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Effect of Ca$^{2+}$ and Fe$^{2+}$ on the Precipitation of Calcium Carbonate and Iron Carbonate Solid Solutions and on Scale Inhibitors Retention

by

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ABSTRACT

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Mineral scale formation is important to many areas of science and engineering, from drinking water treatment to oceanography to oil and gas production. In some cases mineral deposition is beneficial, as in water treatment for heavy metal or arsenic removal, and sometimes it is deleterious, as occurs in oil and gas production due to co-produced water. In either case, understanding the mechanisms of precipitation and inhibition is critical. Work in this thesis has focused on the impact of metal ions on mineral scale formation, and control. The results reveal that the addition of metal ions in the pill solution significantly improved the retention of scale inhibitors. Both BHPMP and DTPMP returns were significantly extended by the addition of Ca$^{2+}$ and Fe$^{2+}$. Also trace levels of Zn$^{2+}$ significantly enhanced the performance and retention of both BHPMP and DTPMP. The enhanced scale inhibition may be caused by a complex of metal ions with amine group of polyamino- polyphosphonates.

It is known that the effectiveness of inhibitors varies upon the type of scale formed where it has been mentioned in the literature that common calcium carbonate inhibitors are not effective for preventing iron carbonate. Therefore, this work was also intended to investigate the impact of calcium and iron ions in the co-precipitation of iron-calcium carbonate solid solutions (Fe$_x$Ca$_{1-x}$CO$_3$). Three different experimental methods were applied to investigate and predict the precipitation of Fe$_x$Ca$_{1-x}$CO$_3$: Free drift, continuous feeding, and constant composition experiments. The results from all methods showed that calcium carbonate was kinetically favored to precipitate rather than iron carbonate when the solution is supersaturated with respect to calcium carbonate and iron carbonate. In the constant composition experiments a series of solid solutions of iron-calcium carbonate ranging from calcium-rich to iron-rich was precipitated.
Based upon the experimental results and the theoretical derivation, a new model in a form of logistic function was developed to predict the stoichiometry of Fe$_x$Ca$_{1-x}$CO$_3$ as a function of the aqueous solution composition. The model showed an excellent representation for the experimental results with $R^2$ greater than 0.97 and 0.88 for Fe$_x$Ca$_{1-x}$CO$_3$ and Ba$_x$Ca$_{1-x}$CO$_3$, respectively.

The experimental equipment and procedures described in this work provide an effective means of producing and handling oxygen sensitive solid solutions. The precipitation kinetics of a number of solid solutions in aquatic systems could be studied by adapting the experimental design developed herein.
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1. INTRODUCTION

1.1. Background and Objectives:

Water usually contains multiple cations and anions. When the solution become supersaturated due to co-mixing and changes in conditions, the ions may precipitate as solid solutions. Better understanding of the solid solution formation from the aqueous solutions is needed to predict and prevent solid formation in various water treatment processes. Several studies have examined the thermodynamics of solid solution formations in geochemical processes where equilibrium condition may be assumed [Lippman, 1980; Plummer 1987; Plummer and Busenberg, 1987; Glynn and Reardon, 1990; Königsberger and Gamsjäger, 1990; Gamsjäger. et al., 2000; Pina and Putnis, 2002, Astilleros, et al., 2003; Pina et al., 2004]. However, solid solutions formation is rarely at equilibrium in industrial water treatment processes. The key parameters needed for the prediction of solid solutions formation for industrial water treatment processes are the stoichiometry of solid solution formation and kinetics at different aqueous compositions and conditions. If these parameters were known, scientists and engineers would be able to project, with precision, the incorporation of ions from waters into minerals. They would also helps to infer the physicochemical conditions of natural crystallization environments.

The precipitation of pure calcium carbonate and iron carbonate has been extensively investigated over wide range of environmental conditions. [Reddy and Nancollas, 1970; Nancollas, 1976; Kazmierczak, et al., 1982; Johnson, 1990; Jonson and Tomson., 1991; Tomson et al., 1991; Braun, 1991; Greenberg and Tomson, 1992; Stefán, 2003; Yean et al, 2008]. Due to the abundance of calcium and iron in natural
environments, solid solutions of calcium and iron carbonates commonly form in natural rock and processing equipment. However, little information is available about the co-precipitation of iron-calcium carbonate solid solutions.

Typically, precipitation is studied by preparing a supersaturated solution and following the concentration of the lattice ions with time. This method is known as free drift. Using free drift is particularly problematic to study solid solution formation, because as the concentrations decrease the solid stoichiometry frequently changes. In addition, the amount of solid solution formed is often very small as the reaction approaches equilibrium. Most of these restrictions have been overcome, in this research for the first time, by modifying the method of constant composition, introduced by Tomson and Nancollas, 1978. The method of constant composition was used to study the mineralization stoichiometry and kinetics of calcium phosphates, [Tomson and Nancollas, 1978; Koutsoukos, et al., 1979], and other pure solid phases such as calcium carbonate, calcium sulfate, etc.[ Koutsoukos, et al.,1980; Kazmierczak, et al., 1982; Zhang and Nancollas, 1992]. This approach has the ability to hold the supersaturation of the aqueous solution at a constant value for long periods of time. At very low supersaturation, macroscopic quantities of stochiometric and highly crystalline material can be formed and collected for analysis. It also solves the difficulty of determining the stoichiometry of precipitation when the experiment has appreciable reduction in the initial concentrations of crystal lattice ions during the reaction. This method also enables one to study one composition of solid solution at a time, at specific supersaturation conditions. Using constant composition method enables researchers to study the influence
of pH, ionic strength, seed type, and degree of supersaturation with a precision hitherto unobtainable.

This work was intended to; 1) develop an experimental design to be workable for oxygen sensitive salts, and also to be applicable for studying the stoichiometry and kinetics of crystal growth of solid solutions in addition to a single salt; 2) develop a correlation to predict the stoichiometry of iron/calcium carbonate solid solutions as a function of aqueous supersaturation with respect to the pure solid phases; 3) evaluate the influence of metal ions, e.g., Ca$^{2+}$, and Fe$^{2+}$ on inhibitor retention and release.

1.2. Impact of Solid Formation on Industry:

Solid solution of calcium carbonate and iron carbonate are widely observed in natural water. They are also common carbonate salts typically found in the municipal water, wastewater industries, and oil and gas production wells. They play an important role in processes used to control the solubility of ions in most natural waters [Grandia et al., 2008]. Ferrous carbonate has been recognized as a protective layer that effectively inhibits or reduces the corrosion rate [Foss, 2006; Dugstad et al., 200; Tomson and Johnson, 1991]. Also positive scaling of calcium carbonate in the pipe wall of municipal water is often advocated as a mean of corrosion mitigation [Merril et al, 1977]. However, recent evidences suggest that ferrous carbonate may be more important to forming an adherent protective layer. The formation of iron carbonate and calcium carbonate solid solution can be useful for corrosion control, Figure 1.1.
Figure 1.1: A thin layer of iron deposit formed on a production tubing in one of the water supply wells, [Nasr-El-Din et al. 2001].

Excessive formation of either calcium and iron carbonate is found to have an adverse effect on equipment and tube plugging. In desalination technology, the fouling of heat transfer surfaces by the growth of minerals is a serious limitation to the use of evaporative techniques, Figure 1.2, [Elliot, M. N., 1969 and 1970]. Minerals may accumulate in the pumps; valves and production lines, which eventually cause a severe decline in the fluid flow, Figure 1.3. Also as suspended particles in water these minerals, especially in the water injection, may cause formation damage [Salma, 2000; Przybylinski, 2001].

Figure 1.2: Heat exchanger before and after the minerals formation.
Figure 1.3: Calcium carbonate scale covering pump intake of an oil producers. [Nasr-El-Din et al., 2006].

Treating the problems arising from formation of solid solutions is probably very costly. In oil and gas industry, the wells are deeper and more expensive. The cost of workover rigs to remove the solids formed is about $5,000/day. It is also important to consider the cost that might result from the decline of production due to salt formation, especially when the price of the barrel of oil exceeds $100. Equipment free of deposits operates more efficiently and economically. Nevertheless, the chemistry and the stoichiometry of the precipitation of solid solutions are still poorly understood.
2. BACKGROUND AND LITERATURE REVIEW

2.1. Basic Equations of CO₂ System:

Carbon dioxide plays an important role in the precipitation and dissolution processes of calcium carbonate an iron carbonate. Carbon dioxide gas dissolves in water to an extent controlled by its partial pressure, and by its interaction with other ions in the water, [Lasaga 1997; Butler 1982]. The concentration of carbon dioxide in solution is normally expressed by Henry's law:

\[ \{ \text{CO}_2 \} = K_H P_{\text{CO}_2} \]  

Where,

\( \{ \text{CO}_2 \} \) : activity of dissolved carbon dioxide in mole/L  

\( K_H \) : Henry's law constant in mole/liter/atm, \( 10^{-1.5} \) at 25 °C, [Stumm and Morgan, 1981]  

\( P_{\text{CO}_2} \) : partial pressure of CO₂ in atm, \( 10^{-3.5} \) atm, [Stumm and Morgan, 1981]  

At higher temperature, CO₂ is less soluble; \( K_H \) decreases to \( 10^{-1.7} \) at 50 °C, [Butler 1982].

When CO₂ is in contact with water, it hydrates to produce carbonic acid, H₂CO₃, according to the following reaction:

\[ \text{CO}_2 (aq) + \text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{CO}_3 (aq) \]  

The reaction in Eq. 2.1.2 is slow if compared to the ionization of H₂CO₃, [Butler 1982]. Only about 1% of the dissolved CO₂ exists as H₂CO₃; the remainder exists as dissolved CO₂, [Lasaga 1997; Butler 1982; Shakhshiri 2008]. In literature, the sum of dissolved CO₂ and hydrated CO₂ is commonly referred as H₂CO₃.

Carbonic acid is a weak acid; in basic solution it dissociates to yield proton [H⁺], bicarbonate ion [HCO₃⁻], and carbonate [CO₃²⁻] according to the following reactions:

\[ \text{H}_2\text{CO}_3 \xrightarrow{K_a} \text{H}^+ + \text{HCO}_3^- \]  

Eq. (2.1.3)
At equilibrium:

\[ K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \] Eq. (2.1.5)

\[ K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \] Eq. (2.1.6)

The temperature dependences of the equilibrium constant are available in the literature. For the first ionization constant, \( K_{a1} \), [Shedlovsky and MacInnes 1935]:

\[ pK_{a1} = \frac{-17052}{T} + 215.21 \log(T) - 0.12675 (T) - 545.56 \] Eq. (2.1.7)

For the second ionization constant, \( K_{a2} \), [Harned and Scholes 1941]:

\[ pK_{a2} = \frac{2902.39}{T} + 0.0239 (T) - 6.498 \] Eq. (2.1.8)

Butler provided tabulated values for the first and second ionization constant of carbonic acid for a temperature ranges from 0 to 200°C, [Buutler, 1982]. In dilute solutions at 25°C, \( K_{a1} \) and \( K_{a2} \) are approximately \( 4.2 \times 10^{-7} \), and \( 4.8 \times 10^{-11} \), respectively. By using Eq.s 2.1.1 to 2.1.6 along with pH equation (\( pH = -\log a_{H^+} \)), one can calculate the dependence of carbon species’ concentration on pH. For an open system, the concentrations distribution of \( H_2CO_3 \), \( HCO_3^- \), \( CO_3^{2-} \), and total \( CO_3 \) as a function of pH at 55°C, and \( P_{CO_2} = 0.0085 \) atm is illustrated in Figure 2.1.1. At low pH, the total dissolved carbonate exists in the form of carbonic acid, \( H_2CO_3 \), whereas at high pH, carbonate ions, \( CO_3^{2-} \), predominate. At moderate pH (7.0 – 8.0), bicarbonate ions, \( HCO_3^- \), predominate.
2.2. Driving Force:

It is prudent to know the kinetic driving force before discussing the mechanisms of nucleation and crystal growth. The chemical potential of a component is the driving force responsible for its transfer from a phase where the chemical potential is higher to a phase where the chemical potential is lower at same temperature and pressure. The chemical potential is commonly denoted by $\mu$, in unit of $\text{kJ/mol}$ or $\text{kcal/mol}$ [Bodek et.al., 1988]. The deference in chemical potential of a substance in two different states 1 and 2:

$$\Delta \mu = \mu_1 - \mu_2$$  \hspace{1cm} \text{Eq. (2.2.1)}

where:

$$\mu = \mu_0 + RT \ln a$$

$\mu_0 =$ the chemical potential at standard state, joule/mole.

$R =$ Gas constant, 8.314 joule/mol/K

$T =$ Absolute temperature, in K unit

$a =$ Activity.
Several authors suggest a dimensionless driving force, $\sigma_\mu$, derived from chemical potentials [Garside, 1984; Sohnel, 1981; Leeuwan and Blomen, 1979; Sohnel and Garside, 1979, Sohnel et al. 1977]. Rearranging Eq. 2.2.1, for the difference in chemical potential to reach equilibrium state, produces a dimensionless driving force, $\sigma_\mu$, that is independent of the activity unit:

$$\sigma_\mu = \frac{\Delta \mu}{RT} = \ln\left(\frac{a_i}{a_{ie}}\right)$$

Eq. (2.2.2)

where,

$a_i$ and $a_{ie}$ : the activity of component $i$ in bulk solution and at equilibrium in any unit, respectively.

Making the substitution $a_i = \gamma_i c_i$ in Eq. 2.2.2 produces the following equation:

$$\sigma_\mu = \ln\left(\frac{\gamma_i c_i}{\gamma_{ie} c_{ie}}\right)$$

Eq. (2.2.3)

where,

$c_i$ = concentration of component $i$ in bulk solution at any unit

$c_{ie}$ = concentration of component $i$ in bulk solution at equilibrium at any unit

$\gamma_i$ : ionic activity coefficient; equation needed to calculate the activity coefficient is provided at the end of this section.

A slightly different dimensionless driving force based on solution activities is recommended by Neilsen [Neilsen 1983; Nielsen 1986].

$$\sigma_a = \left(\frac{a_i}{a_{ie}} - 1\right)$$

Eq. (2.2.4)
The chemical potential based driving force \( \sigma_\mu \) in Eq. 2.2.2 relates to the activity based driving force \( \sigma_a \) in Eq. 2.2.4 by the following equation, [Johnson, 1990]:

\[
\sigma_\mu = \ln\left( \frac{a_i}{a_{i,eq}} \right) = \ln\left( \frac{a_i - a_{i,eq}}{a_{i,eq}} + 1 \right) \quad \text{Eq. (2.2.5)}
\]

\[
\sigma_\mu = \ln(\sigma_a + 1) \quad \text{Eq. (2.2.6)}
\]

At low supersaturation, i.e. \( \sigma_a << 1 \):

\[
\sigma_\mu = \ln(\sigma_a + 1) = \sigma_a \quad \text{Eq. (2.2.7)}
\]

It should be expected that the two dimensionless approaches give similar results but not identical. Other researchers use dimensioned driving force [Kazmierczak et al. 1982; Nancollas and ready 1971; Tomson and Nancollas 1979; Greenberg and Tomson, 1991]:

\[
\sigma_m = \left[ (a_{\text{cation}} a_{\text{anion}})^{1/2} - K_{SP}^{1/2} \right] \quad \text{Eq. (2.2.8)}
\]

Where,

\( \sigma_m \): driving force in molal units, molal units are not temperature dependent

\( K_{SP} \): the thermodynamic solubility product

\( a_i \): the ion activity of cation and anion in the bulk solution; \( a_i = \gamma_i c_i \)

\( c_i \): concentration of component \( i \) in bulk solution in molal unit

\( \gamma_i \): ionic activity coefficient.

Several equations are available in the literature to calculate the activity coefficient. Each equation is workable within certain range of ionic strength, [Stumm and Morgan 1997;
Sawyer, 2003]. One of the common used equation is what so called Davies equation, [Stumm and Morgan 1997; Sawyer, 2003]:

\[
\log \gamma = -AZ^2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \\
\text{Eq. (2.2.9)}
\]

where,

\[
A = 1.82 \times 10^6 (\varepsilon T)^{3/2}; \ A \approx 0.5 \text{ at } 25 \text{ °C}, \text{ [Stumm and Morgan 1997]}
\]

\(\varepsilon\) : dielectric constant

\(Z\) : the charge on the ion for which the activity coefficient is being determined.

\(\mu\) : ionic strength.

The constant 0.3 is sometimes also taken as 0.2). It reduces to a simple Debye-Hückel model if the "0.3\(\mu\)" part is removed. The Davies equation is frequently used in geochemical modeling, [Parkhurst, Plummer, and Thorstenson, 1980; Stumm and Morgan, 1981]. Note that Davies equation expresses all dependence on the solution composition through the ionic strength. Ionic strength of a solution can be calculated by the following expression:

\[
\mu = \frac{1}{2} \sum_i C_i Z_i^2 \\
\text{Eq. (2.2.10)}
\]

where,

\(C_i\) : the concentration of ion \(i\), in mole/L

\(Z_i\) : the charge on the ion \(i\).

It has been reported that Davis equation, Eq. 2.2.9, is workable for solution with ionic strength up to 0.5 M. There is a general believe that, yet, there is no satisfactory relation which provides a good estimation for activity coefficient at ionic strength greater than 0.5 M, [Sawyer, 2003].
Driving force definition is widely used to describe the stability of an aqueous solution. When the solution contains higher concentrations of dissolved solute than their equilibrium concentration it is called “supersaturated”. In the industry, supersaturation is the best indicator to predict salt formation. The ability to predict salt formation has two major applications; first, it helps in planning and designing the production facilities. For example, in oil industry the likelihood that salt can form in producing wells and equipment can be predicted for given water compositions injected for water flooding or pressure maintenance. If several waters are available for injection, then the water that is least likely to cause salt problems can be selected. Secondly, it helps to determine the composition of produced water most likely to form salt (scale) and the location where salt is likely to occur, [Cowan and Weintritt 1976]. A way to predict deposit formation is to use the supersaturation ratio as shown:

\[ SR = \frac{IAP}{K_{SP(T,P)}} \]  

Eq. (2.2.11)

where,

- SR : the supersaturation ratio
- IAP : ion activity product
- \( K_{SP(T,P)} \) : solubility product; it is a function of temperature and pressure.

Where:

- If SR > 1, the solution is supersaturated therefore solid phase may form.
- If SR = 1, the solution is saturated.
- If SR < 1, the solution is undersaturation and scale will not form.
Sometimes the logarithm of the SR, called the saturation index (SI), is used for prediction, as it also used in this research:

\[ SI = \log \frac{IAP}{K_{SP(T,P)}} \]  

Eq. (2.2.12)

where:

- If SI > 0, the solution is supersaturated
- If SI = 0, the solution is saturated
- If SI < 0, the solution is undersaturation.

2.3. Nucleation:

The vast majority of the minerals formed in the earth are the result of the combined processes of nucleation and crystal growth. Nucleation is the atomic process by which atoms of a reactant phase rearrange themselves into a cluster of the product phase large enough to be thermodynamically stable. Further enlargement of this cluster is then termed crystal growth, [Lasage 1997; Stumm and Morgan 1996].

2.3.1. Nucleation Mechanisms:

The mechanisms of nucleation are classified based upon the process that initiates growth. Two basic nucleation mechanisms have been recognized, homogeneous and heterogeneous [Lasaga, 1997]. Heterogeneous nucleation requires a preexisting foreign crystalline substance such as dust or reactor wall. The one not fundamentally calling for the presence of the foreign substances, even though it can be influenced by them, is called homogeneous nucleation. It is virtually impossible to have industrial water clean enough for homogeneous nucleation to occur. It is doubtful whether homogeneous nucleation ever exists. [Mullin, 1961; Walton 1967; Nancollas 1979; Randolph and
Larson 1988]. Thus, in the precipitation study the actual type of nucleation should be considered.

2.3.2. Saturation Zones:

Figure 2.3.1 depicts three different saturation zones: undersaturation, metastable, and Labile. In the undersaturation zone neither nucleation and crystal growth occurs, whereas, both nucleation and crystal growth occur in the labile zone. Below the labile zone the nucleation rate is virtually zero and the solution can be stable for long periods of time. However, in this metastable zone crystal growth can occur, without nucleation, if seed material is seeded to the solution, Stumm and Morgan 1997; Lasaga 1997; Zhang and Nancollas 1990].

![Solubility diagram](image)

**Figure 2.3.1**: Solubility diagram, (adapted from Zhang and Nancollas, 1990).

Solution with low supersaturation may remain stable indefinitely without nucleating. This is because the solution is in its metastable position and is not in its lowest energy state. Enough energy must be supplied to push the solution from its resting point toward nucleation. If the energy delivered is very small, the solution may return
back to its metastable position. To illustrate the concept of metastable solution and the influence of foreign matters, a closer look at surface thermodynamic should be taken.

Nucleation requires a phase change. The total free energy change due to nucleus formation consists of energy gained from making bonds and of work required to create a surface [Lasaga, 1997; Stumm and Morgan 1996]. Therefore, the total free energy change, \( \Delta G \), due to forming a stable nucleus in solution equals the sum of the free energy of the bulk solid plus the surface free energy [Mullin 1961; Randolph and Larson 1988; Lasaga 1998; Stumm and Morgan 1996]. Nucleation would be impossible if the product is not thermodynamically favored; therefore a usual requirement for nucleation is that the bulk free energy has to be negative (\( \Delta G_{\text{bulk}} < 0 \)). In Eq. 2.3.1, the bulk free energy is proportional to the volume of the nucleus, and the surface free energy is proportional to the surface area of the solid.

\[
\Delta G (\text{total}) = -\Delta G_{\text{bulk}} + \Delta G_{\text{surface}}
\]

where,

\( \Delta G_{\text{bulk}} \) is Bulk free energy of the solid (always negative)

\( \Delta G_{\text{surface}} \) is Surface free energy.

Assuming spherical particle:

\[
\Delta G = - (4/3) \pi r^3 \Delta G_v + 4\pi r^2 \Delta G_s
\]

where:

\( \Delta G_v \) : bulk free energy per unit volume of solid

\( \Delta G_s \) : surface free energy per unit area of solid

\( r \) : nucleus radius.
Plot of $\Delta G$ versus particle radius shows that the maximum $\Delta G^*$ occurs at some critical radius, $r_c$, Figure 2.3.2.

Figure 2.3.2: Free energy change as a function of nucleus radius (reproduced), [Randolph and Larson 1988].

Putting the derivative of Eq. 2.3.2 with respect to $r$ equal to zero and solving for $r_c$.

$$-4\pi r^2 \Delta G_v + 8\pi r \Delta G_s = 0 \quad \text{(Eq. (2.3.3))}$$

$$r_c = \frac{2\Delta G_s}{\Delta G_v} \quad \text{(Eq. (2.3.4))}$$

Nuclei smaller than $r_c$ require an increase in free energy to grow. The maximum total free energy change, $\Delta G^*$, can be viewed as an energy barrier. If not enough energy exists for stable nuclei to form, crystallization will not occur, and the solution will remain metastable.

The above equation also explains the “Ostwald-Ripening”, a process by which larger particle grow at the expense of smaller ones [Nancollas 1979; Neilson 1983]. Particles, smaller than the stable size, should preferentially dissolve. Eq.2.3.4 also provides a relation between the solution supersaturation and the size of stable particle, $r_c$.

The bulk free energy per volume can be defined as, [Stumm and Morgan 1997]
\[ \Delta G_s = \frac{RT \ln S}{V_m} \]  \hspace{1cm} \text{Eq. (2.3.5)}

where,

- \( S \): solution supersaturation
- \( V_m \): molar volume in m\(^3\) per mole
- \( R \): gas constant
- \( T \): temperature.

By substituting \textbf{Eq. 2.3.5} below into \textbf{Eq. 2.3.4} yields

\[ \ln S = \frac{2\Delta G_s V_m}{RTr_c} \]  \hspace{1cm} \text{Eq. (2.3.6)}

\textbf{Eq. 2.3.6} is called Gibbs-Thomson equation, \cite{Johnson1990}. As the supersaturation increases, the stable particle size becomes smaller.

\subsection*{2.3.3. Impact of Foreign Matter:}

The reduction in the surface energy of the nucleus by foreign matter and also by the wall of pipe and vessel that act as nucleating site as other foreign substances, can be illustrated by analyzing the free energy required to create a surface. Indeed, the level of the energy barrier comes from the work required to create a surface. For a metastable supersaturated solution, in the case of homogenous nucleation

\[ \Delta G_{surf} = \bar{Y}_{cw}A \]  \hspace{1cm} \text{Eq.2.3.7}

where,

- \( \bar{Y}_{cw} \): the interfacial free energy of the crystal to be formed in J/m\(^2\) (assumed to be independent of the crystal size), \cite{StummMorgan1996}
- \( A \): is the surface area of the formed crystal in m\(^2\).
Surface energy is assumed to be constant over the range of sizes of interest in the nucleation, [Stumm and Morgan 1996]. Table 2.3.1 gives values of $\tilde{Y}$ for various minerals. For many minerals, data on $\tilde{Y}$ values are missing. An interesting correlation for simple inorganic salt between $\tilde{Y}$ and the logarithm of the aqueous solubility of the crystal has found by Nielsen, Figure 2.3.3, [Nielsen 1986].

In the presence of foreign material, heterogeneous nucleation, the surface energy term expressed as

$$\Delta G_{\text{surf}} = Y_{\text{cw}} A_{cw} + (Y_{\text{cs}} - Y_{\text{sw}}) A_{cs}$$  \hspace{1cm} \text{Eq. 2.3.8}$$

Where,

the suffixes CW, CS, and SW refer to crystal-water, crystal-seed, and seed-water, respectively. When the surface of the seeds matches well with the formed crystal:

$$Y_{\text{cs}} \rightarrow 0$$  \hspace{1cm} \text{Eq.2.3.9}$$

$$Y_{\text{sw}} = Y_{\text{cw}}$$  \hspace{1cm} \text{Eq.2.3.10}$$

Therefore:

$$\Delta G_{\text{surf}} = Y_{\text{cw}} (A_{cw} - A_{cs})$$  \hspace{1cm} \text{Eq.2.3.11}$$

As shown in Eq.2.3.11, the presence of foreign materials decreases the energy needed to form new crystals and as a consequence decreasing the energy barrier (free energy of formation, $\Delta G$). If the surface area of the foreign material is too large, the surface energy may become negative and the activation energy barrier vanishes, [Stumm and Morgan, 1996].
Table 2.3.1: Surface free energies between minerals and water or melts, [adopted from Lasaga 1998]

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>( \sigma ) (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorite</td>
<td>CaF(_2)</td>
<td>120°</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO(_3)</td>
<td>97°</td>
</tr>
<tr>
<td>Witherite</td>
<td>BaCO(_3)</td>
<td>115°</td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO(_3)</td>
<td>125°</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO(_4\cdot2)H(_2)O)</td>
<td>26°</td>
</tr>
<tr>
<td>Celestine</td>
<td>SrSO(_4)</td>
<td>85°</td>
</tr>
<tr>
<td>Barite</td>
<td>BaSO(_4)</td>
<td>135°</td>
</tr>
<tr>
<td>F-apatite</td>
<td>Ca(_5)(PO(_4)(_3))F</td>
<td>289°</td>
</tr>
<tr>
<td>OH-apatite</td>
<td>Ca(_3)(PO(_4)(_3))\cdot)OH(_2)(_2)O)</td>
<td>87°</td>
</tr>
<tr>
<td>OCPp</td>
<td>Ca(_4)H(PO(_4)(_3))(_x)H(_2)O)</td>
<td>26°</td>
</tr>
<tr>
<td>Portlandite</td>
<td>Ca(OH)(_2)</td>
<td>66°</td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(CH(_2))(_2)</td>
<td>123°</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeOOH</td>
<td>1600°</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe(_2)O(_3)</td>
<td>1200°</td>
</tr>
<tr>
<td>Zincite</td>
<td>ZnO</td>
<td>77°</td>
</tr>
<tr>
<td>Tesserite</td>
<td>CuO</td>
<td>690°</td>
</tr>
<tr>
<td>Gibbsite(001)</td>
<td>Al(OH)(_3)</td>
<td>140°</td>
</tr>
<tr>
<td>Gibbsite(100)</td>
<td></td>
<td>483°</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO(_2)</td>
<td>350°</td>
</tr>
<tr>
<td>Amorph. Silica</td>
<td>SiO(_2)</td>
<td>48°</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al(_2)Si(_2)O(_5)(OH)(_4)</td>
<td>&gt;200°</td>
</tr>
<tr>
<td>Water-air</td>
<td>H(_2)O</td>
<td>71.96°</td>
</tr>
<tr>
<td>Sodium disilicate melt</td>
<td>Na(_2)Si(_2)O(_5)</td>
<td>55°</td>
</tr>
<tr>
<td>Pyrite(100)</td>
<td>FeS(_2)</td>
<td>315°</td>
</tr>
<tr>
<td>Pyrite(111)</td>
<td>FeS(_2)</td>
<td>4733°</td>
</tr>
<tr>
<td>Lithium disilicate melt</td>
<td>Li(_2)Si(_2)O(_5)</td>
<td>201°</td>
</tr>
<tr>
<td>Iron melt</td>
<td>Fe</td>
<td>204°</td>
</tr>
<tr>
<td>Nickel melt</td>
<td>Ni</td>
<td>255°</td>
</tr>
<tr>
<td>Aluminium melt</td>
<td>Al</td>
<td>93°</td>
</tr>
</tbody>
</table>

Figure 2.3.3: The interfacial tension between crystal and aqueous solution as a function of the logarithm of the solubility, [adapted from Lasaga 1998]
2.4. Crystal Growth:

The growth does not usually take place by the direct placement of atoms in solution to a growing face. Rather, there are several steps the atoms follow before arriving to their final place on the growing face. Figure 2.4.1 shows the basic processes whereby atoms transferred from the parent phase (aqueous phase) to the new growing phase (solid phase). The steps of these processes can be summarized as, [Lasaga 1998]:

1) transport of atom through the solution (parent phase),

2) attachment of atoms to the surface,

3) movement of atoms on the surface,

4) attachment of atoms to edges or kinks.

Figure 2.4.1: The basic atomic processes involved during crystal growth, [adopted from Lasaga, 1998].

The processes in step 1 differ from the processes in steps 2-4; the former represents the transport processes in which the atoms transport through a boundary layer in an aqueous phase; whereas, the later involves the processes occur on the surface, [Lasaga 1998]. The important issue, however, is to differentiate transport processes from surface processes and decide which, if any, controls the rate of crystal growth. The transport and
surface processes, both occur normally in series and the slowest process would control
the rate of the overall growth reaction. For example, if the surface reaction is exceedingly
fast and could place the atoms or molecules at a very fast rate, then the crystal would
grow only as fast as the reactant atoms could get to the surface. In this case the overall
growth rate would be determined by the rate of the transport processes. In the literature
this case is termed transport-controlled growth. On the other hand, if the rate of surface
reaction is very slow compared to the transport rate, the overall growth rate would be
determined by the rate-limiting surface reaction. The process is called the surface-
controlled growth.

There have been no solid rules to determine whether the reaction is diffusion
control or surface control. However, in the literature, there are some ideas have been
reported that help to determine the dominant mode of crystal growth [Lasaga 1998):

1) if the concentration gradient in the reactants within the media surrounding the
growth phase is very small, the rate of growth should be surface controlled,
[Tsukamoto and Sungawa 1985; Tsukamoto and Onuma 1991]. It is hard to use
this technique due to the difficulty of in-situ measurement of the concentration
gradient, [Lasaga, 1998].

2) if the rate is independent of steering rate, this give high probability that the
reaction rate is surface controlled.

3) In aqueous media, the activation energy for diffusion is around 5 kcal/mole. So, if
the activation energy of the reaction is much higher than 5 kcal/mole, then it is an
indication of surface controlled reaction.
2.5. Topography of Crystal Surface:

The feature of crystal faces (topography) whether the surface is rough or smooth is also important during the surface processes. Surface-controlled reaction has rate much more sensitive to the surface topography [Jhonson 1990; Lasaga 1998]. Smooth surface is associated with the slow growth while the rough surfaces are more akin to fast growth. Also, the growth sites are not energetically equivalent. **Figure 2.5.1**, displays different growth sites during crystal growth: smooth, edge, and kink sites. Edge and smooth surface sites are less favorable than kink sites. This is because three faces of the incorporated unit in the kink site will bind with crystal [Johnson 1990].

