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RICE UNIVERSITY

THE TEMPERATURE AND IONIC STRENGTH DEPENDENCE
OF THE SOLUBILITY PRODUCT CONSTANT OF FERROUS PHOSPHONATE

by
STEPHEN FRIEDFELD

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

The Temperature and Ionic Strength Dependence of the Solubility Product Constant of Ferrous Phosphonate

by

Stephen Friedfeld

The formation of ferrous phosphonate precipitate and its dissolution were monitored in a batch experiment for a range of temperatures and ionic strengths. The precipitate was found to be $\text{Fe}_{2.5}\text{HNTMP}$, where NTMP is a phosphonate compound. Using a complexation and speciation model, concentrations of free iron and phosphonate were calculated, from which the solubility product constant was derived for each temperature and ionic strength. The temperature (K) and ionic strength (M) dependence of the negative logarithm of the ferrous phosphonate solubility product constant (pK_{sp}) was thus determined:

$$pK_{\text{sp}} = 39.54 - 6.14\sqrt{IS} + 2.18IS - 1315/T.$$

Simulated calculations using actual field data to compare iron and calcium phosphonates predicted ferrous salts to form in all instances and calcium salts to form occasionally. Further, a relationship was established whereby the concentration of free iron in a calcium-iron-phosphonate system can be predicted.

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Chapter 1

Introduction

Scale or deposit formation in water systems is an ongoing problem. Scaling occurs in biological and physiological systems and in such diverse industrial applications as oil and gas pipelines and wells, boilers, and cooling systems. Effective prevention of scale in these industrial applications, particularly in the oil and gas industry, often requires injecting inhibitors into the affected areas. The inhibitors most likely adsorb onto or precipitate within the rock formation to control scale; after a “shut in” period, the inhibitors undergo a slow release into the produced stream whereby they prevent scale. The precise mechanism of inhibition, however, is not known. Scale and scale prevention ultimately cost billions of dollars annually, and thus insights into the mechanisms of inhibitor fate and transport are needed.

Although much research has been directed toward the process of adsorption that follows an inhibitor injection or “squeeze” (Leung and Nancollas, 1978; Gill and Nancollas, 1981; Breen *et al.*, 1990; Jordan *et al.*, 1995), several authors indicate that the precipitation mechanism may prove to be more important (Carlberg, 1983; Malandrino *et al.*, 1995; Browning and Fogler, 1996). The reaction of divalent metal cations--most notably calcium--with phosphonate inhibitors results in a precipitated salt; calcium phosphonate has been the focus of most inhibitor precipitation work (Kan *et al.*, 1994; Tomson *et al.*, 1994; Frostman *et al.*, in press). Because of the abundance of ferrous iron

(Fe²⁺) from natural sources or corrosion in scaling systems, iron should also form salt precipitates with phosphonate, despite the fact that its precipitation has yet to be observed in the field.

The purpose of this research was to gain insight into the fate of phosphonate inhibitors in the ferrous system following squeeze applications. Specific objectives were as follows:

1. Determine the complexation constants of each likely component of the ferrous-phosphonate system.
2. Form and isolate a ferrous phosphonate precipitate and quantitatively analyze the salt.
3. Induce dissolution of the precipitate to obtain the temperature and ionic strength dependence of the solubility product constant and thermodynamic properties of ferrous phosphonate.
4. Establish a relationship between ferrous iron, calcium, and their phosphonate salts as it pertains to gas and oil well field conditions.

Knowledge of the temperature and ionic strength dependence of the solubility of ferrous phosphonates will be of assistance in determining whether ferrous phosphonate should form in the field under various conditions, and if so, in determining the release of phosphonate into the produced brine. In addition, this information may be of use in corrosion systems, as a ferrous phosphonate protective layer or film on pipe walls may be forming and thus extending the lifetime of the pipe. Further, this work could apply to future research focusing on the relationship between calcium and ferrous phosphonate salts, as well as the phosphonate salts of other metals.

Chapter 2

Background and Literature Review

2.0 Introduction

The purpose of this chapter is to present an overview of scale formation and precipitation as it relates to the release of inhibitors into produced brine. This review begins with a background discussion of the presence of iron in many natural and industrial systems and the formation of common iron-based compounds which deposit as mineral scale; corrosion is also discussed. The method of squeezing inhibitors to control scale and corrosion is examined, along with a review of adsorption and precipitation mechanisms. The next section gives an overview of relevant thermodynamic theory and equilibrium chemistry. Specifically, dissolution, solubility, and saturation, as well as crystal growth and nucleation, are addressed. The following section applies the thermodynamic theory and equilibrium chemistry to the precipitation of ferrous phosphonates and introduces complexation and speciation theory. Finally, the chapter concludes with the significance of this research and its broader applications.

2.1 Background

2.1.1 The Prevalence of Iron in Water Systems

Iron is an important element in both natural and industrial aquatic systems. Iron is a common element in the Earth's crust; changes in environmental conditions brought about by biological reactions as well as chemical reactions with soils that contain iron-based compounds contribute an appreciable amount of iron to natural and industrial systems (Patton, 1986; Sawyer *et al.*, 1994). In addition, corrosion that occurs in the formation waters of oil and gas production wells and water purification, electricity generation, and chemical production processes considerably adds to the concentration of iron in these environments. Iron exists in water in both the partially oxidized ferrous state (Fe^{2+}) and the fully oxidized ferric state (Fe^{3+}), increasing the complexity of iron studies. Though compounds containing ferric iron are generally insoluble, anoxic conditions can reduce the iron to the ferrous form, where solution typically occurs more readily.

Iron in drinking water does not cause any known harmful effects to humans, but increased levels of iron in water exposed to air (oxygen) cause negative aesthetic effects, since the oxidized iron produces turbidity and a noticeable taste, even at low levels (Sawyer *et al.*, 1994). Furthermore, the presence of iron can support iron-feeding bacteria in distribution systems. Iron also forms an oxide scale commonly known as rust on many steel and iron surfaces as well as "red water" in subsurface waters, resulting from a colloidal form of ferric oxide (Fe_2O_3) (Cowan and Weintritt, 1976); other scales that form can restrict fluid flow or damage equipment. Despite the many negative aspects of its

presence in water, iron can contribute positively to water systems by creating a coating or thin film on water pipes which protects the interior surface from corrosion and nodule-formation, ultimately lengthening the lifetime of the pipe (Cowan and Weintritt, 1976; Lane, 1993) and reducing costs. The presence of iron in most natural and industrial water systems and its complexity create a unique and worthwhile opportunity for research.

2.1.2 Mineral Scale Formation

Solubility is broadly defined as the amount of a substance that will dissolve in a given amount of another substance (Webster's, 1991). Sawyer *et al.* (1994) note that any substance, no matter how "insoluble", is soluble to some degree. Precipitation of solid materials, then, will occur if the solvent--water, for example--contains ions that form compounds of limited solubility or if there exists a change in the physical conditions or water composition that lowers the solubility below the concentrations of ions currently in solution (Patton, 1986). Such physical condition changes include a drop in pressure, a temperature or pH change, or flow rate fluctuation (Cowan and Weintritt, 1976; Oddo and Tomson, January 1994), for example. The precipitation that occurs is either suspended in solution or adheres to a wall or surface; that precipitate which adheres to a surface is known as mineral scale, or simply scale.

Scale occurs when two mixing solutions or waters are said to be incompatible. Incompatible waters are stable and present no scaling problems when independent of other systems; however, upon mixing, two or more incompatible waters contain dissolved ions

which form a precipitate. Several types of scale commonly persist in oilfield waters especially, as seen in Table 2.1.

Table 2.1. The most common scales found in oilfield waters. Reproduced from Patton, 1986, p. 50. Note: Primary Variables are those factors which affect the scales' solubility.

Name	Chemical Formula	Primary Variables
Calcium Carbonate (Calcite)	CaCO_3	Partial Pressure of CO_2 , Temperature, Total Dissolved Salts
Calcium Sulfate Gypsum (most common) Hemi-Hydrate Anhydrite	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ CaSO_4	Temperature, Total Dissolved Salts, Pressure
Barium Sulfate	BaSO_4	Temperature, Pressure, Total Dissolved Salts
Strontium Sulfate	SrSO_4	Temperature, Pressure, Total Dissolved Salts
Iron Compounds Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferric Hydroxide Ferric Oxide	FeCO_3 FeS $\text{Fe}(\text{OH})_2$ $\text{Fe}(\text{OH})_3$ Fe_2O_3	Corrosion, Dissolved Gases, pH

From Table 2.1 it is readily apparent that iron compounds form many common oilfield scales.

Mineral scale formation is not limited to industrial environments alone. Many biological and physiological processes precipitate a form of scale, either beneficial or detrimental. For example, in addition to the iron compounds in Table 2.1, a form of iron phosphate known as vivianite-- $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ --is found in the anaerobic conditions created by wastewater sludge and sediments (Al-Borno and Tomson, 1994). Further,

natural beneficial scale formation occurs in bone and tooth growth, mollusk shells, and sucrose formation; negative scale deposits include kidney stones and arthritis (Gerbino, 1996).

The current study, though, does focus on industrial scale, and because all aspects of water utilization systems produce mineral scale deposits, their many negative consequences are widespread. Scale deposits are an important consideration in the petroleum industry and water purification, wastewater treatment, and steam and hot water heating systems. Problems that scale causes include production losses by reduced heat transfer; emergency shut-downs; damaged or ruined equipment; downtime; and plugged injection wells, all of which can potentially result in losses of millions of dollars (Cowan and Weintritt, 1976; Oddo and Tomson, January 1994). It is therefore evident that the prediction of which scale types will form under various conditions and the prevention of such scaling deposits have the potential to impact many aspects of water-related industries.

2.1.3 Corrosion

Controlling scale is inherently connected to the prevention of corrosion. Corrosion has been historically documented for over 130 years (Naval Research Laboratory, 1957); obviously the complete control and prevention of corrosion have yet to be achieved. Corrosion is defined by Lane (1993) as “the degradation of a metal by an electrochemical reaction.” Common corrosion products include iron oxide compounds, especially brown

iron oxide (Fe_2O_3) (hematite) or black iron oxide (Fe_3O_4) (magnetite). Though a protective film of corrosion products can form (Johnson, 1990), there exist many negative aspects of corrosion, which include creating discolored or dirty water; producing an off-taste or odor to water; plugging pipelines; causing leaks to develop from perforation of piping; and lowering heating or cooling efficiency (Lane, 1993). Rengstorff *et al.* (1984) discuss the relationship of mechanical wear and corrosion with scale. They note that several possible interaction phenomena exist as the result of the presence of surface deposits, ranging from a film that forms that resists corrosion losses and lowers mechanical wear losses to conditions where corrosion losses are added to mechanical losses. Other research (Tilman *et al.*, 1985) has found that corrosion rates for steels in deaerated water from iron mines were higher than rates from lead mines, emphasizing the need to quantify scale formation of iron salts, especially as it may relate to corrosion. As with scale deposits, problems related to corrosion create enormous monetary losses. According to a 1995 study (NACE, 1997), the corrosion of metals cost the United States almost \$300 billion per year, or around 4.2% of the Gross National Product. This study accounts avoidable corrosion--which is incurred by a failure to use the best available anti-corrosion technology--for over \$100 billion of that total.

2.1.4 Scale and Corrosion Control with Inhibitors

Because of the potential damage and costs of scale and corrosion, in addition to the desire to improve water quality in all aspects of water distribution and use, much

research has focused on scale and corrosion control by the use of additives or inhibitors (for example, Vetter, 1972; Leung and Nancollas, 1978; Gill and Nancollas, 1981; Oddo *et al.*, 1982; Tomson, 1983; Cushner *et al.*, 1990; van der Leeden and van Rosmalen, 1990; Graham and Sorbie, 1990; He *et al.*, 1994). Common inhibitors used in oilfield applications especially which have been effective include polyphosphates, phosphonates, carboxylates, and sulfonates (Black *et al.*, 1991).

The current study focuses on phosphonate inhibitors in general, and on nitrilotri-(methylenephosphonic acid) in particular (NTMP) (Figure 2.1). Phosphonates are widely used in industry for scale and corrosion control and in such diverse applications as boiler water treatment and textile applications, to name a few (Tomson *et al.*, 1994; Monsanto, 1986). The advantages of phosphonates in scale prevention lie in their ability to slow or prevent scale deposition and crystal growth processes and their stability over a wide range of temperatures and pressures (Browning and Fogler, 1996). Further, commercial scale inhibitor phosphonates are deemed “practically non-toxic” when ingested and only slightly irritating to the skin (Monsanto, 1986).

Figure 2.1. Structure of NTMP. Nitrilotri(methylene phosphonic acid), or NTMP, is a common inhibitor used for scale control and corrosion control.

2.1.4.1 Inhibitor Squeeze Treatment

In oilfield wells, three principal options exist for introducing an inhibitor into the affected target areas: (1) injecting a trace concentration of inhibitors into the surface equipment; (2) injecting these inhibitors downhole using a treatment string; or (3) squeezing an inhibitor into the formation so that the inhibitor will undergo a slow release when production resumes (Street *et al.*, 1989). The first option does not protect the production tubing and the second option is considerably expensive; thus, an inhibitor squeeze, which protects near-wellbore formation, production tubing, and surface equipment (Street *et al.*, 1989) is a desirable option for scale control.

In a squeeze treatment, the liquid inhibitor is pumped down a well and into the formation under low differential pressure, where the inhibitor either adsorbs and/or reacts to form a precipitate on the formation. See Figure 2.2. Specifically, the well is temporarily taken out of production and a high concentration of commercial inhibitor is diluted to 0.5-5% using either produced water or synthetic or natural brine. The mixture is known as an “inhibitor pill”, and is pushed into the formation following a pre-flush in which an acid or chelant is added to the well to clean production tubing and perforations (Gerbino, 1996). Following the injection of the inhibitor pill into the well, an overflush volume of water or brine is injected and the well is “shut in” for up to three days to allow exposure of the pill to more formation (Cowan and Weintritt, 1976; Gerbino, 1996). Typically, an initial large release of chemical followed by a slow release of a few parts per million or less of the inhibitor into the production stream occurs; the inhibitor

Figure 2.2. Squeeze procedure for a gas- or oil-producing well. In a squeeze treatment, a liquid inhibitor “pill” is pumped down a well and into the formation following a pre-flush of acid; after an overflush volume is injected, the well is shut-in, usually for two days, to allow exposure of the pill to the rock formation. When production is resumed, the inhibitor is slowly released into the production stream at a concentration which is generally sufficient to prevent scale formation. Reproduced from Gerbino (1996).

remains at this concentration for “millions of barrels of brine production” (Kan *et al.*, 1994; Shuler and Jenkins, 1989; Hunter, 1992). This concentration of inhibitor is usually sufficient in preventing scale formation (Hunter, 1992). Once the level of inhibitor drops below a pre-determined or pre-calculated minimum, however, the well must be resqueezed to maintain a necessary level of scale inhibition. A resqueeze treatment may be needed anywhere from several weeks to several years (Street *et al.*, 1989); the “ultimate design goal”, though, is for a single treatment of the well over the well’s lifetime (Gerbino, 1996).

2.1.5 Mechanisms of Retention: Adsorption and Precipitation

Once the inhibitor, or phosphonate in this case, is squeezed into the well, two proposed mechanisms control its retention in the formation: adsorption and precipitation. Adsorption is an interfacial phenomenon--fluids in a rock formation are present but separated from the rock surfaces by a boundary, and interfacial interaction occurs when an additive is injected into the formation (Cowan and Weintritt, 1976). In an adsorption squeeze, molecular forces bind the liquid inhibitor to the rock surfaces (Carlberg, 1983). Either chemical or physical adsorption occurs. Chemical adsorption (also chemisorption) results from strong specific intermolecular forces and leads to the formation of chemical compounds; it is considered permanent or irreversible sorption. Physical adsorption occurs as the result of relatively nonspecific weak attractive forces between molecules. The physically adsorbed molecule is not attached to a particular site, but instead can move freely about the surface (Cowan and Weintritt, 1976; Sawyer *et al.*, 1994). Physical

adsorption is generally reversible and is therefore desirable in adsorption squeezes, whereby the inhibitor slowly desorbs into the producing stream. This desorption returns that level of inhibitor which prevents scale formation. Because a “useful life” of a squeeze treatment is generally lengthened by transporting the inhibitor a greater distance from the wellbore, the overflush volume is used to accomplish this in adsorption inhibitor squeezes such that the number of sorption sites is saturated (Carlberg, 1983; Hunter, 1992).

The precipitation squeeze uses a different mechanism from adsorption squeezes—it is based on the process of forming a salt in the formation, with a dissolution process controlling its slow release into the producing brine (Hunter, 1992). In particular, phosphonates react with divalent metal cations (for example, calcium or ferrous iron) during the shut-in period, after which the cation-phosphonate precipitates redissolve into the produced fluid to slow or prevent scaling (Malandrino *et al.*, 1995; Browning and Fogler, 1996). Although precipitation squeezes are not fully understood, proposed theories indicate that the governing mechanisms of such squeezes range from pure precipitation to complex models that couple adsorption and precipitation phenomena (Malandrino *et al.*, 1995). The design of precipitation squeezes, again to transport the inhibitor farther from the wellbore, must consider the reaction between the rock formation and phosphonic acids (phosphonates). Thus, acidization followed by an appropriate overflush volume is required to move the chemical away from the wellbore effectively (Carlberg, 1983; Hunter, 1992).

Research has shown that precipitation and subsequent dissolution of the metal-phosphonate salts “enhance treatment lifetimes by increasing the amount of phosphonate retention during the shut-in period and slowing the release characteristics of phosphonates into produced fluids during production” (Browning and Fogler, 1996 and references therein). Other evidence also supports this type of squeeze treatment as an effective means of scale inhibition: Malandrino *et al.* (1995) cite numerous authors who claim that precipitation squeezes result in longer lifetimes when compared to adsorption squeeze processes.

Materials that tend to adsorb strongly would also likely form precipitates, and thus it is difficult to distinguish between these two mechanisms. Because of this difficulty, either mechanism could probably be used to describe the system when in actuality only one mechanism may indeed be controlling the system (Frostman *et al.*, in press; Sposito, 1984). Despite the importance of adsorption, this work focuses on precipitation as the governing mechanism and especially on the solubility and complexation of ferrous iron phosphonate.

