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Retardant effect of different additives on gypsum nucleation

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The main object of the present paper is the measurement of the induction period for gypsum nucleation when NTMP, citric acid and PBTC are separately added in solutions as additives, by using a well-assessed laser light scattering technique previously devised for the measurement of induction times. The measured induction period values are used to estimate the values for the interfacial tension between gypsum crystals and the mother solution for the additive concentration level of 0.01 g/L at the fixed temperature T=25°C. The obtained values are then compared to those estimated in the absence of any additive in the mother liquor, showing that NTMP is the stronger retardant among those studied, at least in the tested experimental conditions.

1. Introduction

Gypsum (calcium sulfate dehydrate) is a sparingly soluble salt whose precipitation is unwanted in several processes, such as sea water desalination, water distillation, industrial water recovery in cooling tower technology and hydrometallurgical operations. In such processes, gypsum scale deposition may have several disadvantages: scales offer a resistance to the heat flow when crystallize on heat transfer surfaces and they can accumulate in pipelines, orifices and other flow passages seriously impeding the process flow; moreover, calcium sulfate scales constitute, together with calcium carbonate scales, the major cause of fouling in reverse osmosis membranes. An accounted technique to hinder or delay gypsum scale formation is the addition of additives in solution, which retards calcium sulfate formation. These compounds are added to any given treatment in very small quantities (*ppm*) so they are called "threshold inhibitors" to describe the mechanism of scale inhibitor at sub-stoichiometric ratios. This threshold effect is explained by an adsorption of the inhibitor onto the crystal growth sites of sub-microscopic crystallite which are initially produced in the supersaturated solution, interfering with crystal growth and altering the morphology of those that grow. This process can prevent crystal growth or at least delay it for

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prolonged periods of time. Therefore, scale inhibition by threshold inhibitor is based on kinetic and not thermodynamic effects (Amjad, 1996). The proper selection of an antiscalant additive depends upon the water chemistry and the system design. A number of investigation have reported that the precipitation of calcium sulfate is significantly reduced in the presence of water soluble additives such as special type of polymers/copolymers with carboxyl groups (Lioliou *et al.,* 2006), organophosphorus compounds derivative of phosphonic acid (Klepetsanis *et al.,*1998; Liu and Nancollas, 1973; Demadis *et al*., 2004), organic phosphate esters (El Dahan *et al*., 2000), citric acid (Prisciandaro *et al*., 2003), anionic and cationic surfactants (Mahmoud *et al.,* 2004) and some metal ions (Hamdona *et al*., 2007). Among phosphonates, the nitrilotri-methylene phosphonic acid (NTMP) is used as a cost-effective gypsum scale inhibitor in circulating cooling water treatment, industrial boilers and heat exchangers (Klepetsanis *et al.,* 1998). Due to its high complexation capacity toward Ca^{2+} and Mg^{2+}, the 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) is also widely used as an inhibitor of corrosion and to avoid the formation of calcite and gypsum scale deposits in boilers and refrigeration circuits (Salvado *et al*., 1999; Lanxess, 2005). In Figure 1 is reported the schematic representation of the three additives used in this work as inhibitors of the nucleation of gypsum.

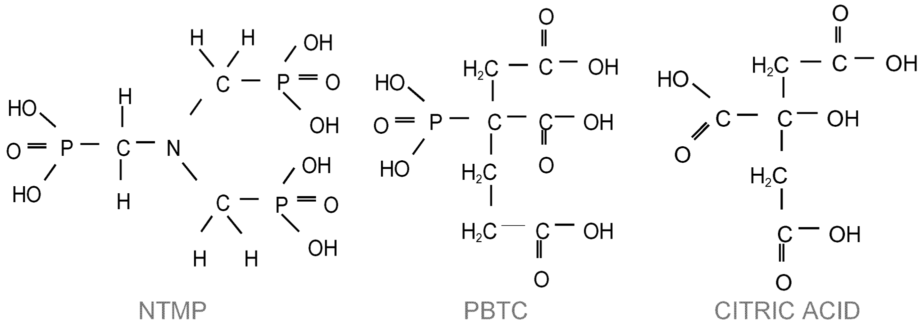

Figure 1. Additives used as inhibitors for gypsum nucleation.

The study of the effect of an additive on the gypsum nucleation can be carried out by evaluating the induction period (t_{ind}) defined as the time that elapses between the onset of supersaturation and the formation of critical nuclei, or embryos. This time primarily depends on solution supersaturation and temperature and from its dependence on supersaturation it is possible to determine the interfacial tension (γ_S) among crystals and the surrounding solution.