![Figure 2.5.1](image)

**Figure 2.5.1**: Growth sites on a crystal surface. A is smooth surface site, B is edge site and C is kink site [Johnson 1990].

2.6. Methods of Precipitation Processes:

In the laboratory, precipitation experiments are generally conducted by one of the four precipitation processes methods: free drift, pH stat, continuous feeding, and constant composition. Each method has advantages and disadvantages. The selection of each method depends on the objectives of the experiment.
2.6.1. Free Drift and pH-stat:

In the free drift procedure, the change in ion concentration with respect to time is monitored while the solution supersaturation and pH drift freely. In this method, also due to precipitation processes and as a consequence changing initial concentration, ionic strength changes as well. Thus, changes in pH and ionic strength may affect the reaction kinetics and the solubility of some solid phases.

In the pH-stat method, the kinetic of reaction is studied at constant hydrogen ion activity, but the concentrations of the precipitating ions still drift during the experiment. As the supersaturation changes, the solution may be metastable with different solid phases, [Tomson and Nancollas 1978; Koutsoukos, et al., 1980; Kazmierczak, et al., 1982].

The concentration changes during pH stat and free drift experiments are typically small, requiring precise analytical measurements to produce clear numerical result, [Tomson and Nancollas, 1978].

In the free drift and pH-stat experiment, several empirical power law equations are frequently employed in modeling crystal growth. Many researchers successfully used the following second order rate equation to fit the precipitation data for a number of sparingly soluble electrolytes, for example, CaCO₃, CaSO₄, BaSO₄, CaHPO₄, and FeCO₃, [Nancollas and reddy 1971; Nancollas 1979; Johnson 1990; Greenberg and Tomson 1991].

\[
\frac{dM_+}{dt} = k((a_+ a_-)^{1/2} - K_s^{1/2})^2
\]

Eq. 2.6.1

Where,
\[ \frac{dM_+}{dt} : \text{change in cation concentration with time.} \]

k : rate constant

\[ a : \text{activity of cation and anion of the crystal lattice} \]

\[ K_{sp} : \text{thermodynamic solubility product.} \]

Neilsen and others used a similar equation, [Neilsen 1983; Neilsen 1986; Johnson 1990]:

\[ \frac{dM_+}{dt} = k \left[ \left( \frac{a_+ a_-}{K_{sp}} \right)^{1/2} - 1 \right]^2 \quad \text{Eq. (2.6.2)} \]

The temperature dependence of the rate constants and the solubility have similar functional forms, [lasaga 1997; Johnson 1990]

\[ K = Ae^{-E/RT} \quad \text{Eq. (2.6.3)} \]

where,

A : pre-exponential factors; A and \( A_{sp} \) are different for \( k \) and \( K_{sp} \)

E : activation energy; \( E_a \) for \( k \), and enthalpy \( \Delta H_m^o \) for \( K_{sp} \).

2.6.2. Continuous Feeding:

In the continuous feeding method, the reaction solution is continuously fed with the constituent ions. In this method, the ion concentrations increase with time. The change in ion concentration with respect to time is monitored while the solution supersaturation and pH change continuously. Due to continuous feeding of the constituent ions into reaction solution, ionic strength changes. Nevertheless, continuous feeding method enables one to observe the precipitation interaction between different solid phases when the solution containing more than one cations.

The interaction between the constituent ions can be studied by comparing the actual
in-situ measured concentrations in the solution with the calculated concentrations in the effluent stream under the condition of no-reaction. The calculated concentrations of ions in the effluent (under the assumption of perfect mixing, no reaction, and adsorption) can be calculated by using the integrated form of effluent concentration in continuous stirred tank reactor, CSTR. The equation is derived by mass balance of each of the ions in solution:

\[ C_{\text{eff}}(t) = C_{\text{infl}} + (C_0 - C_{\text{infl}}) \exp \left( -\frac{t}{\tau} \right), \tag{2.6.4} \]

where,

- \( C_{\text{eff}}(t) \): concentration of the ion in the effluent at time \( t \) in mg/L
- \( C_{\text{infl}} \): concentration of the ion in the influent stream in mg/L
- \( C_0 \): initial concentration of the ion in the reactor
- \( t \): time in minutes
- \( \tau \): the characteristic retention time in minutes, \( (V/Q) \)
- \( V \): solution volume in mL,
- \( Q \): flow rate in mL/min.

**Note:** In section 2.7 and 2.8, the precipitation interaction of calcium carbonate and iron carbonate was studied by using the free drift, and the continuous feeding methods.

### 2.6.3. Constant Composition:

This method was first developed by Tomson and Nancollas in 1978. In the constant composition method, all the important parameters: the initial concentrations of cations and anions, pH, ionis strength, are held constant by the selective addition of
titrant solutions, [Tomson and Nancollas 1978; Koutsoukos, et al., 1980; Kazmierczak, et al., 1982; Zhang and Nancollas, 1992]. Figures 2.6.1 and 2.6.2 show the shape of the trends of concentration, pH and volume of titrant added with time in a constant composition experiment. In this approach the kinetic of the reaction is studied as a function of titrant solution addition, [Tomson and Nancollas, 1978; Zhang and Nancollas 1992; Wang et al., 2005].

Figure 2.6.1: Concentration of constituent ion and volume of titrant added in constant composition method.

Figure 2.6.2: pH and ionic strength in constant composition method.

Wang et al. used the following equation to study the growth kinetic in term of flux density, [Wang et al. 2005]:

\[
J = \frac{C_p \, dV/dt}{S_A m_s}
\]

Eq. (2.6.5)
Where,

\[ J : \text{the flux in mol s}^{-1} \text{ m}^{-2} \]

\[ C_p : \text{concentration of precipitate, it has any arbitrary value} \]

\[ \frac{dv}{dt} : \text{titantr curve gradient} \]

\[ S_A : \text{specific surface area} \]

\[ m_s : \text{initial seed mass.} \]

Wang et al. did not consider the increase in effective surface area due to crystal growth. However, Zhang and Nancollas studied the kinetic in term of flux by using an equation similar to Wang et al.'s equation with taking to the account the influence of the increase in surface area, [Zhang and Nancollas 1992]:

\[
J = \frac{C_p \, dV/dt}{S_0 \left( \frac{m}{m_0} \right)^p}
\]

Eq. (2.6.6)

Where,

\[ J : \text{the flux in mol s}^{-1} \text{ m}^{-2} \]

\[ C_p : \text{concentration of precipitate, it has any arbitrary value} \]

\[ \frac{dv}{dt} : \text{the slope of titration curve} \]

\[ S_0 : \text{initial effective surface area} \]

\[ m : \text{mass of crystal at time } t \]

\[ m_0 : \text{mass of crystal at time } t = 0 \]

\[ p : \text{is parameter of growth type; for isotropic three dimensional growth } p = 2/3, \]

[Oosterhout and Rosmalen 1980]; for two direction, \( p = 1/2 \); and for one direction, \( p = 0 \), [Barone et al., 1983]
The initial effective surface area, at \( t = 0 \), is related to the total effective surface area at time \( t \) by the following equation, [Christoffersen and Christoffersen 1976; Zhang and Nancollas 1990]:

\[
S_e = S_0 (m/m_0)^p \tag{2.6.7}
\]

Where \( S_e \) and \( S_0 \) are the effective and initial surface areas of the crystals; and \( m \) and \( m_0 \) are the masses of the crystals at time \( t \) and \( t = 0 \), respectively.

Rewriting Eq. 2.6.6:

\[
\log \log \left( \frac{dV}{dt} \right) = \log \left( \frac{JS_0}{C_p} \right) + p \log \left( \frac{m}{m_0} \right) \tag{2.6.8}
\]

Thus, \( p \) value can be obtained by plotting a number of values of \( \log(dv/dt) \) versus \( \log(m/m_0) \), [Zhang and Nancollas 1990]. The above equation requires a perfectly smooth titration curve.

The approach below produces more accurate value for \( p \) and \( J \), [Zhang and Nancollas 1990]. From the volume of titrant addition, \( V \), the total mass of crystal can be calculated:

\[
m = m_0 + M C_p V \tag{2.6.9}
\]

where, \( M \) : the molecular weight in gram per mole.

Substituting of Eq. 2.6.9 into Eq. 2.6.6 produces Eq. 2.6.10:

\[
J = \frac{C_p}{S_0} \frac{dv/dt}{\left( 1 + M C_p V / m_0 \right)^p} \tag{2.6.10}
\]

Integrating Eq. 2.6.9 with initial condition \( V = 0 \) at \( t = 0 \), produces Eq. 2.6.11 and 2.6.12:
\[
J = \frac{C_p}{S_0} \left( \frac{V_c}{t} \right)
\]

Eq. (2.6.11)

\[
V_c = \frac{\left( 1 + \frac{MC_p V}{m_0} \right)^{1-p} - 1}{(1 - p) \left( \frac{MC_{pp}}{m_0} \right)}
\]

Eq. (2.6.12)

where,

- \( V_c \): the corrected amount of titrant for a constant effective surface area, in liter.
- \( M \): the molecular weight of the precipitated solid solution in g/mole.
- \( V \): the actual amount of titrant added in liter.
- \( m_0 \): the mass of crystal, in grams, at \( t = 0 \).
- \( C_p \): the concentration of the precipitated solid solution, mol/L.
- \( p \): the parameter of growth type, [Zhang and Nancollas; 1992].
2.7. Iron (II)-Calcium Carbonate: Precipitation Interaction: Free drift*

2.7.1. Introduction:

Calcium carbonate and iron carbonate minerals are widely observed in oilfield industry. They are also common carbonate salts typically found in the municipal water and wastewater industries. Calcium is commonly present in the formation brine while iron could either be inherently present in the formation brine or released from the formation rock and production strings due to intervention treatments and/or corrosion process.

There is a close relation between the formation of scale and the corrosion. Ferrous carbonate deposit has been recognized as protective layer that effectively inhibits or reduces the corrosion rate [Foss, 2006 and Dugstad et al., 2001]. Also positive scaling of calcium carbonate in the pipe wall of municipal water is often advocated as a mean of corrosion mitigation [Marril et al, 1977]. However, recent evidence suggests that ferrous carbonate may be more important to forming an adherent protective layer. Both iron carbonate and calcium carbonate formation can be useful for corrosion control. On the other hand, excessive formation of either mineral is found to have an adverse effect on tube plugging. They may accumulate in the pumps; valves and production strings, which eventually cause a sever decline in the fluid flow. Also their suspended particles in water, especially in the water injection, may cause formation damage. Therefore, understanding of their chemistry is an important element in the water and oil industries. Most of previous studies have reported results about the kinetics of calcium carbonate solubility

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The content of this section has been published at SPE 114064. 2008. H.A. Al-Saiari, S.Yean, M.B. Tomson, and, A.T. Kan. It was reproduced here as submitted and the only changes here are the numbering of tables and figures, which have been renumbered to adhere to the format of this thesis.
and deposition. Few reports have been found about ferrous iron carbonate precipitation. This is probably due to the difficulties of establishing an anoxic system to precipitate ferrous carbonate in the laboratory. In spite of the fact that formation of mixed scale of both calcium and iron carbonate, \( \text{Fe}_x\text{Ca}_{1-x}\text{CO}_3 \), has been observed in several oil wells and water treatment plants, not enough results have been presented in the literature showing the interactions of both simultaneously.

Earlier studies, conducted by Johnson and Tomson, investigated the kinetics of pure iron carbonate and how they impact oilfield corrosion [Jonson et al., 1991 and Tomson et al., 1991]. Braun studied the solubility of pure iron(II) carbonate at different temperature and reported that the rate-determining step of the dissolution reaction is \( \text{FeCO}_3(\text{s}) + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^- \) [Braun, 1991]. Also Greenberg et al., studied the solubility and dissolution of pure iron carbonate at different temperatures [Greenberg et al., 1992]. A study, conducted by Herzong et al., investigated the effect of iron oxide particles and ferrous iron on the calcium carbonate nucleation and growth at room temperature [Herzong et al., 1989]. He found that a trace concentration of \( \text{Fe}^{2+} \) strongly inhibited the calcite growth but not aragonite growth and also inhibited the transformation of aragonite into calcite. Similar results have been also reported by Langerak et al., during his study of the influence of phosphate and iron on the extent of calcium carbonate precipitation during anaerobic digestion at 30 °C [Langerak et al., 1999]. The influence of impurities on the growth rate of calcite at 20 °C was studied by Meyer [Meyer, 1984]. He found that Fe (II) had the lowest concentration, among the tested impurities, required to halve the initial growth rate.
As mention above, most of the previous studies either have investigated only the precipitation of pure iron carbonate, pure calcium carbonate or the effect of iron in the calcite precipitation only at low temperature (room temperature). Whereas, oilfields have temperatures higher than 45 °C. Also, most of the published reports did the study only in batch systems and did not investigate the effect of continuous feeding of the constituents. Therefore, this work was intended to:

- Studying the interaction between ferrous iron and calcium in a supersaturated alkaline solution and investigate the influence of each constituents (Fe\(^{2+}\) and Ca\(^{2+}\)) on the solubility of iron carbonate and calcium carbonate at high temperature (55 - 65 °C) in both batch system (BS) and continuous stirred tank reactor (CSTR).
- Comparing the crystalline shape of pure iron carbonate, calcium carbonate and mixed solid of iron-calcium carbonate.
- Determining experimentally the actual molar ratio of ferrous iron to calcium in the precipitated solid.

2.7.2. Experimental technique and Design

2.7.2.1 Preparation of Solutions:

Bulk stock solutions were prepared for the CSTR experiments. Whereas in batch system experiments the salts of ferrous iron, calcium and bicarbonate were directly added to a deoxygenated-deionized-water (DDIW) right before the experiment. A solution of sodium chloride (NaCl) was prepared by adding sodium chloride salt, supplied by Fisher Scientific (S-671-500), to DI water pre-filtered by 0.45 μm filter. Similarly, calcium and bicarbonate solutions were separatedly prepared by adding salts of calcium chloride and
sodium bicarbonate (Fisher Scientific, S233-500), to DI water. Then, they were sparged with 1% carbon dioxide gas for at least one hour. Iron (II) sulfate heptahydrate (FeSO4.7H2O), from Acros Organic, was used as ferrous iron source in all the experiments. Ferrous iron solution was prepared to avoid the oxidation of iron. First, a pre-measured volume of DDIW in a separate vial was prepared. A known weight of iron sulfate heptahydrate solid was quickly added to a deoxygenated 10 ml plastic syringe and then dissolved with small volume of the previously prepared DDIW. Then, the solution was transferred to the original three-valve-cap glass vial by vacuum and kept under 1% CO2 gas to prevent oxygen contamination.

2.7.2.2. Experimental Apparatus:

One of the major difficulties in studying the kinetics of ferrous iron in the laboratory generally comes from the difficulty of designing a rigorous anoxic system. The experiments were performed in a glass reaction vessel covered with six-hole steel cap. The hole in the middle of the cap was used for two functions; as a gas outlet and also to pass the bar of the two-way agitator through. The second hole was used alternatively for both temperature measurements and pH meter electrode. The third hole was used for collecting samples while the fourth one was connected to the gas inlet line. The fifth and sixth holes were only utilized as inlet lines during the CSTR experiments to continually feed the reactor with iron, calcium and bicarbonate solutions. Iron and calcium solutions entered into the reactor from one line while bicarbonate entered from a separate line to avoid premature precipitation of carbonate salts. A water circulation bath was used for temperature control. The solution was thoroughly mixed with a two-way agitator. CO2 (1% and balance is N2) gas was used to deoxygenate the pumps and solution lines before
transferring the solutions into them. Oxygen gas absorber was connected right to the cylinder’s gas outlet to remove trace of oxygen that might be present with the reactor’s inlet gas. Figure 2.7.1 shows the actual experimental apparatus.

![Figure 2.7.1: Picture of actual experimental apparatus.](image)

2.7.2.3. Experimental Procedures:

In batch reactor experiments, 500 ml of 0.01 M NaCl solution was initially added to the reactor vessel. The temperature was digitally controlled on the monitor of the water bath. In addition, portable thermometer was inserted through one of the hole of the steel cap. The DI water had been deoxygenated by sparging with a 1% CO2 gas in N2 for at least one hour. The dissolved oxygen content was then measured by a colorimetric analysis (CHEMets Kit) to make sure that the DI water in the reactor is oxygen free (less than 5 ppb). Then, a specific weight of sodium bicarbonate powder was added directly to the reactor vessel as carbonate source. Before adding the salts, the pH had been monitored until no change on pH was observed. Afterward, iron and then calcium salts were added to the reactor vessel.
In the CSTR experiments the sequence and the procedures were quite different. Two liters of 0.5 M NaCl solution were prepared and deoxygenated by 1% CO₂ gas. 500 ml of this NaCl solution was transferred to the reactor cell and kept under CO₂ sparging. Another portion of it was used to preparing calcium, iron and bicarbonate solutions to avoid significant change in the ionic strength of the final solution. Three separate pumps were used; each solution was transferred by vacuum to each pre-deoxygenated pump. Three pumps were operated at equal flow rate, 20 ml/hr, for a total flow rate of 60 ml/hr. Figure 2.7.2 shows schematic of the CSTR experiments.

![Figure 2.7.2: Schematic of experiment procedures.](image)

2.7.2.4. Analytical Technique:

The concentrations of iron, calcium and bicarbonate were measured by collecting samples from the reaction cell each 10 minutes. The sampling line was first flushed with two milliliters, and then, another eight milliliters was removed from the reactor by a syringe for analysis. The sample was filtered with 0.45 μm filter before performing the
analysis to remove the suspended solids of calcium and iron carbonate. Two grams of the filtered sample were then transferred into the Hach-spectrophotometer vial and then diluted to 25 grams with DI water for iron measurement. Total alkalinity was also measured in-situ to minimize the error that might result from further precipitation. The alkalinity measurement was performed by titrating with 0.05 N HCl using Bromcresol Green-Methyl Red Indicator Powder (Hach Permachem Reagents). The total alkalinity was assumed to be equal to the bicarbonate concentration under the experiment conditions. Figure 2.7.3 shows the ionization of carbonic acid with pH in an open system in equilibrium with 1% CO₂ at 55 °C. Calcium measurement was done by transferring another one gram of the filtered sample into nine grams of 2% HNO₃. The calcium concentration was measured later after finishing the experiment by inductive coupled plasma (ICP). The Saturation index and ionic strength were calculated by using Visual Minteq software version-2.53. Saturation index (SI) is defined by the following equation:

\[
SI_{\text{siderite}} = \log_{10} \frac{a_{\text{Fe}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{\text{SP,siderite}}(T,P)}
\]

Eq. (2.7.1)

\[
SI_{\text{calcite}} = \log_{10} \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{\text{SP,calcite}}(T,P)}
\]

Eq. (2.7.2)

Where \(a_{\text{Fe}^{2+}}, a_{\text{Ca}^{2+}}, a_{\text{CO}_3^{2-}}\), and \(K_{\text{sp}}\) are the activities of ferrous iron, calcium, and carbonate and solubility product constants of the precipitated solids.

The calculated concentrations of iron, calcium and bicarbonate in the effluent of CSTR system under the assumption of perfect mixing, no reaction and adsorption were
calculated by using the integration form of effluent concentration in CSTR. The equation was derived by mass balance for each of the ions in solution.

\[
C(t) = C_{in} \left(1 - \exp\left(\frac{-t}{\tau}\right)\right) + \left(C_0 \exp\left(\frac{-t}{\tau}\right)\right)
\]

Eq. (2.7.3)

Where, \(C(t)\) is the concentration of the ion in mg/L at time \(t\). \(C_{in}\) is the concentration of the ion in the influent stream in mg/L. \(C_0\) is the initial concentration of the ion in the reactor. \(t\) is time in minutes, \(\tau\) is the characteristic retention time in minutes, \((V/Q)\).

![Figure 2.7.3: Ionization constant of carbonic acid at 1% CO\(_2\) and 55 °C.](image)

2.7.2.5. Solid Preparation:

The solid analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM) was collected after the suspended salt in the reaction solution settled in the bottom of reaction vessel. The CO\(_2\) gas was kept flowing during this process to avoid oxidation processes. The supernatant fluid was then slowly sucked from the reactor. The remaining wet solid was kept to dry at 70 °C. The dry solid was washed with DI water to remove residual of background electrolyte due to evaporation. Eventually, the solid was dried again by following the same aforementioned steps.
2.7.3. Result and Discussion:

2.7.3.1. The Interaction Between Iron-II and Calcium in Batch System:

Series of experiments have been conducted to study the precipitation interaction between ferrous iron and calcium in a batch reactor in 0.01 M NaCl solution at temperatures of 45, 55 and 65 °C. The ferrous iron to calcium molar ratio was varied in each experiment by changing calcium concentrations while keeping iron and bicarbonate concentrations constant. Table 2.7.1 summarizes the experimental conditions such as the initial concentrations, saturation index (SI), ionic strength (IS) and Fe/Ca molar ratio. Figure 2.7.4 shows the change of ferrous iron concentration with time at different iron-calcium molar ratios. In the absence of calcium (Fe/Ca molar ratio = 1:0), the concentration of ferrous iron in the solution dropped approximately by 60% after one hour. The figure also shows that the presence of calcium ions in a solution containing ferrous iron, at Fe/Ca molar ratios 1:1 and 1:2, had no significant effect on the solubility of ferrous iron. However, they slightly reduced the rate of precipitation of siderite in the solution during the first half of the experiment if compared with that of no calcium. When calcium concentration was increased to about 800 mg/L in the initial solution (Fe/Ca molar ratio = 1:10), the drop in iron concentration significantly reduced to approximately 10%. Moreover, more increasing in calcium concentration (Fe/Ca molar ratio = 1:50), [Ca] = 4000 mg/L, no noticeable drop in ferrous iron concentration was observed during the course of the experiment. Figure 2.7.5 shows the concentrations of calcium at different Fe/Ca molar ratios. The increase in calcium concentration resulted in an increase in the SI value of calcite. No change in calcium concentration was observed at Fe/Ca molar ratio 1:1 and 1:2, respectively. A little drop in calcium concentration was
observed at higher ratios (1:10 and 1:50). Although the drop in calcium concentrations was not significant, but was probably due to increasing the saturation index of calcium carbonate.

Table 2.7.1: Summary of experimental conditions of the batch experiments.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>[Fe], mM</th>
<th>[Ca], mM</th>
<th>[HCO3], mM</th>
<th>SI, Siderite</th>
<th>SI, Calcite</th>
<th>Molar Ratio: Fe:Ca</th>
<th>T, °C</th>
<th>pH</th>
<th>Ionic strength</th>
<th>[NaCl], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>1.90</td>
<td>0</td>
<td>4.0</td>
<td>2.53</td>
<td>-</td>
<td>1:0</td>
<td>55</td>
<td>7.55</td>
<td>0.020</td>
<td>0.01</td>
</tr>
<tr>
<td>B-2</td>
<td>1.90</td>
<td>1.90</td>
<td>4.0</td>
<td>2.49</td>
<td>0.51</td>
<td>1:1</td>
<td>55</td>
<td>7.53</td>
<td>0.025</td>
<td>0.01</td>
</tr>
<tr>
<td>B-3</td>
<td>1.90</td>
<td>3.80</td>
<td>4.0</td>
<td>2.45</td>
<td>0.77</td>
<td>1:2</td>
<td>55</td>
<td>7.52</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>B-4</td>
<td>1.90</td>
<td>19.0</td>
<td>4.0</td>
<td>2.22</td>
<td>1.23</td>
<td>1:10</td>
<td>55</td>
<td>7.45</td>
<td>0.072</td>
<td>0.01</td>
</tr>
<tr>
<td>B-5</td>
<td>1.90</td>
<td>95.0</td>
<td>4.0</td>
<td>1.81</td>
<td>1.50</td>
<td>1:50</td>
<td>55</td>
<td>7.31</td>
<td>0.275</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 2.7.4: Concentration of iron at various FICMR (1:0,1,2,10 and 50) at 55 °C.
2.7.3.2. Interaction Between Iron-II and Calcium in CSTR System (continuous feeding):

Iron carbonate and calcium carbonate salts have different solubility-product constants, ($K_{sp}$ at 25 °C), $10^{-10.55}$ and $10^{-8.30}$, respectively [Sawyer, 2003]. The cation precipitating first may impair the chance of precipitation of the other by consuming the available carbonate in the solution. In order to avoid the lack in the availability of carbonate ions in the solution during the experiment due to precipitation and complexes formation, similar experiments were conducted but in continuous stirred tank reactor. This was also to evaluate the impact of continuous feeding more clearly. The molar concentration of bicarbonate in the influent was designed to be always greater than the sum of molar concentration of both ferrous iron and calcium. Also, to reduce the effect of variation in the ionic strength during the precipitation process, all the CSTR experiments were conducted in 0.5 M NaCl solution at 55 °C.

Figure 2.7.6 compares the calculated concentrations of ferrous iron and calcium in the case of no reaction to the actual in-situ measured concentration in solution with time. The pH was also measured during the experiment, Figure 2.7.7. The concentrations of ferrous

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Ca(1:1)</th>
<th>Ca(1:2)</th>
<th>Ca(1:10)</th>
<th>Ca(1:50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>20</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>40</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>50</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>60</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>70</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>
iron, calcium and bicarbonate in the inflow stream were 274.9 mg/L, 2657.8 mg/L and 4492.4 mg/L respectively. The drop in ferrous iron concentration was noticed first. This occurred at \( \text{SI}_{\text{siderite}} \approx 1.6 \), Figure 2.7.8. At this \( \text{SI}_{\text{siderite}} \) the calcium concentration was only about 100 mg/L, much lower than what was observed in batch studies (Figures 2.7.4 and 2.7.5) to inhibit siderite nucleation and growth. Iron carbonate continued to precipitate until calcium concentration reached about 300 mg/L, at \( \text{SI}_{\text{aragonite}} \approx 2.0 \), and aragonite started to nucleate and grow, which resulted in inhibiting siderite growth. Siderite inhibition by aragonite continued until the \( \text{SI}_{\text{siderite}} \) reached about +3.0 (after 110 min) at which it appeared that both aragonite and siderite were able to grow simultaneously (Figure 2.7.6). Whether they formed arkarite \([\text{CaFe(CO}_3)_2]\) or some less well defined mineral such as ferroin calcium carbonate is not yet known, but this is probably an ideal experimental approach to study these phase relationships in the future.

Analogous experiments were performed exactly under the same conditions in the absence of calcium to clearly validate the impact of calcium in the solution supersaturated with ferrous iron. Figure 2.7.9 shows the trends of ferrous iron concentrations in the presence and absence of calcium. Iron concentrations exhibited the same behavior in both cases during the first seventy minutes. However, thirty minutes later, iron carbonate precipitation accelerated and then dropped to almost zero. The accelerated precipitation of iron carbonate in the absence of calcium ions was probably due to the buildup of bicarbonate concentration in solution. As a result, it can be inferred that calcium has a strong impact on the precipitation of ferrous carbonate. Its presence impaired the precipitation of siderite at high SI values during a continuous feeding of ferrous iron into the solution.
The effect of iron in a solution supersaturated with calcium was also studied. Figure 2.7.10 shows the change in calcium concentration in the presence and absence of ferrous ions. The presence of ferrous iron in solution did not show significant impact on the extent of calcium carbonate precipitation. In the presence of ferrous ions there was a small increase in the concentration of calcium in solution, but not significant. The precipitation of siderite at the beginning did not also substantially affect the threshold precipitation of calcium carbonate.

Generally, the precipitation of iron carbonate at the beginning and the precipitation of calcium carbonate afterward and the inhibition of iron carbonate precipitation accompanied with the precipitation of calcium carbonate most likely explains some of the field cases where pure siderite scale was found in the bottom of the tubing and pure calcium carbonate scale was found in the top when the formation brine contains high concentration of iron and calcium.

![Graph](image)

**Figure 2.7.6**: Concentrations of iron and calcium with time in CSTR at 55 °C.
Figure 2.7.7: pH reading in CSTR at 55 °C.

Figure 2.7.8: Saturation index (SI) and Ionic Strength

Figure 2.7.9: Iron concentrations in the solution in the presence and absence of calcium in CSTR at 55 °C.
2.7.4. Effect of Temperature:

Iron carbonate precipitation in the oilfield is known to be sensitive to temperature. Figure 2.7.11 shows the change in iron concentration with time in a batch reactor, all at initial Si$_{\text{siderite}}$ 2.6 at three different temperatures (45, 55 and 65 °C). No change in iron concentration was observed at 45 °C whereas the concentration gradually decreased at 55 °C and sharply dropped at 65 °C. Figure 2.7.12 shows the iron concentration in a batch system, but in the presence of calcium at a molar ratio of iron-to-calcium 1:10 at 65 °C. The drop in concentration of iron was drastically reduced when the calcium co-existed in the solution. The drop of iron concentration in the experiment with similar iron-to-calcium molar ratio (1:10) at 65 °C was higher than that observed at 55 °C. Therefore, presence of calcium significantly reduced the effect of increased temperature.

Similar experiments were performed but in CSTR system instead. Figure 2.7.13 shows the concentration trends of both iron and calcium at 55 °C and 65 °C. As expected, the drop on concentrations was slightly higher at 65 °C than that at 55 °C of
both calcium and iron. At the end of three hours the system converted to batch by closing all the influent lines. This was intended to evaluate the stability of cations in solution. Surprisingly, no appreciable further drop in concentrations was observed. Figure 2.7.14 shows the SI values before and after the shut-in at $55 \, ^\circ\mathrm{C}$.

Figure 2.7.11: Iron concentrations in the solution at different temperatures in BS.

Figure 2.7.12: Iron concentrations in the solution in the presence of calcium at $65 \, ^\circ\mathrm{C}$ in a batch reactor.
Figure 2.7.13: Iron and calcium concentrations in the solution in at 55 °C and 65 °C.

Figure 2.7.14: SI value of siderite, aragonite and calcite at 55 °C.

2.7.5. XRD and SEM analysis:

Several solid samples were collected for XRD and SEM analysis; three from CSTR experiments and another three from the batch experiments. The XRD analysis showed that the solid collected from the reactor containing only calcium was mixed calcite and aragonite. Whereas, the solid collected from the experiments of solution containing both ions of iron and calcium was entirely aragonite. This revealed that the presence of ferrous iron in solution changed the calcium carbonate salt from the stable
form (calcite) into a metastable form (aragonite). Aragonite typically has higher solubility than calcite but lower solubility than vaterite and other forms of amorphous calcium carbonate salts [Plummer et al., 1982 and Brecevic et al., 1989]. These results are very consistent with the results previously found (at 25 °C) by Herzong, et al., (1989) where they reported that ferrous iron strongly inhibited calcite growth but not aragonite growth and the trace amount of ferrous iron also inhibited the transformation of aragonite into calcite. Also Langerak, et al., (1999) reported that iron did not inhibit the deposition of calcium carbonate, however it did inhibit the growth of calcite but not the formation of aragonite.