2.2 General Theoretical Approach

2.2.1 Thermodynamic Theory and Equilibrium Chemistry

As stated in Chapter 1, a principal objective of this work is to determine the temperature and ionic strength dependence of the solubility of ferrous phosphonate; this information should be of assistance in determining the release of phosphonate concentration into the produced brine, thereby increasing the squeeze lifetime, if indeed ferrous phosphonate forms in real water systems. An understanding of thermodynamic concepts, equilibrium theory, and scale deposition mechanisms is necessary to achieve the stated objective.

The First and Second Laws of Thermodynamics (Denbigh, 1971; Stumm and Morgan, 1981; Blandamer, 1992) serve as a basis for deriving expressions relevant to chemical equilibria in solution. The First Law states that the change in internal energy (dE) of a closed system is the sum of heat transferred to the system (dq) and work done on the system (dw). For finite changes,

$$\Delta E = q + w. \quad (2.1)$$

The Second Law states that the total entropy change for a closed system is the sum of the entropy changes inside the system and the entropy transferred to the system, or

$$dS_{\text{sys}} = dS_{\text{int}} + dS_{\text{sur}}. \quad (2.2)$$

The entropy transferred to the system is defined as

$$dS_{\text{sur}} = \frac{dq}{T}. \quad (2.3)$$

Equilibrium is a reversible process, and occurs when $dS_{\text{int}}=0$. For a spontaneous process--also called an irreversible or natural process-- $dS_{\text{int}}>0$.

Equilibrium relationships can be formed by combining the laws of thermodynamics and making appropriate assumptions. For a closed system in which only expansion work is done,

$$dw = -PdV \quad (2.4)$$

and at equilibrium for a system of fixed composition

$$dq = TdS_{\text{sys}}. \quad (2.5)$$

Thus, the combined First and Second Laws give

$$dE = TdS - PdV. \quad (2.6)$$

For a given S and V at equilibrium, $dE=0$. A system at equilibrium rests at its minimum energy. Thermodynamics is built upon this relationship as well as several other fundamental relationships which themselves represent an equilibrium state. The enthalpy and Gibbs free energy are two such thermodynamic properties of systems. The enthalpy and its differential are:

$$H = E + PV \text{ and } dH = TdS + VdP. \quad (2.7, 2.8)$$

The Gibbs free energy and differential are:

$$G = H - TS \text{ and } dG = -SdT + VdP. \quad (2.9, 2.10)$$

For a finite change in the system, equation 2.9 at constant temperature becomes

$$\Delta G = \Delta H - T\Delta S. \quad (2.11)$$

These equations are quite valuable since they depend upon temperature and pressure (Stumm and Morgan, 1981), conditions which can be held constant in laboratory settings. One useful property measured at constant pressure, in fact, is the heat capacity C . The heat capacity is defined as

$$C = \frac{dq}{dT} \quad (2.12)$$

which, at constant pressure, becomes

$$C_p = \frac{dq_p}{dT} = \left(\frac{dH}{dT} \right)_p \quad (2.13)$$

The Gibbs free energy and its related properties can be rearranged to show the relationship of the different components of a closed system. For systems of variable composition, in which the mole number of a component in a solution changes as the result of a phase transformation or chemical reaction, partial differentials are used to carry through these manipulations. In particular, for the Gibbs free energy

$$G = G(P, T, n_1, n_2, \dots, n_k)$$

where n_i is the mole number of component i . Thus, the total differential based on the above equation is

$$dG = \left(\frac{\partial G}{\partial P} \right)_{T; n_i} dP + \left(\frac{\partial G}{\partial T} \right)_{P; n_i} dT + \sum \left(\frac{\partial G}{\partial n_i} \right)_{P; T; n_j} dn_i \quad (2.14)$$

The term $\left(\frac{\partial G}{\partial n_i} \right)_{P; T; n_j}$ from equation 2.14 is known as the partial molar Gibbs free energy and defines the chemical potential of component i . That is,

$$\mu \equiv \left(\frac{\partial G}{\partial n_i} \right)_{P;T;\eta_j} \quad (2.15)$$

The chemical potential μ is defined as the amount by which the capacity of the phase for doing work is increased per infinitesimal unit amount of substance added (Denbigh, 1971). Similarly, for a pure substance, μ is the *molar* free energy of that substance (*cf.* partial molar).

The chemical potential is a fundamental component of equilibrium concepts. An equation to describe a so-called “ideal solution” is based on the analogous equation for an ideal gas. From the ideal gas law, $V=nRT/P$; and, from equation 2.10 at constant temperature, $dG=VdP$. Thus,

$$dG = nRT \frac{dP}{P} \quad \text{or} \quad dG = nRT d(\ln P) \quad (2.16)$$

Integrating this equation from a standard pressure P° to a pressure P and dividing by the number of moles n yields (for each component i)

$$\mu_i = \mu_i^\circ(g) + RT \ln P_i \quad (2.17)$$

Extrapolating equation 2.17 for ideal solutions gives

$$\mu_i = \mu_i^\circ(\text{sol}) + RT \ln x_i \quad (2.18)$$

where $\mu_i^\circ(\text{sol})$ is a function of temperature and pressure and x_i is the mole fraction of component i in solution. The value of μ_i° depends upon the units chosen to express concentration; for example, mole fraction or pressure is often used. Typically two reference states are used: the pure compound with x_i and a molar solution ($C=1$ M) extrapolated from infinite dilution.

For real solutions, idealized concentrations known as activities replace the mole fraction. The activity is used because, as solutions of salts, acids, or bases become more concentrated, their quantitative effect decreases continuously below the calculated molar concentrations as the result of charge interactions at these higher concentrations. The activity is thus the effective concentration (Sawyer *et al.*, 1994). Equation 2.18 then becomes

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (2.19)$$

where a_i is the activity of that component. Using molar units, the activity and the real concentration are related through the activity coefficient γ_i via

$$a_i = \gamma_i M_i. \quad (2.20)$$

Thus, the chemical potential in a real solution is

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i M_i. \quad (2.21)$$

2.2.1.1 Chemical Reactions and Equilibrium

In a constant temperature and pressure system, equilibrium occurs when $\sum \mu_i dn_i = 0$. Further, spontaneous reactions occur when $\sum \mu_i dn_i < 0$. These results apply to chemical reactions to describe equilibrium conditions. A chemical reaction is represented as

where the ν 's represent stoichiometric coefficients of reactants A and B and products C and D. This equation can also be written more simply as

$$\sum \nu_i \mu_i = 0 \quad (2.23)$$

where M_i is the molecular weight of component i and ν_i is the stoichiometric coefficient of i . The reactants' coefficients are negative; the products' coefficients are positive. For mixtures of components, the equation for the chemical potential in terms of the activity of component i ($\{i\}$) can be substituted into the above equation, resulting in

$$\Delta G = \sum \nu_i \mu_i^\circ + RT \sum \nu_i \ln \{i\} \quad (2.24)$$

or

$$\Delta G = \Delta G^\circ + RT \ln \prod \{i\}^{\nu_i} \quad (2.25)$$

where the standard Gibbs free energy of reaction is given by

$$\Delta G^\circ = \sum \nu_i \mu_i^\circ. \quad (2.26)$$

Equation 2.25, in terms of reaction 2.22, becomes

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{C\}^{\nu_c} \{D\}^{\nu_d} \dots}{\{A\}^{\nu_a} \{B\}^{\nu_b} \dots}. \quad (2.27)$$

The reaction quotient Q is

$$Q = \prod \{i\}^{\nu_i} = \frac{\{C\}^{\nu_c} \{D\}^{\nu_d} \dots}{\{A\}^{\nu_a} \{B\}^{\nu_b} \dots}. \quad (2.28)$$

Thus equation 2.27 becomes

$$\Delta G = \Delta G^\circ + RT \ln Q. \quad (2.29)$$

At equilibrium, $\Delta G=0$, and Q becomes Q_{eq} or K , the equilibrium constant. That is,

$$K \equiv Q_{eq} = \left(\frac{\{C\}^{\nu_c} \{D\}^{\nu_d} \dots}{\{A\}^{\nu_a} \{B\}^{\nu_b} \dots} \right)_{eq}. \quad (2.30)$$

Substitution therefore gives equation 2.31, a central relationship in thermodynamics:

$$\Delta G^\circ = -RT \ln K. \quad (2.31)$$

2.2.1.2 Solubility Product

When a solute dissolves in a solvent, the ions on the solute's surface migrate into the solvent until the solute is completely dissolved or the saturation limit is reached. When a salt is in equilibrium with the solvent, a representative reaction and corresponding equilibrium condition can be written:

$$K = \frac{\{A^{+n}(aq)\}^m \{B^{-m}(aq)\}^n}{\{A_mB_n(s)\}}. \quad (2.33)$$

The salt in the denominator of equation 2.33 exists as a solid; its concentration is considered constant at equilibrium. The solid concentration is assumed constant because only the surface area of the solid is in contact with the solvent and, in a saturated solution, ions leave the surface at the same rate at which ions are deposited by the solution (Sawyer *et al.*, 1994). Thus, $A_mB_n(s)$ is a constant, K_s , and equation 2.33 becomes

$$K = \frac{\{A^{+n}(aq)\}^m \{B^{-m}(aq)\}^n}{K_s} \quad (2.34)$$

or

$$\{A^{+n}(aq)\}^m \{B^{-m}(aq)\}^n = KK_s = K_{sp}. \quad (2.35)$$

The term K_{sp} is called the *solubility product constant*. The solubility product constant can be used to determine the level of saturation of a given solution. In an unsaturated solution, $\{A^{+n}\}^m \{B^{-m}\}^n < K_{sp}$. In an oversaturated solution, $\{A^{+n}\}^m \{B^{-m}\}^n > K_{sp}$. Saturation is discussed in Section 2.2.2.2 below. The solubility product constant relates the solubilities of different salts to one another. Further, the K_{sp} allows mathematical

treatment of the equilibrium condition as well as the prediction of the effect of adding common ions to a solution containing a sparingly soluble salt. A commonly calculated value is the pK_{sp} :

$$pK_{sp} \equiv -\log K_{sp}. \quad (2.36)$$

All other things being equal, the greater the value of the pK_{sp} , the more “insoluble” the salt.

2.2.2 Scale Deposition Mechanisms

Figure 2.3 (Cowan and Weintritt, p. 204) illustrates a general overview of scale deposition mechanisms. As illustrated in the figure, several processes are involved in scale formation--namely, dissolution and solubilization; supersaturation; and nucleation, precipitation, and crystal growth (Cowan and Weintritt, 1976).

Figure 2.3. An overview of scale deposition mechanisms. Reproduced from Cowan and Weintritt (1976), p. 204.

2.2.2.1 Temperature Effects on Solubility

As noted in Section 2.1.2, all solids are soluble to some degree. The solubility of a substance can be affected by a number of factors, including temperature, solute particle size, the presence of impurities, or the solvent. An increase in temperature, for instance, typically causes the solubility of a solute in a solvent to increase. Notable exceptions are some of the compounds that deposit as scale. Many of these salts undergo a “negative solubility effect”, and are so-called inversely soluble (Mullin, 1961) because the salts’ solubilities decrease with an increase in temperature.

Although many equations have been proposed to correlate and predict solubility data, no universal equation has been written. Instead, the temperature dependence of solubility is usually expressed by one of two general equations:

$$c = A + Bt + Ct^2 + \dots \quad (2.37)$$

or

$$\log x = \frac{a}{T} + b. \quad (2.38)$$

In the equation 2.37, c is the mass of solute per given mass of solvent; t is the temperature in °C or °F; A , B , and C are constants found in the literature for many common solute-solvent systems. In equation 2.38, the solubility is expressed as the mole fraction x of non-solvated solute in the solution; T is absolute temperature; a and b are constants (Mullin, 1961). Stumm and Morgan (1981) (p. 70) also present a set of arguments describing the influence of temperature on the equilibrium constant, leading to the final expression

$$\ln K = B - \frac{\Delta H_o}{RT} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R} T + \frac{\Delta c}{6R} T^2 \quad (2.39)$$

where ΔH_o and B are constants and $\Delta a = \sum \nu_i a_i$, etc. This equation was derived from the integration of the equations

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \text{and} \quad \frac{d\Delta H^\circ}{dT^2} = \Delta C_p^\circ = \Delta a + \Delta b T + \Delta c T^2.$$

Thus, certain thermodynamic properties--enthalpy (H), for example--can be obtained directly from an expression for the temperature-dependent equilibrium constant K .

2.2.2.2 Solubility and Saturation

A saturated solution is one which is in equilibrium with the solid phase. In a saturated solution, the product of the molar concentrations of a salt's constituent ions (raised to the respective stoichiometric coefficient) equals the solubility product constant. In an under- or subsaturated solution, this product is less than the K_{sp} ; in an over- or supersaturated solution, the product of molar concentrations of constituent ions exceeds the K_{sp} (Sawyer *et al.*, 1994).

Solubility and precipitation depend upon the degree of saturation. Specifically, "labile" (unstable) and "metastable" solutions represent oversaturated conditions where spontaneous precipitation (in the absence of solid nuclei) will and will not occur, respectively (Mullin, 1961). Furthermore, different precipitates may form--by undergoing a phase transformation--as the saturation changes. Stumm and Morgan (1981) discuss an "active" and "inactive" form of the compound. They describe an active form as a "very

fine crystalline precipitate with a disordered lattice”, generally formed from highly supersaturated solutions. This active form of the crystal or precipitate persists in a metastable solution and may age or mature into a stable inactive form. Inactive solids have ordered crystals and are formed in solutions that are only slightly oversaturated. Various factors that affect the activity of the solid phase are: (1) the lattice energy; (2) the degree of hydration; (3) solid solution formation; and (4) the free energy of the surface (Stumm and Morgan, 1981).

Figures 2.4a and 2.4b qualitatively describe the relationship of solubility and saturation for a given concentration and temperature or pH, respectively. In Figure 2.5a by Miers (see Mullin, 1961 for reference), the solid line represents the normal solubility curve for the salt; the so-called supersolubility curve is the upper dashed line. Unlike the normal solubility curve, the supersolubility curve is not well-defined, and its position in the diagram depends on the degree of agitation of the solution (Mullin, 1961). As per the diagram, three zones are formed: (1) the stable (unsaturated) zone, where crystallization is impossible; (2) the metastable zone, where spontaneous precipitation is not likely but growth would occur if a seed crystal were placed in solution; and (3) the labile (supersaturated) zone, in which spontaneous crystallization is likely to occur. Precipitation can occur by cooling the solution at a constant concentration (line ABC); evaporating the solution at a constant temperature (line AB'C'); or a combination thereof (curve AB''C''). Figure 2.4b (from Stumm and Morgan, 1981) is a schematic showing concentration ranges versus pH for various levels of saturated solutions. From the diagram, the active form of the solid phase is in the metastable region. The active

Figure 2.4. Two representations of the relationship between solubility and saturation. The figures show three saturation zones--labile, metastable, or stable--for concentrations as a function of (a) temperature and (b) pH. (a) is reproduced from Mullin (1961), p. 27; (b) is reproduced from Stumm and Morgan (1981), p. 235.

precipitate is more soluble than the inactive precipitate, but it may slowly convert to the solid stable phase.

2.2.2.3 Nucleation and Crystal Growth

The formation of a solid phase develops from a supersaturated solution. Figure 2.5 (Stumm and Morgan, 1981) depicts the processes involved in nucleation and crystal growth. A general knowledge of these processes is helpful in understanding not only the formation of ferrous phosphonate (or other) mineral scales, but also dissolution and inhibition mechanisms.

Stumm and Morgan (1981) define nucleation as “the formation of the new centers from which spontaneous growth can occur.” Prior to nucleation, continuous formation and dissolution of clusters occurs; when the concentration of the solute is high enough, the clusters become sufficiently large to yield crystallites and then crystals. Cluster formation of ions or molecules is represented by the following (Walton, 1967; Stumm and Morgan, 1981):

After crystal growth, large crystals may eventually form from ripening.

Figure 2.5. Schematic diagram depicting the processes involved in nucleation. Reproduced from Stumm and Morgan (1981), p. 311.

Homogeneous Nucleation

As indicated, a certain degree of supersaturation must be achieved before nucleation can occur. Stable nuclei will only form, however, if an energy barrier to nucleation is overcome, analogous to the activation energy barrier of a chemical reaction (Walton, 1967; Stumm and Morgan, 1981). The free energy of formation of a nucleus is the sum of the free energies of formation of the bulk of the particle and the surface:

$$\Delta G_j = \Delta G_{\text{bulk}} + \Delta G_{\text{surf}}. \quad (2.40)$$

For a spherical nucleus, the bulk-free energy term is

$$\Delta G_{\text{bulk}} = -jkT \ln \frac{a}{a_0} \quad (2.41)$$

where j is the number of molecules or ions in the nucleus--in volume terms, $j = 4\pi r^3/3V$, where V is the volume of the nucleus; k is Boltzmann's constant; T is absolute temperature; and a/a_0 is the oversaturation ratio, where a and a_0 represent the actual and equilibrium activities of the solutes. The free energy of formation of the surface is given by

$$\Delta G_{\text{surf}} = 4\pi r^2 \sigma \quad (2.42)$$

where σ is the interfacial energy. Combining equations 2.40 through 2.42 gives

$$\Delta G_j = \frac{-4\pi r^3}{3V} kT \ln \frac{a}{a_0} + 4\pi r^2 \sigma. \quad (2.43)$$

When ΔG_j is plotted as a function of size r (at constant values of V and σ) for different values of oversaturation, the activation energy barrier to the nucleation process (ΔG^*) decreases with increasing degrees of oversaturation (Johnson, 1990). Because small

crystals are more soluble than larger crystals, the energy barrier is related to the additional energy required to form more soluble nuclei and thus is due to the surface energy term.

