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Development and Testing of an Electrochemical Model for PWR Steam Generator Crevice Environments

Technical Report

Development and Testing of an Electrochemical Model for PWR Steam Generator Crevice Environments

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REPORT SUMMARY

The crevice formed by the tube/tube support plate (tube/TSP) intersection in a pressurized water reactor (PWR) steam generator is a concentration site for nonvolatile impurities from steam generator water. Researchers developed an electrochemical model to study the steam generator crevice environment, and the model was benchmarked with data from several laboratory and in situ plant studies.

Background

Concentrated solutions that form in crevices over time contribute to several forms of steam generator tube corrosion, including intergranular attack/stress corrosion cracking (IGA/SCC), pitting, and wastage. It is extremely difficult to measure impurity concentrations within actual steam generator crevices, so data from heated crevice autoclaves were used to benchmark a model relating bulk water to crevice chemistry.

Objective

To develop an electrochemical, convection-diffusion model for studying steam generator crevice environments based on the application of mass, momentum, energy conservation and charge transfer laws in porous media and pore solutions.

Approach

The model described in this report is based on four previously developed chemical, electrochemical, and thermal hydraulic models by Dombrovski, Chun, Millett, and MacDonald. Water is continually evaporated from steam generator crevices as a result of nucleate boiling at steam generator tubes. Saturated water is drawn into the crevice to replace exiting steam, and this countercurrent flow of steam and water is driven by capillary pressure at the steam-liquid interface. Impurities migrate into the crevice by means of saturated water, and the system eventually becomes thermodynamically limited when the solution's boiling point reaches the primary water temperature. The model uses the laws of conservation of mass, momentum, energy, the momentum of chemical species, boiling point elevation, and capillary pressure. The system's chemical equilibrium is calculated by applying solubility limits to any dissolved species. The electrochemical model is solved using an electric circuit analogy and assumes that anodic and cathodic reactions occur in the crevice solution and on the wall of the tube or support plate.

Results

The model was benchmarked with data from three heated crevice autoclaves. In each case, model predictions and experimental data were in excellent agreement. The thermal hydraulic model predicts that highly permeable crevices will allow concentration of liquid and impurities in the middle of the crevice, where it will first become thermodynamically limited. In densely packed crevices, there will initially be a steam blanketed region in the center of the crevice. Impurities will concentrate at the interface between the liquid and the steam. As time passes, the concentrated solution diffuses into the steam-blanketed region towards the center of the crevice. The mass of impurities predicted in the crevice is a linear function of exposure (the product of time of exposition and bulk water impurity concentrations), regardless of whether the crevice is initially fully wetted or steam blanketed. The model predicts, as expected, that the ratio significantly influences crevice pH. The new electrochemical model was compared to MacDonald's model with good agreement. There is a very large diffusion current at the interface between the non-concentrated and the concentrated regions in the crevice, which determines the electrochemical potential behavior between the two regions.

EPRI Perspective

The model described in this report was integral to developing the new integrated exposure diagnostic parameter in Revision 5 of the Secondary Water Chemistry Guidelines. Along with data from the heated crevice autoclaves, the model has shown that it is possible to predict local crevice chemistry from bulk water chemistry by applying the laws of mass, momentum, energy, and charge conservation to porous media and pore solution.

Keywords

Secondary water chemistry
Crevice
Steam generator
Corrosion

ABSTRACT

A localized electrochemical model has been developed to study PWR steam generator crevice environments. The model accounts for the accumulation of species in tube/tube support plate crevices. The model considers a two-phase countercurrent flow of water and steam within a porous deposit, driven by capillary forces. It is based on the application of mass, momentum and energy conservation and charge transfer laws in porous media and pore solutions. Convection and diffusion processes are taken into account.

Several homogeneous reactions (hydrolysis of the products of the anodic reaction, saturation reactions and the autoprotolysis of water) are considered as well as electrochemical reactions (metal dissolution, hydrogen evolution and oxygen reduction). Internal and external environments are coupled through charge conservation.

