

## Antiscalants for Gypsum Precipitation in Industrial Equipments: Comparison among Different Additives

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The aim of the paper is to measure the antiscalant effect of different additives on gypsum precipitation by evaluating the induction period for nucleation. Different additives (NTMP, PBTC, citric acid, NaCl) are added to a supersaturated solution, and through a well-assessed laser light scattering technique previously devised, the induction times have been measured, and then used to estimate the activation energy for gypsum nucleation for a fixed additive concentration (0.05 g/l), with the temperature varying in the range 15 - 45°C.

A comparison among different additives allowed to confirm which is the most active in retarding gypsum scale formation, and a comparison among the estimated activation energies allowed an insight in the induction time nucleation mechanisms.

### 1. Introduction

Calcium sulphate, CaSO<sub>4</sub>, in mineral form is commonly called gypsum and occurs abundantly in many areas of the world. In natural deposits, the main form is the dihydrate. Some anhydrite is also present in most areas, although to a lesser extent. Mineral composition can be found in Table 1 (Lancia et al., 2011). The hemihydrate (stucco) is normally produced by heat conversion of the dihydrate from which 3/2xH<sub>2</sub>O is removed as vapor. The resulting powder is also known as plaster of Paris. Stucco has the greatest commercial significance of these materials. It is the primary constituent used to fabricate products and in formulated plasters used in job- or shop-site applications. About 23 million metric tons of gypsum are consumed annually (Lancia et al., 2011). About 80% is processed into the commercially usable hemihydrate. Uses of gypsum are in fabricated and/or formulated building materials, Portland cement set regulation, and agricultural soil conditioning.

Gypsum is also obtained as a by-product of various chemical processes. The main sources are from processes involving scrubbing gases evolved in burning fuels that contain sulphur (Prisciandaro et al 2010), such as coal used in electrical power generating plants, and the chemical synthesis of chemicals, such as sulfuric acid, phosphoric acid, titanium dioxide, citric acid, and organic polymers. Besides these processes, gypsum precipitation is an undesirable occurrence in several processes - e.g. sea water desalination, water distillation, industrial water recovery (Mazziotti di Celso and Prisciandaro, 2013) and hydrometallurgical operations- in which gypsum scale deposition occurs: in particular, the solubility of all calcium sulfate forms decreases with increasing temperature starting from 40°C, as reported in Figure 1, a fact that is responsible for the formation of scale mostly constituted by a mixture of calcium sulfate dihydrate (gypsum) and calcium sulfate anhydrous (anhydrite).

Table 1. Gypsum properties.

Common name	Molecular formula	Composition % <sub>w</sub>		
		CaO	SO <sub>3</sub>	Combined H <sub>2</sub> O
anhydrite	CaSO <sub>4</sub>	41.2	58.8	-
gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	32.6	46.5	20.9
stucco	CaSO <sub>4</sub> x ½ H <sub>2</sub> O	38.6	55.2	6.2

Calcium sulfate scale formation may have several disadvantages: in particular, when scales crystallize on heat transfer surfaces, they offer a resistance to the heat flow and can accumulate in pipelines, orifices and other flow passages seriously impeding the process flow. Moreover, calcium sulfate scales, together with calcium carbonate scales, are the major cause of fouling in reverse osmosis membranes, resulting in a continuous decline in desalted water production thus reducing the overall efficiency and increasing operation and maintenance costs. In this view, the comprehension of nucleation and crystal growth mechanisms of that regulate the gypsum precipitation is fundamental. An accounted technique to hinder or delay gypsum scale formation is the addition of additives in solution, which retards calcium sulfate formation. Many substances, organic as well as inorganic, have been tested as additive for their capability of retarding the unwanted gypsum precipitation process. As regards inorganic additives, aluminium ions are the most active among those studied (Saring and Mullin, 1982; Sarig et al, 1986), enhancing the degree of agglomeration of gypsum crystals and reducing the overall growth and nucleation rate. Moreover, an experimental work has showed that chloride salts (NaCl and CaCl<sub>2</sub>) influence gypsum nucleation by retarding nucleation kinetics (Prisciandaro et al, 2001). Among the organic species whose effect on gypsum precipitation was tested, polymeric additives were the most used, and mainly polyelectrolytes (Smith and Alexander, 1970; Amjad and Hooley, 1986), polyphosphates and phosphonates (Liu and Nancollas, 1975; Klepetsanis et al, 1999; Wilson et al., 1999, Prisciandaro et al., 2006-2009). All cited authors agree on the circumstance that these polymeric species are effective in retarding the kinetic of gypsum crystal nucleation and growth, and their action depends on pH and on polymer concentration. Moreover, the citric acid has been proved to have a strong inhibiting effect on gypsum nucleation (Prisciandaro et al., 2003-2005; Badens et al., 1999). Finally, various inorganic alkali solutions such as sodium hydroxide, potassium hydroxide and ammonium and sodium bicarbonate have been effectively used to remove calcium sulfate, but they are usually referred to as converting solutions, since calcium sulfate is converted to calcium carbonate or calcium hydroxide, and these are in turn removed with acid (Cowan and Weintritt, 1976). The proper selection of an antiscalant additive depends upon the water chemistry and the system design. However, the knowledge of the fundamental thermodynamic properties that regulate the crystallization, particularly the nucleation process, such as the activation energy for nucleation, is of major importance.