The main object of the present paper is the measurement of the induction period for gypsum nucleation when NTMP, PBTC and citric acid are singly added in solutions as an additive at 25°C, by using a well-assessed laser light scattering technique for the measurement of t_{ind} previously devised (Lancia *et al.,* 1999).

The measured induction period values are used to estimate the values for the interfacial tension between gypsum crystals and the mother solution for each additive concentration level. The obtained values are then compared to those estimated in the absence of additives in the mother liquor (Lancia *et al.,* 1999).

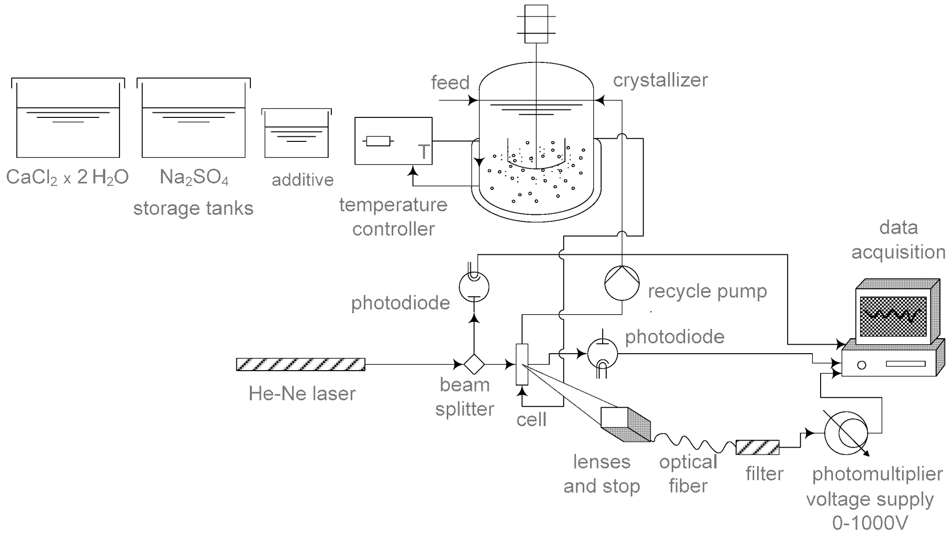

Figure 2. Experimental apparatus.

2. Material 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 (Lancia *et al.,* 1999). Supersaturated solutions of calcium sulfate were prepared by mixing clear aqueous solutions of reagent-grade $CaCl_2 \cdot 2H_2O$ and Na_2SO_4. The additive solutions were prepared for each level of concentration by adding in turn NTMP ($C_3H_{12}NO_9P_3$ as 50% w/w solution in water), PBTC ($C_7H_{11}O_9P$ as 50% w/w solution in water, available under the commercial name of Bayhibit® AM kindly provided by Lanxess Deutschland GmbH, Leverkusen), citric acid ($C_6H_8O_7$ anhydrous) to bidistilled water. After their preparation and their ions concentration determination all the solutions were filtered, by using a 0.45 μm 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 Na_2SO_4 solution and then fed to the reactor. The equimolar concentration of $CaCl_2 \cdot 2H_2O$ and Na_2SO_4 in the reactor varied between 50 and 132.2 mol/m^3, while the additive concentration (namely c_{NTMP}, c_{PBTC}, c_{CA}) was 0.01 g/L. The supersaturation ratio was calculated considering the liquid–solid equilibrium between Ca^{2+} and SO_4^{2-} ions and solid $CaSO_4 \cdot 2H_2O$, as described by the following equation:

$$\mathrm{Ca}^{2+} + \mathrm{SO}_4^{2-} + 2\mathrm{H}_2\mathrm{O} = \mathrm{CaSO}_4 \cdot 2\mathrm{H}_2\mathrm{O} \tag{1}$$

so that it is:

$$\sigma = \frac{a_{Ca^{2+}} a_{SO_4^{2-}} a_{H_2O}^2}{K_{ps}} \tag{2}$$

where a_J represents the activity of the J species (J= Ca^{2+}, SO_4^{2-} and water) expressed as the product of the molality (m_J) and the activity coefficient (γ_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 0.01 g/L while changing the supersaturation ratio in the range 2.06 – 4.66. The temperature was fixed at 25°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_{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 (±10%) results.

3. Results

Figure 3 shows the dependence of induction period on supersaturation ratio for T=25°C and $c_{additive}$=0.01 g/L. The figure shows that the induction period for gypsum nucleation continuously decreases with increasing supersaturation. Above all, from this figure it appears very clear that NTMP is the additive that mostly increases the induction period, thus retarding the nucleation, followed by citric acid and then by PBTC. This last, at least in the tested experimental conditions, does not augment a lot the induction period values with respect to the absence of any additive.