The model solves separately the thermal hydraulics, chemistry and electrochemistry. The model predicts the solution chemistry, potential distribution and corrosion rate inside the cavity as a function of time.

The model has been benchmarked against three sets of experimental data. It predicts that the mass of ionic species accumulated inside the crevice is a LINEAR function with the exposure, defined as the time of exposition times the bulk water concentration of the species. The crevice is initially steam-blanketed and slowly becomes wetted as the impurities migrate into the steam-blanketed region.

The model predictions were compared to a model developed by MacDonald. Agreement is found. Both models predict that the electrochemical potential in the crevice is independent of the external polarization.

The model is very versatile and can be applied to any bulk chemistry and any alloy system with any corrosion rate.

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INTRODUCTION

Over the past two decades, steam generator (SG) corrosion has been one of the major problems associated with operating pressurized water type nuclear reactors (PWR). The cost of steam generator corrosion alone to the US industry between 1984–1988 was approximately 1.8 billion dollars.[1] However, in the past ten years, plant operators have considerably limited the impact of corrosion on nuclear plant productivity. US plant capability factors reached an all time high of 82.6% in 1995 compared to 71.7% five years earlier.[2] The number of steam generator tubes repaired has steadily decreased between 1995 and 1998, as more degraded steam generators are replaced.[3] However, there is further room for productivity increases and cost savings.

Materials improvements and advances in water chemistry have played important roles in limiting the impact of SG corrosion. Most early steam generator tubing (prior to the late 1970s) was made from mill annealed alloy 600, which is susceptible to intergranular attack and stress corrosion cracking in both secondary and primary water chemistries. After the late 70s, much of the alloy 600 was thermally treated, which yielded improved performance. Many of the new and replacement steam generators contain thermally treated alloy 690 tubing. This tubing has approximately twice as much chromium (30% versus 50%). The percentage of tubes repaired by tube material is shown in Figure 1-1.[4]

The vast majority of steam generator tube repairs have been performed on mill annealed alloy 600 tubing. This does not mean that the newer steam generator tubing will not experience degradation problems but the performance of thermally treated alloy 600 and alloy 690 to date has been far superior to that of mill annealed alloy 600 tubing.[4]

Despite the recently improved performance, component degradation due to stress corrosion cracking and other corrosion processes continues to be a significant concern to the operators of pressurized water reactors and is potentially life limiting in many cases.

Steam generator replacement reached a record high in 1997 and 1998 and is expected to decrease over the next few years. Steam generators were replaced at Point Beach 2, Mihama 3, McGuire 1, Almaraz 2, Tricastin 2, Ohi 2, Salem 1, and McGuire 2 during 1997, and St. Lucie 1, Byron 1, Tihange 3, Braidwood 1, Kori 1, and Ikata 1 in 1998. As of the end of 1998, 11 utilities in the US, 7 in Europe and 2 in Japan have replaced a total of 150 steam generators at 51 nuclear units. The steam generators replaced in 1997-98 had an average of 12.6 effective full power years.

