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Influence of Supersaturation, Temperature and Rotational Speed on Induction Time of Calcium Sulfate Crystallization

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Abstract: Calcium sulfate is a very important product of precipitation reactions in various branches of industry. The most common applications include building materials, impression materials in dentistry, immobilizing casts and an inactive ingredient of tablet excipients. It is also used as a drying agent and color glaze. In this paper, influence of various conditions, i.e., substrates concentration (supersaturation), temperature and rotational speed on induction time was investigated. The range of investigated parameters was 0.15–0.35 M for concentration with step of 0.05 M, 298–323 K with step of 5 K for temperature, and 1.67–8.33 s\(^{-1}\) for rotational speed with change every 1.67 s\(^{-1}\). The experiments were performed using visual and turbidimetric methods. It was proven that increase in all three investigated parameters resulted in shorter induction time. The turbidimetric method was found to be more precise, but still insufficient for concentrations below 0.15 M. Moreover, as a result of data analysis, a simple method of induction time calculation was proposed when arbitrary measurements in various concentrations are known.

Keywords: induction time; precipitation; calcium sulfate; crystallization with chemical reaction

1. Introduction

Crystallization is one of the most important processes in industry. In many branches, such as pharmaceutical [1,2], agricultural [3], and food industries [4], demand for crystalline products is constantly growing. Apart from the quantity, other requirements that need to be met for such products are high purity, specific shape and size of crystals, as well as appropriate properties [5].

Precipitation of sparingly soluble solids can be either a desired process or an undesired one, depending on the case. Phosphonic acid can be produced in a number of routes [6] among which there are several ones involving precipitation. The occurrence of such crystalline product in this case will make the purification step more difficult. Sparingly soluble solids can also deposit on the surface of equipment. In pipes it decreases their diameters by clogging [7]. When the layer of calcium sulfate is present, the heat exchange is compromised. In membrane processes it can limit the recovery in reverse osmosis systems as well as in forward osmosis systems [8,9]. To end up with a well-determined average particle size of the crystals during, e.g., the processing of cane sugar, both the nucleation and growth need to be rigorously controlled [3].

Calcium sulfate dihydrate is one of the hardly soluble salts and it is a side product, for example, in the desulfurization process of flue gases. Among various methods of SO\(_2\) emission reduction the most widely used is desulfurization. The crystal habit of the produced gypsum is an important aspect of wet limestone scrubbing, since it significantly affects the by-product dewatering properties, and consequently the economics of the whole process [5]. The crystallization of calcium sulfate has been intensely investigated
Crystals formation, although it is described by number of authors, is still an issue in industry to which full explanation has not been delivered. The more information is extracted from various perspectives, the closer one is to understanding and properly describing this phenomenon. Influence of temperature and concentration is discussed in a variety of papers, but until now, there was no report on a simple and effective way of determining induction time based on a few points of known values of solution supersaturation. In industrial practice rotational speed is an equally important parameter. Proper determination of the influence of mixing on induction time of a given compound can help to define proper working conditions.

Nucleation is the initial stage in the crystallization process [13] and is stochastic in its nature [14]. It is described as the process of random generation of those small particles of the new phase that have the ability to irreversibly overgrow to macroscopic sizes [15]. During this phenomenon, crystals of organic and inorganic substances are formed from the solution. The nucleation kinetics should be measured for better control of final crystal properties such as size distribution, purity, form, and habit.

The precipitation process is in the range of primary nucleation. Its kinetics can be measured either by adopting a metastable zone width or by induction time method [16,17]. Despite the fact that the metastable zone width method is less labor intensive, the induction time method seems to have higher accuracy and is easier to analyze [17]. The time which elapses between achievement of constant supersaturation and first observed change of phase (appearance of the first crystals) is different for each system and is called the induction time ($t_{in}$) [18]. Therefore, it is “a measure of the ability of a supersaturated solution to remain in the state of metastability” [19]. More precisely, one can define it as the sum of the time of critical nucleus formation, $t_n$, and its growth to detectable size—observed first as changing properties of solution, $t_g$ [13,16]:

$$t_{in} = t_n + t_g$$

Currently, no exact theory regarding nucleation exists, but more and more studies confirming the presence of two stages of the process could be found (Söhnel and Mullin, 1988) [20,21].

Crystal growth to detectable size can be defined in various ways, such as the first “appearance” of crystals, the onset of a change of some physical properties of solution, etc. [21]. The subjective assessment of the emergence of a new phase in solution is not very exact. Therefore, a method of accurate measurement of the nucleation phenomenon is necessary if precise data about induction period is needed. Detailed knowledge of the crystallization kinetics allows for full control of the process and achievement of the final product with desired properties: size of crystals, humidity, and purity. The detection of the new phase is indicated by the appearance of crystals as an effect of increasing size of crystal nuclei. The determination is possible as long as it exceeds a reasonable period of time. This condition arises from the limitations of many of measuring devices, which tend to fail when $t_{in}$ is smaller than 5 s [22,23]. For successful measurement of short induction time, we need very fast and sensitive devices which can measure changes in solution properties before visual confirmation.

The induction time depends on many factors. It is considerably influenced not only by the initial and process conditions such as supersaturation (concentration) and temperature, but also, among others, by mixing condition (stirring rate), type and composition of solvent [16,18,19,24].

One of the most important factors influencing induction time are ion collisions which create crystal nuclei [25]. A larger number of ions (increase in supersaturation level) in the solution increases the probability of nucleation. “The induction period decreases
exponentially with supersaturation, which suggests that the nucleation rate increases exponentially" [26].