Figures 2.7.15a to 2.7.15c show the crystal shape taken by SEM of the solids collected from the experiments of pure iron carbonate, pure calcium carbonate and a mix of both, respectively. Pure iron carbonate (siderite) showed a poorly defined plate-like shape whereas calcite showed trigonal-hexagonal shape. Conversely, the shape of mix-iron-calcium carbonate showed to be dependant on the iron calcium molar ratio. Its crystal shape varied between the poorly defined shape of siderite and the well-organized crystalline shape of calcite. It was shown to be closer to the crystal shape of siderite when the iron content is high and closer to aragonite when the iron content was low, Figures 2.7.15c – 2.7.15e.
Photo 2.7.15: a) Pure iron carbonate (Siderite), Batch System at 55 °C; b) pure calcium carbonate (Calcite), CSTR at 55 °C; c) mixed iron-calcium carbonate at molar ratio iron-to-calcium 1:10 (Batch System at 55 °C; d) Mixed iron-calcium carbonate at molar ratio iron-to-calcium 1:50 (Batch System at 55 °C; e) Mixed iron-calcium carbonate (CSTR at 55 °C).
2.8. Effect of calcium and iron (II) ions in the precipitation of calcium carbonate and iron carbonate: Continuous Feeding*

2.8.1. Introduction:

Most subsurface waters produced with hydrocarbons contain a high concentration of bicarbonate ions as a result of high carbon dioxide (CO₂) partial pressure. CO₂ dissolves into formation brine to convert to a weak carbonic acid, as follows:

\[ \text{CO}_2(g) \rightarrow \text{CO}_2(aq) \]  
Eq. (2.7.1)

\[ \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq) \]  
Eq. (2.8.2)

Aqueous carbonic acid (H₂CO₃) is a weak acid that dissociates in two steps (Sawyer et al. 2003):

\[ \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \]  
Eq. (2.8.3)

\[ \text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-} \]  
Eq. (2.8.4)

The weak carbonic acid formed from the contact of carbon dioxide can readily dissolve certain minerals, such as calcium carbonate, to form the soluble calcium, iron, and, further, bicarbonate ions in the formation water. Because of changes in conditions, precipitation of calcium and iron salts occurs. These are also common carbonate salts typically found in the municipal water and wastewater industries. Calcium is commonly present in the formation brine, while iron either could be inherently present in the formation brine or could be released from the formation rock and production strings because of intervention treatments or corrosion processes.

*The content of this section has been published at SPE J. 2010. H.A. Alsaiai, A. Kan, M. Tomson. It was reproduced here as submitted and the only changes here are the numbering of tables and figures, which have been renumbered to match the format of this thesis.
Scale formation and corrosion are closely related. Positive scaling of calcium carbonate and iron carbonate in the pipe walls of municipal water lines and oil-production lines has been advocated as a means of corrosion mitigation (Merrill et al. 1977; Dugstad et al. 2001; Foss et al. 2006). However, excessive formation of either mineral has been found to have an adverse effect on tube plugging. Also, their suspended particles in water, especially in water injection, may cause formation damage. Therefore, an understanding of their chemistry is an important concern in the water and oil industries.

Sparse information has been reported about the kinetics of iron carbonate solubility and deposition. This is probably because of the difficulties of establishing an anoxic system to precipitate ferrous carbonate in the laboratory. Despite the fact that formation of mixed scale of both calcium carbonate and iron carbonate, Fe$_x$Ca$_{1-x}$CO$_3$, has been observed in several oil wells and water-treatment plants, not enough results have been presented in the literature showing the interactions of both simultaneously. Earlier studies investigated the precipitation and dissolution kinetics of pure iron carbonate and how they affect oilfield corrosion (Braun 1991; Johnson and Tomson 1991; Tomson and Johnson 1991; Greenberg and Tomson 1992). The influence of impurities on the growth rate of calcite and siderite at room temperature was also studied by several researchers (Meyer 1984; Herzong et al. 1989; van Langerak et al. 1999). Recently, Alsaiari et al. (2008) exclusively studied the interaction and crystal shape of mixed iron carbonate/calcium carbonate at 55°C in a batch reactor. They found that the presence of ferrous iron inhibited calcite growth but not aragonite growth.

As mentioned, most of the previous studies have investigated only the precipitation of pure iron carbonate or pure calcium carbonate, or the effect of iron in the calcite
precipitation only at low temperature (room temperature). On the other hand, the processes in oil fields are at high temperatures. In addition, most of the previous work was carried out only in batch systems and did not investigate the effect of continuous feeding of the constituents. Therefore, this work was intended to study the interaction between ferrous iron and calcium in a supersaturated alkaline solution and to investigate the influence of each constituent (Fe\(^{2+}\) and Ca\(^{2+}\)) on the solubility of iron carbonate and calcium carbonate at high temperature. It was also intended to determine experimentally the actual molar ratio of ferrous iron to calcium in the precipitated solid.

2.8.2. Experimental Methods and Materials

2.8.2.1. Solution Preparation:

A stock solution of 0.5 M sodium chloride (NaCl) was prepared by adding NaCl salt to deionized water prefiltered by a 0.45-\(\mu\)m filter. NaCl solution was used as a background solvent to preparing iron (II), calcium, and bicarbonate solutions. Iron (II) sulfate heptahydrate (FeSO\(_4\)·7H\(_2\)O) was used as a ferrous-iron source in all the experiments. Ferrous-iron solutions were prepared carefully to avoid successive oxidation of iron. First, a premeasured volume of NaCl solution was transported into a sealed multivalve bottle. The NaCl solution was deoxygenated by sparging with 1\% CO\(_2\) gas [balance is nitrogen (N\(_2\))] for at least one hour. Preweighed salt of iron sulfate heptahydrate was transported quickly into a 10-mL plastic syringe preflushed with CO\(_2\) gas. The syringe piston was then pushed to the end till almost no gas was left inside the syringe. The syringe was connected to the bottle through one valve. Iron salt in the syringe was dissolved by drawing back-and-forth some of the deoxygenated NaCl
solution in the sealed bottle, Figure 2.8.1. Further sparging by 1% CO$_2$ gas was applied to expel trace amounts of oxygen that might have entered through salt dissolution. The bottle was kept under a small positive pressure to prevent contamination with air. Similarly, calcium and bicarbonate solutions were prepared separately by adding salts of calcium chloride and sodium bicarbonate to deoxygenated 0.5 NaCl solutions.

Figure 2.8.1: Iron (II) solution preparation.

2.8.2.2. Experimental Apparatus:

One of the major difficulties in studying the kinetics of ferrous iron in the laboratory generally comes from the difficulty of designing a rigorous anoxic system. The experiments were performed in a glass reaction vessel covered with a six-hole steel cap, similar to that used by Al-Borno and Tomson (1994). The hole in the middle of the cap was used for two functions: as a gas outlet and as a passage for the bar of the two-way agitator. The second hole was used alternatively for temperature measurements and a pH meter electrode. The third hole was used for collecting samples, while the fourth hole was connected to the gas-inlet line. The fifth and sixth holes were used only as inlet lines for iron, calcium, and bicarbonate solutions. Iron and calcium solutions entered together into the reactor from one line, while bicarbonate entered from a separate line to avoid
premature precipitation of carbonate salts. A water-circulation bath was used for temperature control. The solution was thoroughly mixed with a two-way agitator. CO₂ (1% in N₂) gas was used to deoxygenate the pumps and solution lines before transferring the solutions into them. An oxygen-gas absorber was connected to the gas-cylinder outlet to remove the impurities and trace of oxygen that might be present with the reactor inlet gas. **Figure 2.8.2** is a schematic of the apparatus used.

![Figure 2.8.2: Schematic of experiment procedures in CSTR.](image)

### 2.8.2.3. Experimental Procedures:

A 500-mL volume of 0.5 M NaCl solution was initially added to the reactor vessel. The 0.5 M NaCl was used to alleviate the rapid increase in the ionic strength that might occur from the continuous feeding of the ions into the reactor solution. The temperature was controlled digitally on the monitor of the water bath. In addition, a portable thermometer was inserted through one of the holes of the steel cap. The NaCl solution in the reactor vessel was deoxygenated by sparging with a 1% CO₂ gas in N₂ and simultaneously stirring with a two-way agitator for at least 1 hour. One percent CO₂ was
used to buffer the solution and prevent rapid increase in the pH from carbonate addition. Based upon experience and estimated mass-transfer rate, the characteristic exchange time (τ) for CO₂ gas is estimated to be a few minutes. The dissolved oxygen content was then measured by a colorimetric analysis to make sure that the oxygen content in the initial solution was less than 5 ppb. Three separate pumps were used to deliver solutions to the reactor. Each solution was transferred by vacuum to each predeoxygenated pump. The concentrations of the calcium, iron, and bicarbonate were varied on the basis of the purpose of each experiment. Three pumps were operated at equal flow rates, 20 ± 0.01 mL/h, for a total flow rate of 60 mL/h.

The CO₂ gas was passed through a separate vessel containing 0.5 M NaCl solution under the same reaction temperature. The presaturation of gas with water, before it enters the reactor, was aimed at minimizing further saturation of CO₂ inside the reactor that may result in a reduction in the initial solution volume. In addition, the agitator speed was adjusted not only to provide mixing but also to minimize the effect of bubbling that might escape with the outlet gas during the course of experiment.

2.8.2.4. Analysis and Sampling Procedure:

The actual concentrations of iron, calcium, and bicarbonate were measured by collecting samples from the reactor every 10 minutes. The sampling line was first flushed with 2 mL of the actual solution. Subsequently, another 8 mL was removed from the reactor by a syringe for analysis. The sample was filtered with a 0.45-μm filter before performing the analysis to remove the suspended solids of calcium carbonate and iron carbonate. Two grams of the filtered sample were then transferred into the spectrophotometer vial and then diluted to 25 g with deionized water for iron
measurement. With a preliminary comparison using inductive coupled plasma (ICP), virtually identical analytical results were obtained, approximately ±0.1%. Total alkalinity was also rapidly measured in-situ to minimize further precipitation of carbonate salts. The alkalinity measurement was performed by titrating with 0.05 N HCl using bromcresol green/methyl red indicator powder. The total alkalinity was assumed to be equal to the bicarbonate concentration under the experimental conditions. Calcium-concentration measurements were made by transferring another 1 g of the filtered sample into 9 g of 2% HNO₃. The calcium concentration was measured later at the end of experiment by ICP. Solid samples were taken periodically for scanning-electron-microscope/energy-dispersive X-ray and X-ray analysis. Each confirmed the chemical results; therefore, they are not included.

2.8.3. Results and Discussion

2.8.3.1. Iron Carbonate/Calcium Carbonate Precipitation Interaction:

The interaction between the constituent ions was studied by comparing their actual in-situ measured concentrations in the solution with the calculated concentrations in the effluent stream under the condition of no-reaction. The calculated concentrations of iron, calcium, and bicarbonate in the effluent (under the assumption of perfect mixing, no reaction, and adsorption) were calculated by using the integrated form of effluent concentration in CSTR. The equation was derived by mass balance of each of the ions in solution:

\[ C_{eff}(t) = C_{int} + (C_0 - C_{int}) \exp\left(-\frac{t}{\tau}\right). \]

Eq. (2.8.5)
where, $C_{\text{eff}}(t)$ is the concentration of the ion in the effluent at time $t$ in mg/L. $C_{\text{infl}}$ is the concentration of the ion in the influent stream in mg/L. $C_0$ is the initial concentration of the ion in the reactor, $t$ is time in minutes, $\tau$ is the characteristic retention time in minutes, $(V/Q)$, $V$ is the solution volume in mL, and $Q$ is flow rate in mL/min.

**Figure 2.8.3** shows the trends of measured and calculated concentrations of ferrous iron, calcium, and bicarbonate. Neither ferrous iron nor calcium was initially present in the reactor except the electrolyte background (0.5 M NaCl). The concentrations of ferrous iron, calcium, and bicarbonate in the inflow stream were 274.9, 2657.8, and 4492.4 mg/L, respectively. The figure explicitly displays four distinguished regions in terms of iron-concentration behavior. The first region represents a transition of solution from its stable undersaturated state to a metastable state, supersaturated. This region extended until approximately 18 minutes. In this region, the saturation indices of siderite and calcite were shifted from negative to positive values, **Figure 2.8.4**. The SI is defined by the following equations:

$$\text{SI}_{\text{siderite}} = \log_{10} \frac{a_{Fe^{2+}} \cdot a_{CO_3^-}}{K_{sp,\text{siderite}}(T,P)}$$  \hspace{1cm} \text{Eq. (2.8.6)}$$

and

$$\text{SI}_{\text{calcite}} = \log_{10} \frac{a_{Ca^{2+}} \cdot a_{CO_3^-}}{K_{sp,\text{calcite}}(T,P)}.$$  \hspace{1cm} \text{Eq. (2.8.7)}$$

$a_{Fe^{2+}}$ is the activity of ferrous iron in solution, $a_{Ca^{2+}}$ is the activity of calcium in solution, and $a_{CO_3^-}$ is the activity of carbonate in solution. $K_{sp,\text{siderite}}$ is the solubility product constant of siderite ($\text{FeCO}_3$), and $K_{sp,\text{calcite}}$ is the solubility-product constant of calcite ($\text{CaCO}_3$). $K_{sp}$ values of siderite and calcite are shown in Table 2.8.1.
**Figure 2.8.3:** Shows the four different regions exhibited in term of iron concentration changes in CSTR at 55 °C. (■) in-situ measured calcium concentration. (▲) in-situ measured ferrous iron concentration. (- -) calculated calcium concentration by equation 9. (---) calculated iron concentration by equation 9.

**Figure 2.8.4:** Change in saturation index (SI) with time. (●) SI siderite. (▲) SI calcite. (■) SI aragonite.
TABLE 2.8.1—SOLUBILITY-PRODUCT
CONSTANTS
OF SIDERITE AND DIFFERENT TYPES
OF CALCIUM CARBONATE

<table>
<thead>
<tr>
<th>Type of Calcium Carbonate</th>
<th>Solubility Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siderite*, FeCO₃, at 25°C</td>
<td>10⁻¹⁰.⁵⁵</td>
</tr>
<tr>
<td>Calcite*, CaCO₃, at 25°C</td>
<td>10⁻⁸.₃₀</td>
</tr>
<tr>
<td>Aragonite**, CaCO₃, at 30°C</td>
<td>10⁻⁸.²</td>
</tr>
<tr>
<td>Vaterite**, CaCO₃, at 30°C</td>
<td>10⁻⁷.₉</td>
</tr>
<tr>
<td>Monohydrate†, CaCO₃, at 30°C</td>
<td>10⁻⁷.₂</td>
</tr>
<tr>
<td>Amorphous††, CaCO₃, at 30°C</td>
<td>10⁻⁶.₅</td>
</tr>
</tbody>
</table>

* Sawyer et al. (2003)
** Plummer and Busenberg (1982)
† Kralj and Brečević (1995)
†† Brečević and Nielsen (1989)

No precipitation was noticed in Region 1, and no change in the color of the solution was observed. The SI_{siderite} at the end of Region 1 was ~0.6, while SI_{calcite} and SI_{aragonite} remained negative. However, in the second region, iron started to precipitate; no precipitation of calcium was observed. This was probably because iron carbonate has lower solubility than calcium carbonate, which resulted in a higher supersaturation index of siderite than calcite and aragonite. Despite of the presence of calcium, iron continued to precipitate because of the continuous increase in the supersaturation of siderite, reaching up to SI = 2.0 at the end of Region 2. These results are consistent with the results, published previously by Alsaiari et al. (2008), on batch experiments where lower concentration of calcium (~76–160 mg/L Ca²⁺) did not inhibit the nucleation and growth of siderite. This region extended until 70 minutes. The third region was confined between 70 and 120 minutes. Surprisingly, it was noticed that precipitation of iron carbonate in this region was completely stopped although the saturation index of siderite was high.
This observation was confirmed by comparing the slope of the lines of the measured iron concentrations with that calculated over the time interval of this region. Because the time interval was short, a straight line was a good assumption for both trends (R value > 0.99). The slope of the measured iron concentration was 0.53, and that of the calculated iron concentration was 0.49 (Table 2.8.2). Larger slope of the line of the measured concentration confirmed that siderite nucleation and growth were not only completely inhibited but also a small quantity of the previously precipitated siderite seeds probably redissolved into the solution, or perhaps iron ions in the solid exchanged with calcium ions. Siderite inhibition continued at this region; on the other hand, calcium carbonate precipitated instead. The SI of calcite was ~1.3 when the calcium precipitation began. The precipitation of calcite or aragonite can be attributed to the increase in their supersaturation and also probably to the availability of the active sites for crystal growth provided by the siderite seeds previously formed at the second region. In addition, calcium carbonate has a higher reaction-rate constant than that of iron carbonate. The reaction-rate constant of calcium carbonate at 25°C is five orders of magnitude greater than the rate constant of iron carbonate (Greenberg 1986; Kazmierczak 1978). Calcium carbonate precipitation in this region resulted in a drop in SI_{siderite}, but the SI_{siderite} was still higher than the value at which siderite started to precipitate at Region 2. A change in the color of the solution was gradually observed from light gray at the second region to a cloudy white at the third region. It is difficult to account for the stop in the siderite precipitation. But this result was somewhat in agreement with the results observed in batch experiment at 1:50 Ca/Fe molar ratio where little precipitation in calcite was observed and no precipitation of siderite was noticed (Alsayari et al. 2008). An increase in
the complex formation is probably not the only reason that accounts for this phenomenon because the bicarbonate was fed to the solution continuously at high concentration. But it could be ascribed to the incorporation of calcium into the active sites of siderite crystals. This region is probably important in explaining how serious the corrosion process is when iron carbonate scale is formed in significant quantity in an environment having high calcium concentration.

**TABLE 2.8.2—SUMMARY OF EQUATIONS, SLOPES, AND REGRESSION ($R^2$) VALUES OF IRON- AND CALCIUM-ION TRENDS IN SOLUTION AT DIFFERENT REGIONS FROM THREE DIFFERENT EXPERIMENTS**

<table>
<thead>
<tr>
<th>Experime nt Number</th>
<th>Reaction</th>
<th>No Reaction</th>
<th>Equation</th>
<th>$R^2$</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11708</td>
<td>Fe$^{2+}$ = 0.999</td>
<td>Fe$^{2+}$ = 0.990</td>
<td>0.492t+16.36</td>
<td>8</td>
<td>0.535t+15.19</td>
<td>2</td>
</tr>
<tr>
<td>11308</td>
<td>Fe$^{2+}$ = 0.999</td>
<td>Fe$^{2+}$ = 0.942</td>
<td>0.044t+0.782</td>
<td>8</td>
<td>0.033t+2.30</td>
<td>8</td>
</tr>
<tr>
<td>11308</td>
<td>Ca$^{2+}$ = 0.999</td>
<td>Ca$^{2+}$ = 0.998</td>
<td>3.655t−116.2</td>
<td>8</td>
<td>1.371t+179.6</td>
<td>8</td>
</tr>
<tr>
<td>11708</td>
<td>Fe$^{2+}$ = 0.999</td>
<td>Fe$^{2+}$ = 0.982</td>
<td>0.437t+11.63</td>
<td>8</td>
<td>0.300t+6.24</td>
<td>3</td>
</tr>
<tr>
<td>11708</td>
<td>Ca$^{2+}$ = 0.999</td>
<td>Ca$^{2+}$ = 0.869</td>
<td>4.339t−184.8</td>
<td>8</td>
<td>1.498t+177.6</td>
<td>7</td>
</tr>
<tr>
<td>21208</td>
<td>Fe$^{2+}$ = 0.999</td>
<td>Fe$^{2+}$ = 0.985</td>
<td>1.160t−80.73</td>
<td>8</td>
<td>0.567t−2.415</td>
<td>7</td>
</tr>
<tr>
<td>21208</td>
<td>Ca$^{2+}$ = 0.999</td>
<td>Ca$^{2+}$ = 0.984</td>
<td>4.280t−145.9</td>
<td>8</td>
<td>2.179t+125.9</td>
<td>4</td>
</tr>
</tbody>
</table>

*Concentrations are in mg/L and time is in minutes (see text and figs. 8 and 9).

**Region 3 showed stalling in iron carbonate precipitation when calcium carbonate starts to precipitate. Region 4 showed precipitation of both iron and calcium carbonate.
In the fourth region, siderite was able to reprecipitate once again along with calcite or aragonite. The simultaneous precipitation of both most likely was because of the heavy buildup of the supersaturation of both minerals, at which the influence of calcium was diminished. The precipitation of siderite in this region was confirmed as it was in the third region, by comparing the slope of the lines of measured and calculated concentrations over the time interval of interest (in this case, Region 4; see Table 2.8.2). The slope of the line of the in-situ measured concentration was a little lower than that of the calculated value, ~0.30 and 0.44, respectively. Comparing the two trends of calcium and iron reveals that the rate of calcite precipitation was higher than that of siderite. This is in agreement with the reported values of rate constants of calcium carbonate and iron carbonate as mentioned. It will be explained further in the following subsection. This region of interaction may be important during the formation of adherent protective films on steel pipe to minimize corrosion rate.

It is known that the pH and ionic strength have an effect on the solubility of minerals. No significant changes in the pH and ionic strength were observed. Because of the continuous feeding of bicarbonate, calcium, and iron ions into the solution, the solution ionic strength gradually increased from ~0.47 to 0.53 M. Also, the solution pH increased and then gradually dropped within a small range; see Figure 2.8.5. The decrease in pH was attributed to the release of protons from bicarbonate ions into the solution as a result of calcium carbonate and iron carbonate precipitations, as in Eq. 2.8.8:

\[ x \text{Fe}^{2+} + (1-x)\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{Fe}_x\text{Ca}_{1-x}\text{CO}_3^{(s)} + \text{H}^+ , \quad \text{Eq. (2.8.8)} \]
2.8.3.2. Molar Ratio:

The molar ratio of calcium to iron in the precipitate was studied by considering the region at which the calcium carbonate and iron carbonate have precipitated simultaneously (Region 4, Figure 2.8.3). This region of spontaneous precipitation of siderite and aragonite (or calcite) appeared after approximately 2 hours and lasted until the end of the CSTR experiment. The amount of calcium and iron precipitated at each time was calculated by subtracting the in-situ-measured concentration from the calculated concentration that should exist if no precipitation occurs, as shown in Figures 2.8.6 and 2.8.7.
Figure 2.8.6: Straight line correlation of measured and calculated concentrations of iron in the region of simultaneous precipitation used in the calculation of simultaneous molar ratio of iron and calcium in the precipitate (exp 011708). (♦) Calculated concentration of ferrous iron. (▲) Measured concentration of ferrous iron.

Figure 2.8.7: Straight line correlation of measured and calculated concentrations of calcium in the region of simultaneous precipitation used in the calculation of simultaneous molar ratio of iron and calcium in the precipitate (exp 011708). (♦) Calculated concentration of calcium. (▲) Measured concentration of calcium.

Three CSTR experiments at different initial concentrations of ferrous iron, calcium, and bicarbonate were performed at 55°C for this purpose. Table 2.8.3 summarizes the concentrations of the constituent ions in the inflow stream of each experiment. As mentioned, in this region, the calcium and iron precipitate alongside each other. A linear relation of calcium and iron concentrations with time was assumed in this region. It was found that the molar ratio of calcium to iron in the precipitated solid varied in each experiment. Their molar ratios in the precipitated solid were proportional to their molar...
ratios in the influent stream. The higher the calcium/iron molar ratio is in the influent, the higher the molar ratio is in the precipitated solid. This phenomenon might be attributed to the increase of the solution supersaturation. Figure 2.8.8 illustrates the result of experiment 21208 as an example; all of the results are summarized in Table 2.8.4.

![Graph](image)

**Figure 2.8.8:** Ratio of calcium to iron in the precipitated solid, exp 021208.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Fe^{2+}</th>
<th>Ca^{2+}</th>
<th>HCO_3^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>11308, M 10^{-3}</td>
<td>0.53</td>
<td>56.84</td>
<td>63.11</td>
</tr>
<tr>
<td>11708, M 10^{-3}</td>
<td>4.92</td>
<td>66.32</td>
<td>73.63</td>
</tr>
<tr>
<td>21208, M 10^{-3}</td>
<td>12.17</td>
<td>66.32</td>
<td>73.63</td>
</tr>
</tbody>
</table>
The composition of the iron/calcium carbonate solid having the chemical formula $(\text{Fe}_x\text{Ca}_{1-x}\text{CO}_3)$ varied on the basis of the experimental condition, where $x$ varied between 0.004 and 0.16. The values of $x$ were actually close to what had been reported in real analysis results of oilfield-scale samples reported by Nasr-El-din et al. (2002). More research should be conducted to pinpoint the parameters affecting the value of $x$ in the solid of iron/calcium carbonate.

Furthermore, the molar ratio of calcium to iron in the influent stream was compared with that in the precipitated solid. This was performed by linearly plotting the molar ratio in the influent vs. the molar ratio in the precipitated solid. Because of the high experimental error that might arise from the analysis of low constituent concentrations, the relation was calculated in two ways: on the basis of the actual measurement and on the basis of the linear correlations of the spontaneous precipitation in Region 4. Both results gave similar numbers, with $R$ values greater than 0.99 (Fig. 2.8.9). The relation of the actual measurements was found to be as follows:

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Influent Stream</th>
<th>Influent Measured</th>
<th>Influent Calculated*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope</td>
<td>$R^2$</td>
</tr>
<tr>
<td>21208</td>
<td>5.45</td>
<td>5.28</td>
<td>0.5676</td>
</tr>
<tr>
<td>11708</td>
<td>13.47</td>
<td>30.02</td>
<td>0.9041</td>
</tr>
<tr>
<td>11308</td>
<td>106.20</td>
<td>254.15</td>
<td>0.9588</td>
</tr>
</tbody>
</table>

* The ratio was determined in two ways: on the basis of the real measurements and on the basis of the linear correlation of the real measurements.
\[
\frac{\text{ratio}_{\text{solid}}}{\text{ratio}_{\text{influent}}} = 2.39, \quad \text{Eq. (2.8.9)}
\]

where \( \text{ratio}_{\text{solid}} \) is calcium/iron molar ratio in the precipitated solid and \( \text{ratio}_{\text{influent}} \) is calcium/iron molar ratio in the influent.

![Relation between molar ratio in inflow and in solid](image)

**Figure 2.8.9:** Relation between calcium-ion molar ratio in influent and precipitated solid at 55 °C. (●) Based on the actual measurement. (■) Based on the correlation derived from straight line.

It was found that the ratio has a constant value of 2.39 (greater than unity). This reveals that calcium ion has a higher preference to precipitate than iron, although the saturation index of calcium carbonate (calcite and aragonite) was lower than that of siderite during the experiment. In addition, calcium carbonate (calcite and aragonite) has higher solubility-product constant than siderite. This phenomenon can be explained by comparing the behavior of iron and calcium ions in the solution. There are several factors that might explain this phenomenon. One of them is probably the characteristic water-loss-rate constant of calcium ions and ferrous-iron ions in water. The rate constant of the formation of metal-ligand complexes in water depends on two factors: the characteristic water-loss rate for the metal ion and the outer sphere association constant for the metal-
ligand pair (Pagenkopf 1978). All metal ions are hydrated in water solution. Many of them coordinately attach to six water molecules to form octahedrons. The water molecules coordinated to a metal ion exchange with those in the solvent. The exchange mechanism involves water loss from the inner coordination sphere of the metal followed by rapid scavenging of the available site by another water molecule.

\[ M(OH_2)_n+OH_2^+ = M(OH_2)_{n-1}OH_2^+ + H_2O, \]  
Eq. (2.8.10)

where \( M \) represents metal (\( \text{Ca}^{2+} \) and \( \text{Fe}^{2+} \)).

The rate of water exchange is dependent upon the particular metal ion. Calcium ion has higher water-loss-rate constant than ferrous ions (Pagenkopf 1978). Calcium can easily and rapidly lose water molecules, to subsequently attach to carbonate ligands in the solution. The stability constant of calcium-/bicarbonate-ion pairs is similar to that of iron, Eqs. 2.8.11 and 2.8.12, but the calcium concentration is much higher.

\[ \frac{[\text{CaHCO}_3^-]}{[\text{Ca}^{2+}][\text{HCO}_3^-]} = 10^{1.26} \quad \text{(Sawyer et al. 2003)} \]  
Eq. (2.8.11)

\[ \frac{[\text{FeHCO}_3^-]}{[\text{Fe}^{2+}][\text{HCO}_3^-]} = 10^{0.23} \quad \text{(Greenberg et al. 1986).} \]  
Eq. (2.8.12)
3. THERMODYNAMIC EQUILIBRIA OF SOLID-SOLUTION AQUEOUS-SOLUTION (SSAS) SYSTEMS

3.1. Introduction:

Minerals in nature, e.g., calcium, iron, magnesium, carbonate, and sulfate, usually contain a certain portion of impurities, [Deer et al., 1963; Cowan and Weintritt, 1976; Pellant 2002]. The study of incorporation of impurities into the solid has been started since the late of 18th century, as a result of the need for high purity chemical reagent, [Glayn 1990]. It is also of great interest to the field of rock water interactions, and to many other processes in industry. Lately, many researchers have studied the thermodynamics of solid solution formation in geochemical processes where equilibrium condition may be assumed. [Lippman, 1980; Plummer 1987; Plummer and Busenberg, 1987; Glynn and Reardon, 1990; Königsberger and Gamsjäger, 1990; Gamsjäger. et al., 2000; Pina and Putnis, 2002, Astilleros, et al., 2003; Pina et al., 2004].

Distribution coefficients were usually used to express the partitioning of impurity ions between the aqueous-phase and the solid-phase, [Stumm and Morgan,1981]. The distribution coefficient is theoretically derived from the thermodynamic equilibrium condition in a binary solid-solution-aqueous-solution system AC-BC-H2O:

\[
\{A^+\}\{C^-\} = K_{AC}a_{AC} = K_{AC}X_{AC}Y_{AC} \quad \text{Eq. (3.1.1)}
\]

\[
\{B^+\}\{C^-\} = K_{BC}a_{BC} = K_{BC}X_{BC}Y_{BC} \quad \text{Eq. (3.1.2)}
\]

Where,

\{A^+\}: the activity of A\(^+\) in the aqueous solution

\{B^+\}: the activity of B\(^+\) in the aqueous solution

\{C^-\}: the activity of C\(^-\) in the aqueous solution
\( K_{AC} \): the solubility product of the pure phase of AC

\( K_{BC} \): the solubility product of the pure phase of BC.