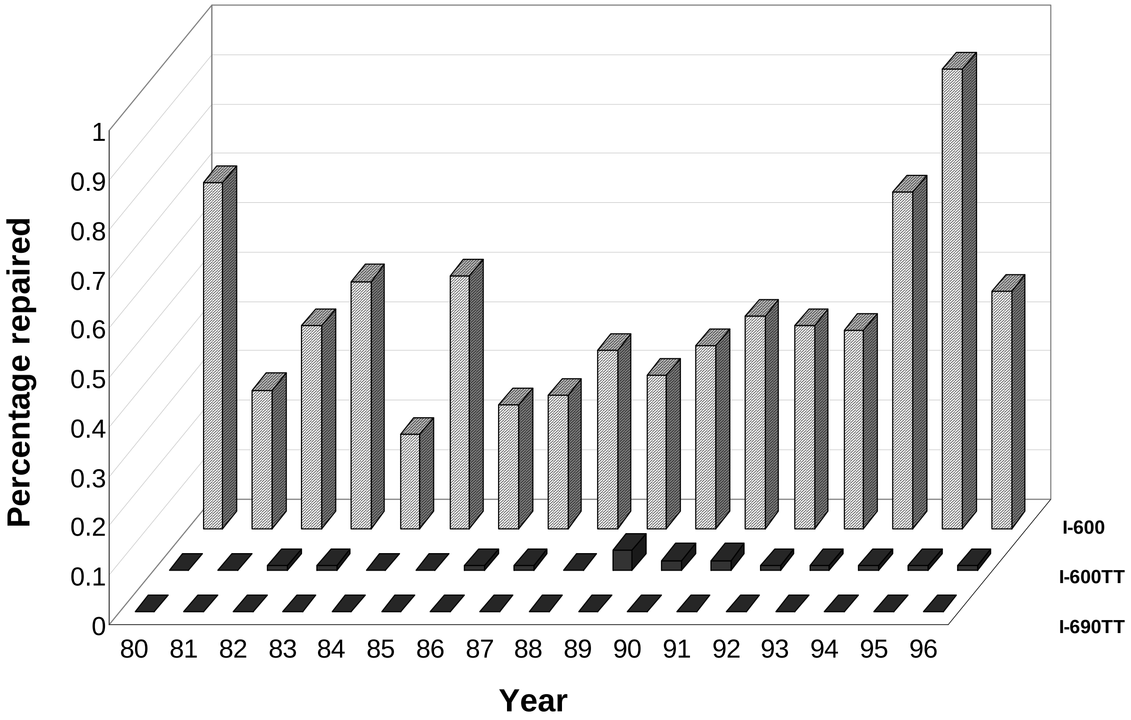


Figure 1-1
Percentage of tubes repaired by tube material

The impact to a utility of having to replace steam generators is substantial. The duration of generator replacements range between 18-365 days, with doses received by changeout personnel ranging between 60-2141 man rems, and replacement costs ranging from 37-230 million dollars, excluding replacement power costs. Replacement steam generators have been ordered for at least 20 additional plants. These orders indicate that steam generator replacement activity will continue during the next several years.

The latest report issued by EPRI tracking reported steam generators problems from 1975 to 1998 contains information on 230 operating plants and covers major steam generator issues and degradation mechanisms encountered.[3]

PWR steam generators are subject to a variety of degradation mechanisms. Corrective action for significantly degraded tubes includes removing the tube from service by plugging. Figure 1-2 shows the number of steam generator tubes plugged as a percentage of tubes in service on a worldwide basis.[3] During the last ten years, approximately 0.49% of the steam generator tubes in service have been plugged each year and this percentage remains relatively constant. The major causes of steam generator tube plugging have changed with time from wastage, then to denting, and finally to side stress corrosion cracking (SCC) and intergranular attack (IGA) today. SCC and IGA have been responsible for approximately 40% of the tubes plugged during the last ten years.[3]

