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The Fate of Phosphonate Inhibitors in Oil & Gas Reservoirs: Validation of the SqueezeSoft™ Computer Program

by

Malene Abena Watson

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

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HOUSTON, TEXAS

FEBRUARY, 2002
Abstract

The Fate of Phosphonate Inhibitors in Oil & Gas Reservoirs: Validation of the SqueezeSoft™ Computer Program

by

Malene Abena Watson

The deposition of material that has precipitated out of solution can cause problems that plague a variety of engineering and biological processes. Scale formation in cooling towers, boilers, and oil/gas operations are prevented with chemical inhibitors such as nitritolotriis (methylene phosphonic acid). The release of this phosphonate from solid material is studied with batch and dynamic flow experiments. The corresponding observations can be incorporated into SqueezeSoft™, a computer program, written by the Rice University Brine Chemistry Consortium. This work attempts to examine SqueezeSoft™'s ability to identify the placement of inhibitor during a squeeze treatment and the corresponding reactions that occur. SqueezeSoft™ has been found to correctly predict the profile of inhibitor injected into a column packed with core material. Because this program is based on theory and not on empirical findings, it can be expanded to other more general applications.
ACKNOWLEDGEMENTS

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CHAPTER 1: Introduction

1.1 PROBLEM STATEMENT

The precipitation of unwanted chemicals from aqueous solutions plagues scientists and engineers in a variety of fields ranging from medicine to petroleum. The precipitation of stones in the kidneys and scale in production lines are just a few examples. The deposition of scale from naturally occurring minerals on equipment when changes in pressure and temperature occur has been identified as a major problem generally occurring in systems that involve the usage of large quantities of water. These systems include, but are not limited to, distribution lines, hot-water heaters, heat exchangers, cooling towers, boilers, and oil/gas drilling operations and production [1].

The petroleum industry spends hundreds of millions of dollars each year trying to eliminate scaling downhole so that it will not cause problems in wells and equipment thereby reducing productivity [2]. Typically, the formation of scale is prevented with the use of chemical inhibitors. According to the literature [3], inhibitors prevent the deposition of minerals by blocking the nucleation of their crystals, which allows brine to flow through equipment without scaling. Since the manner in which the inhibitors work has not been sufficiently researched [4],[5]; practicing engineers do not have a good method of determining the type of inhibitor needed nor accurately calculating the amount required for a “squeeze” operation (the injection of inhibitor into rock formations). To some degree, the design of a squeeze treatment is trial and error [6]. It is for this reason that further study of the chemistry of chemical inhibitors and their performance during a
squeeze treatment is necessary. The mechanisms that dictate how inhibitors are placed in rock formation and then react will be the focus of this work.

1.2 OBJECTIVES

Investigating the chemistry of the adsorption/desorption properties of nitrilotris (methylene phosphonic acid) (NTMP), a commonly used scale inhibitor, will allow for further understanding of its solution chemistry which is applicable to its placement in the subsurface environment during a squeeze treatment. The primary research goals of this thesis are to examine the chemical properties of NTMP as it interacts with the solid/solution interface, relate the findings of this work to the mechanisms that occur during a squeeze treatment, and evaluate the SqueezeSoft™ computer program based on solution chemistry criteria.

1.2.1 ADSORPTION/DESORPTION STUDIES

A series of adsorption/desorption studies were previously performed by members of the Rice University Brine Chemistry Consortium (BCC) research group to determine the adsorption/desorption properties of NTMP. The adsorption isotherm of NTMP and BaSO₄ was found to be irreversible. Because the data from their research did not include equilibrium concentrations below 0.5 mg/L, batch experiments in this work were performed to determine if similar hysteretic behavior occurs. A possible third Ca-H-NTMP phase may have been found, although further research is required to be certain. Additionally, previous BCC research identified solubility as the controlling mechanism
for desorption. A series of batch experiments with varied pH, calcium concentration, and ionic strength were performed. The results of this work did not support the proposed theory that desorption is governed by solubility.

1.2.2 COLUMN STUDIES

A series of column studies were used to simulate a squeeze treatment shut-in (a 24 to 72 hour period of time when the inhibitor is allowed to reach equilibrium with the rock formation). The information derived from this study will allow for the comparison of the SqueezeSoft™ program to laboratory data derived in this work. Table 1-1 lists the general parameters for five of the six column studies performed. The last column study will be discussed in detail in Chapter 5.

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<td>Core Material</td>
<td>Frio Sandstone</td>
</tr>
<tr>
<td>Particle Size</td>
<td>250 – 710 microns</td>
</tr>
<tr>
<td>Pore Volume</td>
<td>11 mL</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.46</td>
</tr>
<tr>
<td>Column ID</td>
<td>1.6 cm</td>
</tr>
<tr>
<td>Column Length</td>
<td>11.7 cm</td>
</tr>
<tr>
<td>Shut-In Period</td>
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In each experiment, a column packed with core material was injected with inhibitor and shut-in for 24 hours. After which, the core material was removed from the column and extracted. Both the injection rate and inhibitor concentration was varied so that the placement of inhibitor in the solid phase could be studied under different conditions.
The concentrations derived from these analyses were used to reconstruct the profile of the solid phase inhibitor concentration, which SqueezeSoft™ outputs. The solid phase concentration was used for comparison purposes rather than the liquid phase so that the actual placement of inhibitor could be studied.

A final column study was performed to eliminate uncertainties caused by impurities in the core material, error introduced by serial dilutions, and pH measurements taken at room temperature instead of 70°C (the temperature of the column in the temperature bath). In this last study, a column was packed with pure calcite crystals (420 – 600 µm) and reagent grade powder enabling the determination of the relative significance of specific surface area and the degree of adsorption. Also, the entire squeeze process was simulated (preflush, injection, shut-in, and resumed production). This particular study may have revealed a highly insoluble Ca-H-Phn phase.

1.2.3 SQUEEZEWOOD™ PROGRAM

SqueezeSoft™ was written under the premise that the inhibitor reacts with calcite to form a phosphonate-calcium complex, which adsorbs to the surface of the mineral thereby preventing the nucleation or growth of scale. In order to investigate the robustness of this computer program, solid phase distribution obtained from the laboratory studies was compared to SqueezeSoft™’s prediction.
SqueezeSoft™ was written to simulate the entire squeeze process; beginning with the preflush and ending with the inhibitor return curve. Five of the six laboratory experiments only simulated the first half of the process, injection through shut-in. For this reason, the computer program was modified to stop after shut-in and the inhibitor return curve was replaced with a postflush subroutine.
CHAPTER 2: Background

The fundamental principles of chemistry are essential to developing the technology needed to repair former damage done to the natural environment as well as to prevent future problems from occurring. Aqueous chemistry is based on chemical equilibria, which is needed to understand the processes that govern the chemical composition of natural waters. The study of water chemistry is composed of several topics including, but not limited to the precipitation and dissolution of solid phase chemicals, the equilibrium and kinetics that determine which reactions will occur and their corresponding rates, the nucleation and growth of crystals in aqueous solutions, and the adsorption and transport of chemicals in aqueous environments. All of these areas of study are required to comprehend a variety of problems ranging from scale in cooling towers, boilers, and oil/drilling operations to physiological issues such as osteoporosis and kidney/bladder stones. The precipitation, dissolution, and adsorption of calcium-phosphonate complexes will be the focus of this work.

2.1 CHEMICAL EQUILIBRIUM

The chemical equilibrium of a natural body of water is obtained through several chemical reactions and biological processes. Chemical reactions taking place in an aqueous solution can be addressed using thermodynamics or kinetics. Thermodynamics allows for the determination of changes in chemical energy in both forward and reverse reactions. Kinetics is the study of the rate of a chemical reaction as it approaches
equilibria. Both areas of study are important for the determination of the composition of aqueous species.

2.1.1 CHEMICAL THERMODYNAMICS

Chemical thermodynamics describes changes in chemical composition resulting from reactions that cause chemical species to transition between liquid, solid, and gaseous phases while approaching equilibrium. A chemical system will experience spontaneous and irreversible changes during a state of nonequilibrium until a final state of equilibrium has been obtained. Once chemical equilibrium has been achieved, the system will remain constant until a new stress is placed on it.

2.1.1.1 GIBBS FREE ENERGY

The change in equilibrium from an initial state to final state at constant temperature and pressure is given by the Gibbs free energy as shown in Equation 2-1:

\[ \Delta G = \Delta H - T \Delta S \, , \]  

(2-1)

where, \( \Delta G \) = the Gibbs free energy (kJ/mole),
\( \Delta H \) = the change in enthalpy (kJ/mole),
\( T \) = the absolute temperature (K), and
\( \Delta S \) = the change in entropy (kJ/mole-K).

The change in Gibbs free energy can also be described as the initial change in energy minus the final change in energy as displayed in Equation 2-2:
\[ \Delta G = \Delta G_{\text{initial}} - \Delta G_{\text{final}}, \]  

(2-2)

where, \( \Delta G \) = the standard state free energy (kJ/mole),  
\( \Delta G_{\text{initial}} \) = the initial standard state free energy (kJ/mole), and  
\( \Delta G_{\text{final}} \) = the final standard state free energy (kJ/mole).

The free energy for the general reaction, \( aA + bB = cC + dD \), is defined in Equation 2-3:

\[ \Delta G = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}, \]  

(2-3)

where, \( \Delta G_{\text{products}} \) = the free energy of the products of a reaction (kJ/mole) and  
\( \Delta G_{\text{reactants}} \) = the free energy of the reactants in a reaction (kJ/mole).

Based upon the previously mentioned reaction, the free energy can be expressed as follows:

\[ \Delta G = \Delta G^0_{\text{products-reactants}} + cRT \ln a_C + dRT \ln a_D - aRT \ln a_A - bRT \ln a_B, \]  

(2-4)

Equation 2-4 can be rearranged as shown in Equation 2-5 to give:

\[ \Delta G = \Delta G^0 + RT \ln \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}, \]  

(2-5)

\( Q \), the reaction quotient, is defined in Equation 2-6:
\[ Q = \frac{(a_c)^c (a_o)^d}{(a_A)^a (a_o)^b}, \quad (2-6) \]

The reaction quotient is equal to the thermodynamic equilibrium constant, \( K \), when the free energy (\( \Delta G \)) is zero. Therefore, Equation 2-5 reduces to (Equation 2-7):

\[ \Delta G_f^0 = -RT \ln K, \quad (2-7) \]

Equation 2-5 can be used to determine whether a particular reaction is thermodynamically favored. If \( \Delta G \) is positive, then the reaction will not proceed spontaneously. Thermodynamics is not the only factor that determines whether a reaction will occur. Kinetics is important because thermodynamics only predicts whether a reaction will take place, but kinetics determines how long it will take to reach a state of equilibrium [7].

Equation 2-7 describes the standard state free energy of reaction. This term can be divided into the free energy of formation due to chemical interactions and the free energy of formation due to coulombic interactions as illustrated in Equation 2-8:
\[ \Delta G_{\text{tot}}^0 = \Delta G_{\text{chem}}^0 + \Delta G_{\text{coul}}^0 \]  

(2-8)

where, \( \Delta G_{\text{tot}}^0 \) = the free energy of reaction (kJ/mole),  
\( \Delta G_{\text{chem}}^0 \) = the intrinsic free energy (kJ/mole), and  
\( \Delta G_{\text{coul}}^0 \) = the Coulombic term (kJ/mole).

Generally, the free energy due to chemical reactions, \( \Delta G_{\text{chem}}^0 \), is associated with covalent bond making and breaking. The Coulombic term, is defined below in Equation 2-9, it represents the electrostatic work done while moving ions through the interfacial potential gradient [8]:

\[ \Delta G_{\text{coul}}^0 = \Delta Z F \Psi \]  

(2-9)

where, \( \Delta Z \) = the change in charge of surface species,  
\( F \) = the Faraday constant (96,485 C/mole), and  
\( \Psi \) = the surface potential (V).

2.1.1.2 THE EFFECTS OF TEMPERATURE, IONIC STRENGTH, & PRESSURE ON CHEMICAL EQUILIBRIUM

Three parameters that affect a system's equilibrium are temperature, ionic strength (IS), and pressure. One example of the affects of temperature is the manner in which the equilibrium constant varies with temperature is shown in Equation 2-10, where the change in enthalpy is assumed independent of temperature:
\[
\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),
\] (2-10)

where, \( K_1 \) = the equilibrium constant at \( T_1 \),
\( K_2 \) = the equilibrium constant at \( T_2 \),
\( T_1 \) = the first temperature (usually 298 K),
\( T_2 \) = the second temperature (K),
\( \Delta H^0 \) = the change in enthalpy (kJ/mole), and
\( R \) = the universal gas constant (8.314 J/mole-K).

The ionic strength of an aqueous solution is defined below in Equation 2-11:

\[
IS = \frac{1}{2} \sum_i C_i z_i^2,
\] (2-11)

where, \( C_i \) = the concentration of species \( i \) in solution (mole/liter) and
\( z_i \) = the charge on species \( i \) in solution.

This parameter directly affects the activity of species in aqueous solution where the
activity is defined in terms of concentration rather than mole fraction in Equation 2-12:

\[
a_i = \gamma_i C_i,
\] (2-12)

where, \( a_i \) = the activity of species \( i \) in solution (mole/liter) and
\( \gamma_i \) = the activity coefficient of species \( i \) in solution.

The activity coefficient is used to determine the degree to which the concentration of
species \( i \) deviates from its activity due to ionic chemical species in solution. Several
equations have been developed to predict activity coefficients. Table 2-1 lists four
commonly used equations.
Table 2-1. Equations Used to Predict Activity Coefficients Based on Ionic Strength and Other Parameters [7].

<table>
<thead>
<tr>
<th>Equation Name</th>
<th>Equation</th>
<th>Ionic Strength Limit</th>
</tr>
</thead>
</table>
| DeBye-Hückel                   | \(
\log \gamma = A z^2 \sqrt{IS} \\
1 + Ba \sqrt{IS}
\) | IS \(\leq 0.01\) M |
| Extended Debye- Hückel         | \(
\log \gamma = - A z^2 \sqrt{IS} \\
1 + Ba \sqrt{IS}
\) | IS \(\leq 0.1\) M |
| Gunstelberg                    | \(
\log \gamma = - A z^2 \sqrt{IS} \\
1 + \sqrt{IS}
\) | IS \(\leq 0.1\) M |
| Davies                         | \(
\log \gamma = - A z^2 \sqrt{IS} - 0.31 \\
1 + \sqrt{IS}
\) | IS \(\leq 0.5\) M |
| Pitzer Specific Ion Interactions | \(\log \gamma = f(\text{ion interactions})\) | IS \(\sim 30\) M |

All of the equations listed in Table 2-1 use another parameter, A. This variable is defined in Equation 2-13:

\[
A = 1.823 \cdot \frac{10^6}{(DT)^{1/2}}, \quad (2-13)
\]

where, \(D\) = the dielectric constant of the solvent and \(T\) = the absolute temperature (K).

The Extended Debye-Hückel equation uses two additional parameters, a, the hydrated ion size, and B, which is defined below in Equation 2-14:

\[
B = \frac{50.3}{(DT)^{1/2}}, \quad (2-14)
\]

The third parameter affecting chemical equilibria, pressure, generally has a smaller affect than does temperature or ionic strength. One example is the ion product of water. This
constant increases by a factor of more than two when the pressure increases from one atmosphere to 1000 atmospheres.

2.1.2 KINETICS

The kinetic rate constant determines how quickly a reaction will advance toward equilibrium. Equations 2-15 through 2-17 define the characteristic forward rate constant, characteristic reverse rate constant, forward rate constant, and reverse rate constant:

\[ A + B \leftrightarrow C + D \]  \hspace{1cm} (2-15)

\[ R_f = k_f (A)(B) \]  \hspace{1cm} (2-16)

\[ R_r = k_r (C)(D) \]  \hspace{1cm} (2-17)

where, \( k_f \) = the characteristic forward rate constant (M\(^{-1}\)sec\(^{-1}\)),
\( k_r \) = the characteristic reverse rate constant (M\(^{-1}\)sec\(^{-1}\)),
\( R_f \) = the forward rate constant (M/sec), and
\( R_r \) = the reverse rate constant (M/sec).

When a system is at equilibrium, the forward rate constant is equal to the reverse rate constant and the thermodynamic equilibrium constant, \( K \), is generally given by the ratio of the rate constants (Equation 2-18):

\[ K = \frac{k_f}{k_r} = \frac{(C)(D)}{(A)(B)} \]  \hspace{1cm} (2-18)
2.2 PRECIPITATION & DISSOLUTION

The precipitation and dissolution of chemical species in natural waters and water treatment processes regulate the concentration of dissolved species in aqueous solutions. A solution is defined as saturated with respect to a particular solid phase when it can not dissolve additional solid. If additional solid material is added to the system, the solution will become supersaturated and solid material will precipitate rather than dissolve. Conversely, an undersaturated solution will continue to dissolve any solid added to the system until the solution has reached saturation. These definitions are not absolute because slightly supersaturated solutions can remain stable for indefinite periods of time. The saturation of a solution with respect to a solid material depends on how soluble it is. For the generic reaction (Equation 2-19) listed below, the intrinsic solubility of a solid is illustrated in Equation 2-20:

\[ A_xB_y(s) \leftrightarrow A_xB_y(aq) \leftrightarrow zA^{x+} + yB^{y-}, \quad (2-19) \]

\[ S = \frac{[A_xB_y(aq)]}{[A_xB_y(s)]}, \quad (2-20) \]

where, \( S \) = the intrinsic solubility (M) and \( [\cdot] \) = the activity of the constituents inside the braces (M).

The activity of a pure solid is unity; therefore, Equation 2-20 simplifies to the expression in Equation 2-21:

\[ S = [A_xB_y(aq)], \quad (2-21) \]
The ion activity product (IAP) is equal to the intrinsic solubility divided by the thermodynamic equilibrium constant as show in Equation 2-22:

$$IAP = \frac{S}{K} = \{A^{\text{y}+}\}^x \{B^{\text{z}−}\}^y,$$  \hspace{1cm} (2-22)

The solubility product, $K_{sp}$, is different from IAP in that $K_{sp}$ is equal to the product of the activities of the anion and cation as displayed in Equation 2-23:

$$K_{sp} = \{A^{\text{y}+}\} \{B^{\text{z}−}\},$$  \hspace{1cm} (2-23)

The saturation index (SI) is defined as the ratio of the IAP to the $K_{sp}$. As shown in Equation 2-24, the SI is equal to zero when the ion product and solubility product are equivalent [9]:

$$SI = \log\left(\frac{IAP}{K_{sp}}\right)$$  \hspace{1cm} (2-24)

The solution is supersaturated if $SI > 0$, undersaturated if $SI < 0$, and at equilibrium if $SI = 0$. 
2.2.2 COMPLEX FORMATION

Metal ions in solution will form complexes in an attempt to improve their molecular stability. The formation of complexes may result from the development of covalent bonds between a metal ion and a ligand, which is the anion that bonds with the metal to form a coordination compound. Often particles contain surface groups that behave as ligands as demonstrated in Equation 2-25:

\[ \equiv S - OH + M^{z+} \leftrightarrow S - OM^{(z-1)+} \]  \hspace{1cm} (2-25)

The \( S-OH \) terms represents a solid with a hydroxyl group on the surface. The \( OH^- \) ion is capable of complexing metal ions in solution. Because of the metal ion's strong affinity for surface coordination sites, the concentration of metals on the solid is much higher than in solution.

In addition to the formation of monodentate surface complexes, as was shown in Equation 2-25, bidentate complexes can form, this is illustrated in Equation 2-26:

\[ \overset{\text{S-OH}}{\text{S-OH}} + \text{Me}^{2+} \leftrightarrow \overset{\text{S-O Me}}{\text{S-O Me}} + 2\text{H}^+ \]  \hspace{1cm} (2-26)

Figure 2-1 shows two kinds of surface complexes, inner-sphere and outer-sphere. Inner-sphere complexes have a stronger attraction primarily due to covalent bonding. Outer-
sphere complexes are metal ions that are not as closely bound to the surface because of their waters of hydration. Because metal ions compete with $\text{H}^+$ ions, complex formation is competitive. The primary surface complexation mechanism is ligand exchange occurring between the ligand and hydroxyl ion; which is also a competitive process.

![Diagram of surface complexes](image)

**Figure 2.1. Surface Complex Formation Involving Inner-Sphere and Outer-Sphere Complexes.**

More than one ligand may associate with a metal complex simultaneously because the surface ligand can only occupy a portion of the metal’s coordination sphere. There are two types of ternary complexes, type A and type B as shown below in Equations 2-27 and 2-28, respectively:

\[
S - OH + M^{2+} + L^- \leftrightarrow S - OM - L + H^+ \quad (2-27)
\]
\[ S - OH + L^- + M^{2+} \leftrightarrow S - L - M^{2+} + OH^- \]  \hspace{1cm} (2-28)

### 2.2.1 CARBONATE EQUILIBRIUM

The solubility of carbonate species is very important in natural water systems. Metal ions tend to form more stable complexes with carbonates than hydroxides, which is why carbonates control the solubility of metals. Calcium, magnesium, and other metals in solution are dependent on the carbonate concentration. A general expression for carbonate equilibrium in a system open to the atmosphere is illustrated in Equation 2-29:

\[ CaCO_3(s) + CO_2(g) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \]  \hspace{1cm} (2-29)

Equations 2-30 through 2-34 represent the equilibrium relationships required for carbonate calculations:

\[
\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_1 \hspace{1cm} (2-30)
\]

\[
\frac{[H^+][CO_3^{2-}]}{[H_2CO_3]} = K_2 \hspace{1cm} (2-31)
\]

\[
\frac{[H_2CO_3]}{P_{CO_2}} = K_H \hspace{1cm} (2-32)
\]

\[
[H^+][OH^-] = K_w \hspace{1cm} (2-33)
\]

\[
[Ca^{2+}][CO_3^{2-}] = K_sp \hspace{1cm} (2-34)
\]
All of these equations can be substituted into the charge balance shown in Equation 2-35 below:

$$2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$  
(2-35)

Figure 2-2 is a plot displaying the equilibrium of calcium carbonate solid in the presence of pure water for an open system. Equations 2-30 through 2-34 were used to calculate the values in the plot. The partial pressure of CO₂ in the atmosphere is assumed to be 10⁻³.⁵ atmospheres.

