Rigorous Modeling of the Kinetics of Calcium Carbonate Deposit Formation - CO2 Effect

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Introduction

The kinetics of CaCO3 deposition on flow surfaces is of widespread interest in many engineering applications, notably cooling tower water systems and both thermal and membrane desalination processes. Comprehension of the kinetics of this system is closely allied to scale control efforts.

The complexity of the CaCO3 precipitation system arises from the need to consider the combined role of several mass transfer, chemical reaction processes and flow effects. Kinetic models proposed in various studies are based on highly simplified assumptions.1–14 We have recently derived a rigorous kinetic model which considered all processes involved in the precipitation system but included the simplification that the CO2 hydration reaction was instantaneous.15 This article completes our previous work by analyzing the effect of the CO2 hydration reaction.

Precipitation mechanisms

The system considered is the same as that analyzed in our previous article and consists of wall deposition of a crystallizing CaCO3 scale layer from a supersaturated solution in isothermal turbulent flow through a tube (Figure 1).

The overall reaction involved in the wall crystallization process of CaCO3 is

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3(s) + \text{CO}_2 + \text{H}_2\text{O} \quad (1)$$

The main processes involved are the surface crystallization reaction

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(s) \quad (2)$$

which is followed by shifts of the ionic species participating in the process

$$\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (3)$$

$$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (4)$$

CO2 kinetics in carbonate systems

It is well established that the ionic species involved in the second dissociation constant of carbonic acid (H+, HCO3-, and CO3^{2-}) are at instantaneous equilibrium during the precipitation process. This is not the case for the first dissociation constant of carbonic acid since the reactant CO2 is not in an ionic state.

The hydration and dehydration of CO2 in carbonate solutions occur by the following parallel reaction mechanisms16–18:

Acidic Mechanism:

$$\text{CO}_2 + \text{H}_2\text{O} \quad \text{IC}_1 \quad \text{H}_2\text{CO}_3 \quad \text{IC}_1^{-1} \quad \text{HCO}_3^- + \text{H}^+ \quad (5)$$

$$\text{HCO}_3^- \quad \text{IC}_3 \quad \text{CO}_3^{2-} + \text{H}^+ \quad (6)$$

Alkaline Mechanism

$$\text{CO}_2 + \text{OH}^- \quad \text{IC}_3 \quad \text{HCO}_3^- \quad (7)$$

$$\text{HCO}_3^- + \text{OH}^- \quad \text{IC}_3 \quad \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (8)$$

Equations 5 and 7 describe finite rate reactions since the composition and decomposition of the CO2 species occur through modification of the chemical structure of the CO2 molecule. However Eqs. 6 and 8 describe instantaneous reactions since they involve only proton exchange.19

Table 1 summarizes correlations for the rate coefficients of reactions (5) and (7), while Table 2 lists the equilibrium constants of the instantaneous reactions (6) and (8).

Model Equations

The diffusional transport of the reacting species (H+, OH-, CO3^{2-}, HCO3-, Ca^{2+}, CO2) are given by

$$-D_i \frac{d^2c_i}{dx^2} = R_i \quad (9)$$

where $D_i$ is the diffusion coefficient of species $i$, and $R_i$ is the reaction rate of the reacting species described by
Figure 1. Transport of the reacting species from the solution bulk to the crystallizing layer.

Table 1. Rate Coefficients of the CO₂ Reactions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Rate Coefficient</th>
<th>Units</th>
<th>Reported Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinsent et al.²⁰</td>
<td>k₁</td>
<td>1/s</td>
<td>log k₁ = 329.85 - 110.541·log T - 17265.4</td>
</tr>
<tr>
<td>Usdowski et al.²¹</td>
<td>k₁</td>
<td>1/s</td>
<td>log k₁ = 13.558 - 3617.1</td>
</tr>
<tr>
<td>Pinsent et al.²⁰</td>
<td>k₃</td>
<td>mol·s⁻¹</td>
<td>log k₃ = 13.635 - 2558.5</td>
</tr>
<tr>
<td></td>
<td>k₃</td>
<td>mol·s⁻¹</td>
<td>log k₃ = 14.09 - 5368.9</td>
</tr>
</tbody>
</table>

R_{CO₂} = +k₁[CO₂] - k₁[H₂CO₃] + k₃[CO₂] ÷ [OH⁻] - k₃[HCO₃⁻] (10)

R_{H⁺} = +k₁[CO₂] - k₁[H⁺][HCO₃⁻] - k₃[CO₂] · K₅[H⁺] + k₃[HCO₃⁻] (11)

R_{OH⁻} = -k₃[CO₂][OH⁻] + k₃[HCO₃⁻] + k₁[CO₂] - k₃K₅[H₂CO₃] / K₅[OH⁻] (12)

R_{HCO₃⁻} = +k₁[CO₂] - k₁[H₂CO₃] + k₃[CO₂] · [OH⁻] - k₃[HCO₃⁻] (13)

