PHASE AND ELECTROLYTE EQUILIBRIUM

MODELING IN DOWNHOLE

ENVIRONMENTS

By

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NOMENCLATURE

- a Activity, mol/kg solvent.
- a⁰ Hard sphere radius, Angstorm units.
- a, b Constants used in Equation (2.4), dimensionless
- A_i Constants used in Equation (3.30), dimensionless.
- AAPD Average Absolute Percentage Deviation, percentage
- A, B Molal Debye-Huckel parameters, dimensionless.
- A^{*} Constant defined by Equation (2.15), kmol²/kpa m⁶.
- B' Constant defined by Equation (2.16), kmol/m³.
- B_{i,j} Temperature Coefficients for Equilibrium Constants (Used in Equation 3.34), mol/kg Kⁿ (n = -1, 0, or 1).
- b Bias in a property, percentage
- b⁰ Deviation function describing the departure of the mean ionic activity coefficient of an electrolyte from that predicted by the Debye-Huckel expression, mol/l.
- CAO Equilibrium concentration of the hydrogen ion at the gas/liquid interface, mol/l
- C_{ii} Binary interaction parameter, dimensionless.
- d Amount dissociated in liquid phase, dimensionless.
- D Percentage Deviation in a Property, percentage.
- f Fugacity, kpa.

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- F total Amount of feed, moles.
- G Gibbs free energy, Joules.
- H Henry's Law constant, kpa-kg solvent/mol solute.
- I Ionic strength, Coulomb mol²/kg².
- k_M Mass transfer coefficient in the liquid film, m/sec.
- ks Surface reaction rate constant, m/sec.
- Ki, VLE Vapor/liquid equilibrium constant, dimensionless.
- K Equilibrium constant, mol/kg water.
- K_{SP} Solubility product, mol/kg water.
- m Molality, mol/kg solvent.
- M Apparent molality or stoichiometric concentration of the weak electrolyte in the aqueous phase, mol/kg solvent.
- M_s Molar Strength, Coulomb mol/kg.
- n Number of Components in a System.
- N_{AZ} Molar flux of the hydrogen ion at the gas/liquid interface, kg mol/m² sec.
- P Pressure, kpa.
- R Ideal Gas Law Constant, kpa m³/kmol K.
- S_c Source term defined by Equation (B-5), dimensionless.
- T Temperature, K.
- V Volume, m³.
- x Liquid phase mole fraction, dimensionless.
- y Gas-phase mole fraction, dimensionless.

- z Ionic charge, Coulomb.
- Z Compressibility factor, dimensionless

Greek Variables

- α Constant used in Equation (2.4).
- γ Activity coefficient.
- ρ Density, g/cc.
- φ Fugacity coefficient.
- ω Acentric factor
- ξ Dielctric constant.
- μ Chemical potential.

Subscripts

- C Critical.
- g Gas.
- i ith species.
- j jth species.
- l Liquid
- m Electrolyte of concentration 'm'.
- s Solid.

W Water

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Superscript

- L Liquid.
- S Solid
- t Total.
- V Vapor.

CHAPTER 1

INTRODUCTION

Oil and gas wells produce varying amounts of gases such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), water (H_2O), and organic acids. These gases dissolve in water and form a weak acidic solution that is corrosive.

The economic impact of corrosion is tremendous. The cost of corrosion in the United States alone has been estimated to be between \$8 billion and \$126 billion per year (Jones, 1991). The above figure takes into account only the direct economic costs of corrosion. The indirect costs (such as the shut down of an industrial unit, expenditure on corrosion control) resulting from actual or possible corrosion are very difficult to evaluate and are probably greater.

Corrosion is a serious problem in the oil and gas industry. The loss of metal in a pipeline may lead to failure that could potentially cause an explosive situation. A severely corroded well may have to be shut down, at least temporarily, leading to loss of production. Corrosion increases the cost of production due to increased spending on corrosion control. The severity of the damage and the enormity of the expense associated with corrosion has promoted a wide range of research activity.

Corrosion in oil and gas wells is controlled by the use of corrosion resistant materials for construction, protective coatings on the tubing and casing, and the use of inhibitors. The type of corrosion control varies from well to well and is dependent on specific well conditions. Generally, more than one corrosion control method may be necessary.

The use of corrosion resistant materials (e.g., chrome steel, nickel steel) for controlling corrosion is a very reliable, but costly method. These materials must be resistant to both sulfides and carbonates in order to provide a long term solution to the corrosion problem. Further, the process of determining whether a particular material is acceptable for use in a specific case involves the experimental modeling of the actual well conditions before finalizing the use of that material in a well (Tuttle, 1990). At high concentrations, oxygen and strong mineral acids attack even corrosion resistant alloys (Tuttle, 1987).

A more economical, but less reliable, method is the use of protective coatings. The coatings can be plastic, inorganic, metallic, or non-metallic. Coatings isolate the material from the corrosive environment and prevent the material from being attacked (Newton and Hausler, 1984). Coatings are often inapplicable in situations where severe erosion and high temperature could occur. OKLAHOMA STATE UNIVERSITY

Corrosion inhibitors (e.g., sodium nitrite, ethylene glycol etc.) are used extensively in oil and gas wells. Most of the commonly used inhibitors are organic chemicals with polar and non-polar parts (Newton and Hausler, 1984). The polar group attaches to the metal while the non-polar group promotes the formation of a protective oil film over the inhibitor layer. The effectiveness of the inhibitor depends on the ability of the inhibitor to cover the metal surface completely. Effective coverage of the metal surface may be hampered due to chemical or mechanical reasons. Sometimes the inhibitor may not be compatible with the surface of the metal and may not adhere to the surface of the metal. If the velocity of flow is higher than the erosional velocity then the inhibitor may be washed away. In certain high pressure wells, organic inhibitors do not penetrate the entire depth of the well (Bilhartz, 1952) and result in severe corrosion of the lower zones of the tubing. The remote location of many wells may also make inhibition difficult and expensive.

The phenomenon of corrosion in oil and gas wells is highly complicated and is not understood completely. A survey of the literature shows that the corrosion in an oil or gas well depends on many factors such as CO₂ and H₂S concentrations, the system temperature and pressure, fluid velocity, the corrosion product formed, relative amounts of liquid water and hydrocarbon vapor, liquid phase pH, the flow regime encountered downhole, phase behavior, concentrations of ions in the water phase, oxygen contamination downhole, and the presence of microorganisms. These phenomena are interrelated, and understanding the corrosion process or predicting the corrosion rate accurately is difficult.

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Authors have used different classification for corrosion. Fontana (1986) has classified corrosion as: galvanic or two-metal corrosion, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, and hydrogen damage. However, corrosion occurring downhole can be classified broadly as uniform corrosion and localized corrosion (Liu, 1991). Overall weight loss and thinning of the corroded material is referred to as uniform corrosion, while the appearance of grooves and pits is called localized corrosion.

The need for a mechanistic tool for corrosion prediction is great. The mathematical modeling of downhole corrosion is complicated because a multiphase, multicomponent, heterogeneous system in turbulent flow with mass transfer, and chemical reactions has to be modeled. Crolet and Bonis (1984) emphasized corrosion prediction involves not only forecasting the risk of corrosion, but also the possibility of a lack of corrosion. Thus, corrosion prediction helps in material selection, and the use of coatings and inhibitors. A reliable method for corrosion prediction would be a valuable tool which would help reduce production and operating costs.

A comprehensive mathematical model for predicting corrosion rates was developed by Liu (1991). The model included modules for thermodynamic phase equilibria calculations, electrolyte equilibrium computations, mass transfer calculations, and corrosion rate calculations. All of these modules were incorporated into a user friendly software, named DREAM (Downhole Corrosion Prediction Program), to predict the corrosion rate.

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1.1 OBJECTIVES OF THIS WORK

The principal objective of the present work was to refine DREAM to establish a consistent and generalized framework for phase and electrolyte equilibrium computations in gas wells. In DREAM simulations, phase and electrolyte equilibrium computations are performed initially to estimate the quantity of the liquid and the vapor phases and the composition of the species present at the gas-liquid interface. The compositions at the

vapor-liquid interface are used to obtain the composition at the surface of the piping where corrosion occurs. Accurate estimation of the composition at the gas-liquid interface is important for correct corrosion rate calculations.

Another objective of this work was to include hydrogen sulfide in the electrolyte equilibrium module to enable the prediction of hydrogen sulfide induced corrosion. The previous version of DREAM (Version 3.0) could predict corrosion induced by CO₂ alone.

The final objective of this work was to evaluate the performance of the phase and electrolyte equilibrium model with experimental data for the following binary systems: CO_2 -H₂O, and H₂S-H₂O. The performance of the old model, DREAM (Version 3.0) was also evaluated and compared with the performance of the new model (DREAM 3.3).

CHAPTER 2

LITERATURE REVIEW

This chapter discusses corrosion, the factors influencing corrosion in gas wells, models used for corrosion prediction, electrolyte equilibrium modeling, and the phase equilibrium model used in DREAM 3.0. The corrosion process is defined and described briefly. Several factors that influence corrosion in gas and oil wells are analyzed. Some of the corrosion prediction models developed at Oklahoma State University are discussed. The need for electrolyte equilibrium modeling and the importance of the approach used in this work, as applied to downhole environments, is explained. The phase equilibrium model used in DREAM 3.0 is also documented.

2.1 Corrosion Fundamentals

Corrosion may be defined as the deterioration or destruction of a material or its properties due to a reaction with the environment. In the oil and gas industry, corrosion refers primarily to the destruction of metal, either through a chemical or an electrochemical reaction with a given environment.

The mechanism by which corrosion proceeds is quite complicated. The presence of liquid water is a necessary factor for corrosion in oil and gas wells (Tuttle and Hamby, 1977). Corrosion proceeds through an electrochemical mechanism in which water plays the role of the electrolyte. A driving force and a complete electrical circuit are necessary for current flow. The potential difference existing on the surface of the metals or alloys used in the construction of the tubing provides the necessary driving force. The electrical circuit is completed by the presence of the electrolyte which conducts electrical current from the anode to the cathode. The greater the conductivity of the electrolyte, the greater the rate of corrosion.

2.2 Factors Influencing Downhole Corrosion

A survey of the literature shows that the phenomenon of downhole corrosion is dependent on many factors. The presence of CO_2 and H_2S , the partial pressures of CO_2 and H_2S , the presence of water, the pH of the produced water, the temperature along the well string, the presence of corrosion product layers, the water chemistry, the flow regime, and the nature of steel influence the corrosion rate (Videm and Dugstad, 1989; Bradley, 1986; Crolet and Bonis, 1983; Kuznetsov, 1981; Bradburn, 1977; de Waard and Milliams, 1976; Shock and Sudbury, 1951).

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The corrosion of steel equipment in oil and gas wells has been observed for the past several decades. Bacon and Brown (1943) observed serious corrosion in fittings and orifice plates in some gas wells. The gas contained nearly 1% CO₂ and traces of H_2S . The pH of the produced water varied between 5.0 and 6.0 at the wellhead. Bacon and Brown (1943) concluded that the damage to the pipe was probably due to erosion-corrosion in turbulent two-phase flow. Erosion-corrosion in turbulent two-phase flow is

possible, provided there is a sufficient amount of solids making contact with the wall (Shock and Sudbury, 1951).

Several authors (Videm and Dugstad, 1989; Bradley, 1986; Crolet and Bonis, 1983; de Waard and Milliams, 1976; Shock and Sudbury, 1951; Zitter, 1973) proposed that the partial pressures of CO_2 and H_2S affected the corrosion rate by controlling the acidity of the medium. Bradley (1986) proposed a rule-of-thumb to predict the corrosiveness of a well using the partial pressure of CO_2 as an index. A partial pressure above 15 psia indicates a corrosive well. If the partial pressure of the corrosive gases is between 7-15 psia, the well will probably be corrosive. According to Bradley, partial pressure of less than 7 psia indicates a non-corrosive well. Videm and Dugstad (1989) observed that the corrosion rate varied exponentially with the partial pressure of CO_2 with the exponent ranging between 0.5 and 0.8.

Bradburn (1977) stated that the corrosion rate in a well increases with increasing amount of water produced in the well. The amount of carbonic acid produced in a well would depend on the carbon dioxide concentration and the water production. Bradburn (1977) concluded that if two wells produced the same amount of water with a magnitude of difference in the carbon dioxide concentration, then the well with the higher carbon dioxide concentration would be more corrosive. OKLAHOMA STATE UNIVERSITY

Using the principles of fluid mechanics, Videm and Dugstad (1989) concluded that when the corrosion process is controlled by mass transfer, the corrosion rate varies with the water flow rate raised to a power of 0.8 for a fully developed turbulent flow. Gatzke

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and Hausler (1984) extended this to the gas production rate and proposed an empirical correlation to demonstrate the effect of gas and water flow rates on downhole corrosion.

The effect of pH on the corrosion rate has also been studied extensively. Shock and Sudbury (1951), found that corrosion took place at pH values less than 5.5. The authors also concluded that the corrosion phenomenon could be explained satisfactorily by correlating corrosion with acidity rather than with galvanic action or current flow. A relationship between corrosion and acidity was also confirmed by Ewing (1955) who observed a distinct change in the appearance of the solution and the corrosion rates at pH values close to 6. Experiments conducted by Videm and Dugstad (1987) indicated that increasing the acidity of the solution increased the ferrous ion (Fe²⁺) concentration in solution, and concluded that the corrosion rate increases with decreasing pH and is most pronounced below a pH of 3.8.

Temperature has an indirect effect on the corrosion rate. Changes in temperature cause changes in pH, flow rate, solubility of the various species found in water, the reaction rate, potential difference, and the properties of the corrosion product layer. Kuznetsov (1981) performed gravimetric tests in autoclaves and observed that corrosion rate increases exponentially with temperature up to a temperature of 60 °C. The rate of increase of corrosion was retarded above 60 °C, and the corrosion rate reached a maximum value at 80 °C. He also observed a steady fall in the corrosion rate above 80 °C.

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The temperature at which the corrosion rate reaches a maximum is called the scaling temperature. At this temperature, the local pH, and the Fe^{++} concentration formed at the steel surface are such that a protective film is formed (de Waard et al., 1991). The

scaling temperature is likely to be dependent on flow rate and increases with increasing flow rate. Kuznetsov suggested that under dynamic conditions the process is subject to a mixed anodic-cathodic control at low temperatures and an anodic control at high temperatures. Polarization curves for steel showed that at higher temperatures the anodic process was retarded owing to corrosion product deposition, leading to a drop in the corrosion rate.