\( a_{AC} \): the solid phase activity of AC

\( a_{BC} \): the solid phase activity of BC

\( X_{AC} \): the solid phase mole fraction of component AC

\( X_{BC} \): the solid phase mole fraction of component BC

\( \gamma_{AC} \): the solid phase activity coefficient of AC

\( \gamma_{BC} \): the solid phase activity coefficient of BC

Dividing Eq. 3.1.1 by Eq. 3.1.2 produces what so called distribution coefficient:

\[
D = \frac{X_{AC}}{X_{BC}} \quad \text{Eq. (3.1.3)}
\]

Eq. 3.1.3 does not provide information about the activity of ion \( \{C\} \), and therefore the solubility of the solid-solution is lost. Geochemists have often used another expression to overcome this problem. They express the solubility of solid-solution \( A_{1-x}B_xC \), [Glynn and Reardon 1990], as follow

\[
\text{IAP}_{SS} = \{A^+\}^{1-x}\{B^+\}^x\{C^-\} = K_{ss} \quad \text{Eq. (3.1.4)}
\]

Where,

\( \text{IAP}_{SS} \): the observed ion activity product

\( K_{ss} \): the applicable solubility constant at a given temperature and pressure for a given solid solution composition \( A_{1-x}B_xC \).
3.2. Lippmann Diagram:

Instead of considering the stoichiometric dissolution, Lippmann (1978, 1980, 1982) adopted the fundamental law of equilibrium thermodynamic, $\mu_{ia} = \mu_{ib}$, to derive the solubility expression for solid solutions. This adoption should be valid for any component $i$ distributed between two phases A and B at thermodynamic equilibrium and at constant temperature and pressure. Thermodynamic equilibrium, adopted by Lippmann, in a system with a binary solid solution $A_{1-x}B_xC$ is defined by the law of mass action equations, Eq.3.1.1 and Eq.3.1.2. If Eq.3.1.1 and Eq.3.1.2 hold true at thermodynamic equilibrium, so must their sum or any other arithmetic combination. Lippmann added Eq.3.1.1 and Eq.3.1.2 together and then defined the “total solubility product” variable $\sum \Pi$, where

$$\sum \Pi = (\{A^+\} + \{B^+\})\{C^-\}$$

At equilibrium:

$$\sum \Pi_{eq} = (\{A^+\}_{eq} + \{B^+\}_{eq})\{C^-\}_{eq} = K_{AC}X_{AC}Y_{AC} + K_{BC}X_{BC}Y_{BC}$$

$$\sum \Pi_{eq} = K_{AC}X_{AC}Y_{AC} + K_{BC}X_{BC}Y_{BC}$$

where,

$$\sum \Pi_{eq}$$ is the value of the solubility product variable at thermodynamic equilibrium. Plot of $\sum \Pi_{eq}$ versus $X_{AC}$ in Eq.3.1.7 is known as “solidus”, [Lippmann 1980]. For a complete description of the solid-solution aqueous-solution system at thermodynamic equilibrium, a second relation was also derived by substituting the activity fractions of ions in the aqueous phase in Eq.3.1.1 and Eq.3.1.2 to produce what so called “solutus”:
\[ \Sigma \Pi_{eq} = \frac{1}{\left( \frac{X_{A,eq}}{K_{AC}Y_{AC}} + \frac{X_{B,eq}}{K_{BC}Y_{BC}} \right)} \]  
Eq. (3.1.8)

Where,

\[ X_{A,eq} = \frac{\{A^+\}}{\{A^+\} + \{B^+\}} \]  
Eq. (3.1.9)

\[ X_{B,eq} = \frac{\{B^+\}}{\{A^+\} + \{B^+\}} \]  
Eq. (3.1.10)

If the activity coefficients of solid phase and aqueous phase are known, then, the two curves, “solidus” and “solutus” of Lippmann diagram can be plotted used to predict the solubility of any solid-solution at thermodynamic equilibrium, [Lippmann 1980, Glynn and Reardon, 1990; Grandia et al. 2008]. For solid solution, \( A_{1-x}B_xC \), the activity coefficients can be calculated using the following equation, [glynn 1990; Bruno 2007]

\[ \ln \gamma_{AC} = X_{BC}^2 [a_0 - a_1 (3X_{AC} - X_{BC}) + a_2 (X_{AC} - X_{BC})(5X_{AC} - X_{BC}) + ...] \]  
Eq.(3.1.11)

\[ \ln \gamma_{BC} = X_{AC}^2 [a_0 + a_1 (3X_{BC} - X_{AC}) + a_2 (X_{BC} - X_{AC})(5X_{BC} - X_{AC}) + ...] \]  
Eq.(3.1.12)

Where,

the parameters \( a_i \) are dimensionless fitting parameters, sometimes referred as excess free-energy parameters, [Glynn and Reardon]. The first two terms in Eq.3.1.11 and Eq.3.1.12 are generally considered to accurately represent the dependence of \( \gamma_{AC} \) and \( \gamma_{BC} \) composition, [Glynn and Reardon 1990; 1992]. If the difference in the sizes of the constituent ions in the solid solution is small, the first parameter, \( a_0 \), is usually sufficient to describe the solid solution, [Urusov 1974; Glynn and Reardon 1990].
3.3. Ideal and Non-ideal Solid Solutions:

Due to the lack in the experimental data and as a result the values of parameters $\alpha_i$, for simplicity, people usually assume an ideal solid solution (all the activity coefficients of the components are unity). The ideality treatment of solid solution is still controversial. However, there is a general consensus about the factors that control the degree of ideality, [Bruno, 2007]:

1) the similarity in size between the substituting and the host ion, and

2) the similarity in crystal lattice.

Table 3.3.1 shows the ionic radiuses of some of the ions commonly exist in water. The ions, Cd$^{2+}$ and Ca$^{2+}$, have similar ionic radii and having same crystal class. As reported in the literature, the experimental value and the calculated value of the partition coefficient between Cd$^{2+}$ and calcite were close when the system was treated as an ideal. On the other hand, Sr$^{2+}$ and Ba$^{2+}$ have larger sizes than calcite, and they belong to different crystallographic systems, so, their partitioning coefficients differ in more than two order of magnitude which suggest strong non-ideality, [Tesoriero and Pankow, 1996; Curti, 1999; Purno 2007].
### Table 3.3.1: the ionic radius of some of the common ions (Adapted from Purno 2007).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.78</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.95</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>1.49</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>0.93</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>1.13</td>
</tr>
<tr>
<td>Au⁺</td>
<td>1.37</td>
</tr>
<tr>
<td>Tl⁺</td>
<td>1.49</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.78</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.99</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>1.27</td>
</tr>
<tr>
<td>Pd²⁺</td>
<td>0.80</td>
</tr>
<tr>
<td>Ag²⁺</td>
<td>0.93</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>1.43</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.91</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.83</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.83</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Calcite (stable calcium carbonate) and siderite both belong to the hexagonal crystal system. This group includes also dolomite (Ca-Mg-CO₃), and magnesite (MgCO₃), [Cowan and Weintritt 1976]. On the other hand, aragonite (metastable calcium carbonate) crystallizes in the orthorhombic system; this system includes strontionite (SrCO₃), and witherite (BaCO₃), [Cowan and Weintritt 1976]. The ion size of calcium
and iron are not quite similar (Ca$^{2+}$ = 0.99 Å, Fe$^{2+}$ = 0.83 Å), Table 3.3.1. In addition, aragonite and siderite belong to a different crystal lattice. Therefore, the assumption of aragonite-siderite, and also calcite-siderite as an ideal solid solution may not be accurate. To plot Lippmann diagram for aragonite-siderite system, one needs to get the value of the parameter, $\alpha_i$. Glynn tabulated the values of $\alpha_i$ for several minerals, [Glynn]. According to Glynn, two values of $\alpha_i$ (2.56, and 4.18) have been reported for a rhombohedral Ca-Fe-CO$_3$ at 50°C. Because of the scarcity in the available data, the average value, $\alpha_i = 3.37$, was considered to create Lippmann diagram. Figure 3.3.1 displays a series of solid solutions and aqueous solutions composition for siderite-aragonite solid-aqueous system at 55°C. The two curves, solidus and the solutus, were plotted using Equations 3.1.7 and 3.1.8. The activity coefficients of the solid solutions were calculated using Equations 3.1.11 and 3.1.12. $K_{sp,aragonite}$ and $K_{sp,siderite}$ at 55°C are $10^{-8.44}$ and $10^{-10.77}$, respectively. Points P1, and P2 give the aqueous and solid phase compositions, respectively, of a system at thermodynamic equilibrium with respect to a Fe$_{0.97}$Ca$_{0.03}$CO$_3$. Points, T1 and T2, give the composition of either an aqueous phase or solid phase if the solid dissolves or precipitate at congruent stoichiometric saturation. Figure 3.3.2, shows Lippmann diagram of same siderite-aragonite solid solution described in Figure 3.3.1 if ideal solid solution is assumed. The shape of the solidus and solutus changed which consequently lead to different predicted values of aqueous and solid compositions. Thus, using inaccurate assumption and thermodynamic data lead to inaccurate stoichiometric predictions of solid solutions compositions.
Figure 3.3.1: Lippmann Diagram for siderite-aragonite solid solution at 55 °C. Blue line (top) represents “solidus”, the composition in solid phase: Pink line (bottom) represents “solutus”, the composition in aqueous phase.

Figure 3.3.2: Lippmann Diagram for siderite-aragonite at 55 °C if ideal solid solution is assumed. Blue line (top) represents “solidus”, the composition in solid phase: Pink line (bottom) represents “solutus”, the composition in aqueous phase.
4. SOLID SOLUTIONS OF IRON CALCIUM CARBONATE AT CONSTANT COMPOSITION

4.1. Introduction:

Understanding of the solid solution formation from the aqueous solutions is needed to predict and prevent solid formation in various water treatment processes. Several studies have examined the thermodynamics of solid solution formations in geochemical processes where equilibrium condition may be assumed [Lippman, 1980; Plummer 1987; Plummer and Busenberg, 1987; Glynn and Reardon, 1990; Königsberger and Gamsjäger, 1990; Gamsjäger. et al., 2000; Pina and Putnis, 2002, Astilleros, et al., 2003; Pina et al., 2004]. However, solid solutions formation is rarely at equilibrium in industrial water treatment processes. The key parameters needed for the prediction of solid solutions formation for industrial water treatment processes are the stoichiometry of solid solution formation and kinetics at different aqueous compositions and conditions. If these parameters were known, scientists and engineers would be able to project, with precision, the incorporation of ions from waters into minerals. They would also helps to infer the physicochemical conditions of natural crystallization environments.

Typically, precipitation is studied by preparing a supersaturated solution and following the concentration of the lattice ions with time. This method is known as free drift. Using free drift is particularly problematic to study solid solution formation, because as the concentrations decrease the solid stoichiometry frequently changes. In addition, the amount of solid solution formed is often very small as the reaction approaches equilibrium. Most of these restrictions have been overcome, for the first time, by modifying the method of constant composition, introduced by Tomson and Nancollas,
1978. This approach has the ability to hold the supersaturation of the aqueous solution at a constant value for long periods of time. At very low supersaturation, macroscopic quantities of stochiometric and highly crystalline material can be formed and collected for analysis. It also solves the difficulty of determining the stoichiometry of precipitation when the experiment has appreciable reduction in the initial concentrations of crystal lattice ions during the reaction. This method also enables one to study one composition of solid solution at a time, at specific supersaturation conditions. Using constant composition method enables researchers to study the influence of pH, ionic strength, seed type, and degree of supersaturation with a precision hitherto unobtainable. This work was intended to; 1) develop an experimental design to be workable for oxygen sensitive salts, and also to be applicable for studying the stoichiometry and kinetics of crystal growth of solid solutions in addition to a single salt; 2) develop a correlation to predict the stoichiometry of iron/calcium carbonate solid solutions as a function of aqueous supersaturation with respect to the pure solid phases.

4.2. Experimental Procedure:

4.2.1. Experimental Apparatus and Design:

A picture and a schematic of experimental design are shown in Figures 4.2.1 and 4.2.2, respectively. The design has the flexibility to deal with oxygen-sensitive ferrous ions. All fluid delivery lines (Peek Tubing) and experimental apparatus were pre-flushed with argon gas several times before conducting the experiment. The titrant containers, titrant syringes, and titrant lines were connected to the flushing gas cylinder and reaction cell by three-way valves to easily flush the lines and containers in an oxygen-free
environment. An oxygen gas absorber (SUPELCO, Model 503088) was connected to the outlet of the gas cylinder as an additional measure to trap the trace concentration of oxygen in the gas cylinder. The precipitation reactions were performed in a double-walled glass reaction vessel connected to a water bath for temperature control. The titrant delivery lines were dipped in a separate double-walled glass vessel connected to a water bath to maintain the titrant solutions to be at same temperature as the reaction solution. A digital caliber was connected to a syringe pump and a PC to track the amount of titrant-solution added during the precipitation processes.

Figure 4.2.1: Picture of the experimental design and its basic components
4.2.2 Reaction Solution Preparation:

Reagent grade chemicals and deionized water were used to prepare the reaction and titrant solutions. Magnetite powder (Aldrich grade) with a particle size less than 5 micron was used as seed materials. In a typical experiment, nitrogen gas with 1% CO₂ was sparged through 600 ml of 0.5 M NaCl solution in water-jacked Pyrex cell to exclude oxygen. 1.0 % CO₂ gas was used to stabilize the concentration of total carbonate. The sparging process was maintained throughout the entire time of each experiment. The oxygen content was measured at the beginning and at the end of each experiment by a colorimetric analysis technique. (O₂ content was less than 5 ppb). The solution in the reaction cell was supersaturated with respect to calcium carbonate and iron carbonate by addition of sodium bicarbonate salt (Fisher grade), calcium chloride dehydrate salt (EMD
grade), and ferrous chloride 4-hydrate salt (J.T. Bakker grade). The salts were added to
the reaction cell after elapsing one hour of the sparging processes. The amount of salts
added was based upon the level of supersaturation required for precipitating a specific
composition of Fe$_x$Ca$_{1-x}$CO$_3$ solid solution. A known amount of de-aerated seed crystals
was added to the reaction solution to induce the precipitation.

4.2.3. Titrant Preparation:

Two titrants, each in a separate container, were used to maintain the experiment
conditions at constant thermodynamic driving force (constant pH, ionic strength, and
initial concentrations). Titrant-1 contained the cations (calcium and ferrous ions) while
titrant-2 contained anions (bicarbonate and hydroxide ions). Titrant-1 was prepared by
adding calcium chloride dehydrate (EMD, assay 99.0-105%) and sodium chloride
(SIGMA-ALDRICH, assay 99.0%) salts to DI water. The solution was sparged with
argon gas (ultra high purity) for about two hours. Ferrous chloride 4-hydrate salt
(J.T.BAKER, assay 101.5%) was added into the titrant container afterward to avoid the
oxidation of ferrous ions. Similarly, titrant-2 was prepared by adding sodium hydroxide
solution (TRISTAR, 1.000±0.002N), sodium chloride salt (SIGMA-ALDRICH, assay
99%), and sodium bicarbonate salt (Fisher grade), to DI water and, then, the mixture was
deoxygenated by argon gas. At the end of the de-oxygenation processes the titrant
containers were maintained at a little positive pressure to prevent contamination with air.
Samples were collected from each titrant for analysis. The equations below were
developed to calculate the total concentrations of cations and anions in titrants. These
equations are similar to what has been reported by Jingwu and Nancollas for a pure solid
phase, [Jingwu and Nancollas, 1992], but modified to include both Ca$^{2+}$ and Fe$^{2+}$. For the reaction:

\[ x\text{Fe}^{2+} + (1-x)\text{Ca}^{2+} + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}_{1-x}\text{Fe}_x\text{CO}_3(\text{s}) + \bar{n}\text{H}^+ \]  

Eq. (4.2.1)

where: $0 \leq x \leq 1$, and $0 \leq \bar{n} \leq 2$

**Titrant-1:**

\[ [\text{CaCl}_2]_{\text{Titr}} = 2[\text{CaCl}_2]_{\text{Sol}} + [\text{CaCl}_2]_{\text{Ppt}} \]

Eq. (4.2.2)

\[ [\text{FeCl}_2]_{\text{Titr}} = 2[\text{FeCl}_2]_{\text{Sol}} + [\text{FeCl}_2]_{\text{Ppt}} \]

Eq. (4.2.3)

\[ [\text{FeCl}_2]_{\text{Ppt}} = \frac{x}{(1-x)}[\text{CaCl}_2]_{\text{Ppt}} \]

Eq. (4.2.4)

\[ [\text{NaCl}]_{\text{Titr}} = 2[\text{NaCl}]_{\text{Sol}} - 2C_{\text{Ppt}} \]

Eq. (4.2.5)

\[ C_{\text{Ppt}} = [\text{CaCl}_2]_{\text{Ppt}} + [\text{FeCl}_2]_{\text{Ppt}} \]

Eq. (4.2.6)

**Titrant-2:**

\[ [\text{NaHCO}_3]_{\text{Titr}} = 2[\text{NaHCO}_3]_{\text{Sol}} + [\text{NaHCO}_3]_{\text{Ppt}} \]

Eq. (4.2.7)

\[ [\text{NaHCO}_3]_{\text{Ppt}} = C_{\text{Ppt}} \]

Eq. (4.2.8)

\[ [\text{NaOH}]_{\text{Titr}} = \bar{n}C_{\text{Ppt}} \]

Eq. (4.2.9)

Where,

The subscripts Titr, Sol, and Ppt refer to the titrant solution, reaction solution, and the precipitate concentration, in mol/L, respectively. $C_{\text{Ppt}}$ in Eq. 4.2.6 is the concentration of the precipitate; any value can be selected for $C_{\text{Ppt}}$. To have enough volume of titrant addition during the course of the experiment, it is recommended to select small concentration for $C_{\text{Ppt}}$ ($\leq 0.1$ mol/L) when the precipitation rate is slow and large concentration ($> 0.1$ mol/L) when the precipitation rate is high. $\bar{n}$ is the average number
of protons bound to a carbonate ion which can be expressed as shown in the following equation:

$$\bar{n} = \frac{[\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3]}{C}$$  \hspace{1cm} \text{Eq.}(4.2.10)

Where,

$C$ is the concentration of total carbonate. The value of $\bar{n}$ is calculated from the ionization constant of carbonates, pH, and total carbonate concentration, or can be read from an alkalinity titration. Plot of $\bar{n}$ as a function of pH at 55°C is shown in Figure 4.2.3.

![Figure 4.2.3: Average number of protons bound per carbonate ion as function of solution pH at IS = 0.5 M and 55°C. Total carbonate was calculated by mass balance equation. The activity coefficient of the proton was calculated by using Davies equation. The ionization constants of carbonate, $K_{a1}$ and $K_{a2}$, at 55°C were obtained from SSP Software ($pK_1 = 6.286$ and $pK_2 = 10.157$)](image)

4.2.4. Precipitation Technique at Constant Composition Method:

pH dropped as precipitation occurred according to the following reaction

$$x\text{Fe}^{2+} + (1-x)\text{Ca}^{2+} + \text{HCO}_3^- = \text{Ca}_{1-x}\text{Fe}_x\text{CO}_3^{(s)} + \text{H}^+$$  \hspace{1cm} \text{Eq.}(4.2.11)
The output of the pH (Orion pH electrode) in the controller (EUTECH-alpha-pH2000w) was constantly compared with a preset value. The difference in electric potential triggered a motor of a syringe pump (Harvard Apparatus-Infusion/Withdrawal Pump) to deliver titrants from two syringes (SGE- 100 ml class syringe) into the reactor cell thereby maintaining a constant thermodynamic driving force. The processes repeated each time pH dropped. The amount of titrants added into the reaction solution with time during the course of the experiment was tracked by a digital recording caliber (WIN-2 RS232 INTERFACE) connected to a PC. Samples from the reaction solution were collected each 10 minutes for analysis.

4.2.5. Experiment Tactic and Ideal Experiment:

The tactic used in this work was based upon trial and error. A series of experiments was conducted, each at different initial concentrations of lattice ions at 55°C. The concentrations of calcium and bicarbonate ions were selected to be within the precipitation zone of calcium carbonate, and also to reflect the concentrations that commonly exist in the natural waters and industrial brines. On the other hand, ferrous iron concentrations were designed to be within the precipitation zone of iron carbonate and outside the precipitation region of ferrous hydroxide ([Fe^{2+}] < 10^{-2.4} M, and pH ≤ 7.5). Visual MINTEQ package and SPP software were used to diagnose the precipitation regions.

The concentrations of lattice ions were varied in each experiment by assuming an arbitrary value for x in the chemical formula, Fe_xCa_{1-x}CO_3, then the reaction and titrant solutions were prepared as described in Eqs. 4.2.2-4.2.10. The concentrations of calcium
and ferrous ions were then monitored during the course of the precipitation experiment. The first experiment was usually considered as non-ideal due to the change in the concentrations of lattice ions. The level of change in the concentrations was corresponding to how much the assumed value, x, was far from the accurate value. In the subsequent experiment, the value of x was projected by performing a mass balance on the concentrations of iron and calcium ions in the preceding experiment. The titrant concentrations were then adjusted accordingly. The procedures were repeated for several iterations until no appreciable change in the concentrations of iron, calcium, and bicarbonate was observed in the reaction solution. Two to three experiments were generally needed to reach constant composition versus time. The acceptable change in lattice ion concentrations was within 2% for calcium and iron ions, and 5% for bicarbonate. At this point, the constant composition experiment was considered successful in which the rate of titrant addition is characteristic of growth rate and Fe/Ca ratio is characteristic of stoichiometry of the solid solution formed. Plots of the concentrations of constituent ions and amount of titrant added, for ideal experiments, were shown in the discussion section.

4.2.6. Analyses and Sampling Procedures:

The concentrations of iron, calcium and bicarbonate in the reaction solution were measured periodically by collecting samples from the reactor cell. Before collecting the sample, the sampling line was flushed with 10 milliliters of the reaction solution. Five milliliters of the reaction solution were withdrawn by a plastic syringe. The sample was filtered through a 0.45 μm filter to remove suspended solids. One half (0.5) gram of the
filtered samples was then transferred into a vial and diluted with 10 grams of 2% HNO₃ to be within the measurable range. Calcium and iron concentrations were measured at the end of the experiment using an inductive coupled plasma atomic emission spectrophotometer (ICP-AES). Total alkalinity was measured immediately after sampling to minimize further precipitation of carbonate salts. The alkalinity measurement was performed by transferring 4 ml of the filtered sample to a small glass tube precedingly containing green-methyl red indicator powder. Then, the sample was titrated with 0.05 N HCl till the end-point. At the end point, the sample color turned from blue to red. The total alkalinity was calculated by using the equation below:

\[
Alk = \frac{[HCl] \cdot Vol_{HCl}}{Vol_{sample}}
\]

Eq. (4.2.12)

Where,

Alk : total alkalinity in mol/L

[HCl] : concentration of hydrochloric acid in mol/L

Volₜₜₜ : added volumes of HCl in liter

Volₜₜₜ : volumes of sample in liter.

4.2.7. Crystal Analysis:

At the end of precipitation experiments, aqueous solution was rapidly removed from the reaction cell and the leftover crystals were dried in-situ inside the reaction cell with ultra pure argon gas at 60 °C and 1 atm. The crystals were left for couple of days, and then analyzed using X-ray diffraction (XRD), a scanning electron microscope, SEM (FEI Quanta 400 ESEM FEG), and Energy-dispersive X-ray spectroscopy (EDX) systems.
4.3. Result and Discussion

4.3.1. Formation of aragonite:

Calcium carbonate occurs in several polymorphic forms. Calcite and aragonite are the common types of calcium carbonate exist in the nature and in the industrial processes. The values of the thermodynamic solubility product constants of aragonite and calcite at 55°C are $10^{-8.44}$ and $10^{-8.71}$, respectively, [SSP, Tomson and Kan, Rice University]. The solubility product constant of aragonite is about 0.27 SI units higher than that of calcite at 55°C. Although the difference in $K_{sp}$ is not significant, but it is probably worthy to mention that aragonite was the predominant calcium carbonate solid formed along with siderite during the precipitation processes. Figure 4.3.1 shows the XRD analysis of one of the collected sample for calcium-rich solid solution, $(\text{Fe}_{0.014}\text{Ca}_{0.986}\text{CO}_3)$. Surprisingly, even at approximately 1.4 % iron content in the solid solution, aragonite was formed. This revealed that the metastable calcium carbonate (aragonite) is probably the preferable form in the presence of iron ions. These results were consistent with the results previously reported by Herzong, et al., (1989) and Langerak, et al., (1999). They reported that ferrous iron inhibited calcite growth but not aragonite growth. The inhibition effect on calcite formation probably results from the presence of ferrous iron, not in solid solution, but in the aqueous solution. Nevertheless, to the best knowledge of the author, no reports are available in the literature showing the conditions at which calcite forms along with iron.

The peaks of XRD analysis of one of the iron-rich-solid sample $(\text{Fe}_x\text{Ca}_{1-x}\text{CO}_3, x=\sim1)$ was displayed in Figure 4.3.2. Some of the analysis peaks in Figure 4.3.2 are in
good agreement with the peaks reported by Johnson for pure siderite sample, [Johnson 1990]. However, the vast majority of the peaks was in a good agreement with magnetite peaks. This was probably due to the pre-existence of magnetite as crystal seeds and also probably due to oxidation of iron carbonate during drying processes. It had been observed that, during the drying processes, the color of the solid gradually changed from white to green and then, eventually, either to brown and black based upon the content of iron on the precipitated solid solution. This observation is consistent with what has been reported in the literature. According to Chai and Navrotsky (1994), the final product of siderite decomposition is hematite (Fe$_2$O$_3$) in an oxidizing atmosphere, magnetite (Fe$_3$O$_4$) in a CO$_2$ atmosphere and in vacuum, and magnetite and wüsite (FeO) in an inert atmosphere, [Chai and Navrotsky, 1994].

Figure 4.3.1: XRD analysis of calcium-rich solid solution, Fe$_{0.01}$Ca$_{0.99}$CO$_3$. The white peaks are the analysis peaks and the blue peaks are the matching peaks of aragonite.
Figure 4.3.2: XRD analysis of calcium-rich solid solution, Fe$_{0.01}$Ca$_{0.99}$CO$_3$. The white peaks are the analysis peaks and the blue peaks are the matching peaks of aragonite.

4.3.2. Composition of Iron/Calcium-Carbonate Solid Solutions:

A series of iron-calcium carbonates solid solutions, ranging from calcium-rich to iron-rich, was forced to precipitate by changing the initial supersaturation of pure phases in reaction solution. The experimental conditions (initial concentrations of lattice ions, composition of pure phases in the solid, saturation indexes of pure phases, pH and temperature) are summarized in Table 4.3.1. Each constant composition experiment had different initial aqueous concentrations of calcium and iron, and calcium to iron molar ratio. The difference in supersaturation with respect to pure iron carbonate and calcium carbonate increased gradually from Experiment-1 to Experiment-9. The supersaturation was expressed by saturation index (SI) with respect to pure phases. The saturation index of the pure iron carbonate is defined as
\[ SI_{FeCO_3} = \log\frac{a_{Fe^{2+}}a_{CO_3^{2-}}}{K_{SP,FeCO_3}(T,P)} \]  
Eq. (4.3.1)

And the saturation index of the pure calcium carbonate is defined as

\[ SI_{CaCO_3} = \log\frac{a_{Ca^{2+}}a_{CO_3^{2-}}}{K_{SP,CaCO_3}(T,P)} \]  
Eq. (4.3.2)

where,

\[ a_{Fe^{2+}}, a_{Ca^{2+}}, \text{ and } a_{CO_3^{2-}} \] are the aqueous activities of ferrous ions, calcium ions, and carbonate, respectively. \( K_{SP,FeCO_3} \) and \( K_{SP,CaCO_3} \) are the thermodynamic solubility products constant of FeCO\textsubscript{3} and CaCO\textsubscript{3}, respectively. The ion activities and SI were calculated using SSP software, developed by Tomson and Kan, Rice University.
Table 4.3.1: Summary of the experimental conditions of constant composition experiments

<table>
<thead>
<tr>
<th>EXP#</th>
<th>T,°C, IS, M ±0.02</th>
<th>Ca²⁺, mg/l</th>
<th>Fe²⁺, mg/l</th>
<th>Alk, a ' Fe²⁺, Ala, ca₂⁺ a ' Fe²⁺, eq</th>
<th>pCa₂⁺</th>
<th>pFe²⁺</th>
<th>pCa₀,eq</th>
<th>pFe₀,eq</th>
<th>pH, ±0.02</th>
<th>SIₐragonite a</th>
<th>SIₐ siderite a</th>
<th>Seed type</th>
<th>XₐFe CO₃ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55 0.5</td>
<td>2783</td>
<td>25.10</td>
<td>213.0</td>
<td>11.38</td>
<td>0.064</td>
<td>3.570</td>
<td>0.017</td>
<td>7.1</td>
<td>1.04</td>
<td>1.12</td>
<td>Fe₀.01Ca₀.99CO₃</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>55 0.5</td>
<td>2304</td>
<td>136.0</td>
<td>212.0</td>
<td>9.83</td>
<td>0.355</td>
<td>1.029</td>
<td>0.005</td>
<td>7.37</td>
<td>1.03</td>
<td>1.93</td>
<td>magnetite</td>
<td>0.025</td>
</tr>
<tr>
<td>3</td>
<td>55 0.5</td>
<td>1511</td>
<td>177.6</td>
<td>219.0</td>
<td>6.89</td>
<td>0.501</td>
<td>1.488</td>
<td>0.007</td>
<td>7.29</td>
<td>0.88</td>
<td>2.08</td>
<td>magnetite</td>
<td>0.151</td>
</tr>
<tr>
<td>4</td>
<td>55 0.5</td>
<td>1093</td>
<td>178.3</td>
<td>181.4</td>
<td>5.19</td>
<td>0.517</td>
<td>1.558</td>
<td>0.007</td>
<td>7.28</td>
<td>0.60</td>
<td>1.94</td>
<td>magnetite</td>
<td>0.367</td>
</tr>
<tr>
<td>5</td>
<td>55 0.5</td>
<td>957.7</td>
<td>153.7</td>
<td>284.4</td>
<td>4.68</td>
<td>0.448</td>
<td>0.817</td>
<td>0.004</td>
<td>7.42</td>
<td>0.90</td>
<td>2.23</td>
<td>magnetite</td>
<td>0.442</td>
</tr>
<tr>
<td>6</td>
<td>55 0.5</td>
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<td>155.9</td>
<td>155.8</td>
<td>4.68</td>
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<td>2.358</td>
<td>0.011</td>
<td>7.19</td>
<td>0.40</td>
<td>1.73</td>
<td>magnetite</td>
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</tr>
<tr>
<td>7</td>
<td>55 0.5</td>
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<td>169.9</td>
<td>170.6</td>
<td>2.65</td>
<td>0.518</td>
<td>1.631</td>
<td>0.008</td>
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<td>1.84</td>
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<td>1.182</td>
<td>0.006</td>
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<td>0.14</td>
<td>1.93</td>
<td>magnetite</td>
<td>0.933</td>
</tr>
<tr>
<td>9</td>
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<td>88.31</td>
<td>289.9</td>
<td>1.37</td>
<td>0.287</td>
<td>0.896</td>
<td>0.004</td>
<td>7.4</td>
<td>0.35</td>
<td>2.01</td>
<td>magnetite</td>
<td>0.99</td>
</tr>
</tbody>
</table>

a. Saturation indexes were calculated by SSP-Software.
b. Molar fraction of ferrous iron in solid solution.
Figure 4.3.3 show the trends of the ion concentrations of calcium, iron and alkalinity with time of one of ideal experiments, (Fe$_{0.37}$Ca$_{0.63}$CO$_3$). The concentrations of the constituent ions were held constant during the course of the experiment. The pH, the actual amount of titrant added, and the corrected amount of titrant added are shown in Figure 4.3.4. Plots of all the remaining conducted experiments were shown at the end of this section, Figures 4.3.1a through 4.3.9b. The corrected amount of titrant added in Figure 4.3.4 represents the amount of titrant added per constant effective surface area of seed material. This is because the effective surface area available for crystal growth increases as the crystals grow. As a result, this leads to a more rapid addition of titrant.

According to Zhang and Nancollas (1992), Eq. 4.3.3 was used to calculate the corrected amount of titrant added for a constant effective surface area as a function of actual amount of titrant added, [Zhang and Nancollas; 1992]. For the derivation of Eq. 4.3.3, see Eqs. 2.6.6 through 2.6.12.

$$V_c = \frac{\left(1 + \frac{MC_{\text{ppt}}V}{m_0}\right)^{1-p} - 1}{(1-p)\left(\frac{MC_{\text{ppt}}}{m_0}\right)} \quad \text{Eq. (4.3.3)}$$

$V_c$: the corrected amount of titrant for a constant effective surface area, in liter.

$M$: the molecular weight of the precipitated solid solution in gram per mole.

$V$: the actual amount of titrant added in liter.

$m_0$: the mass of crystal, in grams, at $t = 0$.

$C_{\text{ppt}}$: the concentration of the precipitated solid solution, mol/L.

$p$: the parameter of growth type, $p = 2/3$ for isotropic three dimensional growth, [Zhang and Nancollas; 1992].
**Figure 4.3.3:** Iron, calcium, and bicarbonate concentrations in the precipitation experiment of Fe$_{0.37}$Ca$_{0.63}$CO$_3$ solid solution. (+) aqueous calcium concentration in mg/l. (*) aqueous iron concentration in mg/l. (■) Alkalinity concentration in mg/l. The first 20 minutes of the experiments was ignored for precipitation stabilization.