Influence of supersaturation was investigated by a number of researchers [11,27]. Ziegenheim et al. [27] investigated precipitation kinetics of gypsum over quite a large range of concentrations: from 0.04 M to 0.2 M. Their research was mainly focused on recognition of kinetics, but they found that over this range of concentrations the induction time decreased by 2 orders of magnitude as concentration increased. Worthwhile to notice is that tested volumes were very small (50 cm$^3$) and investigated concentrations also were relatively low. Influence of volume on kinetic conditions is also reported in the literature [14], and the volumes used in the described paper reflect purely laboratory conditions.

Temperature impact was also investigated by a number of researchers. The influence of temperature on induction time of calcium sulfate was investigated in the work of Hoang et al. [7], which confirms that higher temperature favors a significant decrease in induction period. Klepetsanis et al. [28] investigated precipitation of calcium sulfate in the temperature range of 25 °C to 80 °C but the research was focused on kinetics of reaction. In this case, induction time was only used as a mean to determine precipitation kinetics. In addition, Alimi et al. [18] investigated dependence of induction time on temperature and supersaturation. From this dependence, it was possible to distinguish between the homogeneous and heterogeneous nucleation mechanisms. It was also observed that the induction period depends highly on the lattice cation/anion molar ratio. It is more important for the lower supersaturations.

In the case of mixing conditions, there is no information on such investigations. Such research is reported in this paper.

1.1. Induction Time Calculation

Mathematical considerations on induction time are based on a classical nucleation theory (CNT). Recently, many studies [29,30] have been carried out to measure gypsum induction time and described by CNT. On the other hand, there are papers confirming that gypsum precipitation is a multi-stage process and can be described by “Non-Classical Nucleation Theory” [31,32], thus making the CNT unsuitable for describing complex pathways in crystallization process [33]. There are articles in which research was conducted on the precipitation of gypsum from aqueous solutions, observing the formation of the other two forms of gypsum, namely anhydrous and hemihydrate [34]. Nevertheless, for assessment of induction time—the first observed change of phase solutions—the CNT is suitable. The induction time is defined as the time which elapsed between achievement of supersaturation and the formation of critical nuclei. Thus, one can conclude that it depends on the nucleation rate [35]. Induction time is considered inversely proportional to nucleation rate ($J$) [19] and can be expressed with the following formula:

$$ t_{in} \propto \frac{1}{J} $$

(2)

while the nucleation rate (rate of nucleus formation) is given by an Arrhenius equation:

$$ J = A \cdot \exp\left(\frac{-\Delta G}{kT}\right) $$

(3)

where:

- $k$—Boltzmann constant (J/K);
- $A$—Pre-exponential factor (-);
- $T$—Absolute temperature (K);
- $\Delta G$—Gibbs free energy for the formation of the crystalline phase (kJ/mol), which can be defined as:

$$ \Delta G = \frac{\beta \delta^3 V_m^2}{k^2 T^2 (\ln S)^2} $$

(4)
where:
- $S$—supersaturation ratio (-);
- $V_m$—molar crystal volume ($\text{m}^3/\text{mol}$);
- $\delta$—interfacial energy of the nucleus-solution system ($\text{J/m}^2$);
- $\beta$—shape factor (-).

After substitution of Equation (4) to Equation (3) and the result to Equation (1) one can obtain the following formula:

$$\ln(t_{in}) = K + \frac{\beta \delta^3 V_m^2}{k^3 T^3 (\ln S)^2} \tag{5}$$

This equation describes the curve of the induction time as a function of supersaturation but only at constant temperature. The slope of this straight line ($B$) is defined as:

$$B = \frac{\beta \delta^3 V_m^2}{k^3 T^3} \tag{6}$$

Of course, there are a lot of approaches to describe induction time. One of them is a model proposed by Söhnel [21]. It is based on interfacial tension between the crystal and aqueous solution as a fundamental parameter in modeling of both nucleation and crystal growth [18]. Söhnel proposed the following equation:

$$\log(t_{in}) = A + \frac{B}{(\log S)^2} \tag{7}$$

where $A$ is constant and $B$ is slope, given by:

$$B = \frac{\beta \delta^3 V_m^2 N_A}{(2.3RT)^3} \tag{8}$$

Equation (8) has the same form as the equation of Gibbs free energy. It is created by substituting the equation for Boltzmann constant (Equation (9)) from Equation (7) with changed logarithm base. Boltzmann constant is described as:

$$k = \frac{R}{N_A} \tag{9}$$

where:
- $R$—universal gas constant ($\text{J/mol} \cdot \text{K}$);
- $N_A$—Avogadro’s number (1/mol).

Calculation of induction time requires knowledge of certain values, namely: solution supersaturation and constant in the formula proposed by Söhnel [22]. This equation is only valid for measurements carried out at constant temperature and with varying concentration. As a consequence, all induction time calculations in this paper were carried out based on results obtained at various concentrations.