**Figure 2-2.** Plot of CaCO₃(s) in Equilibrium with Aqueous Solution for an Open System. T = 25°C, P_{CO₂} = 10⁻³.⁵, pK₁ = 6.3, pK₂ = 10.25, pK₃ = 1.5, and pK₇ = 14.
Figure 2-2 is representative of conditions generally found in fresh water systems. Typically, the pH range between 5 and 8 are of most interest. In that range, the dominant species is bicarbonate; carbonate does not play a significant role until the pH exceeds 10. Figure 2-3 is quite different than Figure 2-2 because the CO$_2$ (g) is not allowed to escape the aqueous solution. The HCO$_3^-$ concentration is still of greatest importance although its concentration levels off at approximately $10^{-2}$ M. Also, the H$_2$CO$_3$ concentration is no longer a constant value in a closed system. In fact, the carbonic acid concentration decreases once the pH drops below 6.
Figure 2-3. Plot of CaCO₃(s) in Equilibrium with Aqueous Solution for a Closed System. T = 25°C, TOTCO₃ = 7 x 10⁻³ M, pK₁ = 6.3, pK₂ = 10.25, pK₃ = 1.5, and pK₄ = 14.

2.2.3 PHOSPHATE EQUILIBRIUM

Both industrial processes and biomineralization processes involve the precipitation and dissolution of phosphate salts. Metal phosphates may contain considerable lattice defects and impurities complicating solubility determinations. Calcium phosphates have been studied more than the other alkaline earth phosphates. They naturally occur in many classes of rock. Due to the reuse of water, calcium phosphate scale deposits are commonly found in cooling towers and boilers.
Hydroxyapatite (HAP) is only formed in solutions that have been supersaturated for a long time because it is the most thermodynamically stable calcium phosphate [10]. Table 2-2 lists HAP and other less stable phases.

**Table 2-2. Calcium Phosphate Salts Precipitated in Supersaturated Solutions. [11]**

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Solubility Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite (HAP)</td>
<td>Ca$_5$(PO$_4$)$_3$OH</td>
<td>4.7 x 10$^{-39}$</td>
</tr>
<tr>
<td>Tricalcium Phosphate (TCP)</td>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>1.20 x 10$^{-39}$</td>
</tr>
<tr>
<td>Octacalcium Phosphate (OCP)</td>
<td>Ca$_4$H(PO$_4$)$_3$ · 2 · 5 H$_2$O</td>
<td>1.25 x 10$^{-37}$</td>
</tr>
<tr>
<td>Dicalcium Phosphate Dihydrate (DCPD)</td>
<td>CaHPO$_4$ · 2 H$_2$O</td>
<td>2.49 x 10$^{-7}$</td>
</tr>
</tbody>
</table>

Equations 2-36 through 2-42 illustrate the protonation of phosphoric acid and the formation of calcium phosphate salts:

\[
H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad (2-36)
\]

\[
H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad (2-37)
\]

\[
HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad (2-38)
\]

\[
CaH_2PO_4^+ \rightleftharpoons Ca^+ + H_2PO_4^- \quad (2-39)
\]

\[
CaHPO_4^- \rightleftharpoons Ca^+ + HPO_4^{2-} \quad (2-40)
\]

\[
CaPO_4^{2-} \rightleftharpoons Ca^+ + PO_4^{3-} \quad (2-41)
\]

\[
CaOH^- \rightleftharpoons Ca^+ + OH^- \quad (2-42)
\]
When calcium phosphates initially precipitate from solution, an amorphous phase forms. Figure 2-4 displays phosphoric acid in equilibrium with pure water at different pH values.

![Plot of Phosphate in Equilibrium with Aqueous Solution](image)

**Figure 2-4.** Plot of Phosphate in Equilibrium with Aqueous Solution. $T = 25^\circ C$, TOTP$_4$ = $10^{-2}$ M, pK$_{a1}$ = 2.1, pK$_{a2}$ = 7.2, pK$_{a3}$ = 12.3, and pK$_{w}$ = 14.

The pH range of most interest for natural water systems ranges between pH 5 and 8. In this range, H$_2$PO$_4^-$ and HPO$_4^{2-}$ dominate. The equilibrium reactions of phosphonates and calcium resemble those of phosphoric acid and calcium.
2.2.4 NUCLEATION

Before calcium carbonate or calcium phosphonate can precipitate, the solution must become supersaturated. Precipitation develops in three stages: 1) nucleation (development of critical cluster), 2) crystal growth (crystallites formed), and 3) aging or ripening (formation of larger crystals). Figure 2-5 illustrates the process that a supersaturated solution must undergo before a crystal will form.

Nucleation begins when a fine particle spontaneously develops in a supersaturated solution (a small foreign particle may also serve as a nucleus). If two solutions are mixed together to produce a supersaturated solution, the time from when they are initially mixed until a precipitate is visibly detected is referred to as the induction time. The induction time is an exponential function of the initial concentration of precipitated species in solution.
Figure 2-5. Nucleation and Crystal Growth Processes[8]

Tomson et al. [12], [13] have developed a semi-empirical model to for the determination of the affect that inhibitors have on nucleation time (Equation 2-43):
\[ \log(t_{\text{ind}}^{\text{inh}}) = \log(t_{\text{ind}}^0) + b_{\text{inh}} C_{\text{inh}} \]  

(2-43)

where, \( t_{\text{ind}}^{\text{inh}} \) = the induction time with the inhibitor,  
\( t_{\text{ind}}^0 \) = the induction time without the inhibitor,  
\( b_{\text{inh}} \) = the inhibitor effectiveness term, and  
\( C_{\text{inh}} \) = the concentration of inhibitor added.

Initially, microcrystalline precipitates develop and then form well-defined crystals under slightly supersaturated conditions. Once the degree of supersaturation has reached a critical supersaturation point, the particles become smaller and less perfect. The rate of nucleation will continue at a constant rate until the induction period has ended.

2.2.4.1 HOMOGENEOUS NUCLEATION

Homogenous nucleation occurs when nuclei are formed from species precipitated out of solution. After the energy barrier has been surpassed, stable nuclei develop. The free energy of formation for a nucleus is defined in Equation 2-44:

\[ \Delta G_j = \Delta G_{\text{bulk}} + \Delta G_{\text{surf}} \]  

(2-44)

where, \( \Delta G_j \) = the free energy of formation of a nucleus (kJ/mole),  
\( \Delta G_{\text{bulk}} \) = the free energy gained from making bonds (kJ/mole), and  
\( \Delta G_{\text{surf}} \) = the free energy of work required to create a surface (kJ/mole).

The bulk free energy is defined below in Equation 2-45:
\[ \Delta G_{\text{bulk}} = -jkT \ln S = -jkT \ln \frac{a}{a_0} \] (2-45)

where, \( j \) = the number of molecular units in the nucleus \((j=4\pi r^3/3V; V = \text{the molecular volume (cm}^3\text{)}\) and \( r = \text{the nucleus radius (cm)}\),
\( k = \text{the Boltzman constant (J/K)}\),
\( T = \text{the absolute temperature (K)}\),
\( S = \text{the saturation ratio}\),
\( a = \text{the actual concentration of the solute, and} \)
\( a_0 = \text{the equilibrium concentration of the solute.} \)

Interfacial energy determines the thermodynamics and kinetics of nucleation. Surface free energy is defined in terms of interfacial energy, \( \gamma \) \((\text{mJ/m}^2)\), (Equation 2-546):

\[ \Delta G_{\text{surf}} = 4\pi r^2 \gamma \] (2-46)

Therefore, the free of energy of nucleus formation can be expanded as shown in Equation 2-47:

\[ \Delta G_j = -\frac{4\pi r^3}{3V} kT \ln S + 4\pi r^2 \gamma \] (2-47)

Figure 2-6 illustrates the free energy of formation of nuclei is higher for the more stable phase, curve A, and lower for the less stable phase, curve B.
Figure 2-6. A Schematic Plot of the Free Energy of Formation of Clusters from Solution as a Function of Size [8].

The rate at which nuclei form, $J$, can be expressed according to traditional rate theory (Equation 2-48):

$$J = \bar{A} \exp \left(-\frac{\Delta G^*}{kT}\right)$$

(2-48)

where, $\bar{A}$ = a factor related to the efficiency of collisions between molecules.

The rate of nucleation is governed by the interfacial energy, degree of supersaturation, efficiency and frequency of collisions, and temperature.

Interfacial energy is defined differently for homogeneous nucleation (Equation 2-49) than for heterogeneous nucleation (Equation 2-49) which is discussed in the next section.

$$\Delta G_{\text{surf}} = \bar{\gamma}_{\text{cw}} A$$

(2-48)
\[ \Delta G_{\text{int, erf}} = \tilde{\gamma}_{cw} A_{cw} + (\tilde{\gamma}_{cs} - \tilde{\gamma}_{sw}) A_{cs} \]  

(2-49)

where, \( \tilde{\gamma}_{cw} \) = the cluster-water interfacial energy (mJ/m²),
\( \tilde{\gamma}_{cs} \) = the cluster-substrate interfacial energy (mJ/m²), and
\( \tilde{\gamma}_{sw} \) = the substrate-water interfacial energy (mJ/m²).

The clusters will spread themselves across the substrate if their attachment to each other is strong, \( \tilde{\gamma}_{sw} = \tilde{\gamma}_{cw} \). If \( \tilde{\gamma}_{sw} \gg \tilde{\gamma}_{cw} \), the precipitate will probably form a continuous coating on the substrate grain. Normally, homogeneous nucleation will not occur unless the degree of supersaturation is high. Under high supersaturation conditions, the initially formed crystallites will be extremely small and amorphous.

2.2.4.2 HETEROGENEOUS NUCLEATION

Heterogeneous nucleation is very important in natural systems because suspended particles are common place [7]. When foreign particles initiate the nucleation process, it is referred to as heterogeneous and the initial concentration of the species in solution no longer controls the rate of nucleation. A precipitation event may begin as a homogeneous mechanism and then transition into a heterogeneous process if the nuclei generated are used to form new solid material. Solid particles are only formed in supersaturated material because the formation of organized crystal lattice nuclei, from random molecules in solution consumes energy. Because of this energy requirement, less energy is used during heterogeneous precipitation because foreign matter already present in solution can act as nuclei [14]. Figure 2-7 demonstrates that heterogeneous nucleation has a significantly smaller energy barrier to overcome than does homogeneous nucleation.
The Ostwald Step Rule states that the least stable solid will precipitate first because the nucleation rate is larger for the less stable phases. The more soluble phase has a lower cluster-water interfacial tension.

![Diagram](image)

**Figure 2-7. Schematic Representation of the Ability of Solid Substrate to Catalyze the Nucleation Process [8].**

2.2.5 CRYSTAL GROWTH

The mechanisms of crystal growth are not well known but they are described as occurring in two phases, diffusion of ions from bulk solution to the crystal surface and reactions at the solid surface. The Burton, Cabrera, and Frank (BCF) theory states that on the surface of a solid, crystals will adsorb onto kinks and screw dislocations and then become incorporated into the crystal lattice. As crystals deposit themselves onto the nuclei surface, they continue to grow according to Equation 2-50:
\[ \frac{dC}{dt} = -kS(C - C^*)^n, \]  
(2-50)

where, \( C \) = the concentration of the limiting ion in solution (moles/liter), 
\( t \) = the time (s), 
\( k \) = the rate constant \( \left( \frac{mg}{liter \ mole} \left( \frac{mole}{liter} \right)^n \frac{1}{s} \right) \), 
\( S \) = the surface area available for precipitation (mg/liter), and 
\( C^* \) = the saturation concentration (moles/liter).

If the diffusion rate of the ions to the crystal surface controls the rate of crystal growth, \( n \) will equal one; but if the reaction at the crystal surface governs the crystal growth rate, \( n \) will be equal to a different value. The rate constant is dependent on the conditions of the solution and the nature of the solid material that is precipitated.

2.2.5.1 CALCIUM CARBONATE CRYSTAL GROWTH

Several authors have defined the growth rate of CaCO\(_3\) (calcite) as shown in Equation 2-51:

\[ \frac{d[CaCO_3]}{dt} = k_{-1}[Ca^{2+}][CO_3^{2-}] + k_{-1}[Ca^{2+}][HCO_3^-] + k_{-2}[Ca^{2+}][HCO_3^-]^2, \]  
(2-51)

Calcite crystal growth is generally caused by heterogeneous nucleation on particle surfaces in freshwater and processes involving calcareous organisms in seawater.
2.2.5.2 GROWTH INHIBITORS

Crystal growth can be retarded or prevented when adsorbed molecules block the deposition of lattice ions. It is believed that the modification of the morphology of crystal phases inhibits the crystallization process [15]. Trace amounts of organic matter and phosphates can poison the crystal surface of calcite. It has been suggested that growth is prohibited because the adsorbing ions inhibit the creation of steps on the surface by adsorbing to active growth sites. Nygren [16] has proposed that phosphonate inhibition occurs when kinks along the steps are blocked. According to Suzuki [17], "The phosphorous-containing anions show an intense inhibition for the crystallization of calcium carbonate. The effect of polyphosphates on the retardation of crystallization is much larger than that of orthophosphate and the aminopolyphosphonates such as ethylenediaminetetra(methylene phosphonic acid) and hydroxyethylidene-1,1-diphosphonic acid quench the crystal growth completely at very low concentrations". In addition to the prevention of crystal growth, some of these "inhibitors" may prevent dissolution as well. It seems that the attachment of ions at kink sites in mononuclear steps may be responsible for the precipitation and dissolution of ionic solids like calcite. He [18] et al. has produced an inhibitor model which predicts the inhibitor efficiency for barium sulfate scale control by incorporating experimental nucleation and inhibition data (Equation 2-52):
\[ C_{\text{inh}} = \frac{[\log(t_{\text{inh}}) - \log(t_0)]}{b}, \]  

(2-52)

where, \( C_{\text{inh}} \) = the effective inhibitor concentration (mg/L),
\( t_{\text{inh}} \) = the induction period with inhibitor,
\( t_0 \) = the induction period without the inhibitor, and
\( b \) = the inhibitor efficiency (L/mg).

2.2.6 SURFACE PRECIPITATION

As ions precipitate and adsorb onto mineral surfaces, they may form a complex with the surface functional groups. Surface precipitation may be described as a process bridging the gap between complex formation and bulk solution precipitation. Initially, when the adsorbate concentration is low, the surface complexation process dominates. As the concentration of adsorbate increases, so does the surface complex and surface precipitate concentration until the surface sites become saturated. At this stage, surface precipitation is the primary mechanism occurring.

2.2.7 AGING OR RIPENING

When solid material is first formed, it may not be the most thermodynamically stable form. This material is referred to as amorphous rather than crystalline. With time, the structure may change to a more stable phase. This process is referred to as aging. Ripening occurs as the crystal’s size increases with time. Small particles have such high surface energies that the solution concentration in equilibrium with them is higher than for large particles. Larger crystalline material will continue to grow causing the solution concentration to decrease and smaller particles to dissolve back into solution. Figure 2-8 is an example of phosphate crystal maturing from an amorphous phase to a more stable
crystalline phase. Notice the initial induction period before nucleation takes place followed by phase transformation and finally the development of a stable crystalline phase.

![Diagram showing the stages of precipitation kinetics]

**Figure 2-8. Idealized Precipitation Kinetics[14]**

2.3 SOLID/SOLUTION INTERFACE

Most reactions take place at physical discontinuities, such as the interface between solid material and aqueous solutions. Table 2-3 lists some of the forces that act on molecules at the surface of substrate. Chemical and coulombic forces create the strongest bonds.
Table 2-3. Summary of Primary Forces Affecting Solid/Solution Interfaces.

<table>
<thead>
<tr>
<th>Interfacial Force</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Extend over short distances, i.e. covalent bonding</td>
</tr>
<tr>
<td>Electrostatic or Coulombic</td>
<td>Stretches out over longer distances, caused by electrostatic attraction between two point charges</td>
</tr>
<tr>
<td>Orientation Energy</td>
<td>Other electric force caused by dipole-dipole interactions</td>
</tr>
<tr>
<td>Dispersion or London-van der Waals</td>
<td>Another electric force due to synchronized dipoles that attract each other</td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>Hydrogen ion allows two electron pair clouds to bind two polar molecules</td>
</tr>
</tbody>
</table>

2.3.1 ADSORPTION

Adsorption is the transition of a chemical from the solution phase to the solid phase; this process is controlled by the physical/chemical properties of those phases. The degree of adsorption is influenced by several factors including temperature, pressure, ionic strength, and available surface area. Physical adsorption is a reversible process that tends to be governed by London-van der Walls forces and occurs in low or moderate temperature ranges. Conversely, chemical adsorption is caused by chemical interactions. Stumm [19] categorizes these interactions into three groups (Table 2-4). Intermolecular interactions are very important for adsorption in water, sediment, and soils. The manner in which a solute interacts with a solid surface is determined by the reactions listed in the table.
Table 2-4. Intermolecular Interactions at the Solid-water Interface [19]

<table>
<thead>
<tr>
<th>Chemical Reactions with Surfaces</th>
<th>Surface Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface Complexation</td>
</tr>
<tr>
<td></td>
<td>Surface Ligand Exchange</td>
</tr>
<tr>
<td></td>
<td>Hydrogen Bond Formation</td>
</tr>
<tr>
<td>Electrical Interactions at Surfaces</td>
<td>Electrostatic Interactions</td>
</tr>
<tr>
<td></td>
<td>Polarization Interactions</td>
</tr>
<tr>
<td>Interactions with Solvent</td>
<td>Hydrophobic Expulsion</td>
</tr>
</tbody>
</table>

Adsorption isotherms are used to describe the relationship between the amount of chemical associated with the solid and the amount in solution at a constant temperature. The two most commonly used isotherms are the Langmuir and Freundlich. The Langmuir adsorption isotherm is based on assumed monolayer coverage; the adsorption energy for each adsorption site is the same for every adsorbate. Figure 2-9 shows that only one adsorbate may attach itself to an adsorption site (symbolized by the triangle’s apex) as more adsorbates are diffusing through the bulk layer of solution to the mineral surface.

![Figure 2-9. Langmuir Adsorption Process Illustrating Monolayer Coverage](image)
Once all of the adsorption sites have been filled, additional sorption cannot take place.

Equation 2-53 represents the mathematical expression of this isotherm [20]:

\[ q = q_{\text{max}} \frac{K_{\text{ads}} C}{1 + K_{\text{ads}} C}, \]  

(2-53)

where, \( q \) = the amount adsorbed on the solid (mg/kg), 
\( K_{\text{ads}} \) = the adsorption coefficient (L/mg), 
\( q_{\text{max}} \) = the maximum amount of adsorbent on the solid (mg/kg) and, 
\( C \) = the amount in solution at equilibrium (mg/L).

Equation 2-54 is a rearrangement of Equation 2-53, producing a linear plot that can be used to obtain the values of \( q_{\text{max}} \) and \( K_{\text{ads}} \). Phosphate adsorption by sedimentary soil is typically represented with a Langmuir isotherm:

\[ \frac{C}{q} = \frac{1}{q_{\text{max}} K_{\text{ads}}} + \frac{C}{q_{\text{max}}}, \]  

(2-54)

The Freundlich isotherm is an empirical equation that also describes adsorption (Equation 2-55). The empirical constant, \( n \), is generally less than one. It models data from heterogeneous soils quite well [19]:

\[ q = K_f C^n, \]  

(2-55)

where, \( K_f \) = the Freundlich adsorption coefficient \( \left( \frac{mg}{kg} \left( \frac{L}{mg} \right)^n \right) \) and 
\( n \) = the empirical dimensionless constant.
Taking the logarithm of both sides linearizes the previous equation as shown in Equation 2-56:

\[ \log q = \log K_f + n \log C. \]  \hspace{1cm} (2-56)

These two isotherms are compared by vanLoon [21] in the following manner: "The Freundlich relation differs from that of the Langmuir in that not all sites on the surface are considered equal but rather that adsorption becomes progressively more difficult as more and more adsorbate accumulates. Furthermore, it is assumed that once the surface is covered, additional adsorbed species can still be accommodated." Both of these equations have been used to model the transport of scale inhibitors in rock formation [22].

A linear expression for the partitioning of a chemical between the solid and solution phase is described by the distribution coefficient, \( K_d \) (L/kg), shown in Equation 2-57 [23]:

\[ K_d = \frac{C_s}{C_w}, \]  \hspace{1cm} (2-57)

where, \( C_s \) = the total concentration of adsorbate on the solid (mg/kg) and \( C_w \) = the total concentration of adsorbate in the aqueous phase (mg/L).

The value of \( K_d \) is dependent upon the properties of the solid material, solution, and solute itself.
2.3.2 SURFACE CHARGE & THE ELECTRIC DOUBLE LAYER

Surface charge is very important because it determines whether particles will aggregate, affects the fate of contaminates associated with particulate matter, and governs the degree to which dissolved chemicals will adsorb to solid material. Many oxides, carbonates, and silicates possess surfaces charge which is greatly affected by pH. The point of zero charge is the pH at which the electric charge on the solid surface is equal to zero. Surface charge can develop in one of three ways: 1) chemical reactions at the solid surface, 2) lattice imperfections, and 3) adsorption of hydrophobic chemicals. Surface charge usually develops when the solid surface is hydrated, protonated, or deprotonated [24]. Proton transfer reactions and surface complexation between metal ions and ligands create a net surface charge on hydrous oxide surfaces. Equation 2-58 displays the various contributions of charge on a surface:

\[
\sigma_p = \sigma_o + \sigma_H + \sigma_{IS} + \sigma_{OS}, \tag{2-58}
\]

where, \( \sigma_p \) = the total net surface charge (C/m\(^2\)),
\( \sigma_o \) = the permanent structural charge (C/m\(^2\)),
\( \sigma_H \) = the net proton charge (C/m\(^2\)),
\( \sigma_{IS} \) = the inner-sphere complex charge (C/m\(^2\)), and
\( \sigma_{OS} \) = the outer-sphere complex charge (C/m\(^2\)).

Permanent structural charge may be caused by substituted cations in the crystal lattice while net proton charge is due to the association of \( \text{H}^+ \) ions and \( \text{OH}^- \) ions to the solid surface. Inner-sphere and outer-sphere complex charges are caused by the complexation
of ligands with metal ions in the crystal lattice (inner-sphere complex) or ligands associated with metal ions but separated by water molecules (out-sphere complex).

The Electric Double Layer (EDL) theory predicts the bulk concentration required for high adsorption density as well as surface charge reversal. When a particle equilibrates with water a charged surface develops at the interface because of the hydrophobicity of its ions. If positively charged functional groups are less hydrophobic than the negatively charged ones, the surface will have a net positive charge and attract dissolved negative ions from solution. The layer of negatively charged ions surrounding the solid particle may attract another layer of positively charged ions as illustrated in Figure 2-10.

The Gouy-Chapman theory states that the surface charge density, \( \sigma_p \), is a function of the surface potential, \( \psi_o \), as shown in Equation 2-59:

\[
\sigma_p = \left(8RT\varepsilon\varepsilon_0C \times 10^1\right)^{1/2}\sinh\left(Z\psi_oF/2RT\right)
\]  

(2-59)

where, \( R \) = the gas constant (8.314 J/mole K),
\( T \) = the absolute temperature (K),
\( \varepsilon \) = the relative dielectric constant of water (78.5 @ 25°C),
\( \varepsilon_0 \) = the permittivity of free space (8.854 x 10^{-12} C^2/J m),
\( C \) = the concentration (M), and
\( Z \) = the ionic charge.