For a spherical cluster, the ΔG_{bulk} term can be rewritten as follows:

$$kT \ln \frac{a}{a_0} = \frac{2V\sigma}{r}, \text{ or } r = \frac{2V\sigma}{kT \ln \frac{a}{a_0}}. \quad (2.44)$$

The activation energy ΔG^* to nucleation, the maximum value of ΔG_j , can thus be calculated by substituting the equation for r (denoted r_j when the particle radius is “critical” for spontaneous crystallization) into the equation for ΔG_j . Thus, equation 2.43 becomes

$$\Delta G_j = \frac{4\pi}{3V} \left(\frac{2V\sigma}{kT \ln \frac{a}{a_0}} \right)^3 kT \ln \frac{a}{a_0} + 4\pi \left(\frac{2V\sigma}{kT \ln \frac{a}{a_0}} \right)^2 \sigma.$$

Simplifying this expression, ΔG^* is a function of the surface energy, volume, and supersaturation ratio as follows (Mullin, 1961; Walton, 1967; Stumm and Morgan, 1981):

$$\Delta G^* = \frac{16\pi\sigma^3 V^2}{3[kT \ln \frac{a}{a_0}]^2}. \quad (2.45)$$

Heterogeneous Nucleation

In the previous section, nucleation as a homogeneous process—that is, a process in which the influence of solids other than the precipitating phase is ignored—was considered. The influence of impurities on nucleation is important (Walton, 1967); true spontaneous nucleation, in which impurities are negligible, is rarely encountered. Mullin (1961)

presents the following explanation of heterogeneous nucleation. For a “foreign” particle or seed to induce nucleation, the free energy change of formation of a critical nucleus under heterogeneous conditions ($\Delta G'_{\text{crit}}$) must be less than the corresponding free energy change associated with homogeneous conditions (ΔG_{crit}); that is,

$$\Delta G'_{\text{crit}} = \phi \Delta G_{\text{crit}} \quad (2.46)$$

where ϕ is a factor less than one. Figure 2.6 illustrates a typical interfacial energy diagram for three phases in contact--the solid surface, the crystalline deposit, and the liquid. It has been suggested (see references in Mullin, 1961) that the value of ϕ is determined by the contact angle θ in Figure 2.6, and can be expressed as:

$$\phi = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}. \quad (2.47)$$

Thus, when $\theta=180^\circ$, $\phi=1$ and $\Delta G'_{\text{crit}} = \Delta G_{\text{crit}}$; when $0<\theta<180^\circ$, $\Delta G'_{\text{crit}} < \Delta G_{\text{crit}}$; and when $\theta=0$, $\Delta G'_{\text{crit}} = 0$. These cases correspond respectively to: complete non-affinity between the crystalline deposit and the solid surface; partial affinity, where heterogeneous nucleation occurs more easily than homogeneous nucleation because less free energy of nucleation is required; and complete affinity, which corresponds to the seeding of a supersaturated solution with small crystals of the solute.

Crystal Growth

Once particles in a supersaturated solution have developed beyond a critical size r_j they begin to form visible crystals. Crystal growth occurs in three successive steps: (1)

Figure 2.6. Interfacial interaction between a crystal, a liquid, and a solid surface. The angle θ is the contact angle between the crystalline deposit and the solid surface. Reproduced from Mullin (1961), p. 110.

transport of the solute to the solution interface; (2) adsorption of the solute at the interface; and (3) lattice formation (Stumm and Morgan, 1981). Growth kinetics are determined by interface-controlled growth or diffusion-controlled growth.

Interface-controlled growth fits a general rate law formula:

$$\frac{dc}{dt} = -k's(c - c_0)^n \quad (2.48)$$

where c_0 is the concentration in the immediate proximity of the crystal surface; s is the surface area; k is a rate constant that depends on the diffusion coefficient; and n is the order of the reaction. Diffusion-controlled growth--or dissolution--is characterized by the rate equation

$$\frac{dc}{dt} \cong -ks(c - c_0). \quad (2.49)$$

In equation 2.49 the rate constant k depends on both the diffusion coefficient and the extent of turbulence in solution (Stumm and Morgan, 1981). Dissolution occurs more rapidly than crystal growth, and different faces of a crystal usually grow and dissolve at unequal rates (Mullin, 1961).

Inhibition of Nucleation and Crystal Growth

The mechanisms of nucleation and crystal growth inhibition are not fully understood; however, it is generally accepted that “small amounts of soluble foreign constituents may alter markedly the growth rate of crystals and their morphology” (Stumm and Morgan, 1981) at the interface. Recent research (Black *et al.*, 1991) has specifically investigated the binding of phosphonate inhibitors to inorganic surfaces. This work used scanning and transmission electron microscopy to examine the morphology of crystals with and without inhibitors to study specifically the effects of the additives on crystal growth.

Black *et al.* (1991) found that two recognition factors at the interface must be simultaneously satisfied: the first is related to structural aspects of the inorganic surface; the second is related to the charge on the inhibitor. Furthermore, it was observed that pH has a great effect on the reactivity of phosphonates (and other inhibitors) in solution with divalent metal cations, since the pH controls the degree of protonation on the phosphonate groups. Thus, a pH in which the phosphonate groups are doubly deprotonated can satisfy the charge balance at the surface and dictate the complexing with metals that occurs. The authors found that when the inhibitor is incorporated into the inorganic surface, additional layers of the inorganic solid are “disrupted” and the growth rate is slowed. Thus, it is apparent that nucleation and crystal growth theory can give insight into the mechanism of inhibition, and thus the fate of phosphonates in waters containing high levels of divalent metal cations.

2.3 Complex Solution Chemistry of Ferrous-NTMP

An understanding of the solution chemistry of NTMP and its interaction with ferrous systems as a function of ionic strength and temperature is necessary to help predict the fate of these inhibitors downhole. The solution and complexation chemistry is needed to determine the solubility product constant. The solubility product constant, in turn, should reveal insight into ferrous phosphonate formation and dissolution.

The dissolution of a ferrous phosphonate precipitate is given by

where Phn is the phosphonate NTMP and x is the stoichiometric coefficient. As seen in Figure 2.1, NTMP has six ionizable protons; thus, the distribution of species depends strongly on pH. The solubility product corresponding to equation 2.50 is:

$$K_{sp} = (Fe^{2+})^x \{H^+\}^{(6-2x)} (Phn^{6-}). \quad (2.51)$$

In equation 2.51, parentheses represent concentrations in molarity; $\{H^+\}$ is the proton activity in solution, equal to 10^{-pH} ; superscripts inside brackets or parentheses represent the ionic charge and superscripts outside refer to the power to which the concentration is raised (Frostman *et al.*, in press). Therefore, to calculate the K_{sp} the free concentrations of Fe^{2+} and Phn^{6-} in solution are needed, and can be determined by using a speciation model and the measured total concentrations of iron and phosphonate.

Proton association and calcium complexation with NTMP have been studied and serve as a basis for this research (Tomson *et al.*, 1994; Kan *et al.*, 1994; Frostman *et al.*, in press). Figure 2.7 represents the general scheme for the solution chemistry of ferrous-

Figure 2.7. A representation of all the NTMP and iron (II) complexes to be considered. Stepwise association constants (logarithm to base ten) are to the right or just above the respective arrows. The constants K_1 to K_6 are proton association constants; K_{11} to K_{51} are iron complexation constants.

NTMP. The first proton of NTMP associates with the nitrogen, and is assumed not to be displaced by Fe^{2+} when complexing occurs; the association constant is reported as $\log K_1^N(\text{NTMP})=12.3$ (Carter *et al.*, 1967). The remaining protons associate successively from H_1Phn^{5-} to H_6Phn^0 . In addition, these highly charged anions should form complexes with divalent metal ions such as Fe^{2+} (Tomson *et al.*, 1995).

The six association constants for NTMP were determined by acid/base titration data (Frostman *et al.*, in press). The only constants required, then, are the nine complexation constants. Because of experimental and numerical difficulties encountered in determining the complexation constants of calcium phosphonates, Tomson *et al.* (1995) derived a numerical model based on electrostatic effects that assumes the constants are a linear function of charge. (See Tomson *et al.*, 1995 for a detailed explanation of the model.) This same model was used for determining the analogous constants of ferrous-NTMP. The model is divided into two parts: the successive association of protons to a deprotonated NTMP ion and the complexation of Fe^{2+} with the phosphonate ligands. For NTMP, the proton association follows the general equation:

with

$$K_i = \frac{(H_iPhn^{(6-i)-})}{\{H^+\}(H_{i-1}Phn^{(7-i)-})} \quad (2.53)$$

The equilibrium constant is modeled according to Tomson *et al.* (1995) as

$$\log K_i = a_{H^+} + b_{H^+}|q_{i-1}| \quad \text{for } i \geq 2 \quad (2.54)$$

where a_{H^+} and b_{H^+} are speciation constants determined from speciation data and $|q_{i-1}|$ is the absolute value of the charge of the $(i-1)$ th species--the species with one less proton that is being protonated. Similarly, complexation with ferrous iron is as follows:

and the corresponding equilibrium constant is given by

$$K_{ij} = \frac{(Fe_jH_iPhn^{(6-i-2j)-})}{(Fe^{2+})(Fe_{j-1}H_iPhn^{(8-i-2j)-})}. \quad (2.56)$$

As before, the equilibrium constant is modeled as

$$\log K_{ij} = a_{Fe^{2+}} + b_{Fe^{2+}}|q_{2j-2+i}| \quad \text{for } i \geq 1, j \geq 1. \quad (2.57)$$

The values for the a and b constants are determined from experimental titration data. Because the NTMP proton association constants are already known, and the $a_{Ca^{2+}}$ was determined not to improve the model fit (thus assuming that the analog $a_{Fe^{2+}}$ also would not improve the fit), only the $b_{Fe^{2+}}$ constant is needed. With that one term, then, all complexation constants can be calculated for the ferrous-NTMP system, allowing for the calculation of all species at a given pH, leading to the determination of the K_{sp} .

2.4 Environmental Significance Of This Work

Precipitation processes obviously are important to the understanding of the fate of inhibitors in industrial systems. Precipitation processes, as indicated in Section 2.1.2, also play an important physiological role. The solubility product dictates the conditions under which a solid will dissolve or precipitate. Thus, determining the K_{sp} at various conditions gives a broad perspective of how a particular precipitate behaves. Further, insight may be gained regarding precipitation *mechanisms* from the K_{sp} .

Knowledge of ferrous phosphonate precipitation potentially has important environmental consequences. For instance, Fe-NTMP may form a protective layer against corrosion, which can potentially release toxic metals into water systems in the environment (Greenberg, 1986). Thus, the prevention of corrosion is an important public health concern. Further, iron removal in waters may be carried out by precipitation processes. Finally, because iron is a natural element in the Earth's crust and waters, a better understanding of iron chemistry could lead to future work with ferrous and ferric systems.

Chapter 3

Experimental Procedures

3.0 Introduction

An apparatus was built to create an anoxic environment to study the temperature and ionic strength dependence of the solubility of iron (II) phosphonate. After the iron phosphonate precipitate was formed and washed, its dissolution was monitored by determining the total concentrations of iron and phosphonate in the liquid. The dissolution experiments were sequential such that a single batch of the precipitate was dissolved in a particular ionic strength solution at a given temperature and, after reaching equilibrium, the solution temperature was changed until a new equilibrium was established. This procedure occurred continuously for three different ionic strengths (IS) between 1 M and 3 M and at 25, 50, and 70°C for each ionic strength.

3.1 Reagents Used

3.1.1 Materials Description

The following reagents were used in the experiments described in this chapter. Ferrous iron was obtained from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Sigma Chemical Co., 100.4% or Fisher Scientific Co., 100.3%). The IS electrolyte was NaCl (Fisher Scientific Co., 99.4%). The buffer (at about pH 4.4) was made from CH_3COOH (EM Science, 99.7%) and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (Fisher Scientific Co., 99.7%). The acid and base solutions used were 1 N HCl (Fisher Scientific Co.), 1 N NaOH (Hach Co.), and 8 N KOH (Hach Co.) (used in determining the stoichiometry). Finally, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (Aldrich Chemical Co., 99+%) was used for the fixed total iron experiments.

3.1.2 Phosphonate Solution

The NTMP was Dequest® 2000 (Monsanto Co., 50%). Because Dequest® is a commercial grade chemical, the solubility test results are more likely to predict actual field precipitation and dissolution. The phosphonate solution was prepared by placing about 25 mL deionized water in a 250 mL beaker which was in a cold water bath. Approximately 12 g NaOH pellets (Fisher Scientific Co.) was added slowly to the deionized water and allowed to dissolve. To this solution 40 g Dequest® 2000 was added very slowly since the reaction is exothermic and evolves much gas. The cooled solution's pH was measured and NaOH was added via a Hach digital titrator to bring the

solution to a final pH of 6.8. The final calculated concentration of phosphonate in the solution was 0.669 M NTMP.

3.2 Description of Anoxic Apparatus

The apparatus (Figure 3.1) built for the purpose of determining the solubility of iron (II) phosphonates maintained rigorously anoxic conditions by using an alternating vacuum and purge system. The apparatus design combined previous efforts to study ferrous iron chemistry (Greenberg, 1986; Al-Borno & Tomson, 1994). Pulling a vacuum on a flask and then opening a connection to another flask also allowed for the transfer of materials from one vessel to another without exposure to oxygen. Compressed pre-purified 99.998% argon gas (Trigas Industrial Gases) entered the system via a Firestone valve (ACE Glass Inc.) to ensure that the pressure in the system never exceeded 1 atm while maintaining a constant positive pressure on the system (US Patent #4,131,129). The gas then flowed to a vacuum/purge manifold (ACE Glass Inc.), where two-way valves were connected to two 5 L flasks (ACE Glass Inc.) and a 1 L round-bottomed jacketed reaction vessel (ACE Glass Inc.) which rested upon a magnetic stirrer (Fisher Scientific Co.). The valves alternately allowed for a gas purge or a vacuum pull on the attached flasks. A Neslab circulating bath maintained a given temperature to $\pm 0.1^{\circ}\text{C}$. The connections in the apparatus were all made with high-vacuum hoses so that no air could enter the system. Further, a 316 SS lid with an O-ring was clamped (ACE Glass Inc.) onto the reaction vessel. The lid had ten 1/8 in OD Cajon adapters distributed on its surface: eight for sampling/injection, and two-way valves connected to SS tubing

secured with O-rings on the other two adapters. System components combined in the reaction vessel and samples were taken by disposable syringes (Becton Dickinson & Co.) through septa (Alltech Associates, Inc.) in the adapters.

Figure 3.1. Schematic of the apparatus used to deoxygenate the system to study the dissolution of ferrous phosphonate. The system used an alternating vacuum and argon gas purge method to eliminate oxygen. Dissolved oxygen studies showed that the system was able to remove oxygen to below 100 ppb.

3.3 Analytical Methods

3.3.1 Concentration Measurements

Samples were withdrawn in the dissolution experiments to measure the total iron and phosphonate concentrations, usually several times a day over a period of at least two days. 12" 20-G Stainless steel needles (Popper and Sons, Inc.) were attached to 30 mL plastic disposable syringes and samples were taken through the septa on the reaction vessel's lid. The samples were then filtered through 0.45 μm filters (Gelman Sciences AutoPack™ Acrodisc® Syringe Filters) into 30 mL plastic centrifuge cuvettes for storage. The centrifuge tubes were capped and placed in a cool water bath if the temperature of the solution was 50 or 70°C to bring the temperature down to 25°C. Then the sample was divided into two independent samples, one to measure the total phosphonate concentration and one to measure the total iron concentration. Each split sample was appropriately diluted so that the concentration of iron or phosphonate would be in a desired range for spectrophotometric analysis--namely, 0-3.00 mg/L for Fe and 0-2.50 mg/L for phosphonate.

3.3.1.1 Hach Iron and Phosphonate Measurements

A Hach DR/2000 Spectrophotometer (Hach Co.) was used for the concentration measurements. Total iron was measured using the Hach FerroVer® method in which a powder pillow was placed into a cuvette containing a 25 mL sample; a reference cuvette contained a 25 mL sample without a powder pillow. Each Hach FerroVer® Powder

Pillow contains 1,10-phenanthroline and a sodium sulfite reducing agent. The absorbance of an orange complex in the sample cell was measured at 510 nm by the spectrophotometer, and the results reported in mg/L Fe.

Phosphonate measurements were obtained by using the blue ascorbic acid PhosVer3® method for phosphates at 890 nm in which potassium persulfate was added to the sample and then UV oxidized. To measure phosphonate concentrations instead of total phosphates, however, the reference cuvette contained potassium persulfate and PhosVer3® in the sample as opposed to deionized water. By using the sample itself in the reference cell, free phosphates were subtracted from total phosphates and only phosphonates were measured.

3.3.1.2 Calibration Curve for Phosphate Measurements

Because the spectrophotometric methods were used continuously throughout the dissolution experiments, a calibration curve for phosphates--the basic method used to measure phosphonates--was developed to assure a high level of accuracy. Hach provided standard phosphate ampoules which were successively diluted to various concentrations within the desired range. The method of standard additions was used to obtain the calibration curve in Figure 3.2, where a least-squares regression fit produced $r^2=1.000$.

3.3.2 Precipitate Stoichiometry and Characterization

The stoichiometric determination of the precipitate formed is needed to calculate the solubility product for each ionic strength and temperature. The stoichiometry was

Figure 3.2. Standard phosphate calibration curve. A calibration curve for the phosphate Hach measurement, which is the method used to measure phosphonates, was created to confirm the accuracy of the spectrophotometer. The standard phosphonate concentrations were made with standard phosphate ampoules; the fitted curve correlation gave $r^2=1.000$.

obtained using dissolution measurements in which a sample was taken from the reaction vessel, filtered, and dissolved in acid. The solution from which the samples were withdrawn was at 3 M IS, 25°C after the completion of the dissolution experiments. The precipitate collected on the filter was then washed by backflushing the filter. To backflush, Nalgene tubing (1/8 in ID) about six inches in length was attached to the effluent end of the filter and to a disposable syringe, and deionized water was pushed through to force the precipitate into a clean beaker. 1 N HCl was added to the beaker to dissolve the precipitate, and water was added to dilute the solution. The solution was neutralized with NaOH or KOH until the pH was around 6 or 7, as tested by pH paper

(Hydriion Papers). The resulting solution was stirred using a magnetic stirrer and then measured for total phosphonate and total iron concentrations using the Hach spectrophotometric methods. The average ratio of iron to phosphonate for eight independent experiments gave the overall precipitate stoichiometry.