The study of the effects of an additive on gypsum nucleation can be carried out by evaluating the induction period, defined as the time elapsing between the onset of supersaturation and the formation of critical nuclei. this time primarily depends on solution supersaturation and temperature and is the sum of two components: nucleation time ( $t_n$ ), related to the appearance of the critical nuclei, and growth time ( $t_g$ ), connected to the growth process leading from critical nuclei to measurable crystals. Depending on the relative values of these two time periods, induction time can be influenced by nucleation alone ( $t_n \gg t_g$ , nucleation-controlled induction period), by both mechanisms ( $t_n \approx t_g$ , nucleation-and-growth-controlled induction period) or by growth alone ( $t_n \ll t_g$ , growth-controlled induction period)

This research group has tested the effect of different kind of additives to delay gypsum nucleation, and namely citric acid (CA), NTMP and PBTC; moreover, the effect of an excess of chlorine in solution was studied. In this paper, a comparison of the activation energies for gypsum nucleation estimated in the presence of different additives is reported, through the measurement of induction times, providing a method to compare the retardant effect of the tested additives.

## 2. Materials and Methods

The experimental apparatus consists of a stirred reactor with a related optical device and is schematically shown in Figure 2. The detailed description of the apparatus is reported elsewhere (Prisciandaro et al., 2001). Supersaturated solutions of calcium sulfate were prepared by mixing clear aqueous solutions of reagent-grade CaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>. The additive solutions were prepared for each level of concentration by adding in turn NTMP (C<sub>3</sub>H<sub>12</sub>NO<sub>9</sub>P<sub>3</sub> as 50% w/w solution in water), PBTC (C<sub>7</sub>H<sub>11</sub>O<sub>9</sub>P as 50% w/w solution in water, available under the commercial name of Bayhibit® AM kindly provided by Lanxess Deutschland GmbH, Leverkusen), CA (citric acid, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> anhydrous), and sodium chloride (NaCl) to bidistilled water.

After their preparation and their ions concentration determination all the solutions were filtered, by using a 0.45  $\mu\text{m}$  filter and a vacuum pump in order to eliminate all foreign material inevitably present in the solution, and then mixed directly into the reactor. The additive aqueous solution was added to the  $\text{Na}_2\text{SO}_4$  solution and then fed to the reactor. The additive concentration (namely  $C_{\text{NTMP}}$ ,  $C_{\text{PBTC}}$ ,  $C_{\text{CA}}$ ) was 0.05 g/l, while as for the effect of an excess of chlorine in solution, the excess of  $\text{Cl}^-$  ions with respect to equimolar conditions has been defined as follows:

$$E = \frac{[\text{Cl}^-] - [\text{Cl}_{\text{eqm}}^-]}{[\text{Cl}_{\text{eqm}}^-]} \quad (1)$$

where  $\text{Cl}^-$  is the molar concentration of chlorine in solution and  $\text{Cl}_{\text{eqm}}^-$  is the chlorine introduced in solution through the equimolar feed as  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . All experiments have been carried out for a fixed value of chlorine excess, namely  $E=0.5$ , that from a previous experimentation has been recognized an industrial reliable amount (Prisciandaro et al., 2001).