1.2. Calculation of Solution Supersaturation

For each trial the solution supersaturation was calculated. In order to do this, Equation (10) was used [5,18,23,28]:

$$S = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} - a_{\text{H}_2\text{O}^2}}{K_{sp}} = \frac{m_{\text{Ca}^{2+}} \cdot m_{\text{SO}_4^{2-}} \cdot \gamma_{\text{Ca}^{2+}} \cdot \gamma_{\text{SO}_4^{2-}} - a_{\text{H}_2\text{O}^2}}{K_{sp}} \tag{10}$$

where $a_i$, $m_i$ and $\gamma_i$ are the activity (mol/m$^3$), concentration in molality (mol/kg solvent) and activity coefficient for ingredient $i$, respectively, and $\gamma_{\text{H}_2\text{O}^2}$ is the activity of water, which can be calculated from the osmotic coefficient. $K_{sp}$ is the solubility product of gypsum.
There are many equations describing activity coefficient, but two of them are the most commonly used. They are Debye–Hückel and Bromley (modified Debye–Hückel) equation. Both equations are used for solutions of strong electrolytes but there is a small but significant difference. Namely, the first equation can be used only for small values of ionic strength while the second one provides approximation to the activity coefficient variation over the entire range of ionic strength values. It is a linear function described by the following expression [36]:

\[
\log \gamma_i = \frac{-A\gamma \cdot |Z^+Z^-| \cdot I^{0.5}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.06B) |Z^+Z^-| I}{(1 + |Z^+Z^-| I)^2} + BI + CI^2
\]  

(11)

where:
- \(z^+, z^-\) — Charge of ion (cation or anion) (-);
- \(A\gamma, \rho, C\) — Constants (-);
- \(I\) — Ionic strength (-);
- \(B\) — Individual ions values (-).

The values used in Equation (11) were taken from the work of Bromley [36] and are presented in Table 1. These values allow to determine the supersaturation of the system in the case of gypsum precipitation.

**Table 1. Values used in Bromley equation [36].**

| Constant | Value | Unit |
|----------|-------|------|
| \(A\gamma\) | 0.509 | kg\(^{1/2}\)/mol\(^{1/2}\) |
| \(\rho\) | 1 | kg\(^{1/2}\)/mol\(^{1/2}\) |
| \(C\) | 0.05 | - |
| \(B_{Ca^{2+}}\) | 0.0374 | - |
| \(\delta_{Ca^{2+}}\) | 0.119 | - |
| \(B_{SO_4^{2-}}\) | 0 | - |
| \(\delta_{SO_4^{2-}}\) | -0.4 | - |

The algorithm for supersaturation calculation is as follows. First, calculation of the ions molality in solution is performed using the equation:

\[
m_i = \frac{n_i}{m_{solvent}} = \frac{V \cdot C_i}{m_{solvent}}
\]  

(12)

where:
- \(n_i\) — Amount of moles of compound in solution (mole);
- \(V\) — Volume of solution in reactor (0.3 dm\(^3\));
- \(m_{solvent}\) — Mass of solvent (kg);
- \(C_i\) — Concentration of compound (mol/dm\(^3\));

Then the ionic strength of solution for various concentrations is calculated using the following formula:

\[
I = \frac{1}{2} \sum_{i=1}^{n} m_i z_i^2
\]  

(13)

where:
- \(n\) — Number of ions in solution;
- \(z_i\) — Charge of ion;
- \(m_i\) — Molality concentration of ion.

Next, calculation of the activity coefficient should be performed. Because of high ionic strength of investigated solutions, calculations were made based on Bromley Equation (11)
and values from Table 1. Moreover, in the formula for the activity coefficient, the absolute values of ion charges and stoichiometric coefficients of the precipitated salt were substituted. Calculations also required knowledge of individual ion values per salt. It was calculated based on the following formula:

\[
B = B_{Ca^{2+}} + B_{SO_4^{2-}} + \sigma_{Ca^{2+}} \cdot \sigma_{SO_4^{2-}}
\]

(14)

After substitution of the values from Table 1 following result was obtained:

\[
B = 0.0347 + 0 + 0.119 \cdot (-0.4) = -0.0102
\]

In the next step, the thermodynamic solubility product was calculated using empirical equation [5,18,23]:

\[
\log K_{sp} = 390.9619 - 152.6246 \log T - 12545.62 T + 0.0818493 T
\]

(15)

The solubility product depends on temperature and thus calculations were made for the whole investigated temperature range. The results are presented in Table 2. As one can notice, its value is changing with temperature.

**Table 2. Thermodynamic solubility product.**

| T (K) | log \( K_{sp} \) | \( K_{sp} \) (10^5) |
|-------|----------------|----------------------|
| 298.15 | -4.37257 | 4.24 |
| 303.15 | -4.37168 | 4.25 |
| 308.15 | -4.37527 | 4.21 |
| 313.15 | -4.38296 | 4.14 |
| 318.15 | -4.39398 | 4.04 |
| 323.15 | -4.40820 | 3.91 |

Determination of water activity value is a necessary step to calculate supersaturation. If the concentration of a soluble compound rises, the activity coefficient of water decreases below a value of 1. Activity of water should be determined using Equation (16). This correlation contains osmotic coefficient (\( \phi \)) which should be determined using Bromley theory [36]:

\[
(a_{H_2O}) = -\phi M_{H_2O} \sum v c_i
\]

(16)

where:
- \( M \)—Molar mass (kg/mol);
- \( v \)—Stoichiometric coefficient of ion of dissolved compounds (-);
- \( c \)—Concentration of compound (mol/dm^3).