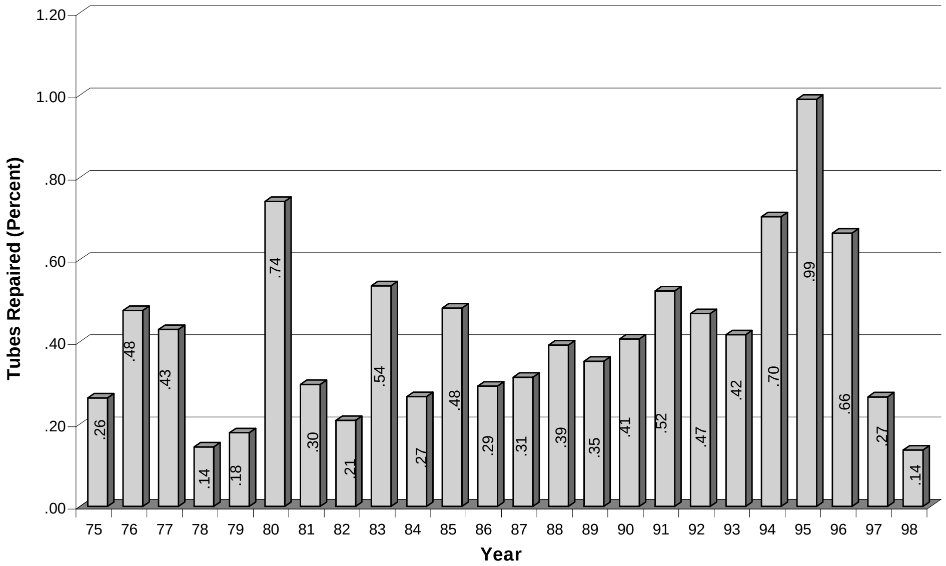


Figure 1-2
Percentage of steam generator tubes plugged worldwide

Although overall degradation in SGs has been decreasing, there are indications of increased local degradation at tube/tube support plate intersections.[4] As plants age, this phenomenon is aggravated. To better prevent this type of corrosion, a good understanding of corrosion processes in tube/tube support plate crevices is essential. SCC results from a combination of three factors: a sensitized material, the presence of tensile stress and an aggressive environment. Sensitization occurs when grain boundaries are depleted in carbides and chromium. The depleted chromium alloy in the grain boundaries is much less corrosion resistant than the surrounding grains. The grain boundary is aggressively corroded. The knowledge of the environment in the crevice as a function of the bulk chemistry and the operating parameters may enable advances in water chemistry in order to better control degradation processes.

In this thesis, we are concerned primarily with the characterization of the crevice environment and in particular the modeling of concentration and electrochemical processes which occur in the restricted geometries of crevices and cracks on the secondary side. These processes can promote the development of an environment that results in premature degradation. A schematic of the crevice and the locations of crevices in steam generators are given in Figure 1-3. Typical dimensions of a crevice are a 0.50 in (1.27 cm) diameter tube, 10 mils (0.025 cm) width and 1.0 in (2.54 cm) height.[1]