Electron microprobe analysis by energy dispersive spectrometry (EDS) was used to determine analytically the components of the precipitate (by Department of Geology and Geophysics, Rice University, Houston, TX). Further characterization of the precipitate was obtained using x-ray diffraction (by Department of Geology and Geophysics, Rice University, Houston, TX).

3.4 Experimental Design and Procedures

3.4.1 Deoxygenation of the System

Experiments were run to ensure that the apparatus was sufficiently deoxygenating the system, and thus suitable for ferrous iron experiments. A previous study on the precipitation kinetics of ferrous carbonate indicated that levels of oxygen below 40 ppb were required to maintain a reduced iron state (Johnson, 1990). The deoxygenation requirement for kinetics studies is much more demanding, however, than that for equilibrium studies. In these experiments, deionized water was placed in the sealed reaction vessel, and the dissolved oxygen (DO) content of withdrawn 5 mL samples was measured using a DO probe (Yellow Springs Instrument Co., Inc.) after each purge/vacuum step to determine the reduction in dissolved oxygen levels. The DO probe used a KCl/AgCl filling solution. Because each withdrawn water sample was exposed to the atmosphere for these measurements, a constant flow of argon was run through the samples to keep the deoxygenated liquid degassed. The DO level in the deionized water before any vacuum/purge steps was around 5000 ppb; after four steps, the level dropped to an average of 100 ppb, and by the fifth step the DO content in the water dropped below 100 ppb to around 40-50 ppb. The DO meter's detection limit is 100 ppb, and thus any levels below this are estimates. When ferrous iron oxidizes to ferric iron, it turns red-brown in color, indicating oxidation. Thus, the DO content results, in addition to the color as an oxidation indicator, verified that the apparatus sufficiently deoxygenated the system and was a valid method for studying ferrous iron chemistry.

3.4.2 Obtaining the Complexation Factor

The $b_{\text{Fe}^{2+}}$ coefficient, or complexation factor, which ultimately leads to the calculation of all complexation species in solution, was determined by modifying procedures used to yield the same coefficient for calcium phosphonate (Kan *et al.*, 1994), assuming that the divalent-metal cations behaved similarly and were stoichiometrically equivalent. Titrations were performed to measure the $b_{\text{Ca}^{2+}}$ coefficient and the pH change upon the addition of NaOH was recorded and used for the calculation of the coefficient. The measurements for iron were analogous except that anoxic conditions were considered, and thus appropriate modifications were used. For example, the pH change for the titration of NaOH into a solution containing 5 mM Ca^{2+} was isolated and used as the basis of comparison with the iron experiments. In the anoxic apparatus, all of the reagents other than iron—including the exact amount of NaOH titrated into the calcium solution—were combined and deoxygenated in the deoxygenation flask and brought to the reaction vessel which contained the iron. This combination then represented that isolated point in the calcium titration. The experiments were run at 70°C; the reagents used were 0.16 M NaOH, 1 M NaCl, 5 mM Fe^{2+} in approximately 0.1 L deionized water, and 1 mM NTMP. The 1 mM phosphonate was obtained by using exactly 2.0 mL (Gilmont syringe) of a solution of 7.48 g Dequest® 2000 in 250 mL deionized H_2O . The $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in the reaction vessel was placed in approximately 0.01 L deionized water. In early experiments in which the ferrous chloride was in the reaction vessel as a powder and not in solution, the vacuum pulled some of the crystals into the lid's O-ring and thus altered the concentration of iron. To avoid this problem, the crystals were added to a small

amount of deionized water in the reaction vessel; this solution was deoxygenated before adding the remaining reagents.

3.4.2.1 pH Measurement

The solution pH before and after addition to iron was measured and the average change in pH over several identical experiments was used for the calculation of the $b_{\text{Fe}^{2+}}$ coefficient. In an effort to measure the pH of a deoxygenated solution, the KCl filling solution (Orion® Ross® 3 M KCl Reference Electrode Filling Solution) of the pH electrode (Orion® Ross®) itself was deoxygenated before filling the electrode. Phthalate and borate buffers were used to calibrate the pH meter (Fisher Scientific Co.), and each buffer was flushed with Ar gas before measuring the pH.

After at least four vacuum/purge steps to deoxygenate the solution without iron, the deoxygenation flask's stopper was removed and the pH of this solution recorded. This deoxygenated solution's flask was then stoppered again and a vacuum pulled that solution to the reaction vessel to combine with the iron solution. The pH of the total solution after mixing for about one to two minutes was taken by lifting the SS lid and inserting the electrode into the solution. The lid was replaced, but was not airtight since the electrode's wire was under the lid preventing a complete seal. The pH of the stirred solution was measured, and the pH per 1 mL addition of a relatively concentrated titrating iron solution of approximately 0.3 M Fe^{2+} was recorded. Argon gas was used because it was believed that it would provide a relatively heavy cover of head space so that even with exposure to the atmosphere for less than ten seconds to add or remove the electrode,

the solution would be unaffected by oxygen. Further, a more rigorous approach to measure pH while avoiding exposure to the air was considered in which the pH electrode would be inserted in one of the lid's openings and fitted securely. However, the electrode did not fit through the adapter opening and thus the method described above, applying a positive pressure of argon gas, was considered an appropriate alternative as the exposure to the atmosphere was minimized.

3.4.3 Seed Crystal Preparation

Experiments to create an iron (II) phosphonate precipitate followed general methods and procedures used to yield calcium phosphonate (Frostman *et al.*, in press). Sufficient quantities of the starting reagents were used so that the ratio of iron to phosphonate was approximately 5:1 to assure that the system would yield a sufficient amount of iron (II) phosphonate with which to perform dissolution experiments. The volume of the Dequest® solution (described in Section 3.1.2) used gave a final concentration of 0.02 M phosphonate in 900 mL total. The volume of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ used gave a final concentration of 0.1 M Fe^{2+} . The iron chloride appeared to have some oxidized crystals, and thus might have caused slight oxidation of the solution (see below). The other reagents were 1 M HCl, 1 M NaOH, 0.01 M acetic acid as a buffer, 0.7 M NaCl to give a 1 M IS solution, and 850 mL deionized water. The precipitation was done at 70°C and the reaction was continuously stirred.

Because of the need for all reagents to remain anoxic, each solution or pure reagent to be titrated into the water-salt-acetate solution was deoxygenated in the apparatus, withdrawn into a plastic disposable syringe whose tip was covered with Parafilm "M" (American National Can™) immediately upon removal from the lid, and then stored in a controlled atmosphere glove box (Labconco Corp.) until all the reagents were prepared. When all of the titrating reagents and the water-salt-acetate solution inside the reaction vessel were deoxygenated, the titrating reagents' syringe needles were each placed in a septum on the reaction vessel lid. Thus, phosphonate, reduced iron, acid, and base could be titrated into the remaining solution. In making the Fe(II)-NTMP precipitate, a type of constant composition method (Tomson and Nancollas, 1978) was employed in which concentrations of reagents and conditions (especially pH) do not change as the solution precipitates out the desired solid. To use this method, 1 mL of iron was injected into the solution, and then 1 mL phosphonate solution was injected immediately following. This procedure was carried out for about 25 mL total of both iron and phosphonate. The pH was monitored as described below.

3.4.3.1 pH Measurements Using an Immersed Electrode

The pH of the solution needed to be measured to ensure that a precipitate was formed at constant composition, as this method overcomes the problems of size and size distribution changes and irreproducibility associated with a non-constant composition precipitation technique (Tomson and Nancollas, 1978). Thus, as part of the constant composition method, acid and/or base was added to adjust the pH when it changed upon

precipitate formation. The pH was originally measured by immersing the electrode--whose filling solution had previously been deoxygenated--in the solution. As noted in Section 3.4.2.1, this method of measuring pH obviously introduces the likelihood of oxidation. The desired pH for precipitate formation was 5.7, as this represents actual downhole conditions; this pH was maintained by adding appropriate amounts of acid and/or base as a precipitate formed. After the precipitation was completed, the immersed electrode was removed from the reaction vessel and the lid was sealed.

The solution yielded a large amount of a thick off-white precipitate which settled overnight. The settled solution had a layer of orange at the precipitate/solution interface, indicating that the iron at the interface had oxidized. It was concluded, as before, that immersing the pH electrode into the solution exposed the system to too much oxygen and oxidized the precipitate (at the interface).

3.4.3.2 pH Measurements Using Withdrawn Samples

Because of the oxidation caused by the obvious exposure to the air using the electrode-immersion technique, precipitation experiments were performed in an entirely sealed vessel. To measure pH “continuously”, then, withdrawn 5 mL samples throughout the precipitation were taken. The pH of these samples indicated the need to add acid or base to adjust the pH to 5.7. Further, the pH after each addition was recorded in the experiment described in Section 3.4.3.1; these pre-recorded pH’s served as a guide in approximating the appropriate amount of acid or base needed after each 1 mL addition of either iron or phosphonate. Thus, a near-constant pH was maintained during seed crystal

preparation. Approximately 75 mL of a slurry precipitate formed, which settled within about a half hour.

3.4.3.3 Washing the Precipitate

The settled precipitate had a thin layer (≈ 0.25 cm) of orange at the solution/precipitate interface, most likely the result of impurities in the original ferrous chloride used. This slight amount of oxidized precipitate was easily removed using the following procedure. A vacuum was pulled on the waste flask, and the two-way valve connecting the reaction vessel and the waste flask was lifted so that its attached stainless steel tubing inside the reaction vessel was brought up to the “orange” level. The valve was turned to complete the connection between the SS tubing and the waste flask. Thus, a vacuum was pulled on the supernatant orange layer only. This method was used to remove the supernatant liquid after each wash of the remaining clean precipitate.

For each wash, a deoxygenated washing solution was introduced into the precipitate; this mixture was then stirred for several hours, and allowed to settle for several hours, all at 70°C. The mother liquor was then removed to the waste flask using the above procedures, and the next wash was begun. The precipitate used in the dissolution experiments was washed nine times with approximately 675 mL solutions containing a buffer of 0.05 M NaAc, 0.05 M HAc, and 0.7 M NaCl. The buffer fixed the solution pH at around 4.4. The concentration of total iron in the supernatant was sampled between each wash; the amount of iron rapidly dropped from over 5000 ppm to 27 ppm by the ninth wash. The phosphonate was also measured periodically; its concentration

was 9 ppm by the ninth wash. An attempt was made to dry the precipitate in the glove box and then later in the sealed reaction vessel. Because of the requirement for anoxic conditions, however, the precipitate never fully dried. Instead, about 40 mL of the wet precipitate was used in the solubility experiments (the remainder of the precipitate was stored in the glove box or used in the constant-iron experiments (see Section 3.4.4.1 below)).

3.4.4 Solubility Experiments

For the solubility experiments, the iron (II) phosphonate precipitate was equilibrated systematically at varying conditions of ionic strength and temperature. A deoxygenated solution containing a buffer of 0.05 M sodium acetate, 0.05 M acetic acid and an appropriate amount of NaCl was transferred from the deoxygenation flask to the reaction vessel which contained the washed Fe-NTMP precipitate. The conditions started at 1 M IS and 70°C. After equilibrium was reached on the continuously stirred sample, as determined by a constant concentration of iron and phosphonate for several hours, the temperature was lowered to 50°C and equilibrium was again established. The temperature was then lowered to 25°C until a new equilibrium was obtained. Because many scaling salts are inversely soluble (Chapter 2), the experiments were run from a higher to a lower temperature so that the reprecipitation did not occur (assuming that Fe-NTMP also was an inversely soluble salt). The condition was then changed to 2 M IS, and the temperature was elevated to 70°C. The temperature changes were repeated at 2

M IS; the solution condition was then changed to 3 M IS and again the temperature changes were repeated. Typically, the solution was allowed to equilibrate for at least 48 to 72 hours to assure that equilibrium was established, with samples being taken every few hours to measure the total concentrations of iron and phosphonate.

3.4.4.1 Attempt to Use a Fixed Iron Concentration

The pH was held constant by using the acetic acid/acetate buffer to reduce mathematical complexity. A constant ferrous iron concentration simplifies the solubility product calculations, requiring measurement of only phosphonate in each sample taken. Thus, an attempt was made to add a relatively large amount of reduced iron (0.1 M) to the system during the dissolution. Though this method of approach was desirable, the deoxygenated iron/acetate/salt solution added to the precipitate caused the solution's color to change from off-white to a deep red-orange when left overnight, indicating oxidation. An attempt to repeat this experiment using a more rigorous approach with deoxygenated crystalline FeCl_2 combined with the remaining reactants still caused oxidation to occur when the solution was left overnight.

To avoid oxidation as in the previous attempts to add iron, a preparation flask was added to the apparatus to obtain even *more* deoxygenation. This round-bottomed flask was added between the deoxygenation vessel and the reaction vessel and contained a stopcock at its inlet and outlet. Iron chloride (to yield a 1 M IS solution) was added to this new flask and then deoxygenated. The remaining solution reagents were deoxygenated in the deoxygenation flask and subsequently added to the FeCl_2 in the

preparation flask. The solution was stirred and left overnight. Because oxidation did occur, the solution was discarded and instead $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)$ was added to yield a 1 M IS final solution. It was believed that the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)$ was more resistant to oxidation in the crystalline form than ferrous chloride; however, the solution oxidized after about 8 hours, yielding a light orange colored solution with a large amount of settled reddish precipitate. Since all the constant-iron experiments were done continuously, it was possible that oxidized orange residue from the reaction vessel's walls contaminated the solution. To test the ferrous ammonium sulfate solution's resistance to oxidation, an independent solution was made in the preparation flask and immediately stored in the glove box. Oxidation did occur after about 20 hours, indicating that the limits of deoxygenation were not great enough to prevent oxidation when large amounts of iron were present. Thus, it was decided not to add excess iron and to measure both the total concentrations of iron and phosphonate instead, as described in the solubility experiments in Section 3.4.4.

Chapter 4

Results and Discussion

4.0 Introduction

In this chapter the results of the experiments described in Chapter 3 are presented and discussed. First, the results of the ferrous phosphonate stoichiometry experiments are shown along with results from the instrumental analyses. Then some qualitative aspects of the ferrous phosphonate seed material are described. Next, speciation and complexation theory as it relates to the current study is presented, along with the approach used to determine the solubility product constant. The results of the solubility dissolution batch experiment are presented; the data are shown explicitly and are summarized for each temperature and ionic strength condition. Further, an equation for pK_{sp} as a function of ionic strength and temperature is given. Finally, the conditional solubility products are used with real field data to compare calcium- and ferrous-phosphonate complexes.

4.1 Characterization of the Ferrous Phosphonate Seed Material

4.1.1 Stoichiometry

Eight independent experiments were run to determine the stoichiometry of the ferrous phosphonate solid. Table 4.1 contains the results of these experiments, indicating the total iron and total NTMP concentrations (mM) present in each solid sample. The mean (and standard deviation) of the Fe:NTMP ratio in the solid was 2.46 (0.18). The stoichiometry of the precipitate, using the general stoichiometry $Fe_xH_{6-2x}Phn$ (where *Phn* represents NTMP) presented in Chapter 2, is thus assumed to be $Fe_{2.5}HNTMP$, rounding to the nearest small whole-number ratios. Furthermore, this value is supported by:

- the chemical formula of NTMP, $(^2O_2P-CH_2)_3-N^+H$ (see Figure 4.1), and
- data for an amorphous form of Ca-NTMP with the stoichiometry $Ca_{2.5}HNTMP$.

The relatively large standard deviation of about 7% may partially be explained from the method of crystal formation, where a semi-constant composition was used instead of a completely constant composition because of the need for an anoxic environment. The size and size distribution of the solid particles may change during the course of the reaction (formation) when a constant composition is not used (Tomson and Nancollas, 1978). In addition, a commercial inhibitor was used instead of pure NTMP, since results using Dequest® would be more applicable to field work. The commercial inhibitor contains impurities such as phosphoric and phosphorous acids, which may interfere with the solubility of the solid. As with solubility studies using calcium-inhibitor

Table 4.1. Summary of experimental data for determining Fe-NTMP stoichiometry. Samples were taken at the conclusion of the dissolution experiments; thus, the precipitate had undergone temperature changes of 25-70°C for ionic strengths between 1 and 3 M over a period of about 7 weeks. These samples were taken from the final T and IS condition: 25°C, 3 M.

Sample Number	Fe _T (mM)	NTMP _T (mM)	Fe _T / NTMP _T
	(x 10 ⁻³)	(x 10 ⁻³)	
1	2.507	0.928	2.70
2	19.159	8.746	2.19
3	12.087	4.816	2.51
4	8.953	3.796	2.36
5	12.534	4.666	2.69
6	9.132	4.005	2.28
7	14.414	5.987	2.41
8	4.118	1.639	2.51
Mean			2.46
Standard Deviation			0.18

Figure 4.1 A probable structure of HNTMP^{5-} in the solid phase $\text{Fe}_{2.5}\text{HNTMP}$. The sp^3 -hybrid nitrogen is very basic with an estimated ionization constant of $10^{-12.3}$ and its hydrogen is therefore difficult to remove.

precipitates, ferrous phosphonate salts also likely exhibit “complicated precipitation and dissolution chemistries” as the result of the formation of multiple phases, persistence of thermodynamically unstable phases, and development of non-stoichiometric phases from the incorporation of impurities and lattice defects (Frostman *et al.*, in press).

Despite the likely sources of error, and assuming the above stoichiometry is representative of the actual precipitate stoichiometry, the K_{sp} is calculated from the equation:

$$K_{sp} = (Fe^{2+})^{2.5} \{H^+\} (NTMP^6). \quad (4.1)$$

A molar ratio of 2.5:1:1 for Fe:H:NTMP is quite reasonable, especially considering the initial or amorphous phase of Ca-NTMP that exists in a metastable state has this same stoichiometry (Frostman *et al.*, in press). A second phase for Ca-NTMP was formed after the initial precipitate had undergone a dialysis-filtration process, and was found to have the stoichiometry Ca_3NTMP . It is important to compare calcium- and ferrous-inhibitor salts because, of the divalent metal cations prevalent in industrial brines, Ca^{2+} - and Fe^{2+} -phosphonate precipitates are believed to be among the most insoluble. Thus, the solids formed by these two cations may dictate the fate of inhibitors and the length of a squeeze lifetime.