**Figure 4.3.4:** (○) actual volume of titrant added in milliliters. (△) The corrected volume of titrant added due to change in surface area of the crystal seeds in the precipitation experiment of Fe$_{0.37}$Ca$_{0.63}$CO$_3$. (▲) pH reading.
4.3.3. Theoretical Derivation of Solid Solution Stoichiometry as a Function of Aqueous Solution Composition:

In a given aqueous solution containing seed crystals and supersaturated with more than one solid phase, the rate of growth of a solid solution, e.g. (Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3}), based on kinetics and reaction probability can be expressed by the following relation:

\[ \text{Rate} = \{\text{driving force}\} \{\text{probability of reaction of ions in solution}\} \quad \text{Eq. (4.3.4)} \]

For pure calcium carbonate solid (CaCO\textsubscript{3}) the rate equation can be expressed as:

\[ \text{Rate}_{\text{CaCO}_3} = k_{\text{CaCO}_3} (a_{\text{Ca}^{2+}} - a_{\text{Ca}^{2+},\text{eq}})^m \cdot \left( \frac{a_{\text{Ca}^{2+}}}{a_{\text{Ca}^{2+}} + a_{\text{Fe}^{2+}}} \right) \quad \text{Eq. (4.3.5)} \]

where,

Rate\textsubscript{CaCO\textsubscript{3}} : rate of precipitation of calcium carbonate in mol L\textsuperscript{-1} s\textsuperscript{-1}

\[ a_{\text{Ca}^{2+}} : \text{activity of calcium at time zero} \]

\[ a_{\text{Ca}^{2+},\text{eq}} : \text{activity of calcium at equilibrium} \]

\[ m : \text{reaction rate and assumed to be 1.0} \]

\[ \frac{a_{\text{Ca}^{2+}}}{a_{\text{Ca}^{2+}} + a_{\text{Fe}^{2+}}} : \text{probability that Ca}^{2+} \text{ will be added to the solid mixture.} \]

Similarly, for iron carbonate solid (FeCO\textsubscript{3}), the rate equation can be expressed as:

\[ \text{Rate}_{\text{FeCO}_3} = k_{\text{FeCO}_3} (a_{\text{Fe}^{2+}} - a_{\text{Fe}^{2+},\text{eq}})^m \cdot \left( \frac{a_{\text{Fe}^{2+}}}{a_{\text{Ca}^{2+}} + a_{\text{Fe}^{2+}}} \right) \quad \text{Eq. (4.3.6)} \]

At constant composition precipitation of Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3}, the rate of Fe\textsuperscript{2+} addition is related to the rate of Ca\textsuperscript{2+} addition via fixed parameter, \( \zeta \), therefore:
\[
\frac{Rate_{FeCO_3}}{Rate_{CaCO_3}} = \zeta
\]
Eq. (4.3.7)

\[R_{Total} = Rate_{FeCO_3} + Rate_{CaCO_3}\]
Eq. (4.3.8)

Where: \(R_{Total}\) is the total rate of titrant addition to maintain a constant composition of solid solution \(Fe_xCa_{1-x}CO_3\).

\[Rate_{FeCO_3} = x \ R_{Tot}\]
Eq. (4.3.9)

\[Rate_{CaCO_3} = (1-x) \ R_{Tot}\]
Eq. (4.3.10)

Rearranging Eqs. 4.3.9 and 4.3.10 leads to:

\[
\frac{Rate_{FeCO_3}}{x} = \frac{Rate_{CaCO_3}}{1-x}
\]
Eq. (4.3.11)

where,

\(x\) is the molar composition of \(FeCO_3\) in the precipitated solid solution, \(Fe_xCa_{1-x}CO_3\).

Rearranging Eq. 4.3.11 and substituting Eq. 4.3.7 leads to:

\[
\frac{Rate_{FeCO_3}}{Rate_{CaCO_3}} = \frac{x}{1-x} = \zeta
\]
Eq. (4.3.12)

Rearranging Eq. 4.3.12 and substituting for \(\zeta\):

\[
x = \frac{1}{1 + \frac{1}{\zeta}}
\]
Eq. (4.3.13)

\[
x = \frac{1}{1 + \frac{Rate_{CaCO_3}}{Rate_{FeCO_3}}}
\]
Eq. (4.3.14)

Eq. 4.3.14 is a form of logistic function. Substituting Eqs. 4.3.5 and 4.3.6 in Eq. 4.3.14 leads to:
where,

$x_{Fe CO_3}$: molar composition of siderite in the precipitated solid solution of Fe$\_x$Ca$_{1-x}$CO$_3$

$\mathrm{ks}$: the ratio of rate constant of pure phases; $kS = \frac{k_{Ca CO_3}}{k_{Fe CO_3}}$

$a_{Fe^{2+}}$: activity of iron in solution at initial condition

$a_{Fe^{2+}, eq}$: activity of iron in solution at equilibrium

$a_{Ca^{2+}}$: activity of calcium in solution at initial condition

$a_{Ca^{2+}, eq}$: activity of calcium in solution at equilibrium

The activity at equilibrium can be calculated from solution pH and thermodynamic solubility product. It is assumed that the thermodynamic solubility product constant, $K_{sp}$, of pure phases can be used also to calculate the equilibrium concentrations of the constituent ions of the solid solution end-members. The typical expression of thermodynamic solubility product is:

$$K_{sp(T,P)} = a_{cation, eq} \cdot a_{anion, eq}$$  \hspace{1cm} \text{Eq. (4.3.16)}

$$a_{cation, eq} = \frac{K_{sp(T,P)}}{a_{anion, eq}}$$  \hspace{1cm} \text{Eq. (4.3.17)}

For carbonate solid solution, applying mass balance for total carbonate; Eq. 4.3.17 can be expressed as:

$$a_{cation, eq} = \frac{K_{SP} \cdot a_{H^+} \cdot K_{a1} \cdot K_{a2} \cdot K_{H} \cdot P_{CO_2} \gamma_{CO_2} \gamma_{gas}}{K_{a1} \cdot K_{a2} \cdot K_{H} \cdot P_{CO_2} \gamma_{gas}}$$  \hspace{1cm} \text{Eq. (4.3.18)}
Where,

\( K_{sp} \) : thermodynamic solubility product in molal unit, \( m^2 \)

\( a_{H^+} \) : activity of hydrogen, \( m \)

\( K_{a1} \) : first ionization constant of \( H_2CO_3 \), \( m \)

\( K_{a2} \) : second ionization constant of \( H_2CO_3 \), \( m \)

\( K_H \) : Henry's constant, \( m \cdot \text{atm}^{-1} \)

\( P_{CO_2} \) : partial pressure of \( CO_2 \), \( \text{atm} \)

\( \gamma_{CO_2} \) : Fugacity coefficient of \( CO_2 \), unitless.

4.3.4. Validating Theoretical Model with The Experimental Results of \( Fe_xCa_{1-x}CO_3 \):

To validate the model in Eq. 4.3.15 the experimental results of solid solution composition at 55°C were plotted in Y-axis versus \( \frac{(a_{Ca^{2+}} - a_{Ca,eq}) \cdot a_{Ca^{2+}}}{(a_{Fe^{3+}} - a_{Fe,eq}) \cdot a_{Fe^{3+}}} \) in X-axis. Figure 4.3.5 shows the experimental results and the trend produced from the theoretical model in Eq. 4.3.15. The trend of the theoretical model is in a good agreement with the experimental results with regression coefficient \( (R^2) \) greater than 0.97. The value of \( k_s \), in Eq. 4.3.15 was obtained by non-linear least square curve fitting. \( k_s \) was found to be 0.019. \( k_s \) does not have a unit because it represents the ratio of the rate constants of end members, \( k_s = \frac{k_{CaCO_3}}{k_{FeCO_3}} \). Macro SolvStat.xls package was used to obtain the regression statistics of the theoretical model, [Billo, 2001]. The value of \( k_s \), the standard deviation of \( k_s \), and the regression coefficient were shown in Table 4.3.2.
Figure 4.3.5: Molar composition of solid solution, Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3} versus 
\[ \frac{(a_{Ca^{2+}} - a_{Ca,eq}) \cdot a_{Ca^{2+}}}{(a_{Fe^{2+}} - a_{Fe,eq}) \cdot a_{Fe^{2+}}} \] 
at 55 °C Circles (+) represent actual experimental data. Line, --, represents the theoretical model in Eq. 4.3.15.

The value of ks of Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3} solid solution was further investigated and computed by using the values of rate constants of the pure phases reported in the literature. Reddy and Nancollas, 1970, reported the value of rate constant of pure calcium carbonate at 25°C. Greenberg and Tomson, 1991, reported the rate constant of pure iron carbonate at temperatures between 27-76 °C. Both researchers used a crystal seeds technique and similar forms of the rate equation. Using Arrhenius equation and the reported values of rate constants of pure calcium carbonate and iron carbonate, the rate constants of pure calcium carbonate and iron carbonate at experimental condition herein were calculated. Table 4.3.3 summarizes the rate equations, rate constants, and the parameters (activation energy, temperatures, and the surface area of seed materials) used to calculate the rate constant at 55°C. The calculated value of ks is 0.01. This value is close to the value of the theoretical model; it is higher than the value calculated from the reported rate constant by only a factor of two. The difference between these two values can be attributed to several factors: seeds type (magnetite was used in this work instead
of pure calcite and siderite), the overlap between the nucleation and crystal growth processes, and experimental errors. More research has to be done to address the impact of these factors, but the agreement is surprisingly good.

Table 4.3.2: The correlation coefficients, standard deviation of the coefficients, and regression coefficient of Fe$_x$Ca$_{1-x}$CO$_3$ system.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_s$</td>
<td>0.0196</td>
<td>0.0025</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3.3: Summary of rate equations and rate constants reported by Reddy and Nancollas (1970), and Greenberg and Tomson (1991).

<table>
<thead>
<tr>
<th>Rate Equation$^a$</th>
<th>Reddy and Nancollas</th>
<th>Greenberg and Tomson</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{dCa}{dt} = -kS(m_{Ca}^2 \cdot m_{CO_3}^2 - K_{sp}^{1/2})$</td>
<td>$\frac{dFe}{dt} = -kS((m_{Ca}^2 \cdot m_{CO_3}^2)^{1/2} - K_{sp}^{1/2})^2$</td>
<td></td>
</tr>
<tr>
<td>Activation Energy, $E_a$</td>
<td>$E_a = 33$ kj/mole</td>
<td>$E_a = 108.3$ kj/mole</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
<td>27 °C</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>0.3 m$^2$/g</td>
<td>1.05 m$^2$/g</td>
</tr>
<tr>
<td>$k^c$</td>
<td>$k = 16.1 \frac{L^2}{mol \cdot m^2 \cdot s}$</td>
<td>$k = 391.8 \frac{L^2}{mol \cdot m^2 \cdot s}$</td>
</tr>
<tr>
<td>$k^d$ at 55 °C</td>
<td>$k = 54.4 \frac{L^2}{mol \cdot m^2 \cdot s}$</td>
<td>$k = 5478.1 \frac{L^2}{mol \cdot m^2 \cdot s}$</td>
</tr>
<tr>
<td>$k_s$</td>
<td>$k_s = \frac{k_{CaCO_3}}{k_{FeCO_3}} = 0.01$</td>
<td></td>
</tr>
</tbody>
</table>

---

$^a$ Rate Equation

$^b$ Activation Energy

$^c$ Rate constant

$^d$ Rate constant at 55 °C
a. S is surface area. Values were substituted for rate equation to test the consistency between the two equations. Both produced similar results with a relative error between 3 to 6%.

b. $E_a$ of calcium carbonate where obtained from Wasylenki, et al., 2005.

c. Rate constant of calcium carbonate of Reddy and Nancollas was rearranged to be consistent with the unit reported by Greenberg and Tomson.

d. Rate constant of pure phases at 55°C was calculated by using Arrhenius equation $k = A e^{E_a/RT}$.

The plot of solid solution composition, Y-axis, as a function of the difference in the aqueous solution supersaturation with respect to pure iron carbonate and calcium carbonate, X-axis, was shown in Figure 4.3.6. As shown in Figure 4.3.6, at $\Delta S_I = 0$, ($\Delta S_I = S_{FeCO_3} - S_{CaCO_3}$, Eqs. 4.3.1 and 4.3.2) the crystallized solid solution was calcium-rich with probably trace amount of iron carbonate ($FeCO_3 < 2\%$). In contrast, at $\Delta S_I \geq 1.5$, the crystallized solid solution was iron-rich. In order to crystallize an equi-molar solid solution of iron/calcium carbonate ($Fe_{0.5}Ca_{0.5}CO_3$) at 55°C, 1 atm, and 0.5 M electrolyte solution (NaCl), the aqueous solution should be supersaturated with respect to siderite approximately thirteen times more than the supersaturation of aragonite ($SI_{sid}-SI_{cal} \approx 1.1$). For example, if calcium concentration in water is 1000 mg/L, the concentration of iron should be $\sim 82$ mg/L to allow an equi-molar of iron-calcium carbonate solid solution to precipitate.

The formation of calcium-rich solid solution at $\Delta S_I = 0$ reveals that calcium carbonate was kinetically favored over iron carbonate in spite of its higher solubility. Also, it probably indicates that the presence of calcium ions impairs the precipitation rate of iron carbonate. This observation is consistent with what has been observed in the previous batch and continuous feeding experiments. It was observed that the precipitation rate of iron carbonate was markedly impacted when calcium ions were present at certain
concentration in aqueous solution, $[Ca^{2+}] > 350 \text{ mg/L}$. This result probably explains the field observation where the deposit materials on the pipe are rich with calcium carbonate and has low content of iron carbonate ($FeCO_3 < 10\%$) [Naser-Eldin, et al., 2000]. This phenomenon is also in a good agreement with what has been noticed by Putnis et al. with respect to barium sulfate (barite; $BaSO_4$) and strontium sulfate (celestite; $SrSO_4$), [Putnis, et al., 1992]. Barium sulfate has lower solubility as iron carbonate, ($Ksp=10^{-9.97}$ at 25°C, ;Stumm & Morgan) than strontium sulfate($Ksp=10^{-6.63}$ at 25°C, ;Stumm & Morgan). Putnis et al., found that the threshold supersaturation value was around 10,000 for barium sulfate and 100 for strontium sulfate. Therefore, one can conclude that at low $\Delta SI$, the pure phase having higher solubility precipitates first and probably constitutes the core of the solid solution. This phenomenon is probably attributed to the difference in the characteristic water loss rate constant of the free ions in solution and/or probably due to the difference in the interfacial free energy of the pure endmembers which might result in different values of the energy barriers.

![Figure 4.3.6](image.png)

**Figure 4.3.6**: Molar composition of solid solution, $Fe_xCa_{1-x}CO_3$, as a function of the difference in the supersaturation with respect to pure end members at 55°C.
4.3.5. Validating Theoretical Model with The Experimental Results of Ba\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3}:

Further to validate the new theoretical correlation in Eq.4.3.15, the barium/calcium carbonate solid solution type was selected. Ba/CaCO\textsubscript{3} was chosen because the thermodynamic solubility constant values of BaCO\textsubscript{3} and CaCO\textsubscript{3} are similar, $10^{-8.1}$ and $10^{-8.44}$, respectively. The experimental results of solid solution composition of barium/calcium carbonate at 45°C were plotted in Y-axis versus $(a_{Ca^{2+}} - a_{Ca,eq}) \cdot a_{Ba^{2+}}$ in X-axis. The experimental conditions (initial concentrations of lattice ions, composition of pure phases in the solid, pH and temperature) of Ba\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3} precipitation are summarized in Table 4.3.4. Figure 4.3.7 shows the experimental results and the trend resulted from using the new theoretical model in Eq.4.3.15. The trend of the theoretical model was also in a good agreement with the experimental results with regression coefficient ($R^2$) greater than 0.88. The value of $k_s$, in Eq.4.3.15 was obtained by non-linear least square curve fitting. $k_s$ was found to be 2.65. The value of $k_s$, the standard deviation of $k_s$, and the regression coefficient were shown in Table 4.3.5. Since the value of $k_s$ of Ba\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3} is higher than the value found for Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3}, one should expect that barium carbonate has lower rate constant than calcium carbonate at 45°C. Yet, no reported values of the rate constant of pure barium carbonate have been found in the literature. Therefore, more research has to be done to validate the value of $k_s$ of Ba\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3} found herein.

Since the model shows good representation for the experimental results of two different types of solid solution at two different temperatures, we expect that the model
can be used as a tool for predicting the stoichiometry of other solid solution formation when the water is supersaturated with respect to the pure phases.

**Table 4.3.4:** Summary of the experimental conditions of constant composition experiments of $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solution.

<table>
<thead>
<tr>
<th>EXP#</th>
<th>T,°C, ±0.02</th>
<th>IS, M</th>
<th>Ca$^{2+}$, mg/l</th>
<th>Ba$^{2+}$, mg/l</th>
<th>Alk, pH, ±0.02</th>
<th>$a_{\text{Ca}^{2+}}$, mM</th>
<th>$a_{\text{Ba}^{2+}}$, mM</th>
<th>$a_{\text{Ca}^{2+},eq}$, mM</th>
<th>$a_{\text{Ba}^{2+},eq}$, mM</th>
<th>Seed type</th>
<th>$X_{\text{FeCO}_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>0.5</td>
<td>951.5</td>
<td>100.8</td>
<td>122.5</td>
<td>7.91</td>
<td>4.795</td>
<td>0.116</td>
<td>0.319</td>
<td>0.110</td>
<td>calcite</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>0.5</td>
<td>395.5</td>
<td>1389</td>
<td>112.0</td>
<td>8.25</td>
<td>2.033</td>
<td>1.628</td>
<td>0.067</td>
<td>0.029</td>
<td>calcite</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>0.5</td>
<td>386</td>
<td>1381</td>
<td>117.0</td>
<td>8.26</td>
<td>1.993</td>
<td>1.619</td>
<td>0.064</td>
<td>0.027</td>
<td>calcite</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>0.5</td>
<td>110.0</td>
<td>1337</td>
<td>118.0</td>
<td>8.42</td>
<td>0.584</td>
<td>1.616</td>
<td>0.031</td>
<td>0.013</td>
<td>calcite</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>0.5</td>
<td>101.4</td>
<td>1400</td>
<td>110.8</td>
<td>8.40</td>
<td>0.539</td>
<td>1.682</td>
<td>0.033</td>
<td>0.014</td>
<td>calcite</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
<td>0.5</td>
<td>50.56</td>
<td>1272</td>
<td>157.2</td>
<td>8.45</td>
<td>0.271</td>
<td>1.549</td>
<td>0.026</td>
<td>0.011</td>
<td>calcite</td>
</tr>
<tr>
<td>7</td>
<td>45</td>
<td>0.5</td>
<td>44.75</td>
<td>2979</td>
<td>140.6</td>
<td>8.3</td>
<td>0.229</td>
<td>3.471</td>
<td>0.053</td>
<td>0.023</td>
<td>calcite</td>
</tr>
</tbody>
</table>

a. Molar fraction of ferrous iron in solid solution.

**Table 4.3.5:** The correlation coefficients, standard deviation of the coefficients, and regression coefficient of $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ system.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ks</td>
<td>2.65</td>
<td>1.26</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.88</td>
<td>-</td>
</tr>
</tbody>
</table>
4.3.6. SEM images and EDX analysis:

The SEM images provide information about the spatial distribution of the crystals and knowing whither the nucleation and crystal growth of Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3} occurred on the bulk aqueous solution or on the surface of the crystal seeds. An increase in the crystal size of the seed material was observed in all the SEM images taken for the solid at the end of the experiment. This observation revealed that the growth of iron-calcium carbonate crystals most likely occurred only on the surface of seed materials. SEM images of the surface of magnetite seeds before and after the precipitation experiments, at X = 0.37 and 1.0 in the formula Fe\textsubscript{x}Ca\textsubscript{1-x}CO\textsubscript{3}, were shown in Figure 4.3.8. SEM images of the crystal growth on surfaces of two other different types of seed material: zero iron powder (Aldrich grade), and experimentally pre-prepared Fe\textsubscript{0.01}Ca\textsubscript{0.99}CO\textsubscript{3} crystals, are
shown in Figures 4.3.9 and 4.3.10. The grow and alteration of the spherical shape of zero iron due to precipitation, and the increase in the crystal size of the Fe_{0.01}Ca_{0.99}CO_3 supported the assumption that the precipitation of Fe_{x}Ca_{1-x}CO_3 solid solutions occurred on the surface of seed materials.

Further, EDX analysis was conducted and the analysis results of three different surfaces: Fe_{0.01}Ca_{0.99}CO_3, Fe_{>0.99}Ca_{<0.01}CO_3, pure zero iron powder, were shown as an example. The analysis of EDX on the surface of calcium-rich solid solution, Fe_{0.01}Ca_{0.99}CO_3, displayed a large peak of calcium atoms as shown in Figure 4.3.11. The large peaks of calcium atom and the small peaks of iron atom were proportional to the high content of calcium atom and low content of iron atom in the analyzed surface of the solid solution. In contrary with Fe_{0.01}Ca_{0.99}CO_3, a large peak of iron was observed for iron-rich solid solution (Fe_{>0.99}Ca_{<0.01}CO_3) and for pure zero iron samples, Figures 4.3.12 and 4.3.13. Similarly, the sizes of the peaks were proportional to the content of iron and calcium atoms in these samples. The quality of EDX analysis was not good enough to obtain further information on Fe/Ca ratio in iron-calcium carbonate solid solutions surfaces.
Figure 4.3.8: SEM images of the crystal before and after the experiment. (a) SEM image of pure magnetite used as crystal seeds before the experiment. (b) SEM image after the precipitation experiments of Fe$_{0.37}$Ca$_{0.63}$CO$_3$. (c) SEM image of after the precipitation experiments of Fe$_{1.0}$Ca$_{0.0}$CO$_3$. 
Figure 4.3.9: SEM images of crystal before and after the experiment. (a) SEM image of pure zero iron powder used as crystal seeds before the experiment. (b) SEM image after the precipitation experiments of Fe$_{1.0}$Ca$_{0.0}$CO$_3$. 
Figure 4.3.10: SEM images of the crystal before and after the experiment. (a) SEM image of pure zero iron used as crystal seeds before the experiment. (b) SEM image after the precipitation experiments of Fe$_{1.0}$Ca$_{0.0}$CO$_3$. 
Figure 4.3.11: EDAX analysis of a sample of calcium-rich solid solution (Fe_{0.01}Ca_{0.99}CO_3). Large peak of calcium and small peak of iron reflect the content of iron and calcium in the precipitate.

Figure 4.3.12: EDAX analysis of a sample of iron-rich solid solution (Fe_{1.0}Ca_{0.0}CO_3). Large peak of iron and small peak of calcium reflect the content of iron and calcium in the precipitate.

Figure 4.3.13: EDAX analysis of a sample of zero iron powder. Large peak of iron reflects the content of iron. The very small peaks are probably due to the impurity in the sample of zero iron powder.
Figure 4.3.1a: Calcium and iron concentration during the course of experiment 1 (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

Figure 4.3.1b: pH value during the course of experiment 1.

Figure 4.3.2a: Calcium and iron concentration during the course of experiment 2. (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

Figure 4.3.2b: pH value during the course of experiment 2.
**Figure 4.3.3a:** Calcium and iron concentration during the course of experiment 3. (■) calcium concentration in mg/L, (●) ferrous iron concentration in mg/L.

**Figure 4.3.3b:** Ph value during the course of experiment 3.

**Figure 4.3.4a:** Calcium and iron concentration during the course of experiment 4. (■) calcium concentration in mg/L, (●) ferrous iron concentration in mg/L.

**Figure 4.3.4b:** Ph value during the course of experiment 4.
**Figure 4.3.5a:** Calcium and iron concentration during the course of experiment 5. (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

**Figure 4.3.5b:** pH value during the course of experiment 5.

**Figure 4.3.6a:** Calcium and iron concentration during the course of experiment 6. (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

**Figure 4.3.6b:** pH value during the course of experiment 6.
Figure 4.3.7a: Calcium and iron concentration during the course of experiment 7. (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

Figure 4.3.7b: pH value during the course of experiment 7.

Figure 4.3.8a: Calcium and iron concentration during the course of experiment 8. (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

Figure 4.3.8b: pH value during the course of experiment 8.
Figure 4.3.9a: Calcium and iron concentration during the course of experiment 9. (■) calcium concentration in mg/L, (♦) ferrous iron concentration in mg/L.

Figure 4.3.9b: pH value during the course of experiment 9.
5. CONSTANT COMPOSITION STUDY OF CRYSTAL GROWTH OF MIXED CALCIUM FERROUS CARBONATE SALT*

5.1. Introduction:

Oilfield brines have a lot of impurities. When the brines become supersaturated due to co-mixing and changes in conditions, they usually form mixed salts with cation-substitution. Barium-strontium sulfate is a common example, it is often found in suspended matters in ocean water and in marine sediments, [Lakatos, et al., 2007; Lakatos 2005]. Similarly, calcium-magnesium carbonate is common in fresh water interfaces and in sedimentary rock, [Magaritz, et al., 1980] Ankerite is a mixed calcium-iron carbonate salt which forms in iron rich hydrothermal veins, [Hendry et al., 2000]. Calcium-ferrous carbonate is often found in ground water, oilfields and in corrosive environments containing calcium-bearing water, [Yean et al., 2008; Nase-Eldin, et al., 2002; Tomson and Jonson, 1991] It has been suggested that the cation content of water is not controlled by equilibrium with pure salts, [Monnin and Cividini, 2006]. In case of iron-calcium carbonate, the iron/calcium content in the water is often not controlled by pure siderite or calcite, but by equilibrium with Fe/Ca-substituted siderite or calcite. The precipitation kinetics of co-precipitated calcium-iron carbonate is important because these mixed salts or a defined crystal lattice with substituted ion often co-exist in oilfield production lines. Constant composition method has been conducted to study the dissolution kinetics of pure calcium phosphate and calcium carbonate salts, Tang, et al., 2003; Tomson and Nancillas, 1978; Kazmierczak, et al., 1982].

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Dual constant composition studies of multi-cation carbonate salts are more practical and may have more applications, as will be shown below. These studies may help to design the proper treatment and to select the right inhibitor that might work better. This is more critical when the scale contains ferrous carbonate, because most of the inhibitors tested in the literature show either weak inhibition or adverse effects toward iron-containing salts, [Foss, et al., 2006; Kriel, et al., 1994]. To improve our knowledge of oilfield mineral thermodynamics, it is important to know the actual composition of the salt formed. This enables comparison of the precipitation and dissolution kinetics as either individual pure salts and as components of a mixture. Also it will help in obtaining the correct thermodynamic data, instead of using the data of pure salts. In many cases, the thermodynamic calculations show that the water is undersaturated with respect to pure salts, while it may be supersaturated in the presence of mixed salts or a defined crystal lattice with substituted ion, [Stumm and Morgan 1996].

Unlike calcite which can be easily studied in laboratory, individual and mixed carbonates need special experimental design. Several researchers have studied the kinetics of precipitation and dissolution of the individual phases of ferrous carbonate [Greenberg, 1984; Johnson, 1990]. Sujin et al. 2008, studied the kinetics of ferrous carbonate in the presence of citrate. Alsaiari et al. 2008, studied the interaction of calcium and ferrous ions in carbonate solution using conventional methods. So far, the studies in most of the published reports on the kinetics of iron carbonate have been performed under spontaneous precipitation methods of pure salts. When precipitation or dissolution occurs, many factors (such as pH, ionic strength, and thermodynamic driving force) change together. This paper studies the crystal growth kinetics of calcium-iron carbonate
salts in strictly anoxic conditions by constant composition method in which all parameters are kept constant. The apparatus allows for accurate, rapid determination of the solid stoichiometries of salt components under various field conditions.

5.2. Experimental Methods and Materials:

5.2.1. Experimental Apparatus and Procedure:

The schematic of experimental design is shown in Figure 5.1. It provides the flexibility to deal with oxygen-sensitive ferrous ions. The experiments were performed in a double-walled glass reaction vessel connected to a water bath for temperature control. All fluid delivery lines and experimental apparatus were preflushed with argon gas. The titrant lines were connected to the flushing gas cylinder and reaction cell by three-way valves to easily flush the lines and containers in an oxygen-free environment. An oxygen gas absorber was used as an additional measure to purify the trace concentration of oxygen in the gas cylinder. The temperature of the water bath was digitally controlled.

Figure 5.1: Schematic of Experimental Design of Constant Composition.
A 600 ml volume of distilled water (DI) was initially added to the reaction vessel. Sodium chloride and sodium bicarbonate were then added to the DI water. The solution was thoroughly mixed with a magnetic stirrer covered with polytetrafluoroethylene (PTFE). The reaction solution was then sparged with 1% CO₂ gas (balance was nitrogen, certified mixture) to remove dissolved oxygen. Carbon dioxide gas was used for deoxygenation because argon or nitrogen sparges the CO₂ from the solution and reduces the initial concentration of total carbonate. The deoxygenation process lasted for about one hour and the pH of solution was monitored. After the end of the deoxygenation, no change in solution pH was observed. The dissolved oxygen content was then measured by a colorimetric analysis technique, Figure 5.2, to make sure that the oxygen content in the initial solution was less than 5 ppb. Ferrous chloride-tetra-hydrate salt was added followed by addition of calcium chloride dihydrate salt. This step was performed at room temperature to minimize the potential of premature precipitation of calcium-iron carbonate solid. Samples were withdrawn from the reaction solution to measure calcium, iron and bicarbonate concentrations. Seed crystals of calcium iron carbonate, prepared from preliminary experiments, were then added to the reaction solution. The seeds were delivered into the solution in form of a slurry by quickly withdrawing 20 ml of the deoxygenated solution into 30 ml plastic syringe. In this experiment, two titrants were used to maintain the pH, ionic strength, and concentrations constant. The addition of titrants was triggered by a pH change when crystal growth occurred. The output of the pH in the controller was constantly compared with a preset value and the difference in electric potential triggered a motor of a syringe pump to deliver titrants from two syringes into the reactor cell thereby maintaining a constant thermodynamic driving force. The
amount of titrants added into the reaction solution with time during the course of the experiment was tracked by a digital recording caliper connected to a PC.

**Figure 5.2:** (a) The Color in The Ampoule right after Immersing it in the Reactor Vessel after One Hour of Sparging with 1% CO$_2$ Gas. (b) It Shows The Reading of The Dissolved Oxygen Based on The Color Intensity. The Reading is Ranged from 0 to 40 ppb.

**5.2.2. Analyses and Sampling Procedures:**

The concentrations of iron, calcium and bicarbonate in the reaction solution were measured periodically by collecting samples from the reactor cell. The sampling line was first flushed with five milliliters of the solution. Subsequently, another five milliliters was withdrawn by a plastic syringe for analysis. The samples were filtered through a 0.45 μm filter to remove the suspended solids of calcium and iron carbonates. One half (0.5) gram of the filtered samples was then transferred into the Hach-spectrophotometer vial and diluted to 10 grams with DI water for iron measurement. Total alkalinity was also rapidly measured in-situ to minimize further precipitation of carbonate salts. The alkalinity measurement was performed by titrating with 0.05 N HCl using green-methyl red indicator powder. The total alkalinity was assumed to be equal to the bicarbonate concentration under experimental conditions. Calcium concentration measurements were done by transferring another one gram of the filtered sample into nine grams of 2%
HNO₃. The calcium concentrations were measured at the end of the experiment using an optical inductive coupled plasma (O-ICP) spectrophotometer.