The effect of temperature on corrosion could also be explained in terms of the corrosion product layers formed. The precipitation of a corrosion product in itself does not necessarily result in the formation of a protective film (de Waard et al., 1991). Kuznetsov (1981) found that at temperatures below 60 °C the corrosion process formed a soft, non-cohesive permeable film which has a smudge-like appearance and is easily removed by flowing fluids. Above 60 °C the crystals of the corrosion product were stronger, more compact, and less permeable. This could account for the deviation from the exponential increase in corrosion rate. At temperatures close to 120 °C, the amount of film deposited increased and the permeability of the oxide layer decreased, possibly preventing the metal from corroding further. Similar observations have been reported by de Waard et al. (1991) and Ikeda et al. (1984) and confirmed in the experiments conducted by Shoesmith et al. (1980).

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Crolet (1983) and Crolet and Bonis (1983) concluded that water chemistry is more important in forecasting downhole corrosion rate than temperature or partial pressure of CO_2 . The presence of certain species in the produced water greatly affects the rate of corrosion. Chloride ion is corrosive, but only in the presence of oxygen. The bicarbonate

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ion alters the pH of the produced water and affects the corrosion rate. The presence of compounds such as calcium carbonate and calcium chloride also have a significant effect on the acidity of the produced water. In general, chemical species that increase the acidity of the produced water increase the corrosion rate.

Another important factor that affects the corrosion rate is the nature of the dispersed and the continuous phases along the production string. Water may form an emulsion with the hydrocarbon liquid that is present in the downhole environment. Choi et al. (1989) found a marked increase in the corrosion rate at a water cut of 40% or more. The increase in the corrosion rate was attributed to the phase inversion from oilcontinuous phase to water-continuous phase at water cut values close to 50%. However, in certain wells pitting corrosion occurred at water cuts less than 30%. The pitting corrosion was attributed to the flow velocity. The corrosion rate also increased with the flow velocity, irrespective of the type of emulsion. Choi et al. (1989) reasoned that in the oil-in-water emulsion (o/w) the flow velocity increased both the local turbulence and the contact time of the water phase with the tubing material. In the water-in-oil emulsion (w/o), an increase in flow velocity increased the corrosion rate by washing off the iron carbonate protective film and by increasing the mass transfer through the pores of the iron carbonate layer. Juswandi (1995) developed a mathematical model to predict the location of phase inversion in a gas/oil well and concluded that the oil viscosity and the turbulence in the liquid phase have a significant effect on the phase inversion.

The flow regime has a profound effect on the corrosion rate. The type of flow regime present is dependent on the fluid properties and pipe size. Johnson et al. (1991) found that corrosion rates in slug flow could be seven times higher than the corrosion rates in annular flow. Johnson et al. (1991) also concluded that the corrosion rates increased with increasing flow rates because the protective corrosion product film was washed away by the flowing fluids.

Apart from all the factors discussed above, the nature of the steel used in the construction of the tubing and casing also determines the corrosion rate. Different types of steel corrode differently, since their response to flow rates vary (Videm and Dugstad, 1989; Videm and Dugstad, 1987). However, the presence of small amounts of chromium was shown to improve resistance to corrosion appreciably (Videm and Dugstad, 1989; Ikeda et al. 1984).

2.3 Previous Models for Corrosion Prediction

Various models have been proposed from time to time to predict the nature and rate of corrosion in a gas well. A brief discussion of the corrosion prediction models developed at Oklahoma State University is given below.

2.3.1. The Model of Robertson (1988)

One of the earliest attempts at predicting the nature of downhole corrosion was made by Robertson (1988). The onset of water condensation was assumed to be the point in the tubing above which corrosion occurred. Robertson developed an easy-to-use

computer program which predicted the location of the water condensation zone in gas wells. The program, called DOWN*HOLE (Robertson, 1988), combined an existing thermodynamic phase equilibrium calculation package (Erbar, 1980) with subroutines for the calculation of the fluid flow phenomena. The subroutines for fluid flow were developed by Robertson (1988).

The thermodynamic phase equilibrium calculation package calculated the phase behavior of the produced fluids at high temperature and pressure. The thermodynamic package of DOWN*HOLE used the industrially tested GPA*SIM (Erbar, 1980), which used the Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972) to calculate the thermodynamic properties. Liquid densities were calculated by the COSTALD method (Hankinson et al., 1979). The pipeline was divided into 500 feet sections and the thermodynamic properties were calculated for each section. The SRK equation predicted vapor densities to within 4-5% while the liquid phase densities were predicted by the COSTALD method to within 2-4% (Robertson et al., 1988).

The fluid flow calculation subroutines, added by Robertson, calculated the pressure profile along the well string. These subroutines used four methods to calculate the pressure profile along the production string. The pressure profile calculation included the simple linear pressure profile method, a two-phase homogeneous flow method, the Orkiszewski flow regime dependent correlation method, and the Yao-Sylvester mist-annular flow regime method (Robertson, 1988). The linear model assumed a linear pressure and temperature profile along the well depth. The other three models assumed either a linear enthalpy profile or a linear temperature profile along the length of the well.

After the pressure drop was estimated, the flash calculations were carried out using GPA*SIM (Erbar, 1980).

The calculation of the surface tension and the fluid viscosity is essential for the estimation of the two phase flow pressure drop. The surface tension of the fluid produced downhole was taken to be the surface tension of water at that temperature. Fluid viscosities were calculated by one of the following three methods:

- the hydrocarbon liquid phase viscosity is determined by the method of Beggs and Robinson (1975),
- liquid water phase viscosity was determined by a simple curve fit (Robertson, 1988), and
- 3. the method of Lee et al. (1966) was used to estimate the gas phase viscosity.

The model of Robertson (1988) generated a pressure-temperature diagram of the gas well system. The pressure-temperature diagram included the water and hydrocarbon rich dewpoint curves and a pressure traverse of the production string at a given flow rate (Robertson et al., 1988). The program was also equipped with an option to determine the fluid velocity at various points along the tubing. The difference in the fluid velocity and the erosional velocity is called the excess velocity. The excess velocity was used as an indicator of the well corrosivity.

2.3.2 <u>The Model of Liu and Erbar (1990)</u> his step cover the equilable of the corrosion rate along the depth of the pipeline incorporating the principles of fluid mechanics, mass transfer, and surface reaction rates was developed by Liu and Erbar (1990). In this model, the key corrosive specie was the hydrogen ion in aqueous solution. This model predicted uniform corrosion rates in the absence of protective films, using the following formula:

$$N_{AZ} = \frac{C_{AO}}{\frac{1 - X_{AO} / 2}{k_{M}} + \frac{1}{k_{S}}}$$
(2.1)

where

 C_{AO} = equilibrium concentration of the hydrogen ion at the gas-liquid interface, X_{AO} = mole fraction of the hydrogen ion in the liquid film at the gas-liquid interface,

 k_M = mass transfer coefficient in the liquid film, and

 k_s = surface reaction rate constant.

The first step in the use of this model involved the use of the DOWN*HOLE program (Robertson, 1988). The program calculated the downhole temperature and pressure profile, liquid and gas density, the liquid and the gas flow rate at each section, and the flow regime of the downhole two-phase flow. All these values were used as input for the corrosion rate calculations.

The second stage of the model computed the downhole pH at different depths. This step gave the equilibrium concentration of the hydrogen ion in the liquid film at the gas-liquid interface.

The third step was the calculation of the two-phase flow parameters, the mass transfer coefficient, and reaction rate constants from data reported in literature (Liu and Erbar, 1990). The final step involved the corrosion rate calculation from Equation (2.1). The model neglected the presence of protective films, and predicted the worst case corrosion rate.

2.3.3 The Model of Liu (1991)

Liu (1991) modified his earlier model (Liu and Erbar, 1990) for corrosion prediction by including the effect of protective films on the corrosion rate. In this model Liu also eliminated the need for gross assumptions such as diffusion control or reaction rate control made in the previous model.

Electrolyte equilibrium computations used in the previous model (Liu and Erbar, 1990) were adapted to the principles of Edwards et al. (1978). The electrolyte equilibrium module estimated the temperature dependent equilibrium and Henry's constants. The activities of the molecular species (i.e., CO_2 and H_2S) were estimated from the Henry's constants. These relationships were then used to estimate the pH of the system. All activity coefficients were determined from the work of Kerr (1980). The concentrations of all other species at the gas-liquid interface were estimated from the calculated pH.

The corrosion rate was calculated by using the mass transfer equations in each of the following layers: turbulent layer, diffusion layer, and the corrosion product layer. In this model, the corrosion product layer was considered as another diffusion layer, and the mass balance equation for the diffusion layer was solved for the corrosion product layer to yield the concentrations at the pipeline surface.

2.3.4 The Model of Liu and High (1993)

Further modifications of the corrosion rate calculations were made by Liu and High (1993) and incorporated into software named DREAM. The phase equilibrium module used GPA*SIM, but the program structure of GPA*SIM was altered so that the resulting code was smaller. The three-phase flash calculation procedure was changed. The new flash calculation method used the objective function of Bunz et al. (1991).

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The pressure drop calculation module used the flow regime dependent correlations. The first part of the pressure drop calculation involved the flow regime estimation; the second part calculated the pressure drop with modified literature models. Three flow regimes that werte modeled in this program are: bubble flow, slug flow, and annular flow. Churn flow was included in the slug flow regime. The pressure drop calculations for bubble flow were taken from the correlation by Orkiszewski (1966). The slug flow pressure drop was calculated from the model by Sylvester (1987). The pressure drop in the annular flow regime used the Yao and Sylvester (1987) model and was the same correlation used by Robertson (1988).

Two modifications were made to the uniform corrosion rate calculation module from the previous model (Liu, 1991). The numerical scheme used in the computation of the differential equation for the mass balance in the diffusion layer was changed. The model of Liu (1991) used a process of quasi-linearization (Na, 1979) before writing the equation in the finite difference form. The model of Liu and High (1993) iterarted on the non-linear source term to solve the differential equation (Patankar, 1980). The other change was the modification of the correlation for the diffusivity of the species in the iron carbonate film. The effective diffusivity was correlated (Liu and High, 1993) based on the experimental data reported in literature (Ikeda et al., 1984).

2.4 Electrolyte Equilibrium Modeling

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A description of electrolytic systems and the impact of electrolyte equilibrium modeling on corrosion rate predictions are described in this section.

Various fields ranging from astronomy to zymology are critically dependent on the nature and the behavior of aqueous electrolytes. Many geological processes are modeled in terms of the equilibrium existing between the electrolyte (aqueous phase) and the ions (various mineral phases). Electrolytic behavior significantly affects the metallurgical operations in the extraction of metals, such as iron and aluminum, and the design of furnaces. The distribution and the activity of the species in aqueous solutions, affected by electrolyte behavior, are pertinent to corrosion engineers concerned with pipeline corrosion and solid deposition in gas and oil wells. Electrolytes control the chemical

reaction equilibria in aqueous solutions, thereby influencing industrially important processes such as sour water stripping for pollution control, regenerative flue gas scrubbing for SO_2 removal, plating processes, chemical and biochemical unit operations (e.g., oxidation, fermentation etc.), and ion exchange operations.

Generally, multiple phases are involved in electrolytic systems. Common industrial processes involve aqueous electrolytic solutions in equilibrium with another phase. The other phase could be

- 1. a vapor (e.g., acid gas scrubbing, distillation of HNO₃ or HCl)
- 2. a liquid (e.g., metal extraction in hydrometallurgy), or
- 3. a solid (e.g., adsorption, ion-exchange).

In downhole gas wells, electrolytes in the liquid phase are in constant contact with vapors consisting primarily of low molecular weight hydrocarbons (C_1 and C_2), CO_2 , and H_2S .

The estimation of the vapor-liquid and electrolytic behavior is important in the design of oil and gas wells. Estimation of properties such as phase density, surface tension, and viscosity affect the pressure drop in gas and oil wells. Pressure drop calculations and the flash calculations are coupled. Vapor-liquid and electrolyte equilibrium calculations also provide estimates of the quantity and composition of the various phases present in the downhole environment. The electrolyte equilibrium module calculates the concentration of all the species at the gas-liquid interface. The liquid phase concentration of components such as H^+ , HS^- , S^{2-} , HCO_3^- , and CO_3^{2-} determine the acidity/alkalinity of the solution. The species at the gas-liquid interface are transported to

the metal surface where corrosion reactions occur. Thus, accurate estimation of phase and aqueous electrolyte behavior is essential to predict corrosion rates correctly.

Despite the fact that electrolytic systems are encountered in many disciplines of science and engineering, the ability to predict their vapor-liquid behavior is extremely limited. When the solvent is sufficiently polar, electrolytes dissociate into ions. The ionization effects introduce a high amount of non-ideality to the system. The presence of multiple phases further complicates the matter. Although the thermodynamic basis for such systems has been documented, there is no satisfactory understanding of the physical chemistry of aqueous systems containing volatile weak electrolytes (Mather, 1986).

Systems containing volatile weak electrolytes are modeled in two steps. Vaporliquid equilibrium is primarily modeled using classical equations of state. Aqueous electrolyte equilibrium is described in terms of temperature dependent dissociation constants. Such modeling introduces error when certain factors such as liquid phase dissociation and/or liquid phase reactions are neglected while building the model.

Traditional modeling of systems containing volatile weak electrolytes, using cubic equations of state, has proven to be inaccurate and unreliable (Friedemann, 1987). Friedemann (1987) showed that a typical equation of state based flash calculation does not predict the phase compositions accurately (Table I). While the compositions of the inerts are predicted quite closely, the acid-gas component distribution is inaccurate. This inaccuracy is glaring in the liquid phase prediction vis-à-vis the experimental data of Wilson (1978).

TABLE I

Comparison of Flash Calculations With and Without Providing for Aqueous Phase Dissociations

Temperature = 300 °F

Pressure = 500 psia

Component	Vapor (mol %)	Vapor (mol %)	Vapor (mol%)	Liquid (mol %)	Liquid (mol %)	Liquid (mol %)
	Experimental	without	with	Experimental	without	with
		dissociation	dissociation		dissociation	dissociation
NH ₃	1.57	2.07	1.75	2.02	1.56	1.84
CO ₂	29.20	28.98	29.10	0.60	0.15	0.36
H ₂ S	4.68	5.00	4.79	0.52	0.08	0.36
H ₂ O	13.93	14.52	14.40	96.83	98.18	97.14
N ₂	6.40	6.26	6.32	0.0024	0.00	0.00
CH4	10.09	9.86	9.97	0.0065	0.01	0.01
H ₂	34.13	33.35	33.70	0.0227	0.03	0.03
D.C.	r:1	(1007)				

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Reference: Friedemann (1987)

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The capability of an equation of state to predict the vapor-liquid behavior can be improved by providing for aqueous phase dissociation. Friedemann (1987) used this approach to improve upon the results obtained in Table I for the system studied by Wilson (1978). The improved results have also been tabulated in Table I. A comparison of the flash calculation results indicate that the inclusion of the aqueous phase dissociations reduced the error in the composition prediction of acid-gas components by nearly twothirds.