R_{CO₃²⁻} = +k₁[CO₂] - k₁[H⁺][CO₃²⁻] + k₃K₅K₂[CO₂] · [OH⁻] - k₃[H⁺][CO₃²⁻] / K₂ (14)

R_{Ca⁺²⁺} = 0 (15)

The species H₂CO₃ can be eliminated from Eqs. 10 and 13 using the equilibrium condition

As in our previous article, the surface integration step involved in CaCO₃ crystallization is described by the following reaction expression:²³

J_{CaCO₃} = k₉([Ca⁺²⁺][CO₃²⁻]) - K_{SP} (16)

where k₉ (m⁷/s·mol) is assumed to depend on temperature according to the Arrhenius equation

\[ \ln k₉ = \ln A - \frac{E}{RT} \] (18)

Comparison between CO₂ hydration reaction and CO₂ diffusion

Values of the acidic and alkaline reaction rates, respectively, were calculated using the rate coefficients listed in Table 1 and are displayed in Figure 2 as functions of the pH level at a total alkalinity of 200 ppm as CaCO₃. Figure 3 displays similar plots for a total alkalinity of 500 ppm.

It is seen that there is a pH range where the rate limiting step is the acidic reaction, a pH range where the rate limiting step is the alkaline reaction, and there is a pH range where both reactions are important and cannot be neglected. The dominant mechanism may be assumed to be that where one of the reaction rates (acidic or alkaline) is at least five times higher than that of the alternative mechanism. Table 3 summarizes pH limits of the dominant reaction based on the aforementioned criterion.

Since the CO₂ concentration becomes vanishingly small at high pH levels, the dominant mechanism affecting the CaCO₃

Table 2. Equilibrium Constants of the Instantaneous Reactions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Equilibrium reaction</th>
<th>Equilibrium Constant</th>
<th>Reported Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plummer and Busenberg²²</td>
<td>[H⁺][HCO₃⁻] / [CO₂]</td>
<td>K₁</td>
<td>[ \log K₁ = -356.3094 - 0.06091964 \cdot T + \frac{21834.37}{T} + 126.8339 \cdot \log T - 1684915 ]</td>
</tr>
<tr>
<td>Plummer and Busenberg²²</td>
<td>[H⁺][CO₃²⁻] / [HCO₃⁻]</td>
<td>K₂</td>
<td>[ \log K₂ = -107.8871 - 0.0325849 \cdot T + \frac{5151.79}{T} + 58.92561 \cdot \log T - 553713.9 ]</td>
</tr>
<tr>
<td>Harned and Hamer²³</td>
<td>[H⁺][OH⁻]</td>
<td>K₅</td>
<td>[ \log K₅ = 22.801 - 0.010365 \cdot T - 4787.5 - 7.1321 \cdot \log T ]</td>
</tr>
</tbody>
</table>
precipitation process is the acidic \( CO_2 \) hydration reaction. The relative extents of the \( CO_2 \) reaction and of the \( CO_2 \) diffusion may be evaluated by comparing the typical reaction time of the acidic reaction with the typical diffusion time of the \( CO_2 \) species. The typical reaction time is given by\(^{25}\)

\[
t_{Ac} = \left( k_1 + \frac{k_{-1}}{K_5} [H^+] [HCO_3^-] \right)^{-1}
\]

(19)

where \( k_1 \) and \( k_{-1} \) are the acidic forward and backward reaction constant, respectively and \( t_{Ac} \) the typical reaction time for alkali and acidic mechanisms, respectively.

The typical diffusion time is given by

\[
t_D = \frac{D_{CO_2}}{k_{CO_2}^2}
\]

(20)

where \( D_{CO_2} \) is the diffusion coefficient of the \( CO_2 \) species at 25°C and \( k_{CO_2} \) is the mass-transfer coefficient of the \( CO_2 \) species.

Table 4 displays the difference between the diffusion time and the acidic reaction time at various \( Re \) numbers and various total alkalinity levels. Since the \( CO_2 \) diffusion and the reaction occur simultaneously, the dominating effect is the process occurring more rapidly. It is seen that at the lowest \( Re \) number of 4,400 the reaction time of 2.75–6.43 msec is much more rapid than the diffusion time that requires 251 msec. This trend is reversed at high \( Re \) numbers. For \( Re = 22,200 \) the diffusion time of 1.71 ms is more rapid than the reaction time of 2.75–6.43 msec.

**Influence of the \( CO_2 \) hydration reaction on the \( CaCO_3 \) precipitation rate**

The influence of the \( CO_2 \) hydration reaction on the precipitation rate was analyzed by comparing results calculated assuming \( CO_2 \) equilibrium\(^{15}\) with results taking into account the kinetics of the \( CO_2 \) reaction. Table 5 lists values of the parameters adopted in the simulation study. The range of chemical parameters analyzed was: total alkalinity of 100–500 [ppm as \( CaCO_3 \)] and calcium of 100–400 [ppm]. The range of \( Re \) numbers was 4,400 to 22,200.