5.2.3 Titrants Preparation:

Two separate titrants were used, one for cations of the precipitant and the other for anions. Titrant-1 contained calcium and ferrous ions while titrant-2 had bicarbonate and hydroxide ions. Titrant-1 was prepared by adding calcium chloride and sodium chloride salts to DI water. The solution was sparged with argon gas (ultra high purity) for about one hour. Ferrous chloride salt was added afterward to avoid the oxidation of ferrous ions. Similarly, titrant-2 was prepared by adding sodium hydroxide solution (1N) and sodium chloride salt to the DI water and the mixture was deoxygenated by argon gas. Sodium bicarbonate salt was added at the end of deoxygenation process. This is because argon gas may sparge the carbon dioxide of the carbonate and eventually reduce the concentration of total carbonate. The equations below were developed to calculate the total concentration of cations and anions in titrants as described below:

For the reaction: \( xCa^{2+} + (1-x)Fe^{2+} + HnCO_3^{n-2} = Ca_xFe_{1-x}CO_3(s) + nH^+ \)  

where: \( 0 \leq x \leq 1 \)

\( Titrant-1: \)

\[
[CaCl_2]_{Titr} = 2[CaCl_2]_{Sol} + [CaCl_2]_{Ppt} \quad \text{Eq. (5.2)}
\]

\[
[FeCl_2]_{Titr} = 2[FeCl_2]_{Sol} + [FeCl_2]_{Ppt} \quad \text{Eq. (5.3)}
\]

\[
[FeCl_2]_{Ppt} = [x/(1-x)][CaCl_2]_{Ppt} \quad \text{Eq. (5.4)}
\]

\[
C_{Ppt} = [CaCl_2]_{Ppt} + [FeCl_2]_{Ppt} \quad \text{Eq. (5.5)}
\]
\[ [\text{NaCl}]_{\text{Titr}} = 2[\text{NaCl}]_{\text{Sol}} - 2C_{\text{Ppt}} \quad \text{Eq. (5.6)} \]

**Titrant-2:**

\[ [\text{NaHCO}_3]_{\text{Titr}} = 2[\text{NaHCO}_3]_{\text{Sol}} + [\text{NaHCO}_3]_{\text{Ppt}} \quad \text{Eq. (5.7)} \]

\[ [\text{NaHCO}_3]_{\text{Ppt}} = C_{\text{Ppt}} \quad \text{Eq. (5.8)} \]

\[ [\text{NaOH}]_{\text{Titr}} = \bar{n} C_{\text{Ppt}} \quad \text{Eq. (5.9)} \]

Where:

\[ [\text{M}]_{\text{Titr}} \] is the total concentration of "M" in titrant solution, \([\text{M}]_{\text{Sol}}\) is the total concentration of "M" in reaction solution, \(C_{\text{Ppt}}\) is an arbitrary concentration, in mol/L, for salt precipitation in reaction solution, \(\bar{n}\) is the degree of formation or the average number of protons bound to a carbonate ion in the reaction solution, which may be expressed as shown in the following equation:

\[ \bar{n} = \frac{[\text{HCO}_3^-] + 2[H_2CO_3]}{C} \quad \text{Eq. (5.10)} \]

Where \(C\) is the concentration of total carbonate. Plot of \(\bar{n}\) as a function of pH, shown in Figure 5.3.

**Figure 5.3:** Average number of protons bound per carbonate ion as function of pH at IS = 0.5 M.
5.3. Results and Discussion

5.3.1. Composition of Calcium-Iron Carbonate Salt:

The composition of mixed calcium-ferrous carbonate salt at constant composition experimental conditions was determined. Precipitation of the supersaturated solution was initiated by introduction of 0.175 g of prepared calcium-iron carbonate crystals into the reaction solution. This was intended to induce crystal growth and avoid nucleation. When crystal growth started, change in electrode potential occurred due to release of protons into the reaction solution as shown in equation 1. In this method, titrant solutions containing the lattice ions were simultaneously added into reactor solution to restore the initial conditions and compensate for changes due to crystal growth, thereby maintaining a constant composition in the solution.

The tactic used in this study to determine the Ca/Fe precipitation ratio was based upon trial and error. Several experiments were performed, each at different initial concentrations of lattice ions at 48°C. The concentrations of calcium, ferrous iron and bicarbonate were selected to reflect the concentrations that commonly exist in oilfield brines. The concentrations of lattice ions were varied in each experiment by assuming an arbitrary value for x in the formula; Ca$_x$Fe$_{1-x}$CO$_3$. Then the solutions were prepared based upon the value of x. The trends of calcium and ferrous ions were then monitored during the course of the experiment, Figures 5.4 and 5.5. The representative experiment was considered as the one in which no changes in concentrations of iron, calcium, and bicarbonate was observed.
Figure 5.4: Normalized ferrous concentrations during trial and error experiments at various Fe/Ca molar ratio at 48°C. The first trial was at $x=0.25$, then the value of $x$ was reduced in each trial until constant composition was obtained.

Figure 5.5: Normalized calcium concentrations during trial and error experiments at various Fe/Ca molar ratios at 48°C. Calcium concentration did not change because calcium ion concentration was much greater than ferrous ion concentration.

The concentrations of calcium, iron and bicarbonate in the reaction solution in the successful experiment were $65\times10^{-3}$ M, $4.2\times10^{-4}$ M and $3.5\times10^{-3}$ M, respectively. The pH value was kept constant at $\sim 7.15 \pm 0.05$, Figure 5.6. The concentration of CO$_2$ gas was 1%. The average attached proton, $\bar{n}$, was 1.1. The saturation indexes with respect to calcite and siderite were 0.97 and 0.68, respectively. The saturation index (SI) was calculated by ScaleSoftPitzer software, developed by Tomson and Kan at Rice University. SI is defined by equations 11 and 12:
\[ SI_{\text{siderite}} = \log_{10} \frac{a_{\text{Fe}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{sp,\text{siderite}}(T, P)} \]  

Eq. (5.11)

\[ SI_{\text{calcite}} = \log_{10} \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{sp,\text{calcite}}(T, P)} \]  

Eq. (5.12)

where,

\( a_{\text{Fe}^{2+}} \) is the activity of ferrous iron in solution, \( a_{\text{Ca}^{2+}} \) is the activity of calcium in solution, and \( a_{\text{CO}_3^{2-}} \) is the activity of carbonate in solution. \( K_{sp,\text{siderite}} \) is solubility product constant of siderite (FeCO_3) and \( K_{sp,\text{calcite}} \) is solubility product constants of calcite (CaCO_3). The value of \( x \) in this experiment was found to be 0.013 Ca/Fe. Figure 5.7 shows the concentration trends of calcium and ferrous ions (at \( x = 0.013 \)). The change on concentrations of iron and calcium was within about ±3%. Bicarbonate concentration was measured at the beginning and at the end of the experiment. The change in bicarbonate concentration was within ±4%. This study showed that at these experimental conditions, calcium and ferrous ions reacted with bicarbonate according to the following stoichiometries:

\[ x\text{Ca}^{2+} + (1-x)\text{Fe}^{2+} + 1.1\text{HCO}_3^- = \text{Ca}_x\text{Fe}_{1-x}\text{CO}_3(\text{s}) + 1.1\text{H}^+ \quad , x = 0.013 \]  

Eq. (5.13)

The result was further investigated and confirmed by analytical technique of elemental analysis of the solid sample. Energy-dispersive X-ray spectroscopy (EDAX) was used. The peaks of the elements are shown in Figure 5.8. The longer peak of calcium and shorter peak of iron reflected the larger amount of calcium in the precipitated salt. Other elements found in the plot were as expected from the electrolyte solution. The molar ratio was calculated based on the weight percentage of calcium and iron in the sample. It was found that the molar ratio of calcium to iron was 0.986: 0.014. This result was close and
comparable to the result obtained from the solution analysis above; 0.987: 0.013. The precipitated salt contained trace amount of iron and this probably due to the low content of ferrous iron in solution.

In previous publications, Alsaiari et al. 2009\textsuperscript{18}, showed that calcium-ferrous carbonate can form at different molar ratios due to changing the initial experimental conditions and the precipitation ratio changes due to the precipitation during the course of the experiment. This study was conducted using conventional kinetic studies (spontaneous precipitation) where several factors change simultaneously. Unlike spontaneous precipitation, constant composition seeded growth facilitated the determination of the precipitated salt stoichiometry. Thus, the composition of any oilfield salt can be accurately determined at specific field conditions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{pH_values.png}
\caption{pH Values with Time of The Reaction Solution in The Representative Experiment, $x=0.013$}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{ion_concentrations.png}
\caption{Concentrations of Calcium and Ferrous Ions in The Reaction Solution with Time in A Representative Experiment, $x = 0.013$.}
\end{figure}
5.3.2. Crystal Growth Kinetics:

In the previous conventional studies of the kinetics of crystal growth, the concentrations of the constituent ions and other conditions change with time during the reaction. However, the beauty of the design in this work is that not only constant conditions of all parameters were maintained but also the kinetics of mixed salt was easily studied. Results of one of the typical experiments at 31 °C have been discussed. The crystal growth experiment lasted for about two hours. A typical plot of solution concentrations and of the amount of mixed titrant added as a function of time is shown in Figures 5.6, 5.7, and 5.9. This reveals that the chemical potential, as assumed, was constant. In other words, the crystal growth of the mixed calcium-ferrous carbonate salt had a constant mass transport. Wang et al. 2006, proposed an equation of crystal growth of pure salt at constant composition. The mass flux of the calcium-iron carbonate crystals can be easily determined at any time when the slope of titrant curve, amount of initial crystal added for growth, and specific surface area are known. From the curve of titrant added versus time, Figure 5.9, the mass flux of calcium-ferrous carbonate can be calculated. The specific surface area, SSA, of calcium-ferrous carbonate seed crystals
initially added was calculated from the SEM analyses under the assumption of spherical particle shape (average particle diameter, \( d_p \) was \( \sim 3 \, \mu m \)). SSA is the external surface area of the adsorbent per unit mass and was defined as follow:

\[
SSA = \frac{SA}{\text{mass}} = \frac{SA}{\rho V}
\]

where,

SA is surface area of particles in m\(^2\), \( \rho \) is density of solid in kg/m\(^3\), V is volume of particle in m\(^3\). Because the precipitated solid was a mixture of calcium carbonate and iron carbonate, the density of the mixed salt was calculated based upon the mole fraction and the densities of its individual salts. SSA was found to be 0.678 m\(^2\)/g. Consequently, the mass flux was found to be about 0.0218 g/m\(^2\).min, (2.18x10\(^{-4}\) mol/m\(^2\).min). During this experiment, the calcium-ferrous carbonate surface available for growth increased more than three fold. The value was compared with the SEM analysis results of calcium-ferrous carbonate crystal size before and after the experiment. The results are comparable where the particle size of the crystal increased, as shown in Figures 5.10 and 5.11.

Crystal growth equilibrium is not instantaneous because the precipitated ions must first diffuse from the solution to the external surface of the seed crystals. The mathematical description of mass transfer may be derived by integrating the Fick’s first law of diffusion. Accordingly, the following simple equation was obtained:

\[
J_A = k_c(C_i - C_s)
\]

where,

\( J_A \) is the mass flux, mole/m\(^2\).min. \( k_c \) is mass transfer coefficient, m/s. \( C_i \) and \( C_s \) are the concentrations of molecules in the bulk solution and at the external surface, respectively. Based upon calcium carbonate as the predominant solid phase the mass transfer
coefficient can be estimated, \( J_A = 2.18 \times 10^{-4} \text{ mole/m}^2\text{.min} \), and \( C_i = 0.0035 \text{ mol/l} \). \( C_i \) was considered as bicarbonate ion concentration because calcium ions were in excess. Also, the attachment rate of ions onto the crystal surface was assumed to be much faster than the diffusion rate, i.e., it was assumed that \( C_s = 0 \) for analysis. Based upon the above assumption, the mass transfer coefficient, \( k_c \), was found to be about \( k_c = 1.04 \times 10^{-6} \text{ m/s} \). The value of \( k_c \) and the curved trend of amount of titrant added, **Figure 9**, reveals that the reaction of crystal growth of calcium ferrous carbonate was probably surface reaction rate limited, because the particle size only a few microns.

**Figure 5.9**: Amount of Mixed Titrant Added as A Function of Time in The Crystal Growth Experiment, \( x = 0.013 \).

**Figure 5.10**: SEM Picture of Calcium-Ferrous Carbonate Crystal before The Crystal Growth Experiment.
Figure 5.11: SEM Picture of Calcium-Ferrous Carbonate Crystal after The Crystal Growth Experiment.
6. MECHANISTIC UNDERSTANDING OF ROCK/PHOSPHONATE INTERACTIONS AND THE EFFECT OF METAL IONS ON INHIBITOR RETENTION*

6.1. Introduction:

Mineral scale formation is a persistent problem in oil and gas production, especially in older reservoirs with increased water production and drawdown. Inhibitor squeezes are commonly used to deposit a suitable scale inhibitor in the formation. During an inhibitor squeeze treatment, a predetermined volume of the inhibitor solution is pumped into the formation and followed by injecting another volume of brine or diesel to place the inhibitor further away from the wellbore and allowing it to react with the existing rock. During production following a squeeze treatment, the inhibitor is slowly desorbed or dissolved into the formation water.

Earlier efforts have focused on describing what happens and when to resqueeze (Hong and Shuler 1988; Rogers et al. 1990). More recent papers have advanced the knowledge of inhibitor reactions under various production conditions (Benton et al. 1993; Sweeney and Cooper 1993; Lawless et al. 1993; Sorbie et al. 1994; Jordan et al. 1994; Jordan et al. 1995; Jordan et al. 1997; Lawless and Smith 1998; Smith et al. 2000; Collins 2003). The primary conclusions from several previous studies (Al-Thubaiti et al. 2004; Kan et al. 2004a; Kan et al. 2004b; Tomson et al. 2006) of NTMP(aminotri(methylene phosphonic acid))-calcite reaction are: (1) The extent of NTMP retention by carbonate-rich formation rock is limited by the amount of calcite that can dissolve prior to inhibitor-induced surface poisoning; (2) calcite-surface poisoning effect is observed after approximately
20 molecular layers of phosphonate surface coverage that retards further calcite dissolution; and (3) the consequence of retarded calcite dissolution is that less basic ion, \( \text{CO}_3^{2-} \) is released into solution, leaving the solution more acidic; therefore, more soluble calcium phosphonate solid phases form. The inhibitor return concentration can be altered by changing the inhibitor concentration in the pill. The ability to control the high inhibitor return may be useful in initial water breakthrough where high inhibitor return is desired. Kan et al. (2005) also compared the retention of NTMP, DTPMP (diethylenetriamine penta (methylene phosphonic acid)), BHPMP (bis-hexamethylenetriamine penta (methylene phosphonic acid)), and PPCA (phosphinopolycarboxylic acid) with pure calcite, a calcite-rich chalk rock, a calcite and clay-rich formation rock from Guerra Ranch, McAllen, Texas, and a quartz sandstone with very little calcite from Frio formation, Galveston County, Texas. Similar inhibitor returns were observed in both calcite-rich and low-calcite rock, suggesting that calcite is the primary solid responsible for phosphonate retention. Clays or other minerals play a secondary role in phosphonate retention. The retention of the polymer-based inhibitors is much lower than phosphonates. The data show that BHPMP provides the highest squeeze life at \( \text{MIC} > 50 \text{ mg/L} \). DTPMP is the preferred inhibitor at \( \text{MIC} \) between 1 and 50 mg/L and NTMP is the preferred inhibitor at \( \text{MIC} < 0.3 \text{ mg/L} \).

Calcium ion (\( \text{Ca}^{2+} \)) is the predominant divalent metal ion in most oilfield produced waters. Previously, several reports indicated that \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) have a strong effect on inhibition of barite by common inhibitors (Fernandez-Diaz et al. 1990; Boak et al. 1999; Collins 1999). Collins (1999) observed a clear change in crystal habit between barite growth in the presence and absence of Ca. Xiao et al. (2001) noted that Ca significantly
enhanced the inhibitor efficiency; however, Ca had no effect on barite nucleation time in the absence of scale inhibitor. Collins (1999) reported a similar effect of Ca with polyaspartate as a barite inhibitor. The enhanced inhibition efficiency may be attributed to the reduction of net negative charge of the polyion due to complexation of the polyaspartate with divalent cations (Tomson et al. 2003).

In this work, the influence of metal ions, e.g., Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$ on the inhibitor retention and release was evaluated in both laboratory simulation and field case studies. These metal ions were either originally added to the inhibitor pill solutions or generated in-situ because of the dissolution of reservoir minerals by acidic inhibitors.

6.2. Methods:

6.2.1. Laboratory Squeeze Simulation:

Two scale inhibitors were examined in the present study. The active components in the inhibitors are H$_{10}$DTPMP and H$_{10}$BHPMP, respectively. The chemical structures and molecular weights of H$_{10}$DTPMP and H$_{10}$BHPMP are given in Fig. 6.1.

Figure 6.1: Chemical structure of two common scale inhibitors, diethylenetriamine penta(methylene phosphonic acid) (DTPMP) and bishexamethylenetriamine penta(methylene phosphonic acid) (BHPMP).
The squeeze simulation experiments were done with the totally contained squeeze simulation apparatus discussed previously (Tomson et al. 2006), Figure 6.2. “Totally contained” squeeze simulation refers to the approach wherein the carbonates that dissolve during the inhibitor/core reaction are contained in a column apparatus to simulate the inhibitor/core reaction during squeeze treatments. In a typical squeeze simulation, approximately 30 g calcite was packed in a 1.6-cm ID column to a length of 12 cm and a PV of 15 ml. The squeeze was done by injecting 1 part (2.7 to 3.3 ml) of scale inhibitor, followed by 4 to 5 parts of overflush solution (11.2 to 12.3 ml) under 75 psig pressure. The inhibitor pill typically reached ~18% of the total column length after the inhibitor pill was injected and displaced nearly to the end of the column after the overflush solution was injected. Then, the column was shut-in under pressure overnight. A “cationic” brine containing ~ 0.05 M CaCl₂·2H₂O in 1 M NaCl and an “anionic” brine containing 0.03 M NaHCO₃ in 1 M NaCl were prepared. Before the inhibitor return experiments, equal volumes of both brines were mixed and bubbled with water saturated with CO₂ (100%) gas. This synthetic brine, used as the return brine, was saturated with respect to calcite at 158°F (pH ~ 5.6) to simulate typical brine in a formation.

Procedure:
- Pre-flush
- Inhibitor Pill
- Over-flush
- Shut-in overnight
- Flow back

Column Characteristic:
- 30 g calcite
- 1.6 cm ID column
- 12 cm length
- 15 ml pore volume

Figure 6.2: Experimental design.
For each experiment, several liters of return brine were pumped into the column from the reverse direction (opposite direction from pill injection direction) to simulate production after a squeeze treatment. Typically, the return inhibitor concentration will reduce to a sub-mg/L level after approximately 100 PV of flow and the inhibitor return concentration will eventually approach a constant value after a large volume of return flow. At this point, the experiment was stopped and the solid phase was pushed out from the column. The solid was divided into six equal sections, dissolved in concentrated HCl, and analyzed for phosphorus, calcium, magnesium, and iron concentrations.

Squeeze simulations with both scale inhibitors were compared at 4 wt% active inhibitor concentrations. The inhibitor pill matrix contained 1 M NaCl, and one of the 3 cationic salts: 0 to 0.33 M CaCl₂·2H₂O, 0.0-0.01 M Fe(NH₄)₂(SO₄)₂ or 0.0 to 0.05 M MgCl₂·6H₂O. The amount of Ca added to the inhibitor pill was equal to 0 to 4.3 mole Ca per phosphonate, Table 6.1. For the Fe²⁺ experiments (experiments 11 through 13, Table 6.2), the iron-free inhibitor pill solution was prepared and degassed using a vacuum pump. Prior to the inhibitor pill injection, Fe(NH₄)₂(SO₄)₂ salt was added to the deoxygenated, acidic inhibitor pill solution and the solution was quickly mixed to dissolve the solid, and then the solution was injected into the column containing CO₂ saturated brine. No Fe²⁺ oxidation was observed in these experiments. The Fe²⁺ concentration used in this study was much lower than both Ca²⁺ and Mg²⁺ concentrations. At Fe²⁺ concentrations > 0.01 M, iron phosphonate precipitate was observed in the inhibitor pill even though the pH value of the inhibitor pill was less than unity. Previously, Al-Thubaiti (2003) characterized an acidic iron phosphonate and a calcium phosphonate salt phase. Under the experimental conditions of the present study, no iron,
calcium, or magnesium phosphonate was observed in the inhibitor pill for a period of 24 hours.

The calcium, magnesium, iron, and phosphonate concentrations in various solutions were measured by inductively coupled plasma atomic emission spectrophotometer. HACH colorimetric method was used to analyze low phosphonate concentrations and the pH was monitored with an in-line pH electrode.
Table 6.1. Experimental parameters and inhibitor return data of eight inhibitor squeeze simulation experiments where the inhibitor pill contained various concentrations of Ca$^{2+}$.

<table>
<thead>
<tr>
<th>No.</th>
<th>Pill composition</th>
<th>Mass of phn return</th>
<th>Obs return vol. (L)</th>
<th>Mass balance</th>
<th>Phase III$^a$ return conc. (mg/L)</th>
<th>Crystalline phase solubility product ($pK_{sp}$)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_{10}$DTPMP</td>
<td>0.0704</td>
<td>0.0</td>
<td>0.0146</td>
<td>175.2</td>
<td>42.4, 99.2, 29.9 (27.4)</td>
</tr>
<tr>
<td>2</td>
<td>H$_{10}$DTPMP</td>
<td>0.0713</td>
<td>0.011</td>
<td>0.0145</td>
<td>214.7</td>
<td>37.7, 127.2, 56.8 (51.5)</td>
</tr>
<tr>
<td>3</td>
<td>H$_{10}$DTPMP</td>
<td>0.0706</td>
<td>0.033</td>
<td>0.0147</td>
<td>201.7</td>
<td>21.5, 90.3, 73.3 (68.4)</td>
</tr>
<tr>
<td>4</td>
<td>H$_{10}$DTPMP</td>
<td>0.0704</td>
<td>0.100</td>
<td>0.0146</td>
<td>237.7</td>
<td>19.8, 112.1, 101.0 (93.4)</td>
</tr>
<tr>
<td>5</td>
<td>H$_{10}$DTPMP</td>
<td>0.0706</td>
<td>0.307</td>
<td>0.0151</td>
<td>212.4</td>
<td>22.3, 82.0, 93.2 (90.1)</td>
</tr>
<tr>
<td>6</td>
<td>H$_{10}$BHPMP</td>
<td>0.0665</td>
<td>0.000</td>
<td>0.0143</td>
<td>166.9</td>
<td>93.9, 61.6, 6.1 (4.7)</td>
</tr>
<tr>
<td>7</td>
<td>H$_{10}$BHPMP</td>
<td>0.0714</td>
<td>0.102</td>
<td>0.0149</td>
<td>212.4</td>
<td>70.1, 78.4, 54.9 (50.2)</td>
</tr>
<tr>
<td>8</td>
<td>H$_{10}$BHPMP</td>
<td>0.0692</td>
<td>0.299</td>
<td>0.0149</td>
<td>205.8</td>
<td>70.8, 83.6, 40.7 (35.9)</td>
</tr>
</tbody>
</table>

a. Injection volume is the total volume of inhibitor pill and overflush solution that was injected into the column. b. Values in parentheses are the remaining mass of phosphonate (\( \square \) mols) on the solid phase that was analyzed at the end of the experiments. c. The constant return inhibitor concentrations established in phase III. d. The solubility products are calculated with the solution pH, Ca$^{2+}$, and phase III phosphonate concentrations using the phosphonate speciation equations, (Kan, et al., 2004; Tomson et al., 1994) and a stoichiometries of Ca$_3$H$_4$DTPMP or Ca$_4$H$_2$BHPMP.
Table 6.2. Experimental parameters and inhibitor return of seven inhibitor squeeze simulation experiments where the inhibitor pill contained various concentrations of Mg²⁺ or Fe²⁺.

<table>
<thead>
<tr>
<th>No.</th>
<th>Pill composition</th>
<th>Inhibitor</th>
<th>Me Ion conc. (M)</th>
<th>Phn Conc. (M)</th>
<th>Me Ion/Phn ratio</th>
<th>Mass of Phn return (µmol)</th>
<th>Mass of Metal ion return (µmol)</th>
<th>Total inj vol (L)ᵃ</th>
<th>Phase I (µmol)</th>
<th>Phase II (µmol)</th>
<th>Phase IIIb (µmol)</th>
<th>Mass balance Phn</th>
<th>Phase IPhase IIPhase III Mass balance Mg²⁺ or Fe²⁺</th>
<th>Obs return vol (L)</th>
<th>Phase III phn return conc (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>H₁₀DTPMP</td>
<td>-</td>
<td>0.070</td>
<td>-</td>
<td>175.2</td>
<td>0</td>
<td>0.0146</td>
<td>42.4</td>
<td>99.2</td>
<td>29.9</td>
<td>0.98</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Mg²⁺</td>
<td>H₁₀DTPMP</td>
<td>0.071</td>
<td>0.056</td>
<td>0.792</td>
<td>222.3</td>
<td>176.1</td>
<td>0.0151</td>
<td>17.99</td>
<td>83.37</td>
<td>120.8</td>
<td>120.8</td>
<td>0.99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Mg²⁺</td>
<td>H₁₀DTPMP</td>
<td>0.071</td>
<td>0.056</td>
<td>0.792</td>
<td>197.4</td>
<td>147.3</td>
<td>0.0151</td>
<td>17.52</td>
<td>94.87</td>
<td>82.7</td>
<td>110.3</td>
<td>0.99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Fe²⁺</td>
<td>H₁₀DTPMP</td>
<td>0.073</td>
<td>0.001</td>
<td>0.014</td>
<td>209.6</td>
<td>8.76</td>
<td>0.0148</td>
<td>25.20</td>
<td>112.50</td>
<td>63.4</td>
<td>56.9</td>
<td>0.96</td>
<td>1.43</td>
<td>2.67</td>
</tr>
<tr>
<td>12</td>
<td>Fe²⁺</td>
<td>H₁₀DTPMP</td>
<td>0.073</td>
<td>0.010</td>
<td>0.142</td>
<td>218.2</td>
<td>34.1</td>
<td>0.0149</td>
<td>31.29</td>
<td>107.21</td>
<td>60.9</td>
<td>50.3</td>
<td>0.91</td>
<td>1.64</td>
<td>13.64</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>H₁₀BHPMP</td>
<td>-</td>
<td>0.067</td>
<td>-</td>
<td>166.9</td>
<td>0</td>
<td>0.0143</td>
<td>93.9</td>
<td>61.6</td>
<td>6.1</td>
<td>16.54</td>
<td>0.97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Fe²⁺</td>
<td>H₁₀BHPMP</td>
<td>0.066</td>
<td>0.011</td>
<td>0.160</td>
<td>172.6</td>
<td>27.66</td>
<td>0.0151</td>
<td>62.6</td>
<td>61.6</td>
<td>38.9</td>
<td>34.2</td>
<td>0.95</td>
<td>3.71</td>
<td>7.41</td>
</tr>
</tbody>
</table>

a. Injection volume is the total volume of inhibitor pill and overflush solution that was injected into the column.

b. Values in parentheses are the remaining mass of phosphonate (µmols) on the solid phase that was analyzed at the end of the experiments.

c. Fe concentration in the solid phase was not measured; the value in parentheses is estimated from mass balance.
6.3. Field Studies:

Field “H” is a sandstone reservoir in central Saudi Arabia that produces super light crude oil (°API > 50). The sandstone formation contains 68 to 97% quartz, 0–19% Na feldspar, 0–21% clays, 0–1% calcite, 0–4% anhydrite, 0–1% chlorite, and 0–7% ankerite. The last two minerals contain iron. Nasr-El-Din et al. (2002, 2003) did extensive acid stimulation and inhibitor squeeze studies in this field. Most vertical wells in this field are gravel packed and contain an electrical submersible pump to lift oil. Scale was observed downhole near the pump intake and gravel pack, possibly because of the rising temperature near the pump and the high pressure drop across the gravel pack. Both carbonate and sulfide scales were noted in these wells. A novel inhibitor squeeze treatment was performed in more than 50 wells. However, the present study will focus on two wells: H-1 and 66 (Saiari et al. 2004). The composition of the produced waters from these two wells is given in Table 6.3. The inhibitor squeeze formulations for these two wells were similar. Before the squeeze treatment, the tubing was first preflushed with about 21 bbls of KCl solution. The main stage of the inhibitor pill treatment consisted of an emulsified DTPMP pill containing a strong acid and a Ca-source. This was followed by a pH-controlled fluid containing Na₂CO₃. Portions of both fluids were injected alternatively into the formation. The overflush was done using a large volume of diesel. Samples were collected once the well was put on production. The concentrations of Ca, Mg, Fe, and P in the aqueous solutions that were separated from the samples were measured by ICP.
Table 6.3. Brine chemistry and well conditions of wells H-1 and H-66.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Well Name</th>
<th>Units</th>
<th>Well Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>(mg/L)</td>
<td>H-1 1,819</td>
<td>H-66 2,695</td>
<td>Gas/Day (Mcf/D) 4</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>(mg/L)</td>
<td>H-1 73</td>
<td>H-66 94</td>
<td>Oil/Day (B/D) 441</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>(mg/L)</td>
<td>H-1 703</td>
<td>H-66 717</td>
<td>Water/Day Downhole 341</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>(mg/L)</td>
<td>H-1 -</td>
<td>H-66 -</td>
<td>Temp (°F) 152</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>(mg/L)</td>
<td>H-1 3,300</td>
<td>H-66 4,720</td>
<td>Temp Well Head (°F) 144</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>(mg/L)</td>
<td>H-1 1,150</td>
<td>H-66 1,160</td>
<td>Pressure Downhole 2,675</td>
</tr>
<tr>
<td>Alkalinity**</td>
<td>(mg/L)</td>
<td>H-1 197</td>
<td>H-66 213</td>
<td>Pressure Well Head (psia) 221</td>
</tr>
<tr>
<td>pH (measured STP)</td>
<td>pH</td>
<td>H-1 6.90</td>
<td>H-66 7.70</td>
<td></td>
</tr>
</tbody>
</table>

6.4. Results and Discussion:

Kan et al. (2005) proposed that the shape of inhibitor return curve is controlled by the dissolution of various Ca-inhibitor solid phases. In Figure 6.3 is plotted DTPMP and BHPMP return concentrations following a 4 wt% acidic H₁₀DTPMP and H₁₀BHPMP squeeze simulation. Also plotted in Figure 6.3 are the corresponding Ca₃H₄DTPMP or Ca₄H₂BHPMP negative logarithmic ion products (pIP). The return curves are characterized with 3 phases: Phase I represents the initial return of the residual phosphonate that remained in solution after reacting with the solid phase. This residual phosphonate typically returned within the first 3 PV. Phase II represents the return of a high-solubility inhibitor salt and Phase III represents the return of a low-solubility inhibitor salt. The return concentration was typically > 1 mg/L for phase II and < 1 mg/L for Phase III when the return brine contained 0.025 M Ca at 158°F. Phase III salt apparently corresponds to the crystalline Ca-inhibitor phase that was extensively studied by Kan et al. (1994) and Frostman et al. (1998).
Using the solution speciation model for DTPMP (Tomson et al. 1994), and assuming a stoichiometry of Ca$_3$H$_4$DTPMP, the solubility products estimated from Phases II and III of DTPMP return concentrations, are $10^{-52.3}$ and $10^{-53.8}$. Similarly, the solubility product, estimated from phase III BHPMP return concentrations, is $10^{-39.9}$ by assuming a stoichiometry of Ca$_4$H$_2$BHPMP and the speciation model of Kan et al. (2004b). Interestingly, the phase II DTPMP return showed a constant ion product of $10^{-52.3} \pm 0.14$ between 27 and 678 PV, while the ion product for BHPMP was changing continuously during the Phase II BHPMP return. It is likely that DTPMP return in the Phase II regime is caused by dissolution of a distinctive solid phase that has a characteristic solubility product ($K_{sp} = 10^{-52.3}$). There may be multiple Ca-BHPMP solid phases formed with the
BHPMP/calcite reaction, because there is a continuous variation in the calculated ion product. Much more DTPMP (76% of the total phosphonate injected) than BHPMP (44% of the total phosphonate injected) was retained in the calcite column after the first 3 PV of return flow. The difference in DTPMP and BHPMP reactions with calcite has to be related to their molecular structure, Figure 1. For BHPMP, there are six methylene groups on the triamine backbone to separate the five phosphonate groups. Therefore, there are much less electrostatic interactions among the functional groups than that of DTPMP, where the five phosphonate groups of the DTPMP molecule are closer to each other and, as a result, the electrostatic interactions among them become important. Therefore, the metal salts of these two phosphonates may have very different solubilities. In the following sections, the effects of Ca$^{2+}$, Mg$^{2+}$, or Fe$^{2+}$ on the inhibitor retention and return are compared for these two inhibitors.