Aqueous phase dissociation can be described in terms of the following generalized ionic equilibria.

$$AB \leftrightarrow A^+ + B^-$$
 (2.2)

The ionic equilibrium can be described in terms of the equilibrium constant and the ionic activities as given below.

$$K = \frac{[a_{A^{+}}][a_{B^{-}}]}{[a_{AB}]}$$
(2.3)

Typically, concentrations are expressed in terms of molality and ionic activity coefficients. Ionic activity coefficients are calculated from empirical models.

The ionization effects can be studied by means of molecular and empirical models. Molecular models are based on the effects of the various types of forces on the structural and thermodynamic properties and are defined by particle interactions. Empirical models are usually derived from excess Gibbs energy or the Helmholtz energy (Renon, 1986). Various properties such as mean activity coefficients of molecular solutes, excess partial molar volumes, enthalpies, entropies, and heat capacities can be derived from the excess Gibbs energy or the Helmholtz energy.

This work utilizes a combination of molecular and empirical models to describe the phase and electrolyte equilibrium in gas wells. The generalized thermodynamic framework is based on a molecular approach by Edwards et al. (1978). The constituent properties required to complete the framework are based on empirical approaches and are described in detail in Chapter III of this work.

An important feature of any empirical approach is the number of adjustable parameters. In the electrolytic systems encountered in most industries, there are numerous species resulting in a large number of binary or even ternary interactions. The inability to measure binary interaction parameters, directly and independently (Renon, 1986), necessitates multi-property, multi-parameter regression. Approximate methods are available for parameter regression, the specific problem is to take into account many properties at the same time, to check the validity of the parameters and the model, and achieve the phase equilibrium computations. Using a model with a very small number of adjustable parameters would therefore be advantageous.

A new approach to predicting phase equilibria by Chen et al. (1994) has been used in this work. This model uses a single molecular interaction parameter for aqueous binary mixtures. The model has the capability to predict phase equilibria for light hydrocarbons and inert gases encountered in gas wells using the Soave-Redlich-Kwong equation of state. Further, this model has been extensively tested over an extensive range of published
experimental data. Chen et al. (1994) indicated that the model predicted partial pressures with errors on the order of the uncertainty in the experimental measurements.

2.5 The Phase Equilibrium Model used in DREAM

Phase equilibrium calculations give the quantity and composition of the liquid and vapor phases at every point along the gas well. The rate of corrosion depends on the amount of condensed water in the tubing and the concentration of the acidic components. The change in the temperature and pressure from the wellhead to the bottomhole changes the amount of water condensed at various locations in the well.

The Soave-Redlich-Kwong (Soave, 1972) equation of state used to model the behavior of the molecular components in both the vapor and the liquid phases is described below:

$$P = \frac{RT}{(V-b)} - \frac{a\alpha}{V(V+b)}$$
(2.4)

where a, b, and α are constants and are given by:

$$a = \frac{0.42747 R^2 T_c^2}{P_c}$$
(2.5)

$$b = \frac{0.08664 \text{ R } T_{\text{C}}}{P_{\text{C}}}$$
(2.6)

$$\alpha = [1 + (0.48508 + 1.55171 \,\omega - 0.15163 \,\omega^2) (1 - T_r^{0.5})]^2$$
(2.7)

In Equation (2.7), ω is the pure component acentric factor and can be taken from GPA*SIM (Erbar, 1980). T_r is the reduced temperature and is given by:

$$T_r = \frac{T}{T_c}$$
(2.8)

For mixtures the following rules apply:

$$(a\alpha)_{mix} = \sum \sum x_i x_j (a\alpha)_{ij}$$
(2.9)

$$(\mathbf{a}\alpha)_{ij} = (1 - C_{ij}) \left[(\mathbf{a}\alpha)_i (\mathbf{a}\alpha)_j \right]^{0.5}$$
(2.10)

$$(b)_{mix} = \sum x_i b_i \tag{2.11}$$

where C_{ij} is the binary interaction parameter. The values for C_{ij} are taken from GPA*SIM (Erbar, 1980) for all binaries. The interaction between different species in the fluid can be categorized as

- 1. molecule-molecule interaction
- 2. ion-ion interaction
- 3. molecule-ion interaction.

These interactions can be binary, ternary, or even higher (i.e., multiple particle interaction) in nature. Studying or accounting for all of these interactions in the model is virtually impossible. To simplify the computation process only binary molecule-molecule interaction is accounted for and is defined in Equation (2.10).

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Flash calculations estimate the quantity of the liquid and vapor at any point in the system. The vapor-liquid equilibrium constant, $K_{i,VLE}$, is calculated as a ratio of the fugacity coefficients.

$$K_{i,VLE} = \frac{\phi_i^L}{\phi_i^V} = \frac{y_i}{x_i}$$
(2.12)

The vapor-liquid equilibrium constant values are used in the flash calculations. The two-

phase flash calculation can be determined from the Rachford-Rice criterion (Smith and Van Ness, 1987):

$$f(L/F) = \frac{\sum Z_i (1 - K_{i,VLE})}{K_{i,VLE} + \frac{L}{F} (1 - K_{i,VLE})} = 0$$
(2.13)

Equation (2.13) was solved by means of a Newton-Raphson iteration technique by providing an initial guess for the value of L/F.

The fugacity coefficients can be calculated from the SRK equation of state using the following formulae:

$$\ln \phi = \frac{b_i}{b_{mix}} (Z-1) - \ln (Z-B^*) - \frac{A^*}{B^*} \left[\frac{2(a\alpha)_i}{(a\alpha)_{ij}} - \frac{b_i}{b_{mix}}\right] \ln (1 + \frac{B^*}{Z})$$
(2.14)

where,

$$A^{*} = \frac{(a\alpha)_{mix} P}{R^{2} T^{2}}$$
(2.15)

$$B^* = \frac{b_{mix} P}{RT}$$
(2.16)

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The compressibility factor, Z, can be calculated from Equation (2.4) rewritten as:

$$Z^{3} - Z^{2} + (A^{*} - B^{*} - B^{*2}) Z - A^{*} B^{*} = 0$$
(2.17)

CHAPTER 3

MODEL DEVELOPMENT

The principal objective of this work, is to establish a consistent, generalized framework for the phase and electrolyte equilibrium computations required for corrosion prediction in downhole gas wells. This chapter discusses the physical model of the downhole system, the generalized electrolyte equilibrium model developed as part of this work, and the numerical technique for coupled phase and electrolyte equilibrium calculations.

3.1 Physical Model

The system downhole can be described as one in which natural gas, with or without formation water, leaves the reservoir and enters the tubing at high temperature and pressure (Liu, 1991). The decrease in pressure and temperature experienced by the upward flowing gas, may cause water condensation to occur in some part of the well. The gas flow rates in most of the wells encountered are very high, so the flow is in the annular or the slug flow regime.

The downhole corrosion phenomenon has been viewed as a three layer model as shown in Figure 1 (Liu, 1991). The three layers are the turbulent film layer, the diffusion layer, and the corrosion product layer. The corrosive species at the gas-liquid interface

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Figure 1 Physical Model of Downhole System

are first transported through the turbulent liquid film. Interfacial shear and wall roughness strongly influence the transport of the various species through the turbulent layer. In the diffusion layer, molecular diffusion and ion migration are the dominant mechanisms. In a multicomponent corrosion process encountered downhole, surface electrochemical reactions set up an electric field. Hence, the mass transport expression in the diffusion region includes the effect of the concentration gradients and the electric potential. Finally, the corrosive species diffuse through the corrosion product layer to reach the metal surface. Corrosion reactions occur at the tubular surface, and a corrosion product may be formed. The corrosion product layer protects the piping material. The diffusion of CO_2 and H_2S through the corrosion product layer is highly dependent on the temperature (de Waard et al., 1991; Ikeda et al., 1984; Kuznetsov, 1981; Shoesmith et al., 1980).

The system encountered downhole can be represented by Figure 2. At a given temperature and pressure, the weak electrolyte and water will equilibrate between the liquid and the vapor phase. In the liquid phase, weak electrolytes exist in two forms: molecular and ionic. The chemical equilibrium between the molecular and ionic forms of the electrolytes is described by the dissociation constant. Electrolytic dissociation occurs only at very high temperatures in the vapor phase. Such high temperatures are not prevalent in gas wells. Therefore, vapor phase dissociation was neglected.

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In Figure 2, the phase equilibrium is determined by the molality of the molecular (not ionic) solute; that molality is in turn affected by the chemical dissociation equilibrium. Since ions are not volatile, the phase equilibrium of the system is not governed by the total electrolyte concentration in the liquid phase; only by the concentration of the liquid phase



Figure 2 Vapor-Liquid Equilibrium in a Downhole System

electrolyte that exists in the molecular (undissociated) form.

3.2 Model Formulation

The equilibrium conditions for phase equilibria can be derived using the concept of Gibbs free energy, G. For an open system with n components, like the one considered downhole, the condition of equilibrium can be written as:

$$dG^{t} = -S dT + V dP + \sum \mu_{i} dn_{i}$$
(3.1)

where μ_i is the chemical potential of component i and is defined as the change in the Gibbs free energy of a system as a result of the addition of dn_i moles of component i at constant temperature and pressure, holding the moles of the other components constant.

According to the second law of thermodynamics, the total Gibbs free energy of a closed system at a constant temperature and pressure is minimum at equilibrium, i.e.,

$$dG^{t} = 0$$
 (3.2)

Figure 2 depicts the downhole system at equilibrium. At the gas-liquid interface at Equation (3.2) reduces to

$$\mu_i^L = \mu_i^V \tag{3.3}$$

i.e., the chemical potential of component i in the liquid phase and the vapor phase are the same. The chemical potentials can be related to the mole fraction (or concentration) by means of the fugacity as follows:

$$d\mu_i = \mathbf{RT} \, \mathbf{d} \, \ln \mathbf{f}_i \tag{3.4}$$

The fugacity of the ith component in a mixture is defined as

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$$\mathbf{f}_{i} = \mathbf{y}_{i} \, \boldsymbol{\phi}_{i} \, \mathbf{P}. \tag{3.5}$$

From Equation (3.3) and Equation (3.4) the following condition exists at equilibrium:

$$\mathbf{f}_{i}^{L} = \mathbf{f}_{i}^{V} \tag{3.6}$$

Substituting Equation (3.5) into Equation (3.6):

$$\mathbf{y}_{i} \mathbf{\phi}_{i}^{\mathrm{V}} = \mathbf{x}_{i} \mathbf{\phi}_{i}^{\mathrm{L}} \tag{3.7}$$

The gas-phase mole fraction, y_i , is known. The fugacity coefficient, ϕ , is calculated for both the vapor and the liquid phase using the Soave-Redlich-Kwong equation of state as described in Chapter II (Equations 2.4 to 2.17). The calculation of the liquid phase mole fraction, xi, is described in this chapter.

The following assumptions were made in the model development:

- 1. The concentrations of the species across the gas-liquid interface are in thermodynamic equilibrium.
- 2. The system is at steady state.
- 3. Electroneutrality holds in the bulk liquid and also at the liquid-solid interface.
- 4. All the inorganic ions present in the formation water do not necessarily take part in the corrosion reactions but do contribute to the electroneutrality of the solution.
- Precipitation is a sufficient condition for film formation.
- Iron dissolution kinetics are neglected.

This model uses assumptions (1) and (2) to determine the concentrations of the species in the liquid and vapor phases. These concentrations are used to estimate the pH OKT.AHOMA STATE UNIVERSITY

of the system and the boundary conditions in the mass transport expressions for the subsequent three layers.

3.2.1 Concentration at the Gas-Liquid Interface

The thermodynamic analysis of aqueous weak electrolytes in this model is based on the following four principles outlined by Edwards et al. (1978):

- 1. Overall mass balance in the liquid phase,
- 2. Electroneutrality in the bulk liquid,
- 3. Chemical equilibrium between the undissociated (molecular) and the dissociated (ionic) forms of the weak electrolyte in the liquid phase, and
- 4. Vapor-liquid equilibrium for the molecular solute.

The equilibrium relationship at the gas-liquid interface can be summarized as follows (Sundaram et al., 1996):

$$H_2O_{(g)} \leftrightarrow H_2O_{(l)}$$
 (3.8)

$$\mathrm{CO}_{2(\mathrm{g})} \leftrightarrow \mathrm{CO}_{2(\mathrm{l})}$$
 (3.9)

The ionic dissociation reactions at the gas-liquid interface are given below:

$$H_2O_{(1)} + CO_{2(1)} \leftrightarrow HCO_3^- + H^+$$
(3.10)

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$
(3.11)

$$H_2O_{(1)} \leftrightarrow H^+ + OH^-$$
 (3.12)

If H₂S is present, the following relations are included:

$$H_2S_{(g)} \leftrightarrow H_2S_{(1)}$$
 (3.13)

$$H_2S_{(1)} \leftrightarrow HS^- + H^+$$
 (3.14)

$$HS^- \leftrightarrow S^{2-} + H^+$$
 (3.15)

The tubulars and casings could react with the carbonic acid or the sulphurous acid present and form iron carbonate, calcium carbonate, and/or iron sulfide. The corrosion product layers so formed could retard the rate of corrosion in the gas well. This model is based on the assumption that precipitation is a sufficient condition for film formation. In the presence of these protective corrosion product films, the following relations should be taken into consideration.

$$(FeCO_3)_s \leftrightarrow Fe^{2+} + CO_3^{2-} \tag{3.16}$$

$$(CaCO_3)_s \leftrightarrow Ca^{2+} + CO_3^{2-}$$
 (3.17)

$$(\text{FeS})_{s} \leftrightarrow \text{Fe}^{2+} + \text{S}^{2-}$$
 (3.18)

The assumption of electroneutrality for the mixture of charged species can be written as:

$$\Sigma \mathbf{z}_{\mathbf{i}} \mathbf{m}_{\mathbf{i}} = \mathbf{0} \tag{3.19}$$

where z_i is the charge associated with the i^{th} ionic species and m_i is the corresponding concentration.