4.1.2 Results Using Instrumental Analysis

Analyses of the solid were determined using X-ray diffraction (XRD) and an electron microprobe. Two samples were analyzed using XRD: the first sample was an

“initial” precipitate that had been washed (see Section 3.4.3.3) five times and then stored in an airtight glove box; the second sample was an “aged” precipitate taken from the solution after completion of the solubility experiments (Section 3.4.4). Thus, the second sample was washed nine times before undergoing the temperature and ionic strength changes discussed in Section 3.4.4. The results in Figure 4.2 show that sharp peaks for NaCl appear in each sample at ~ 31 and 46 $2\text{-}\theta$, as expected. Although no similar sharp peaks exist that reveal a crystalline ferrous phosphonate solid, the rounded “hump” centered at around 26 $2\text{-}\theta$ in both XRD results indicates that it is possibly a microcrystalline solid.

The electron microprobe results gave an average stoichiometry for the initial precipitate of $\text{Fe}_{1.66}\text{H}_{2.68}\text{NTMP}$. Caution must be used, however, in obtaining a molar ratio of elements in a solid from an electron microprobe since this instrument is site-specific, meaning different points of analysis on a single slide can produce different results. Further, as discussed above, several factors can interfere with the stoichiometry of a given solid, and may therefore explain the inconsistent molar ratio results. The electron microprobe results were instead able to confirm qualitatively the composition of the solid and the absence of other elements (Figure 4.3).

Figure 4.2. X-ray diffraction (XRD) diagrams. The X-ray patterns for a so-called initial precipitate (top figure) and an aged precipitate (bottom) of ferrous phosphonate show strong peaks for Na and Cl because NaCl was the electrolyte in which the precipitate was formed/matured. Although no sharp peaks exist to reveal a crystalline structure, the rounded “hump” in the figures suggests that the solid may be microcrystalline.

Figure 4.3. Electron microprobe results. The electron microprobe analysis of ferrous phosphonate confirms that the constituents of the solid are iron and phosphorus. Further, strong peaks for sodium and chloride exist, as the solid was prepared in a 1 M ionic strength NaCl-electrolyte solution. From the figure, there were no impurities in the solid. Note that 9843 FS is the number of counts on the P peak.

4.2 Qualitative Results

Qualitative experiments were run on the Fe-NTMP precipitate to test its reactivity and stability against oxidation. Ten milliliters of a ferrous phosphonate solution at ~5.5 pH was left in a small open beaker at room temperature. Settling occurred after several hours. The color remained off-white for over 30 hours, after which time the color changed to a light orange, indicating oxidation. In another “stability” test, about 30 mL of the precipitate solution was centrifuged (3000 rpm, 30 min) and the supernatant liquid was removed. The remaining settled particles were washed with deionized water and collected on a 0.45 μm filter, backflushed out of the filter into a 25 mL vial, and left open to the atmosphere. The fine particles remained an off-white color for about two days, after which time the color changed to pink/light orange.

Fe-NTMP’s reactivity with a strong base was tested. In the oxygen-free glove box, 1 mL of deoxygenated 8 N KOH was added to 10 mL of the precipitate. Immediately the solution turned dark green/brown; another mL of KOH was added to this solution, and similar changes were observed. After about two days, the ferrous-phosphonate/base solution changed color to an orange/brown mixture. Further, the reactivity of Fe-NTMP with calcium-containing salts was qualitatively observed. Approximately 10 mL of a 70 mM deoxygenated solution of CaCl_2 was added to 10 mL of a deoxygenated ferrous phosphonate solution in the glove box; no visible changes occurred. Similarly, 5 mL of a 70 mM deoxygenated solution of CaCO_3 was added to 10 mL Fe-NTMP, and again no visible effects were observed.

4.3 Speciation and Complexation

4.3.1 Derivation of Phosphonate Equilibrium Speciation Equations

A speciation and complexation model was introduced in Section 2.3 in which a deprotonated NTMP (H_0Phn^{6-}) was successively protonated to form H_6Phn^0 , and iron complexed with several partially protonated phosphonate ions. Again, a value for K_1^N was determined separately for NTMP ($\log K_1^N=12.3$) but will be used in the derivation following Tomson *et al.* (1994, 1995). The remaining proton association reactions and constants (that is, K_2-K_6) (see Figure 2.7) for the general reaction

are given by

$$K_i = \frac{(H_iPhn^{(6-i)-})}{\{H^+\}(H_{i-1}Phn^{(7-i)-})} \quad (4.3)$$

Thus, the concentration $(H_iPhn^{(6-i)-})=K_i\{H^+\}(H_{i-1}Phn^{(7-i)-})$. Through continued substitution, then, an arbitrary species $(H_iPhn^{(6-i)-})$ can be expressed in terms of equilibrium constants, free phosphonate concentration, and the pH:

$$(H_iPhn^{(6-i)-}) = K_1^N K_2 K_3 \dots K_i \{H^+\}^i (Phn^{6-}) \text{ for } i > 3. \quad (4.4)$$

A cumulative formation constant is used to simplify the expressions:

$$\beta_1 \equiv K_1^N \text{ and } \beta_i \equiv K_1^N K_2 K_3 \dots K_i \text{ (for } i > 3). \quad (4.5)$$

From Chapter 2, it was seen that the K_i 's are modeled as a linear function of charge according to the equation

$$\log K_i = a_{H^+} + b_{H^+}|q_{i-1}| \quad \text{for } i \geq 2. \quad (4.6)$$

The α_{H^+} and b_{H^+} terms are speciation constants determined from titration data and $|q_{i-1}|$ is the absolute value of the charge of the $(i-1)$ th species.

The method of determination of b_{H^+} combines the mass balance of phosphonate in the system with the electroneutrality condition (charge balance equation). The mass balance of the phosphonate species is given by

$$C_{Phn} = (Phn^{6-}) + \sum_{i=1}^6 (H_i Phn^{6-i}) \quad (4.7)$$

Substituting equations 4.4 and 4.5 into 4.7 and factoring out the free phosphonate concentration, (Phn^{6-}) , results in the following expression:

$$(Phn^{6-}) = \frac{C_{Phn}}{1 + \sum_{i=1}^6 \beta_i \{H^+\}^i} \quad (4.8)$$

Further, the electroneutrality condition for the phosphonate equilibrium is given by

$$(Na^+) + (H^+) = 6(Phn^{6-}) + \sum_{i=1}^6 (6-i)(H_i Phn^{6-i}) + (OH^-) \quad (4.9)$$

where (Na^+) refers only to the net amount of strong base (NaOH) added (as the Na^+ and Cl^- from added NaCl exactly “cancel one another” with respect to charge balance). Thus, via substitution of equations 4.4 and 4.5 into 4.9 and rearrangement, the concentration of base required to reach a certain pH is given by equation 4.10:

$$(Na^+)_{calc} = 6(Phn^{6-}) + \sum_{i=1}^6 (6-i)\beta_i \{H^+\}^i (Phn^{6-}) + (OH^-) - (H^+) \quad (4.10)$$

The value of free phosphonate from equation 4.8 can be used in equation 4.10. The only unknown in 4.10 is β_i , which is indirectly a function of b_{H^+} , since the other terms represent measurable quantities. If the a_{H^+} term is also required (as for NTMP), then at least two titration points are needed to solve equation 4.10. A solution for this equation is obtained by using a set of titration data and the following iteration procedure:

1. an a_{H^+} and a b_{H^+} value are assumed
2. K_i values from a_{H^+} and b_{H^+} are calculated using equation 4.6
3. a datum point (pH, C_{Phn} , $(Na^+)_{meas}$) is selected
4. the right-hand side of 4.10 ($(Na^+)_{calc}$) is then calculated
5. the residual-squared, r^2 , is calculated: $((Na^+)_{calc} - (Na^+)_{meas})^2$
6. steps 3-5 are repeated for all data points
7. r^2 is summed over all data points under consideration
8. new values for a_{H^+} and b_{H^+} are assumed by the method of nonlinear least squares adjustment or by trial-and-error
9. steps 2-7 are repeated until there is no change in the value for a_{H^+} and b_{H^+}

Table 4.2 contains the speciation constants a and b as a function of ionic strength (IS, in molality) and temperature (T, in Kelvin). These functions, determined by Frostman *et al.* (in press), were used in the calculations in this study to determine the free phosphonate and free iron concentrations. Because the a_{H^+} and b_{H^+} constants are specific to NTMP, they can be used to represent proton association for this inhibitor regardless of the metal that is complexing with NTMP in solution.

The ionic strength dependence in the reported functions for the a_{H^+} and b_{H^+} speciation constants in Table 4.2 is a function of molality (moles/kg H_2O), whereas the concentrations for total phosphonate and iron--and thus all other complexes, since all of the speciation and complexation concentrations are related--were reported and calculated

in units of molarity (moles/L solution). The difference between using molality and molarity for determining all of the constants is very slight, however, and was calculated

Table 4.2. Functional formulas for the proton association constants for NTMP. IS = ionic strength (molal) and T = temperature (K) (reproduced from Frostman *et al.*, in press).

Parameter	NTMP
a_{H^+}	$2.296 - 0.567\sqrt{IS} + 0.184IS - \frac{314}{T}$
b_{H^+}	$1.439 - 0.160\sqrt{IS} + 0.0255IS - \frac{54.3}{T}$

to result in a final change of $\Delta pK_{sp} \sim 0.02$. Therefore, pK_{sp} values do not change for all practical purposes, and it was decided then that using molar concentrations would not affect the final results significantly.

4.3.2 Derivation of Equations for Complexation with Ferrous Iron

A similar approach to that used for proton association with phosphonates is used to model complexation with ferrous iron and determine the complexation factor, $b_{Fe^{2+}}$. The experimental method for determining the complexation factor was discussed in Section 3.4.2. The general complexation reactions are given by the equation

and the corresponding equilibrium constants are given by

$$K_{ij} = \frac{(Fe_i H_i Phn^{(6-i-2j)})}{(Fe^{2+})(Fe_{j-1} H_i Phn^{(6-i-2j)})} \text{ for } i \geq 2, j \geq 1. \quad (4.12)$$

Through repeated substitution, the concentration of an arbitrary iron-phosphonate complex can be given by an equation similar to 4.4:

$$(Fe_i H_i Phn^{(6-i-2j)}) = \beta_{ij} (Fe^{2+})^i (H^+)^j (Phn^{6-}) \quad (4.13)$$

where β_{ij} is a cumulative formation constant for complex ions:

$$\beta_{ij} \equiv K_1^N K_2 \dots K_i K_{i1} K_{21} \dots K_{ij} = \beta_i K_{i1} K_{21} \dots K_{ij}. \quad (4.14)$$

Again, the complexation constants are modeled as a linear function of charge (using the charge of the species with one less iron ion in the complex):

$$\log K_{ij} = a_{Fe^{2+}} + b_{Fe^{2+}} |q_{2j-2+i}| \text{ for } i > 1, j \geq 1. \quad (4.15)$$

According to Tomson *et al.* (1994), the analogous $a_{Ca^{2+}}$ value was found not to significantly improve the model's fit to the data. It was assumed that the $a_{Fe^{2+}}$ value likewise would not improve the fit for the iron system. Hence,

$$\log K_{ij} = b_{Fe^{2+}} |q_{2j-2+i}| \text{ for } i > 1, j \geq 1. \quad (4.16)$$

The following describes the mathematical method for calculating $b_{Fe^{2+}}$; this method follows that above for phosphonate proton association, but with an added mass balance equation for the iron present in the system. The mass balance equations are:

$$C_{Phn} = (Phn^{6-}) + \sum_{i=1}^6 (H_i Phn^{6-i}) + \sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} (Fe_i H_i Phn^{6-i-2j}) \quad (4.17)$$

and

$$C_{Fe} = (Fe^{2+}) + \sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} (j) (Fe_i H_i Phn^{6-i-2j}). \quad (4.18)$$

(Note: in the summation of the j values in equations 4.17 and 4.18 and below, when the limit $(6-i)/2$ is a half-integer, the number is rounded up to the next integer.) The electroneutrality condition is

$$(Na^+) + 2(Fe^{2+}) + (H^+) = \sum_{i=0}^6 (6-i)(H_iPhn^{(6-i)}) + \sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} (6-2j-i)(Fe_jH_iPhn^{6-i-2j}) + (Cl^-) + (OH^-) \quad (4.19)$$

where (Na^+) again refers to the net amount of strong base (NaOH) added and (Cl^-) represents the concentration of counter-ions to C_{Fe} ; *i.e.*, $(Cl^-)=2C_{Fe}$, since ferrous ions were added as $FeCl_2 \cdot 4H_2O$. Via substitution and rearrangement of terms, the mass balance equations can be solved in terms of free phosphonate and free iron concentrations. The (Phn^{6-}) concentration is given by

$$(Phn^{6-}) = \frac{C_{Phn}}{1 + \sum_{i=1}^6 \beta_i \{H^+\}^i + \sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} \beta_{ij} (Fe^{2+})^j \{H^+\}^i}. \quad (4.20)$$

By substitution of equation 4.20 into 4.18, the total concentration of iron becomes

$$C_{Fe} = (Fe) + \frac{\sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} (j) \beta_{ij} (Fe^{2+})^j \{H^+\}^i C_{Phn}}{1 + \sum_{i=1}^6 \beta_i \{H^+\}^i + \sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} \beta_{ij} (Fe^{2+})^j \{H^+\}^i}. \quad (4.21)$$

Therefore, for known total concentrations of iron and phosphonate at a given pH, equation 4.21 can be solved via iteration. Once an (Fe^{2+}) concentration is determined from this iteration, the concentration of free phosphonate can be calculated by substituting

(Fe^{2+}) into equation 4.20. Finally, an optimum value for $b_{Fe^{2+}}$ can be determined from the electroneutrality equation (rearranged):

$$(Na^+)_{calc} = 6(Phn^{6-}) + \sum_{i=1}^6 (6-i)(H_i Phn^{(6-i)}) + \sum_{i=1}^6 \sum_{j=0}^{(6-i)/2} (6-i-2j)(Fe_j H_i Phn^{6-i-2j}) + 2[C_{Fe} - (Fe^{2+})] + (OH) - (H^+) \quad (4.22)$$

Similar to the procedure outlined in Section 4.3.1,

1. a $b_{Fe^{2+}}$ value is assumed
2. β_i values from $b_{Fe^{2+}}$ are calculated using equation 4.16
3. a datum point (pH, C_{Phn} , $(Na^+)_{meas}$) is selected
4. the right-hand side of 4.22 is calculated (from (Fe^{2+}) and (Phn^{6-}))
5. the residual-squared, r^2 , is calculated: $((Na^+)_{calc} - (Na^+)_{meas})^2$
6. steps 3-5 are repeated for all data points
7. r^2 is summed over all data points under consideration
8. a new value for $b_{Fe^{2+}}$ is assumed by the method of nonlinear least squares adjustment or by trial-and-error
9. steps 2-7 are repeated until there is no change in the value for $b_{Fe^{2+}}$

4.3.2.1 Complexation Factor Results and Discussion

A computer program written in FORTRAN (Appendix A) for Ca-inhibitor studies was used to calculate the value for $b_{Fe^{2+}}$ given a data set of input parameters, such as ionic strength, temperature, and pH values from titrations, as well as using the iterative method outlined above. Table A.1 contains the input parameters for this program; Figure A.1 contains the output. The value for $b_{Fe^{2+}}$ converged at 0.86; this value is used throughout this study to determine the K_{ij} complexation constants. The final value of the pK_{sp} changed by less than 0.015 (or, around 0.05%) when the functional form of $b_{Ca^{2+}}$ was used

for $b_{\text{Fe}^{2+}}$ for temperatures and ionic strengths other than 25°C and 1 M. Thus, although the value for $b_{\text{Fe}^{2+}}$ was based on the $b_{\text{Ca}^{2+}}$ value at 25°C and 1 M IS, no temperature and ionic strength dependence was placed on the iron complexation factor because the values of the complexation constants were assumed not to vary significantly in the temperature and ionic strength ranges of this study. Thus, the K_{ij} 's from Figure 2.7 can be tabulated; the results are in Figure 4.4.

The value of the iron complexation factor can be interpreted using outer-sphere complex formation and ligand field theory arguments. An outer-sphere complex is the result of a central metal (M) cation (iron) reacting with a ligand (L) (phosphonate). The associated equilibrium constant is obtained from the general equation for divalent metal cations:

and the equilibrium constant K_{os} is given by

$$K_{\text{os}} = \frac{\text{ML}^{(2-n)+}}{(\text{M}^{2+})(\text{L}^{n-})} \quad (4.24)$$

Morel and Hering (1993) give a theoretical expression for K_{os} derived from statistical and electrostatic interactions:

$$K_{\text{os}} = \frac{4000\pi N_A \alpha^3}{3} \exp\left(\frac{-z_M z_L e^2}{4\pi\epsilon_0 \epsilon k T \alpha}\right) \exp\left(\frac{-z_M z_L e^2 \kappa}{4\pi\epsilon_0 \epsilon k T (1 + \kappa \alpha)}\right) \quad (4.25)$$

where κ is the Debye-Hückel ion atmosphere parameter, given by

$$\kappa^2 = \frac{2000e^2 N_A I}{\epsilon_0 \epsilon k T} \quad (4.26)$$

Figure 4.4. Complexation and speciation constants for the NTMP and iron (II) complexes considered. See also Figure 2.7. 1 m IS, 298 K values for K_i : 12.3, 6.47, 5.35, 4.23, 3.10, 1.98.

and the remaining constants (with SI units) are:

N_A = Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$); α = distance of closest approach (m); z_M = charge on metal ion (+2 for ferrous iron); z_L = charge on ligand (*e.g.*, -2 for $\text{H}_4\text{Phn}^{2-}$); ϵ_0 = permittivity of a vacuum ($8.834 \times 10^{-12} \text{ Jm}^{-2}$); ϵ = dielectric constant of water (78.54 at 25°C); k = Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$); e = electron charge ($1.60 \times 10^{-19} \text{ C}$); T = temperature (K); I = ionic strength (molal).