The supersaturation ratio was calculated considering the liquid–solid equilibrium between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions and solid  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , as described by the following equation:



so that it is:

$$\sigma = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} a_{\text{H}_2\text{O}}^2}{K_{ps}} \quad (3)$$

where  $a_J$  represents the activity of the  $J$  species ( $J = \text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and water) expressed as the product of the molality ( $m_J$ ) and the activity coefficient ( $\gamma_J$ ), and  $K_{ps}$  is the solubility product of gypsum. The concentration values of the  $J$  species were calculated by solving a numerical model based on the equilibria that take place in the aqueous solution. The activity coefficients in the supersaturated solution were calculated by using Bromley's method and are reported in detail elsewhere (Prisciandaro et al., 2006). All experiments have been carried out for the additive concentration of 0.05 g/l, or, in the case of  $\text{NaCl}$ , at a fixed chlorine excess  $E=0.5$ , with the supersaturation ratio  $S$  equal to 4.0. The temperature was varied in the range 15–45°C. The induction period was evaluated by measuring the intensity of scattered and transmitted light signals as a function of time. Such signals have been processed to evaluate  $t_{\text{ind}}$  by adopting two parallel procedures, one graphical and the other one numerical. These procedures, described in detail elsewhere (Lancia et al., 1999), gave quite similar ( $\pm 10\%$ ) results.

### 3. Results

In Figure 2 the smoothed curves of  $I_{\text{trans}}/I_0$  and  $I_{\text{sca}}/I_0$  are reported as a function of time for a supersaturation ratio  $S=4$ , in the presence of a fixed concentrations added to the solution ( $\text{CA}$ ;  $\text{NTMP}$  and  $\text{PBTC}$ ;  $C_{\text{additive}}=0.05$  g/l;  $E=0.5$ ), at the temperature of 25°C. The figure shows that the system optical properties remain unchanged until nucleation occurs in solution: then, signals of transmitted light register a modification, in particular,  $I_{\text{trans}}/I_0$  starts to decline while  $I_{\text{sca}}/I_0$  begins to grow. This change in system optical properties, which is a measure of the induction period, is clearly affected by the presence of an additive in solution.

As a matter of fact it is clear, by comparing the curves, that when an additive is added to the solution, induction time increases, and gypsum nucleation is thus retarded. The analysis of the figure shows that a chlorine excess poorly delays the nucleation,  $\text{PBTC}$  is quite effective, citric acid is a rather strong retardant, and  $\text{NTMP}$  is the strongest retardant among the studied additives.

Experimental data of induction periods for different temperatures at a fixed additive concentration were used to estimate the activation energy for gypsum nucleation according to an Arrhenius relationship:

$$t_{\text{ind}} = A \exp\left(-\frac{E_{\text{act}}}{RT}\right) \quad (4)$$

where  $A$  is a constant,  $R$  the gas constant and  $E_{\text{act}}$  the activation energy.