Osmotic coefficient was calculated according to following formula [36]:

\[
1 - \phi = 2.303 A |z^+ z^-|^0.5 \sigma (\rho \sqrt{T}) - 2.303 (0.06 + 0.6 B) \frac{I}{2} \psi (al) - 2.303 B \frac{I}{2}
\]

(17)

where:

\[
\sigma (\rho \sqrt{T}) = \frac{3}{(\rho \sqrt{T})^3} \left[ 1 + \rho \sqrt{T} - \frac{1}{1 + \rho \sqrt{T}} - 2 \ln \left( 1 + \rho \sqrt{T} \right) \right]
\]

(18)

\[
\psi (al) = \frac{2}{al} \left[ \frac{1 + 2al}{(1 + al)^2} - \frac{ln(1 + al)}{al} \right]
\]

(19)

\[
a = \frac{1.5}{|Z^+ Z^-|}
\]

(20)
2. Materials and Methods

2.1. Solutions Preparation

Two reagents were used to prepare appropriate solutions: calcium chloride dihydrate (VWR International) and sodium sulfate (VWR International). Both of them were of analytical purity, kept under anhydrous conditions. The calculated amount of reagents was weighed on an analytical balance (accuracy +/− 0.0001 g) in a balance room and transferred quantitatively to flasks. All solutions were prepared in 0.5 dm³ flasks by dissolving salts in deionized water (Hydrolab, Poland). Prepared solutions were left in sealed glass flasks and stored in a dark and dry container. Both solutions were prepared in a number of concentrations equal to 0.15, 0.20, 0.25, 0.30 and 0.35 mol/dm³.

The preparation procedure for both visual and turbidimetric measurement was the same, although measurement was different. Equal volumes of 150 cm³ of both solutions were placed in separate vessels and agitated using magnetic stirrer at constant temperature for about 30 min to achieve thermal equilibrium. The solutions were equimolar. The mixing of two solutions (Na₂SO₄ and CaCl₂) of a given concentration took place directly in the jacked reactor (working volume: 0.3 dm³) kept at a constant set temperature using thermostat (Huber Ministat).

2.2. Measurement Procedure

Induction time was measured using two methods: turbidimetric and visual. Each measurement was repeated three times and the obtained data were averaged.

Turbidity measurements were performed using a special equipment consisting of: digital meter (MULTI 3510 IDS) for digital IDS sensor (VISO TURBO 900-P) connected to a computer via dedicated software for collecting data (MULTI LAB USER). Such set up allowed to gather results of measurement directly in a spreadsheet file in very short time intervals (1 s). Moreover, during each measurement the turbidity probe was always immersed in the solution at the same height and at the same angle. This was necessary to obtain repeatable results.

Turbidimetric method is based on measuring the critical nuclei formation with detectable size. Appearance of visible crystals (with size larger than critical size) causes changes in intensity of transmitted light along the detector [27].

In the case of visual assessment of the induction time videos were recorded by digital camera (LUMIX Quad Indicator) illustrating the turbidity of the solution over time. Based on the recorded film, the change in the solution turbidity could be determined.

During tests the influence of the following parameters on induction time were examined: concentration, temperature, and rotational speed. The following ranges were selected:

- Concentration: 0.15–0.35 M (0.05 M interval).
- Temperature: 298–323 K (5 K interval).
- Rotational speed: 1.67–8.33 s⁻¹ (1.67 s⁻¹ interval).

Each of above-mentioned parameters were examined under constant conditions. When the determining the influence of temperature the supersaturation and rotational speed were at constant level. The investigated ranges were selected in such a way that the resulting induction time was long enough to be observable and short enough to be reasonable.

3. Results and Discussion

3.1. Influence of Concentration

The first investigated parameter was concentration. All measurements were made at constant temperature 298 K and with mixing rate of 1.67 s⁻¹.

The exemplary turbidity measurement results are presented in Figure 1. As it could be observed, the higher the concentration the shorter induction time. In the case of concentration of 0.15 M the induction time was found to be equal to 160 s, for 0.20 M it was 92 s, for 0.25 M—69 s, for 0.30 M—49 s, and for 0.35 M—28 s. Change in concentration
between two neighboring values was constant and equal to 0.05 M, but difference between induction time for subsequent values of concentration becomes smaller when concentration increases. What is also quite interesting, the point at which precipitation starts is also more clearly marked with increasing concentration.

![Figure 1. Influence of concentration on induction time: • 0.15 M; ■ 0.20 M; ♦ 0.25 M; ▲ 0.30 M; × 0.35 M.](image)

In Table 3 the results of visual observations are presented. For an easier comparison between investigated concentrations a time-lapse from exactly the same time points are presented. As one can observe, with increasing concentration the turbidity of solution becomes visible faster. The pink color is a result of using colored cooling agent in the thermostat. The results obtained using both methods are similar.

In Figure 2 induction time is presented as a function of concentration. The effect is clearly visible: time decreases with increasing concentration and so the slope is negative. This result is as expected. The reason is that more concentrated solutions have a higher supersaturation and thus a higher driving force for nucleation to occur. In most research obtained points lay along a straight line \[37,38\]. In the case of the presented measurements, the result for lowest concentration is visibly out of range. The reason can be that the smallest concentration and thus supersaturation results in smaller concentration of ions and, as a consequence, the number of successful collisions is smaller. Therefore, determination of the exact moment at which turbidity increases can be hard. Excluding this one point from the chart one can obtain an almost exactly straight line (Figure 3) with Pearson’s correlation coefficient almost equal to 1. It means that the relationship between concentration (supersaturation) in the range between 0.2 and 0.35 M and induction time is linear.

