of the crystals (Parisi and Chianese, 2012): according to Mullin (2001), the overall surface of the suspended solid is proportional to the 2<sup>nd</sup> moment of the population density if the crystal surface shape factor is constant. Thus the light intensity can be considered, on first approximation, proportional to the 2<sup>nd</sup> moment  $M_2$ :

$$I = c \cdot \int_0^{L_{\text{max}}} n(L) \cdot L^2 dL = c \cdot M_2 \quad (9)$$

Where c is a constant. The proposed model was implemented by using the gPROMs package with three fitting parameters: G, B and the “c” constant in Eq(9). In particular, the values of G and B were derived by the median size and the magma density measured by the Malvern particle sizer, and the constant c were estimated by the best fitting of the nephelometric signal profile during the first 5 min after nucleation.

In Figure 4 the experimental and the simulated nephelometric signal profiles are compared, clearly showing a very good agreement between the two.

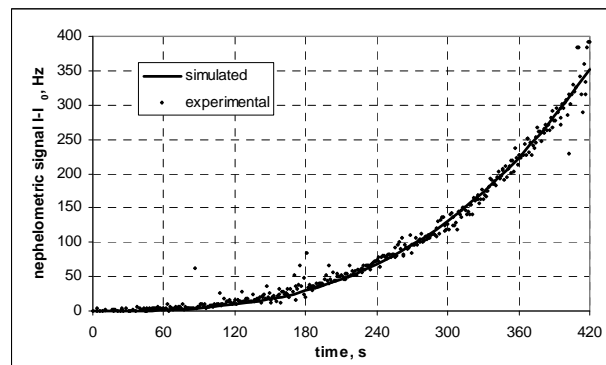


Figure 4: experimental and simulated nephelometric signal profiles for run P1.

## 5. Conclusions

The adopted nephelometer was proven to be a valid tool for the experimental investigation on the nucleation of potassium sulphate crystals from aqueous solution. It allowed an accurate detection of nucleation and of the increase of crystal mass in the first period of time after nucleation. The successful use of a simplified model, based on a direct proportionality between the recorded signal and the 2<sup>nd</sup> moment of the population density, confirmed that the nephelometric signal intensity is representative of the overall crystal surface evolution at the starting of the crystallization operation. The fitting of the nephelometric signal during the first period of time after nucleation appears, thus, a promising and easy technique to estimate the kinetics of both nucleation and growth rate at starting of crystallization process.

### List of symbols

b	cooling rate, °C/h
B	Primary nucleation rate, #/m <sup>3</sup> s
c	concentration, kg of solute/m <sup>3</sup> of solution
G	linear crystal growth rate, m/s
I	nephelometric signal intensity, Hz
$k_v$	volume shape factor
L	crystal dimension, m
$M_2$	second order moment of the population density function, m <sup>2</sup>
$M_3$	third order moment of the population density function, m <sup>3</sup>
$M_T$	magma density, kg of solid/m <sup>3</sup> of slurry
$n(L)$	population density function, #/(m <sup>3</sup> of slurry m)
t	time, s

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$t_{ind}$  induction time, s  
T temperature, °C  
 $\rho_{cryst}$  crystals density, kg /m<sup>3</sup>  
 $\sigma$  relative supersaturation

subscript

0 initial value  
eq equilibrium value  
met metastability

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