6.4.1. Effect of Ca$^{2+}$ on Inhibitor Return:

In Table 6.1, the inhibitor pill composition was listed in Columns 2 through 7. In Columns 8 through 10 are listed the total mass of inhibitor that was returned from Phases I, II, and III. Note that the mass of inhibitor in Phase III (Column 10) included the mass that was eluted in Phase III and the inhibitor mass that was on the solid phase. The values in parentheses of Column 10 are the measured solid phase inhibitor mass. A large fraction of Phase III solid was retained in the column when the experiments were terminated. In Column 11 of Table 6.1 is listed the inhibitor mass balance. The mass balance is defined as the mass ratio of the amount of phosphonate that was recovered from both the solution phase and the solid phase at the end of the experiment divided by
the amount of phosphonate that was injected at the beginning of the experiment (the ratio of the summation of Columns 8 through 10 to Column 7). The phosphonate mass balance of these experiments were very good (Tables 6.1 and 6.2), indicating excellent quality control. In Column 12 is listed the total volume of synthetic brine that was used in the inhibitor return experiments. Column 13 lists the constant inhibitor return concentrations observed in Phase III. Column 14 lists the observed solubility products that were calculated from the Phase III brine composition and inhibitor return concentrations. Among these eight experiments, the average crystalline phase solubility products of $10^{-53.6 \pm 0.2}$ for Ca$_3$H$_4$DTPMP and $10^{-40.2 \pm 0.3}$ for Ca$_4$H$_2$BHPMP were observed and they were within experimental errors (Kan et al. 1994; Kan et al. 2004a; Frostman et al. 1998). Therefore, one may conclude that the addition of Ca$^{2+}$ does not affect the solubility of the crystalline-phase.

In Figures 6.4a and 6.4b are plotted the initial phosphonate return for the first 3 PV (Phase I) of the eight experiments in Table 6.1. Note that the unreacted phosphonate concentrations returned at nearly 1 PV. The inhibitor concentration decreased to below 100 mg/L for DTPMP and below 500 mg/L for BHPMP within 3 PV. The mass of inhibitor that returned within Phase I is strongly influenced by the amount of Ca$^{2+}$ added to the inhibitor pill. Figure 6.4c plots the percentage of cumulative inhibitor mass returned in Phase I. The DTPMP loss in Phase I was 24% in the absence of added Ca$^{2+}$ and it was reduced to approximately 10% when 0.033M Ca$^{2+}$ was added to 4 wt% DTPMP pill, which was equivalent to 0.5 mole Ca$^{2+}$/mole DTPMP in the inhibitor pill. Similarly, BHPMP loss in Phase I was 56% and was reduced to 33% when 0.1 M Ca$^{2+}$ was added to 4 wt% BHPMP, which was equivalent to 1.4 moles Ca/mole BHPMP in
inhibitor pill. However, phosphonate return in Phase I was not reduced further when Ca concentration in the inhibitor pill was increased from 0.1 to 0.33 M.

Figure 6.4: Plots of the first three pore volumes of (a) DTPMP return concentrations, where the inhibitor pill contained 4% H10DTPMP and various Ca concentrations; (b) BHPMP return concentrations, where the inhibitor pill contained 4 wt% H10BHPMP and various Ca concentrations; and (c) plot of the percentage of accumulative inhibitor mass that returned in three pore volumes (phase I) versus Ca concentration in inhibitor pill. One pore volume = 0.015 L.
In Figures 6.5a and 6.5b are plotted the long term inhibitor return concentration vs. the number of PV for the eight experiments in Table 6.1. As discussed previously, the return concentration eventually reduced to a level similar to the solubility limit of the crystalline phase. Figure 6.5c plots the percentage inhibitor that was left in the column at the end of the experiments. The addition of 0.033 to 0.1 M Ca\(^{2+}\) to the inhibitor pill significantly extended the inhibitor squeeze life. However, increasing the Ca\(^{2+}\) concentration above 0.1 M showed no additional advantage in extending the inhibitor squeeze life. At the end of squeeze simulation experiment, a considerable amount of phosphonate was retained inside the column. Assuming that the phosphonate will continue to elute from the column at the crystalline solubility limit if the experiments was not terminated, the potential return volume can be significantly extended by the addition of Ca\(^{2+}\). As shown in Figure 6.5a, the sharp decline in DTPMP concentration during the transition of Phase II DTPMP solid to Phase III DTPMP solid was replaced with a gradual decline in DTPMP concentration in Phase II, indicating possibly multiple Ca-DTPMP solid phases formation during Phase II in the presence of additional Ca\(^{2+}\) in the pill.

In Figure 6.5d is plotted the solid phosphonate distribution in the column at the end of the experiments where the x-axis is the distance from the pill injection side of the column and the y-axis is the phosphonate concentration of the solid phase. Most of the inhibitor mass was precipitated within the first 18% of the column length, which corresponded to the pill injection. Apparently, much less inhibitor was precipitated while the inhibitor pill was pushed towards the end of the column during the overflush. When Ca was added to the inhibitor pill, more phosphonate was retained in the solid phase during the overflush.
injection. From this data, the maximum effect on phosphonate retention was observed in the presence of 0.5 to 1.0 mole Ca\(^{2+}\)/mole DTPMP or BHPMP. The predominant effect of Ca\(^{2+}\) in pill solution is the reduction of initial phosphonate return in the first 3 PV, which is more than double the useful squeeze life. The addition of Ca\(^{2+}\) to inhibitor pill increased phosphonate precipitation throughout the injection volume, and the major portion of the precipitation occurred when inhibitor pill solution contacted the core material near the front of the core. Similar near-wellbore precipitation is expected during squeeze operation. Ca\(^{2+}\) and other divalent ions can be retained in the formation by ion exchange mechanism as discussed by Kan et al. (2008). A pretreatment with divalent metal ions is expected to enhance inhibitor retention during squeeze treatment (Kan et al. 2008).

a.

b.
6.4.2. Effect of Fe$^{2+}$ and Mg$^{2+}$ on Inhibitor Return:

In Table 6.2 is listed 5 other squeeze simulation experiments where 0.05 M Mg$^{2+}$, or 0.001 to 0.01 M Fe$^{2+}$ was added to the inhibitor pill. Data of Experiments 1 and 6 are also included in Table 6.2 for comparison. As with Table 6.1, Columns 2 through 9 are listed the inhibitor pill composition. Columns 10 through 17 are listed the mass of both inhibitor and metal ion eluted in Phases I through III and the corresponding mass balances. Column 18 lists the total volume of brine that flowed through the column and Column 19 lists the phase III constant return concentrations. Experiments 9 and 10 are replicate experiments in which the inhibitor pill contained 0.05 M Mg$^{2+}$. 

---

**Figure 6.5:** Plots of the return concentrations versus the number of pore volumes of flow for (a) DTPMP where the inhibitor pills contain 4 wt% H10DTPMP and various concentrations of Ca; (b) BHPMP where the inhibitor pills contain 4% H10BHPMP and various concentrations of Ca; (c) plot of the percentage of inhibitors that was left on the solid phase at the end of the squeeze simulation experiments, and (d) plot of the solid phase DTPMP distribution in the column at the end of the return flow, where the y-axis is DTPMP concentration (moles/Kg) and x-axis is the column length with distance (cm) from the Pill injection end of the column. One pore volume = 0.015 L.
Figures 6.6a through 6.6c plot the DTPMP and BHPMP returns from the first 3 PV of inhibitor return of the experiments given in Table 6.2, where the effect of Mg$^{2+}$ on DTPMP return is compared in Figure 6.6a, the effect of Fe$^{2+}$ on DTPMP return is compared in Figure 6.6b, and the effect of Fe$^{2+}$ on BHPMP return is compared in Figure 6.6c. Similar to that observed with Ca$^{2+}$ in the inhibitor pill, both Mg$^{2+}$ and Fe$^{2+}$ in the inhibitor pill reduced the initial phosphonate return in the first 3 PV. In Figure 6.6d is plotted the percentage of the cumulative inhibitor return of these seven experiments. The percentage of cumulative inhibitor return in the presence of 0.1 M Ca$^{2+}$ (Experiments 4 and 7) is also included in Figure 6.6d. Interestingly, 0.05 M Mg$^{2+}$ reduced the inhibitor loss in the first 3 pore volumes (PV) to an extent similar to that noted with 0.1 M Ca$^{2+}$. It is surprising that low concentrations of Fe$^{2+}$ (0.001 to 0.01 M Fe$^{2+}$) in the inhibitor pill also reduced the inhibitor loss in the first 3 PV. The molar ratio of Fe$^{2+}$ to phosphonate in the pill was in the range of 0.014 to 0.142 for these two experiments, which was significantly lower than the Mg$^{2+}$/phosphonate and Ca$^{2+}$/phosphonate ratios in the inhibitor pill of the other experiments shown in Figure 6.6d.
b.

![Graph](image)

No Me

$\text{Fe (0.001 M)}$

$\text{Fe (0.01 M)}$

DTPMP Conc. (mg/L)

No. of Pore Volumes

c.

![Graph](image)

No Me

$0.01 \text{ M Fe}$

BHPMP Conc. (mg/L)

No. of Pore Volumes

d.

![Graph](image)

% Accumulative Phn Return

<table>
<thead>
<tr>
<th>DTPMP</th>
<th>BHPMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca 0.1 M</td>
<td>Ca 0.1 M</td>
</tr>
<tr>
<td>Mg 0.05 M</td>
<td>Mg 0.05 M</td>
</tr>
<tr>
<td>Mg 0.001 M Fe</td>
<td>Mg 0.001 M Fe</td>
</tr>
<tr>
<td>Fe 0.01 M</td>
<td>Fe 0.01 M</td>
</tr>
<tr>
<td>Ca 0.1 M</td>
<td>Fe 0.01 M</td>
</tr>
</tbody>
</table>
Figure 6.6: Plots of the first three pore volumes returns of (a) DTPMP concentration, where the inhibitor pills contained 4% H10DTPMP and 0 and 0.05 M Mg2+; (b) DTPMP concentration, where the inhibitor pill contained 4% H10DTPMP and 0 - 0.01 M Fe2+; (c) BHPMP concentration, where the inhibitor pill contained 4% H10BHPMP and 0 - 0.01 M Fe2+; and (d) plot of the percentage of accumulative inhibitor return in three pore volumes of return flow of nine experiments with different Ca2+, Mg2+, or Fe2+ and phosphonate composition in the pill. The first 6 columns are DTPMP data and last three columns are BHPMP data. The pill composition is listed in the x-axis. One pore volume = 0.015 L.

In Figure 6.7a through 6.7c are plotted the long-term DTPMP and BHPMP returns from the seven experiments of Table 6.2, and Figure 6.7d is plotted the percentage phosphonate mass that was retained in the column. Similar to the effect of Ca2+ observed before, the addition of either Mg2+ or Fe2+ increased both the observed return flow volumes and the amount of inhibitor retained by the solid phase at the end of the experiments. Therefore, we may conclude that the 3 metal ions enhanced phosphonate retention. Note that Mg2+ appeared to increase the Phase III DTPMP return concentrations in Experiments 9 and 10. Similarly, Fe2+ appeared to increase the Phase III return concentration of BHPMP, but it did not change the DTPMP return concentration. It is not clear how Mg2+ or Fe2+ in inhibitor pill affected the phosphonate solid stoichiometry and solubilities. Magnesium ion containing salt was generally more soluble than calcium and ferrous ion salts. For example, the solubility product of magnesium phosphate, expressed as Mg3(PO4)2, is 10^{-24}, while the solubility product of calcium phosphate, expressed as Ca3(PO4)2, is 10^{-29} whereas the solubility product of ferrous phosphate, Fe3(PO4)2·8H2O, is 10^{-37.6} (Gustafsson 2005; Al-Borno and Tomson 1994). Similarly, it was suggested that magnesium phosphonate is more soluble than calcium phosphonate and ferrous phosphonate (Tantayakom et al. 2005; Friedfeld et al. 1998). Mg2+ was also observed to reduce the overall rate of hydroxyapatite crystal growth.
(Ca₅(PO₄)₃OH) by adsorption of magnesium ion at active growth sites and stabilization of growth precursor phases (Nancollas et al. 1976).

a.

![Graph A](image A)

b.

![Graph B](image B)

c.

![Graph C](image C)
Figure 6.7: Plots of the return concentration versus the number of pore volumes of return flow for (a) DTPMP, where the inhibitor pills contained 4 wt% H10DTPMP and 0 and 0.05 M Mg$^{2+}$; (b) DTPMP, where the inhibitor pill contained 4% H10DTPMP and 0 - 0.01 M Fe$^{2+}$; (c) BHPMP, where the inhibitor pill contained 4 wt% H10BHPMP and 0 and 0.01 M Fe; and (d) plot of the percentage of inhibitor mass that remained on the solid phase at the end of experiments for nine experiments with different Ca$^{2+}$, Mg$^{2+}$, or Fe$^{2+}$ and phosphonate composition in the pill. The first 6 columns are DTPMP data and last three columns are BHPMP data. The pill composition is listed in the x-axis. One pore volume = 0.015 L.

Figure 6.8 plots (a) Mg$^{2+}$ vs. DTPMP concentration in the Phase II effluent (Exp 10) and (b) Fe$^{2+}$ vs. DTPMP concentration in the Phase II effluent (Exp. 12). Also plotted in Figure 6.8 are the solid phase (c) DTPMP and Mg$^{2+}$ distribution of Experiments 10 and (d) DTPMP and Fe$^{2+}$ distribution of Experiment 12, where the x-axis is the column length determined from the inhibitor pill injection point of the column. In Figures 6.8c and 6.8d, the solid-phase DTPMP distribution of Experiment 1 (dashed line) was also plotted for comparison. The ratio of Mg$^{2+}$/DTPMP in the Phase II effluent was 0.83 ± 0.06, which was similar to that of the inhibitor pill (0.79). The ratio of Fe$^{2+}$/DTPMP in
Phase II effluent varied from approximately 0.39 to 0.08 with a mean of $0.13 \pm 0.07$, while the inhibitor pill contained 0.14 mole Fe$^{2+}$ per mole phosphonate. These data suggest that Mg$^{2+}$ and Fe$^{2+}$ might be coprecipitated with DTPMP and Ca$^{2+}$ at a ratio similar to that in the inhibitor pill. The addition of Mg$^{2+}$ and Fe$^{2+}$ improved the precipitation of phosphonate during both the pill injection and the overflush stages. Both Mg$^{2+}$ and Fe$^{2+}$ appear to be evenly distributed in the column. Therefore, one may assume that these metal ions may not be coprecipitated with phosphonate in phase III. Instead, these metal ions might be ion exchanged with Ca$^{2+}$ in calcite. If this is the case, then the metal ions may not affect the long-term inhibitor in Phase III return.

a. [Graph showing a linear relationship between Mg concentration and DTPMP concentration with a slope of 0.79]

b. [Graph showing a linear relationship between Fe concentration and DTPMP concentration with a slope of 0.14]
Figure 6.8: Plots of (a) Mg$^{2+}$ versus DTPMP concentrations in the effluent during Phase II return of Exp 10, where the inhibitor pill contains 0.05 M Mg$^{2+}$; (b) Fe$^{2+}$ versus DTPMP concentrations in the effluent during Phase II return of Exp 12, where the inhibitor pill contains 0.01 M Fe$^{2+}$; (c) the solid phase DTPMP and Mg$^{2+}$ concentration of Exp 10 and the solid phase DTPMP concentration of Exp 1 (no metal ions added to pill) versus the distance into the column from the pill injection end of the column; and (d) the solid phase DTPMP and Fe$^{2+}$ concentration of Exp 12 and the solid phase DTPMP concentration of Exp 1 versus the distance into the column from the pill injection end of the column. Also plotted in Figs. 7a and 7b are the quality lines that represent the Mg/DTPMP and Fe/DTPMP ratios in the inhibitor pill.
6.4.3. Field Case Study: Inhibitor Return:

The field squeeze treatment and return of wells H-1 and H-66 (Nasr-El-Din et al. 2003) present two interesting case studies to be compared with the results of laboratory studies. The formation is sandstone with less than 1 wt% calcite (Nasr-El-Din et al. 2003). In the two squeeze treatments, a strong acid was added to the inhibitor pill dissolved considerable amounts of $\text{Fe}^{2+}$ from the iron-bearing formation. In addition, $\text{Ca}^{2+}$ was added to the pill solution.

The inhibitor squeeze treatment was proven to be very successful with each squeeze treatments lasting over 800 days. In Figure 6.9 are plotted DTPMP returns from Wells H-1 and H-66 (a, b), $\text{Fe}^{2+}$ to DTPMP ratio in the return fluids of these two wells (c, d), and the cumulative mass of DTPMP returned from these two wells (e). In Figures 6.9a and 6.9b are also plotted the negative logarithmic ion products of calcium phosphonate salt (p$\text{IP}$) by assuming a stoichiometry of $\text{Ca}_3\text{H}_4\text{DTPMP}$, and the data are given in Table 6.4 (see following discussion). In order to compare the laboratory to field data, the produced water volume was normalized by dividing the produced water volume with the total volume of water in the injection fluids (204 bbls for H-1 and 183 bbls for H-66). Because the inhibitor pill was pushed with diesel in volumes equivalent to four times the water volume, the initial inhibitor return would take five times the volume of injected water for the residual phosphonate to be produced from the well (i.e., the initial phosphonate return may take up to 15 PV of water flow, instead of 3 PV). Interestingly, both Wells H-1 and H-66 return curves showed the characteristic 3 phase returns. DTPMP concentration in the return fluids reduced to below 210 mg/L (0.36 and 0.27 mM) within the first 15 PV of flow. In both cases, the data exhibit a high solubility phase
(Phase II, ~18 mg/L) between 15 and 800 PV and the inhibitor return concentration decreased to the lower solubility phase after nearly 800 PV.

As shown in Figure 6.9c and 6.9d, Fe co-eluted with DTPMP at a ratio of 0.6 to 1.0 mole Fe per DTPMP, indicating that approximately 0.6 to 1 mole of Fe$^{2+}$ was coprecipitated with DTPMP. This is consistent with previous observation that approximately 1 mole Mg$^{2+}$ coprecipitated with Ca$^{2+}$ and DTPMP. In both H-1 and H-66 returns, approximately 10% DTPMP mass in the inhibitor pill was returned within 3 PV (Figure 6.9e). Similarly, we observed approximately 10% DTPMP returned in the laboratory observations when Ca or Mg was added to the pill (Figure 6.6d).
Figure 6.9: Plots of DTPMP return concentrations and logarithmic ion product (pIP) of Ca3H4DTPMP stoichiometry versus the number of pore volumes for the inhibitor return data of (a) H-1 well; (b) H-66 well; plots of Fe versus DTPMP concentrations from the return flow of (c) H-1 well; and (d) H-66 well; and (e) plot of the percentage of accumulative DTPMP mass returned from wells H-1 and H-66. One pore volume = 204 bbls (H-1) and 183 bbls (H-66).
The squeeze treatments were very successful, with < 30% DTPMP returned after > 800 days production for both wells. The excellent DTPMP retention in the sandstone formation may be attributed to the high Ca\(^{2+}\) concentration that was added to the inhibitor pill and high Fe\(^{3+}\) concentration that was dissolved in-situ from the formation.

In order to calculate the ion products from the return data of H-1 and H-66, a realistic downhole pH must be estimated. From the brine chemistry listed in Table 3, the downhole calcite saturation index for these two wells, estimated with ScaleSoftPitzer\(^{\text{TM}}\), are 0.43 and 1.22, which may not be reasonable. It was assumed that the predominant uncertainty was the reported pH values. The downhole pH values were estimated to be 6.37 and 6.36, for Wells H-1 and H-66 respectively, if one assumed that downhole conditions to be at equilibrium with calcite. The corresponding calculated pH values at STP conditions would be 6.47 pH for both wells. In Columns 1 through 5 of Table 6.4 are listed the downhole well conditions. The brine chemistry and squeeze treatments for these two wells were nearly identical, except that H-66 produces 4.4 times more water than H-1 well. In Columns 6 through 8 are listed the duration of production that corresponds to the Phase II return, the total volume of water treated during Phase II return, and the mean Ca\(_3\)H\(_4\)DTPMP solubility product. Columns 9 through 11 list the duration of production that corresponds to Phase III return, the total volume of water treated during Phase III return, and the mean Ca\(_3\)H\(_4\)DTPMP solubility product. These solubility products are within experimental errors to that reported previously for the solubility products of two calcium phosphonate phases (Kan et al. 2005). As shown in Table 6.4, the predominant volume of production was under Phase III inhibitor return.
conditions. Similar to that observed in the laboratory, the presence of Fe$^{2+}$ does not appear to influence the Phase III return of DTPMP.

These field inhibitor data support our mechanistic model of inhibitor retention following a squeeze treatment. It is very important to identify the controlling mechanism of return concentrations. At least two solid phase solubility products were identified for phosphonate. Depending on the minimum inhibitor need (MIC) of particular well conditions, the crystalline phase solubility limit may or may not be sufficient to protect the well. In many common well conditions with low scaling tendency, such as this case study, the minimum inhibitor needed is lower than the crystalline phase solubility limit. In such conditions, a squeeze treatment may last for several years of production. However, some wells may encounter more severe scaling potential, in which case a squeeze treatment needs to be formulated that extends the Phase II return. This could be achieved by proper formulation of the inhibitor pill composition and pH, as demonstrated in this work and in an earlier paper (Kan et al. 2005).

The implication of this study is that inhibitor squeeze treatment can be improved by adding a compatible cation and control acidity of the pill. Addition of cations and optimizing the pH of the inhibitor pill improves the retention of phosphonate and the distribution of phosphonate in the formation. The precipitation-based model can be used to predict the inhibitor retention and return in the field squeeze treatments.
7. ENHANCED INHIBITOR TREATMENTS WITH THE ADDITION OF ZINC*

7.1. Introduction:

Mineral scale formation is a persistent problem in oil and gas production (Collins 2003; Rogers et al. 1990). Scale inhibitors are typically added to the production well either by continuously injection via a treat stream or by a bullhead treatment to force an inhibitor pill into the formation. In either case, both inhibition efficiency and inhibitor retention are significantly affected by their interaction with divalent cations. The interaction of the alkaline earth cation with scale inhibitors have been widely studied (Kan et al. 1994; Tomson et al. 1994, 2006; Friedfeld et al. 1998; Kan et al. 2000, 2004, 2005; Benton 1993; Boak et al. 1999; Graham et al. 1997). The inhibition efficiency of common scale inhibitors is significantly enhanced in the presence of Ca$^{2+}$ and Mg$^{2+}$ (Boak et al. 1999; Xiao et al. 2001b; He et al. 1996). It is proposed that the synergistic effect of Ca$^{2+}$ and inhibitors is caused by the formation of the Ca-Inh solution complex that is favorably adsorbed onto the nuclei (Tomson et al. 2003). Trace concentration of heavy metal ions, such as Mn$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$, are in the brine. The first transition series metal ions have many interesting chemical properties. These metal ions have been shown to enhance both scale (Breen et al. 1991; Barouda et al. 2007) and corrosion inhibition (Kuznetsov 2006; Demadis et al. 2005, 2006) properties of a phosphonate scale inhibitors. The primary retention mechanism for scale inhibitors following a bullhead treatment into the formation is precipitation of scale inhibitors with calcium (Kan et al. 2004; Jönsson and Jönsson 1995; Jordan et al. 1994, 1997; Sorbie et

*The content of this chapter has been published at SPE J. 2009. A. Kan, G. Fu, D. Shen, H. Alsaiaari, M. Tomson. It was reproduced here as submitted and the only changes here are the numbering of tables and figures, which have been renumbered to adhere to the format of this thesis.
According to a previous study, the following three conclusions were made for scale inhibitor retention following a squeeze: (1) The extent of inhibitor retention by carbonate-rich formation rock is limited by the amount of calcite that can dissolve before inhibitor-induced surface poisoning; (2) Surface poisoning effect is observed after approximately 20 molecular layers of inhibitor coverage that retards further mineral dissolution; (3) The consequence of retarded calcite dissolution is that the pore solution is acidic and more soluble calcium inhibitor solid phases form. Recently, it was observed that trace level of Fe$^{2+}$ in the connate brine significantly enhances the squeeze life and, evidently, Fe$^{2+}$ coproduced with inhibitor during its return (Tomson et al. 2008). Thus, the interaction of heavy metal ions with scale inhibitors must also play a significant role in squeeze retention.

7.2. Transition Metal Ion Interactions with Scale Inhibitors:

The primary functional groups in scale inhibitors are phosphate, phosphonate, carboxylate, and amine. The alkaline earth cations, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, are the predominant divalent metal ions in produced brine. The first transition element cations, from Mn$^{2+}$ to Zn$^{2+}$ have 3d$^5$ to 3d$^{10}$ subshell electrons. Attraction of these inner electrons to the nucleus leads to an overall decrease in cation radii and increase in electronegativity as compared to Ca$^{2+}$. Note that the alkaline earth cations and Mn$^{2+}$(3d$^5$) are classified as Pearson hard cations, which form strong ionic bonds with Pearson hard bases, which are common ligands in natural brines and inhibitors [e.g., OH$^-$, HCO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$, H$_n$PO$_4^{n-3}$, and carboxylates (Langmuir 1997)]. Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ are classified as borderline hard and soft acids and their bonding shows increasing covalency.
with soft bases (e.g., the amine group in the aminophosphonates). The metal/ligand complex stabilities increase in the order of Ca < Mn < Fe < Co < Ni < Cu ≈ Zn, and this order is often referred to as the Irving-Williams order (Irving and Williams 1948, 1953). Table 7.1 lists the stability constants of metal ion ligand stability constants of acetate, hydrogen phosphate, glycine, and ethylenediamine (Stumm and Morgan 1996; Popov et al. 2001; Sawada et al. 1987, 1989) and phosphonates, where MP is methylphosphonate, AMP is aminomethylphosphonate, NTMP is nitrilotris(methyl phosphonate), and EDTMP is ethylenediamine tetra(methylene phosphonate), with the data from Popov et.al. (2001), Sawada et. al. (1987, 1989), and Motekaitis et al. (1976). The complex between phosphate and all metal ions is electrostatic in nature and the stability constants of phosphate with alkaline earth ions and the first transition series ions are very similar. The complex stability constants between carboxylic acid and metal ions are approximately 1.5–1.9 log unit lower than that of phosphate except for the complex with ferrous ion. The stability constant of ferrous acetate is more than two orders of magnitude larger than the corresponding Ca complex. Because glycine has both carboxylate and amine functional groups, the ferrous glycine stability constant is also high. The strong complex between carboxylate and ferrous iron may have some implication in scale inhibition of ferrous salt. For example, Yean et al. (2008) observed strong inhibition of ferrous carbonate formation by citrate. On the other hand, the stability constants for the amines (glycine and ethylenediamine) with transition metal ions (Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺) are much higher than that of phosphate and acetate. The stability constants of the Cu²⁺ and Zn²⁺ complexes of glycine and ethylenediamine are approximately five and 11
orders of magnitude larger than that of the alkaline earth ions, respectively, indicating the stronger covalency in the complex of \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), and amine (Pearson soft base).

<table>
<thead>
<tr>
<th></th>
<th>Ethylenediamine</th>
<th>Glycin</th>
<th>HPO(_2)^{-}</th>
<th>Acetat</th>
<th>Methylene Phosphonate</th>
<th>Aminoethylene Phosphonate</th>
<th>Nitrilotrimethylene Phosphonate</th>
<th>Ethylenediamine tetramethylenephosphonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ba}^{2+} )</td>
<td>0.8</td>
<td>—</td>
<td>1.1</td>
<td>1.3</td>
<td>1.17</td>
<td>6.34</td>
<td>—</td>
<td>—</td>
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<tr>
<td>( \text{Sr}^{2+} )</td>
<td>0.9</td>
<td>2.15</td>
<td>1.1</td>
<td>1.4</td>
<td>1.34</td>
<td>6.52</td>
<td>—</td>
<td>—</td>
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<tr>
<td>( \text{Ca}^{2+} )</td>
<td>0.11</td>
<td>1.4</td>
<td>2.75</td>
<td>1.6</td>
<td>1.67</td>
<td>7.86</td>
<td>9.36</td>
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<tr>
<td>( \text{Mg}^{2+} )</td>
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<td>2.7</td>
<td>3.05</td>
<td>1.9</td>
<td>2</td>
<td>7.52</td>
<td>8.43</td>
<td></td>
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<tr>
<td>( \text{Mn}^{2+} )</td>
<td>2.73</td>
<td>3.2</td>
<td>—</td>
<td>1.4</td>
<td>2.5</td>
<td>3.6</td>
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<tr>
<td>( \text{Fe}^{2+} )</td>
<td>4.28</td>
<td>10.8</td>
<td>3.65</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>13.5</td>
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</tr>
<tr>
<td>( \text{Co}^{2+} )</td>
<td>5.89</td>
<td>5.1</td>
<td>3.15</td>
<td>1.5</td>
<td>2.2</td>
<td>4.5</td>
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<td>17.11</td>
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<tr>
<td>( \text{Ni}^{2+} )</td>
<td>7.52</td>
<td>6.2</td>
<td>3.05</td>
<td>1.4</td>
<td>2.3</td>
<td>5.3</td>
<td>11.7</td>
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<tr>
<td>( \text{Cu}^{2+} )</td>
<td>10.55</td>
<td>8.6</td>
<td>4.144</td>
<td>2.2</td>
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<td>8.1</td>
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</tr>
<tr>
<td>( \text{Zn}^{2+} )</td>
<td>5.71</td>
<td>5.4</td>
<td>3.35</td>
<td>1.6</td>
<td>2.6</td>
<td>5</td>
<td>14.6</td>
<td>18.76</td>
</tr>
</tbody>
</table>

*Stumm and Morgan (1996)
**Popov et. al. (2001)
†Sawada et. al. (1987, 1989)
‡Motekaitis et. al. (1976)

Because MP does not contain an amine group, the stability constants are similar to that of phosphate (i.e., the stability constants for MP with all metal ions are similar). The stability constants for the transition ions and AMP, NTMP, and EDTMP are much higher than that with alkaline earth metal ions because of the presence of amine groups in these three phosphonates. The very high stability constant for EDTMP may be caused by coordination of the metal ions with both nitrogen atoms of the EDTMP ligand.
Motekaitis et al. 1976). Sawada et al. (1987, 1989) concluded that the nitrogen atom of the ligand is protonated in the presence of an alkaline earth cation. However, the protonation occurs on the free O− of the NTMP ligand in the presence of transition metal ion. Therefore, these results suggest that the transition metal ion−N complex is very strong and is not displaceable by a proton. From the study, one may conclude that the solution chemistry of polymeric carboxylate and phosphonates may be similar in the presence of alkaline earth metal ions. The strong interaction between aminophosphonate and transition metal ions may affect the inhibition properties of aminophosphonates. Similarly, the strong interaction between Fe$^{2+}$ and carboxylate may have some implication to both the inhibition and squeeze applications of polymeric inhibitors, which has been studied by (Yean et al. 2008).

7.3. Solubility of Metal Phosphate and Metal Carboxylate Salts:

Some inhibitors are better squeeze chemicals than others. Kan et al. (2004) have shown that the retentions of NTMP and DTPMP are nearly 80%, while the retentions of BHPMP and PPCA are not as good. The retentions of BHPMP and PPCA are only 43% and 39%, where percent retention is defined as the percentage of inhibitor mass that is retained in the core after the highly soluble phase is returned in 3 pore volumes of flow. Previous work has shown that phosphonate reaction during squeeze treatments involves a series of self-regulating reactions with calcite and other minerals. However, excess calcite does not improve the retention of phosphonate because of the surface poisoning effect of the inhibitor (Tomson et al. 2008). It is proposed that by including Zn$^{2+}$, and possibly Cu$^{2+}$, or Fe$^{2+}$, an inhibitor pill could significantly extend the squeeze life because
the solubility of transition metal salts of phosphonates and polymers are expected to be much lower than the corresponding alkaline metal salts. **Table 7.2** lists the solubility products of the magnesium, calcium ferrous iron, cupric and zinc phosphate, and oxalate salts. The last row of **Table 7.2** shows the change in root mean logarithmic solubility product (pK$_{sp}$) between the calcium and zinc salts, which are 1.3 for the two phosphate salts and 0.5 for the two oxalate salts. The solubilities of the corresponding cupric salts are similar to that of the zinc salts. To date, no systematic work has been done to evaluate the effects of zinc in scale inhibitor squeeze treatment. The objective of this work is to evaluate the interaction of Zn$^{2+}$ and Ca$^{2+}$ with scale inhibitors in squeeze simulation and in scale inhibition.

