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Effect of residence time on the degree of $CaCO_3$ precipitation in the presence of an anti-scalant☆

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HIGHLIGHTS

- Effect of residence time and of anti-scalant SHMP on $CaCO_3$ precipitation in a CSTR
- As expected increase of the anti-scalant SHMP dosage reduced $CaCO_3$ precipitation.
- However unexpectedly increase of the residence time decreased $CaCO_3$ precipitation.
- This decrease is shown to arise from increased SHMP adsorption on $CaCO_3$ particles.

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ABSTRACT

The present work examines the effect of residence time on the degree of $CaCO_3$ precipitation in a continuous flow stirred tank reactor in the presence of the inhibiting additive sodium hexametaphosphate (SHMP). The degree of $CaCO_3$ precipitation and the degree of SHMP adsorption on the crystallizing particles were both measured in a series of experiments performed with solutions at the same initial supersaturation level residing in the reaction vessel at various retention times in the range of 20 to 150 min. Variation of the SHMP concentration in the feed gave the anticipated trend of a decrease in the degree of $CaCO_3$ precipitation with an increase in inhibitor concentration. However, surprisingly, increase of the residence time at a constant SHMP dosage level led to a diminished degree of $CaCO_3$ precipitation. The rate of SHMP adsorption on the crystallizing $CaCO_3$ particles was found to vary inversely with the square root of residence time. This result suggests that adsorption of the SHMP inhibitor on the crystallizing $CaCO_3$ particles is a slow, diffusion-controlled process. Precipitation is increasingly inhibited at an increased residence time due to the augmented level of the adsorbed SHMP inhibitor. A diffusion-controlled adsorption model enabled successful correlation of all kinetic data.

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1. Introduction

Scale deposition on flow surfaces is a difficulty encountered with waters containing ions of sparingly soluble salts. Scale precipitation occurs whenever process conditions lead to the creation of supersaturation with respect to one or more of the sparingly soluble salts. This problem is widely encountered in cooling water systems and in water desalination processes. It is usually controlled by dosage of minute concentrations of certain chemical additives ("anti-scalants") which are able to delay precipitation of a sparingly soluble salt from its supersaturated solution. Since such low dosages represent a small fraction of the stoichiometric concentration of the affected species, the suppression mechanism cannot be rationalized by chemical interactions. The inhibition process is of physical nature and is known to involve adsorption of additive molecules on active growth sites of the crystallization surface [1,2]. However, the fundamentals of inhibition mechanisms from their quantitative aspects are poorly understood so that effects of operating parameters on inhibition effectiveness are largely unpredictable [3].

One of the most widely studied scaling species is $CaCO_3$. Its inhibition has been mostly examined in seeded batch experiments. The present work examines the kinetics of $CaCO_3$ precipitation in a continuous flow stirred tank reactor in the presence of the inhibiting anti-scalant sodium hexametaphosphate (SHMP, "Calgon").

A widely used approach in kinetic studies of inhibited precipitation is to assume that crystallization is retarded by the adsorption of inhibitor molecules on crystal growth sites. In many instances the Langmuir adsorption model, which assumes equilibrium conditions, has been successfully used to describe empirically the reduction in crystal growth rates by the presence of an inhibitor [2,4].

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The above approach can be exemplified by the study of Nancollas and Reddy [5] in which the precipitation kinetics of $CaCO_3$ in the presence of various organic inhibitors was investigated in a batch seeded system. The precipitation rate was analyzed using the following kinetic expression:

$$-\frac{\mathrm{dCa}}{\mathrm{dt}} = k \times (\mathrm{Ca}-\mathrm{Ca}^*)^2 \tag{1}$$

where k is a rate coefficient in units of L/mol min per mg/L seeds, Ca is the instantaneous concentration of dissolved calcium and Ca^* is the final equilibrium concentration. The variation of the rate coefficient k with inhibitor concentration p was reasonably well correlated on the basis of the Langmuir equation:

$$\frac{k}{k_0} = \frac{1}{1+K\times p} \tag{2}$$

where k_0 is the value of the rate coefficient in the absence of an inhibitor and K is an equilibrium adsorption constant. As usual, the pseudo-equilibrium concentration Ca^* was found to increase with inhibitor concentration. The Langmuir adsorption model has been similarly applied for correlating kinetic data on the inhibitory effect induced by trace metal ions on the precipitation of $CaCO_3$ in batch seeded systems [6,7].

In all batch seeded investigations of $CaCO_3$ precipitation in the presence of inhibiting additives, the degree of precipitation was universally observed to increase with time. A study of $CaCO_3$ precipitation in a continuous flow stirred tank reactor without the presence of an inhibitor also indicated either an increase in the degree of precipitation with increase of residence time or an asymptotic constant value [8]. A striking result observed in this study of $CaCO_3$ precipitation in the presence of an inhibitor in a stirred tank reactor is that increase of residence time induced a decrease rather than an increase in the degree of precipitation.