Surface charge can have a large impact on ionic reactions and mechanisms especially at low ionic strengths. At the total dissolved solids values of actual oil field brines the double layer thickness is generally less than an ionic radius and therefore the
overwhelming impact of surface charge is greatly reduced. In addition, adsorption of phosphate and phosphonates, studied in this work and work performed by the Rice University Brine Chemistry research group, has been shown [17] to take place by adsorbing essentially aqueous neutral species such as $\text{CaPO}_4^-$ or Ca-Phn (see Chapter 4 for details). Therefore, the impact of surface charge may not be as important in practice, as otherwise expected from conventional double layer theory. Yet, testing of such assumptions using electrophoresis is recommended.

![Figure 2-10. Illustration of The Electric Double Layer Theory.](image-url)
2.3.2.1 POINT OF ZERO CHARGE

The pH value when the surface charge is zero is referred to as the point of zero charge (pzc) or pH_{pzc}. If the surface charge is governed by protonation and deprotonation of the surface, the pH_{pzc} is also the pH_{pzc or pzc} or pH point of zero net proton charge. The point of zero charge for an oxide can be determined from the cationic charge and radius of the central ion. Changes in the pzc are caused by changes in hydration, cleavage, and crystallinity. The pzc of mineral salts are dependent on pH and the activity of potential determining ions.

2.3.3 HYDROUS OXIDE SURFACES

Oxides, abundant compounds in natural waters, become covered with surface hydroxyl groups in the presence of water. The functional groups on hydroxides are similar to those found in soluble ligands. Table 2-5 lists important surface complex formation equilibria. These surface ligands are capable of complex many different species.

According to Dzombak and Morel [25], there are four characteristic criteria for all surface complexation models:

1. Adsorption occurs at specific surface coordination sites
2. Adsorption reactions are described by mass law equations
3. Surface charge is a result of surface complex formation
4. Adsorption surface charge effect accounted for by applying a correction factor derived from the electric double layer theory to the mass law constants for surface reactions.

**Table 2-5. Surface Complex Formation Equilibria (Adapted [8]).**

<table>
<thead>
<tr>
<th>Acid-Base Equilibria</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv S-OH + H^+ \leftrightarrow \equiv S-OH_2^+$</td>
<td></td>
</tr>
<tr>
<td>$\equiv S-OH + OH^- \leftrightarrow \equiv S-O^- + H_2O$</td>
<td></td>
</tr>
</tbody>
</table>

**Metal Binding**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv S-OH + M^{2+} \leftrightarrow \equiv S-OM^{(z-1)+} + H^+$</td>
<td></td>
</tr>
<tr>
<td>2 $\equiv S-OH + M^{2+} \leftrightarrow (S-O)_2M^{(z-2)+} + 2H^+$</td>
<td></td>
</tr>
<tr>
<td>$\equiv S-OH + M^{2+} + H_2O \leftrightarrow \equiv S-OMOH^{(z-2)+} + 2H^+$</td>
<td></td>
</tr>
</tbody>
</table>

**Ligand Exchange**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv S-OH + L^- \leftrightarrow \equiv S-L + OH^-$</td>
<td></td>
</tr>
<tr>
<td>2 $\equiv S-OH + L^- \leftrightarrow \equiv S_2L^+ + 2OH^-$</td>
<td></td>
</tr>
</tbody>
</table>

**Ternary Surface Complex Formation**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv S-OH + L^- + M^{2+} \leftrightarrow \equiv S-L-M^{2+} + OH^-$</td>
<td></td>
</tr>
<tr>
<td>$\equiv S-OH + L^- + M^{2+} \leftrightarrow \equiv S-OM-L^{(z-2)+} + H^+$</td>
<td></td>
</tr>
</tbody>
</table>

Surface charge on hydrous oxides develops as a result of reactions on the surface. The mean surface charge is a function of pH as shown in Equation 2-60:

$$
\frac{C_A - C_B + [OH^-] - [H^+]}{a} = \{ SOH_2^+ \} - \{ SO^- \} = Q
$$

(2-60)

where, $C_A$ = the concentration of acid added to the system (moles/liter),
$C_B$ = the concentration of base added to the system (moles/liter),
a = the quantity of oxide used (kg/liter),
$Q$ = the surface charge (mole/kg),
[ ] = concentration in moles/liter, and
{ } = concentration in moles/kg.
The specific surface area can be used to calculate surface charge in coulombs per meter squared instead of moles per kilogram as shown in Equation 2-61:

\[
\sigma = \frac{Q}{S} = F\left(\Gamma_{H^+} - \Gamma_{OH^-}\right)
\]  

(2-61)

where, \(\sigma\) = the surface charge (C/m\(^2\)),
\(F\) = the Faraday constant (96,485 C/mole),
\(S\) = surface area (m\(^2\)/kg),
\(\Gamma_{H^+}\) = the adsorption density of H\(^+\) (moles/liter), and
\(\Gamma_{OH^-}\) = the adsorption density of OH\(^-\) (moles/liter).

The acidity constant for hydroxides can be used to determine the uptake and release of protons. Equations 2-62 and 2-63 define the acidity constant for a generic hydroxide:

\[
K'_{a1} = \frac{[SOH][H^+]}{[SOH_2^2]}
\]  

(2-62)

\[
K'_{a2} = \frac{[SO^-][H^+]}{[SOH]}
\]  

(2-63)

As protons are removed from the hydroxide, surface charge is reduced and the acidity of neighboring sites is impacted. The surface reactions of hydroxides are similar to those of carbonate, phosphates, and other types of minerals.
2.4 TRANSPORT

Adsorption is one of several parameters that affect the fate and transport of chemicals through porous media as well as large bodies of water; others include advection, diffusion, dispersion, and reaction. Advection moves mass from one point to another (i.e., with the flow of groundwater), while diffusion is the result of mass movement due to random motion and gradients in concentration. The dispersion of mass is caused by heterogeneities in the medium, which create variations in the velocity and flow path. Reactions can create or destroy mass as it flows through porous media. All of these mechanisms affect the fate of chemicals as they advance through porous material.

2.4.1 TRANSPORT THROUGH POROUS MEDIA

Many different numerical analyses have been done to describe transport through porous media. An illustrative example of the derivation and application of a characteristic transport equation for a squeeze treatment is described by Kan et al. [26] who divided the process of adsorption into four stages: “1) molecular diffusion, 2) dissolution of mineral from sandstone, 3) adsorption, and 4) solid phase maturation.” They used the kinetics and equilibrium mechanisms coupled with these four stages of adsorption to describe the transport of phosphonate inhibitors through rock formations. The transport equation employed (Equation 2-64) describes the radial flow of nonconservative chemicals through porous media. This equation incorporates the assumption that instantaneous equilibrium occurs:
\[
R \frac{\partial C}{\partial t} = D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \right] - V_w \frac{\partial C}{\partial r},
\]

(2-64)

where, \( R \) = the retardation factor,
\( C \) = the concentration of inhibitor in the aqueous phase (mg/L),
\( t \) = the time (s),
\( D \) = the dispersion coefficient (m\(^2\)/s),
\( r \) = the radius (m), and
\( V_w \) = the linear velocity of water (m/s).

The retardation factor in Equation 2-64 accounts for adsorption, the first term on the right side represents dispersion, and the second term represents advection.

2.4.2 TRANSPORT IN NATURAL WATER

Transport can also occur in lakes, rivers, and other bodies of water as trace ions associate themselves with particulate matter. The amount of soluble species that a particular body of water can contain is referred to as its carrying capacity. The complexation of trace metals by ligands will increase their solubility. Some metal complexes are more stable than others; therefore, certain metal ions are preferentially complexed. Due to a limited quantity of organic material available, certain ions compete for complexing materials others (ions that do not form stable complexes) are affected very little by the presence of organic ligands.

Natural waters contain inorganic particulate matter like hydroxides and organic material such as humic acid. Guy et al. [27] have identified three solid/solution interactions of great importance in natural waters:
1. Metal-clay colloid ion-exchange reactions,
2. Metal adsorption onto hydrous oxides, and
3. Metal adsorption onto humic acid-clay colloids.

The adsorption of metal ions onto particulate matter occurs quickly, in a matter of minutes to hours. Conversely, desorption can take months, years, or even decades.

The adsorption capacity of a particular body of water is directly related to its sediment load. In addition, particle size effects the adsorption capacity, for example a decrease in particle size creates an increase in adsorption capacity.

Trace elements can be transported in natural waters whether they are dissolved or associated with particulate matter. Dissolved elements will be transported solely with the water. Adsorbed metals will move with the particles. Obviously, larger and heavier particles will move in a pattern very different from the water. Generally, the transport of particles is dependent on its size and the turbulence of the water.

Trace metals can be adsorbed to sediment, fall to the bottom of a lake or river, and later be released from the solid material. As stated previously, desorption is a very slow process. Rarely does a chemical completely desorb from a solid material in the natural environment. There are a few situations that can increase the rate of desorption, such as physical disturbance of soil, oxygen depletion which creates a reducing environment, and
biological activity which is the most common method of remobilization of trace metals from sediments [7].

2.5 PRACTICAL APPLICATIONS

The basic principles of precipitation and dissolution chemistry effect a variety of fields such as chemistry, bone and tooth formation, industrial scale, desalination, and kidney stones [28],[29]. The unwanted development of calcium salts is a common theme in the areas of scale formation and biological mineralization. The nucleation and growth of crystals has significant implications for both industry and the field of medicine.

2.5.1 SCALE

Cowan & Weintritt [30], the authors of Water-Formed Scale Deposits, define scale as "a secondary deposit of mainly inorganic chemical compounds caused by the presence or flow of fluids in a system at least partially man-made." This definition does not include paraffins or asphaltenes nor does it distinguish between real scale (such as CaCO₃) or pseudoscale (a product of two or more man-introduced chemicals). Throughout this text, scale will be used to describe naturally occurring mineral deposits that have precipitated from produced brine.

Primary scale deposits of concern in the petroleum industry are listed in Table 2-6. Scale can occur in rock formations, wellbores, production tubing, and surface equipment. As
newer methods of recovery develop, which involve even larger amounts of water, the prevention of scale will become more significant to oil producers.

Scale deposits result from commonly occurring minerals that have precipitated from produced fluids. There are three minerals in particular that are ubiquitous in the natural environment; each one develops in a different manner. The ability of calcium carbonate to remain in solution is affected by changes in the partial pressure of carbon dioxide, temperature, and ionic strength. As produced fluids are brought to the surface; the reduction in gas pressure raises the pH, a process that is the primary cause of carbonate scaling [31]. Conversely, decreases in temperature and high concentrations of sodium chloride can increase the solubility of calcium carbonate. Ostroff [1] states that the “crystals of calcium sulfate are smaller than those of calcium carbonate, so the scale is generally harder and denser than carbonate scales.” These crystals are produced when the pressure and temperature decrease; as well as when two incompatible waters, one containing high calcium and the other containing high sulfate, are mixed together. Barium sulfate is the most difficult scale to remove and is one of the least soluble minerals in water [32],[33]. Unlike calcium carbonate and calcium sulfate, decreases in temperature reduce the solubility of barium sulfate.
Table 2-6. Typical Scale Deposits (*Most commonly encountered) [34]

<table>
<thead>
<tr>
<th>Name</th>
<th>Common Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Sulfate*</td>
<td>Hemi-Hydrate</td>
<td>CaSO$_4\cdot$ 1/2 H$_2$O</td>
</tr>
<tr>
<td>Calcium Sulfate*</td>
<td>Anhydrate</td>
<td>CaSO$_4$</td>
</tr>
<tr>
<td>Calcium Sulfate*</td>
<td>Gypsum</td>
<td>CaSO$_4\cdot$ 2H$_2$O</td>
</tr>
<tr>
<td>Calcium Carbonate*</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Barium Sulfate*</td>
<td>Barite</td>
<td>BaSO$_4$</td>
</tr>
<tr>
<td>Strontium Sulfate</td>
<td>Celestite</td>
<td>SrSO$_4$</td>
</tr>
<tr>
<td>Ferrous Carbonate</td>
<td>Siderite</td>
<td>FeCO$_3$</td>
</tr>
<tr>
<td>Ferrous Sulfide</td>
<td>Marcasite</td>
<td>FeS</td>
</tr>
<tr>
<td>Ferrous Hydroxides</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Goethite</td>
<td>$\alpha$-FeO $\cdot$ OH</td>
</tr>
<tr>
<td></td>
<td>Lepidocrocite</td>
<td>$\gamma$-FeO $\cdot$ OH</td>
</tr>
<tr>
<td></td>
<td>Limonite</td>
<td>Fe $\cdot$ OH $\cdot$ nH$_2$O</td>
</tr>
<tr>
<td>Ferric Oxide</td>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Iron Hydroxide Magnetite</td>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
</tr>
</tbody>
</table>

Generally, minerals deposit on equipment when brine becomes supersaturated and the free energy of the particle nucleation is overcome. This enables aggregates to grow to a critical size via two different mechanisms – homogeneous and heterogeneous nucleation [8]. In reality, these mechanisms take place to some degree simultaneously. Once nucleation has commenced, several deposit growth mechanisms may occur – agglomeration, nucleation at the surface of a crystallite, adsorption, and phase transition [35].

Scale in gas and oil wells can prevented in a number of ways [36]:

1. Limit production to reduce pressure drop
2. Inject inhibitor into surface equipment
3. Inject inhibitor into via treat string
4. Squeeze inhibitor into rock formation
Option number four is generally the most successful because the inhibitor that is retained by the reservoir will slowly be released into the produced fluids preventing future scale formation.

2.5.1.1 SCALE INHIBITORS

In order to prevent scaling, a variety of chemicals are used to inhibit crystal nucleation or growth. These chemicals behave in a number of ways to suppress scaling. They function as dispersants, anti-precipitants, sequesterants, chelating agents, crystal modifiers, or sludge conditioners [30]. Phosphonate-containing inhibitors are known to prevent scale deposition by altering the rate of nucleation or growth of mineral crystals [37]. This mechanism is believed to be surface controlled and dependent on the degree of supersaturation [38]. A prolonged induction period may be caused by an increase in surface tension between the crystal lattice and aqueous solution from the presence of inhibitors [39]. Because they co-precipitate with divalent cations to form a stable phase, their dissolution mechanisms play a major role in their release into the environment [40]. It has been proposed by Kan et al. [41] that phosphonates prevent scaling by forming a complex with Ca\(^{2+}\) (which has dissolved from naturally occurring calcite in the rock formation) that adsorbs to the mineral surface. If a certain amount of Ca-Phosphonate has covered the surface of the mineral before the nucleus has reached a critical nucleus size, scaling is inhibited [42]. While Ca\(^{2+}\) improves the performance of phosphonates, Mg\(^{2+}\) reduces their effectiveness [43]. Research performed by Leung [44] and Nancollas suggest that less than 5% of the active surface sites must be blocked for effective
inhibition. Some believe that these inhibitors prevent scaling by adsorbing and desorbing to and from the mineral surface because of electrostatic forces [45]. There are a number of conflicting opinions about how phosphonates inhibit scale. For example some believe that phosphonates are adsorbed to the surface and other suggest that the dominant mechanism is precipitation. There is also disagreement as to whether phosphonates prevent nucleation, crystal growth, or both. Once these issues are definitively sorted out, the mechanisms that determine the precipitation and dissolution of inhibitors can be exploited for the optimization of squeeze treatments.

A number of different chemical inhibitors are capable of delaying, decreasing, or completely preventing scale. Specifically three groups of inhibitors are generally used: phosphonates, phosphoric acid esters, and polymers [46]. The inhibitor that is used throughout this study is nitrilotris (methylene phosphonic acid) (NTMP), an amino tri-phosphonate molecule (Figure 2-11). NTMP was chosen primarily because it [5]:

1. Sufficiently inhibits scale at low concentrations
2. Demonstrates stability over a wide range of conditions
3. Effectively inhibits several different kinds of scale
4. Phosphonate concentration relatively easily measured

Interestingly, this inhibitor is known to form an unstable initial amorphous precipitate which eventually transforms into a less stable crystal [47].
The commercial form of NTMP, DEQUEST® 2000; is a 50% active acid developed by Monsanto Chemical Company [48].

![NTMP Molecular Structure](image)

**Figure 2-11. NTMP Molecular Structure**

Table 2-7 lists the characteristics that are applicable to this study. Additionally, this particular chemical is used to prevent scale in cooling towers and boilers as well as to control water hardness in textile bleaching. This chemical is said to have a “threshold effect,” which means that normally only a few milligrams per liter are required for the prevention of precipitation. Monsanto states in its technical bulletin [48] that NTMP is hydrolytically stable and capable of functioning over a wide pH range. Furthermore, it is usually effective in squeeze treatments for several weeks (for wells with extremely persistent scaling problems) to several years.
Table 2-7. DEQUEST 2000® Properties [48]

<table>
<thead>
<tr>
<th>Dequest 2000® Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibition of typical scales</td>
</tr>
<tr>
<td>Corrosion inhibition</td>
</tr>
<tr>
<td>Resistant to water degradation</td>
</tr>
<tr>
<td>Compatibility with other treatment chemicals</td>
</tr>
<tr>
<td>Control of iron fouling</td>
</tr>
<tr>
<td>Stability in acidic and basic solutions</td>
</tr>
<tr>
<td>Soluble in most brines</td>
</tr>
<tr>
<td>Selective adsorption or precipitation</td>
</tr>
</tbody>
</table>

Monsanto also claims that DEQUEST® 2000 is rated as being “practically non-toxic,” although it is slightly irritating to the skin and eyes. They have reported that this product slowly degrades in the natural environment, although Nowack [49] states that it is not degradable; instead it is removed from the aqueous environment through sorption and water treatment operations through anaerobic digestion. According to Monsanto, this phosphonate also has negligible COD and BOD as well as low toxicity toward several cold and warm water fish species.

2.5.1.2 SQUEEZE TREATMENTS

The fate and transport of NTMP in rock formations during a squeeze treatment is central to this research. Squeeze treatments are frequently used in the petroleum industry to prevent scale from depositing in the well bore area, production lines, and surface equipment [50]. Typically, a small volume of a particular chemical inhibitor at relatively high concentrations is injected and pushed deep into the rock formation followed by an overflush of filtered produced brine or KCl solution (Figure 2-12). Once the inhibitor is in place, it is left there for 24 to 72 hours – this is called the “shut-in” period. After shut
in, production is resumed and an initial spike in inhibitor concentration appears followed by a slow release of inhibitor at concentrations as low as 0.1 to 1 mg/L.\[51],[52]\] Theoretically, this concentration should be sufficient to delay the nucleation/growth kinetics of crystals in the produced fluid for several years.\[30]\]

Figure 2-12. Schematic of Squeeze Treatment

The manner in which the inhibitor reacts with the rock formation depends on whether adsorption or precipitation is taking place. Most likely, both are occurring simultaneously\[53]\]. If the adsorption mechanism is dominant, the inhibitor is adsorbed to the surface of the formation immediately after injection and slowly desorbs once
production is resumed [54]. This type of squeeze treatment is believed to be less
damaging to the formation because a precipitate may plug the well bore area [55].
Alternatively, if precipitation dominates, the inhibitor forms a solid upon its addition to
the formation. Produced fluid flows past the precipitated solid slowly dissolving it. In
most cases, the rock formation has to be acidified. This will provide a source of calcium
for the inhibitor to complex with [56]. Precipitation squeeze operations may last longer
than adsorption squeeze treatments and are recommended for wells that have large
production rates [43],[5]. Studies done by Fogler et al. suggest that the inhibitor return
curve is governed by the slow dissolution of Ca-Phn precipitates lodged in the pore throat
of rock formations [57]. The mechanism of inhibition that actually occurs is dependent
on the rock formation.

2.5.1.3 SQUEEZE SOFT™

SqueezeSoft™ is an Excel Visual Basic program designed to predict squeeze treatments
for oil and gas wells. This program makes use of the characteristics of the rock
formation, produced fluids, injected inhibitor solution, and observed field data from
previous squeeze treatment(s). It also uses a decision tree in the form of several
subroutines to decide which Ca-NTMP species will form. The products of the reaction
between inhibitor and calcite determine the concentration of inhibitor in the return curve.
Table 2-8 lists the statements used in those subroutines. SqueezeSoft™ also uses
ScaleSoftPitzer™, another computer program that calculates scaling tendencies, to
suggest which inhibitor to use, predict minimum inhibitor concentration required, and plot the inhibitor return curve.

Table 2-8. SqueezeSoft™ Logic

1. The primary reaction site is calcite in the formation rock.
2. Calcite dissolution is inhibited once the inhibitor is adsorbed or precipitated onto the surface.
3. Two protons from NTMP are consumed to dissolve one mole of calcium from the clean calcite surface.
4. If the solution is supersaturated with respect to CaH₂Phn, then CaH₂Phn will precipitate and inhibit further calcite dissolution.
5. If the solution is undersaturated with respect to the acidic CaH₂Phn solid, then two additional protons will be consumed to dissolve one more mole of calcium.
6. If the solution is supersaturated with respect to Ca₂₅HPhn, then Ca₂₅HPhn will precipitate and inhibit further calcite dissolution.
7. If the solution is undersaturated with respect to the CaH₂Phn or Ca₂₅HPhn solid phases, additional calcium may dissolve to reach simultaneous equilibrium with both Ca₂₅HPhn and CaCO₃ solid phases.
8. If the solution reaches saturation with respect to CaCO₃ and is undersaturated with respect to Ca₂₅HPhn, a Ca-H-Phn solution complex will adsorb onto the calcite surface following a linear adsorption isotherm.

SqueezeSoft™ uses a mass transport equation similar to the one used in the Markov Chain Method (MCM) [58] to calculate NTMP, calcium, carbonate, and pH as a function of time and space. This method allows for the analysis of spatial, non-homogeneous, and kinetic systems. It is based on the assumption that molecular concentrations are
equivalent anywhere in a given compartment and may vary from compartment to compartment. This type of box model was used for simplicity.

The spatial one-dimensional probability of mass transfer due to transport is defined below (Equation 2-65):

\[ \alpha = \frac{v \Delta t}{\Delta x}, \quad (2-65) \]

where \( \alpha \) = the probability of mass transfer flow, 
\( v \) = the uniform velocity of flow (m/s), 
\( \Delta t \) = the unit time (s), and 
\( \Delta x \) = the compartment size (m).

Equation 2-66 defines the probability of mass transfer through diffusion in one direction:

\[ d = \frac{D \Delta t}{(\Delta x)^2}, \quad (2-66) \]

where \( d \) = the probability of mass transfer through diffusion in one direction and 
\( D \) = the Fick's diffusion coefficient (m\(^2\)/s).