A mass balance between the undissociated and the dissociated forms of the molecular species yields the following two equations:

$$m_{CO_2} + m_{HCO_2^-} + m_{CO_2^{2-}} = M_{CO_2}$$
 (3.20)

$$m_{H_2S} + m_{HS'} + m_{S^{2-}} = M_{H_2S}$$
 (3.21)

The variables appearing in Equation (3.20) and Equation (3.21) have units of concentration (mole/kg solvent).

For dissociation of the molecular and the ionic species the following relations hold:

$$K_{W} = \frac{m_{H^{+}} m_{OH^{-}} \gamma_{H^{+}} \gamma_{OH^{-}}}{m_{H_{2}O} \gamma_{H_{2}O}}$$
(3.22)

$$K_{1, CO_{2}} = \frac{m_{HCO_{3}^{-}} \gamma_{HCO_{3}^{-}} m_{H^{+}} \gamma_{H^{+}}}{m_{H_{2}O} \gamma_{H_{2}O} m_{CO_{2}} \gamma_{CO_{2}}}$$
(3.23)

$$K_{2, CO_{2}} = \frac{m_{CO_{3}^{2^{-}}} \gamma_{CO_{3}^{2^{-}}} m_{H^{+}} \gamma_{H^{+}}}{m_{HCO_{3}^{-}} \gamma_{HCO_{3}^{-}}}$$
(3.24)

$$K_{1, H_2S} = \frac{m_{HS'} \gamma_{HS'} m_{H^+} \gamma_{H^+}}{m_{H_2S} \gamma_{H_2S}}$$
(3.25)

$$\mathbf{K}_{2, H_{2}S} = \frac{\mathbf{m}_{S^{2}} \gamma_{S^{2}} \mathbf{m}_{H^{+}} \gamma_{H^{+}}}{\mathbf{m}_{HS^{-}} \gamma_{HS^{-}}}$$
(3.26)

The solubility products of the corrosion product layers are estimated from the following relations:

$$K_{SP FeCO_3} = \frac{m_{Fe^{2+}} \gamma_{Fe^{2+}} m_{CO_3^{2-}} \gamma_{CO_3^{2-}}}{a_{FeCO_3}}$$
(3.27)

$$K_{SP CaCO_3} = \frac{m_{Ca^{2+}} \gamma_{Ca^{2+}} m_{CO_3^{2-}} \gamma_{CO_3^{2-}}}{a_{CaCO_3}}$$
(3.28)

$$K_{SP FeS} = \frac{m_{Fe^{2+}} \gamma_{Fe^{2+}} m_{S^{2-}} \gamma_{S^{2-}}}{a_{FeS}}$$
(3.29)

Equations (3.19 and 3.22 to 3.29) contain 9 equations and 9 unknowns (viz., m_{H^+} , m_{OH^-} , $m_{HCO_3^-}$, $m_{CO_3^{--}}$, m_{HS^-} , $m_{S^{--}}$, m_{H_2O} , m_{CO_2} , m_{H_2S}). All the unknowns can be expressed in terms of m_{H^+} and substituted into Equation (3.19) and solved to obtain the following expression involving the molality of the hydrogen ion:

$$A_1 m_{H^+}^4 + A_2 m_{H^+}^3 + A_3 m_{H^+}^4 + A_4 = 0$$
 (3.30)

where,

$$A_{1} = \gamma_{H^{+}}^{2} (A_{5} + A_{6} + A_{7})$$
(3.31)

$$A_2 = 1.0$$
 (3.32)

$$A_3 = -(A_8 + A_9 + A_{10}) \tag{3.33}$$

$$A_4 = -\frac{2}{\gamma_{H^*}^2} (A_{11} + A_{12})$$
(3.34)

$$A_{5} = \frac{K_{SP FeS}}{\gamma_{Fe^{2+}} K_{1, H_{2}S} K_{2, H_{2}S} m_{H_{2}S} \gamma_{H_{2}S}}$$
(3.35)

$$A_{6} = \frac{K_{SP FeCO_{3}}}{\gamma_{Ee^{2+}} K_{1, CO_{2}} K_{2, CO_{2}} \gamma_{H_{2}O} \gamma_{CO_{2}} m_{H_{2}O} m_{CO_{2}}}$$
(3.36)

$$A_{7} = \frac{K_{SP CaCO_{3}}}{\gamma_{Ca^{2+}} K_{1, CO_{2}} K_{2, CO_{2}} \gamma_{H_{2}O} \gamma_{CO_{2}} m_{H_{2}O} m_{CO_{2}}}$$
(3.37)

$$A_{8} = \frac{K_{W} \gamma_{H_{2}O} m_{H_{2}O}}{\gamma_{OH'} \gamma_{H^{+}}}$$
(3.38)

$$A_{9} = \frac{K_{1, CO_{2}} m_{CO_{2}} \gamma_{CO_{2}} m_{H_{2}O} \gamma_{H_{2}O}}{\gamma_{H^{+}} \gamma_{HCO_{3}^{-}}}$$
(3.39)

$$A_{10} = \frac{K_{1, H_2S} m_{H_2S} \gamma_{H_2S}}{\gamma_{H^+} \gamma_{HS^-}}$$
(3.40)

$$A_{11} = \frac{K_{1, CO_2} K_{2, CO_2} m_{H_2O} \gamma_{H_2O} m_{CO_2} \gamma_{CO_2}}{\gamma_{CO_3^{2-}}}$$
(3.41)

$$A_{12} = \frac{K_{1, H_2S} K_{2, H_2S} m_{H_2S} \gamma_{H_2S}}{\gamma_{S^{2-}}}$$
(3.42)

The corrosion rate along the well depth also depends on the ionic species present in the produced water. The quantity of the ionic species present in the production water is estimated from the water analysis. Generally, the water analysis supplied for the prediction of corrosion rates is not electroneutral. In this work the sodium ion concentration is adjusted to satisfy the charge balance.

The solution of Equation (3.30) yields the pH from which the concentrations of all the other species are calculated. The estimation of the parameters and the constants required for solving Equation (3.30) are detailed in the remaining part of this section.

Chemical dissociation constants are strong functions of temperature and very weak functions of pressure (Helgeson, 1969). All dissociation constants used in this work are functions of temperature alone. The chemical dissociation constants used in this work are calculated using the correlations by Edwards et al. (1978) and Kawazuishi and Prausnitz (1987). The generic equation for the dissociation constant can be expressed as: OKTAHOMA STALE UNIVERMENT

 $\ln K_{i} = B_{i,1} / T + B_{i,2} \ln T + B_{i,3} T + B_{i,4}$ (3.43)

The constants Bi, j are given in Table II.

The solubility products of the corrosion product layers are also functions of temperature. Liu (1993) fit the following equation for the solubility product of iron carbonate to the data reported by Garrels and Christ (1965).

TABLE II

Temperature Coefficients for Equilibrium Constants

Species	B _{i, 1}	B _{i, 2}	B _{i, 3}	B _{i, 4}	Valid	Reference	
					Range (⁰ C)		
CO ₂	-12092.1	-36.7816	0.0	235.482	0-225	1	
H ₂ S	-18034.7	-78.0719	0.092	461.716	0-275	2	
HCO ₃ .	-12431.7	-35.4819	0.0	220.067	0-225	1	
HS	-406.004	33.889	-0.054	-214.559	0-225	2	
H ₂ O	-13445.9	-22.4773	0.0	140.932	0-225	1	

Reference 1: Edwards et al. (1978)

Reference 2: Kawazuishi and Prausnitz (1987)

$$\ln K_{sp CaCO_3} = -65.92499 - 0.09288796 T + 14.6247 \ln T - \frac{2784.51}{T}$$
(3.44)

The data reported by Helgeson (1969) for the solubility products of iron carbonate and iron sulfide have been correlated (Liu, 1993) as:

$$\ln K_{\rm sp \ FeCO_3} = -20.0717 + 0.003165 \ T - 6.318 \ x10^{-5} \ T^2$$
(3.45)

$$\ln K_{sp \, FeS} = 31.0813 - \frac{2.02024 \, x \, 10^4}{T} - 2.0026 \, x \log (T) \tag{3.46}$$

The activity coefficients of the ionic species are calculated by the B-dot method (Lewis and Randall, 1961) using the following expression by Helgeson (1969):

$$\log \gamma_{i} = \frac{-A Z_{i}^{2} \sqrt{I}}{1 + a^{0}_{i} B \sqrt{I}} + b^{0} I$$
(3.47)

where I is the ionic strength defined by

$$I = 0.5 \Sigma z_i^2 m_i$$
 (3.48)

The activity coefficient is the ratio of the activity of a substance and the concentration of the substance. The activity coefficient can be defined to take a value of unity under ideal conditions. Two types of ideality are generally used: one leading to Raoult's law and the other leading to Henry's law (Prausnitz, 1969).

If the activity coefficients (γ) are defined with reference to a solution that is ideal over the entire range of composition (Raoult's law) then for both the solute and the solvent

$$\gamma \to 1.0 \text{ as } x \to 1.0$$
 (3.49)

If the activity coefficients are defined with reference to an ideal dilute solution, then the following two equations hold:

$$\gamma_1 \rightarrow 1.0 \text{ as } \mathbf{x}_1 \rightarrow 1.0 \text{ (Solvent)}$$
 (3.50)

$$\gamma_2 \rightarrow 1.0 \text{ as } \mathbf{x}_2 \rightarrow 1.0 \text{ (Solute)}$$
 (3.51)

The Henry's constants are defined as the ratio of the fugacity to the concentration in a dilute solution.

$$H = \frac{f_2}{x_2} (x_2 \to 0.0)$$
 (3.52)

The activity coefficient represents the deviation from ideality. The deviation for the completely dissociated solute is given by the first term in Equation (3.47). Charged ions exert long-range electrostatic forces upon one another even in dilute electrolytic solutions, lowering the activity coefficients significantly (Garrels and Christ, 1965). The effects of the long-range electrostatic forces have been evaluated using the Debye-Huckel theory and several useful equations similar to Equation (3.47) have been proposed to evaluate activity coefficients (Lewis and Randall, 1961; Klotz, 1950). The activity coefficients are expressed in terms of the molal Debye-Huckel parameters (A and B) and are functions of temperature (Helgeson, 1969):

$$A = \frac{1.8246 \times 10^6 \sqrt{\rho_w}}{(\varepsilon_w T)^{3/2}}$$
(3.53)

$$B = \frac{50.29 \times 10^8 \sqrt{\rho_w}}{\sqrt{\varepsilon_w T}}$$
(3.54)

where ρ_w represents the density of water and ε_w represents the dielectric constant of water. An equation was fit (Liu, 1993) to the density and dielectric constant of water data reported by Helgeson (1967). The term a^0 in Equation (3.47) represents the distance of closest approach of ions in an electrolyte solution. Thus a^0 may be thought of as the effective diameter of the particular species in solution. This quantity is an empirical parameter, but has a magnitude slightly larger than values of ionic diameters. The deviation in the value of the ionic diameter is possibly due to the envelope of the water molecules that surround the ions in aqueous solution (Garrels and Christ, 1965). The values for a^0 used in the model are those reported by Klotz (1950). The value of a^0 varies significantly with temperature. Due to the lack of data for most ions at higher temperatures and the absence of any computational procedure available in the literature (Helgeson, 1969), the values for the hard sphere radius available at 25 °C are used in the model.

The second term in Equation (3.47) represents the deviation of the ionic activity coefficient from that prescribed by the Debye-Huckel expression at 25 $^{\circ}$ C. This deviation function is represented by the term b⁰ and accounts for the short range (Van der waals) interactions between solute species. These interactions are of three types (Edwards et al., 1978):

- (1) molecule-molecule,
- (2) ion-ion, and
- (3) molecule-ion.

The quantity b^0 has been found to be dependent on temperature, but independent of concentration at ionic strengths of 0.5 or more in most electrolyte solutions at 25 ${}^{0}C$ (Helgeson, 1969). Helgeson (1969) concluded that b^0 approaches zero at temperatures

close to 300 $^{\circ}$ C. A correlation has been fit (Liu, 1993) to calculate the variation of b⁰ with temperature using the data reported by Kharaka et al. (1988) and Helgeson (1969).

The activity coefficients of the molecular species are calculated by a different procedure. The activity coefficients of CO_2 and H_2S are calculated as the ratio of the Henry's law coefficients in an electrolyte of given concentration (m) to that in pure water (Kharaka and Mariner, 1985; Helgeson, 1969).

$$\gamma_{\rm CO2} = H_{\rm m, \, CO2} / H_{\rm W, \, CO2} \tag{3.55}$$

$$\gamma_{\rm H2S} = H_{\rm m, \, H2S} \,/\, H_{\rm W, \, H2S} \tag{3.56}$$

The generic equations for the Henry's constants for H_2S and CO_2 are functions of both temperature and molar strength (Kharaka et al., 1988) and are given below:

$$\ln (H_{CO_2}) = 21.2572 - 0.017603 T - 1.0312 M_s - \frac{3885.6}{T} + \frac{0.4445}{M_s} + \frac{0.0012806 T}{M_s}$$
(3.57)

$$\ln (H_{H_2S}) = 11.1255 - 0.0071704 T - 0.2905 M_s - \frac{2021.5}{T} + \frac{0.5705}{M_s}$$

$$-0.0001574 T M_s - \frac{46.2 M_s}{T} - \frac{0.001777 T}{M_s}$$
(3.58)

where Ms is the molar strength defined by

$$\mathbf{M}_{\rm s} = 0.5 \sum \mathbf{z}_{\rm i} \, \mathbf{m}_{\rm i} + 1.0 \tag{3.59}$$

The Henry's law coefficients for CO_2 and H_2S in an electrolyte are calculated by using the molar strength of the electrolyte from Equation (3.59). The Henry's law coefficients for CO_2 and H_2S in water are calculated by using a value of 1.0 for M_s in Equation (3.57) and Equation (3.58).

The activity of water in dilute solutions is calculated using the following formula (Kharaka and Mariner, 1985; Garrels and Christ, 1965)

$$\gamma_{\rm H2O} = 1 - 0.017 \sum m_{\rm i} \tag{3.60}$$

3.2.2 Coupled Phase and Electrolyte Equilibrium Calculations

A new method for the computation of phase and electrolyte equilibrium, based on the work of Friedemann (1987) with interaction parameters for phase equilibrium calculation from Chen et al. (1994) has been incorporated in this work. The model calculates the dissociation of the weak electrolytes in the liquid phase and uses the corrected value of the concentrations to update the vapor-liquid equilibrium constants.