The value of the outer-sphere complex stability constant calculated using equation 4.25 can be compared to the value of the complexation constant obtained from equation 4.16 for a given species. For example, the equilibrium constant associated with FeH_4Phn^0 is $\log K_{41} = b_{\text{Fe}^{2+}}(2)$, or $0.86 \times 2 = 1.72$, using equation 4.16. The same value, $\log K_{\text{os}} = 1.72$, is obtained using equation 4.25 when the value for the distance of closest approach (ion size) is $\alpha = 2.2 \times 10^{-10} \text{ m}$ (2.2 Angstroms). Because this distance is about half that of a water molecule (which is generally considered the average distance of approach of a ligand to a metal), complexation between Fe^{2+} and Phn^{6-} is only *partially* explained by outer-sphere complexing. That is, extra energy is required to overcome repulsive forces at that close a distance (2.2 Å) to stabilize the ligands with respect to the central metal atom.

Ligand field stabilization energy (LFSE) is the difference in stability that is the result of ligands approaching a metal. Because it contains an incomplete outer d shell, Fe^{2+} experiences a LFSE upon complex formation. Thus, the ligand association energy (also called hydration energy) for iron is greater than if no LFSE existed, as seen in Figure 4.5 (reproduced from Morel and Hering, 1993). Thus, the difference between the smooth curve and the hydration energy of Fe^{2+} in Figure 4.5 is in fact the LFSE. Thus, the

complexation of iron and phosphonate is due in part to outer-sphere complexation *and* to electronic interactions in the inner sphere.

Figure 4.5. Hydration energies of the divalent cations of the first row of transition metals. The solid symbols indicate measured hydration energies, while the open circles are corrected for the LFSE (ligand field stabilization energies). The difference between the smooth curve and the solid circles is the value of the LFSE. Reproduced from Morel and Hering (1993), p. 329.

4.3.2.2 Method of Determining Free Concentrations of Iron and Phosphonate

The values for free phosphonate and free iron concentrations (*i.e.*, (Phn^6) and (Fe^{2+})) were determined using a spreadsheet calculation. With a spreadsheet set-up, the concentration of each ion in solution could be connected via an equation similar to 4.13. A change in the concentration of free iron, for example, would cause all related values to change accordingly. The iterative method for the calculations used in this study was performed using the Goal Seek function in Microsoft Excel 5.0 (1993) with a convergence criterion of 1E-21. The Goal Seek function operates by iteratively changing an independent cell value to obtain a pre-determined value in a dependent cell, given an initial guess for the independent value. A flow-diagram in Figure 4.6 details the method of calculation. Finally, the K_{sp} and pK_{sp} were calculated from the converged concentrations of free iron and phosphonate.

Figure 4.6. A flow diagram summarizing the calculations required to obtain the concentrations of free iron and free phosphonate (NTMP) in solution. Values for the K_i and K_{ij} constants are calculated from the input parameters; the equilibrium constants are then used to calculate the concentration of each species in solution, based on initial guesses of the free iron and phosphonate concentrations. The difference between the calculated and measured values of total Fe^{2+} and Phn^{6-} is minimized by changing values of free Fe^{2+} and Phn^{6-} until this difference approaches zero (convergence criterion: $1E-21$).

4.4 Solubility Results

4.4.1 Dissolution Experimental Data

Table 4.3 contains the results from the consecutive dissolution experiments described in Section 3.4.4. The data in the table are divided into nine sections, with each section corresponding to a given dissolution condition with respect to ionic strength (M) and temperature (°C). The data are listed chronologically; the columns labeled Phn_T and Fe_T refer to the measured concentrations of phosphonate (specifically NTMP) and iron in the solution. The columns labeled Phn_f and Fe_f contain values that were calculated using the method described above in Section 4.3.2; these values are used with equation 4.1 to calculate the pK_{sp} 's listed in the last column.

Figure 4.7 is a plot of the pK_{sp} values in Table 4.3 as a function of time. Because the dissolution of ferrous phosphonate was a batch experiment, the points in Figure 4.7 represent consecutive calculated pK_{sp} values. The data are divided into sections corresponding to those in Table 4.3. The temperature and ionic strength conditions were held so that equilibrium, determined by a constant or near-constant measured concentration of total iron and phosphonate, was maintained for several hours. Each T and IS condition lasted for at least one day; all but two conditions were maintained for at least two days (the exceptions were 25°C, 2 M IS and 70°C, 3 M IS; equilibrium was established relatively quickly for these conditions). The last condition is anomalous in that the temperature and ionic strength were kept constant for several weeks, as opposed

Table 4.3. Summary of chronological experimental solubility data for Fe-NTMP. The initial ionic strength was 1 M; the temperature was 70°C, and eventually was lowered to 50 and then to 25°C. The IS was increased to 2 M and 3M, and the same temperature cycle was run for each IS. $K_{sp} = (Fe^{2+})^{2.5} \{H^+\} (Phn^{6-})$ and $pK_{sp} = -\log K_{sp}$.

Time (h)	T (°C)	IS (M)	pH	Phn _T (M) (x 10 ⁻⁵)	Fe _T (M) (x 10 ⁻⁵)	Phn _r (M) (x 10 ⁻¹⁶)	Fe _r (M) (x 10 ⁻⁵)	pK _{sp}
5.50	70	1	4.48	0.16	8.70	0.05	8.70	31.919
17.00	70	1	4.48	1.05	6.26	0.35	6.24	31.444
18.50	70	1	4.48	1.28	6.20	0.43	6.17	31.370
20.50	70	1	4.48	1.43	5.78	0.48	5.76	31.399
23.00	70	1	4.48	1.47	6.99	0.49	6.96	31.183
24.00	70	1	4.48	1.38	6.21	0.46	6.19	31.337
41.50	70	1	4.48	1.64	6.36	0.55	6.32	31.239
47.00	70	1	4.48	1.61	6.14	0.54	6.11	31.284
48.50	70	1	4.48	1.86	4.69	0.63	4.66	31.511
63.50	50	1	4.48	0.94	3.60	0.55	3.59	31.855
68.50	50	1	4.48	0.95	3.37	0.55	3.35	31.923
72.00	50	1	4.48	1.07	3.89	0.62	3.87	31.716
88.50	50	1	4.48	0.97	3.53	0.57	3.51	31.863
93.25	50	1	4.48	1.09	3.78	0.63	3.76	31.740
96.25	50	1	4.48	1.42	3.38	0.83	3.37	31.745
115.25	50	1	4.48	1.29	3.53	0.75	3.52	31.741
123.75	25	1	4.48	0.96	4.10	1.19	4.08	31.378
126.25	25	1	4.48	1.00	3.77	1.23	3.75	31.454
136.25	25	1	4.48	1.34	4.19	1.66	4.16	31.211
141.25	25	1	4.48	1.08	3.74	1.34	3.72	31.425
146.75	25	1	4.48	1.15	3.74	1.42	3.72	31.400
159.50	25	1	4.48	1.18	4.56	1.45	4.53	31.177
164.75	25	1	4.48	1.33	4.75	1.63	4.72	31.083
166.75	25	1	4.48	1.50	5.09	1.84	5.05	30.957
186.75	25	1	4.48	1.26	4.85	1.56	4.82	31.080
232.25	25	1	4.48	1.24	5.00	1.52	4.98	31.055
238.00	70	2	4.42	0.97	4.62	0.73	4.60	31.400
255.75	70	2	4.42	1.27	4.07	0.96	4.05	31.417
259.75	70	2	4.42	1.44	4.45	1.09	4.42	31.269
281.25	70	2	4.42	1.55	3.90	1.17	3.88	31.380
285.75	70	2	4.42	1.03	3.86	0.78	3.84	31.565
304.50	70	2	4.42	1.09	3.21	0.83	3.19	31.742
307.50	70	2	4.42	1.41	3.76	1.07	3.74	31.458
309.50	70	2	4.42	1.15	3.89	0.87	3.87	31.510
325.50	50	2	4.42	1.48	3.92	1.88	3.89	31.170
329.00	50	2	4.42	1.57	4.82	1.99	4.78	30.923
377.50	50	2	4.42	1.26	4.24	1.61	4.21	31.153
379.75	50	2	4.42	1.33	3.85	1.70	3.83	31.234
385.50	50	2	4.42	1.37	4.29	1.75	4.26	31.104
395.67	25	2	4.42	1.17	4.53	3.04	4.50	30.805
399.50	25	2	4.42	1.27	4.40	3.29	4.37	30.801
404.00	25	2	4.42	1.33	4.22	3.46	4.18	30.827
409.50	25	2	4.42	1.72	5.17	4.45	5.12	30.499
420.25	25	2	4.42	1.34	4.28	3.49	4.25	30.808
422.25	25	2	4.42	1.24	4.48	3.24	4.44	30.791

Table 4.3 continued

Time (h)	T (°C)	IS	pH	Phn _T (M) ($\times 10^{-5}$)	Fe _T (M) ($\times 10^{-5}$)	Phn _T (M) ($\times 10^{-16}$)	Fe _T (M) ($\times 10^{-5}$)	pK _{sp}
429.25	70	3	4.38	1.03	3.04	1.00	3.03	31.678
449.50	70	3	4.38	0.80	3.24	0.77	3.23	31.720
472.25	70	3	4.38	1.02	3.40	0.99	3.38	31.562
494.50	50	3	4.38	1.11	3.23	1.80	3.21	31.358
496.00	50	3	4.38	0.72	2.74	1.17	2.73	31.723
501.25	50	3	4.38	0.70	3.67	1.12	3.66	31.421
515.75	50	3	4.38	0.76	3.21	1.23	3.20	31.527
519.75	50	3	4.38	1.05	3.03	1.70	3.03	31.445
521.50	50	3	4.38	0.56	3.26	0.90	3.25	31.647
539.00	50	3	4.38	0.92	3.11	1.48	3.09	31.483
541.75	50	3	4.38	0.66	3.40	1.07	3.39	31.528
543.00	50	3	4.38	0.58	3.29	0.94	3.28	31.615
549.50	50	3	4.38	0.77	3.06	1.25	3.05	31.572
551.00	50	3	4.38	0.60	3.85	0.97	3.84	31.435
561.50	50	3	4.38	0.85	3.66	1.38	3.65	31.337
563.00	50	3	4.38	1.15	3.51	1.87	3.49	31.253
569.75	25	3	4.38	0.63	4.18	2.04	4.16	31.021
581.50	25	3	4.38	0.76	3.60	2.48	3.58	31.101
589.50	25	3	4.38	0.86	3.42	2.81	3.40	31.102
607.00	25	3	4.38	0.78	3.94	2.55	3.92	30.991
631.50	25	3	4.38	0.78	4.59	2.54	4.57	30.826
653.25	25	3	4.38	1.16	3.96	3.78	3.93	30.817
654.50	25	3	4.38	1.37	4.66	4.45	4.61	30.572
658.50	25	3	4.38	0.74	4.21	2.41	4.19	30.943
677.00	25	3	4.38	0.97	3.87	3.18	3.84	30.916
1193.50	25	3	4.38	1.05	5.32	3.42	5.28	30.539

Figure 4.7. Plot of the consecutive pK_{sp} values over a seven-week period. The arrows point to the values of the pK_{sp} that were obtained for a particular ionic strength and temperature condition.

to several days. Since this condition was the final one, the stability of the precipitate solubility was tested here. Figure 4.7 shows that the final value reached at the end of the three-week period (1193.5 h) is considerably lower than most of the pK_{sp} values obtained for that condition with the exception of the pK_{sp} at 409.5h and 654.5 h. Hence, the solubility of the solid may have increased over the longer time period, possibly because of slower kinetics at 25°C.

Upon completion of these experiments, the temperature was increased to 70°C while the solution's IS was still 3 M to determine if the solubility would decrease to the pK_{sp} average value of 31.653 for 3 M IS, 70°C in the original experiment. The solution was maintained at these conditions for approximately ten days, with four samples taken over this period of time. The mean and standard deviation were: $pK_{sp}=30.943\pm0.115$. Thus, the solubility decreased slightly upon returning the temperature to 70°C; however, the new mean solubility product was close to that of the 25°C, 3 M IS experiment than the previous 70°C condition.

4.4.2 Mean pK_{sp} Results

From Figure 4.7 it is apparent that a general trend was established for each temperature and ionic strength condition. For many of these conditions, however, there appears to be one or two outliers which deviate from that trend. Thus, the average pK_{sp} and standard deviation were calculated for each T/IS division (Table 4.4). The average

Table 4.4. Summary statistics for solubility data. The mean pK_{sp} values plus one standard deviation are for each temperature and ionic strength condition of Table 4.4.

Time Range (h)	T (°C)	IS (M)	pH	Mean pK_{sp}	Std. Dev.
5.5-48.5	70	1	4.48	31.410	0.216
63.5-115.25	50	1	4.48	31.798	0.081
123.75-232.25	25	1	4.48	31.222	0.180
238-309.5	70	2	4.42	31.468	0.142
325.5-385.5	50	2	4.42	31.117	0.118
395.67-422.25	25	2	4.42	30.755	0.126
429.25-472.25	70	3	4.38	31.653	0.082
494.5-563	50	3	4.38	31.488	0.133
569.75-1193.5	25	3	4.38	30.883	0.198

values lie between 30.755 (for 25°C, 2 M IS) and 31.798 (for 50°C, 1 M IS). All of the standard deviations are below 0.200 except that for 70°C, 1 M IS. When the mean pK_{sp} data are plotted as a function of time, the resultant Figure 4.8 appears to be a “normalized” version of Figure 4.7. The trends indicated in Figure 4.7 become much more apparent in Figure 4.8. A cyclic behavior appears to form when the temperature is lowered from 70 to 50 to 25°C within one ionic strength—namely, the pK_{sp} mean value drops successively. When a new ionic strength condition is introduced, and the temperature is returned to 70°C, the pK_{sp} values return to a level higher than that at the previous condition, followed by a drop in pK_{sp} with a decrease in temperature. The only exception is the first condition at 70°C, 1 M IS, which is lower than the corresponding pK_{sp} mean for 50°C.

4.4.2.1 Explanation of Deviation

Several factors may explain the different behavior of the first set of data. One possibility is that, because this is the first dissolution condition, the solid may be in an initial phase, that is, a microcrystalline phase which has not undergone any phase transformation. As different temperatures and ionic strengths are introduced to the solution later in the experiment, the solid may undergo a phase change to a more mature solid, after which point the solid behaves in a regular fashion. It was found for Ca-DTPMP (where DTPMP is a related phosphonate-based inhibitor), for example, that the

Figure 4.8. Plot of the mean pK_{sp} values over time for each temperature and ionic strength condition. The trends that characterize the data are easily observed when the mean pK_{sp} values for each temperature and ionic strength condition are plotted as a function of time. With the exception of the first set of conditions, the solubility decreases as temperature decreases for a given ionic strength. Further, the solubility of the ferrous phosphonate increases as the ionic strength is increased but then decreases when the IS is further increased.

initial precipitates were so-called amorphous and slowly transformed to a less soluble phase (Kan *et al.*, 1994). Further, it is possible that the impurities associated with the commercial inhibitor dictate the dissolution of the precipitate because it is the first set of conditions (Frostman *et al.*, in press), implying that these impurities still existed while the data were collected. Finally, it is possible that the precipitate was not washed thoroughly before the dissolution experiments began. The solid was washed nine times; however, total iron in the mother liquor initially was in great excess compared to phosphonate (16:1 molar ratio) even after the ninth wash. Because of the excess of iron, the amount of ferrous phosphonate that could dissolve, as dictated by the true solubility product constant, was greatly decreased. In support of this is the $\text{Fe}_T:\text{Phn}_T$ ratio, which begins at around 54 and then decreases to around 3~4 for the remainder of much of the data set. Figure 4.9 is a plot of the logarithm of the concentration of total iron or phosphonate in the batch dissolution experiments as a function of time. From this figure, the ratio of iron to phosphonate appears to be stable after the initial experiments, as indicated. Thus, the apparent solubility of this first set of experiments does not follow the general trend established in the remaining conditions and the impact of impurities needs to be studied.

4.4.3 Ionic Strength and Temperature Dependence

Figure 4.10 is a plot of the mean pK_{sp} as a function of ionic strength (M). From this figure, it can be seen for all three temperatures that, with the exception of the data from 70°C, 1 M IS, the mean pK_{sp} value decreases as the ionic strength is increased, reaching a low point at 2 M IS, and then increases again as the ionic strength is increased

Figure 4.9. Plot of log concentration over time. From the figure, total iron and total phosphonate in the batch dissolution experiments maintain a near-constant ratio throughout the experiment, with the exception of the data for the initial conditions.

Figure 4.10. Plot of mean pK_{sp} as a function of ionic strength. A plot of the mean pK_{sp} values as a function of ionic strength essentially summarizes the information obtained from Figure 4.8, showing explicitly the dependence of the solubility product constant on the range of IS solutions considered in this study.

Figure 4.11. Plot of mean pK_{sp} as a function of temperature. Similar to data summary of Figure 4.10, this graph shows the dependence of the mean pK_{sp} on temperature. With the exception of the 70°C 1 M IS data, the pK_{sp} increases as the temperature is increased (that is, solubility decreases as temperature increases).

to 3 M IS. The increase in pK_{sp} at 3 M IS, however, leads to a value lower than that at 1 M IS. Figure 4.11 shows the general trend found in most scaling precipitates that, as temperature increases, the solubility decreases. This property of inverse solubility, discussed in Chapter 2, is apparent from the rise in mean pK_{sp} as the temperature is increased. The only exception to this is again the pK_{sp} from the initial condition.

