

## Inhibition of Formation of Magnesium Hydroxide by Polymers: The Role of Molecular Architecture

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### ABSTRACT

In thermal desalination process by multistage flash (MSF) desalination, magnesium hydroxide (brucite) is a major component of the alkaline (or “soft”) scale formed at lower temperatures than the “hard” calcium sulfate scale. Brucite formation has also been reported during lime softening process. During the last three decades various additives have been developed to control precipitation of scale forming salts. This study is focused on the evaluation of synthetic poly(acrylic acids) with functional groups (carboxylic acid, -COOH) which have the potential to act as inhibitors for brucite scale. Two poly(acrylic acids) were tested with molecular weights (MW) 2,000 (PAA2k) and 6,000 (PAA6k), respectively. They were present in solutions supersaturated with respect to brucite and the spontaneous precipitation was monitored by the solutions electrical conductivity. Both polymers were effective inhibitors of the crystal growth of the supercritical nuclei forming in the solutions. The effect of the polymers as brucite inhibitors was compared with 1-hydroxyethylidine 1,1-diphosphonic acid (HEDP). The efficiency of inhibition followed the order: HEDP > PAA2k > PAA6k.

**Keywords:** brucite, precipitation, kinetics, inhibition, polyacrylic acid, HEDP

### INTRODUCTION

Magnesium hydroxide,  $Mg(OH)_2$ , fouling of heated seawater and water circulating in cooling towers and boilers is a significant operational problem with serious implication on energy consumption and corrosion of metallic parts of industrial equipment due to the evolution of corrosive gases from the decomposition of intermediate salts including hydromagnesite.<sup>1,2,3</sup> Magnesium hydroxide scale is favored at higher temperatures while at lower (<80°C) temperatures alkaline earth carbonate scales are predominant.<sup>4,5</sup> Magnesium hydroxide scale deposits predominate in cases in which boiling takes place at ambient pressure while alkaline earth carbonate scale make up the most of scale deposits

at lower temperatures encountered in vacuum distillation equipment.<sup>6</sup> Despite intensive research over the past few decades, there is still considerable ambiguity concerning the mechanism of alkaline scale formation, especially in view of competition with magnesium hydroxide and other salts.<sup>7</sup> A number of methods have been developed to optimize processes by minimizing scale formation, including acid addition, nano-filtration, thermal shock etc.<sup>8,9,10,11</sup> However, so far it seems that the use of antiscalants is the most convenient and effective way to tackle scale formation. Literature is abundant with studies concerning the development and evaluation of eco-friendly, stable, efficient and economic antiscalants<sup>12,13,14,15,16</sup> and still progress is made. Most promising are studies in which the approach adopted is based on the mechanistic investigation of the generation and evolution of scale nuclei of various salts in solutions supersaturated with respect to the respective salts. In the present work we have investigated the spontaneous precipitation of magnesium hydroxide from supersaturated solutions in which the stoichiometry of Mg(total)/OH was 1:2. The concentration monitoring method was adopted using a conductivity probe. Through the appropriate calibration, electrical conductivity was converted into magnesium concentration. The effect of the presence of two poly(acrylic acids), PAAs, with molecular weights 2,000 (PAA2k) and 6,000 (PAA6k), respectively, on the precipitation of magnesium hydroxide was investigated.

## EXPERIMENTAL PROCEDURE

All experiments were done at room temperature ( $25.0^{\circ}\pm 0.5^{\circ}\text{C}$ ). Stock solutions of magnesium chloride were prepared from crystalline  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  and were standardized with atomic absorption spectrometry and with titrations with standard EDTA solution. Sodium hydroxide standard solutions were used for the NaOH needed for the supersaturated solutions. The supersaturated solutions volume totaling 200 mL, were prepared directly in the reactor where they were magnetically stirred at ca. 150 rpm, to ensure homogeneity and avoid the development of locally high supersaturations. In all experiments Mg(total):NaOH was 1:2. The reactor was sealed airtight and the dead air volume above the supersaturated solutions was minimized to avoid intrusion of atmospheric carbon dioxide. Poly(acrylic acids), MW 2,000, PAA2k; MW 6,000, PAA6k, and HEDP used were commercial materials and their stock solutions were prepared on a dry weight basis. A conductivity probe was fitted on the reactor lid which had a sampling port from which samples were withdrawn for analysis of the composition of the aqueous phase. The electrical conductivity of the supersaturated solutions was monitored by a probe standardized with standard potassium chloride solutions.<sup>17</sup> The signal was recorded via A/D interface with a computer. The solids were collected at the end of precipitation and were characterized by powder X-Ray diffraction (XRD) using Cu-K $\alpha$  radiation and by thermogravimetric analysis. The experimental setup is shown in Figure 1.

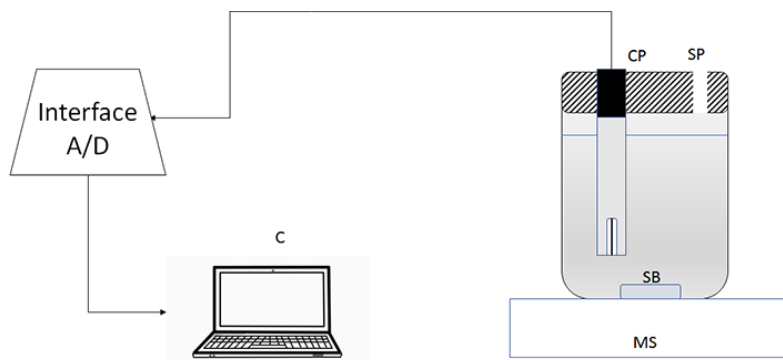


**Figure 1: Experimental setup for the investigation of the spontaneous precipitation in the presence and in the absence of additives: MS: magnetic stirrer; SB: Teflon coated stirring bar; SP: sampling port; CP: conductivity probe; C: computer for data collection and analysis.**