Figure 4 displays limiting pH levels at which the \( CaCO_3 \) precipitation rate based on \( CO_2 \) equilibrium deviates by less than 10% from results calculated in the presence of the \( CO_2 \) hydration reaction. The upper bound of each of the \( Re \) number bands represents absolute deviation levels corresponding to the high calcium and alkalinity concentrations and the lower bound, to the lower calcium and alkalinity concentrations. It is evident that high deviations occur only at the lowest \( Re \) numbers, while deviations are negligibly small at the highest \( Re \) number of 22,200.

**Concluding Remarks**

The analyses described in this article and in our previous publication\(^{15}\) enable prediction of the anticipated \( CaCO_3 \) precipitation rate in scale-prone systems, notably cooling water towers, thermal desalination units and membrane processes. The dominant mechanism under a wide range of conditions is convective mass transfer.

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**Table 3. Extent of the Dominant Mechanism**

<table>
<thead>
<tr>
<th>pH level range</th>
<th>Dominant mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0-8.0</td>
<td>Acidic</td>
</tr>
<tr>
<td>8.0-9.2</td>
<td>Acidic and Alkali</td>
</tr>
<tr>
<td>9.2-10.0</td>
<td>Alkali</td>
</tr>
</tbody>
</table>

**Table 4. Reaction and Diffusion Time at Various Conditions**

<table>
<thead>
<tr>
<th>Total alkalinity (ppm)</th>
<th>Reaction time [msec]</th>
<th>Diffusion time [msec]</th>
<th>Diffusion time [msec]</th>
<th>Diffusion time [msec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>2.75</td>
<td>251</td>
<td>54.1</td>
<td>1.71</td>
</tr>
<tr>
<td>400</td>
<td>3.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>6.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>4.60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5. Parameters used in the Simulation Analyses**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_R )</td>
<td>( 3.68 \times 10^{-5} ) [m^4/(mol sec)]</td>
</tr>
<tr>
<td>( K_p )</td>
<td>( 5.32 \times 10^{-2} ) [mol/m^3]</td>
</tr>
<tr>
<td>( K_5 )</td>
<td>( 1.71 \times 10^{-1} ) [mol/m^3]</td>
</tr>
<tr>
<td>( D_{HOH} )</td>
<td>( 9.31 \times 10^{-3} ) [m^2/sec]</td>
</tr>
<tr>
<td>( pH )</td>
<td>7-11</td>
</tr>
<tr>
<td>( U )</td>
<td>24.25-198 [m/sec]</td>
</tr>
<tr>
<td>( Temp. )</td>
<td>25°C</td>
</tr>
<tr>
<td>( D_{CO_2} )</td>
<td>( 2.00 \times 10^{-5} ) [m^2/sec]</td>
</tr>
<tr>
<td>( D_{HCO_3} )</td>
<td>( 1.13 \times 10^{-5} ) [m^2/sec]</td>
</tr>
<tr>
<td>( D_{Ca} )</td>
<td>( 0.79 \times 10^{-5} ) [m^2/sec]</td>
</tr>
<tr>
<td>( D_{HCO_3} )</td>
<td>( 1.13 \times 10^{-5} ) [m^2/sec]</td>
</tr>
<tr>
<td>( U )</td>
<td>24.25-198 [m/sec]</td>
</tr>
<tr>
<td>( Temp. )</td>
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</tr>
<tr>
<td>( U )</td>
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</tr>
<tr>
<td>( Temp. )</td>
<td>25°C</td>
</tr>
<tr>
<td>( D_{CO_2} )</td>
<td>( 2.00 \times 10^{-5} ) [m^2/sec]</td>
</tr>
</tbody>
</table>

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**Figure 3.** Acidic and alkaline \( CO_2 \) reaction rate and ratio of alkaline to acidity reaction rate as functions of the pH level (total alkalinity of 500 ppm as \( CaCO_3 \)).

**Figure 4.** Absolute deviation ranges according to various total alkalinites, \( Ca^{+2} \) concentrations and \( Re \) numbers.
The analyses hold for systems free from impurities such as Fe$^{2+}$, Fe$^{3+}$, Zn$^{2+}$ and Mg$^{2+}$ which can alter significantly the surface precipitation reaction and enhance the role of the surface reaction mechanism. Predictions based on analyses neglecting the effect of impurities provide an upper limit to the anticipated precipitation rate. Obviously, extension of available data on the effect of impurities on the surface reaction will widen the applicability of theoretical predictions of CaCO$_3$ scaling rates.

**Literature Cited**

22. Flummer LN, Busenberg E. The solubilities of calcite, aragonite and vaterite in CO$_2$-H$_2$O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO$_3$-CO$_2$-H$_2$O. *Geochem Cosmochim Acta.* 1982;46:1011–1040.

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