In a system, where molecular diffusion is far smaller than the flow and a first-order reaction is taking place (Equation 2-67), concentration is expressed in the following manner:

\[ k = k' \Delta t, \quad (k<<1), \quad (2-67) \]
\[ [A_i]_{+\alpha} = (1 - k - \alpha)[A_1] + \alpha[A_0], \quad (2-68) \]

\[ [A_i]_{+\alpha} = (1 - k - \alpha)[A_i] + \alpha[A_{i-1}], \quad (2-69) \]

where, \( A \) = the concentration (mg/L),
\( A_0 \) = the initial concentration (mg/L),
\( k \) = the reaction probability, and
\( k' \) = the first order reaction rate (s\(^{-1}\)).

Equation 2-67 represents the reaction rate as a function of time. Equation 2-68 describes the concentration in the entrance of the reactor while Equation 2-69 represents the concentration in the remaining compartments of the system.

When flow is not considerably greater than diffusion, the equations become a bit more complex (Equations 2-70 through 2-72):

\[ [A_i]_{+\Delta t} = (1 - k - \alpha - d)[A_i] + d[A_{i+1}] + \alpha[A_0] \quad (2-70) \]

\[ [A_i]_{+\Delta t} = (1 - k - \alpha - d)[A_i] + (d + \alpha)[A_{i-1}] \quad (2-71) \]

\[ [A_i]_{+\Delta t} = (1 - k - \alpha - 2d)[A_i] + d[A_{i+1}] + (d + \alpha)[A_{i-1}] \quad (2-72) \]

The boundary compartments are defined by Equations 2-70 and 2-71. Equation 2-72 represents the internal compartments. The equations used in SqueezeSoft™ are similar to these except that they omit the reaction rate term, \( k \).
The Markov Chain Method can be expanded to second-order reactions, dissipative structures, stationary systems, and bi-dimensional processes. Formosinho [58] demonstrates that the MCM solution compares well to the exact solution (Table 2-9) in the range of very high and low D coefficients with the accuracy depending on the chosen compartment size.

<table>
<thead>
<tr>
<th>$k/10^{-3}$</th>
<th>$v/10^{-3}$</th>
<th>$D$</th>
<th>$\Delta x$</th>
<th>MCM Concentration</th>
<th>Exact Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>$\infty$</td>
<td>1/40</td>
<td>0.2000</td>
<td>0.2000</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$10^{-2}$</td>
<td>1/40</td>
<td>0.1899</td>
<td>0.1899</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$5 \times 10^{-4}$</td>
<td>1/40</td>
<td>0.1022</td>
<td>0.1016</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$6.25 \times 10^{-5}$</td>
<td>1/40</td>
<td>0.0385</td>
<td>0.0353</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$6.25 \times 10^{-5}$</td>
<td>1/40</td>
<td>0.0369</td>
<td>0.0353</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$5 \times 10^{-6}$</td>
<td>1/40</td>
<td>0.0216</td>
<td>0.0198</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0</td>
<td>1/40</td>
<td>0.0202</td>
<td>0.0185</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>$10^{-5}$</td>
<td>1/40</td>
<td>0.1445</td>
<td>0.1380</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>$10^{-5}$</td>
<td>1/80</td>
<td>0.0037</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

The error will be less than 15% when Equation 2-73 is less than 0.2.

$$\frac{k}{\left(\frac{v}{\Delta x} + \frac{D}{(\Delta x)^2}\right)} < 0.2 \quad (2-73)$$

The MCM equations can also be obtained through mathematics that is more traditional. Shown in Figure 2-13 is the derivation of Equation 2-78 from the mass transfer equation. The first term on the right hand side of the mass transport equation represents diffusion,
the second term is advection, the third term is adsorption and the last term symbolizes reactions.

\[
\frac{dC}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} \frac{\rho_b}{\eta} \frac{dq}{dt} - k' C
\]

Let \(-\frac{\rho_b}{\eta} \frac{dq}{dt} = \frac{\rho_b}{\eta} \frac{dC}{dt}\)

\[
\frac{dC}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} \frac{\rho_b}{\eta} \frac{dC}{dt} - k' C
\]

\[
\frac{dC}{dt} + \frac{\rho_b}{\eta} \frac{dC}{dt} \frac{dq}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} - k' C
\]

\[
\left(1 + \frac{\rho_b}{\eta} K_d\right) \frac{dC}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} - k' C
\]

Let \(\frac{dq}{dC} = K_d\)

\[
\left(1 + \frac{\rho_b}{\eta} K_d\right) \frac{dC}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} - k' C
\]

Let \(\frac{\rho_b}{\eta} K_d = R\)

\[
R \frac{dC}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} - k' C
\]

\[
\frac{dC}{dt} = D_x \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} - k' C
\]

\[
\Delta C = \left(\frac{D_x}{R (\Delta x)^2} - \frac{v_x}{R} \frac{\Delta C}{\Delta x} - k' \frac{\Delta C}{R}\right) \Delta t
\]

\[
\Delta C = \frac{D_x}{R (\Delta x)^2} (\Delta^2 C) - \frac{v_x}{R} (\Delta C) - k' \frac{\Delta C}{R}
\]

\[
\Delta C = d(\Delta^2 C) - \alpha(\Delta C) - kC
\]

\[
C_{t+1,x} - C_{t,x} = C_{t,x-1} d + C_{t,x-1} \alpha + C_{t,x} - 2C_{t,x} d - C_{t,x} \alpha - C_{t,x} k + C_{t,x+1} d
\]

\[
C_{t+1,x} - C_{t,x} = (C_{t,x+1} - 2C_{t,x} + C_{t,x-1}) d - (C_{t,x} - C_{t,x-1}) \alpha - C_{t,x} k
\]

\[
C_{t+1,x} = C_{t,x-1} (d + \alpha) + C_{t,x} (1 - 2d - \alpha - k) + C_{t,x+1} (d)
\]

Figure 2-13. Derivation of Markov Chain Method from the Mass Transport Equation.
2.5.2 BIOLOGICAL MINERALIZATION

The production and dissolution of bone and tooth minerals are governed by the same mechanisms that control crystal growth. Generally, these compounds contain calcium (calcium phosphates are quite common). Under physiological conditions, the most stable calcium phosphate phase is hydroxyapatite (HAP), which is a significant constituent of the skeleton and teeth [59]. Calcium carbonate and oxalate hydrates are a few other important constituents of biological mineral deposits [60].

The abnormal deposition of calcium containing minerals from supersaturated biological fluids creating calcified heart valves is just one example of how dependent physiology is on crystal growth [61]. Nancollas [62] suspects that precipitation inhibitors in biological fluids may nucleate calcium phosphates when attached to a surface. He also states that the heterogeneous nucleation of minerals such as calcium phosphate is controlled by surface properties of the substrate and the degree of supersaturation [63].

The development of stones in the urinary tract has yet to be thoroughly understood. Urine typically contains concentrations of calcium phosphate and calcium oxalate that are 1000 times greater than saturation and yet in normal functioning bladders, they do not precipitate due to a proposed inhibitor – pyrophosphate [64]. The reason why such high concentrations of minerals in the body do not deposit is one of the more interesting unsolved problems in medicine today. Another areas of study is the formation of bones and teeth and the calcification of cartilage.
CHAPTER 3: Materials and Methods

NTMP adsorption on barium sulfate was evaluated with batch experiments. Its interaction with core material was modeled with a dynamic flow study. In both cases, the temperature was maintained at 70°C with a temperature controlled bath shaker (American Optical, model 406015) and the pH was buffered at approximately 6.4 with the biological buffer, Piperazine-N,N'-bis [2-ethanesulfonic acid] (PIPES), 99% pure, pKₐ = 6.8 @ 25°C, pH range 6.1 to 7.5) or natural buffer, NaHCO₃.

3.1 MATERIALS

Frio sandstone rock was chosen for the column studies because it was obtained from an oil well that had never been used for production. Therefore, there would be less interference from unknown contaminants or inhibitors from previous squeeze treatments. As stated earlier, NTMP was used because it is an effective scale inhibitor commonly used in the oil and gas industry. All other chemicals utilized were at least reagent grade.

3.1.1 SOLID MATERIALS

Two kinds of solid material were used to pack the columns. Frio Sandstone, which was taken from a dry oil well, was utilized in the first five column studies. Pure calcite (Iceland Spar) was employed in the final study to prevent the impurities of natural core material from interfering with the charge balance determination.
3.1.1.1 FRIo FORMATION SANDSTONE

Frio sandstone is weakly cemented, friable sand from the DeLee well. Sandstone is considered a kind of fragmental rock – one of the most common types of reservoir rocks [65]. Ordinarily, sandstones consist of quartz containing silts, clays, carbonates, silica, feldspars, and/or rock fragments. Tables 3.1 – 3.3 list the composition of the Frio Sandstone Formation [66]. The iron content is 2.5% (Table 3-1) but the oxidation state is not known. The core material samples were stored in ambient conditions, therefore any iron (II) present may have been oxidized to iron (III). This might cause interferences with the iron balance calculation discussed in Chapter 5.

Core material was ground using a mortal and pestle, washed with methanol and then deionized water, and finally allowed to air dry. The dry samples were then sieve cut between 500 and 720 μm, collected, and used for the column studies in Chapter 5.

Table 3-1. Elemental Composition of Friable Frio Sandstone (Analysis performed by Reservoirs, Inc., Houston, Texas)

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>80</td>
</tr>
<tr>
<td>Aluminum</td>
<td>13</td>
</tr>
<tr>
<td>Magnesium</td>
<td>3.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>---</td>
</tr>
<tr>
<td>Iron</td>
<td>2.5</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.28</td>
</tr>
</tbody>
</table>
Table 3-2. Mineral Composition of Friable Frio Sandstone

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Relative Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>61</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>17</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3-3. Clay Fractions of Friable Frio Sandstone

<table>
<thead>
<tr>
<th>Clay Fraction</th>
<th>Relative Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>49</td>
</tr>
<tr>
<td>Illite</td>
<td>8</td>
</tr>
<tr>
<td>Smectite</td>
<td>22</td>
</tr>
<tr>
<td>Chlorite</td>
<td>21</td>
</tr>
<tr>
<td>Total Clay</td>
<td>7</td>
</tr>
</tbody>
</table>

Previous experiments performed by the Rice University Brine Chemistry (BCC) research group verifies that the presence or absence of calcium may affect the retention of phosphonates in sandstone as well as the design of a squeeze treatment [9].

3.1.1.2 CALCIUM CARBONATE

Two forms of calcium carbonate were used in the final column study. The majority of the column was packed with Iceland Spar calcite purchased from Ward’s Natural Science Establishment, Inc. (Rochester, New York). Calcite (CaCO₃) is a relatively pure form of calcium carbonate with minor impurities such as Mn, Fe, and Mg. Calcite is a ubiquitous mineral found in oil and gas reservoirs. Ninety-nine percent pure calcium carbonate reagent grade powder was also used. It was obtained from Malinckrodt, Inc. (Paris, KY).
3.1.2 CHEMICALS

NTMP (DEQUEST® 2000) was obtained from the Monsanto Company as a 50% active phosphonic acid. Its molecular weight is 299 g/mole, and its pH is less than two. PIPES, purchased from Sigma, is a biological zwitteron buffer with a pKₐ = 6.8 at 25°C. All other chemicals were reagent grade and were purchased from Fisher Scientific (Fair Lawn, NJ), Malinckrodt, Inc. (Paris, KY), HACH Company (Loveland, CO), or SIGMA Chemical Company (St. Louis, MO) (Table 3-4).

Table 3-4. Reagent Grade Chemicals Used

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Manufacturer</th>
<th>Certification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Molybdate</td>
<td>Malinckrodt</td>
<td>A.C.S. Certified</td>
</tr>
<tr>
<td>Antimony Potassium Tartrate</td>
<td>Fisher Scientific</td>
<td>Certified</td>
</tr>
<tr>
<td>Ascorbic Acid</td>
<td>Fisher Scientific</td>
<td>A.C.S. Certified</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>Fisher Scientific</td>
<td>Certified</td>
</tr>
<tr>
<td>Calcium Chloride Dihydrate</td>
<td>Fisher Scientific</td>
<td>A.C.S. Certified</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>Fisher Scientific</td>
<td>Certified A.C.S. Plus</td>
</tr>
<tr>
<td>Molybdenum Reagent</td>
<td>HACH</td>
<td>------</td>
</tr>
<tr>
<td>PIPES</td>
<td>SIGMA</td>
<td>------</td>
</tr>
<tr>
<td>Potassium Persulfate</td>
<td>Fisher Scientific</td>
<td>Certified</td>
</tr>
<tr>
<td>Sodium Bicarbonate</td>
<td>Fisher Scientific</td>
<td>A.C.S. Certified</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>Fisher Scientific</td>
<td>Certified for Biological Work</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>Fisher Scientific</td>
<td>A.C.S. Certified</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>Fisher Scientific</td>
<td>Certified A.C.S. Plus</td>
</tr>
</tbody>
</table>

The water used in all of the studies was purified with a PCS SYBRON|Barnstead filtration system. This process began with tap water passing through a high capacity ion exchange cartridge, followed by two successive ultrapure ion exchange cartridges. Then the water flows through a final cartridge for the purpose of organics removal. Purified
deionized (DI) water was used for dilution purposes as well as to prepare all standards, reagents, and blanks.

3.2 ANALYTICAL PROCEDURES

Two different studies were performed in this work – batch experiments and column studies. The batch adsorption/desorption experiments were conducted to further investigate the sorptive properties of NTMP at low concentrations. Previously Kan [41] et al. had shown that the adsorption of NTMP onto barium sulfate exhibits hysteretic behavior.

Column work was performed to test the SqueezeSoft™ program. This computer program predicts the inhibitor return curve reasonably well, but the distribution of inhibitor inside the core material had not been verified.

A variety of analytical procedures were used in both sets of experiments. In order to measure the concentration of phosphonates in solution they must be digested first to break the phosphorous – carbon bonds. This allows for the analysis of phosphate, which can be used to back calculate the amount of phosphonate in solution. Phosphonate can be digested using the Autoclave Persulfate Digestion method or the UV Oxidation method. Both methods work well, but due to limited numbers of UV lamps, the autoclave method is preferred when more than four samples are to be analyzed at once. There are also two colorimetric phosphate analyses that can be used, the blue method and the yellow method. The blue method is accurate for concentrations ranging between 0 and 2.5 mg/L.
phosphate. The yellow method can be used for solution containing 2.5 to 45 mg/L phosphate. Solid material containing adsorbed phosphonates were analyzed after extraction. The extract is analyzed for phosphonates via the methods previously described. In addition to phosphonate analysis, aqueous solutions were analyzed for bicarbonate, calcium, and chloride using HACH titration methods. The concentration of calcium in solution was measured using the inductively coupled plasma (ICP) atomic emission spectroscopy or the HACH titration method. The ICP was more useful when multiple samples needed to be analyzed.

3.2.1 AUTOCLAVE PERSULFATE DIGESTION METHOD

The persulfate digestion method was slightly modified from Standard Methods 4500-P B.5 [67]. Six normal hydrochloric acid was prepared from concentrated hydrochloric acid. Sodium hydroxide pellets were used to make six normal sodium hydroxide. A volumetric pipette was employed to deliver 25 mL of sample and 1 mL of 6N HCl into a glass vial containing 0.500 g of potassium persulfate. This mixture was heated to 121°C at an average pressure of 16.5 psig for 30 minutes in an autoclave oven (Amsco Scientific SG-120 Eagle/Century Series). For each set of samples digested, a blank containing 25 mL of buffer solution (1M NaCl, 0.05 M CaCl₂, 5 mM PIPES), 1 mL of 6N HCl, and 0.500 g of potassium persulfate was prepared and digested as well. Once the samples had cooled to room temperature, they were neutralized by adding 1 mL of 6 N NaOH and 4 mL of 1 N NaOH (purchased from Fisher Scientific as such).
3.3.2 ASCORBIC ACID METHOD (THE BLUE METHOD)

The ascorbic acid method was modified from Standard Methods 4500-P E [67]. This method was typically used for the adsorption/desorption batch studies for which all samples contained low concentrations. All reagents were prepared before samples were analyzed in the following manner: 1) 5N HCl was prepared by diluting 420 mL of concentrated HCl with DI water to 1000 mL, 2) 1.372 g of potassium antimonyl tartrate was dissolved with 400 mL of DI water and stored in a glass bottle, 3) 20 g of ammonium molybdate was dissolved in 500 mL of DI water and stored in a glass bottle, and 4) 0.1 M ascorbic acid was prepared by dissolving 1.760 g in 100 mL of DI water and stored in a refrigerator for up to one week. A combined reagent was always prepared directly before use by mixing 50 mL of 5N HCl, 5 mL of potassium antimonyl tartrate solution, 15 mL of ammonium molybdate solution, and 30 mL of 0.1 M ascorbic acid. The 25 mL samples, which had already been digested, cooled, and neutralized, were mixed thoroughly with 5 mL of the combined reagent. The absorbance of each sample was measured 10 to 30 minutes after the reagent had been added using a HACH DR/2000 Direct Reading spectrophotometer with the wavelength set at 880 nm. The absorbance reading was compared to a standard curve that had previously been prepared from standard solutions ranging between 0.5 to 2.0 mg/L NTMP (Figure 3-1).
Figure 3-1. Standard Curve for NTMP in PIPES Buffer Solution. Slope = 2.2792, Intercept = 0.0024, Standard Deviation = 0.02, $R^2 = 0.9995$.

3.3.3 UV OXIDATION PERSULFATE DIGESTION METHOD

The UV oxidation method was modified from the HACH UV Oxidation method [68]. First a volumetric pipette was used to deliver 25 mL of sample into a glass vial and a HACH potassium persulfate powder pillow was added. Next, a UV lamp (HACH company, short-wave, pencil type) was used to oxidize the sample for 30 minutes. A blank was always digested with each set of samples.
3.3.4 MOLYBDOVANADATE METHOD (THE YELLOW METHOD)

The yellow method requires the addition of one milliliter of HACH molybdovanadate reagent to 25 mL of a previously digested sample (when analyzing background PO₄, the sample was not digested and the concentration was reported as read from the spectrophotometer in mg/L PO₄). This mixture was allowed to react for three minutes before being analyzed with the HACH spectrophotometer at a wavelength of 430 nm. The spectrophotometer reports the concentration in mg/L of PO₄, which was converted to mg/L of NTMP, based on the molecular weight of these two molecules using Equation 3-1:

\[
NTMP (mg/L) = PO₄ (mg/L) \times \frac{299}{284.91} \times DF,
\]

where DF = the dilution factor.

The ratio of 299 to 284.91 is the molecular weight of NTMP divided by the molecular weight of three phosphates.

3.3.5 IGNITION EXTRACTION METHOD

The core material used in the column study was extracted via the ignition method [69]. Aluminum weighing boats, labeled and weighed in advance, were used instead of porcelain crucibles because the weight boats were easier to handle and cooled to room temperature rather quickly. Approximately five grams of each sample were placed in a weigh boat and carefully put in a muffle furnace, (Thermolyne 47900) which had been
allowed to cool to room temperature overnight. Next, the temperature was slowly increased to 550°C over a two hour period and maintained at that temperature for an additional hour. Then the samples were removed from the muffle furnace and cooled to room temperature, after which one gram was transferred to a 50 mL centrifuge tube. Each sample was extracted with 50 mL of 0.5 N H₂SO₄ while being mixed thoroughly in a tumbler (Dayton DC Speed Controller, model 4Z8270) for a period of 16 hours. Next, the samples were centrifuged at 3500 rpms for 15 minutes. Finally, the supernatant was removed and analyzed according to sections 3.3.1 or 3.3.3 and 3.3.2 or 3.3.4.

3.3.6 ALKALINITY TITRATION

In order to characterize the carbonate equilibrium in the column during shut-in, the effluent was titrated to estimate the aqueous phase bicarbonate concentration. Each sample was diluted approximately 1:200 with deionized water. Next, the sample was titrated with a HACH 0.1600 ± 0.008 N sulfuric acid titration cartridge and digital titrator to an end-point of about pH 4. The pH was determined with an Accumet model 15 pH meter set to millivolts. The pH meter was standardized with pH 4 (0.04958 M Phthalate solution) and 10 (0.01 M Borax solution) buffer solutions. The millivolts of each buffer solution were measured in advance as well as the air temperature in order to determine the pH. While titrating, millivolt readings were recorded; after this they were converted to pH units (Equations 3-2 and 3-3). The digits from the digital titrator were converted to milliequivalents using Equations 3-4:
\[ pH = \frac{A - B}{C - D}, \quad (3-2) \]

where \( A \) = the mV reading for the pH 4 buffer solution (mV),
\( B \) = the mV reading for the sample (mV),
\( C \) = the slope calculated in Equation 3-3 (dimensionless), and
\( D \) = the pH value for the pH 4 buffer solution (pH units).

\[ C = \frac{A - E}{F - D}, \quad (3-3) \]

where \( E \) = the mV reading for the pH 9 buffer solution (mV) and
\( F \) = the pH value for the pH 9 buffer solution (pH units).

\[ \text{meq/mL} = d \cdot \frac{mL}{800 \text{digits}} \cdot N \cdot \frac{1}{S}, \quad (3-4) \]

where \( d \) = the number of digits used during titration,
\( N \) = the normality of the acid or base (meq/mL), and
\( S \) = the sample size (mL).

The inflection of the titration curve was too weak to determine. For this reason, each sample was back titrated with a HACH 0.1600 ± 0.0007 N sodium hydroxide titration cartridge. The amount of acid used was subtracted from the amount of base used in units of milliequivalents per liter. The concentration of bicarbonate was calculated according to Equation 3-5:

\[ M = \frac{(I_1 - I_2) \cdot DF}{1000}, \quad (3-5) \]

where, \( M \) = the concentration of bicarbonate (mM),
\( I_1 \) = the inflection point from the first titration (meq/mL),
\( I_2 \) = the inflection point from the back titration (meq/mL), and
\( DF \) = the dilution factor.
3.2.7 CALCIUM ANALYSES

The calcium concentration of the effluent samples was also measured to characterize the carbonate chemistry. Calcium can be determined using an ICP or a simple colorimetric titration method. The ICP method requires the samples to be acidified to create a 0.01 N acidic matrix. Standard solutions of 50, 5, and 0 mg/L calcium were also prepared containing 0.01 N acid. The standards and samples were analyzed with a Perkin Elmer Plasma 400 Emission Spectrometer. For quality control purposes, the samples were analyzed in groups of three with the standards run before and after each group. The intensity from the ICP was used to determine the standard curve for each set of three samples and their respective samples.