As discussed in Chapter II of this work, accurate modeling of the phase behavior of the weak electrolytes should include liquid phase dissociations of the molecular species. CO_2 dissociates into HCO_3^- , and CO_3^{2-} , while H_2S dissociates into HS^- , and S^{2-} . The extent of dissociation (d_i) of the molecular species is calculated by the following equations:

$$d_i = \frac{m_i}{M_i}$$
(3.61)

where m_i is the actual (undissociated) concentration of the molecular species in the liquid phase and M_i is the apparent concentration (sum of the undissociated and the dissociated) of the molecular species in the aqueous phase. The effect of the dissociation of the molecular species on the phase equilibrium is incorporated with the vapor-liquid equilibrium calculations. For the liquid phase the component $K_{i,VLE}$ values are corrected to include the extent of dissociation of the weak electrolytes as follows:

$$K_{i,VLE} = \frac{y_i}{x_i d_i}$$
(3.62)

Phase equilibrium calculations are continued with the corrected K_{i,VLE} values.

Chen et al. (1994) performed bubble point calculations for various aqueous binary systems. The results were used to fit binary interaction parameters for these systems. For systems of interest to us (CO_2 -H₂O and H₂S-H₂O) a single molecular interaction parameter has been fit and is given below:

$$C_{ij, CO_2} = 0.457 - \frac{131}{T}$$
(3.63)

$$C_{ij, H_2S} = 0.432 - \frac{104}{T}$$
(3.64)

where T is the temperature in Kelvin.

3.3 Numerical Implementation

The numerical implementation of the model can be described in terms of two major loops. The outer loop accomplishes the phase equilibrium calculations. The inner loop computes the composition of the molecular and the ionic species in the aqueous liquid phase (electrolyte equilibrium computations).

3.3.1 Phase Equilibrium Computations

The overall computation procedure for the phase and electrolyte equilibrium computations is depicted in Figure 3 and is described below:

- 1. The vapor-liquid equilibrium constants (K_{i,VLE}) are calculated from Equation (2.16).
- 2. The dissociation constants are computed (Equations 3.22 to 3.29).
- 3. An iterative calculation is performed to estimate the pH.
- The concentrations of all the molecular and ionic species are calculated from the pH and the dissociation constants.
- 5. The aqueous phase dissociations of the molecular species are then computed (Equation 3.61)
- The vapor-liquid equilibrium constants are modified by including the aqueous phase dissociations (Equation 3.62).
- The phase equilibrium is checked by checking for convergence in the values of K_{i,VLE}. If the phase equilibrium condition is satisfied then corrosion rate computations are initiated.

3.3.2 Electrolyte Equilibrium Computations

The electrolyte equilibrium computation procedure is represented pictorially in Figure 4 and is summarized below:

1. An initial value for pH is calculated by neglecting all second dissociations.



Figure 3 Flow Diagram for Phase Equilibrium Calculation



Figure 4 Flow Diagram for Electrolyte Equilibrium Calculation

- The pH value calculated in step 1 is used to estimate the compositions of all other molecular and ionic species.
- 3. The coefficients of the fourth order equation (Equation 3.30) are computed from the known value of concentrations calculated in step (2) and step (3).
- The fourth order equation (Equation 3.30) is solved by the bisection method. This gives a new value for the pH.
- The concentration of all other species is calculated from the new value of pH obtained in step 5.
- A check is made to ensure that the charge balance converges within a pre-specified tolerance limit.

3.3.2.1 Solution of the Fourth Order Equation

The most important step in computing the concentration of the species at the gasliquid interface lies in obtaining the correct solution for the fourth order equation (Equation 3.30). A detailed description of the nature of the roots of the above equation and the solution procedure is given below.

A fourth order equation has four roots. These roots may be real (positive or negative) or complex. Equation (3.30) is expressed in terms of the concentration of the hydrogen ion. The point of interest as far as this work is concerned is in finding the correct positive root of the equation.

The nature of the roots of Equation (3.30) were examined. If F(x) denotes a polynomial function in 'x', then according to the Descartes rule of signs (Niles, 1978):

- There can be no more positive roots than the number of changes of sign in F(x). The number of positive roots may however be smaller by an even integer because complex roots always occur in pairs.
- There can be no more negative roots than the number of changes of sign in F(-x). The number of negative roots may however be smaller by an even integer because complex roots always occur in pairs.

The constants A_j that appear in Equation (3.30) are functions of equilibrium constants, activity coefficients, and concentrations and are always positive. From Equations (3.31) to Equation (3.42), we know that

- A₁ and A₂ take a positive sign
- A₃ and A₄ take a negative sign

Based on the Descartes rule of signs (Niles, 1978), Equation (3.30) has only one positive root. There are two possibilities for the coefficients in the fourth order equation (Equation 3.30):

- A1 term takes a zero value, or
- A1 term takes a non-zero value.

The specific case of the A_1 term being non zero is taken up for analysis here. To aid the above analysis let Equation (3.30) be represented as $F(m_H^+)$.

1. The number of changes of sign in $F(m_{H}^{+})$ is 1.

2. Hence the maximum number of positive roots for this equation is 1.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes the results obtained as part of this work and discusses the interpretation of these results. The effect of the new method of phase and electrolyte equilibrium computations (Chen et al., 1994) has been evaluated, and the results have been compared with experimental data. A similar evaluation of the old phase equilibrium module (Liu and High, 1993) has also been performed to measure the improvement in the prediction of the system pressure for the two binaries (CO₂-H₂O and H₂S-H₂O). The effect of the new phase equilibrium module on the corrosion rate prediction has been studied. Manual calculations were performed and the results were compared with those from the program to validate the computer code developed as part of this work.

The performance of the model of Chen et al. (1994) and the model of Liu and High (1993) have been evaluated by performing classical bubble point checks at specified temperatures. The modeling results obtained for the bubble pressure predictions were compared with experimental data.

The phase and electrolyte equilibrium model has been incorporated into DREAM. DREAM has been evaluated, and the effect of the electrolyte equilibrium on the corrosion rate has been studied using sixteen test cases. The corrosion rates predicted by the old and the new model were compared with field data.

- 3. Number of changes of sign in $F(-m_{H}^{+})$ is 3.
- 4. The maximum number of negative roots for Equation (3.30) is 3.
- If there are less than three negative roots for Equation (3.30) then the equation can have only one negative root.
- 6. If there is only one negative root then there are two complex roots.
- 7. So in this case, Equation (3.30) has
 - 1 positive root and 3 negative roots, or
 - 1 positive root, 1 negative root, and 2 complex roots.

A similar analysis proves that Equation (3.30) has only 1 positive root even if A₁ is zero.

Since the system has only 1 positive root the equation is solved by bisection which guarantees the calculation of the one real, positive root.

The accuracy of the computer code developed as part of this study for the phase and aqueous electrolyte equilibrium calculation has been verified. In order to verify the accuracy of the FORTRAN subroutines developed, manual calculations were performed for one test case; and the results were compared with the values calculated by the code. The details of the manual calculations and the comparison with the values calculated by the code are given in Appendix B. The liquid phase concentrations calculated manually were found to deviate only in the 6th significant figure from the concentrations computed by the FORTRAN code. The difference can be attributed to round-off errors.

The following formulae have been used in Section (4.1) and Section (4.2) for the purpose of statistical analysis:

Percentage deviation in property 'Y',
$$D = \left(\frac{Y_{calc} - Y_{exp}}{Y_{exp}}\right) \times 100$$
 (4.1)

Bias in property 'Y',
$$b = \frac{\sum (D)}{N}$$
 (4.2)

Average absolute % deviation, AAPD = $\frac{\sum \text{Absolute (D)}}{N} \times 100$ (4.3)

4.1 Analysis of the CO₂-H₂O System

A total of 266 data points from Stewart and Munjal (1970), Takenouchi and Kennedy (1964), Wiebe and Gaddy (1939), Zawisza and Malesinska (1981), Gillespie et al. (1986), and Muller et al. (1988) were used to evaluate the model performance for the CO_2 -H₂O system. A wide range of temperature (32 ^oF - 662 ^oF) and a wide range of

pressure (86.9 psia - 22,038.2 psia) were covered in the analysis. Experimental values of temperature and the liquid phase composition of CO_2 were used to calculate the bubble point pressure of the CO_2 -H₂O binary. The calculated bubble point pressures and the experimental bubble point pressures were compared, and the results are summarized in Tables III and IV.

Table III gives the summary of the results for the CO_2 -H₂O system. The average absolute percentage deviation (AAPD) for the model of Liu and High (1993) is 48.9 %. The AAPD is 14.5 % for the model of Chen et al. (1994). The bias (average) is 24.1 % for the model of Liu and High (1993) and -2.0 % for the model of Chen et al. (1994). For the individual authors studied as part of this work, the AAPD varies from 119.1 % to 20.4 % for the model of Liu and High (1993). For the model of Chen et al. (1994), the corresponding AAPD is 31.3 % to 5.5 %. The model of Chen et al. (1994) performs better for each of the individual authors studied.

Table III also presents the results of the CO_2 -H₂O system classified by reference for the models of Liu and High (1993) and Chen et al. (1994). This analysis has been done, because considerable differences exist in the experimental studies conducted by different authors (Chen et al., 1994).

Figure 5 shows a plot of the AAPD as a function of the total system pressure (on a semi-logarithmic scale) for both the models studied. The model of Liu and High (1993) shows a wider scatter than the model of Chen et al. (1994) over the entire range of pressure studied. The scatter is particularly significant at pressures below 5,000 psia.

TABLE III

Reference	Number of Points	Temperat ure Range (°F)	Pressure Range (psia)	Average Absolute % Deviation (Liu and High)	Bias (Liu and High)	Average Absolute % Deviation (Chen et al.)	Bias (Chen et al.)
1	12	32 - 77	147 - 661	37.0	32.4	28.7	7.2
2	115	230 - 662	1469.2 - 22038.2	20.4	17.5	5.5	0.9
3	62	53 - 167	367.5 - 10290	50.3	46.5	16.5	-3.5
4	15	302 - 392	111.5 - 669.3	119.1	117.6	7.6	6.3
5	20	60 - 250	100 - 2940	87.1	54.0	31.3	-16.6
6	42	248 - 392	86.9 - 1175.9	79.9	-13.1	26.7	5.7
Summary	266	32 - 662	86.9 - 22038.2	48.9	24.1	14.5	-2.0

Summary of the Calculated vs. Measured Bubble Point Pressures for the CO2-H2O System

\$4

- 1. Stewart and Munjal (1970)
- 2. Takenouchi and Kennedy (1964)
- 3. Wiebe and Gaddy (1939)
- 4. Zawisza and Malensinska (1981)
- 5. Gillespie et al. (1986)
- 6. Muller et al. (1988)



Figure 5. Average Absolute Percentage Deviation in the Calculated Bubble Point Pressure as a Function of the System Pressure for the CO₂-H₂O Binary

Table IV classifies the results obtained for the CO_2 -H₂O binary by isotherms. A classification of the data points by isotherm has been done because most authors have measured the liquid phase composition of CO_2 along isotherms, moving from higher to lower pressures. Figure 6 plots the AAPD as a function of temperature. From Figure 6 and Table IV it can be concluded that the model of Chen et al. (1994) performs better than the model of Liu and High (1993) at every isotherm studied. For the individual isotherms analyzed the AAPD of the model of Chen et al. (1994) varies between 1.04 % and 32.70 %, while for the model of Liu and High (1993) the variation in the AAPD is between 3.13 % and 97.11 %.

4.2 Analysis of the H₂S-H₂O System

A total of 472 data points from Selleck et al. (1952), Gillespie and Wilson (1980), Clarke and Glew (1971), Wright and Maass (1932), and Lee and Mather (1977) were used to evaluate the model performance for the H₂S-H₂O system. Temperatures range from 32 0 F to 600 0 F; the pressure range was 5.3 psia to 3,000.0 psia. Experimental values of temperature and the composition of H₂S in the liquid phase were used to calculate the bubble point pressure of the H₂S-H₂O binary. The calculated and experimental bubble point pressures were compared. The deviations are summarized in Tables V and VI.

For this set of data, average absolute percentage deviation (AAPD) is 53.0 % for the model of Liu and High (1993) and 8.6 % for the model of Chen et al. (1994). There is 4

TABLE IV

Temperature	Number	Pressure Range	Average	Average	
(°F)	of	(psia)	Absolute %	Absolute %	
	Points		Deviation (Liu	Deviation (Chen	
			and High, 1993)	et al., 1994)	
32.0	3	147.0 - 441.0	96.90	18.53	
41.0	3	147.0 - 558.6	96.89	28.93	
50.0	3	147.0 - 558.6	96.94	32.70	
53.6	6	735.0 - 4410.0	7.44	6.78	
54.3	1	661.5	6.33	2.37	
60.0	1	735.0	30.85	1.04	
64.4	7	367.5 - 4410.0	17.24	21.89	
77.0	6	294.0 - 5880.0	61.35	21.67	
85.0	1	800.0	83.74	6.91	
87.9	11	100.0 - 7300.0	65.11	30.10	
95.0	8	367.5 - 7350.0	54.53	16.37	
104.0	9	367.5 - 7350.0	57.22	15.89	
122.0	11	367.5 - 10290.0	67.78	22.06	
167.0	14	100.0 - 10290.0	97.11	26.23	
200.0	4	367.5 - 2940.0	68.39	28.95	
230.0	15	1469.2 - 22038.2	13.44	4.77	
248.0	7	86.9 - 413.0	79.44	28.75	
250.0	5	100.0 - 2940.0	50.64	14.36	
284.0	7	94.3 - 470.8	67.01	9.27	
302.0	20	111.5 - 22038.2	95.46	6.05	
320.0	7	127.3 - 504.6	54.63	9.76	
347.0	5	173.6 - 591.6	35.33	10.66	
356.0	7	208.7 - 909.1	56.85	15.05	
392.0	34	267.4 - 22038.2	50.08	22.55	
482.0	15	1469.2 - 11753.7	18.89	8.10	
500.0	15	2938.4 - 22038.2	15.36	4.86	
518.0	12	2938.4 - 17630.6	19.48	4.10	
527.0	10	1469.2 - 11753.7	27.53	7.43	
572.0	10	1469.2 - 8080.7	25.85	6.06	
617.0	6	2203.8 - 5876.8	18.29	4.92	
662.0	3	2938.4 - 4407.6	3.13	2.35	