A curve fit using the statistical code Psi-Plot (1994) was performed to determine pK_{sp} as a function of ionic strength and temperature. Following the functional form of the solubility for $\text{Ca}_{2.5}\text{HNTMP}$ (from Frostman *et al.*, in press), the following general equation was used:

$$pK_{sp} = A + B\sqrt{IS} + C*IS + D/T \quad (4.27)$$

where A, B, C, and D are constants, IS is the ionic strength in molarity, and T is the temperature in Kelvin. The value of K_{sp} from equation 4.27 is a conditional solubility product constant since it is an explicit function of ionic strength. The curve fit result is:

$$pK_{sp} = 39.54(\pm 1.24) - 6.14(\pm 1.63)\sqrt{IS} + 2.18(\pm 0.6)IS - 1315(\pm 205)/T. \quad (4.28)$$

Figure 4.12 shows the curve fit of equation 4.28 for all three temperatures used in this study over a range of ionic strengths. The fitted curves in Figure 4.12 essentially smooth out the curves in Figure 4.10. Furthermore, the pK_{sp} allows for thermodynamic properties to be calculated. For instance, the standard enthalpy change can be calculated from equation 4.28 via the thermodynamic relationship (Stumm and Morgan, 1981) $\ln K =$

$$\frac{-\Delta H^\circ}{RT} + C \text{ such that } -1315 = \frac{\Delta H^\circ}{2.302R}. \text{ Thus, } \Delta H^\circ = -25.2 \text{ kJ mol}^{-1}.$$

Figure 4.12. Curve-fitted values of the pK_{sp} of Fe-NTMP as a function of ionic strength. The pK_{sp} as a function of ionic strength is plotted for the three temperatures used in this study. The curves were made using the fitted functional form in equation 4.28. The variation in Figure 4.10 is corrected for in this figure when equation 4.28 is used.

4.4.3.1 Test of Functional Form

The rigor of the functional form of the pK_{sp} for ferrous phosphonate was tested by changing the pH of the solution after the completion of the solubility dissolution experiments. Hence, the ionic strength was 3 M at 70°C. The pH was lowered to 3.90 (from ~4.4) by the addition of 20 mL of deoxygenated 0.1 M acetic acid. Three samples were taken, at 2, 22, and 33 h after the addition of the acid. The resultant mean pK_{sp} (and standard deviation) for these three samples was 31.925 (0.085). Using the functional form in equation 4.24 at $T=343$ K and $IS=3$, the calculated pK_{sp} was 31.611, a difference from the mean of only 0.99%. This closeness of fit is an indication that the pK_{sp} function determined from this study may be widely applicable to other pH, temperature, and ionic strength conditions, and thus is useful in real field situations.

4.5 Application of Results

4.5.1 Simulations Using Field Data

Because of the relevance of this work to oil and gas production wells, and the apparent influence of calcium and ferrous cations on phosphonate inhibitor fate in precipitation squeezes, the solubility data were used with real field data to simulate precipitation conditions. Ten wells in Texas and Louisiana which have been used in various other inhibitor studies were chosen. The wells and their corresponding characteristics are listed in Table 4.5. The pH, temperature, and ionic strength, along with the concentrations of total calcium and total iron, were used as input parameters in an Excel 5.0 spreadsheet as before; each system was assumed to be independent of other systems. If the value of ferrous iron was 0, then it was set equal to $(Ca^{2+}_T)/100$ because $K_{sp}(CaCO_3) \approx 100 K_{sp}(FeCO_3)$. In addition, the IS (M) was assumed to equal IS (m). Also, the value of total phosphonate was defined for each well as 1 mg/L NTMP; this concentration is representative of phosphonate return concentrations following a squeeze treatment. Finally, the functional form of $b_{Ca^{2+}}$ determined by Frostman *et al.* (in press) was used: $b_{Ca^{2+}} = 1.569 - 0.606\sqrt{IS} + 0.201IS - 206/T$ for the calcium data.

Each simulation was run to determine final concentrations of free iron, calcium, and phosphonate; these values, along with the pH (actually, hydrogen activity), were used with the appropriate stoichiometry of the precipitate to determine the ion product (IP):

$$\begin{aligned} \text{for } Fe_{2.5}HNTMP, \quad IP &= (Fe^{2+})^{2.5}\{H^+\}(NTMP^{6-}) \\ \text{for } Ca_{2.5}HNTMP, \quad IP &= (Ca^{2+})^{2.5}\{H^+\}(NTMP^{6-}) \text{ and} \\ \text{for } Ca_3NTMP, \quad IP &= (Ca^{2+})^3(NTMP^{6-}). \end{aligned}$$

Table 4.5. Input parameters for solubility simulations. Phnr:Fe or :Ca refers to the free phosphonate concentration in the respective simulation. Total phosphonate was set for each well at 1 mg/L, a typical phosphonate return concentration.

Well Name	pH	T (K) (bottom hole)	IS (M)	Fe_T (M) ($\times 10^{-4}$)	Ca_T (M) ($\times 10^{-2}$)	Phnr (M) ($\times 10^{-6}$)	Fe_T (M) ($\times 10^{-4}$)	Ca_T (M) ($\times 10^{-2}$)	Phnr:Fe (M) ($\times 10^{-13}$)	Phnr:Ca (M) ($\times 10^{-14}$)	pK_{sp} $\text{Fe}_2\text{:HPhn}$	pIP $\text{Fe}_2\text{:HPhn}$	pK_{sp} $\text{Ca}_2\text{:HPhn}$	pIP $\text{Ca}_2\text{:HPhn}$	pK_{sp} Ca_3P	pIP Ca_3P
Gladys McCall	4.10	420.78	1.75	6.27	10.30	3.34	6.26	10.3	2.04e^{-6}	4.09e^{-6}	32.107	30.798	21.112	25.955	18.673	22.349
O'Daniel #2	5.37	413.55	0.76	1.36	1.90	3.34	1.36	1.90	1.12e^{-2}	1.95e^{-2}	32.664	29.987	21.697	25.386	19.137	20.877
Pleasant Bayou #2	5.50	424.67	2.91	17.2	24.00	3.34	17.20	24.00	2.87e^{-2}	2.39e^{-3}	32.313	26.955	21.163	23.672	18.807	18.483
High Island A-9 #2	6.00	411.89	1.20	1.25	3.07	3.34	1.24	3.07	0.79	0.41	32.237	28.867	21.262	24.170	18.762	18.927
Huff A	6.50	371.89	0.74	1.61	1.12	3.34	1.59	1.12	5.72	9.40	32.335	28.236	21.242	24.406	18.643	18.882
N.R. Smith #4	6.50	344.11	0.88	1.43	1.20	3.34	1.41	1.20	7.69	21.60	31.873	28.238	20.682	23.969	18.078	18.43
Pretts #1	6.50	374.11	0.73	0.52	1.12	3.34	0.51	1.12	8.56	8.64	32.375	29.296	21.288	24.438	18.689	18.913
A.E. Guerra #43	6.50	444.11	1.40	2.15	16.20	3.34	2.13	16.20	4.70	0.044	32.366	28.007	21.460	23.831	19.005	17.726
Maxus ZEE-6	6.50	388.56	0.23	0.09	0.57	3.34	8.86e^{-2}	0.57	4.03	2.27	33.712	31.527	22.586	25.747	19.884	20.368
Thompson Trustee #1	7.43	374.67	0.75	0.88	1.28	3.34	0.86	1.21	140.00	98.30	32.348	28.449	21.263	24.233	18.670	17.762

$*\text{pK}_{\text{sp}}(\text{Ca}_2\text{:HNTMP}) = 29.34 - 5.39\sqrt{\text{IS}} + 1.79\text{IS} - 1780/T$; $**\text{pK}_{\text{sp}}(\text{Ca}_3\text{NTMP}) = 26.80 - 5.00\sqrt{\text{IS}} + 1.73\text{IS} - 1910/T$

*, ** from Frostman *et al.* (in press)

Figure 4.13 illustrates the results of the simulations; the columns labeled pIP and pK_{sp} in Table 4.5 were used to determine the saturation index (SI), plotted in Figure 4.13. The SI is the difference between the pK_{sp} and the pIP (where $pX = -\log X$). This figure shows the saturation index for each production well as a function of ionic strength. The pK_{sp} 's in Table 4.5 were calculated using the curve-fitted equation corresponding to each precipitate (see footnote in table).

The SI predicts whether a solution will form a precipitate; this prediction is obviously of great importance for scale control. The SI is defined by the equation:

$$SI = \log \left(\frac{IP}{K_{sp}} \right), \text{ or, equivalently, } SI = pK_{sp} - pIP.$$

Any value of $SI > 0$ will form a precipitate, as this implies that the solution is oversaturated with respect to the relevant species; if $SI < 0$, the solution is undersaturated and therefore does not yield a precipitate. Finally, if $SI = 0$, then $pIP = pK_{sp}$ and the solution is saturated and is at equilibrium.

From Figure 4.13 it is apparent that ferrous phosphonate is predicted to precipitate in each well, since $SI > 0$ for each simulation. Further, the figure shows that, if the calcium-phosphonate has the $Ca_{2.5}HNTMP$ stoichiometry, none of these wells would yield this precipitate since each solution is undersaturated with respect to this form. If the calcium salt has the Ca_3NTMP stoichiometry, however, a precipitate is predicted for three of the wells. The degree of saturation of Ca_3NTMP is low relative to the saturation levels of ferrous phosphonate in these three wells, indicating that the iron-based

Figure 4.13. Field data simulation saturation index results. The results of the field data simulations (in which the total phosphonate was set at 1.0 mg/L) are plotted in this figure. The saturation index (SI) as a function of ionic strength is plotted. Those points above $SI=0$ represent supersaturated conditions in which a precipitate will form; similarly, negative values of the SI indicate that the solution is subsaturated, and thus a precipitate will not form. Ferrous phosphonate is predicted to scale in each well; Ca_3NTMP is predicted to form scale in only three of the wells; and $Ca_{2.5}HNTMP$ will not precipitate.

solids are more likely to form than the calcium salts for the given conditions.

Because the *SI* calculations predict both $\text{Fe}_{2.5}\text{HNTMP}$ and Ca_3NTMP to form in some wells, a relationship among ferrous iron, calcium, and phosphonate using these stoichiometries and the respective solubility product constants can be established to predict the concentration of free iron in the water system:

$$\frac{K_{\text{sp}}^{\text{Fe}}}{K_{\text{sp}}^{\text{Ca}}} = \frac{(\text{Fe}^{2+})^{2.5} \{H^+\} (\text{Phn}^{6-})}{(\text{Ca}^{2+})^3 (\text{Phn}^{6-})};$$

therefore,

$$(\text{Fe}^{2+}) = \left(\frac{(\text{Ca}^{2+})^3}{\{H^+\}} \right)^{1/2.5} \left(\frac{K_{\text{sp}}^{\text{Fe}}}{K_{\text{sp}}^{\text{Ca}}} \right)^{1/2.5}, \quad (4.29)$$

an expression for the concentration of free iron. Table 4.6 was constructed using the functional forms derived for the K_{sp} 's of $\text{Fe}_{2.5}\text{HNTMP}$ and Ca_3NTMP and the free concentration of calcium and the pH for each well listed in Table 4.5. The ratio of the free iron concentration calculated with the simulations to that calculated using equation 4.29 ranges from 1-50 (last column of Table 4.6), or, within an order of magnitude. For the most part, the predicted concentrations approach the actual concentrations as the pH is increased. Nonetheless, the free (Fe^{2+}) concentrations calculated with equation 4.29 can serve as a good estimate of actual downhole concentrations, and thus are useful in pre-determining the appropriate concentration of phosphonate inhibitor required to prevent scale.

Table 4.6. Calculation of the concentration of free iron in a system containing calcium, ferrous iron, and phosphonate. The value for $(Fe^{2+})_{f,calc}$ was calculated using equation 4.29; $(Fe^{2+})_{f,sim}$ is the concentration of free iron determined to be in the wells based on the simulation calculations.

pH	$\{H^+\}$ ($\times 10^{-7}$)	$(Ca^{2+})_f$ (M) ($\times 10^{-2}$)	K_{sp}^{Fe} ($\times 10^{-33}$)	K_{sp}^{Ca} ($\times 10^{-19}$)	$(Fe^{2+})_{f,calc}$ (M) ($\times 10^{-4}$)	$(Fe^{2+})_{f,sim}$ (M) ($\times 10^{-4}$)	Ratio of $(Fe^{2+})_{f,sim}$ to $(Fe^{2+})_{f,calc}$
4.10	794.0	10.30	7.81	2.12	0.121	6.26	51.7
5.37	42.7	1.90	2.17	0.73	0.047	1.36	28.9
5.50	31.6	24.00	4.86	1.56	1.130	17.20	15.2
6.00	10.0	3.07	5.79	1.73	0.156	1.24	7.9
6.50	3.16	1.12	4.62	2.27	0.061	1.59	26.1
6.50	3.16	1.20	13.40	8.36	0.060	1.41	23.5
6.50	3.16	1.12	4.22	2.05	0.061	0.51	8.4
6.50	3.16	16.2	4.30	0.99	2.030	2.13	1.1
6.50	3.16	0.57	0.19	0.13	0.020	0.09	4.5
7.43	0.4	1.21	4.49	2.14	0.158	0.86	5.4

4.5.2 Implications of Simulation Results

Although the value of the $b_{Ca^{2+}}$ complexation term is defined by a functional form which is dependent on ionic strength and temperature, the value of $b_{Fe^{2+}}$ at the “original” condition of 25°C, 1 M IS is greater than that of $b_{Ca^{2+}}$ at the same conditions (0.86 *cf.* 0.47). Furthermore, the values for the $b_{M^{2+}}$ terms for Mg, Sr, and Ba have been determined at 70°C and 1 M IS (Table 4.7). These values, along with the calcium and iron (II) $b_{M^{2+}}$ terms at those conditions, shows that the complexation factor is correlated with ionic radius. Though the data set is far from complete, it appears that the complexation factor decreases down a group and increases across a period. This is most likely attributed to the outer-sphere complexation theory and ligand field theory discussed in Section 4.3.2.1. That is, the influence of the outer sphere decreases with each successive element in a group (in equation 4.25, the value of a increases as $\log K_{ij}$ decreases), and the LFSE plays an increasing role in going across each period as a result of the d orbitals of the transition metals. These arguments correlate with electronegativity trends. Figure 4.12 is a plot of the electronegativity of these metals against the complexation factor, b .

Because the simulations compare calcium and iron phosphonate complexes, it is necessary to examine the electron configurations of calcium and iron to determine the effect of electrostatic interactions on LFSE. These configurations are

Table 4.7. Complexation factor values and electronegativities of important divalent metal cations found in many brine solutions. The $b_{M^{2+}}$ values are for 1 M IS, 70°C.

Divalent Metal Cation	$b_{M^{2+}}$ Value*	Electronegativity [#]
Mg^{2+}	0.67	1.31
Ca^{2+}	0.56	1.00
Fe^{2+}	0.86	1.83
	(this study)	
Sr^{2+}	0.42	0.95
Ba^{2+}	0.42	0.89

*with the exception of ferrous iron, b values were obtained by Frostman (1996)

[#]Moore (1972)

Figure 4.14. Relationship between the electronegativity and complexation factor of some metals. The values for the $b_{M^{2+}}$ complexation factor for Mg, Ca, Fe (this study), Sr, and Ba correspond to the electronegativity of the metal (that is, the metal's tendency to acquire an electron). These elements' divalent metal cations are prevalent in natural and industrial water systems, and thus insight into their reactivity behavior can reveal information about scaling tendencies.

thus the third shell is the outer shell for each. As indicated in Section 4.3.2.1, the *d*-orbital electrons of iron require a LFSE when a ligand approaches the metal. Calcium, however, contains no *d* orbitals, and thus has no LFSE. The difference in LFSE may explain the difference in the $b_{M^{2+}}$ values and in the reactivity of both cations, and hence the differences in complexation with phosphonate ligands.

The results from the simulation trials, as discussed above, indicate that $Fe_{2.5}HNTMP$ would precipitate in each well, no $Ca_{2.5}HNTMP$ would be formed, and the matured solid Ca_3NTMP would form in a few wells. The percent speciation for these wells lends insight into explaining this phenomenon. For each simulation, the final concentration of each complex ion is calculated in the spreadsheet (see the flow diagram in Section 4.3.2.2); thus, the percent speciation can be computed using the total amount of species formed. For all but one iron simulation, the greatest percentages of species formed were protonated forms of the phosphonate (mostly H_2Phn^{4-} or H_3Phn^{3-}). In about half the wells the iron-complexed ion $FeHPhn^{3-}$ was also a major species. In contrast, however, the largest percentages of species in the calcium simulations in all ten wells were calcium-complexed ions. Usually $CaHPhn^{3-}$, CaH_2Phn^{2-} , and Ca_2HPhn^- were the predominant species formed. Table 4.8 lists the two or three most abundant species for each well. Therefore, it seems that undersaturated solutions contain large amounts of complexed ions, while supersaturated solutions do not, leading to the suggestion that the $b_{M^{2+}}$ factor determines the precipitation.

Table 4.8. Dominant species present in each solubility simulation. Only the 2 or 3 species existing in the highest percentages are given.