A more simple calcium measurement is advantageous when only a few samples need to be analyzed. Calcium can also be determined via two titration methods: the total hardness and calcium hardness procedures. The HACH total hardness method determines hardness due to magnesium and calcium. This method is useful when the sample is known not to have any magnesium and a sharp endpoint is desired. The sample is buffered with a HACH Hardness 1 Buffer Solution and an indicator is added turning the solution from clear to red. Next, the solution is titrated with 0.08 or 0.8 M EDTA (the concentration is determined based on the sample size) until the color turns from red to pure blue. If magnesium is suspected to be in the sample and only hardness due to calcium is required, the HACH calcium hardness procedure is used. The sample is buffered with an 8 N Potassium Hydroxide Standard Solution and a different indicator is
added. The solution is also titrated with 0.08 or 0.8 M EDTA until the solution turns from pink to blue. Regardless of the colorimetric method used, the amount of calcium in solution can be determined using Equation 3-6:

\[
Ca^{2+} (mg / L) = d \times \frac{1mL}{800{digits}} \times N \times \frac{1mole}{1meq} \times \frac{1}{S} \times \frac{40.01g}{mole} \times \frac{1000mg}{1g} \times \frac{1000mL}{L} \tag{3-6}
\]

3.2.8 CHLORIDE TITRATION

In order to perform a charge balance, the chloride concentration in the effluent of the column studies needed to be determined. This titration was performed using the HACH Mercuric Nitrate method. One milliliter of sample was diluted to 100 mL with deionized water in a glass Erlenmeyer flask and thoroughly mixed on a stir plate. The contents of one diphenylcarbazone powder pillow were added as the diluted solution continued to mix. A digital titrator containing a 2.256 N Hg(NO₃)₂ cartridge was used to add small increments of titrant to the solution until the color changed from pale yellow to light pink. The digits of titrant added to the solution were converted to milliliters and used to calculate the chloride concentration as shown in Equation 3-7:

\[
Cl^- (mg / L) = d \times \frac{1mL}{800{digits}} \times N \times \frac{1mole}{1meq} \times \frac{1}{S} \times \frac{35.453g}{mole} \times \frac{1000mg}{1g} \times \frac{1000mL}{L} \tag{3-7}
\]
3.2.9 HOT HYDROCHLORIC ACID EXTRACTION

When extracting very small quantities of NTMP from the solid phase, a more drastic method was needed. The hot HCl extraction method consisted of placing one gram of solid sample and 2 mL of HCl in a 40 mL glass vial with a stir bar and heating in a 70°C temperature bath for a period of 24 hours for BaSO₄ or 72 hours for CaCO₃. Afterwards, the samples were allowed to cool, diluted to about 37 mL, and centrifuged. The supernatant was removed from the vial and analyzed according to sections 3.3.1 or 3.3.3 and 3.3.2 or 3.3.4 respectively.
CHAPTER 4: ADSORPTION/DESORPTION OF NTMP ONTO BARIUM SULFATE

In order to understand how threshold inhibitors return from the formation during production, numerous desorption studies were performed by the Rice University BCC research group. That research was continued in this thesis at lower concentrations, similar to those found in inhibitor return curves. The characterization of the release of NTMP from core material can be utilized to develop a general theory of inhibitor behavior, which has been incorporated into subroutines employed by SqueezeSoft™ for the design of squeeze treatments.

4.1 BACKGROUND

Previous work investigating the desorption of NTMP from barium sulfate had been done by the BCC where hysteretic behavior was observed (Figure 4-1) [41]. When initial NTMP concentrations of 79 mg/L were used, almost twenty desorption steps were required before the equilibrium concentration dropped to 0.5 mg/L. Yet, the concentration still did not drop to zero. Even when lower initial concentrations were used, many desorption steps were required and the equilibrium concentration converged to a constant concentration as it approaches the adsorption isotherm. These experiments were performed at pH 6.12 and 4.96. Initially, solutions containing as much as 33 mg/L NTMP were used to adsorb phosphonate onto the solid. After numerous successive desorption steps, the solution phase concentration converged to a constant value of approximately 0.43 mg/L for pH 6.12 and 0.56 mg/L for pH 4.96. Interestingly, the ion
product of the pH 6.12 solution corresponds to the solubility product of the Ca$_{23}$HPh$_n$ crystalline phase. An ion product and solubility product that is equal to one another is indicative of a stable crystalline phase being formed. The pH 4.96 solution had an ion product that was less than the corresponding solubility product. Therefore, a less stable, amorphous phase is present at those conditions. Based on these observations, they proposed that an alternative solid phase was formed at pH 4.96.

![Graph](image)

**Figure 4-1. NTMP/Barium Sulfate Desorption Hysteresis**

This different solid phase would explain why the solubility and ion products are different at pH 4.96 and similar at pH 6.12. Fogler [57] has drawn similar conclusions, stating that
varying conditions can cause alternative Ca-Phn phases to precipitate. It was proposed by the BCC research group that crystalline Ca-Phosphonate solubility controls the long-term inhibitor return concentration. If a particular crystalline phase is more soluble than another is, more NTMP will dissolve or desorb into the produced fluids. In both cases, the equilibrium concentration after adsorption was greater than or equal to 0.5 mg/L. This phenomenon had not been investigated at lower inhibitor concentrations. It is for this reason, that similar experiments, featured in this work, were performed at an initial equilibrium concentration of 0.5 mg/L.

4.2 EXPERIMENTAL PROCEDURE

The experiments presented in this thesis were designed to be similar to previous work so that the research would continue where the BCC’s work had ended. All experiments were performed in plastic 50 mL centrifuge tubes (Figure 4-2). The solid to solution ratio, mineral adsorbent, and phosphonate were kept the same.

![Centrifuge Tube with BaSO₄ and NTMP Solution](image)

Figure 4-2. Centrifuge Tube with BaSO₄ and NTMP Solution
The buffer solution consisted of 1 M NaCl, 0.05 M CaCl₂, and 5 mM PIPES. In the research done by the BCC research group, the buffer solution contained sodium acetate or PIPES. In this experiment, only PIPES was used as a buffer. Previously, a glass-jacketed reactor was used to adsorb 450 mL of NTMP solution onto 10 g of barite. Instead of working with 10 g of BaSO₄, approximately one gram was placed in each centrifuge tube followed by 45 mL of a buffer solution initially containing 3.5 mg/L NTMP. Altogether, eight tubes were placed in a shaker water bath set at 70°C and 20 oscillations per minute for a period of 24 hours (Figure 4-3). Four of them contained 1 g of barium sulfate and the other four, used as control samples, did not have any solid material. All tubes had 45 mL of NTMP solution.

Figure 4-3. Centrifuge Tubes in Temperature Bath/Shaker
After adsorption, the tubes were centrifuged at 5000 rpm for 10 minutes. Because fine particles were found floating on top, approximately 43 mL of the supernatant was removed and filtered into a fresh centrifuge tube with a sterile 0.2 μm Nalgene syringe filter leaving behind a residual volume of about 2 mL. Subsequently, 45 mL of buffer solution that did not contain NTMP was added and then the tubes were returned to the water bath for an average of two days each time. This desorption step was repeated more than 20 times. The filtered solutions were analyzed according to Sections 3.3.1 and 3.3.2.

4.3 RESULTS & DISCUSSION

A summary of the measured equilibrium concentration, calculated solid phase concentration, and computed distribution coefficient is listed in Table C-1 in Appendix C. Desorption step four is not shown because the supernatant that was recovered was inadvertently disposed of. After the first three desorption steps, the data in Figure 4-4 appeared to be moving toward the data point Q=111 mg/kg, C=0.03 mg/L; all calculations after the fourth desorption are based on this assumed data point. All volumes are reported in milliliters although they were actually measured in grams. It was assumed that the density of the supernatant is about the same as water, one gram per milliliter.

After the first twenty desorption steps, some of the samples were compromised in the water bath. Thereafter, the data points shown are the average of three samples or less. As the graph shows, the aqueous phase concentration converges at an average value of about 0.12 mg/L, which is even lower than the work done before by the BCC despite the
fact that the pH is slightly higher. Based on the line of reasoning discussed earlier, this may imply that yet another crystalline phase exists. Using the equilibrium concentration (0.12mg/L), pH, temperature, TDS concentration, and calcium concentration; the log $K_{sp}$ is calculated to be about 24.0. This new $K_{sp}$ is in the range of the $K_{sp}$ for CaH$_4$PHN (32.46 @ 1.0 M IS and 70°C) and Ca$_{2.5}$HPhn (23.12 @ 1.0 M IS and 70°C). This result is especially interesting because the computer program, SqueezeSoft™, consistently overestimates the inhibitor return curve concentration.

Figure 4-4. NMTP Desorption Hysteresis
In Figures 4-5 through 4-6, the squares represent the observed inhibitor return concentration; the solid line represents the inhibitor return concentration predicted by SqueezeSoft™. In both cases, the observed inhibitor concentration is slightly lower than the prediction concentration.

Figure 4-5. Inhibitor Return Concentration for the N. R. Smith Well.

Note that the new $K_{sp}$ is incorporated into SqueezeSoft™ for a new prediction curve that will be compared to the data shown in Figures 4-5 and 4-6 in Chapter 6.
Figure 4-6. Inhibitor Return Concentration for the Gladys McCall Well.

Table 4-2 compares the ion product for the Ca-H-NTMP phase based on the NTMP equilibrium concentration of the aqueous phase and other parameters such as pH and temperature. The ion product was calculated by a speciation model that was developed by the BCC.
Table 4-1. Ion Product Comparison between Field Data and Adsorption/Desorption Study.

<table>
<thead>
<tr>
<th></th>
<th>[Phn]_{eq} (mg/L)</th>
<th>T (°F)</th>
<th>TDS (mg/L)</th>
<th>pH</th>
<th>[Ca^{2+}] (mg/L)</th>
<th>Pressure (psig)</th>
<th>pK_{sp}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gladys McCall</td>
<td>0.10</td>
<td>298</td>
<td>96,340</td>
<td>5.96</td>
<td>4130</td>
<td>12910</td>
<td>24.8</td>
</tr>
<tr>
<td>N. R. Smith</td>
<td>0.35</td>
<td>160</td>
<td>50,899</td>
<td>6.68</td>
<td>480</td>
<td>1900</td>
<td>24.2</td>
</tr>
<tr>
<td>O’Daniels</td>
<td>0.35</td>
<td>285</td>
<td>43,624</td>
<td>5.50</td>
<td>760</td>
<td>9000</td>
<td>25.4</td>
</tr>
<tr>
<td>Pleasant Bayou</td>
<td>0.15</td>
<td>305</td>
<td>130,000</td>
<td>6.17</td>
<td>9600</td>
<td>11168</td>
<td>24.9</td>
</tr>
<tr>
<td>Desorption Study</td>
<td>0.12</td>
<td>158</td>
<td>65,791</td>
<td>6.42</td>
<td>2004</td>
<td>14.7</td>
<td>24.0</td>
</tr>
</tbody>
</table>

*Note: IP = [Ca^{2+}][H^+][Phn]^6

The calculated ion product for the equilibrium concentration of NTMP from the adsorption/desorption study is very close to the ones calculated for the Smith and Pleasant Bayou wells. These two wells also have pH values closer to the pH used in the desorption study. The O’Daniels well ion product is least comparable to the laboratory data obtained and it has the lowest pH as well as a low calcium concentration. Pressure does not appear to impact the data in Table 4-2 at all. There could possibly be a different crystalline phase that develops at low concentrations which may be responsible for the low inhibitor return curves typically found in the field.

In order to determine whether the solubility of the crystalline phase governs desorption at low concentrations, an alternative desorption study was performed. Equation 4-1 illustrates the solubility product for calcium and NTMP:
\[ K_{sp}^{Ca, H, Phn} = [Ca^{2+}]^y \cdot [H^+]^z \cdot [NTMP^{6-}], \]  

(4-1)

where, \([Ca^{2+}] = \) the concentration of calcium (moles/liter),  
\([H^+] = \) the concentration of hydrogen ions (moles/liter), and  
\([NTMP^{6-}] = \) the concentration of NTMP (moles/liter).

If one were to reduce the calcium concentration, the inhibitor concentration would be expected to increase because by definition the solubility product must remain constant. Therefore, an increase in the pH would appear to have the same effect. In order to investigate the validity of this assumption, another study was performed where ten different buffer solutions were prepared (Table 4-2).

<table>
<thead>
<tr>
<th>Solution #</th>
<th>pH</th>
<th>NaCl (M)</th>
<th>CaCl₂ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.42</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>1.42</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>4.42</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>9.42</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>6.42</td>
<td>0.100</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>6.42</td>
<td>0.001</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>6.42</td>
<td>0.000</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>6.42</td>
<td>1</td>
<td>0.0005</td>
</tr>
<tr>
<td>9</td>
<td>6.42</td>
<td>1</td>
<td>0.0005</td>
</tr>
<tr>
<td>10</td>
<td>6.42</td>
<td>1</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The first buffer solution was used as a control and had the same composition as was used in the low concentration adsorption/desorption study described previously. The next three solutions were chosen to have pH values less than or greater than the control so that the effect of pH could be determined. Solutions five through seven have low ionic
strengths, and the last three solutions have low calcium concentrations. These compositions were selected to determine whether ionic strength or calcium concentration influence the solubility properties of NTMP adsorbed onto barite. Each centrifuge tube was prepared as before with the exception that the adsorption step was performed differently. Instead of adsorbing NTMP to barium sulfate in each individual tube, about 400 mL of NTMP solution was mixed with 10 g of BaSO4 in a glass reactor to make sure that each sample had the same initial concentration of NTMP on the solid as well as in the solution. After adsorption, three desorptions steps were done in the reactor vessel using only buffer solution #1. The first three desorption steps were kept the same in order to insure that this study is comparable to the previous one. It was also important that the aqueous phase equilibrium concentration after adsorption be about the same as the previous study for comparison purposes. In both studies, the initial adsorption data point occurs near 0.53 mg/L and 119 mg/kg. Varying buffer solutions were used after the third desorption. Figure 4-7 shows the result of this study. Solution #2 (pH = 1.42) had the most dramatic effect. All of the NTMP was removed from the solid during the fourth desorption step. At low pH, the BaSO4 surface is positively charged. In addition, Calcium and NTMP complexes are negligible (~2%). Further protonated NTMP species such as neutral H6NTMP (62% of total NTMP) and positively charged H3NTMP+ (23% of total NTMP) are less likely to adsorb to the solid surface.
Figure 4-7. Alternative NTMP Desorption Hysteresis

With the exception of solution two, solutions one, three, and eight removed the most phosphonate. Therefore, eleven additional desorptions were carried out in these tubes. An NTMP speciation model, discussed in Chapter 6, calculates the individual species in solution based on the pH, total dissolved solids (TDS), calcium concentration, and NTMP concentration. Table 4-3 lists the aqueous phase species in solutions one, three and eight calculated by the NTMP speciation model.
Table 4-3. Speciation of Solutions 1, 3, and 8 in Batch Experiments

<table>
<thead>
<tr>
<th>Solution #</th>
<th>Species in Solution</th>
<th>Percentage in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Control</td>
<td>Ca₂H₂NMTPT⁻</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>Ca₃H₂NMTPT⁺</td>
<td>19%</td>
</tr>
<tr>
<td></td>
<td>Ca₂H₂NMTPT⁻</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>CaH₂NMTPT⁻³⁻</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>CaH₂NMTPT⁻²⁻</td>
<td>7%</td>
</tr>
<tr>
<td>3: pH = 4.42</td>
<td>CaH₂NMTPT⁺</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td>Ca₂H₂NMTPT⁺</td>
<td>13%</td>
</tr>
<tr>
<td></td>
<td>CaH₂NMTPT⁺</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>H₂NMTPT⁻³⁻</td>
<td>9%</td>
</tr>
<tr>
<td></td>
<td>CaH₂NMTPT⁻²⁻</td>
<td>8%</td>
</tr>
<tr>
<td></td>
<td>H₂NMTPT⁻³⁻</td>
<td>7%</td>
</tr>
<tr>
<td>8: [Ca²⁺] = 0.005</td>
<td>CaH₂NMTPT⁻³⁻</td>
<td>35%</td>
</tr>
<tr>
<td></td>
<td>Ca₂H₂NMTPT⁻²⁻</td>
<td>24%</td>
</tr>
<tr>
<td></td>
<td>Ca₂H₂NMTPT⁺</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>H₂NMTPT⁺²⁻</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>HNTMT⁻⁵⁻</td>
<td>4%</td>
</tr>
<tr>
<td></td>
<td>CaH₂N₃NTPT⁻</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>H₂NMTPT⁻³⁻</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>CaH₂NMTPT⁺</td>
<td>1%</td>
</tr>
</tbody>
</table>

The control solution (#1) and acidic solution (#3) have about the same amount of negatively charged species (71% and 62% respectively) and also have a similar trend on the graph in Figure 4-5 after six or seven desorption steps. The figure shows that solutions eight (low Ca²⁺ concentration) and four (low H⁺ concentration) do not dramatically increase the NTMP concentration nor does solution three (high H⁺ concentration) reduce the NTMP concentration. These observations contradict the hypothesis that the solubility of calcium-phosphonate complexes govern the rate of desorption. A possible reason for this discrepancy is that a small amount of NTMP may adsorb to the mineral surface irreversibly. This observation could be easily overlooked at high inhibitor concentrations. In other words, a small portion of the inhibitor may attach
itself to barite regardless of how much calcium, calcium phosphonate complex, and free phosphonate are in solution. Morel [20] and Hering discuss the adsorption of metals to oxide surfaces as well calcite and sulfide minerals. They conclude that if the metal ion is in excess, the surface will behave like metal species and form coordinative bonds with the ligands. In the case of NTMP adsorption onto barium sulfate, the excess of calcium in solution may have caused BaSO₄ to behave like Ca²⁺ and form relatively strong coordinative bonds with NTMP.

Because the concentration of inhibitor on the solid was calculated rather than measured, the barium sulfate remaining at the end of the study was extracted to verify this data (section 3.3.5 and 3.3.4). Initially the Ignition method described in Chapter 3 was used, but less than 50% of the inhibitor was recovered. Therefore, a more drastic extraction procedure was developed that removed about 90% of the NTMP from the solid. Table 4-4 shows the amount of NTMP removed from the solid with time. Approximately one gram of BaSO₄ was extracted with 2 mL of concentrated HCl and then heated at 70°C for a period of 24 hours. Next, the solution was allowed to cool, diluted to approximately 37 mL with DI water, and centrifuged at 2000 rpm for 15 minutes. The solution was centrifuged at a low speed to avoid breaking the glass vial in which the extraction procedure was performed. After centrifugation, the supernatant was removed and filtered as before and analyzed according to sections 3.2.1 and 3.2.2 respectively.
Table 4-4. Amount of NTMP Recovered from BaSO₄ with Increasing Time.

<table>
<thead>
<tr>
<th>Extraction Time</th>
<th>% NTMP Recovered from BaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 minutes</td>
<td>26%</td>
</tr>
<tr>
<td>1 hour</td>
<td>72%</td>
</tr>
<tr>
<td>24 hours</td>
<td>90%</td>
</tr>
</tbody>
</table>

The majority of NTMP was removed in one hour, and yet an additional 23 hours was still required to achieve only 90% recovery. Perhaps the fraction of NTMP that is so difficult to remove from the solid is responsible for the desorption hysteresis. This resistant Ca-H-Phn solid that is sorbed to the barium sulfate surface could be incorporated into the crystal lattice somehow which would explain the 30% recovery of phosphonate commonly found during field squeeze treatments [70] as well as the underprediction of the inhibitor return curve made by SqueezeSoft™.
CHAPTER 5: COLUMN WORK

For the purpose of simulating a squeeze treatment shut-in, several column studies were performed and analyzed. In the first five experiments a known concentration of NTMP was injected into a column packed with Frio sandstone followed by an overflush of sodium chloride solution and then "shut-in" for a period of about 24 hours. After shut-in, the column was flushed with synthetic brine (the postflush) and the effluent and solid material were analyzed for NTMP. In the last column study, Iceland Spar calcite, Ottawa White sand, and reagent grade CaCO₃ powder were used for reasons to be discussed later in section 5.3.