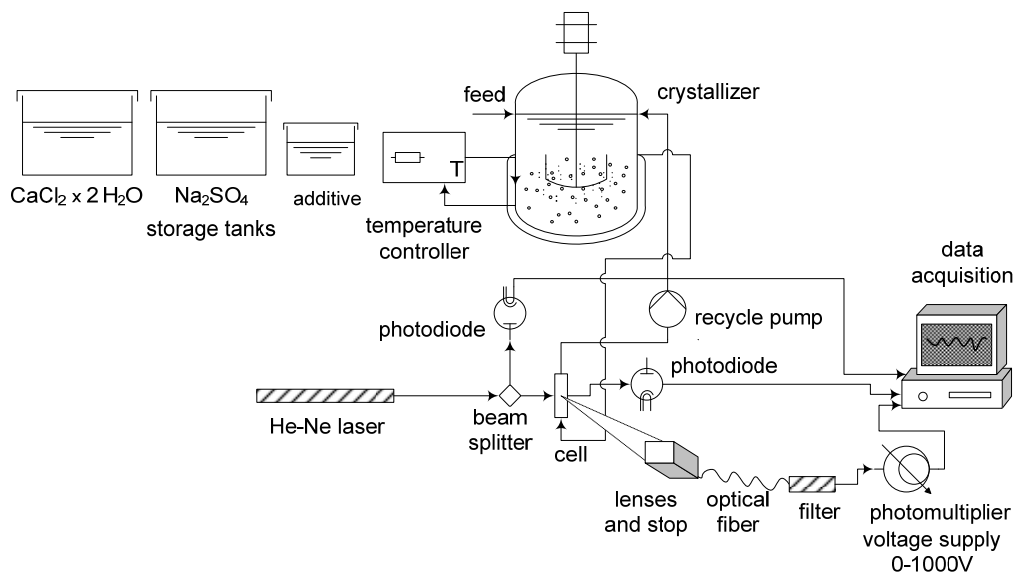


Figure 1. Gypsum precipitation apparatus.

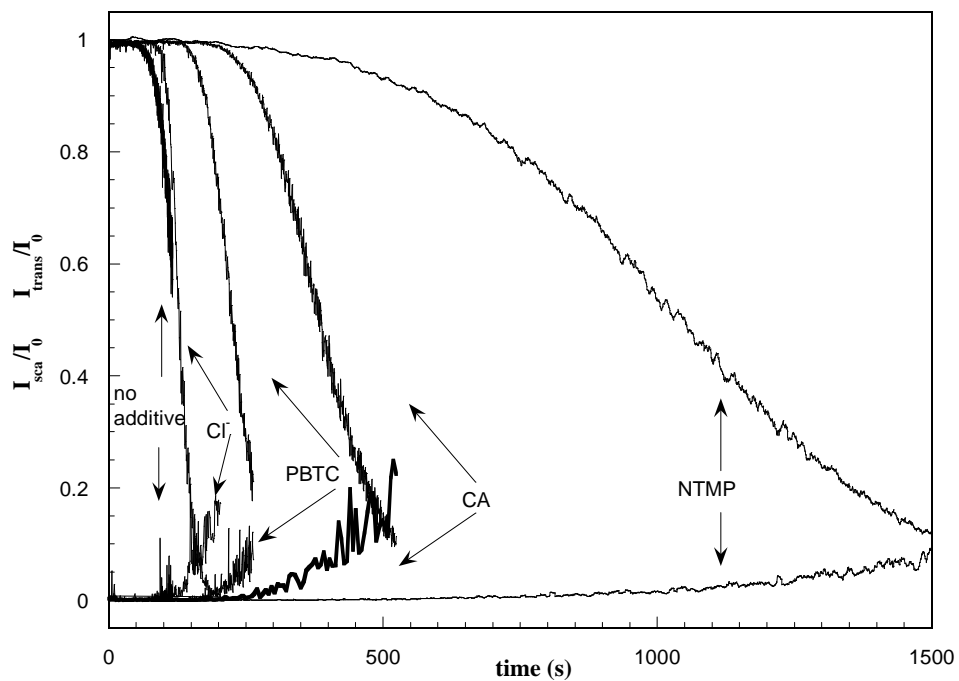


Figure 2. Intensities of the transmitted light ( $I_{trans}/I_0$ , upper curves) and scattered light ( $I_{sca}/I_0$ , lower curves) as a function of time for different additives;  $S=4$ ,  $T=25^\circ\text{C}$ ,  $E=0.5$ ,  $C_{additive}=0.05\text{ g/l}$ .