## RESULTS AND DISCUSSION

Monitoring of the precipitation process was based on changes of the solution conductivity immediately past the preparation of the supersaturated solutions in the reactor. Since solution conductivity is due to the presence of  $\text{Mg}^{2+}$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  ions and in the presence of additives, there is a minor contribution from the respective ions, changes of magnesium and hydroxyl ion concentrations in the supersaturated solutions due to the formation of  $\text{Mg}(\text{OH})_2$  precipitates, caused reduction of the recorded initial values of the solutions electrical conductivity. The concentrations of the related ions in the supersaturated solutions used in the present work were sufficiently low to allow for the use of Fuoss-Onsager equation to correlate electrical conductivity measured with the solution concentration.<sup>18</sup> Since  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations remained constant throughout the precipitation process, the measured solution conductivity,  $\Lambda$ , considering the stoichiometry for the precipitating hydroxide:  $\text{Mg}:\text{OH} = 1:2$ , was correlated with Equation 1:

$$\Lambda = \Lambda_0 - A\sqrt{C_{\text{Mg}^{2+}}} + BC_{\text{Mg}^{2+}} \quad (1)$$

Where  $\Lambda_0$  is the molar conductivity of an infinitely dilute solution, A and B constants and  $C_{\text{Mg}^{2+}}$  the concentration of free magnesium ions in solution. Equation (1) was verified by fitting the electrical conductivity of magnesium chloride solutions with the corresponding known concentrations of magnesium. A typical curve is shown in Figure 2.

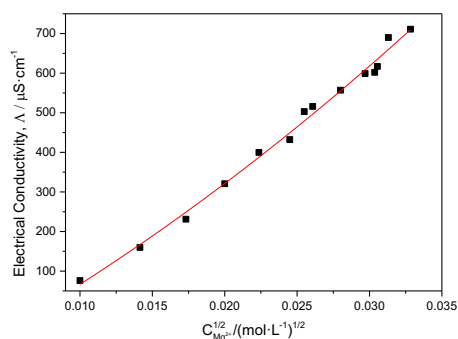


**Figure 2: Fitting of the electrical conductivity measurements of a series of magnesium chloride solutions of known concentrations according to Equation 1.**

All solutions used in the present work were supersaturated with respect to brucite ( $Mg(OH)_2$ ) and the initial solution supersaturation was calculated from the total concentrations of the respective components with an iterative procedure, taking into consideration all equilibria involved. Calculations were done using PHREEQC software.<sup>19</sup>

The solution supersaturation ratio,  $\Omega$ , with respect to  $Mg(OH)_2$  was calculated from Equation 2:

$$\Omega = \frac{(Mg^{2+})(OH^{-})^2}{K_{s,Mg(OH)_2}^0} \quad (2)$$

Where parentheses denote activities of the respective ions and  $K_{s,Mg(OH)_2}^0$  is the thermodynamic solubility product of Brucite. The relative supersaturation with respect to magnesium hydroxide,  $\sigma$ , is defined in Equation 3:

$$\sigma = \Omega^{\frac{1}{3}} - 1 \quad (3)$$

The rates of precipitation were calculated from the slopes of the profiles of magnesium concentration as a function of time at  $t = 0$  (initial rates of precipitation). The dependence of the rates of precipitation,  $R_p$ , on the relative supersaturation,  $\sigma$ , is given by Equation 4:

$$R_p = k_p \sigma^n \quad (4)$$

Where  $k_p$  is the apparent precipitation rate constant and  $n$  the apparent order of precipitation. Experimental conditions and rates measured for solutions over a range of relative supersaturations are summarized in Table 1.

Table 1

**Experimental Conditions and Rates of Precipitation of Magnesium Hydroxide (brucite) in the Absence of Additives.**

| EXP# | $C_{Mg}/\times 10^{-4} M$ | $C_{NaOH} / \times 10^{-3} M$ | $\sigma_{brucite}$ | $R_p/\times 10^{-7} \text{ mol}\cdot\text{s}^{-1}$ |
|------|---------------------------|-------------------------------|--------------------|----------------------------------------------------|
| B101 | 7.14                      | 1.428                         | 3.80               | 2.4                                                |
| B102 | 8.16                      | 1.632                         | 4.37               | 5.0                                                |
| B103 | 8.74                      | 1.748                         | 4.71               | 5.5                                                |
| B104 | 9.10                      | 1.820                         | 4.89               | 7.2                                                |
| B105 | 10.10                     | 2.020                         | 5.41               | 8.8                                                |

Rates of precipitation showed a first order dependence on the relative solution supersaturation, as may be seen in Figure 3, in agreement with early reports.<sup>20</sup> The linear dependence suggested surface diffusion-controlled mechanism.

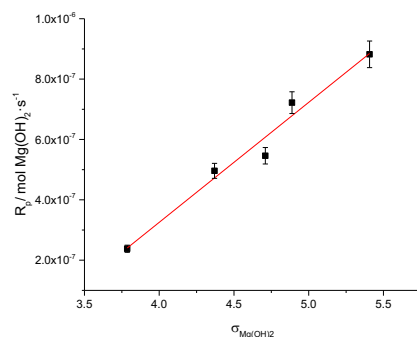


**Figure 3: Plot of the rate of precipitation of magnesium hydroxide from supersaturated solutions as a function of the relative supersaturation with respect to  $Mg(OH)_2$  (brucite); 25°C.**

Analysis of the solid by XRD showed that the precipitate was crystalline Brucite, as may be seen in the diffractogram shown in Figure 4.