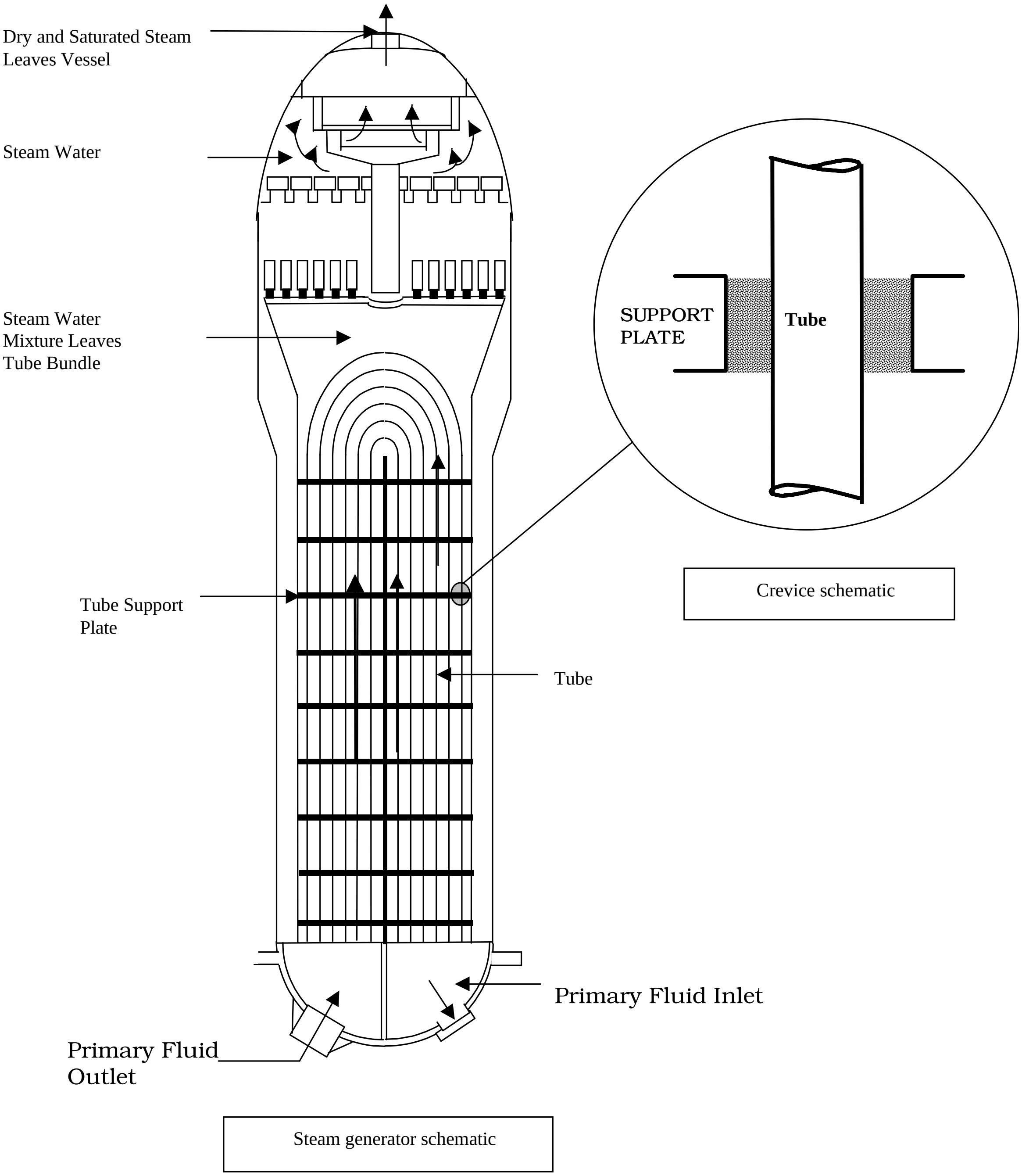


Figure 1-3
Locations and schematic of a crevice in a steam generator

Crevice chemistry is usually different from the chemistry of the bulk environment. In crevices, corrosion products and particulate matter accumulates in the form of porous deposits. Low levels of non-volatile impurities can be efficiently concentrated in the porous corrosion product deposits by a thermal hydraulic mechanism.[1] Pressurized water (16 MPa, 320°C) flows through the tubes of the steam generator. This water is contained in a closed loop consisting of a nuclear reactor and several SGs. Heat is transferred to the secondary fluid (saturated water/steam at 6 MPa and 280°C). The temperature gradient (40°C) across the SG tube coupled with restricted flow rate through the porous media produces boiling in the pore solution. The vapor formed exits the crevice leaving the impurities trapped in the liquid. More liquid containing impurities enters the crevice to replace the exiting steam by capillary forces. If the mechanism results in the production of a sufficiently aggressive environment, localized attack may occur. Prediction of cracking within crevices requires the knowledge of the local electrochemical conditions within the crevice (i.e. pH, electrode potential, concentration of dissolved ions, etc.).

The objective of this thesis is to develop an understanding of the interactions between the local environment and the bulk environment. A model that predicts local chemistry based on mass transport and electrochemical theory is presented in this thesis. It can be used for predicting the effect of operating parameters such as heat flux and feedwater chemistry. Although no experimental work is carried out in this thesis, the model is benchmarked against recent experimental results obtained by Lumsden and Takamatsu.[5]

2

LITERATURE REVIEW

Numerous models have been proposed for the prediction of localized chemistry in crevices in recent years, many of which have been developed specifically for nuclear power plant environments. In the following discussion attention is given to model derivation and solution techniques.

2.1 Dombrovski[6]

Dombrovski developed a transient crevice chemistry model. The crevice is not modeled as a porous media. The time dependent concentration and potential profiles within the cavity region can be analyzed. Transport modes included in the model are diffusion, electromigration, and convection induced by cyclic pumping of crack walls due to tube vibration. The model is versatile and can simulate many metal electrolyte systems. Many homogeneous, precipitation, and electrode reactions can be included.

The model employs Poisson’s equation to predict the electrode potential distribution. The mouth potential is assigned to either zero or the tube’s metal potential and is used as a reference point for potential calculations in the crevice.