Calculated vs. Measured Bubble Point Pressures for the CO₂-H₂O System Classified by Isotherms



Figure 6. Average Absolute Percentage Deviation in the Calculated Bubble Point Pressure as a Function of the System Temperature for the CO₂-H₂O Binary

TABLE V

Reference	Number of Points	Temperature Range (⁰ F)	Pressure Range (psia)	Average Absolute % Deviation (Liu and High)	Bias (Liu and High)	Average Absolute % Deviation (Chen et al.)	Bias (Chen et al.)
1	35	100 - 340	100 - 3000	41.3	22.4	8.5	-1.2
2	27	100 - 600	450 - 3000	36.1	11.7	7.1	-0.8
3	36	32 - 122	6.8 - 13.8	98.1	87.4	13.2	3.5
4	52	41 - 140	5.3 - 71.7	77.2	53.1	11.6	7.6
5	323	50 - 356	22.4 - 967.2	46.8	-16.6	7.8	-0.1
Summary	472	32 - 600	5.3 - 3000	53.0	3.4	8.6	0.9

Summary of the Calculated vs. Measured Bubble Point Pressures for the H2S-H2O System

- 1. Selleck et al. (1952)
- 2. Gillespie and Wilson (1980)
- 3. Clark and Glew (1971)
- 4. Wright and Maass (1932)
- 5. Lee and Mather (1977)
TABLE VI

Calculated vs. Measured Bubble Point Pressures for the H₂S-H₂O System Classified by Isotherms

Temperature	Number	Pressure	Average Absolute	Average Absolute			
(°F)	of	Range (psia)	% Deviation (Liu	% Deviation (Chen			
	Points		and High, 1993)	et al. 1994)			
32.0	3	7.9 - 12.0	215.22	15.57			
41.0	8	5.3 - 22.7	169.95	8.59			
50.0	19	5.9 - 52.4	131.50	11.91			
59.0	9	13.41 - 89.1	106.72	3.08			
68.0	26	7.0 - 196.6	74.54	10.84			
77.0	15	7.6 - 50.7	64.62	15.07			
86.0	37	8.2 - 328.5	57.64	13.37			
100.0	10	50.0 - 360.0	12.78	4.72			
104.0	40	7.2 - 371.4	42.37	14.11			
122.0	38	8.0 - 419.6	48.59	6.92			
140.0	60	12.6 - 612.5	44.06	8.14			
159.9	29	54.3 - 743.3	37.47	6.73			
194.1	43	34.5 - 953.2	35.83	2.97			
200.0	5	120 - 1080	30.71	2.99			
220.0	8	1250 - 3000	33.72	5.00			
248.1	34	71.9 - 967.2	43.29	7.31			
280.0	8	200 - 3000	93.62	11.16			
300.0	4	450 - 3000	67.18	9.55			
302.1	34	100.4 - 957.2	31.88	6.87			
340.0	13	200 - 3000	25.73	11.54			
356.1	16	155.3 - 858.1	31.88	6.87			
400.0	6	450 - 3000	30.89	9.39			
500.0	3	800 - 3000	42.36	7.88			
600.0	4	2000 - 3000	40.89	6.08			

a bias of 3.4 % in the results for the model of Liu and High (1993), while the bias reduces to 0.9 % for the model of Chen et al. (1994).

Figure 7 shows a plot of the AAPD as a function of the total system pressure for both the models studied. The model of Liu and High (1993) shows a wider scatter than the model of Chen et al. (1994) over the entire range of pressure studied for the H_2S-H_2O system.

Table V also presents the results of the H_2S-H_2O system by reference, for the models of Liu and High (1993) and Chen et al. (1994), respectively. As in the case of the CO_2-H_2O binary, an analysis of the data points of individual studies has been conducted because considerable differences exist in the experimental studies conducted by different authors (Chen et al., 1994).

Table VI classifies the results obtained for the H_2S-H_2O system by isotherms because most authors measured the liquid phase composition along isotherms, moving from higher to lower pressures. Figure 8 is a plot of the AAPD as a function of temperature. From Figure 8 and Table IX it can be concluded that the model of Chen et al. (1994) performs better than the model of Liu and High (1993) at every isotherm studied. For the individual isotherms, the AAPD of the model of Chen et al. (1994) varies between 2.97 % and 15.57 %, while for the model of Liu and High (1993) the variation in the AAPD is between 12.78 % and 215.22 %.



Figure 7. Average Absolute Percentage Deviation in the Calculated Bubble Point Pressure as a Function of the System Pressure for the H₂S-H₂O Binary



Figure 8. Average Absolute Percentage Deviation in the Calculated Bubble Point Pressure as a Function of the System Temperature for the H₂S-H₂O Binary

4.3 Discussion

The model of Chen et al. (1994) provides better values for the bubble point pressures than the model of Liu and High (1993), in the temperature and pressure range studied, due to the inclusion of the aqueous phase dissociation in the overall phase equilibrium computation. Instead of using the apparent composition of the weak electrolytes (CO_2 or H_2S) in the liquid phase (Liu and High, 1993), the true composition of the weak electrolytes was used in this work. The corrected compositions result in a better representation of the vapor-liquid equilibrium and an improvement in the phase equilibrium prediction.

The results given in Table III and Table V indicate that the model of Chen et al. (1994) performs better for the H_2S-H_2O binary system than for the CO_2-H_2O binary system. This discrepancy can be explained in terms of the polarity and the acentricity of the molecules.

The polarity of the constituents of a system affect the vapor-liquid equilibrium behavior of the system. Electrostatic forces can arise even in those molecules that do not possess a net electric charge. All molecules that have an uneven spatial distribution of electronic charges about the positively charged nuclei develop a permanent dipole. The greater the asymmetry of the molecule, the greater the dipole moment. H₂O has a dipole moment of 1.8 debye; H₂S has a dipole moment of 0.9 debye; and CO₂ has a dipole moment of 0.0 debye. The wide difference in the polarity of CO₂-H₂O results in a larger error in the prediction of the vapor-liquid equilibrium behavior for the CO₂-H₂O binary (Gerdes et al., 1989).

The acentric factor correlates the extent of deviation of a molecule from simple molecule behavior. The acentric factor is a measure of the acentricity [i.e., the non-central nature of the intermolecular forces (Prausnitz, 1969)]. For simple molecules the acentric factor is 0. The acentric factor increases as the complexity of the molecules increases. An increase in the complexity of a molecule increases its deviation from ideality and introduces a greater error in the modeling of that molecule. The acentric factor for H_2S is 0.095 and the acentric factor for CO_2 is 0.225. The increased non-ideality of CO_2 is a reason for the poorer vapor-liquid equilibrium prediction of the CO_2 -H₂O system.

The modeling results obtained as part of this work have to be studied in the light of certain limitations. Errors in calculating phase equilibria are larger than expected for non-reacting systems for the following reasons (Gerdes et al., 1989):

- Numerous and simultaneous chemical reactions.
- Enhanced non-ideality of the systems due to the electrostatic effects of ions
- Phase and chemical equilibria in a highly polar liquid phase
- Phase and chemical equilibria involving mixtures of non-polar compounds (e.g., CO₂) with highly polar compounds (e.g., H₂O), and
- Difficulty in measuring vapor-liquid equilibrium data.

The problems mentioned above combine to produce larger errors in the measured data for reacting systems vis-a-vis non-reacting systems and increase the chance of errors arising due to the mismatching of the various effects on the modeling process. Unfortunately,

information is not available to quantify the errors in the experimental database used in this study.

The agreement between the various experimental studies is generally poor. For the CO_2 -H₂O binary the data of Takenouchi and Kennedy (1964) are in good agreement with the results of Malinin (1959) but depart sharply from the results of Todheide (1963). For the H₂S-H₂O binary the data of Lee and Mather (1977) are in fairly good agreement with the data of Selleck et al. (1952) at 159.8 ^oF, but at higher temperatures there is a deviation of up to 10 %. This necessitated a statistical analysis of all the data points classified by reference for both the binaries (CO₂-H₂O and H₂S-H₂O) studied as part of this work.

Another area of disagreement is the time required for the attainment of equilibrium between the mixture components. Ellis and Golding (1963) concluded that at least 24 hours were required before equilibrium between H₂O and CO₂ was reached. Malinin (1959) does not report the time required for the attainment of equilibrium in his experiments. Todehide (1963) reported that only 1 hour was required for the attainment of equilibrium. Experimental investigation by Takenouchi and Kennedy (1964) showed that equilibrium was attained in over 3 days at a temperature of 392 ⁰F, and more than 1 week was required at a temperature of 230 ⁰F. All the data for the time required for the attainment of equilibrium detailed above is for the CO₂-H₂O binary. Time required for the attainment of the attainment of equilibrium has not been reported for the H₂S-H₂O binary.

The inherent limitations of the Soave-Redlich-Kwong (SRK) equation of State (Soave, 1972) used in this work introduces a certain degree of error to the modeling results. The SRK equation of state has been used in DREAM for corrosion prediction

because of its excellent predictive capabilities for the phase equilibrium of hydrocarbons. However SRK does not perform well for non-hydrocarbons, especially polar and associative systems (Sandler et al., 1994) like the two binaries (CO₂-H₂O and H₂S-H₂O) of interest in this work. These factors contribute to the deviations obtained in the bubble point pressure predictions.

When model predictions are compared to experimental data, the difference between the prediction and the measurement is examined. The best model would have a lower average relative error, compared to experimental data, than any other model. The above criterion clearly indicates that the performance of the model of Chen et al. (1994) is superior to that of the model of Liu and High (1993). Based on the results obtained it was decided to implement the model of Chen et al. (1994) in DREAM for purposes of phase and electrolyte equilibrium calculations.

4.4 Effect of the Phase and Electrolyte Equilibrium Module on Corrosion Rate Prediction

The model of Chen et al. (1994) has been incorporated in DREAM for phase and aqueous electrolyte equilibrium calculations. The ultimate purpose of DREAM is to predict the corrosion rates in gas wells. The impact of the model of Chen et al. (1994) on the corrosion rate calculations was evaluated. The effect of the old model (Liu and High, 1993) was also evaluated and the results obtained in both these cases were compared with field data. Sixteen test cases were examined to measure the impact of the changed phase equilibria calculation scheme on the corrosion rate calculations. The input data for these sixteen gas wells is given in Tables VII to IX. The conditions prevailing in these wells cover a wide range of temperature, pressure, and concentration.

The corrosion profile for the sixteen test cases is presented in Figures 9 to 24 and can be classified into the following three categories:

1. wells with high or moderately high uniform corrosion,

- 2. wells with low uniform corrosion, and
- 3. wells with pitting corrosion.

Cases I, VII, VIII, IX, X, and XII represent wells with high uniform corrosion. In Case I (Figure 9), the model of Chen et al. (1994) better predicted the corrosion rate than the model of Liu and High (1993) from the wellhead to a depth of 2000 foot and from 6500 foot to the bottomhole. Both the models predicted the same corrosion rates indicating that high corrosion was possible. The caliper survey data indicated that high uniform corrosion occurred in Case I. The model predicted the absence of a protective film, indicating that high corrosion was possible.

In Case VII (Figure 15), the model of Chen at al. (1994) and the model of Liu and High (1993) perform poorly vis-a-vis the corrosion rate indicated by the caliper survey data. The gas well in Case VII contained 2.22 % CO₂ indicating that a high corrosion rate was possible. However the corrosion rate indicated by the caliper survey was much lower than that predicted by the model. between 2000 foot and 3000 foot.

TABLE VII

Well Geometry and Production Data

Case	ID (°)	Depth	Water	Gas	Oil	Wellhead	Bottomhole	Wellhead	Bottomhole
	(in.)	(ff.)	Production	Production	Production	1 emperature	Temperature	Pressure	Pressure
			(bbi/day)	(MSCFD)	(bbi/day)	(F)	(F)	(psia)	(psia)
I	2.441	9700	28	2150	23	130	290	1890	4000
II	2.441	9450	27	1352	8	130	290	1440	4000
III	2.441	9620	124	2800	146	130	290	1270	4000
IV	2.441	11080	20	4000	20	100	230	415	1015
V	2.441	9130	5	4200	32	130	290	1440	4000
VI	1.995	9220	40	3400	92	130	290	1200	2300
VII	2.992	10506	10	3300	62	130	290	1200	2510
VIII	1.995	9540	5	3320	34	130	290	1200	2225
IX	1.995	10350	10	3500	10	130	290	2900	4000
X	2.441	11175	8	440	1	78	190	275	450
XI	2.441	11246	3	413	0	81	200	4700	1600
XII	2.441	10883	10	905	0	95	355	250	800
XIII	1.995	9350	1	150	1	130	290	1180	4000
XIV	1.995	9337	53	528	13	130	290	1560	4000
XV	1.995	9910	7	4600	89	130	290	1200	7000
XVI	1.995	9527	11	3420	58	130	290	2570	4000

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TABLE VIII

Gas Analysis (mole %)

	CH ₄	C_2H_6	C_3H_8	I-C ₄ H ₁₀	N-C4H10	$I-C_5H_{12}$	N-C5H12	C ₆ H ₁₄	C ₇ +	N ₂	CO ₂	H ₂ S
Case I	90.94	4.37	1.14	0.27	0.23	0.13	0.08	0.11	0.27	0.25	2.21	0.00
Case II	91.60	4.39	1.18	0.33	0.25	0.14	0.09	0.13	0.33	0.30	1.26	0.00
Case III	90.10	6.00	1.68	0.45	0.34	0.20	0.12	0.18	0.40	0.22	0.31	0.00
Case IV	95.10	1.92	0.49	0.12	0.11	0.05	0.03	0.11	0.15	0.08	1.84	0.00
Case V	90.17	5.49	1.70	0.54	0.41	0.22	0.15	0.24	0.59	0.23	0.26	0.00
Case VI	88.31	6.90	2.21	0.66	0.50	0.26	0.17	0.23	0.52	0.12	0.12	0.00
Case VII	88.68	5.69	1.69	0.44	0.37	0.20	0.12	0.16	0.28	0.15	2.22	0.00
Case VIII	90.44	5.07	1.36	0.32	0.27	0.15	0.09	0.14	0.32	0.12	1.72	0.00
Case IX	93.55	2.50	0.47	0.10	0.06	0.06	0.04	0.07	0.58	0.10	2.45	0.00
Case X	84.60	7.88	2.64	0.65	0.32	0.32	0.18	0.00	0.17	0.60	2.40	0.00
Case XI	92.04	3.72	0.60	0.14	0.00	0.00	0.00	0.00	0.06	0.09	3.34	0.00
Case XII	92.75	3.24	0.42	0.08	0.00	0.00	0.00	0.00	0.05	0.07	3.40	0.00
Case XIII	89.03	6.74	1.98	0.54	0.40	0.17	0.12	0.12	0.22	0.28	0.40	0.00
Case XIV	88.79	6.73	2.14	0.64	0.48	0.24	0.16	0.20	0.34	0.24	0.04	0.00
Case XV	88.68	5.5	1.65	0.42	0.36	0.20	0.12	0.16	0.37	0.13	2.14	0.00
Case XVI	89.42	6.00	1.84	0.50	0.40	0.22	0.14	0.20	0.40	0.23	0.65	0.00