2. Experimental

The kinetics of continuous flow precipitation of $CaCO_3$ in the presence of the inhibitor SHMP was studied using a 1 m^3 stirred vessel lined with polyester coating (Fig. 1). The volume of the solution in the vessel was maintained at 400 L in all runs. The solution was agitated by a 0.25 HP stirrer operated at 200 rpm.

Inlet feed concentrations in all runs were maintained at the nominal level of $Ca^{2+} = CO_3^{2-} = 20$ mmol/L by dosing into the vessel concentrated solutions of $CaCl_2$, Na_2CO_3 and $NaHCO_3$ and adjusting the CO_3^{2-} concentration by pH-controlled dosage of NaOH. The initial pH of the feed solution before precipitation was around 10.5. The saturation index of the feed solution calculated by Visual MINTEQ ver. 3.0 was 3.38 with respect to calcite and 3.25 with respect to aragonite. These solution conditions represent extremely high supersaturation levels that would cause instantaneous precipitation in the absence of an inhibitor.

The analyses carried out on the vessel exit stream included determination of the residual dissolved Ca^{2+}, CO_3^{2-} and SHMP concentrations and the concentration of adsorbed SHMP in the precipitated particles. The calcium concentration was determined by EDTA titration and the carbonate species were evaluated from analyses of the phenolphthalein and methyl orange alkalinities. The active SHMP inhibitor concentration was determined from the difference between total phosphate and free phosphate concentrations. The phosphate concentration was analyzed by the molybdate spectrophotometric method. The total phosphate concentration was determined by freeing the bound polymeric phosphate through hot acid hydrolysis prior to the phosphate analysis.

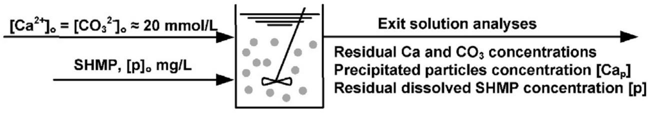

Fig. 1. Schematic diagram of the continuous flow precipitation reactor.

Three series of experiments were carried out in which the concentrated SHMP solution metered into the precipitation vessel provided initial nominal SHMP concentrations corresponding to $P_0 = 5$, 10 and 100 mg/L respectively. The effect of the residence time τ in the reaction volume on the residual supersaturation was investigated at four levels ($\tau = 20$, 40, 80 and 150 min respectively). All runs were carried out at a controlled precipitation temperature of 40 °C. Residual Ca^{2+} and CO_3^{2-} concentrations in the various runs were in the range of 1 to 4 mM.

3. Results and discussion

Table 1 summarizes feed and exit solution analyses.

3.1. Effect of residence time on the residual concentration level

Fig. 2 shows the effect of residence time on the residual calcium carbonate ion product $[Ca^{2+}] \times [CO_3^{2-}]$ in the stirred tank reactor expressed as a percentage of the feed ionic product $[Ca^{2+}]_0 \times [CO_3^{2-}]_0$:

$$Y = \frac{\left[Ca^{2+}\right] \times \left[CO_3^{2-}\right]}{\left[Ca^{2+}\right]_0 \times \left[CO_3^{2-}\right]_0} \times 100 \tag{3}$$

The striking result is the clear trend of an increase in the residual $[Ca^{2+}] \times [CO_3^{2-}]$ level with the increase in residence time τ.

A plausible explanation for this unexpected result is disclosed by analysis of the data of the mass concentration Z of SHMP adsorbed into the $CaCO_3$ particles:

$$Z(\%) = \frac{\text{mass of adsorbed SHMP}}{\text{mass of } CaCO_3 \text{ particle} + \text{SHMP}} \times 100 \tag{4}$$

Measurements showed a clear trend for increased SHMP adsorption levels with increase of residence time in the precipitation vessel. In the first series of experiments in which the nominal SHMP dosed to the feed amounted to $p_0 = 5$ mg/L, values of Z increased with residence time from 0.23 to 0.32%. In the second series at which the nominal SHMP feed dosage was increased to $p_0 = 10$ mg/L, values of Z increased from 0.32% to 0.43%. In the third series conducted at the nominal SHMP feed concentration of $p_0 = 100$ mg/L, SHMP levels values of Z increased from 3.4% to 4.8%.

The increase in the amount of SHMP adsorbed in the precipitated $CaCO_3$ particles with residence time suggests that the augmented inhibition stems from a slow rate-controlling adsorption process. The higher residual CaCO3 supersaturation corresponds to the higher pseudo solubility of CaCO3 generated by the presence of an increased inhibitor concentration.

Data on the equilibrium adsorption of SHMP by $CaCO_3$ particles are available from a study of Corsaro et al. [9] in which SHMP solutions were held in contact with $CaCO_3$ suspensions for 48 h. The data fitted the following Freundlich adsorption expression:

$$q = A \times p^n \tag{5}$$

where q is the amount of SHMP adsorbed (mg per gram $CaCO_3$ particles) and p is the dissolved SHMP concentration (mg per L solution). The coefficient A had the value of 2.2 for $CaCO_3$ particles having a surface area of 20.4 m^2/g and a value of 0.525, for particles of 2.74 m^2/g. In both cases, the exponent n had the same value of 0.60.

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