After analyzing the results, the concentration of 0.25 M was chosen for further investigations.
Table 3. Comparison of turbidity of solution during precipitation for various concentrations.

| Concentration (mol/dm³) | t = 0 (s) | t = 30 (s) | t = 60 (s) |
|--------------------------|-----------|------------|------------|
| 0.15                     | ![Image](image1) | ![Image](image2) | ![Image](image3) |
| 0.20                     | ![Image](image4) | ![Image](image5) | ![Image](image6) |
| 0.25                     | ![Image](image7) | ![Image](image8) | ![Image](image9) |
| 0.30                     | ![Image](image10) | ![Image](image11) | ![Image](image12) |
| 0.35                     | ![Image](image13) | ![Image](image14) | ![Image](image15) |
Figure 2. Induction time as a function of concentration.

Figure 3. Altered induction time as a function of concentration.

3.2. Influence of Temperature

The second analyzed parameter was temperature. In this case, concentration was constant and equal to 0.25 M. Additionally, mixing rate was constant and equal 1.67 s$^{-1}$. Figure 4 presents the results of turbidimetric measurements. As one can notice, a change in induction time with change of temperature can be observed. The longest induction time (49 s) is for temperature 298 K, then it decreases to 41 s for 303 K, 35 s for 308 K, 26 s for 313 K, 18 s for 318 K down to 15 s for 323 K.

Results from the visual method confirm the correctness of the turbidimetric method. Again, for comparison, time-lapse photos taken at the same time point are presented in Table 4. The influence of temperature on induction time is again indisputable. However, it is smoother than in the case of concentration. What is interesting, the result for measurements taken at 298 K is slightly different from the measurements taken previously. There could be many reasons for such discrepancy. It could be caused by some mistakes during preparation of an initial solution, despite keeping extreme caution. In addition, some microimpurities
could be present in the reactor. However, as crystallization is a challenging process such differences in obtained results can happen due to many reasons.

As in the previous case, both methods were comparable. A noticeable difference in the turbidity of solution in Table 5 for the 30 s time-lapse exist between 303 K and 308 K. A very similar result (35 s) was also obtained from measurements using the turbidity probe.

In Figure 5 induction time as a function of temperature is presented. In comparison to Figure 2 where induction time is a function of concentration, this change is more uniform, which is also visible in the presented trend line and its equation. The slope is again negative, which gives increasing influence of temperature as its value is higher. The highest investigated temperature was 323 K as above this value the product of precipitation is no longer calcium sulfate dihydrate (gypsum) only, but calcium sulfate semihydrate is also obtained. Its presence could distort the results.

After analyzing the obtained results, a temperature of 298 K was chosen for further investigations.

3.3. Influence of Rotational Speed

The third examined parameter was rotational speed. In this case, concentration and temperature were constant and equal to 0.25 M and 298 K, respectively. In Figure 6 results of turbidimetric measurements are presented. Again, the highest value of induction time is reported for the lowest rotational speed (67 s). For rotational speeds of 3.33 s\(^{-1}\), 5.00 s\(^{-1}\), 6.67 s\(^{-1}\) and 8.33 s\(^{-1}\) the resulting induction times are 56 s, 53 s, 45 s and 41 s, respectively. For the highest rotational speed, the measuring points are very scattered which results from high turbulence.

The averaged values are illustrated in Figure 7. As expected, an increase in agitation speed causes a decrease in the induction time of calcium sulfate dihydrate crystals. However, the differences characterizing various rotational speeds are much smaller than that observed in the case of concentration and temperature dependences. The slope of the function is, as in previous cases, negative and the overall fit is at good level. The higher the rotational speed is the better the dispersion of molecules of the two species and thus the reaction can take place more effectively.
Table 4. Comparison turbidity of solution during precipitation for various temperature.

| Temperature (K) | t = 0 (s) | t = 30 (s) | t = 60 (s) |
|-----------------|-----------|-------------|-------------|
| 298             | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| 303             | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| 308             | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| 313             | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| 318             | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |
| 323             | ![Image](image16.png) | ![Image](image17.png) | ![Image](image18.png) |
Table 5. Comparison of turbidity of solution during precipitation for various rotational speed.

| Rotational Speed (s⁻¹) | t = 0 (s) | t = 30 (s) | t = 60 (s) |
|------------------------|-----------|------------|------------|
| 1.66                   | ![Image](image1.jpg) | ![Image](image2.jpg) | ![Image](image3.jpg) |
| 3.33                   | ![Image](image4.jpg) | ![Image](image5.jpg) | ![Image](image6.jpg) |
| 5.00                   | ![Image](image7.jpg) | ![Image](image8.jpg) | ![Image](image9.jpg) |
| 6.67                   | ![Image](image10.jpg) | ![Image](image11.jpg) | ![Image](image12.jpg) |
| 8.33                   | ![Image](image13.jpg) | ![Image](image14.jpg) | ![Image](image15.jpg) |

As by definition induction time is inversely proportional to nucleation rate, one can deduce that nucleation rate increases with decreasing induction time.
Figure 5. Induction time as a function of temperature.

Figure 6. Influence of rotational speed on induction time: • 1.67 (s⁻¹); ■ 3.33 (s⁻¹); ▲ 5.00 (s⁻¹); × 6.67 (s⁻¹); ♦ 8.33 (s⁻¹).

However, time-lapse photos in Table 5 taken after 60 s indicate a small change in the turbidity of the solution. Almost in all cases the solution looked similar except for 1.67 s⁻¹ where change is very subtle and 8.33 s⁻¹ where the solution is visibly more turbid. This indicates that the visual method is not precise enough to determine the induction time in this case. Small changes in the measured times for the corresponding speeds make it difficult to subjectively assess the moment at which crystallization occurs.