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TABLE IX

Water Analysis (ppm)

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	Na^+	Ca ²⁺	Mg ²⁺	Ba ²⁺	Sr ²⁺	K ⁺	Fe ²⁺	Cl	SO4 ²⁻	CO32-	HCO ₃ ⁻
Case I	6490	298	38	4	0	0	36	10100	111	0	879
Case II	6280	454	50	2	0	0	0	10300	196	0	313
Case III	127	21	0	3	0	0	0	195	0	0	60
Case IV	20104	326	166	6	0	0	3	30540	800	0	1648
Case V	35	7	1	1	0	0	12	15	0	0	90
Case VI	4580	197	1140	4	0	0	170	10300	32	0	696
Case VII	4740	200	17	1	0	0	74	7490	94	0	257
Case VIII	7110	371	21	20	0	0	0	11500	0	0	335
Case IX	4580	197	1140	4	0	0	0	10300	32	0	696
Case X	31000	7000	900	40	200	130	100	62000	280	0	260
Case XI	31000	7000	900	40	200	130	100	62000	280	0	260
Case XII	31000	7000	900	40	200	130	100	62000	280	0	260
Case XIII	4580	197	1140	4	0	0	170	10300	32	0	696
Case XIV	4580	197	1140	4	0	0	170	10300	32	0	696
Case XV	7830	319	14	13	0	0	1380	12600	0	0	146
Case XVI	5850	564	33	1	0	0	40	9800	218	0	263

 $[2\pi]_{i,j}$

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VALABLES V

Figure 9. Corrosion Rate Profile along Well Depth: CASE I



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Figure 10. Corrosion Rate Profile along Well Depth: CASE II



Figure 11. Corrosion Rate Profile along Well Depth: CASE III



Figure 12. Corrosion Rate Profile along Well Depth: CASE IV



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Figure 13. Corrosion Rate Profile along Well Depth: CASE V



Figure 14. Corrosion Rate Profile along Well Depth: CASE VI



Figure 15. Corrosion Rate Profile along Well Depth: CASE VII



Figure 16. Corrosion Rate Profile along Well Depth: CASE VIII



Figure 17. Corrosion Rate Profile along Well Depth: CASE IX



Figure 18. Corrosion Rate Profile along Well Depth: CASE X



Figure 19. Corrosion Rate Profile along Well Depth: CASE XI



Figure 20. Corrosion Rate Profile along Well Depth: CASE XII



Figure 21. Corrosion Rate Profile along Well Depth: CASE XIII



Figure 22. Corrosion Rate Profile along Well Depth: CASE XIV



Figure 23. Corrosion Rate Profile along Well Depth: CASE XV



Figure 24 Corrosion Profile Along Well Depth: CASE XVI

In Case VIII (Figure 16), the model of Chen et al. (1994) was closer to the caliper survey data from the well head to a depth of 3500 foot. Beyond 3500 foot, the model of Liu and High (1993) performed better. Below a depth of 6500 foot to the bootomhole, both the models predicted a zero corrosion rate and were in perfect agreement with the caliper caliper survey data.

In Case IX (Figure 17) there was a gross over prediction of corrosion rates. However, the model of Chen et al. (1994) was closer to the caliper survey data from the wellhead to a depth of 5500 foot. From 5500 foot to the bottomhole, the model of Liu and High (1993) was in better agreement with the caliper survey data. The model predicted the absence of protective films substantiating the high corrosion rates indicated by the caliper survey data.

In Case X (Figure 18) both the models under predicted the corrosion rates from the wellhead to a depth of 6000 foot. The gas and water production rates were very low for case X indicating that DREAM would predict a low corrosion rate. Beyond a depth of 6000 foot, both the models predicted a low corrosion rate and were in agreement with the caliper survey data.

Case XII (Figure 20) was a well with uniform corrosion from the wellhead to a depth of 4000 foot and zero corrosion from 4000 foot to the bottomhole. The model of Chen et al. (1994) performed better than the model of Liu and High (1993) in predicting uniform corrosion between 500 foot and 1500 foot and once again between 2500 foot and 4000 foot. Both the models under predicted the corrosion rates between 1500 foot and 2500 foot. The model of Chen et al. (1994) predicted very low corrosion beyond 6500

foot, while the model of Liu and High (1993) predicted a very low corrosion beyond 8000 foot.

Cases III, VI, XIII, and XIV represent wells with very low corrosion rates. The caliper data shows corrosion rates below the threshold of detection which is 7 Mils Per Year (MPY). The corrosion rate predicted by both the models were comparable for the wells with very low corrosion rates and were in excellent agreement with the caliper survey data. The corrosion rate predicted by the model was below 7 MPY for Cases III, VI, XIII, and XIV. The model also predicted the formation of a protective film throughout the well, indicating that the wells could be non-corrosive.

The corrosion product film may be removed from the sections of the tubular due to the action of flowing fluids, exposing the wall to corrosive species. The exposed segment of the pipe wall is then subjected to intense corrosion resulting in the formation of localized pits or grooves. This phenomenon is called pitting corrosion and is observed in Cases II, IV, V, XI, XV, and XVI. The caliper survey data represents such pits in Cases II, IV, V, XI, XV, and XVI. Segments of the pipe wall where there are no pits there is no corrosion. DREAM has the capability to predict uniform corrosion only.

In Case II (Figure 10) the model of Chen et al. (1994) predicted a very low corrosion rate below 1000 foot indicating that the uniform corrosion prediction agreed with the caliper survey data. The model of Liu and High (1993) predicted a low corrosion rate below a depth of 3500 foot.

In Case IV (Figure 12), the model of Chen et al. (1994) predicted corrosion rate below 7 MPY throughout the entire depth of the well. The model of Liu and High (1993) predicted a high corrosion rate (greater than 12 MPY) from the well head to a depth of 7500 foot and a low corrosion rate (less than 7 MPY) below 7500 foot. The model also predicted the formation of a protective film throughout the well.

In Case V (Figure 13) the uniform corrosion exhibited by the well was predicted equally well by both the models. Both the models predicted corrosion rates below 7 MPY. The model also predicted that a film was formed below 3850 foot.

The uniform corrosion rate predicted by both the models for Case XI (Figure 19) is high. Both the models over predicted the uniform corrosion rates from a wellhead to a depth of 8500 foot. From 8500 foot to the bottomhole, both the models predicted a very low corrosion rate.

In Case XV (Figure 23) the model of Chen et al. (1994) predicted a high corrosion rate from the wellhead to a depth of 3500 foot and a low corrosion rate (less than 7 MPY) below 3500 foot. Thus the model of Chen et al. (1994) was in consonance with the caliper survey data below a depth of 3500 foot for Case XV. However, the model of Liu and High (1993) was in agreement with the caliper survey data only after a depth of 6000 foot.

In Case XVI (Figure 24), both the models predicted a zero corrosion rate throughout the well and were accurate with regard to uniform corrosion prediction.

Corrosion rate was thought to be a very strong function of the phase and electrolyte equilibrium calculations. The results in Figures 9 to 24 indicated that the corrosion rate was not improved significantly due to an improvement in the phase and the electrolyte equilibrium calculations. The corrosion rate calculation depends on many

modules: phase and electrolyte equilibrium, pressure drop along the production string, mass transfer of the corrosive species to the pipe wall and the corrosion product film to the bulk liquid, and corrosion kinetics. The accuracy of the corrosion prediction depends on the accuracy of each of the modules used.

The phase and electrolyte equilibrium modeling carried out as part of this work incorporated hydrogen sulfide characterization in DREAM. No case studies of actual gas wells containing hydrogen sulfide are available. In order to demonstrate the capability of DREAM to predict phase equilibrium with hydrogen sulfide. Well number 1 was used as an "experimental well". In this well, the composition of hydrogen sulfide was given four values: 0.0 %, 0.1 %, 1.0 %, and 10.0 %; and the gas composition was normalized. All other well operating conditions remained the same as given in Tables VII, VIII, and IX. The pH profile for all these four cases is shown in Figure 25. With an increase in the amount of the hydrogen sulfide, the pH increases till the concentration of H_2S reaches a value of 0.1 % and then decreases. This is due to the fact that dissociation of H_2S is suppressed at concentrations above 0.4 %.

The present work formulated a generalized framework for the coupled phase and electrolyte equilibrium calculations in gas wells and has also verified the accuracy of the generalized model. Even though the improvement in the phase and electrolyte equilibrium computations have not dramatically affected the corrosion rates, this work has succeeded in getting one step closer to the accurate estimation of corrosion rates in gas wells.



Figure 25. pH Profile along Well Depth: Hydrogen Sulfide Induced Corrosion

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be made on the basis of this study:

- The model of Chen et al. (1994) performs better than the model of Liu and High (1993) for the entire range of temperature and pressure tested. Therefore the model of Chen et al. (1994) has been incorporated into DREAM for purposes of corrosion prediction.
- DREAM now has the phase and electrolyte equilibrium calculation necessary to predict corrosion induced by hydrogen sulfide.
- The corrosion rate predictions are not affected significantly due to the new phase and electrolyte equilibrium model.

5.2 Recommendations

The present work can be carried on in the following directions:

1. The corrosion prediction in DREAM does not take into account the dissolution of the iron at the pipe wall. Hence the corrosion product film is assumed to be formed only if

there is sufficient iron (Fe^{2+} ions) in the input water analysis. Iron dissolution is an anodic reaction and can be represented as

$$Fe \leftrightarrow Fe^{2+} + 2e^{-}$$
 (5.1)

The concentration of the iron that dissolves from the tubular can be calculated from the equilibrium potential for the electrode reaction represented by Equation (5.1). The anodic dissolution reaction (Equation 5.1) and the equilibrium potential for the reaction are discussed by Bard and Faulkner (1980).

- 2. In this work precipitation of the corrosion product layer is assumed to be a sufficient condition for film formation. However the precipitation of a corrosion product layer in itself does not necessarily result in the formation of a protective film (de Waard et al., 1991). Johnson and Tomson (1991) concluded that iron carbonate film formation was a slow temperature dependent process and occurred when the supersaturation was 1.3 times the thermodynamic solubility. The accuracy of corrosion rate predictions, in the presence of protective films, needs to be improved by incorporating a suitable model for the product film supersaturation.
- 3. Evaluation of DREAM for the prediction of hydrogen sulfide induced corrosion has not been possible. This work has included hydrogen sulfide characterization in the phase and electrolyte equilibrium module of DREAM. However no case studies of gas wells containing hydrogen sulfide are available. Acquiring field data of gas wells containing hydrogen sulfide would help benchmark DREAM for corrosion rate prediction due to the presence of H₂S.

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APPENDIX A

ERRORS RECTIFIED IN THE PHASE AND ELECTROLYTE EQUILIBRIUM CALCULATION IN DREAM 3.0

Calculational errors were identified and rectified in the phase and electrolyte equilibrium calculation module and the corrosion kinetics module of DREAM 3.0. These errors are listed below.

The principal error in the vapor-liquid equilibrium section of the software occurred in the calculation of the fugacity coefficient. The fugacity coefficient was being calculated as an exponential function, and is given below.

$$\phi = \operatorname{Exp} \left\{ \frac{b_i}{b} (Z-1) - \ln (Z-B^*) - \frac{A^*}{B^*} \left[\frac{2 (a\alpha)_i}{(a\alpha)_{ij}} - \frac{b_i}{b} \right] \ln (1 + \frac{B^*}{Z}) \right\}$$
(A-1)

The program gave an error for large values of the exponential function. In order to avoid this error, the computation scheme was changed so that the program calculated the natural logarithm of the fugacity coefficient. The formula used for computation is shown below:

$$\ln \phi = \left\{ \frac{b_i}{b} (Z-1) - \ln (Z-B^*) - \frac{A^*}{B^*} \left[\frac{2 (a\alpha)_i}{(a\alpha)_{ij}} - \frac{b_i}{b} \right] \ln (1 + \frac{B^*}{Z}) \right\}$$
(A-2)

The terms used in Equation (A-1) and Equation (A-2) are defined in Chapter II of this work.

The fugacity coefficients are used to calculate the vapor/liquid equilibrium constants ($K_{i, VLE}$). The vapor-liquid equilibrium constant ($K_{i, VLE}$) values are defined as

$$K_{i, VLE} = \frac{\phi_i^{L}}{\phi_i^{V}}$$
(A-3)

The change in the computation of the fugacity coefficient is reflected in the computation of the vapor/liquid equilibrium constant as:

$$\mathbf{K}_{i, \text{ VLE}} = \operatorname{Exp}\left[\ln\left(\phi_{i}^{L}\right) - \ln\left(\phi_{i}^{V}\right)\right]$$
(A-4)

The electrolyte equilibrium section of DREAM had not been properly documented in any of the project reports. All data, tables, and equations have now been extensively documented as is reflected in Sundaram et al. (1996). The program has also been documented extensively to reflect these findings.

An error was detected in the calculation of the concentration of the various species at the interface of the diffusion layer and the corrosion product layer. In the calculation of the source term in the nonlinear differential equation used to solve for the interfacial concentration, the second derivative of the concentration gradient $(\frac{dC_j}{dX})$ was used instead of the first derivative. The equation for the source term is given below.

$$S_{c} = -z_{i} \begin{pmatrix} \frac{dC_{i}}{dX} \frac{\sum z_{j}D_{j} \frac{dC_{j}}{dX}}{\sum z_{j}^{2}D_{j}C_{j}} \\ +C_{i} \begin{pmatrix} \frac{(\sum z_{j}D_{j} \frac{dC_{j}}{dX})(\sum z_{j}^{2}D_{j}C_{j}) - (\sum z_{j}D_{j} \frac{dC_{j}}{dX})(\sum z_{j}^{2}D_{j} \frac{dC_{j}}{dX})}{(\sum z_{j}^{2}D_{j}C_{j})^{2}} \end{pmatrix}$$
(A-5)

This error in the corrosion kinetics section has been rectified.