Experimental data of induction period plotted as a function of supersaturation levels can be adequately used, as suggested by Söhnel and Garside (1992), to discriminate whether the appearance of the new solid phase is controlled by gypsum nucleation and/or by growth and to distinguish between homogeneous and heterogeneous nucleation phenomena. This is worth of note in the estimation of some characteristic parameters of primary nucleation, such as the interfacial tension. Since the most likely mechanism that governs the nucleation of gypsum is nucleation (Prisciandaro *et al.,* 2003, 2006) the following equation, derived from homogeneous nucleation equations when nucleation is controlling, was considered (Söhnel and Garside, 1992):

$$\log(t_{ind}) = C + \frac{D}{T^3(\log\sigma)^2} \tag{3}$$

where C is an empirical constant and D is given by:

$$D = \frac{\beta\gamma_s^3 V_m^2 N_A f(\phi)}{(2.3R)^3 \nu^2} \tag{4}$$

in which β is a shape factor, γ_s is the surface energy, N_A is the Avogadro number, R is the gas constant, V_m the molar volume, ν is the number of ions in which the molecule is dissociated and $f(\phi)$ is a correction factor which takes into account the heterogeneous nucleation; in particular, when purely homogeneous nucleation takes place it is $f(\phi)=1$ while when heterogeneous nucleation occurs it is $f(\phi)<1$. Consequently a change in the slope of the equation may indicate a transition from homogeneous to heterogeneous nucleation mechanisms.

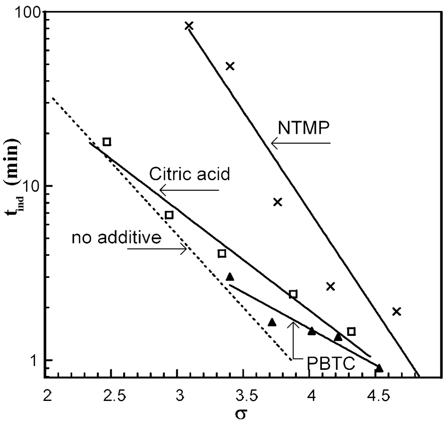

Figure 3. Induction times as a function of σ. T=25°C, $c_{additive}$=0.01 g/L. ----------: no additive; □: citric acid; Δ: PBTC; ×: NTMP.

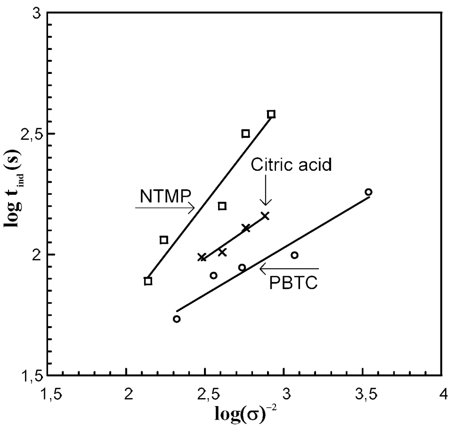

Figure 4. Induction times as a function of σ. T=25°C, $c_{additive}$=0.01 g/L; □: NTMP; ○: PBTC; ×: citric acid.

In this paper, this distinction between the two nucleation regions has been carried out for all t_{ind} experimental data, selecting among them the ones belonging to the homogeneous nucleation region. Figure 4 reports the linearization of the experimental data relative to the homogeneous nucleation region, for $c_{additive}$=0.01 g/l at the temperature of T=25°C, for the three tested additives. From the slope of the straight lines reported in Fig. 4, the values of γ_s reported in Table 1 are obtained (in Eq. (4) it was considered $\beta=16\pi/3$, assuming spherical particle, and V_m=74.69 cm^3/mol). The analysis of the table confirms that NTMP is the stronger retardant among these studied.

Table 1. Interfacial tension values at T=25°C, additive concentration 0.01 g/L.

γ_S (mJ/m^2)	Additive
31.9	-
34.3	PBTC
37.0	Citric acid
46.4	NTMP

4. Conclusions

In this paper, the effect of NTMP, PBTC and citric acid on gypsum nucleation kinetics is studied; at T=25°C and at additive concentration level of 0.01 g/L the retarding effectiveness is NTMP >> citric acid > PBTC, suggesting that NTMP is an effective retardant of the gypsum nucleation from supersaturated solutions containing high concentration of Na$^+$ and Cl$^-$ ions.

5. Acknowledgments

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