As by definition induction time is inversely proportional to nucleation rate, one can deduce that nucleation rate increases with decreasing induction time.
3.4. Crystal Shape Analysis

The dried gypsum precipitate was subjected to microscopic analysis. The CaSO$_4$ crystals appear to look like a fine powder. In Figure 8 microscopic photographs of calcium sulfate dihydrate for varying concentration are presented. For lowest concentration (Figure 8a) crystals are the largest. Additionally, both crystal forms reported for gypsum, namely needle-like and dove tails, can be noticed. As the concentration increases (Figure 8b–e) the observed crystals become smaller. The reason for such situation is rapid nucleation. For low values of concentration and thus supersaturation, the induction time is relatively longer, and the ions can arrange in a more orderly manner. In the case of higher concentrations, the structure of precipitate changed. This does not mean that the structure of gypsum was changed, but it means that at high concentrations (high supersaturation), spontaneous precipitation occurred, which resulted in the very fast precipitation out of the solution with very short induction time and may have resulted in inhibition of the crystals’ growth over time [39]. This resulted in the formation of a large number of crystals, but of small size.

![Graph showing the relationship between induction time and rotational speed](image.png)

**Figure 7.** Induction time versus rotational speed.

A long induction period permits the growth of larger crystals (Figure 8a) while a shorter induction period favors creation of smaller crystals (Figure 8e).

A quite different relationship can be noticed by analyzing photographs of crystals synthesized at different temperatures presented in Figure 9. As one can notice, an increase in temperature caused the precipitation of larger and larger gypsum crystals. Moreover, it can be seen that at higher temperatures (shorter induction times) a large number of polycrystals is formed. All photos show two crystalline forms of calcium sulfate dihydrate. The speed at which crystals precipitate affects their size.

For all investigated rotational speeds both forms of gypsum can also be noticed, as presented in Figure 10a–e. However, the higher the rotational speed the more aggregated crystals appear. In addition, the ratio of dovetail to needle-like shaped crystals is shifted toward dovetail shaped crystals. Additionally, a slight increase in size of particles can be observed but this is not as clear of an increase as in previous cases.
8b–e) the observed crystals become smaller. The reason for such situation is rapid nucleation. For low values of concentration and thus supersaturation, the induction time is relatively longer, and the ions can arrange in a more orderly manner. In the case of higher concentrations, the structure of precipitate changed. This does not mean that the structure of gypsum was changed, but it means that at high concentrations (high supersaturation), spontaneous precipitation occurred, which resulted in the very fast precipitation out of the solution with very short induction time and may have resulted in inhibition of the crystals' growth over time [39]. This resulted in the formation of a large number of crystals, but of small size.

Figure 8. Microscopic photographs (magnification 50×) of obtained calcium sulfate dihydrate for T = 298 K, n = 1.67 s\(^{-1}\) and various concentration: (a) C = 0.15 M; (b) C = 0.20 M; (c) C = 0.25 M; (d) C = 0.30 M; (e) C = 0.35 M.

Figure 8. Microscopic photographs (magnification 50×) of obtained calcium sulfate dihydrate for T = 298 K, n = 1.67 s\(^{-1}\) and various concentration: (a) C = 0.15 M; (b) C = 0.20 M; (c) C = 0.25 M; (d) C = 0.30 M; (e) C = 0.35 M.
polycrystals is formed. All photos show two crystalline forms of calcium sulfate dihydrate. The speed at which crystals precipitate affects their size.

Figure 9. Microscopic photographs (magnification 50×) of obtained calcium sulfate dihydrate for $C = 0.25$ M, $n = 1.67$ s$^{-1}$ and various temperatures: (a) $T = 298$ K; (b) $T = 303$ K; (c) $T = 308$ K; (d) $T = 313$ K; (e) $T = 318$ K; (f) $T = 323$ K.

For all investigated rotational speeds both forms of gypsum can also be noticed, as presented in Figure 10a–e. However, the higher the rotational speed the more aggregated crystals appear. In addition, the ratio of dove tail to needle-like shaped crystals is shifted toward dovetail shaped crystals. Additionally, a slight increase in size of particles can be observed but this is not as clear of an increase as in previous cases.

An obvious conclusion comes to mind, which is that if a specific habit of obtained crystals is desired, then depending on which process parameter(s) is modified, e.g., concentration, temperature or rotational speed, the specific requirement can be met.
Figure 10. Microscopic photographs (magnification 50×) of obtained calcium sulfate dihydrate for C = 0.25 M, T = 298 K and various speeds: (a) n = 1.67 s\(^{-1}\); (b) n = 3.33 s\(^{-1}\); (c) n = 5.00 s\(^{-1}\); (d) n = 6.67 s\(^{-1}\); (e) n = 8.33 s\(^{-1}\).

An obvious conclusion comes to mind, which is that if a specific habit of obtained crystals is desired, then depending on which process parameter(s) is modified, e.g., concentration, temperature or rotational speed, the specific requirement can be met.

4. Calculations

4.1. Supersaturation Calculation

Changes in supersaturation, ionic strength, and activity coefficient as a function of concentration and temperature are presented in Tables 6 and 7. As one can notice, ionic strength in the case of both varying concentration and temperature is above the applicability range of classic Debye–Hückel equation, hence the use of its extended version proposed by Bromley is used. The investigated range of concentrations results in supersaturation level of 4.264 to 12.505. Usually for sparingly soluble substances crystallized by means of chemical reaction, supersaturation level is very high (above 100). However, this is true for low ionic strength of solutions. In the case of high ionic strength, such as for calcium sulfate, such high supersaturation cannot be obtained, and much lower values are accepted. Change in supersaturation for constant temperature and varying concentration...
is three-fold, whereas for constant concentration and varying temperature it is very small. In the case of changing rotational speed both concentration and temperature are constant and therefore supersaturation level will be also constant.