5.1 BACKGROUND

The governing equations used by SqueezeSoft™ to calculate the speciation of the aqueous and solid phases are based on the interaction between NTMP and well known carbonate chemistry. Therefore, a fundamental understanding of carbonate chemistry, inhibitor chemistry, and inhibitor/rock interaction is essential for the analysis of a squeeze treatment. The primary difference between the laboratory simulations and the actual field conditions is probably related to the pressure, for example 1900 to 12,000 psi as compared to 14.7 psi in the laboratory. Pressure is not believed to have a substantial impact for most of these aqueous reactions [8].
5.1.1 CARBONATE CHEMISTRY

Carbonate chemistry in the subsurface is primarily dependent on the dissolution of calcite in the bulk solution. Calcite is a rock forming mineral close in composition to pure calcium carbonate. Magnesium is a common substitute for calcium in the crystal lattice. Less common substitutes for calcium are manganese, iron, and strontium. Calcite, which is ubiquitous in rock formations, has a solubility, which increases with increasing CO₂ pressure and decreasing temperature [34]. Once in solution, calcite will dissociate in the following manner (Equation 5-1):

\[
CaCO₃ \leftrightarrow Ca^{2+} + CO_3^{2-}. \quad (5-1)
\]

Carbonic acid (H₂CO₃) is capable of dissociating into bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) or evolving from solution as carbon dioxide (CO₂) (Equation 5-2):

\[
CO_3^{2-} \leftrightarrow HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2. \quad (5-2)
\]

These reactions occur as brine and other produced fluids are pumped to the surface causing a decrease in the gas pressure and aqueous phase temperature. Once equilibrium has been reached, the concentration of each species may be calculated. Equation 4-1 can be used to calculate the concentration of calcium and carbonate (log K_{sp} = 8.041 @ 25°C and 1 atm). Equation 5-3 can be used to calculate the bicarbonate concentration if K₂,
carbonate, and pH are known. The equilibrium constant, $K_2$, is $10^{-10.328}$ at 25°C and 1 atm:

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 10^{-10.328}. \quad (5-3)$$

Aqueous carbon dioxide can be calculated with Equation 5-5, where the equilibrium constant, $K_1$, is reported at 25°C and 1 atm as well:

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} = 10^{-6.347}. \quad (5-5)$$

Finally, the partial pressure of carbon dioxide ($P_{CO_2}$), may be calculated using Henry's law in Equation 5-6 [21]:

$$K_H = \frac{[CO_2]}{[P_{CO_2}]} = 10^{-1.481}. \quad (5-6)$$

According to the Law of Conservation of Charge, the sum of all of the positive charge and negative charge in solution must equal each other (Equation 5-7); this is referred to as a charge balance. Once the values of all constituents in solution are known, they can be used in a charge balance to verify the accuracy of the measurements used to obtain some or all of them and validate the carbonate chemistry occurring:
\[ 2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]. \] 

(5-7)

5.1.2 INHIBITOR CHEMISTRY

Carbonate chemistry is a complex topic further complicated with the introduction of the phosphonic acid, NTMP. The calculations performed by SqueezeSoft™ are based on the dissolution reactions of calcium carbonate, the solubility product of NTMP, and calcium. The dissolution reaction between calcium and a generic phosphonate is described as follows [3] (Equation 5-8):

\[ Ca_xH_{n-2x}Phn(cr) \rightarrow xCa^{2+} + (n-2x)H^+ + Phn^{n-}, \] 

(5-8)

where, Phn = the phosphonate ligand,
\[ n = \text{the number of ionizable protons on the phosphonate group, and} \]
\[ x = \text{the stoichiometric coefficient.} \]

Equation 5-9 illustrates the solubility product of calcium and phosphonate which is similar to Equation 4-1:

\[ K_{sp} = (Ca^{2+})^x (H^+)^{(n-2x)} (Phn^{n-}). \] 

(5-9)

Frostman discusses the speciation model [71], developed by the BCC research group, which is used to calculate the equilibrium constant for phosphonate. The speciation of calcium and NTMP, which is determined in the model, is illustrated in Figure 5-1.
\[
\begin{align*}
&\text{NMTP}^{6-} \\
\downarrow &\text{HNMTMP}^{5-} \rightarrow \text{CaHNTMP}^{3-} \rightarrow \text{Ca}_2\text{HNTMP}^{1-} \rightarrow \text{Ca}_3\text{HNTMP}^{1+} \\
\downarrow &\text{H}_2\text{NMTP}^{4-} \rightarrow \text{CaH}_2\text{NTMP}^{2-} \rightarrow \text{Ca}_2\text{H}_2\text{NTMP} \\
\downarrow &\text{H}_3\text{NMTP}^{3-} \rightarrow \text{CaH}_3\text{NTMP}^{1-} \rightarrow \text{Ca}_2\text{H}_3\text{NTMP}^{1+} \\
\downarrow &\text{H}_4\text{NMTP}^{2-} \rightarrow \text{CaH}_4\text{NTMP} \\
\downarrow &\text{H}_5\text{NMTP}^{1-} \rightarrow \text{CaH}_5\text{NTMP}^{1+} \\
\downarrow &\text{H}_6\text{NMTP} \\
\downarrow &\text{H}_7\text{NMTP}^{1+}
\end{align*}
\]

**Figure 5-1. NTMP and Ca\(^{2+}\) Speciation used in NTMP Speciation Model & SqueezeSoft™.**

This NTMP speciation model is an interactive spreadsheet that calculates the stability constants, equilibrium concentration, and mole fraction of the Ca-NTMP species in solution. It also determines the free Ca\(^{2+}\), free NTMP\(^{6-}\), and fraction of Ca/NTMP\(^{6-}\) complexes. Equations 5-10 through 5-12 describe the equilibrium relationship of a generic phosphonic acid:

\[
H_{i-1}\text{Phn}^{(n-i+1)-} + H^+ \leftrightarrow H_i\text{Phn}^{(n-i)-} , 
\]

(5-10)

\[
K_i = \frac{(H_i\text{Phn}^{(n-i)-})}{(H^+)(H_{i-1}\text{Phn}^{(n-i+1)-})},
\]

(5-11)
\[ \log K_i = a_{H^+} + b_{H^+} |q_{i-1}|, \quad \text{for } i \geq nN+1, \quad (5-12) \]

where, \( H^+ \) = the concentration of hydrogen ions in solution
\( a_{H^+} \) = a speciation constant determined from experimental titration data,
\( b_{H^+} \) = a speciation constant determined from experimental titration data,
\( q_{i-1} \) = the value of the charge on the \((i-1)\)th species, and
\( nN \) = the number of protons associated with a nitrogen.

A similar set of equations may be written for calcium phosphonate complexes:

\[ Ca_{j-1}H_i Phn^{(n-i-2j+2)^-} + Ca^{2+} \leftrightarrow Ca_jH_i Phn^{(n-i-2)^-}, \quad (5-13) \]

\[ K_{ij} = \frac{(Ca_jH_i Phn^{(n-i-2)^-})}{(Ca^{2+}) (Ca_{j-1}H_i Phn^{(n-i-2j+2)^-})}, \quad (5-14) \]

\[ \log K_{ij} = a_{Ca^{2+}} + b_{Ca^{2+}} |q_{2j-2+i}|, \quad \text{for } i \geq nN+1, j \geq 1, \quad (5-15) \]

where, \( a_{Ca^{2+}} \) = a speciation constant determined from experimental titration data,
\( b_{Ca^{2+}} \) = a speciation constant determined from experimental titration data,
\( q_{2j-2+i} \) = the value of the charge on the \((i-1)\)th species.

Table 5-1 lists the equations used to calculate the speciation constants as a function of ionic strength and temperature. The equilibrium constant can be calculated for any Ca-NTMP complex.

<table>
<thead>
<tr>
<th>Table 5-1. Speciation Constants for NTMP [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>( a_{H^+} )</td>
</tr>
<tr>
<td>( b_{H^+} )</td>
</tr>
<tr>
<td>( b_{Ca^{2+}} )</td>
</tr>
</tbody>
</table>
The $a_{Ca^{2+}}$ constant was not included in the table because this term does not significantly improve the model fit of the data.

Table 5-2 lists the stability constants, equilibrium concentration, and mole fraction calculated by SqueezeSoft™.

<table>
<thead>
<tr>
<th>Species</th>
<th>Stability Constant</th>
<th>Equilibrium Concentration (M)</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNMTMP$^{2-}$</td>
<td>12.30</td>
<td>1.73E-03</td>
<td>5.18E-02</td>
</tr>
<tr>
<td>H$_2$NMTP$^{4-}$</td>
<td>18.98</td>
<td>3.17E-03</td>
<td>9.46E-02</td>
</tr>
<tr>
<td>H$_3$NMTP$^{5-}$</td>
<td>24.52</td>
<td>4.20E-04</td>
<td>1.25E-02</td>
</tr>
<tr>
<td>H$_4$NMTP$^{6-}$</td>
<td>28.93</td>
<td>4.04E-06</td>
<td>1.21E-04</td>
</tr>
<tr>
<td>H$_5$NMTP$^{7-}$</td>
<td>32.19</td>
<td>2.82E-09</td>
<td>8.43E-08</td>
</tr>
<tr>
<td>H$_6$NMTP</td>
<td>34.32</td>
<td>1.43E-13</td>
<td>4.27E-12</td>
</tr>
<tr>
<td>H$_7$NMTP$^{8+}$</td>
<td>35.30</td>
<td>5.25E-19</td>
<td>1.57E-17</td>
</tr>
<tr>
<td>CaHNTMP$^{3-}$</td>
<td>15.06</td>
<td>1.27E-02</td>
<td>3.79E-01</td>
</tr>
<tr>
<td>CaH$_2$NTMP$^{2-}$</td>
<td>21.19</td>
<td>6.50E-03</td>
<td>1.94E-01</td>
</tr>
<tr>
<td>CaH$_3$NTMP$^{1-}$</td>
<td>26.18</td>
<td>2.42E-04</td>
<td>7.24E-03</td>
</tr>
<tr>
<td>CaH$_4$NTMP</td>
<td>30.03</td>
<td>6.55E-07</td>
<td>1.96E-05</td>
</tr>
<tr>
<td>CaH$_5$NTMP$^{1+}$</td>
<td>32.74</td>
<td>1.29E-10</td>
<td>3.85E-09</td>
</tr>
<tr>
<td>Ca$_2$HNTMP$^{1-}$</td>
<td>16.71</td>
<td>7.31E-03</td>
<td>2.19E-01</td>
</tr>
<tr>
<td>Ca$_2$H$_2$NTMP</td>
<td>22.29</td>
<td>1.06E-03</td>
<td>3.16E-02</td>
</tr>
<tr>
<td>Ca$_2$H$_3$NTMP$^{1+}$</td>
<td>26.73</td>
<td>1.11E-05</td>
<td>3.31E-04</td>
</tr>
<tr>
<td>Ca$_3$HNTMP$^{1+}$</td>
<td>17.26</td>
<td>3.34E-04</td>
<td>9.98E-03</td>
</tr>
</tbody>
</table>

In addition to the information in Table 5-2, the model calculated the free calcium fraction to be 0.2566, the free NTMP fraction to be $6.83 \times 10^{-8}$, and the fraction of NTMP complexed by calcium to be 0.8409. This spreadsheet also outputs a surface plot of the total NTMP mole fraction as shown in Figure 5-2:
Figure 5-2. Surface Plot of Ca-H-NTMP Fraction Determined by NTMP Speciation Model (Developed by Rice University Brine Chemistry Consortium Research Group).

These equations coupled with basic carbonate relationships are used by SqueezeSoft™ to determine the species in solution as they react with rock formations. Further research into the interactions that take place between the phosphonates and rock formation will elucidate the mechanisms that determine the amount of inhibitor retained by the formation and the rate at which phosphonate is released.

5.1.3 INHIBITOR/ROCK INTERACTION

The underlying chemical principles of SqueezeSoft™ are based on the conclusions derived from this research group’s previous work. They have proposed the idea that the actual mechanism controlling the scale inhibition process of phosphonates is governed by
the interaction of calcite with the inhibitor. As stated in Chapter 2, calcite is assumed to be the primary reaction site. The dissolution of this mineral is believed to be prevented when the inhibitor covers a certain percentage of its surface or it reacts with the inhibitor to form a precipitate. In either case, the inhibitor is responsible for preventing calcite dissolution. The BCC research group also states that initially, the inhibitor releases two protons as each calcium is complexed by NTMP as shown in Equation 5-9:

$$H_6NTMP + CaCO_3(cr) \rightarrow CaH_4NTMP(aq) + H_2CO_3(aq). \quad (5-9)$$

The CaH_4NTMP that is produced in Equation 5-9, is capable of adsorbing to the CaCO_3 surface as long as the solution remains undersaturated with respect to CaH_4NTMP. Once the solution is supersaturated, CaH_4NTMP will precipitate. This newly formed solid will begin to cover the mineral surface; thereby poisoning the calcite surface and preventing further dissolution. However, if the solution remains undersaturated, CaH_4NTMP will react with the mineral in the following manner:

$$CaH_4NTMP(aq) + CaCO_3(cr) \rightarrow Ca_{2.5}HNTMP(cr) + H_2CO_3(aq). \quad (5-10)$$

If the solution should become supersaturated with respect to Ca_{2.5}HNTMP, then this solid will precipitate to form a barrier around calcite, also poisoning the surface and preventing its dissolution. At this point, if the solution is undersaturated with both CaH_4NTMP and Ca_{2.5}HNTMP, then CaCO_3 will continue to dissolve until the system has reached
equilibrium. Finally, if the solution becomes saturated with calcite but remains undersaturated with CaH₄NTMP and Ca₂.₅HNTMP, a third complex will form. This complex, CaHNTMP⁻, is also able to adsorb onto the calcite surface following a linear adsorption isotherm. Figure 5-3 depicts the interaction between NTMP and the calcite in rock formations.

\[ \text{H}_4\text{NTMP}^{2-} + \text{Ca}^{2+} \rightarrow \text{Calcite} \]

\[ \text{CaH}_4\text{NTMP} \]

\[ \text{Calcite surface is} \quad \text{poisoned by inhibitor} \]

\[ \text{Ca}^{2+}, \text{HCO}_3^- \]

\[ \text{Ca}_2.₅\text{HNTMP} \]

\[ \text{Calcite surface is} \quad \text{poisoned by inhibitor} \]

**Figure 5-3. Illustration of NTMP/Calcite Reactions**

In an actual squeeze operation, the system is shut-in for a period of one to three days after overflush allowing it to reach equilibrium. After shut-in, the oil, gas, and brine, are pumped from the reservoir. Immediately after production is resumed, there is a spike in the concentration of inhibitor in the produced fluid. Over the next few days, this spike drops significantly and levels off at a concentration ranging between 0.5 and 0.1 mg/L.
The residual concentration remains low because the inhibitor desorbs at a rate much slower than it adsorbed. This phenomenon was demonstrated in the adsorption/desorption studies presented in chapter four. Theoretically, the inhibitor concentration will remain at this level until it is exhausted. The placement of the phosphonate and its movement in the system during a squeeze treatment is essential for optimization of this process.

5.2 EXPERIMENTAL PROCEDURE

A series of column studies were designed to simulate a squeeze shut-in in a manner simple enough that it could be modeled relatively easily and yet represent the real process accurately. Glass columns (High Resolution from Pharmacia) with an inner diameter (ID) of 16 mm and a maximum bed height of 6.9 cm were packed with 250 – 710 μm sieved, washed, and dried Frio sandstone. One end was fitted with an adjustable adaptor and the other with a fixed adaptor. Each adaptor has 0.5 mm ID tubing running to a ¼-28 M6 adaptor, which connects the Pharmacia tubing to standard 0.03" ID peek tubing. Before each run, the glass column was washed with phosphate-free Liqui-Nox, rinsed with acetate, and allowed to dry in order to insure a clean surface. Next, the column was packed with 32 – 33 grams of sandstone. Filters were placed at each end of the column in between the core material and the adaptors. These adaptors were equipped with a special mechanism which allows fluid to evenly spread across the cross-sectional area of the column creating plug flow. An excess amount of tubing was attached to the inlet adaptor creating a heating coil. This allowed the injected fluid to reach 70°C before
entering the column. Synthetic brine (1M NaCl, 0.5M CaCl$_2$, 5mM PIPES buffer) was pumped out of a glass bottle that had been degassed with helium, via a high-pressure syringe pump (PHARMACIA LKB Pump P500). Next, the brine flowed through the heating coil, and into the column in an upward flow for a minimum period of 24 hours to force air and other gases out of the pore spaces. After the column was saturated, it was submerged in a 70°C temperature bath. Figures 5-4 and 5-5 illustrate the equipment used.

![Diagram of Glass Column](image)

*Figure 5-4. Diagram of Glass Column*

Following saturation, the inhibitor pill (inhibitor solution) was injected into the column, with another syringe pump (Harvard Apparatus Syringe Infusion Pump 22), through a three-way valve, followed by a 1M NaCl overflush (salt solution that fills the remaining three-fourths of column pore volume).
The inhibitor and overflush were "shut-in" for approximately one day. Following shut-in, fresh synthetic brine solution was used to push the inhibitor and overflush out in the same direction it was injected. This postflush was used to remove residual NTMP from the solid before extraction. The effluent was collected (ISCO ISIS Autosampler) in ten fractions containing about one milliliter each. These fractions were diluted and then analyzed for NTMP, $\text{HCO}_3^-$, $\text{Ca}^{2+}$, and $\text{Cl}^-$ according to sections 3.2.1, 3.2.2, 3.2.6, 3.2.7, and 3.2.8. After the effluent was obtained, the solid material was removed in six sections and analyzed for NTMP according to sections 3.2.5, 3.2.1, and 3.2.4, respectively.

5.3 RESULTS & DISCUSSION

Five different column studies were performed with Frio sandstone. The first column study was used to simulate a simple baseline case. Approximately three milliliters of 1% NTMP was injected into the column at a rate of 3 mL/hr. The concentration of NTMP
sorbed to the solid material was graphed with respect to the cumulative volume in the
column (Figure 5-6).

![Graph showing solid concentration vs. cumulative volume for Column Study #1.
[NTMP] = 10,000 mg/L and Flow Rate = 3 mL/hr.]

Figure 5-6. Solid Concentration vs. Cumulative Volume for Column Study #1.
[NTMP] = 10,000 mg/L and Flow Rate = 3 mL/hr.

This plot shows that the majority of the NTMP was adsorbed in the first four milliliters or
about the first 1.5 hours; after which a residual amount was left on the surface of the
remaining core material. Column studies one, two, four, and five will be compared to a
similar graph generated by SqueezeSoft™ using the same conditions in the Chapter 6. To
verify that no NTMP was lost during injection, a mass balance was performed. Based on
the amount of inhibitor injected, measured in the effluent, and extracted from the solid, the percent recovered was calculated (Equation 5-11). An average of 95% of the NTMP in the system was recovered for the five column studies:

\[
\frac{\text{Mass on Solid}}{\text{Injected Mass} - \text{Mass in Effluent}} \times 100\%. \quad (5-11)
\]

The second column study used a 1% NTMP solution also but was injected at a faster rate (30 mL/hr). Figure 5-7 displays the result from this experiment. As expected, a faster injection rate caused NTMP to be more evenly distributed throughout the column with an average concentration of about 1000 mg/kg. The concentration of inhibitor in the first four milliliters of column study #1 was approximately 2800 mg/kg. About 73% of the NTMP injected was adsorbed in the front half of the column for the first experiment compared to 74% being adsorbed in the front three-fourths of the column in the second column study. It appears that if the flow rate is too slow, some inhibitor may never travel to the far reaches of the reservoir, thereby making the squeeze operation less effective.
Figure 5-7. Solid Concentration vs. Cumulative Volume for Column Study #2.  
[NTMP] = 10,000 mg/L and Flow Rate = 30 mL/hr.

The NTMP concentration was reduced to 0.1% for the third column study. It was hypothesized that the NTMP injected into the system was expected to be depleted before reaching the end of the column at a lower concentration or slower flow rate. The result of this experiment is shown in Figure 5-8.
Figure 5-8. Solid Concentration vs. Cumulative Volume for Column Study #3. 
\([\text{NTMP}] = 1000 \text{ mg/L and Flow Rate} = 3 \text{ mL/hr.}\)

As suspected, the inhibitor concentration drops to almost 5 mg/kg, the average solid phase concentration is 340 mg/kg. This is much less than in the two previous column studies. Approximately 75% of the inhibitor was adsorbed in the first two-thirds of the column. The trend of the line shows that the NTMP concentration will quickly reach zero mg/kg and there will not be enough inhibitor to prevent scaling past about 18 cm. In an actual application, the inhibitor return concentration would be too low to prevent scaling.

In the next column study, the concentration of the inhibitor was increased to 10% and the flow rate was still maintained at 3 mL/hr. Based on previous results, it was anticipated
that the majority of the NTMP would be located in the front half of the column because the flow rate was not high enough to disperse it well. The result of this study is illustrated in Figure 5-9.

![Graph showing inhibitor concentration vs. cumulative volume for Column Study #4.](image)

**Figure 5-9. Solid Concentration vs. Cumulative Volume for Column Study #4.**

\[ [\text{NTMP}] = 100,000 \text{ mg/L and Flow Rate} = 3 \text{ mL/hr}. \]

As predicted, the majority of the NTMP was found in the front of the column, although it does appear to be situated in the first half rather than the first third of the system (column study #1). The average concentration of solid phase NTMP in the first six milliliters is approximately 8200 mg/kg. This concentration is ten times higher than all previous
cases, which is expected because the concentration injected was ten times greater. Almost 75% of the NTMP adsorbed to the core material in the first half of the column; which is similar to the first column study.

In the first four column studies, the effluent pH was measured after it was collected and the pressure was not controlled. In the fifth column study, the pH was measured in-line with a pH cell that holds 200 μL and a flat bottom pH electrode. Additionally, a 75 psi backpressure regulator was used to insure that the carbon dioxide would remain in solution. The flow rate and injected NTMP concentration was the same as in column study #1. Despite the added control in column study #5, the solid phase concentration versus cumulative volume plot (Figure 5-10) looks quite similar to the first column study (Figure 5-6). The magnitude of the plot is smaller, but the general shape is similar. The incorporation of controlled pressure and did not have much affect on the distribution of in the fifth column study.
Figure 5-10. Solid Concentration vs. Cumulative Volume for Column Study #5. [NTMP] = 10,000 mg/L, Flow Rate = 3 mL/hr, and with Backpressure = 75 psi.

Table D-1 in Appendix D lists the solid phase concentration and volume data for all of the column studies.

The mass balance for all of the column studies is within reason except for column study #3 (Table 5-2). Because the concentration of NTMP in the third column study is 10 times lower than previous studies, it was difficult to analyze such low concentrations accurately. This problem was also encountered in the adsorption/desorption studies in chapter four and the last column study, which will be discussed later in this chapter. Due
to the difficulty of extracting less than 1 mg of NTMP per gram of solid, an 80% mass balance is considered to be within reason.

Table 5-3. Mass Balance on Column Studies in Terms of Percent NTMP Recovered from the Solid Phase

<table>
<thead>
<tr>
<th>Column Study #</th>
<th>NTMP Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99%</td>
</tr>
<tr>
<td>2</td>
<td>115%</td>
</tr>
<tr>
<td>3</td>
<td>80%</td>
</tr>
<tr>
<td>4</td>
<td>99%</td>
</tr>
<tr>
<td>5</td>
<td>119%</td>
</tr>
</tbody>
</table>

Based on carbonate chemistry, there should be about twice as many moles of bicarbonate in the effluent as there are moles of calcium. The following charge balance was performed on the effluent collected from column study #5 to verify that the preceding studies were valid (Equation 5-12):

\[
2[Ca^{2+}] + [H^+] + [Na^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [Cl^-] + \sum [NTMP]. \quad (5-12)
\]

The contribution of charge from NTMP was distributed among its respective species in the following manner based on the speciation model developed by the BCC research group (Table 5-4).
Table 5-4. NTMP Speciation at 70°C, pH = 6.3, [NTMP] = 114 mg/L,

\[ \text{[Ca]} = \text{[TDS]} = 956 \text{ mg/L} \]

<table>
<thead>
<tr>
<th>NTMP Species</th>
<th>Charge on Species</th>
<th>Fraction in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(_2)HNTMP(^-)</td>
<td>-1</td>
<td>54%</td>
</tr>
<tr>
<td>Ca(_2)H(_2)NTMP</td>
<td>0</td>
<td>17%</td>
</tr>
<tr>
<td>CaH(_2)NTMP(^2-)</td>
<td>-2</td>
<td>12%</td>
</tr>
<tr>
<td>Ca(_3)HNTMP(^+)</td>
<td>+1</td>
<td>10%</td>
</tr>
<tr>
<td>CaHNTMP(^3-)</td>
<td>-3</td>
<td>5%</td>
</tr>
</tbody>
</table>

The charge balance was deficient almost 66% of the negative charge because there was not enough negatively charged species measured to counterbalance the positively charged species. Several analyses were performed to account for this discrepancy. First, a series of batch experiments were done. In each experiment, approximately one gram of Frio sandstone and 40 mL of solution (Table 5-5) were placed in 50 mL plastic centrifuge tubes. All tubes were placed in the temperature bath/shaker set at 70°C. After 24 hours the tubes were removed and centrifuged. The supernatant from each experiment was analyzed for calcium, alkalinity (bicarbonate), chloride (experiment three only, sodium and chloride cancel each other out in experiment two), and NTMP (only experiment five) (Table 5-5).