Well Name	Fe Simulation	Ca Simulation
	Predominant Species (%)	Predominant Species (%)
Gladys McCall	$\text{H}_4\text{Phn}^{2-}$ (58.7)	$\text{CaH}_3\text{Phn}^{1-}$ (33.2)
	$\text{H}_3\text{Phn}^{3-}$ (20.8)	CaH_4Phn^0 (22.0)
O'Daniel #2	$\text{H}_3\text{Phn}^{3-}$ (59.2)	$\text{CaH}_2\text{Phn}^{2-}$ (32.2)
	$\text{H}_2\text{Phn}^{4-}$ (16.2)	$\text{CaH}_3\text{Phn}^{1-}$ (23.8)
Pleasant Bayou #2	$\text{FeH}_2\text{Phn}^{2-}$ (39.4)	$\text{Ca}_3\text{HPhn}^{1+}$ (32.2)
	FeHPhn^{3-} (18.5)	$\text{Ca}_2\text{HPhn}^{1-}$ (31.2)
High Island A-9 #2		$\text{Ca}_2\text{H}_2\text{Phn}^0$ (25.7)
	$\text{H}_4\text{Phn}^{2-}$ (41.4)	$\text{Ca}_2\text{HPhn}^{1-}$ (34.0)
	$\text{H}_3\text{Phn}^{3-}$ (25.2)	$\text{CaH}_2\text{Phn}^{2-}$ (25.5)
Huff A		$\text{Ca}_2\text{H}_2\text{Phn}^0$ (15.3)
	FeHPhn^{3-} (34.3)	CaHPhn^{3-} (32.3)
	$\text{H}_2\text{Phn}^{4-}$ (31.9)	$\text{Ca}_2\text{HPhn}^{1-}$ (30.6)
N.R. Smith #4		$\text{CaH}_2\text{Phn}^{2-}$ (21.8)
	FeHPhn^{3-} (40.9)	CaHPhn^{3-} (38.1)
	$\text{H}_2\text{Phn}^{4-}$ (27.6)	$\text{Ca}_2\text{HPhn}^{1-}$ (24.7)
Pretts #1		$\text{CaH}_2\text{Phn}^{2-}$ (19.1)
	$\text{H}_2\text{Phn}^{4-}$ (49.6)	CaHPhn^{3-} (31.7)
	FeHPhn^{3-} (16.5)	$\text{Ca}_2\text{HPhn}^{1-}$ (31.2)
A.E. Guerra #43		$\text{CaH}_2\text{Phn}^{2-}$ (21.9)
	HPhn^{5-} (16.2)	$\text{Ca}_2\text{HPhn}^{1-}$ (49.9)
	FeHPhn^{3-} (37.7)	
Maxus ZEE-6		$\text{Ca}_3\text{HPhn}^{1+}$ (37.8)
	$\text{H}_2\text{Phn}^{4-}$ (27.6)	
	$\text{H}_2\text{Phn}^{4-}$ (60.4)	$\text{Ca}_2\text{HPhn}^{1-}$ (32.0)
Thompson Trustee #1		$\text{CaH}_2\text{Phn}^{2-}$ (29.4)
	$\text{H}_3\text{Phn}^{3-}$ (28.3)	
		CaHPhn^{3-} (23.1)
Thompson Trustee #1	FeHPhn^{3-} (53.3)	$\text{Ca}_2\text{HPhn}^{1-}$ (46.0)
	HPhn^{5-} (31.1)	CaHPhn^{3-} (44.2)

Iron present in solution may also be inhibiting calcium-phosphonate precipitation. In fact, both ferrous and ferric iron produce an inhibitory effect on calcite growth at near-neutral pH (Katz and Parsiegla, 1995); thus, it is possible that these ions may influence the growth of Ca-NTMP. These results indicate that ferrous iron is not as effective an inhibitor as ferric; however, ferrous iron in solution is readily oxidized to the ferric form in the presence of oxygen, and thus may contribute to this effect.

The results from the simulations suggest that ferrous phosphonate is likely to form in oilfield wells under the appropriate conditions. Because of the solubility of these precipitates, it is apparent that indeed the ferrous iron in downhole environments may control the fate of squeezed inhibitors, especially phosphonates. That calcium phosphonates are believed to precipitate downhole in wells and have been the subject of many precipitation studies while Fe-NTMP precipitation has not may be the result of the low initial concentrations of ferrous iron, as indicated by Table 4.5. Similarly, the large amount of total calcium found downhole may compensate for the slight degree of supersaturation for the Ca_3NTMP solid, and yield a large amount of calcium phosphonate scale. My data suggest that the potential for ferrous phosphonate to form is high. Thus, this precipitate may especially be important in rust control, by forming a protective layer of scale on the pipeline, as the levels of iron are considerably higher in these systems. Nonetheless, iron exists in most water systems from natural and/or artificial sources, and thus iron precipitation chemistry has widespread applications.

Chapter 5

Conclusions

The following conclusions were formed:

- The stoichiometry of the isolated ferrous phosphonate precipitate is given by $\text{Fe}_{2.5}\text{HNTMP}$, which is supported by NTMP's structure and previous work with calcium phosphonates.
- The complexation factor for iron, $b_{\text{Fe}^{2+}}$, is 0.86 and fits a trend for divalent metal cations which correlates $b_{\text{M}^{2+}}$ with electronegativity.
- The ionic strength and temperature dependence of the solubility product constant of ferrous phosphonate is given by:

$$pK_{\text{sp}} = 39.54 - 6.14\sqrt{IS} + 2.18IS - 1315/T.$$

- Simulations using real field data compared iron and calcium phosphonate scaling tendencies independently. The results showed that, despite the initial low concentrations of iron, the relatively low solubility of Fe-NTMP would enable ferrous iron to compete with calcium for NTMP precipitation.
- Metal-complexed ions in solution were found to be in much greater quantities for those wells which were undersaturated than in oversaturated wells; likewise, in the oversaturated wells, the non-complexed phosphonate ions dominated the speciation.

Chapter 6

Further Research

This research has raised questions which deserve further study. Particularly, the kinetics of ferrous phosphonate precipitation and dissolution should be studied, especially in relation to the other ferrous salts which commonly form downhole. The kinetics may indicate the relative importance of ferrous phosphonate as a scale-former, with respect to competitive effects with other divalent metal phosphonates or other ferrous salts. Further, as with calcium phosphonates, forming another phase of ferrous phosphonate should be attempted, as such information could reveal if the $\text{Fe}_{2.5}\text{HNTMP}$ solid forms downhole or if another precipitate is actually reacting with inhibitors. Also, the precipitation of ferrous iron with other phosphonate inhibitors would allow for a comparison between inhibitors in a ferrous system. Finally, ferric salts and their relative importance to ferrous precipitates could be investigated.

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Appendix A

A computer program written in FORTRAN (see following pages) for determining the $b_{Ca^{2+}}$ complexation term was used to determine this number for iron. The input parameters that were used to determine the $b_{Fe^{2+}}$ coefficient are listed in Table A.1; the corresponding output b value and K_i and K_{ij} constants are in Figure A.1. Because the code was written for calcium complexation studies and the functional form for calcium was used, the reported iron results maintain the “Ca” notation, rather than “Fe”. The code for the program appears on the following pages.

Table A.1. Input parameters required for the FORTRAN program to determine $b_{Fe^{2+}}$.

Parameter	Value	Parameter	Value
# of ionizable protons on the phosphonate	6	a_{H^+}	0.8604
# H's associating with N's in the phosphonate	1	b_{H^+}	1.122
# of data points	4	initial guess for $a_{Fe^{2+}}$	1
C_{Phn}	0.001	initial guess for $b_{Fe^{2+}}$	0.5
C_{Fe}	0.005	$\log K_1^N$	12.3
Ionic Strength (m, assumed $\approx$ M)	1	Temperature (K)	298
$(Na^+)_{meas}$ [=moles NaOH/L]	trial 1: 0.0035 trial 2: 0.0035 trial 3: 0.0035 trial 4: 0.0035	pH	trial 1: 4.75 trial 2: 4.54 trial 3: 4.61 trial 4: 4.61

RESULTS:

aCa .0000, bCa .8558

The data for this analysis was unweighted.

The average squared error = 1.077D-08

Sigma-bCa = one stndrd dev. 1.882D-02

log Beta(1,0) =	12.30	log K1,0 =	12.30
log Beta(1,1) =	16.58	log K1,1 =	4.28
log Beta(1,2) =	19.15	log K1,2 =	2.57
log Beta(1,3) =	20.00	log K1,3 =	.86
log Beta(2,0) =	18.77	log K2,0 =	6.47
log Beta(2,1) =	22.19	log K2,1 =	3.42
log Beta(2,2) =	23.91	log K2,2 =	1.71
log Beta(3,0) =	24.12	log K3,0 =	5.35
log Beta(3,1) =	26.69	log K3,1 =	2.57
log Beta(3,2) =	27.54	log K3,2 =	.86
log Beta(4,0) =	28.35	log K4,0 =	4.23
log Beta(4,1) =	30.06	log K4,1 =	1.71
log Beta(5,0) =	31.45	log K5,0 =	3.10
log Beta(5,1) =	32.31	log K5,1 =	.86
log Beta(6,0) =	33.43	log K6,0 =	1.93
log Beta(6,1) =	.00	log K6,1 =	.00

NaMe	NaCal	pH	f
3.500D-03	3.665D-03	4.750D+00	-1.647D-04
3.500D-03	3.379D-03	4.540D+00	1.214D-04
3.500D-03	3.475D-03	4.610D+00	2.457D-05
3.500D-03	3.475D-03	4.610D+00	2.457D-05

Figure A.1. Output value of $b_{Fe^{2+}}$ and the corresponding K_{ij} constants. “NaMe” is the measured concentration of base (Na^+); “NaCal” is the calculated value upon performing a least-squares regression fit. From Chapter 4, the value of $b_{M^{2+}}$ (for a metal, M) is calculated by minimizing the difference between NaMe and NaCal.

PROGRAM CAPHNb

```

.....
* Program to calculate bCa for Ca-phosphonate complexes.
* Written by M.B.Tomson. Modified by L.M.Frostman
* Version 1. April 9, 1996
.....

.....
* Variables and Constants:
.....
*
*   aCa: aCa+ for phosphonate (read only, keeps input file same)
*   aH: aH+ for phosphonate (read only, keeps input file same)
*   another: 'y' if another iteration will be performed
*   avmsq: average sum of the squares of {NaMe-NaCal}
*   bCa: bCa+ for phosphonate
*   bH: bH+ for phosphonate
*   Beta(i,j): log Beta for the i,j Ca-phosphonate complex
*   CCa: total concentration of calcium (M)
*   Cphn: total concentration of phosphonate (M)
*   deltab: changes in b for next iteration
*   dummyb(i,j): dummy values for Beta(i,j)
*   dummyH: dummy variable for H(ii)
*   EpH(ii), ENaMe(ii): errors in pH and NaMeasured
*   f(ii): function equivalent to Na(measured)-Na(calculated)
*   fbCa, fNaM, fpH: derivatives of f
*   H(ii): hydrogen ion activity
*   i: counting variable for ionization step
*   ii: counting variable for data points
*   j: counting variable for complexation step
*   IS: ionic strength
*   K(i): log of the ith phosphonate ionization constant
*   Kw: dissociation constant for water
*   L: constant accounting for weighting of pH and NaMeas
*   n: number of ionizable protons
*   NaCal(ii): array of calculated Na+ concentrations (M)
*   NaMe(ii): array of measured Na+ concentrations (M)
*   npts: number of data points used in calculations
*   nN: number of protons which associate with nitrogens
*   p(i,j), q(i,j), r(i): matrices to compute new b values
*   pdet: determinant of the p matrix
*   pH(ii): array of measured pH values
*   pKw: pK for dissociation of water
*   sigmabCa: standard deviations in bCa
*   sigmao: arbitrary constant used to compute weights
*   sumsq: sum of the squares of {NaMe-NaCal}
*   T: temperature (K)
*   WpH, WNaMe: weights given to pH and NaMeasured data
*
.....

implicit real*8 (a-z)
integer n, nN, i, ii, j, npts
dimension NaMe(50), NaCal(50), pH(50), H(50), K(0:20, 0:20)
dimension Beta(0:20, 0:20), f(50), dummyb(0:20, 0:20)
dimension EpH(50), ENaMe(50), WpH(50), WNaMe(50), p(5,5), r(5), q(5,5)
character (Len=80) title
character another

```

```

*** Initialize variables and read data from file. ***

Beta = 0.0
dummyb = 0.0
sigmao = 1.0

open (5,file='CaPHN.in')
open (6,file='CaPHN.out')
read (5,*) title
write (6,*) title
print*, title
read (5,*) n,nN,npts,Cphn,CCa,aH,bH,aCa,bCa,IS,T
aH = 0.0 ! this program fits b only
aCa = 0.0 ! this program fits b only

*** Assign values of Ki's for protonation of nitrogens. ***
*** Assign dummy values of Beta for use in derivatives. ***

do i = 1, nN
  read (5,*) K(i,0)
  Beta(i,0) = Beta(i-1,0) + K(i,0)
  dummyb(i,0) = Beta(i,0)
end do

do ii = 1, npts
  read (5,*) Name(ii), pH(ii)
  H(ii) = 10**(-pH(ii))
  EpH(ii) = 1.0
  EName(ii) = 1.0
  WpH(ii) = sigmao**2/EpH(ii)**2
  WName(ii) = sigmao**2/EName(ii)**2
end do

pKw=5.87352-2403.5507/T-1.11956*IS**0.5-0.729137*IS
Kw=10.0**(-pKw)

write(6,900) 'pKw = ',pKw
900 format(1x,A5,f3.4)

*** Calculate how well parameter bCa fits the data. ***

25 p(2,2) = 0.0
r(2) = 0.0
sumsq = 0.0

*** Assign values of Kij's for complexation of phosphonates. ***
*** Assign dummy values of Beta for use in derivatives. ***

do i = (nN+1), n
  K(i,0) = bH * (n-i-1)
  Beta(i,0) = Beta(i-1,0) + K(i,0)
  dummyb(i,0) = Beta(i,0)
end do

do i = nN, (n-1)
  do j = 1, (((n-i-1)/2)+1)
    K(i,j) = bCa * (n-(2*(j-1)+i))
    Beta(i,j) = Beta(i,j-1) + K(i,j)
    dummyb(i,j) = dummyb(i,j-1) + 1.01*K(i,j)
  end do

```

```

end do

*** Calculate the function and it's derivatives at each point. ***

do ii = 1, npts
  Call iteration (freePhn,Cphn,freeCa,CCa,n,nN,Beta,H(ii))

  Call iteration (dummyPhn,Cphn,dummyCa,CCa,n,nN,dummyb,H(ii))
  Call fcalc (dummyPhn,dummyCa,CCa,n,nN,dummyb,NaMe(ii),
    *      NaCal(ii),H(ii),Kw,fbCa)

  dummyH = 10.0**(-1.01*pH(ii))
  Call iteration (dummyPhn,Cphn,dummyCa,CCa,n,nN,Beta,dummyH)
  Call fcalc (dummyPhn,dummyCa,CCa,n,nN,Beta,NaMe(ii),NaCal(ii),
    *      dummyH,Kw,fpH)

  Call fcalc (freePhn,freeCa,CCa,n,nN,Beta,NaMe(ii),NaCal(ii),
    *      H(ii),Kw,f(ii))

  fNaMe = 1.01*NaMe(ii) - NaCal(ii)

  fbCa = (fbCa - f(ii))/(0.01 * bCa)
  fpH = (fpH - f(ii))/(0.01 * pH(ii))
  fNaMe = (fNaMe - f(ii))/(0.01 * NaMe(ii))

  sumsqs = sumsqs + f(ii)**2
  L = fNaMe**2/wNaMe(ii) + fpH**2/wpH(ii)
  p(2,2) = p(2,2) + fbCa**2/L
  r(2) = r(2) + f(ii)*fbCa/L
end do

avsmsq = sumsqs/npts
q(2,2) = 1/p(2,2)

*** Determine if another iteration should be performed. ***

write (*,910) 'aCa = ',aCa,', bCa = ',bCa,', avsmsq = ',avsmsq
910 format (1x,A4,F7.4,A6,F7.4,A11,E12.3)
write (*,*) ' Do Another Iteration, (y/n)?'
read (*,915) another
915 format (A1)

if (another.eq.'y') then
  deltab = q(2,2)*r(2)
  bCa = bCa - deltab
  go to 25
end if

*** Write results to output file. ***

write (6,*) ' '
write (6,*) 'RESULTS:'
write (6,*) ' '
write (6,920) 'aCa = ',aCa,', bCa = ',bCa
920 format (1x,A4,F7.4,A6,F7.4)
write (6,*) ' '
write (6,*) 'The data for this analysis was unweighted.'
write (6,930) 'The average squared error = ',avsmsq
sigmabCa = (q(2,2)*sigmao**2)**(0.5)
write (6,930) 'Sigma-bCa = one stndrd dev. = ',sigmabCa

```



```

      write (6,*) ' '
930 format (1x,A28,1pd12.3)

      do i = 1,n
        do j = 0,(((n-i-1)/2)+1)
          write (6,940) 'log Beta(' ,i,',',j,') = ',Beta(i,j),
*           'log K',i,',',j,') = ',K(i,j)
        end do
      end do

940 format (1x,A9,I1,A1,I1,A4,F7.2,4x,A5,I1,A1,I1,A3,F7.2)
      write (6,*) ' '
      write (6,945)
945 format (6x,'NaMe',8x,'NaCal',9x,'pH',10x,'f')
      do ii=1,npts
        write(6,950) NaMe(ii), NaCal(ii),pH(ii),f(ii)
      end do
950 format (1x,6(1pd12.3))

      End

*****
*      Subroutine used to calculate freeCa and freePhn      *
*****

      Subroutine iteration (freePhn,Cphn,freeCa,CCa,n,nN,Beta,H)
      implicit real*8 (a-z)
      integer i,j,n,nN,nI,maxIter
      dimension Beta(0:20,0:20)

      maxIter = 100
      maxError = 0.000001*CCa
      Sum = 0.0
      max = CCa
      min = 0.0

      if (nN.GT.1) then
        do i = 1,(nN-1)
          Sum = Sum + 10**Beta(i,0)*H**i
        end do
      end if

***      Half-interval iteration to solve for freeCa and freePhn.      ***

      do nI = 1,maxIter
        CaSum = 0.0
        jSum = 0.0

        freeCa = (max + min)/2

        do i = nN,n
          do j = 0,(((n-i-1)/2)+1)
            CaSum = CaSum + 10.0**Beta(i,j) * freeCa**j * H**i
            jSum = jSum + j * 10.0**Beta(i,j) * freeCa**j * H**i
          end do
        end do

        freePhn = Cphn / (1 + Sum + CaSum)
        check = freeCa + jSum * freePhn - CCa

```

```

      if (abs(check) < maxError) exit

      if (check < 0.0) then
        min = freeCa
      else
        max = freeCa
      end if

      if (nI.EQ.maxIter) then
        write (*,*) 'iteration did not converge.'
        write (6,*) 'iteration did not converge.'
      end if
    end do

    Return
  End

*****
*      Subroutine used to calculate the function values.      *
*****

Subroutine fcalc (freePhn, freeCa, CCa, n, nN, Beta, NaMe, NaCal, H, Kw, f)
implicit real*8 (a-z)
integer i, j, n, nN
dimension Beta(0:20,0:20)

Sum = 0.0
CaSum = 0.0

if (nN>1) then
  do i = 1, (nN-1)
    Sum = Sum + (n-i) * 10**Beta(i,0) * H**i
  end do
end if

do i = nN, n
  do j = 0, (((n-i-1)/2)+1)
    CaSum = CaSum + (n-2*j-i) * 10.0**Beta(i,j) * freeCa**j * H**i
  end do
end do

NaCal = freePhn*(n*Sum+CaSum) + 2*(CCa-freeCa) - H + Kw/H
f = NaMe - NaCal

Return
End

```