<table>
<thead>
<tr>
<th><strong>TABLE 7.2</strong>—COMPARISON OF THE SOLUBILITY PRODUCTS OF METAL PHOSPHATES AND METAL OXALATES*</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphates (L)</td>
<td>pK$_{sp}$</td>
<td>Oxalates (L)</td>
</tr>
<tr>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>23.28</td>
<td>MgC$_2$O$_4$</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>28.92</td>
<td>CaC$_2$O$_4$</td>
</tr>
<tr>
<td>Fe$_3$(PO$_4$)$_2$</td>
<td>37.76</td>
<td>—</td>
</tr>
<tr>
<td>Cu$_3$(PO$_4$)$_2$</td>
<td>36.85</td>
<td>CuC$_2$O$_4$</td>
</tr>
<tr>
<td>Zn$_3$(PO$_4$)$_2$·4H$_2$O</td>
<td>35.42</td>
<td>ZnC$_2$O$_4$</td>
</tr>
<tr>
<td>[ \frac{pK_{sp}^{Zn} - pK_{sp}^{Ca}}{n} ]</td>
<td>1.30</td>
<td>[ \frac{pK_{sp}^{Zn} - pK_{sp}^{Ca}}{n} ]</td>
</tr>
</tbody>
</table>

*Data are from the following website on solubility products: [http://www.thelabrat.com/protocols/solubilityproductconstant.shtml](http://www.thelabrat.com/protocols/solubilityproductconstant.shtml)

7.4. Experimental

7.4.1. Materials:

Commercial-grade scale inhibitors are used in this study: nitrilo(methylene phosphonic acid) (NTMP), bis-hexamethylenetriamine-penta(methylene phosphonic)
acid (BHPMP), diethylenetriamine-penta(methylene phosphonic) acid (DTPMP), and polymers with generic composition of phosphinopolycarboxylate (PPCA), maleic acid terpolymer (1000 MW), polyvinylsulfonate (PVS, 15000 MW), and a sulfonate/carboxylate copolymer (1500 MW). Calcite used in this study is reagent grade calcite with a mean particle size of ~10 ± 5 \mu m and has been identified as calcite by X-ray diffraction analysis.

7.4.2. Potentiometric Titration:

All titration experiments were done in a 250 mL Teflon-covered water-jacketed beaker connected to a circulation bath similar to that of Tomson et al. (1994). The pH was monitored with a temperature compensated combination electrode. Approximately 100 mL of solution and electrode were equilibrated at 70°C under N₂. The change in pH was observed with the addition of 20 to 40 increments of sodium hydroxide. The titration of 1.0 mM DTPMP and BHPMP solutions in the presence of 1 mM Ca²⁺ (as CaCl₂·2H₂O), Ba²⁺ (as BaCl₂), or Zn²⁺ (as ZnCl₂) in the solution were tested to observe the effect of metal ion complexation. Titration experiments were also done to evaluate the effect of Zn²⁺ complexation on BHPMP ionization.

7.4.3. Barite Nucleation Kinetics Experiments:

For barite nucleation experiments, the synthetic brine used in the experiments contains 1 M NaCl, 0.089 M CaCl₂·2H₂O and 5 mM PIPES (1,4 piperazinediethanesulfonic acid) at pH 5.2. The experimental protocol is similar to the procedure published by Xiao et al. (2001b) and He et al. (1996), where equal volumes of cation and anion solutions were mixed in a vial and precipitation was detected via turbidity measurement. In each experiment, cationic and anionic solutions were prepared
separately, one with crystallizing cation Ba\(^{2+}\) and another with crystallizing anion \(\text{SO}_4^{2-}\), and both solutions contained the same amount of NaCl and Ca. The two solutions were then added into a glass turbidity cell and rapidly mixed under constant stirring by a Teflon-coated magnetic stirrer. The turbidity of the solution was tracked by a ratio/XR turbidimeter, and the data acquisition was accomplished via a digital multimeter. The final solution contained 1.1 mM Ba and \(\text{SO}_4^{2-}\) before precipitation at a barite saturation index of 2.0 at 25°C. For some experiments, a low concentration of Zn\(^{2+}\) (0–1.4 mg/L) was added to the cationic solution and a scale inhibitor was added to the anionic solution to study the effect of transition metal ions on the scale inhibition of barite. Note that the pH of the solution and temperature of reaction is low; therefore the expected nucleation time in the presence of inhibitors will be moderate. The inhibition time is expected to be exponentially increased at higher pH and temperature (He et al. 1994, 1996).

7.4.4. Laboratory Squeeze Simulation:

BHPMP and PPCA were examined in the present study. The squeeze simulation experiments were done with the totally contained squeeze simulation apparatus discussed previously (Tomson et al. 2006). “Totally contained” refers to the approach wherein the carbonates and inhibitors that dissolve during the inhibitor/core reaction are contained in a column apparatus to simulate the inhibitor/core reaction during squeeze. Typically, this is done by controlling the injection volume (the sum of inhibitor pill and overflush volume) to be \(\sim 96\%\) of the total pore volume. For the purpose of scale-up, we used the injection volume—instead of actual column porosity—to normalize the squeeze simulation results in the following discussion.
For BHPMP experiments, approximately 27 g calcite was packed in a 1.6 cm inner diameter (ID) column to a length of 12 cm and a pore volume of ~15 ml. The porosity of the column was determined by tracer breakthrough studies and the porosity of the column is very reproducible because of the uniform packing material used in this study. The squeeze was done by injecting 1 part (~3 mL) of scale inhibitor, followed by 4–5 parts of overflush solution (~12 mL) under 75 psig pressure. For PPCA experiments, approximately 8 g calcite was packed in a 1.6 cm ID column to a length of 3.5 cm and a pore volume of 4 mL. The squeeze was done by injecting 1 part (~1.6 mL) of scale inhibitor, followed by 1 part of overflush solution (~1.6 mL) under 75 psig pressure. Then, the column was shut in under pressure overnight. A “cationic” brine containing ~0.05 M CaCl₂·2H₂O in 1 M NaCl and an “anionic” brine containing 0.03 M NaHCO₃ in 1 M NaCl were prepared. Before the inhibitor return experiments, equal volumes of both brines were mixed and bubbled with water saturated with CO₂ (100%) gas. This synthetic brine, used as the return brine, was saturated with respect to calcite at 158°F (pH ~5.6) to simulate typical brine in a formation.

For each experiment, several liters of return brine were pumped into the column from the reverse direction (opposite direction from pill injection direction) to simulate production after a squeeze treatment. Typically, the return inhibitor concentration will reduce to a sub-mg/L level after approximately 100 pore volumes of flow and the inhibitor return concentration will eventually approach a constant value after a large volume of return flow. At this point, the experiment was stopped and the solid phase was pushed out from the column. The solid was divided into six equal sections, dissolved in concentrated HCl and analyzed for phosphorus, calcium, and zinc concentrations.
Squeeze simulations with both scale inhibitors were compared at 4 wt% active inhibitor concentrations. The inhibitor pill matrix contained 1 M NaCl, and one of the following cationic salts: 0.3 M CaCl₂·2H₂O or 0.18–0.3 M ZnCl₂ for the BHPMP experiments and 0.25 M CaCl₂·2H₂O or 0.25 M ZnCl₂ for the PPCA experiments. To understand the propagation of Zn²⁺ during the injection phase, the 0.18 M ZnCl₂ in BHPMP experiment was repeated by injecting the inhibitor pill containing Zn²⁺ and an overflush solution to the column. After shut-in overnight, 3 pore volumes of synthetic brine was flowed through the column from the reverse direction to flush out the pore solution and the column was sectioned to analyze the solid phase Zn²⁺ and BHPMP distribution in the core.

The calcium, zinc, phosphonate, and PPCA concentrations were analyzed by inductively coupled plasma atomic emission spectrophotometer (ICP). Detection limit for ICP analysis is typically down to approximately 0.2 mg/L P. At phosphorus concentrations below 0.2 mg/L, the persulfate digestion/ascorbic acid method (Clesceri et al. 1989) was used to analyze phosphonate. The colorimetric method (i.e., the formation of a phosphomolybdic acid and the reduction to form intensely colored molybdenum blue by ascorbic acid method) has a detection limit of 0.02 mg/L P. The potential interferences of this method was discussed previously by Kan et al. (1991) and in Standard Method (Clesceri et al. 1989). There were no known interferences with laboratory samples used in this study. For PPCA analysis, effluent samples were first purified with Sep-Pak C-18 cartridge following the procedure of Xiao et al. (2001b) before the colorimetric determination. pH was monitored with an in-line pH electrode.
7.5. Results and Discussion:

7.5.1. Potentiometric Titration of DTPMP and BHPMP in the Presence of Ca$^{2+}$, Ba$^{2+}$, and Zn$^{2+}$:

Figure 7.1a plots the potentiometric titration of 1 mM DTPMP in the presence of 1 mM Ca$^{2+}$, 1 mM Ba$^{2+}$, and 1 mM Zn$^{2+}$ at 70°C and in 1 M NaCl. As expected, the complexation of DTPMP or BHPMP with Ba$^{2+}$ and Ca$^{2+}$ are much weaker than with Zn$^{2+}$. The strong Zn-Phn complex causes a significant shift of the DTPMP titration curve. When solutions containing 1.0 mM BHPMP and various concentrations of Zn$^{2+}$ were titrated with NaOH, precipitates were always observed when the solution is above 3 pH and before the second inflection point at approximately 7 pH (see Figure 7.1b). The precipitate redissolved into the solution at higher pH.

Figures 7.1. Potentiometric titration of (a) DTPMP and (b) BHPMP in the absence and presence of 1 mM Ca$^{2+}$, Ba$^{2+}$ and Zn$^{2+}$. 
7.5.2. Barite Inhibition Efficiency in the Presence and Absence of Zn\(^{2+}\) and Scale Inhibitors:

**Figure 7.2** shows the induction time of barium sulfate precipitation in the presence and absence of Zn\(^{2+}\) and a scale inhibitor where the turbidity reading vs. reaction time is plotted and BHPMP, DTPMP, or NTMP are used as the scale inhibitors. The induction time is defined as the time lapses between the generation of a supersaturated state by mixing the Ba and sulfate solutions and the observed rapid increase in turbidity reading. As shown in **Figure 7.2a**, Zn\(^{2+}\) alone does not affect the induction time of barite precipitation (~100 seconds). In the presence of BHPMP (0.55 mg/L), the barite induction time increases to ~400 seconds. The induction time is increased to 1,250 seconds when 0.28 mg/L Zn\(^{2+}\) is added to the solution at similar BHPMP concentration (i.e., Zn\(^{2+}\) improved BHPMP inhibition by approximately a factor of three). At higher Zn\(^{2+}\) concentrations, the induction time is further increased to 1,920 seconds (at 1.4 mg/L Zn\(^{2+}\)) [i.e., a factor of 20 times increase in induction time (**Figure 7.2a**)]. Similarly, the induction time is significantly increased when both Zn\(^{2+}\) and DTPMP are present, **Figure 7.2b**. Surprisingly, the presence of Zn\(^{2+}\) impedes the inhibition efficiency of NTMP on barite, **Figure 7.2b**. Breen et al. (1991) also found that Cu\(^{2+}\) and Zn\(^{2+}\) enhance the barite precipitation inhibition of EDTMP (ethylenediamine tetramethylene phosphonic acid) and 1,2 diaminocyclohexane-N,N,N',N'-tetra(methylene phosphonic) acid, but it does not improve barite inhibition efficiency of NTMP. NTMP is not as good a scale inhibitor for barite as BHPMP or DTPMP (He et al. 1994, 1996). These data indicate that the synergistic effect of Zn\(^{2+}\) on barite inhibition is only observed with polyamine polyphosphonates and not with the inhibitors of single amine group.
Figure 7.2: Plots of turbidity versus time for barite nucleation kinetic studies where the barite inhibition study was done in the presence and absence of Zn2+ and (a) BHPMP; (b) DTPMP; and (c) NTMP. The background solution is 1M NaCl, 0.088 M Ca, and 1.1 mM Ba2+ and sulfate at pH 5.2, 25 °C, and barite SI = 2.0.
It is assumed that Zn\(^{2+}\) will not form strong complex with polymeric inhibitors, which do not have the amine functional groups, and, indeed, no such synergistic effect was found in this study with several polymeric inhibitors as shown in Figure 7.3. Figure 7.3 plots the turbidity vs. time of barite nucleation kinetics studies where the barite nucleation times were compared in the presence and absence of (a) PPCA, (b) a maleic acid terpolymer, (c) a sulfonate/carboxylate copolymer, and (d) a polyvinylsulfonate inhibitors and Zn\(^{2+}\). All four inhibitors extended the nucleation time of barite to more than 500 seconds. Even though Zn\(^{2+}\) did not improve the inhibition efficiency of these polymeric inhibitors, more importantly, it did not adversely affect their inhibition performance. Therefore, it may be safe to use Zn\(^{2+}\) in squeeze treatment because it may enhance the retention of polymeric inhibitors.

**Figure.** 7.3 Plots of turbidity versus time for barite nucleation experiments where the solution are in the presence and absence of Zn2+ and (a) PPCA; (b) Maleic acid terpolymer; (c) Sulfonate/carboxylate copolymer; and (d) polyvinylsulfonate. The background solution is 1 M NaCl, 0.088 M Ca, and 1,1 mM Ba2+ and sulfate at pH 6.4, 25 °C, and barite SL = 2.0.

### 7.5.3. Squeeze Simulation
A summary of both BHPMP and PPCA squeeze simulation results are shown in Table 7.3 and Figures 7.4 through 7.9. Figure 7.4 plots the inhibitor return curves of (1) BHPMP in the acid form without additional cation, (2) with the addition of 0.3 M Ca\(^{2+}\), (3) 0.18 M Zn\(^{2+}\), and (4) 0.3 M of Zn\(^{2+}\) to the pill solution. The complete inhibitor return curves are plotted in Figure 7.4a in logarithmic concentration scale on the y axis. The inhibitor return in the first 10 pore volumes is plotted in Figure 7.4b. The mass of inhibitor injected and the mass of the inhibitor return in three pore volumes and the total mass of inhibitors that returned at the end of the experiment were listed in Columns 2 through 4 of Table 7.3. Note that BHPMP alone does not retain well in these squeeze simulations with more than 57% of the inhibitor mass lost in 3 pore volumes (Table 7.3, Column 6). After approximately 350 pore volumes or \(~5.3\) L of return flow by volume, more than 93% of BHPMP was returned (see Columns 7 of Table 7.3) and the BHPMP concentration in the effluent dropped to approximately 0.1 mg/L (Column 8 of Table 7.3 and Figure 7.4a). If we assumed that the minimum inhibitor concentration (MIC) to satisfy the inhibition need is 0.5 mg/L, only 88 pore volumes of flow (\(~1.6\) L, Column 9 of Table 7.3) is returned with BHPMP concentration greater than 0.5 mg/L.

**TABLE 7.3—SUMMARY OF INHIBITOR MASS DISTRIBUTIONS, % RETENTION, % RETURN**
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Mass Injected (mg)</th>
<th>Mass Returned in 3 Pore Volumes (mg)</th>
<th>Total Volume Returned (L)</th>
<th>Total Mass Returned (mg)</th>
<th>% Retention</th>
<th>Equilibrium Return Conc. (mg/L)</th>
<th>Projected Effective Return Volume (L)</th>
<th>NSL (bbl/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHPM P</td>
<td>114</td>
<td>64</td>
<td>5.3</td>
<td>107</td>
<td>43</td>
<td>93</td>
<td>0.1</td>
<td>1.5*</td>
</tr>
<tr>
<td>BHPM P+</td>
<td>142</td>
<td>56</td>
<td>16.8</td>
<td>109</td>
<td>65</td>
<td>23</td>
<td>0.1</td>
<td>4.8*</td>
</tr>
<tr>
<td>BHPM P+ 0.3 M Ca²⁺</td>
<td>143</td>
<td>10</td>
<td>30.3</td>
<td>84</td>
<td>92</td>
<td>59</td>
<td>0.57</td>
<td>109</td>
</tr>
<tr>
<td>BHPM P+ 0.18 M Zn²⁺</td>
<td>155</td>
<td>14</td>
<td>39.2</td>
<td>90</td>
<td>91</td>
<td>58</td>
<td>0.67</td>
<td>113</td>
</tr>
<tr>
<td>PPCA</td>
<td>67</td>
<td>41</td>
<td>6.2</td>
<td>58</td>
<td>39</td>
<td>86</td>
<td>0.36</td>
<td>2.6*</td>
</tr>
<tr>
<td>PPCA+ 0.25 M Ca²⁺</td>
<td>65</td>
<td>18</td>
<td>9.6</td>
<td>57</td>
<td>72</td>
<td>89</td>
<td>0.5</td>
<td>12.6</td>
</tr>
<tr>
<td>PPCA+ 0.25 M Zn²⁺</td>
<td>67</td>
<td>11</td>
<td>10.4</td>
<td>46</td>
<td>83</td>
<td>69</td>
<td>0.5</td>
<td>39</td>
</tr>
</tbody>
</table>

*The effective return volume is the return volume that produced a return concentration greater than the minimum inhibitor concentration of 0.5 mg/L.

a.
Figure 7.4. Plots of inhibitor return versus the number of pore volumes for BHPMP squeeze simulations where 4% acidic BHPMP solution was used as inhibitor pill and 0.3 M Ca\textsuperscript{2+} and 0.18-0.3 M Zn\textsuperscript{2+} are also added to some pill solutions. In Figure 7.4a is plotted the entire return curve where up to 2700 pore volumes of brine was returned and in Figure 7.4b is plotted the initial inhibitor return of the first 10 pore volumes.

Also shown in Figure 7.4, by adding 0.3 M Ca\textsuperscript{2+} to the acidic inhibitor pill, the mass of BHPMP lost in the first 3 pore volumes is significantly reduced and the retention is increased to 65% (Table 7.3, Column 6). After 1,120 pore volumes (~ 16.8 L) of return flow, approximately 77% of BHPMP was returned but the long term effluent BHPMP
concentration also dropped to approximately 0.1 mg/L. The return flow dropped to less
than 0.5 mg/L BHPMP at approximately 320 pore volumes (~4.8 L). Adding 0.18 or 0.3
M Zn\(^{2+}\) to inhibitor pill significantly improved the inhibitor retention (92 and 91%,
respectively). After 2,000 and 2,600 pore volumes (~30 and 39 L, respectively) of return
flow, the effluent BHPMP concentration remains greater than 0.5 mg/L and only
approximately 58–59% of inhibitor returned. Note that the return concentration is nearly
constant after ~1,600 pore volumes of flow for both experiments (see Figure 7.4a). The
mean and one standard deviation of the measured return flow BHPMP concentrations
between 1,600 pore volumes of return flow and the end of the experiments are 0.57 ±
0.06 and 0.67 ± 0.09 mg/L for the 0.18 M and 0.3 M Zn experiments, respectively. No
obvious decline in BHPMP concentration was observed for ~1,000 pore volumes of
return flow (see Figure 7.4a). It is assumed that this constant return concentration
corresponds to the solubility of a Zn-Phn salt (i.e., the return concentration is controlled
by dissolution of a zinc phosphonate salt that precipitated in the formation).

Because the return concentration has reached a constant concentration for the Zn
amended experiments, the experiment was terminated and the solid phase phosphonate
distribution was measured. In each case, the phosphonate mass balance is greater than
90%. To estimate the squeeze life when the experiment is terminated before complete
depletion, Eq. 7.1 is used to calculate the effective return volume by assuming that
BHPMP will return at the constant solubility level until 90% of BHPMP is recovered.
Then, the effective return volume can be calculated from the following mass balance
equation:
Effective Return Vol (L) =
\[
\frac{(0.9 \cdot \text{Inh Mass Injected} - \text{Total Mass Returned})}{\text{Eq. Return Conc. (mg/L)}} + \text{Total Return Vol. (L)}
\]  
Eq. (7.1)

The projected effective return volumes for these two Zn experiments are 109 and 113 L or 7,267–7,533 pore volumes, which are more than 60 times larger than in the absence of cation amended pill.

**Figure 7.5a and 7.5b** plots the solid phase Zn\(^{2+}\) and BHPMP distributions over the entire length of the column and the solid phase Zn\(^{2+}\) vs. BHPMP concentration after just 3 pore volumes of return flow to evaluate the propagation of Zn\(^{2+}\) and BHPMP during injection for the 0.18 M Zn\(^{2+}\) experiment. Note that most of the Zn\(^{2+}\) and BHPMP injected are retained near the well bore as expected because of precipitation reaction. The molar ratio of Zn\(^{2+}\)/BHPMP in the inhibitor pill is 2.5 and the molar ratio of Zn\(^{2+}\)/BHPMP in the solid phase is 2.72 (see **Figure 7.5b**), indicating that most Zn\(^{2+}\) coprecipitated with BHPMP in the front of the column.

**Figures 7.5.** Plots of (a) BHPMP and Zn distribution in the column after injection of 0.18 M Zn\(^{2+}\)/BHPMP pill, overflush and 3 pore volumes of return flow; (2) solid phase Zn versus BHPMP concentrations after injection.
**Figure 7.6** plots $\text{Zn}^{2+}$ vs. BHPMP concentration in both the effluent and the solid phases after more than 2,000 pore volumes of return flow for the 0.18 M and 0.3 M $\text{Zn}^{2+}$ experiments. The molar ratios of $\text{Zn}^{2+}$ to BHPMP in the pill are 2.6 and 4.3 for the two squeeze simulations with $\text{Zn}^{2+}$, respectively. The effluent $\text{Zn}^{2+}$ to BHPMP ratios are 2.59 and 5.69, respectively (see **Figure 7.6a**), indicating that more zinc is returned than phosphonate during inhibitor flowback. Interestingly, the ratios of $\text{Zn}^{2+}$ to BHPMP in the solid (= 1.87, **Figure 7.6b**) for both experiments are similar and lower than that in the pill, indicating that the excess $\text{Zn}^{2+}$ may not be needed. The return performances for these two squeeze simulations are nearly identical. These data support the hypothesis that $\text{Zn}^{2+}$ precipitates with BHPMP at a ratio of $\sim 1.87$ (statistically, this ratio might be 2.00) to form a low solubility solid phase of $\text{Zn}_{1.87}\text{H}_{6.26}\text{BHPMP}$, and this solid material provides the long-term source of BHPMP in the produced water at a low and constant return concentration.

**a.**

**b.**

---

**Figure 7.6.** Plots of (a) effluent $\text{Zn}^{2+}$ versus BHPMP molar concentrations and (b) solid phase Zn versus BHPMP concentrations for the two experiments where 0.18 and 0.3 M $\text{Zn}^{2+}$ were added to the inhibitor pill solution for the squeeze simulation.
Similar squeeze simulations were done with PPCA (Table 7.3 and Figure 7.7). In the absence of added Ca\textsuperscript{2+} or Zn\textsuperscript{2+} in the pill solution, PPCA retention is as low as 39\% (Table 7.3, Column 6). Addition of Ca\textsuperscript{2+} or Zn\textsuperscript{2+} in the pill significantly increased PPCA retention to 72 and 83\%, respectively, with approximately 11\% more retention observed with the Zn\textsuperscript{2+} amended experiment than the Ca\textsuperscript{2+} amended experiment. The return profiles are similar for both Ca\textsuperscript{2+} or Zn\textsuperscript{2+} amended experiments, and both returns are at slightly higher concentrations than the base case without cation added to the inhibitor pill (Figure 7.7). The effective return volume is 39 L in the presence of Zn, which is more than 10 times larger than the base case without any cation amended in the inhibitor pill.

**Figure 7.7:** Plots of inhibitor return versus the number of pore volumes for PPCA squeeze simulations where 4\% PPCA solution was used as inhibitor pill and 0.25 M Ca\textsuperscript{2+} or Zn\textsuperscript{2+} are added to some pill solutions. In (a) is plotted the initial inhibitor return of the first 10 pore volumes and in (b) is plotted the entire return curve where up to 2000 pore volumes of brine was returned.

**Figure 7.8** shows the Zn\textsuperscript{2+} to PPCA concentration in the return flow. Approximately 22 Zn\textsuperscript{2+} is coeluted with each molecule of PPCA. Because PPCA has nominally 50 monomeric carboxylate units per molecule, approximately each Zn molecule is bound with two carboxylate monomers shown in Figure 7.8.
Previously, we observed that the squeeze life can be reasonably characterized by the normalized volume when field squeeze data were compared (Kan et al. 1994). A normalized squeeze life (NSL) may be calculated from the ratio of return volume and the mass of inhibitor used as defined by Kan et al. (1994) for DTPMP (Column 10, Table 7.3, Eq. 7.2a):

$$\text{Normalized Squeeze Life (bbl/Kg)} = \frac{10^6 \cdot \text{Effective Return Vol (L)}}{159 \cdot \text{Mass of Inh Injected (mg)}}$$  \hspace{1cm} \text{Eq. (7.2a)}$$

If the active composition of the inhibitor is known, then NSL can be expressed with common field unit as barrel of brine production per gallon of inhibitor used in a squeeze job (bbl/gal) by multiplying NSL (bbl/Kg) with the activity of the chemical in unit of (Kg of active inhibitor per gallon of inhibitor).

$$\text{Normalized Squeeze Life (bbl/gal)} = \frac{\text{NSL (bbl/Kg)} \times \text{Inhibitor Activity(Kg/gal)}}{\text{Eq. (7.2b)}}$$

The NSL for the squeeze simulations discussed was listed in Column 10 of Table 7.4. When acidic BHPMP is injected into the formation, the NSL is 83 bbl/Kg. When Ca$^{2+}$ is added to BHPMP pill, an NSL of 188 bbl/Kg can be obtained (i.e. a factor of 2.1 increase in projected squeeze life). When Zn$^{2+}$ is added to the inhibitor pill, the NSLs are 4,782
and 4,588 bbl/Kg, which are 52–54 times longer than the base case where no cation is added to the inhibitor pill. Similarly, PPCA NSLs are significantly enhanced with Ca$^{2+}$ and Zn$^{2+}$ amendment.

The BHPMP squeeze simulation is compared to a typical squeeze job, such as that reported by McKinzie et al. (1996) at the Guerra well in south Texas. The well produced 8.5 million scf/D natural gas, 50 B/D oil, and 120 B/D water at the downhole condition of 340°F and 7,000 psig. A 157 Kg BHPMP was injected in a squeeze job. The inhibitor return dropped below 0.5 mg/L after approximately 150 days of production. On the basis of the normalized volume, a PSL can be estimated by Eq. 7.3:

\[
\text{Projected Squeeze Life (day)} = \frac{\text{NSL (B/Kg) \cdot Inh Used in Squeeze Job (Kg)}}{\text{Daily Water Production (B/D)}}
\]

or

\[
\text{Projected Squeeze Life (day)} = \frac{\text{NSL (B/gal) \cdot Inh Used in Squeeze Job (gal)}}{\text{Daily Water Production (B/D)}}
\]

The PSL will be 110 days before it reaches 0.5 mg/L, assuming the NSL in Table 7.3, which is similar in magnitude to that observed for the Guerra well. Note that Guerra brine and well condition is very different from that used in this experiment and a direct comparison needs to be tested. This ballpark comparison certainly suggests that the projections of this study are reasonable. Note that the squeeze life will be strongly dependent on the MIC. Using the Guerra well as an example, 0.5 mg/L BHPMP can control barite scale with barite SI = 1.22 at downhole condition (340°F, 7,000 psi). In fact, the Guerra well downhole barite SI is only 0.21, and, therefore, 0.5 mg/L concentration should be very safe. In fact, this well has produced for 437 days, where the inhibitor concentration eventually dropped to 0.38 mg/L, and no scale has been observed.
Certainly, much works is needed to extend a new proposed squeeze method to field practice. Both the kinetics of precipitation and temperature effects on squeeze performance and inhibition efficiency must be tested. Note that this treatment has only been tested in carbonate type minerals, its efficiency in sandstone formations remains to be tested. However, it is expected that the precipitation of zinc phosphonate in the formation should not be affected by the formation type.

7.7. **Environmental Impact:**

Zinc is found in the air, soil, and water and is present in all foods; in cosmetic/pharmaceutical products, such as vitamin supplements, as an anticorrosion coating as used in galvanized steel and is widely used in completion fluid. Zinc is a trace mineral nutrient and, as such, small amounts of zinc are needed in all animals. In the environment, it will typically adsorb or precipitate, and the level of dissolved zinc in water is typically low. The US Environmental Protection Agency (EPA) has established national secondary drinking water regulations that set nonmandatory water quality standards for 15 contaminants, including Zn$^{2+}$ at 5 mg/L, as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color, and odor (Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals 1992). Figure 7.9 shows the long term Zn$^{2+}$ concentration over 1,000 pore volumes of return flow. The dotted line is the secondary drinking water regulation level (5 mg/L). Zn$^{2+}$ concentration dropped rapidly to below the secondary drinking water regulation level within 26 pore volumes. Because the effluent Zn$^{2+}$ concentration in the return brine dropped below 5 mg/L after ~30 pore volume of flow and eventually
dropped to less than 1 mg/L. At such concentration, it should not pose any environmental risks in the United States if one collects and treats the initial 30 pore volumes of return fluids (i.e., 30 times the volume of injection volume). Assuming an injection volume of 500 bbl, approximately 15,000 bbl of fluids may require treatment to remove Zn before disposal. The regulation in other regions (e.g., United Kingdom and Norway) may be more stringent, and, therefore, its application in these regions may require additional scrutiny. Lastly, Zn potentially can form ZnS scale in sour wells. Therefore, this technology may not be applicable to sour wells, but may suggest a method for sulfide removal, as is being tested by the authors.

**Figure 7.9:** effluent Zn$^{2+}$ concentrations versus number of pore volumes of long term return flow.
8. CONCLUSION:

Water usually contains multiple cations and anions. When the solution become supersaturated due to co-mixing and changes in conditions, the ions may precipitate as solid solutions. In some cases mineral deposition of solid solutions is beneficial, as in water treatment for heavy metal or arsenic removal, and sometimes it is deleterious, as occurs in oil and gas production. In either case, understanding the mechanisms of precipitation and inhibition is important. Therefore, the key parameters needed for the prediction of solid solutions formation for industrial water treatment processes are the stoichiometry of solid solution formation and kinetics at different aqueous compositions and conditions. Due to the abundance of calcium and iron in natural environments, the stoichiometry of solid solutions of calcium and iron carbonates was studied in this work.

Significant accomplishments from this study are 1) the development of a model for predicting the stoichiometry of solid solution as a function of solution composition; 2) development of an experimental design for studying the precipitation kinetics of solid solutions under rigorously anoxic condition, and; 3) studying the impact of metal ions on the inhibitor retention where it was found that addition of metal cations in inhibitor pill increases the inhibitor retention and performance.

In this research, a model was developed in a form of logistic function to predict the stoichiometry of solid solutions. The validity of the model was tested by comparing the model results with the experimental results of two different types of solid solutions: iron-calcium carbonate and barium-calcium carbonate. The model showed an excellent representation for the experimental results with $R^2$ greater than 0.97 and 0.88 for $\text{Fe}_{x}\text{Ca}_{1-x}\text{CO}_3$ and $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$, respectively. Using the model one can predict the incorporation
of ions from waters into solid solution minerals. They also help to infer the
physicochemical conditions of natural crystallization environments.

The experimental equipment and procedures described in this thesis provide an
effective means of producing and handling oxygen sensitive solid solutions. The
precipitation kinetics of a number of other solid solutions in aquatic systems could be
studied by adapting the experimental design developed in this work.

In this research it was also found that scale inhibitor squeeze treatment of
phosphonate type (DTPMP and BHPMP) can be improved by adding compatible divalent
cations to the squeeze pill. The results show that addition of calcium and iron ions with
the inhibitor pill improves the retention of phosphonate and the distribution of the
inhibitor in the formation. In addition trace levels of $\text{Zn}^{2+}$ significantly improves both
BHPMP and DTPMP inhibition efficiency and retention. The enhanced scale inhibition
may be caused by a complex of metal ions with the amine functional group of
polyamino-polyphosphonates. $\text{Zn}^{2+}$ also exhibits a small synergistic inhibition effect with
polymeric carboxylate (PPCA) inhibitors.
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