Table 5-5. Charge Balance Batch Experiments Used to Determine the Source of the Charge Balance Discrepancy.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Solution</th>
<th>Positive Charge (mM)</th>
<th>Negative Charge (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H(_2)O</td>
<td>0.018</td>
<td>0.015</td>
</tr>
<tr>
<td>2</td>
<td>NaCl</td>
<td>0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>CaCl(_2)</td>
<td>3.773</td>
<td>3.623</td>
</tr>
<tr>
<td>4</td>
<td>PIPES</td>
<td>0.348</td>
<td>0.500</td>
</tr>
<tr>
<td>5</td>
<td>NTMP</td>
<td>0.618</td>
<td>0.653</td>
</tr>
</tbody>
</table>
The greatest discrepancy was evident in experiments two and four. Further investigation was done on the NaCl solution because the sodium and chloride should not have undergone any reaction thereby making it the simplest balance to obtain. Sodium was expected to dissociate but not react with any of the other species in solution, and a negligible amount of calcite was anticipated to dissolve in salt water. With the exception of the first experiment (deionized water); it was anticipated that experiment two would have been the simplest. Therefore, a similar set of batch experiments were performed using sodium chloride with core material and sodium chloride with 99.99% pure reagent grade calcium carbonate. The sample containing core material was allowed to equilibrate with two successive sodium chloride solutions to prevent a possible ion exchange process between the calcium in the mineral and sodium in solution from interfering with the calculation. Almost 50% less calcium was dissolved from calcite if the core material was equilibrated with NaCl solution twice. The results of this study show that a different mechanism was responsible for the poor charge balance (Table 5-6). All samples were prepared in duplicate. The chloride concentration was not used in the charge balance because its negative charge is counter balanced by sodium.
Table 5-6. Sodium Chloride Equilibration with Core Material & Calcium Carbonate

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>HCO₃⁻ (mM)</th>
<th>Ca²⁺ (mM)</th>
<th>Mg²⁺ (mM)</th>
<th>Cl⁻ (mM)</th>
<th>Total Positive Charge (mmoles)</th>
<th>Total Negative Charge (mmoles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl/Core - 1</td>
<td>9.210</td>
<td>0.8836</td>
<td>0.6561</td>
<td>0.0023</td>
<td>949</td>
<td>0.0550</td>
<td>0.0377</td>
</tr>
<tr>
<td>NaCl/Core - 2</td>
<td>9.080</td>
<td>0.6478</td>
<td>0.8424</td>
<td>0.0116</td>
<td>927</td>
<td>0.0703</td>
<td>0.0275</td>
</tr>
<tr>
<td>NaCl/CaCO₃ - 1</td>
<td>9.172</td>
<td>0.8151</td>
<td>0.4138</td>
<td>0.0251</td>
<td>945</td>
<td>0.0331</td>
<td>0.0332</td>
</tr>
<tr>
<td>NaCl/CaCO₃ - 2</td>
<td>9.230</td>
<td>0.9560</td>
<td>0.4082</td>
<td>0.0221</td>
<td>972</td>
<td>0.0329</td>
<td>0.0392</td>
</tr>
</tbody>
</table>

Table 5-6 shows an excellent charge balance for calcium carbonate equilibrated with NaCl. Unfortunately, there is still more calcium (positive charge) than can be balanced by bicarbonate (negative charge) in the two samples with core material. Because a reddish brown precipitate was observed in some of the effluent fractions collected in the fifth column study, iron precipitates were suspected of causing the negative charge deficiency. Table 3-1 shows that Frio sandstone contains 2.5% iron. It is possible that some of this iron dissolved from the core material into the aqueous solution to form a ferric complex. This compound may have reacted with bicarbonate or carbonate in solution (resulting from calcite dissolution) to form siderite, FeCO₃. This would account for the absence of more than half of the missing bicarbonate. Unfortunately, ferrous iron, Fe²⁺, is difficult to measure without being oxidized to ferric iron, Fe³⁺.

A few problems in addition to the proposed iron interference were encountered. Temperature was suspected of negatively impacting the pH measurements. The fluid flowing through the in-line pH probe probably equilibrated with the ambient air.
temperature causing the pH readings to be less accurate. The small sample size collected from the effluent posed another problem. One milliliter fractions were obtained from the effluent which were then diluted twice before being analyzed. These serial dilutions may have created an additional margin of error. Lastly, it would be advantageous to replace the synthetic buffer with a natural substitute, bicarbonate. The fluids in rock formation have been under several thousands pounds of pressure for long periods of time during which bicarbonate naturally buffers the pH.

A final column study was performed to rectify the above mentioned problems. This final study was radically different for several reasons. Instead of using core material as a solid surface, pure calcium carbonate (Iceland Spar) was used (Figure 5-11). Second, the entire experiment was performed at room temperature. Finally, 10 mL effluent samples were taken and bicarbonate was used to buffer the pH. To insure that the saturation index of the brine entering column #2 (the primary column) would be zero, synthetic brine was pumped into a column containing pure calcium carbonate before entering the second one.
From crystallography, one knows that adsorption takes place on the active sites of a crystal. The amount of active sites is related to the amount of specific surface area that a crystal has. For this reason, a layer CaCO₃ powder was used in addition to the Iceland Spar to ensure that a detectable amount of NTMP could be extracted from the solid after the squeeze treatment was completed. Therefore, the primary column contained four separate layers. The first layer consisted of 7.01 g of Ottawa white sand, the second layer contained 1.25 g of reagent grade calcium carbonate, the next layer had 4.85 g of Ottawa white sand, and the last layer consisted of 21 g of Iceland Spar calcite (ground and sieved to 425 - 600 µm) (Figure 5-12).

Figure 5-11. Schematic of Final Column Study
Figure 5.12. A Schematic of the Layers of Iceland Spar Calcite, Ottawa White Sand, and CaCO₃ Reagent Grade Powder used in the Second Column.

After the two columns were completely saturated with equilibrated synthetic brine, a different brine solution was prepared with 1.25 M NaCl instead of 1 M NaCl to be used as a tracer. It was injected into the primary column to determine the actual pore volume and degree of dispersion.

Figure 5-13 displays the results of the tracer study. Initially the pore volume was calculated to be about 10.4 mL. The tracer test reflects a pore volume closer to 11 mL with very little dispersion.
Figure 5-13. 1.25 M NaCl Tracer Study.

One pore volume of regular synthetic brine was injected following the tracer test, then an inhibitor pill and overflush was injected directly into the second column bypassing the first one. The system was “shut-in” for a period of 24 hours. After shut-in, the second column was turned around so that the fluid flowing out of the preconditioning column flowed into the outlet of the primary column, which is the opposite direction of flow. A total of 16 pore volumes of synthetic brine was pumped into the preconditioning column and then flowed into the second column to construct a profile of the inhibitor return curve (Figure 5-14).
Figure 5-14. NTMP Inhibitor Return Curve from Column Study #6

Figure 5-14 resembles a typical return curve. Initially there is a spike in inhibitor concentration followed by a long tail of low inhibitor concentration. If the effluent from the column had continued to be collected, the NTMP concentration would eventually fall below 1 mg/L. The first six samples were taken every hour, which translates, to one pore volume or approximately 10 mL. The last sample was taken after 10 hours or about 100 mL (10 pore volumes). Because the first six samples were about 10 mL each they were used to determine the NTMP concentration only. The final sample contained enough solution to be used to determine the concentration of NTMP, calcium, chloride, and
bicarbonate; all of which were used to calculate the charge balance in the effluent (Table 5-7).

<table>
<thead>
<tr>
<th>Sample</th>
<th>NTMP (M)</th>
<th>HCO₃⁻ (M)</th>
<th>Ca²⁺ (M)</th>
<th>Cl⁻ (M)</th>
<th>Calculated Na⁺ (M)</th>
<th>Total Positive Charge (moles)</th>
<th>Total Negative Charge (moles)</th>
<th>Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Brine</td>
<td>0</td>
<td>0.0058</td>
<td>0.0460</td>
<td>0.0920</td>
<td>0.0042</td>
<td>0.0962</td>
<td>0.0953</td>
<td>99.1%</td>
</tr>
<tr>
<td>Equilibrated Synthetic Brine</td>
<td>0</td>
<td>0.0058</td>
<td>0.0458</td>
<td>0.0916</td>
<td>0.0042</td>
<td>0.0958</td>
<td>0.0947</td>
<td>98.9%</td>
</tr>
<tr>
<td>Effluent</td>
<td>0.000154</td>
<td>0.0162</td>
<td>0.0448</td>
<td>0.0896</td>
<td>0.0042</td>
<td>0.0938</td>
<td>0.0929</td>
<td>99.0%</td>
</tr>
</tbody>
</table>

The first set of data was calculated from measurements performed on the synthetic brine before it entered the preconditioning column. The second row contains values calculated from measurements taken from the synthetic brine after it flowed through the preconditioning column. In all cases, the amount of sodium in solution is calculated based on the quantity of NaHCO₃ used to prepare the synthetic brine, the Na⁺ from NaCl is assumed to be counterbalanced by Cl⁻ ions. In the first two sets of data, the amount of bicarbonate in solution is also based on the amount of NaHCO₃ used to make up the synthetic brine. Both of these sets of data have an excellent charge balance. There is an equal amount of negative and positive charge in solution. The charge balance performed on the last effluent sample is deficient by approximately 10% positive charge. This is a significant improvement upon the charge balance calculated from the fifth column study, which was off by about 66%. The fact that the charge balance for the sixth column study is still off by about 10% may be due to experimental error, especially from the
bicarbonate titration. The bicarbonate titration is performed by titration of a 100 mL sample with sulfuric acid while recording the pH reading. This measurement can only be done once because the entire sample is consumed. The calcium, chloride, and NTMP measurements can be done repeatedly because they require considerably smaller sample sizes. The calcium and chloride measurements were repeated to verify the accuracy of their values. The NTMP measurement was not repeated because it contributes very little to the charge balance. It is for these reasons, that the bicarbonate determination is the probable source of error.

The solid phase distribution of NTMP on the solid is quite different than before. The most likely explanation is that the surface area of the crystals used greatly affects the amount of adsorption that takes place. Figure 5-15 shows that the majority of NTMP was adsorbed in the back of the column rather than the front. The amount of inhibitor adsorbed to the Iceland Spar is 20 times less than the amount adsorbed to the core material. Only the CaCO$_3$ reagent powder adsorbed an appreciable amount of NTMP. The Ottawa sand appears to have adsorbed some NTMP, but some powder became intermingled with it while being removed from the column, which may account for the apparent adsorption to the sand.
Figure 5-15. Solid Phase Distribution of NTMP on the Solid in Column Study #6

As shown in Figure 5-12, the front of the column was packed with Iceland Spar calcite with a particle size ranging between 425 – 600 μm. The total surface area of the Iceland Spar, calcium carbonate powder, and NTMP are shown in Table 5-8.

Table 5-8. Total Surface Area of NTMP, Iceland Spar, and CaCO₃ Powder

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Surface Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTMP</td>
<td>36.0</td>
</tr>
<tr>
<td>Iceland Spar Calcite</td>
<td>0.17</td>
</tr>
<tr>
<td>Calcium Carbonate Powder</td>
<td>18.5</td>
</tr>
</tbody>
</table>
The surface area of the Iceland Spar is 200 times lower than that of NTMP and 100 times lower than that of the reagent grade powder. Figure 5-15 shows that the majority of the adsorption took place in the calcium carbonate powder region of the column and the least amount took place in the Iceland Spar area. For this reason, surface area may be a major determining factor for the maximum amount of adsorption that can take place. This is especially important because adsorption is believed to be the primary mode of inhibitor retention for sandstone formations [55].

As discovered with the third column study, a mass balance is difficult to obtain when attempting to extract small amounts of NTMP from a solid surface. The extraction technique described in section 3.2.9 was used to measure the amount of phosphonate adsorbed, but less than 0.5 mg was removed from the solid material. Because so little was initially adsorbed, less than 20% was actually recovered. The fact that such extreme measures was used and only a few tenths of a gram were detected is indicative of the following possible explanations:

1. An extremely insoluble Ca-H-NTMP phase formed that is quite difficult to dissolve in acid and therefore almost impossible to remove with conventional analytical techniques.

2. Ca-H-NTMP adsorbed into the pore spaces of the Ottawa White sand in an irreversible manner.
3. The majority of phosphonate dried onto the aluminum weigh dishes during the Ignition method.

4. NTMP was lost during injection.

Because a mass balance was successfully obtained during previous column studies, it is unlikely there is something fundamentally wrong with the shut-in procedure.
CHAPTER 6: SqueezeSoft™ Program

SqueezeSoft™ is an interactive Excel program developed by the Rice University BCC research group for the prediction of scale inhibitor squeeze treatments in oil and gas wells. A series of laboratory studies were completed to test the ability of this program to accurately simulate a squeeze operation (Chapter 5). The solid phase inhibitor concentration verses distance plot that SqueezeSoft™ generates is compared with fieldwork performed by the BCC research group and laboratory studies done in this work. The comparison between the prediction from SqueezeSoft™ and the field and laboratory data were used to determine the limitations of the program.

6.1 BACKGROUND

Conceptually, a squeeze treatment consists of an inhibitor injection, overflush, and shut-in, followed by resumed production. As the produced fluids are pumped from the reservoir, the inhibitor concentration is monitored and has been found to resemble the curve in Figure 6-1. There is a sudden increase in inhibitor concentration followed by an equally sudden drop that levels off between 0.5 and 0.1 mg/L aqueous phase inhibitor concentration. Most inhibitors are still effective in that range. Once the produced fluid has been pumped for approximately 10 pore volumes, the Ca-Phosphonate complex has matured from an amorphous to a crystalline solid material. The crystalline phase of the solid material is assumed to dictate the solubility of the inhibitor (Chapter 4).
Figure 6-1. Conceptual Model of Squeeze Treatment Return Curve

SqueezeSoft™ was designed to predict the length of inhibition, inhibitor return concentrations, inhibitor placement in formation, and minimum inhibitor concentration required. This program can also store and retrieve squeeze data as well as assist with innovative squeeze design. SqueezeSoft™ accomplishes the above mentioned predictions by incorporating ScaleSoftPitzer™, another program written by this research...
group; recently developed inhibitor chemistry data; proposed inhibitor/rock reactions; 
and ongoing inhibitor adsorption research.

6.1.1 SCALESOFTPITZER™

ScaleSoftPitzer™ is also an interactive Excel program developed by the BCC. It uses 
brine measurements to predict pH, supersaturation, and several other gas and brine 
properties which are based on Pitzer ion-interaction equations. Table 6-1 lists the 
sparsingly soluble salts that are included in the software.

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Barite</td>
<td>BaSO₄</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>CaSO₄·½H₂O</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
</tr>
<tr>
<td>Celestite</td>
<td>SrSO₄</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
</tr>
<tr>
<td>Ferrous Sulfide</td>
<td>FeS</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Fluorite</td>
<td>CaF₂</td>
</tr>
</tbody>
</table>

Figure 6-2 displays the procedure used by this program to calculate scaling tendencies. 
Data is entered based on information gathered about the reservoir, produced fluids, and 
chosen inhibitor. ScaleSoftPitzer™ uses information given by the user to calculate the 
scale index (SI), amount of inhibitor required, and resulting scale inhibition that is 
predicted to occur.
The Pitzer theory of electrolytes is used to determine the SI calculations so that a wider range of temperature, pressure, total dissolved solids (TDS), and cosolvents may be used with empirical methods.
6.1.2 SQUEEZESOFT™ COMPUTER CODE

The SqueezeSoft™ code was written with the assumption that this process can be described by a simple box model. Equations 6-1 and 6-2 are the transport equations used in the program, where \( \alpha = 0.5 \) and \( d = 0.1 \):

\[
[C]_{x,t} = \alpha[C]_{x-1,t-1} + (1 - \alpha - d)[C]_{x,t-1} + d[C]_{x+1,t-1} \quad (6-1)
\]

where, \([C] = \) the concentration (mg/L),
\( \alpha = \) the probability of mass transfer,
\( d = \) the probability of transfer through diffusion,
\( x = \) the distance (ft), and
\( t = \) the time (days).

\[
[C]_{x,t} = (\alpha + d)[C]_{x-1,t-1} + (1 - \alpha - 2d)[C]_{x,t-1} + d[C]_{x+1,t-1} \quad (6-2)
\]

These equations are similar to the Markov Chain Equations for diffusion, described in Chapter 2 (Equations 2-37 and 2-39, respectively), except that the reaction term, \( k \), is not included. Equation 6-1 describes the transport of chemicals as they initially enter the system. Equation 6-2 describes their transport throughout the remaining compartments. The fact that \( k \) is not included is compensated for with a subroutine that reacts the constituents in each compartment before they move to the next one. This subroutine uses another program written by the BCC research group, which calculates the speciation of Ca-H-NTMP under the following conditions Table 6-2:
Table 6-2. Speciation Subroutine That Accounts for the Reaction Occurring in Each Compartment.

<table>
<thead>
<tr>
<th>Option Number</th>
<th>Option Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Speciation Only: TCa$^{2+}$, TNTMP, B$_{net}$, TCO$_3^{2-}$</td>
</tr>
<tr>
<td>2</td>
<td>CaH$_4$NTMP Solubility</td>
</tr>
<tr>
<td>3</td>
<td>Ca$_{2.5}$NTMP Solubility</td>
</tr>
<tr>
<td>4</td>
<td>CaCO$_3$ Solubility</td>
</tr>
<tr>
<td>5</td>
<td>CaCO$<em>3$ &amp; Ca$</em>{2.5}$NTMP Solubility</td>
</tr>
<tr>
<td>6</td>
<td>CaH$_4$NTMP Adsorption</td>
</tr>
<tr>
<td>7</td>
<td>Ca$_{2.5}$NTMP Adsorption</td>
</tr>
<tr>
<td>8</td>
<td>Brine pH from TCaHCO$_3$</td>
</tr>
<tr>
<td>9</td>
<td>TNTMP into Brine</td>
</tr>
<tr>
<td>10</td>
<td>Speciation only from pH, TCa$^{2+}$, TNTM, TCO$_3^{2-}$</td>
</tr>
</tbody>
</table>

The information required for the program to run is entered by the user in the spreadsheet illustrated in Appendix.

In the well data sheet, the concentrations of chemicals in the brine, characteristics of the well, type of inhibitor to be used, and other data relating to the well may be entered by the user (Appendix C, Figure C-1). The squeeze design data sheet allows the user to input the kind of preflush (if any), inhibitor pill, and overflush to be used during the squeeze treatment (Appendix C, Figure C-2). This information is read into the Excel Visual Basic program where the units are converted to the SI system. Next the ScaleSoftPitzer™ subroutine is used to determine the kind and amount of scale that will develop. It is at this point that the squeeze treatment actually begins. The code uses a box model to introduce a preflush, inhibitor pill, overflush, and then resume production. These reactions take place in the first compartment and then the reacted material continues to the next compartment as displayed in Figure 6-5, where P represents the
inhibitor. The first four rows demonstrate how SqueezeSoft™ moves the inhibitor through rock formation as a function of time and distance. At time = 1 and distance = 1, unreacted inhibitor enters the first cell. When time = 2, the remaining inhibitor in the first cell is moved to the second one, and fresh inhibitor is injected into the first cell. As inhibitor advances through the system, its concentration decreases as does the amount of calcite available. This is shown in Figure 6-3 with a P that gets smaller with time and distance as well as the top rectangle (representing calcite) which gets smaller also. The overflush (KCl) moves in a different manner. It simply pushes the reacted inhibitor deeper into the rock formation without reacting with the solid surface or inhibitor.

Figure 6-3. Numerical Simulation of NTMP/Calcite Reactions
This process continues until all of the inhibitor and overflush have been moved into the system concluding the injection process. Next, either a postflush is injected or the inhibitor return curve begins. At the very end, the information determined by SqueezeSoft™ is output as shown in Appendix D, Figures D-1 and D-2.

Figure D-1 displays the hydrogen ion, calcium, and inhibitor concentrations as they vary during the injection period. Both aqueous phase and solid phase inhibitor concentrations are reported. Figure D-2 shows the aqueous phase concentration of the inhibitor that would be desorbed from the rock formation as brine, oil, and/gas is pumped from the well. All aqueous phase concentrations are reported as mg/mL and solid phase concentrations given in normalized concentration units (mg/m²).

6.2 PROGRAM MODIFICATIONS

To simulate the shut-in process, the column was injected with an inhibitor pill, an overflush, and then a synthetic brine postflush. An actual squeeze treatment does not contain a postflush, rather brine is pumped out of the rock formation in a direction opposite that of the injection. For this reason, the SqueezeSoft™ program was altered to reflect this difference. Refer to Appendix E and F to compare the two different versions of the subroutine, which performs this task.

The lines of code that instruct the computer to move the reacted fluids through the reservoir in a direction opposite of how the injected fluids were pumped were replaced
with information regarding a postflush. The postflush consisted of the same synthetic
brine solution and flowed in the identical direction as the preflush. The sole purpose of
using a postflush was to push the inhibitor pill and overflush out of the column so that no
further reactions could take place. The inhibitor return was completely omitted from the
modified version of SqueezeSoft™.

6.4 COMPARISON WITH FIELD DATA

Field data from the Gladys McCall and Smith wells were imported into the
SqueezeSoft™ program. The information obtained about the well, brine, and inhibitor
pill was used to predict the inhibitor return curve. In Figures 6-3 and 6-4 the observed
aqueous phase inhibitor curves are plotted with the predicted inhibitor curve from
SqueezeSoft™. As previously discussed in Chapter 4, the residual concentration that was
predicted by the computer program is greater than what is actually observed in the field.
Based on the adsorption/desorption studies discussed earlier and the suspected low
solubility of the residual Ca-H-NTMP found in column study #6; it is believed that there
is a Ca-H-NTMP phase formed that adsorbs to core material and desorbs at a very slow
rate if at all. This may explain why 30% of injected inhibitor is never recovered. The
overall trends of the observed data and predicted data in Figure 6-4 are very similar
except that SqueezeSoft™ initially under predicts and after 10,000 bbl it over predicts.
Figure 6-4. Field Results from the Gladys McCall Well. \([\text{P}hn] = 41, 190 \text{ mg/L}.\)

Figure 6-5, displays the same pattern as Figure 6-4 except that the observed and predicted data cross each other after 1000 bbl instead of 10000 bbl.
Figure 6-5. Field Results from the N. R. Smith Well. [Phn] = 21, 293 mg/L.

Equation 6-4 is used by SqueezeSoft™ to calculate the $K_{wp}$ value for the Ca$_{2.5}$HPhn phase.

$$K_{wp}^{Ca_{2.5}Phn} = A - 5.32\sqrt{IS} + 1.76IS - 2032T$$ (6-3)

where, $A$ = the experimentally determined $K_{wp}$ value,
$IS$ = the ionic strength (M), and
$T$ = the temperature (K).