Table 6. Supersaturation, molality, ionic strength, and activity of water for various concentration and constant temperature of 25 °C.

| Concentration (mol/dm³) | \( \frac{m_{SO_4^{2-}}}{m_{Ca^{2+}}} \) (mol/kg_solvent) | \( \frac{m_{Na^+}}{m_{Cl^-}} \) (mol/kg_solvent) | I | \( \gamma_{H_{2}O} \) | \( \gamma_{Ca^{2+}} \) | \( \gamma_{SO_{4}^{2-}} \) | S |
|-------------------------|-------------------------------------------------|---------------------------------|---|-----------------|-----------------|-----------------|---|
| 0.15                    | 0.075                                           | 0.150                           | 0.450 | 0.978           | 0.183           | 4.264           |
| 0.20                    | 0.100                                           | 0.200                           | 0.600 | 0.972           | 0.164           | 5.992           |
| 0.25                    | 0.125                                           | 0.250                           | 0.750 | 0.967           | 0.151           | 7.906           |
| 0.30                    | 0.150                                           | 0.300                           | 0.900 | 0.962           | 0.143           | 10.055          |
| 0.35                    | 0.175                                           | 0.375                           | 1.050 | 0.957           | 0.138           | 12.505          |

Table 7. Supersaturation, molality, ionic strength and activity of water for various temperature and constant concentration of 0.25 (mol/dm3).

| Temperature (°C) | \( \frac{m_{SO_4^{2-}}}{m_{Ca^{2+}}} \) (mol/kg_solvent) | \( \frac{m_{Na^+}}{m_{Cl^-}} \) (mol/kg_solvent) | I | \( \gamma_{H_{2}O} \) | \( \gamma_{Ca^{2+}} \) | \( \gamma_{SO_{4}^{2-}} \) | S |
|-----------------|-------------------------------------------------|---------------------------------|---|-----------------|-----------------|-----------------|---|
| 25              | 7.906                                           |                                                |    |                  |                 |                 |    |
| 30              | 7.980                                           |                                                |    |                  |                 |                 |    |
| 35              | 7.955                                           |                                                |    |                  |                 |                 |    |
| 40              | 8.095                                           |                                                |    |                  |                 |                 |    |
| 45              | 8.305                                           |                                                |    |                  |                 |                 |    |
| 50              | 8.582                                           |                                                |    |                  |                 |                 |    |

4.2. Calculation of Induction Time

As mentioned earlier, Equation (7) can be used to calculate induction time but only when its influence on concentration is considered. In the case of temperature impact, supersaturation as well as variable \( B \) depends on this parameter, while for the influence of mixing the temperature and supersaturation are constant. The above limitations make it impossible to calculate the induction times in all presented cases—apart from varying concentration one is reliant on measurements.

In the literature there are very few attempts made to calculate induction time. Usually, they involve many complicated steps or are not given in a straightforward way. In this paper authors present a simple way to obtain induction time of calcium sulfate at a given temperature for chosen concentration within selected range. Calculations were carried out according to the following algorithm.

Based on Equation (8) and values in Table 8 variable \( B \) was calculated. As a temperature-dependent parameter, it greatly influences the slope on the chart describing induction time as a function of supersaturation.

Table 8. Constants in equation on values B [5].

| Constant | Values          | Unit      |
|----------|-----------------|-----------|
| \( N_A \) | 6.023·10^{23}   | 1/mol     |
| \( \delta \) | 0.012           | J/m²      |
| \( R \)    | 8.3145          | J/mol·K   |
| \( V_m \)  | 7.49·10^{-5}    | m³/mol    |
| \( \beta \) | 16.755          | -         |
After substituting values from Table 8 and the selected temperature into the Equation (7), one can obtain value for parameter \( B \). Results for the whole investigated temperature range are presented in Table 9.

Table 9. Changes of value \( B \) as function of temperature.

| \( t \) (°C) | \( T \) (K) | \( B \) |
|-------------|------------|-------|
| 25          | 298.15     | 15.494|
| 30          | 303.15     | 14.740|
| 35          | 308.15     | 14.034|
| 40          | 313.15     | 13.372|
| 45          | 318.15     | 12.752|
| 50          | 323.15     | 12.169|

The curve of induction time as a function of supersaturation is described by Equation (7), in which the coefficient \( B \) comes from Table 9 while the constant \( A \) was determined using the least squares method according to the algorithm presented in Figure 11.

After substituting values from Table 8 and the selected temperature into the Equation (7), one can also read the sought values of the constants \( A \) and \( B \). In this way one can determine the induction time for various concentrations at a given temperature. In Figure 11 two cases are presented: one with all investigated values of supersaturation and one without the smallest value of investigated supersaturations, as this value has an influence on the equation for direct calculation of induction time. As one can notice, in Figure 11a the Pearson’s coefficient is quite high, but the one presented in Figure 11b is closer to unity and thus the fitting is better. Apart from this paper there exist many data on gypsum, thus if there is a need to know the induction time in a given temperature for an arbitrary concentration, then using the described method is simple and definitely less labor intensive than performing experiments. The values read from the chart are in good agreement to values obtained using the least square method.