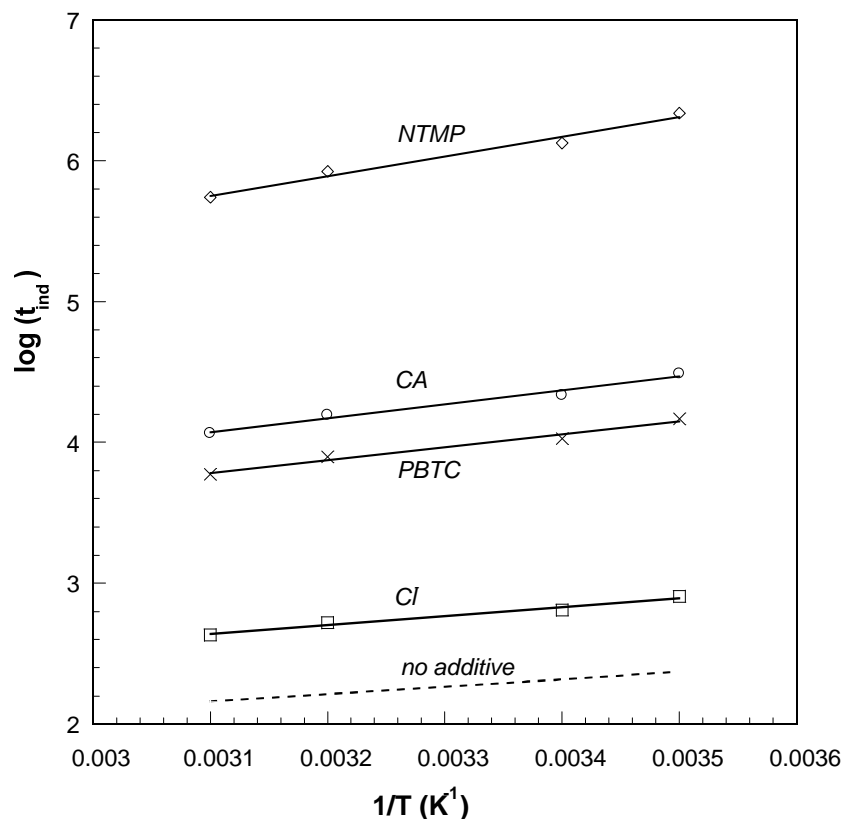


Figure 3. Induction period as a function of the inverse of the absolute temperature for different additives;  $S=4$ ,  $E=0.5$ ,  $C_{\text{additive}}=0.05$  g/l.

Results are showed in Figure 3, confirming that the tested additive are active in the following order: NTMP>CA>PBTC> Cl<sup>-</sup>. Moreover, Eq. (4) is reported as a continuous line in Figure 3; from the slopes of these straight lines the values for the activation energies reported in Table 2 have been obtained. The analysis of the Table reveals that the activation energy (*i.e.* the slope of straight lines) is not strictly connected to the retardant effect of the additive; as a matter of fact it can be observed that the activation energy is the same in the absence of any additive and in the presence of NTMP ( $E_{\text{act}}=30$  kJ/mol), that is the strongest among the tested additives. Furthermore, the activation energy is quite similar when the additive is PBTC or Cl<sup>-</sup> ( $E_{\text{act}}=50$  kJ/mol), that are the less actives among those studied, but higher than in the absence of any additive. The interpretation of this behavior can be found in the action mechanism of the additive, that can be directed toward the inhibition of one of the two mechanisms composing the nucleation time, *i.e.* the nucleation or the growth: Tadros and Mayes (1997), report that a common consensus in the literature is that diffusion-controlled crystal growth processes are associated with activation energy of about 5 kcal/mol ( $\approx 21$  kJ/mol), while reaction controlled growth is associated with higher values ( $>10$  kcal/mol  $\approx 42$  kJ/mol). Therefore, when CA or NTMP are added in solution, the nucleation time is nucleation controlled, but the action of the additive, even if marked, do not change the energy barrier to overcome the critical nuclei, and the activation energy remains almost equal as in the absence of any additive in solution; on the contrary, when PBTC is added in solution or when an excess of chlorine is realized in the reaction vessel, the mechanism changes, and the induction period is controlled by growth. In this case, the retardant effect of the additive is less marked.

Table 2. Activation energy for gypsum nucleation.

Additive	Concentration (g/l)	S	$E_{\text{act}}$ (kJ/mol)
none	-	4	30.0
Cl <sup>-</sup>	$E=0.5^a$	4	49.7
CA	0.05	4	26.9
NTMP	0.05	4	30.3
PBTC	0.05	4	49.9

<sup>a</sup>As defined in Eq. (1)

#### 4. Conclusions

In this paper, the effect of different additives (CA, NTMP, PBTC and NaCl) on gypsum nucleation kinetics is studied at  $T=15-45^{\circ}\text{C}$  and at additive concentration levels in the reactor of 0.05 g/l. Experimental results have been used to estimate the activation energy for the nucleation process. An a posteriori analysis allowed to understand the governing mechanism in nucleation kinetic, i.e. the growth of nuclei.

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