APPENDIX B

EXAMPLE CALCULATION FOR PHASE AND ELECTROLYTE EQUILIBRIUM COMPUTATIONS

A generalized framework for phase and electrolyte equilibrium calculation in gas wells was developed as part of this work. The phase and electrolyte equilibrium model has been coded in FORTRAN. In order to verify the accuracy of the computer code, manual computations were performed for a hypothetical gas well and the results obtained were compared with the values calculated by the computer code. The input well data are summarized in Table X, and Table XI.

The following are the major steps in the computation:

B-1. Use of the input water analysis in corrosion prediction

The water analysis input data gives the concentration of the various ions in the produced water in ppm (parts per million). The concentration of the produced water is converted to molality using the formula given below (Garrels and Christ, 1965):

Concentration in molality =
$$\frac{\text{Concentration in ppm}}{\text{Weight of the ion}} \times 10^{-3}$$
 (B-1)

Table XII gives the weight of the ion and the converted values of the concentrations for the ionic species present in the produced water.

TABLE X

Well Geometry and Production Data for the Hypothetical Well

ID, in.	2.441	
Well Depth, ft.	9450	
Water Production, bbl/day	27	
Gas Production, MSCFD	1352	
Wellhead Temperature, °F	130	
Bottomhole Temperature, °F	290	
Wellhead Pressure, psia	1440	
Bottomhole Pressure, psia	4000	

TABLE XI

Gas Analysis for the Hypothetical Well

Component	Composition (Mole %)
Methane	90.60
Ethane	4.39
Propane	1.18
I-Butane	0.33
N-Butane	0.25
I-Pentane	0.14
N-Pentane	0.09
Hexane	0.13
Heptane Plus	0.33
Nitrogen	0.30
Carbon dioxide	1.26
Hydrogen Sulfide	1.00

TABLE XII

Ionic Species	Concentration (ppm)	Weight (gm)	Charge	Concentration (mol/kg)
Sodium	6280	22.99	+1	2.731622 10-1
Calcium	454	40.08	+2	1.132734 10-2
Magnesium	50	24.31	+2	2.056767 10-3
Barium	2	137.30	+2	1.45664 10-5
Strontium	0	87.62	+2	0
Potassium	0	39.10	+1	0
Iron	0	55.85	+2	0
Chloride	10300	35.45	-1	2.9055 10-1
Sulfate	196	96.06	-2	2.040391 10 ⁻³
Carbonate	0	60.01	-2	0
Bicarbonate	313	61.02	-1	5.13 10 ⁻³
				$\sum z_i m_i = 0.004279546$

Water Analysis for the Hypothetical Well

A calculation shows that the input water is not electroneutral. The electroneutrality of the produced water is adjusted by adjusting the concentration of the sodium ion. For this sample case electroneutrality is satisfied if the sodium ion concentration is adjusted to 0.268882754 mol/kg. The ionic strength is defined by Equation (3.48). The calculated value of ionic strength is 0.315213. The computer code calculates a value of 0.3151994 for the ionic strength.

The molar strength is defined by Equation (3.59). The calculated value for the molar strength is 1.29974. The computer code calculates a value of 1.29976 for the molar strength.

B-2. Calculation of Henry's Constants

The Henry's constant for CO_2 is defined by Equation (3.57). In the downhole environment the value of the Henry's constant for CO_2 ($H_{m, CO2}$) is calculated to be 44.9347, while the code computes a value of 44.9261. In a solution containing CO_2 and water (unit concentration) the Henry's constant for CO_2 (H_{CO2}) is calculated to be 41.92568, while the code calculates a value of 41.90466.

The Henry's constant for H_2S is defined by Equation (3.58). In the downhole environment the value of the Henry's constant for H_2S ($H_{m, H2S}$) is calculated to be 7.162735 while the code computes a value of 7.162951. In a solution containing CO₂ and water (unit concentration) the Henry's constant for H_2S (H_{H2S}) is calculated to be 8.2567915 while the code calculates a value of 8.256908.

B-3. Equilibrium Constants

Equilibrium constants are correlated as functions of temperature. Equation (3.43) defines the equilibrium constants and the parameters required for the computation of the equilibrium constants are given in Table II. The solubility products of the CaCO₃, FeCO₃, and FeS are calculated by Equations (3.44 to 3.46). The values of the equilibrium constants and solubility products calculated manually and the values obtained from the code are given in Table XIII.

B-4. Activity Coefficients

The activity coefficients of the ionic species are calculated using Equation (3.47). The calculated value for the density of water (ρ_W) is 0.9999998 g/cc at 327.5945 K. The code calculates a value of 0.9929709 for the density of water at the same temperature. The calculated value of the dielectric constant of water (ϵ_W) is 149.774787 while the code computes a value of 149.7753.

The molal Debye-Huckel parameters are calculated from Equation (3.53) and Equation (3.54). The calculated values are:

A = 0.5433124, and B = 0.335707.

The values computed by the code are given below:

A = 0.539301, and B = 0.3334095.

TABLE XIII

Comparison of the Values of Equilibrium Constants and Solubility Products Calculated Manually and from the Code

Temperature = 327.5945 K

	Equilibrium Constant or Solubility Product		
Species	Value Obtained from the Code	Value Obtained by manual calculation	
H ₂ O	6.751912 10 ⁻¹⁴	6.9612 10 ⁻¹⁴	
CO ₂	5.246101 10-7	5.24 10-7	
HCO ₃ ⁻	6.984997 10 ⁻¹¹	6.98496 10 ⁻¹¹	
H ₂ S	2.09692 10-7	2.1 10-7	
HS	7.944665 10 ⁻¹⁶	7.944678 10 ⁻¹⁶	
CaCO ₃	1.977257 10 ⁻⁹	1.0 10-9	
FeCO ₃	6.145987 10 ⁻¹²	6.14597 10 ⁻¹²	
FeS	4.77835 10 ⁻¹⁹	4.77255 10 ⁻¹⁹	

The values for the activity coefficients of the molecular species are computed from Equations (3.55, 3.56) and Equation (3.60). The values of the activity coefficients calculated manually and the values obtained from the code are given in Table XIV.

B-5. pH Calculation

The calculation of the concentration at the gas-liquid interface is initialized by neglecting all second dissociations and performing a charge balance. The charge balance is solved to obtain the concentration of the hydrogen ion. The concentration of the hydrogen ion, the equilibrium constants, and the activity coefficients are used to calculate the concentrations of all other molecular and ionic species. The approximate values calculated in this section are used to compute the coefficients of Equation (3.30). Equation (3.30) is solved to obtain the actual pH. From the pH the final concentrations of all other species are once again calculated. This completes the electrolyte equilibrium calculation.

The values of the coefficients of the fourth order equation (Equation 3.30) obtained by manual calculations and that obtained from the code are given in Table XV. Equation (3.30) is solved by the bisection method to obtain the single positive root. The molality of the hydrogen ion is calculated by the computer code to be 2.790563 10^{-4} mol/kg solvent. Equation (3.30) is also solved graphically to confirm the roots obtained from the computer code. The graph of Equation (3.30) for the hypothetical well case is shown in Figure 27. The value of the hydrogen ion concentration obtained graphically is

TABLE XIV

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Comparison of the Values of Activity Coefficients Calculated Manually and from the Code

Temperature = 327.5945 K

	Activity Coefficients		
Species	Value Obtained from	Value Obtained by	
-	the Code	manual calculation	
Sodium	0.692587	0.696712	
Calcium	0.277423	0.278231	
Magnesium	0.3378170	0.339314	
Barium	0.2443524	0.24487	
Strontium	0.2443524	0.24487	
Potassium	0.6602674	0.66411	
Iron	0.277423	0.27830	
Chloride	0.6602674	0.66411	
Sulfate	0.2094366	0.20967	
Carbonate	0.2271096	0.22759	
Bicarbonate	0.7067569	0.710873	
Hydrogen	0.7958558	0.801147	
Hydroxide	0.6771485	0.680873	
Bisulfide	0.6771485	0.680873	
Sulfide	0.2443524	0.2448702	
Carbon dioxide	1.072103	1.07172	
Hydrogen sulfide	0.86751	0.867523	
Water	0.9900706	0.99071	

TABLE XV

Comparison of the Values of the Coefficients of Equation (3.30) Calculated Manually and from the Code

Temperature =	= 327.5945 K
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Value Calculated from the Code	Value Calculated Manually
0.0	0.0
1.0	1.0
-7.771909 10-8	-7.58 10 ⁻⁸
-1.201982 10 ⁻¹⁷	-1.182378 10-17
	Value Calculated from the Code 0.0 1.0 -7.771909 10 ⁻⁸ -1.201982 10 ⁻¹⁷



Figure 26. Graphical Solution for the Concentration of the Hydrogen Ion

2.7833 10⁻⁴ mol/kg solvent and is very close to that obtained by manual calculation. The values of the concentrations of the ionic and molecular species obtained at the gas liquid interface are given in Table XVI.

From the values for the concentrations calculated at the gas-liquid interface a check was made to insure if all the equations used in the electrolyte equilibrium calculation are satisfied. The equations that are used to build up the model developed in this study are discussed in Chapter III. The 9 equations used in the electrolyte equilibrium module are Equation (3.19) and Equations (3.22 to 3.29). The values for the concentrations calculated by the FORTRAN code (as listed in Table XVI) were plugged into Equation (3.19), and Equations (3.22 to 3.29). All of these equations were satisfied.

B-6. Check for the Convergence of Phase Compressibilities

The phase compressibilities are calculated as detailed in Chapter II of this study. In the test case considered the compressibility of the vapor phase was calculated by the computer code to be 0.9537878. Two quantities, A^* and B^* , are used in the calculation of the phase compressibility. The values of A^* and B^* , as computed by the computer code are 0.1551972 and 0.061758 respectively. Using the above values of A^* and B^* , Equation (2.15) reduces to:

$$f(Z) = Z^3 - Z^2 + 0.058524536 Z - 0.013779827 = 0.0$$
(B-1)

The phase compressibility calculated by the computer code (Z = 0.9537878) was plugged into Equation (B-1) and was found to satisfy the equation. Further a graph was

TABLE XVI

Comparison of the Values of Concentrations Calculated Manually and from the Code

Temperature = 327.5945 K

	Concentrations (mol/kg)		
Species	Value Obtained from the	Value Obtained by manual	
	Code	calculation	
Sodium	2.68828 10 ⁻¹	2.68828 10-1	
Calcium	1.132734 10-2	1.132734 10 ⁻²	
Magnesium	2.056767 10 ⁻³	2.056767 10 ⁻³	
Barium	1.456664 10 ⁻⁵	1.456664 10 ⁻⁵	
Strontium	0.0	0.0	
Potassium	0.0	0.0	
Iron	0.0	0.0	
Chloride	2.905501 10 ⁻¹	2.9055 10 ⁻¹	
Sulfate	2.040392 10 ⁻³	2.040391 10 ⁻³	
Carbonate	7.77127 10 ⁻¹¹	7.8716 10 ⁻¹¹	
Bicarbonate	7.93994 10 ⁻⁵	7.882 10 ⁻⁵	
Hydrogen	2.790563 10 ⁻⁴	2.7833 10-4	
Hydroxide	4.476120 10 ⁻¹⁰	4.5864 10 ⁻¹⁰	
Bisulfide	1.996569 10 ⁻⁶	2.017 10-6	
Sulfide	1.979252 10 ⁻¹⁹	1.87572 10 ⁻¹⁹	
Carbon dioxide	2.22257 10-2	2.2223102 10-2	
Hydrogen sulfide	1.650586 10 ⁻¹	1.65068 10 ⁻¹	
Water	1.006976 10 ⁰	$1.00782 \ 10^{0}$	

plotted to study the behavior of the phase compressibility. The graph is shown in Figure 28. The graph of Equation (B-1) has 1 positive root and the value of that root is 0.95.

B-7. Check for the Convergence of the Overall Calculation Scheme

The overall computation of this model is complete only after the phase equilibrium calculation (flash calculation) has converged. The tying of the electrolyte equilibrium calculation with the flash calculation altered the compositions of the flash calculation since the liquid phase dissociations are now taken into account.

The two-phase flash calculations are supposed to converge when the following the three conditions are met:

$$\sum \mathbf{x}_i = 1.0 \tag{B-2}$$

$$\sum \mathbf{y}_i = 1.0 \tag{B-3}$$

$$0 < L/F < 1$$
 (B-4)

where F is the fraction of the feed that is in the liquid state.

For the test case studied the values the liquid phase mole-fraction (x_i) , and the vapor-phase mole-fraction (y_i) have been listed in Table XVII. Both the liquid and the vapor phase mole-fractions add to 1 within the prescribed limits of convergence. The value of L/F is found to be 0.121.



Figure 27. Graphical Solution for the Phase Compressibility



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VITA

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Master of Science

Thesis: PHASE AND ELECTROLYTE EQUILIBRIUM MODELING IN DOWNHOLE ENVIRONMENTS

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TABLE XVII

Final Values Calculated by the Program for the Liquid and the Vapor Phase Mole Fractions

Liquid Phase Mole	Vapor Phase Mole
Fraction	Fraction
1.326051 10 ⁻³	9.041718 10-1
4.293034 10-5	4.381438 10-2
6.867013 10-6	1.177763 10-2
1.346531 10-6	3.293825 10-3
1.052835 10-6	2.495317 10 ⁻³
4.727539 10-7	1.397394 10 ⁻³
2.679693 10 ⁻⁷	8.983295 10-4
3.874879 10-7	1.297587 10 ⁻³
4.832478 10-7	3.293943 10 ⁻³
3.096748 10-7	2.99451 10 ⁻³
4.233842 10-5	1.257127 10 ⁻²
9.92655 10-5	9.96812 10-3
9.9854783 10-1	2.026003 10 ⁻³
$\sum \mathbf{x}_i = 1.000000073$	$\sum y_i = 0.9999996988$
	Liquid Phase Mole Fraction 1.326051 10^{-3} 4.293034 10^{-5} 6.867013 10^{-6} 1.346531 10^{-6} 1.052835 10^{-6} 4.727539 10^{-7} 2.679693 10^{-7} 3.874879 10^{-7} 4.832478 10^{-7} 4.233842 10^{-5} 9.92655 10^{-5} 9.9854783 10^{-1} $\Sigma x_i = 1.00000073$