Originally the value for $A$ in SqueezeSoft™ was 32.92, but using the information derived from the adsorption/desorption studies described in Chapter 4 that number was changed to 33.80. It was assumed that the affect of ionic strength and temperature is small
therefore, the same correction factors for the Ca$_{2.5}$Phn phase were used for this new unidentified phase. Figures 6-6 through 6-9 display the observed inhibitor return curves along with the old and new predictions.

![Graph showing inhibitor concentration vs. volume (bbl) with data points and lines for observed, old prediction, and new prediction.]

**Figure 6-6.** The Observed Inhibitor Return Concentration from the Gladys McCall Well being Compared to SqueezeSoft™'s Old and New Predictions.

In all cases, the $K_{sp}$ value underpredicts the observed inhibitor return curve and the old $K_{sp}$ over predicts the return curve. Figure 6-6 displays the result for the Gladys McCall well, where Table 4-2 lists the field conditions and the calculated ion product.
Figure 6-7. The Observed Inhibitor Return Concentration from the N. R. Smith Well being Compared to SqueezeSoft™’s Old and New Predictions.

The ion product for the well differs from the ion product calculated for the desorption data by about 0.6 log units. The ion product for the N. R. Smith well only differed by 0.3 log units and the new prediction is much closer to the observed data than the old prediction. The amount of variance between the calculated ion product for the field data and laboratory results does not appear to affect the degree to which the prediction closely fits the data as demonstrated in Figure 6-8.
Figure 6-8. The Observed Inhibitor Return Concentration from the O'Daniels Well being Compared to SqueezeSoft™'s Old and New Predictions.

The O'Daniels well has a log ion product of 25.6 which is 1.6 log units greater than the value calculated from the desorption study and yet the new prediction fits the observed data more closely than the old prediction. On the other hand, the ion product calculated for the Pleasant Bayou well is only 0.3 log units greater than value determined from the desorption study and the observed inhibitor curve appears to be just as close to the old prediction as to the new (Figure 6-9). Perhaps the new prediction would be more accurately if the temperature and ionic strength dependence were independently determined for this new phase.
Figure 6-9. The Observed Inhibitor Return Concentration from the Pleasant Bayou Well being Compared to SqueezeSoft™’s Old and New Predictions.

6.5 COMPARISON WITH LABORATORY DATA

The laboratory data was compared to the SqueezeSoft™ program via the solid phase concentration versus distance plot. The trend of column studies one and five (1% NTMP inhibitor solution, 3 mL/hr flow rate) match the computer program output best as shown in Figures 6-10 and 6-11. The output for SqueezeSoft™ shows that the majority of inhibitor resides in the front half of the column followed by a negligible residual concentration in the rest. Apparently, almost all of the inhibitor is consumed before it has
an opportunity to travel the entire length of the column. Both column studies (Figure 6-10 and Figure 6-11) are comparable to the prediction made by SqueezeSoft™.

![Graph showing inhibitor concentration vs. distance](image)

**Figure 6-10. Laboratory Results from Column Study #5.** [NTMP] = 10,000 mg/L, Flow Rate = 3 mL/hr, with Backpressure = 75 psi.

For both column studies #1 and #5 SqueezeSoft™ slightly underpredicts the amount of inhibitor retained by the solid. The majority of the NTMP resides in the front third of the column with a residual amount found in the rest of the column. SqueezeSoft™ satisfactorily predicts the distribution of NTMP on the solid for these conditions. The only difference between column studies five and one are the pressure control.
Each compartment assumes that the inhibitor has sufficient time to reach equilibrium with the solid phase in the column. Unfortunately, squeezing out the inhibitor does not account for changes in the flow rate. Instead, it reduced casing column study 5 to more closely resemble the prediction made by the system, which had a backpressure of 75 psi, the magnitude of the inhibitor return was

Figure 6-11. Laboratory Results from Column Study #1. [NIP] = 0.000 mg/L,

Flow Rate = 3 ml/hr, and with out backpressure.
Figure 6-12 does not compare as well with the prediction because the flow rate was increased from 3 mL/hr to 30 mL/hr. In fact, the phosphonate moved through the system so quickly that it distributed itself more evenly throughout the column.

![Graph showing laboratory results from Column Study #2.](image)

**Figure 6-12. Laboratory Results from Column Study #2.** [NTMP] = 10,000 mg/L, Flow Rate = 30 mL/hr, and with out Backpressure.

Next, column study #4 is compared with the predication from SqueezeSoft™. When 100,000 mg/L NTMP is injected, inhibitor is distributed deeper into the system as illustrated in Figure 6-13. In this case, inhibitor is found in the front two-thirds of the systems. Afterwards, the phosphonate concentration sharply drops to zero.
SqueezeSoft™ models the distribution of inhibitor in the solid phase more accurately when the concentration is varied than when the flow rate is modified.

**Figure 6-13. Laboratory Results from Column Study #4.** [NTMP] = 100,000 mg/L, Flow Rate = 3 mL/hr, and without Backpressure.

Differences in the level-off concentrations of the measured versus the predicted residuals with SqueezeSoft™ clearly need to be addressed. There are probably two sources of these differences, the solid to solution ratio and kinetics. All of the column studies were performed using ground core material that was packed into a column. This procedure changes the solid to solution ratio and flow dynamics. If solid core plugs were used, it should be possible to more realistically test the program's predictions. Secondly, the affects of solid/brine reaction kinetics and the impact of mass transport on those kinetics
might also be the cause of these differences. Neither of these aspects are presently included in SqueezeSoft™. It is recommended that both kinetics and better mass transport limitations be incorporated into future SqueezeSoft™ versions.
CHAPTER 7: Conclusions

7.1 CONCLUSIONS

The results from the batch experiments and column studies provide significant insight into the precipitation and dissolution of calcium phosphonate complexes when they interact with solid surfaces. The following results are described in the remaining sections of this chapter:

1. New crystalline phase identified with a $K_{sp} \equiv 24.0$

2. Extremely insoluble Ca-H-NTMP phase discovered

3. Novel approach to column design using pure CaCO$_3$ crystals

4. Incorporation of new crystalline phase into SqueezeSoft™

7.1.1 ADSORPTION/DESORPTION STUDIES

Two sets of adsorption/desorption studies were done. The first consisted of four identical samples with NTMP adsorbed to BaSO$_4$ in a pH 6.42 buffer solution. The second study was composed of NTMP also adsorbed to barium sulfate but with ten different buffer solutions where the pH, calcium concentration, or ionic strength was varied. Rather than observing a process similar to what was seen before by members of the Rice University BCC, a mechanism other than solubility may control the desorption of NTMP from BaSO$_4$. Previously, members of the BCC discovered that at least two crystalline calcium phosphonate phases exist: Ca$_{2.5}$HNTMP and CaH$_4$NTMP. The results from this study suggest that another crystalline phase may exist at low inhibitor concentration with a $K_{sp}$
of about 24.0. The ion product calculated from the BCC speciation model for the field
data and the desorption study are almost equal to one another. The second study was
performed to determine if the solubility of the crystalline phase at low concentrations
does indeed govern desorption. The results of this study contradict the findings of the
BCC. The use of a highly acidic buffer solution (1.42 pH) to remove NTMP from barium
sulfate was very successful. Even a less acidic solution (4.42 pH) removed a
considerable amount of NTMP in about six desorption steps. Surprisingly the low
calcium solution (0.005 M) desorbed less NTMP than the control. The most interesting
finding from these studies is the low solubility of the Ca-H-NTMP phase formed in the
presence of BaSO4. Despite high temperature and concentrated acid, this calcium-
phosphonate phase requires more than 24 hours for complete dissolution. It is for these
reasons that a different mechanism is suspected of controlling desorption at lower
inhibitor concentrations.

7.1.2 COLUMN STUDIES

A total of six column studies were performed; five with Frio Sandstone core material and
one with a combination of Iceland Spar calcite crystals, Ottawa White sand, and reagent
grade CaCO3 powder. The first four column studies illustrated the dramatic affect that
flow rate and concentration can have on the effectiveness of a squeeze treatment. In
order to have a satisfactory squeeze; a substantial portion of the rock formation must be
saturated with inhibitor. If a large enough area is coated, the inhibitor return
concentration will remain high enough to prevent scaling. When the injection rate of the
inhibitor and overflush is too high, the phosphonate may not have sufficient time to react with calcite. On the other hand, a low injection rate coupled with a high concentration can cause large amounts of Ca-Phosphonate precipitate to from close to the well bore area. Inhibitor concentrations that are too low or too high can cause similar problems. If the concentration is not high enough, an insufficient amount of scale inhibitor will be applied to the core material creating an ineffective squeeze. An excessively high amount of inhibitor may simply be wasteful and costly.

The fifth column study demonstrated the presence of other cations that may form mineral salts such as siderite. The formation of iron carbonate may not be prevented by the particular inhibitor used. Due to the possible interference a sixth column study was performed, wherein the most interesting observations were seen. The surface area was suspected to influence the degree of adsorption that will occur. The use of CaCO₃ with two different surface areas in the last column study revealed that a solid surface with 100 times more surface area adsorbed more than five times as much inhibitor. Just as in the BaSO₄/NTMP batch studies, the calcite crystals had to be extracted with hot, concentrated acid for extended periods of time only to recover a portion of the NTMP. Confirmation of the dependence of adsorption on specific surface area and possibly the formation of a highly insoluble Ca-H-NTMP phase could reveal much information about the precipitation and adsorption mechanisms of calcium phosphonate salts. The use of a pure material in a column study as opposed to natural material proved to unveil more information than anticipated.
7.1.3 SQUEEZE SOFT™ PROGRAM

SqueezeSoft™ is a useful tool capable of assisting in the effective design of a squeeze operation. This computer program enables the user to predict the type and amount of inhibitor required based primarily on information about the well and its fluids. SqueezeSoft™ will output information on the concentration of calcium and inhibitor, as well as the pH during the injection. It will also predict the concentration of inhibitor in the return curve enabling the user to determine the life of the squeeze treatment.

Despite all of the information that SqueezeSoft™ provides, it does have its limitations. This program does not account for mass transport nor does it accurately predict the inhibitor return concentration. In fact, SqueezeSoft™ typically over predicts this concentration. The new $K_{sp}$ value determined from the adsorption/desorption studies was used to predict the return concentration. This new prediction along with the old one, actually bracketed the observed results. Further study of the new crystalline phase could allow for a more accurate determination of the inhibitor return curve.

The comparison between the predictions made by SqueezeSoft™ and the laboratory shut-ins showed how well the computer program models when the concentration or pressure changes. Some of the figures appear to be almost identical. As more information about the solution chemistry of phosphonates is discovered, SqueezeSoft™ could potentially evolve into an excellent tool for the design of squeeze treatments.
7.2 ENVIRONMENTAL SIGNIFICANCE

The placement of phosphonate containing chemicals in rock formation may have environmental significance based on its fate in the natural environment after a squeeze treatment. The ability of acidic phosphonates to sequester metals (as is suspected in the fifth column study) directly impacts their fate in the environment. In general, the study of polyprotic acids such as NTMP can be applied to other polymers and detergents as they make their way to the natural environment via municipal and industrial waste. In addition, an increased understanding of the fundamental nucleation and crystal growth mechanisms can be applied to many other chemical constituents being introduced into the environment.

7.3 FUTURE WORK

There are two areas that could be expanded upon in the adsorption/desorption studies the identification of a third Ca-H-NTMP crystalline phase and its respective stoichiometry and further investigation of the mechanism that controls the desorption of NTMP from a solid surface at low concentrations.

The successful extraction of low levels of phosphonate from a solid material would provide insight into the kinds of scale that is actually formed in rock formations. The determination of whether or not this Ca-Phosphonate complex is truly insoluble under acidic and high temperature conditions as well as how it forms is essential to the understanding of the chemistry of mineral scale deposits.
Several items could be incorporated into SqueezeSoft\textsuperscript{TM} to improve its accuracy and expand its capabilities. The inclusion of a mass transport term into the governing equation would give the program more versatility. Also, the addition of a confirmed third Ca-H-NTMP phase with its ionic strength and temperature dependence could correct the over prediction of the inhibitor return curve. Further column studies using pure calcium carbonate could lead to better understanding of how adsorption and surface area affect the inhibition of mineral deposits. As Ca-Phosphonate behavior is continuously studied, further information derived for other phosphonates could be added to SqueezeSoft\textsuperscript{TM} as well. The interaction of corrosion, hydrate, and halite inhibitors with scale inhibitors during a squeeze treatment could also be used to more realistically describe a squeeze treatment.
BIBLIOGRAPHY


APPENDIX A: Raw Data from Adsorption/Desorption Studies

Table A-1. Adsorption/Desorption Data from Primary Batch Experiment

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APPENDIX B: Raw Data from Column Studies

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<td>5*</td>
<td>10,000</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>10,000</td>
<td>10</td>
</tr>
</tbody>
</table>

*Note: Column study is the only experiment performed with under pressure (75 psi)
### APPENDIX C: SqueezeSoft™ Input Sheets

To run SqueezeSoft Version 1.0 click on the "Run" sheet tab

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Input</th>
<th>Units</th>
<th>Parameters</th>
<th>Input</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ID</td>
<td>Shale-Ind</td>
<td></td>
<td>Na⁺</td>
<td>22,930</td>
<td>mg/l</td>
</tr>
<tr>
<td>Date</td>
<td>9/15/2005</td>
<td></td>
<td>K⁺ (if not known = 0)</td>
<td>(mg/l)</td>
<td></td>
</tr>
<tr>
<td>Operator</td>
<td></td>
<td></td>
<td>Mg²⁺</td>
<td>(mg/l)</td>
<td></td>
</tr>
<tr>
<td>Well Name</td>
<td>Watson</td>
<td></td>
<td>Ca²⁺</td>
<td>2084</td>
<td>mg/l</td>
</tr>
<tr>
<td>Location</td>
<td>Houston</td>
<td></td>
<td>Sr²⁺</td>
<td>(mg/l)</td>
<td></td>
</tr>
<tr>
<td>Field</td>
<td>H-15-2001</td>
<td></td>
<td>Ba²⁺</td>
<td>21</td>
<td>mg/l</td>
</tr>
<tr>
<td>Well Depth</td>
<td>18,000</td>
<td>ft</td>
<td>Fe²⁺</td>
<td>0</td>
<td>mg/l</td>
</tr>
<tr>
<td>Perforation</td>
<td>10.00</td>
<td>ft</td>
<td>Zn²⁺</td>
<td>0</td>
<td>mg/l</td>
</tr>
<tr>
<td>Formation</td>
<td></td>
<td></td>
<td>SO₄²⁻</td>
<td>24</td>
<td>mg/l</td>
</tr>
<tr>
<td>Rock Type</td>
<td>Sandstone</td>
<td></td>
<td>F⁻</td>
<td>0</td>
<td>mg/l</td>
</tr>
<tr>
<td>Porosity</td>
<td>47.00</td>
<td>%</td>
<td>Total Alkalinity</td>
<td>549</td>
<td>mg/l HCO3</td>
</tr>
<tr>
<td>Permeability</td>
<td>(mD)</td>
<td></td>
<td>Acetates</td>
<td>0</td>
<td>mg/l</td>
</tr>
<tr>
<td>Calcite</td>
<td>5.00</td>
<td>%</td>
<td>TDS (measured)</td>
<td>62,519</td>
<td>mg/l</td>
</tr>
<tr>
<td>Clays</td>
<td>8.00</td>
<td>%</td>
<td>Calc. Density (STP)</td>
<td>1.400</td>
<td>g/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ Gas (STP)</td>
<td>0.50</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂S Gas (STP)</td>
<td>0</td>
<td>%</td>
</tr>
<tr>
<td>Gas/Day</td>
<td>1,000</td>
<td>10³ SCF</td>
<td>Total H₂Saq</td>
<td>0</td>
<td>mg/l H₂S</td>
</tr>
<tr>
<td>Oil/Day</td>
<td>50</td>
<td>STB</td>
<td>pH, measured (STP)</td>
<td>7.85</td>
<td>pH</td>
</tr>
<tr>
<td>Water/Day</td>
<td>3,600</td>
<td>STB</td>
<td>Use measured pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-H Temp</td>
<td>90</td>
<td>°F</td>
<td>to calculate SI</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>W-H Temp</td>
<td>70</td>
<td>°F</td>
<td>Here Scale SoftPitzer</td>
<td>4</td>
<td>DTPMP</td>
</tr>
<tr>
<td>B-H Press</td>
<td>3,200</td>
<td>psia</td>
<td>Pick inhibitor for you</td>
<td>1</td>
<td>1st-Yes-No</td>
</tr>
<tr>
<td>W-H Press</td>
<td>160</td>
<td>psia</td>
<td>If No, inhibitor # is</td>
<td>4</td>
<td>#</td>
</tr>
<tr>
<td>MeOH/Day</td>
<td>0</td>
<td>STB</td>
<td>If you select Mixed:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protection Time</td>
<td>120</td>
<td>min</td>
<td>1st inhibitor # is</td>
<td>1</td>
<td>#</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2nd inhibitor # is</td>
<td>2</td>
<td>#</td>
</tr>
</tbody>
</table>

Q C Checks

(I) equiv./liter
(II) meq/liter
(III) Compare exp. and calculated densities.

### Figure C-1. Well Data Input Data Sheet for SqueezeSoft™ Program.
<table>
<thead>
<tr>
<th>Chemical Information:</th>
<th>Shut-In:</th>
<th>Date: 5/15/2001</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product Name</strong></td>
<td><strong>Supplier</strong></td>
<td><strong>Inh. Return Data</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Vol of Brine (bbl)</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td>426</td>
</tr>
<tr>
<td></td>
<td></td>
<td>433</td>
</tr>
<tr>
<td></td>
<td></td>
<td>448</td>
</tr>
<tr>
<td></td>
<td></td>
<td>465</td>
</tr>
<tr>
<td></td>
<td></td>
<td>481</td>
</tr>
<tr>
<td></td>
<td></td>
<td>498</td>
</tr>
<tr>
<td></td>
<td></td>
<td>515</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532</td>
</tr>
<tr>
<td><strong>Preflush:</strong></td>
<td><strong>Input</strong></td>
<td><strong>Unit</strong></td>
</tr>
<tr>
<td>Preflush Volume</td>
<td>1000</td>
<td>bbl</td>
</tr>
<tr>
<td>HCl in Preflush</td>
<td>0</td>
<td>% (wt/wt)</td>
</tr>
<tr>
<td>Corrosion Inhibitor in Preflush</td>
<td></td>
<td>% (wt/wt)</td>
</tr>
<tr>
<td>Biocide in Preflush</td>
<td>% (wt/wt)</td>
<td></td>
</tr>
<tr>
<td>Surfactant in Preflush</td>
<td>% (wt/wt)</td>
<td></td>
</tr>
<tr>
<td><strong>Make-up Fluid Information:</strong></td>
<td>1. KCl, 2. Field Brine, 3. Tap Water, 4. Seawater (Enter 1, 2, 3, or 4)</td>
<td>2</td>
</tr>
<tr>
<td>If Make-up Fluid = 1, Enter KCl Concentration in Preflush</td>
<td>% (wt/wt)</td>
<td>3013, 40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3143, 38</td>
</tr>
<tr>
<td><strong>Inhibitor Pill:</strong></td>
<td><strong>Input</strong></td>
<td><strong>Unit</strong></td>
</tr>
<tr>
<td>Pill Volume</td>
<td>50</td>
<td>bbl</td>
</tr>
<tr>
<td>Active Concentration of Inhibitor in Pill (Check with Supplier)</td>
<td>3.5</td>
<td>lb/bbl</td>
</tr>
<tr>
<td>Is Pill Acidic or Neutralized? (Enter 1-Acidic, 2-Neutralized)</td>
<td>1</td>
<td>6595, 34</td>
</tr>
<tr>
<td>If Pill is Neutralized, Enter pH of Final Pill</td>
<td>pH</td>
<td>13211, 32</td>
</tr>
<tr>
<td>If Pill is Acidic, Check with Supplier for Extra Acid Present in Supplied Inhibitor, Enter &quot;0&quot; If Unknown</td>
<td>moles of HCl/mole Inhibitor</td>
<td>0.19</td>
</tr>
<tr>
<td>If Additional Acid is Added, Enter Acid Concentration as HCl in Pill</td>
<td>% (wt/wt)</td>
<td>41613, 3.6</td>
</tr>
<tr>
<td><strong>Make-up Fluid Information:</strong></td>
<td>1. KCl, 2. Field Brine, 3. Tap Water, 4. Seawater (Enter 1, 2, 3, or 4)</td>
<td>2</td>
</tr>
<tr>
<td>If Make-up Fluid = 1, Enter KCl Concentration in Pill</td>
<td>% (wt/wt)</td>
<td>88089, 1.6</td>
</tr>
<tr>
<td>If Additional Ca is Added to Pill, Enter Ca Concentration in Pill</td>
<td>mg/L</td>
<td>197000, 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>303000, 1.5</td>
</tr>
<tr>
<td><strong>Overflush:</strong></td>
<td></td>
<td><strong>Input</strong></td>
</tr>
<tr>
<td>Overflush Volume</td>
<td>150</td>
<td>bbl</td>
</tr>
<tr>
<td>Make-up Fluid Information:</td>
<td>1. KCl, 2. Field Brine, 3. Tap Water, 4. Seawater (Enter 1, 2, 3, or 4)</td>
<td>2</td>
</tr>
<tr>
<td>If Make-up Fluid = 1, Enter KCl Concentration in Overflush</td>
<td>% (wt/wt)</td>
<td>648000, 1.4</td>
</tr>
<tr>
<td>If Additional Ca is Added, Enter Ca Concentration in Overflush</td>
<td>mg/L</td>
<td>1274000, 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1339800, 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1559400, 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1637600, 0.6</td>
</tr>
<tr>
<td><strong>Simulation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Squeeze Life Simulation</td>
<td>750</td>
<td>days</td>
</tr>
<tr>
<td>Simulation cell size (in unit of bbl)</td>
<td>200</td>
<td>bbl</td>
</tr>
</tbody>
</table>

Figure C-2. Squeeze Design Input Data Sheet for SqueezeSoft™ Program.
APPENDIX D: SqueezeSoft™ Output Sheets

Figure D-1. Output Information from the Inhibitor Injection.

Figure D-2. Output Information from the Inhibitor Return Curve.
APPENDIX E: Original SqueezeSoft™ Program

Complete Visual Basic Program is available upon request to the author or the Committee Chairman, Mason Tomson.

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APPENDIX F: Modified Subroutine of SqueezeSoft™ Program

Complete Visual Basic Program is available upon request to the author or the Committee Chairman, Mason Tomson.