Calculated induction times were compared with the ones obtained from the measurements in Table 10. Moreover, a standard deviation was calculated for each case. As one can see the deviations are of reasonable value—only for one concentration deviation is high. The used method of the least squares is a simple one giving comparable results as well as the equations used proved to be correct. The reason for values of relative error is probably due to high sensitivity of induction time measurement to external conditions. Despite the fact that authors made every effort to perform each trial under exactly the same
conditions including use of the same initial solutions, for each concentration one result was significantly different from the other two. This can cause a slight variation of received averaged values and some greater fluctuations in final calculations.

Table 10. Comparison of the calculated induction times with measured ones.

| Concentration (mol/dm$^3$) | Supersaturation | Average Measured Induction Time (s) | Standard Deviation | Calculated Induction Time (s) |
|---------------------------|-----------------|-----------------------------------|-------------------|-----------------------------|
|                           |                 |                                   |                   |                             |
| 0.15                      | 4.264           | 160                               | 4.81              | 195                         |
| 0.20                      | 5.992           | 92                                | 16.34             | 81                          |
| 0.25                      | 7.906           | 69                                | 6.74              | 56                          |
| 0.30                      | 10.055          | 49                                | 1.35              | 45                          |
| 0.35                      | 12.505          | 28                                | 1.47              | 39                          |

5. Conclusions

The presented paper describes precipitation of calcium sulfate dihydrate in a thermostated reactor. Influence of concentration, temperature and rotational speed is reported. Induction time was measured by means of two methods: turbidimetric and visual. Both methods gave very similar results of induction time. However, the first one proved to be more precise. Moreover, both methods have some limitations. In the case of very short induction times, it would not be possible to perform sufficiently precise measurements using either of them. Classical nucleation theory has limitations regarding gypsum because it forms different structures depending on hydration degree. This work concerns only gypsum production regardless of number of water of molecules. Measurement of induction time with a turbidimetric probe proved to be an effective and simple solution for investigated range of parameters. The turbidity change, that is also confirmed by visual method, coincides with the values obtained from measurements using the turbidity.

In this work a set of experiments concerning measurement of gypsum induction period for nucleation as a function of temperature, rotational speed and concentration was presented. During measurements a new parameter was tested, which is rotational speed. In each of these three cases, the increase in the value of the tested parameter resulted in faster precipitation of calcium sulfate dihydrate and thus shorter induction time. Better control of each parameter would allow to obtain a more desirable form of calcium sulfate dihydrate and improving its properties.

What is more, the calculation of the calcium sulfate–sodium chloride system in water was performed on the basis of available formulas and knowledge of the concentration of feed solutions. In this paper, the induction time was also determined based on the empirical equation using a simple, yet previously not reported method. The measured values are close to the calculated values, which proves the correctness of the method and application of the presented algorithm for determination of the induction time for a given temperature and desired supersaturation level without the need to perform experiments. On the other hand, the measurement of turbidity together with the use of the described equation for the time of induction could be used to determine the supersaturation of solutions in which the classic methods are not effective.

The resulting gypsum sediment was filtered and analyzed using a light microscope. In the obtained sediment samples, two different crystalline forms of gypsum could be observed, namely elongated and twining crystals. Both forms are characteristic for calcium sulfate dihydrate. From analysis of obtained photographs one can conclude, that if a specific habit of obtained crystals in desired, then, depending on which process parameter(s) is modified, e.g., concentration, temperature or rotational speed, the specific requirement can be met.
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Abbreviations

Symbols

- $a$: activity (mol/dm$^3$)
- $A$: constant (-)
- $A_y$: constant (-)
- $B$: constant (-) individual ion values (-)
- $C$: constant (-)
- $C_m$: molar concentration (mol/dm$^3$)
- $f_a$: nephelometric signal (FNU)
- $G$: growth rate (s)
- $\Delta G$: Gibbs free energy (J)
- $l$: ionic strength (mol/dm$^3$)
- $J$: nucleation rate (1/m$^3$s)
- $k$: Boltzmann constant
- $k_a$: area shape factor (-)
- $K_{SP}$: solubility product (-)
- $n$: number of moles (-)
- $N_A$: Avogadro’s number (1/mol)
- $m$: mass (kg) concentration in molality (mol/kg sol)
- $M$: molar mass (kg/kmol)
- $R$: universal gas constant (J/K·mol)
- $S$: relative supersaturation (-)
- $t_{ind}$: induction time (s)
- $T$: temperature (K)
- $V$: volume (m$^3$)
- $V_m$: crystal molar volume (m$^3$/mol)
- $z$: ion charge (-)

Greek letters:

- $\alpha$: degree of conversion (-)
- $\beta$: shape factor (-)
- $\gamma$: activity coefficient (-)
- $\gamma_s$: shear stress (Pa)
- $\delta$: constant (-) surface energy for gypsum (J/m$^2$)
- $\theta$: crystal grow rate (m/s)
- $\mu$: potential (J/mol)
- $\rho$: constant (-)
- $\sigma_a$: relative degree of supersaturation (-)
- $\sigma_c$: dimensionless coefficient being a measure of interaction between neighboring
- $\tau$: time (s)
- $\Phi$: osmotic coefficient (-)
- $\phi$: volume fraction of solid in liquid (-)
- $\nu$: stoichiometric coefficient of ion of dissolved compound

Subscripts:

- $av$: average
- $i$: i-compound
- $ng$: nano gram
- $s^{-1}$: revolution per minute
- $solv$: solvent
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