In the model developed in this work, only the general modeling strategy is based on Dombrovski’s model. When chemical reactions are considered, both models assume that reactions occur instantaneously compared to the transport processes. The solution is always considered at chemical equilibrium. However, the new model solves the chemical equilibrium separately from the thermal hydraulic equations. This is unlike Dombrovski, who solves them together. In her model chemical reactions may generate or consume species in the electrolyte, therefore the rates of these equations are defined as source and sink terms in the continuity equations for the conservation of species. The rates in her model are arbitrarily specified providing they are much faster than the transport processes. Also, neither the specific transport equations nor the calculation of the electrochemical potential is derived from her work.

2.2 Chun[7]

Chun developed a model similar to Dombrovski. Chun’s model is a transient model taking into account chemical and electrochemical reactions and transport of chemical species through diffusion electromigration and convection in a non packed crevice. The convection was due to Eddy induced current. He included a crack growth model that includes tensile stress, crack tip strain and strain rate, crack tip stress, oxide film rupture rate and repassivation.

The main features of Chun's model are the use of an electric circuit analysis technique to construct an equivalent circuit model for localized corrosion processes and the method to calculate the distribution of potential within the crack. None of the mechanical modeling is really applicable to the model outlined in this thesis. However the approach to evaluate the potential is of interest, and is used in the new model. Chun did not employ the Laplace equation as Dombrovski did. He insisted that the Laplace equation can not be used to predict the potential gradient in the very steep concentration gradient region and instead derived an equation based on electroneutrality.

2.3 Millett[1]

Millett's model describes the thermal hydraulic transport processes occurring in porous deposits in the crevices of a steam generator. Important parameters affecting the transport processes in the pore solution include the heat flux and local characteristics such as: porosity, permeability, and the concentration of impurities in the feedwater. The model takes into account diffusion and convection but not electromigration. The main driving force for convection is capillary pressure. The pumping phenomenon utilized in Dombrovski's and Chun's research to predict velocity is not present in a porous media. If the boiling process is very efficient, the model predicts a wetted region quantified by a wetted length and a dryout zone. The model does not predict the concentration of the species in the dryout region. It is assumed that the chemical species remained in the liquid phase.

The model yields predictions for concentration factors, hydrodynamic velocity, temperature and wetted length as functions of time and operating parameters. However, the driving forces in this model are purely thermal and mechanical and no chemical or electrochemical effects are considered. The model was successfully benchmarked against multiple laboratory simulations of crevice concentration processes.[1,8]

The same approach will be used for the new model to describe the transport phenomenon in the packed crevice. The wetted length will be calculated with the same technique Millett developed. Some effort will be carried out to better evaluate certain parameters such as the boiling point elevation, capillary pressure, and heat transfer coefficient.

2.4 MacDonald[9]

MacDonald created a transient packed crevice model that combines some of the features of Millett's model and those of the Coupled Environmental Fracture Model (CEFM) which was written in collaboration with Urquidi-MacDonald to describe stress corrosion cracking.[11]

Diffusion and convection are taken from Millett's model and electromigration is added. Homogeneous chemical reactions and electrochemical reactions are included in the model. The model's outputs are the solution chemistry, potential distribution and corrosion rate within the cavity. The reference potential is the potential of the metal. It is determined using the mixed potential theory. Neither Laplace's equation nor Poisson's equation is used. Instead the electroneutrality equation is incorporated.

Since the rates of chemical reactions are not available, the method used is to combine the continuity equation for the conservation of species to cancel the sink and source terms. Considering the conservation of individual chemical elements, the source and sink terms can be related by an equation. This equation serves to eliminate the source and sink terms. To compensate for the missing equations in the system, MacDonald inserts chemical equilibrium relations for each reaction.

As a result, the final system of equations obtained contains simple linear equations such as electroneutrality, linear partial differential equations (PDEs) such as continuity equations for the conservation of species, and nonlinear PDEs such as chemical equilibrium. It is physically valid but numerically inhomogeneous. The system is solved by inverting the matrix containing the equations.

The convergence is rare outside the default values and therefore even when the model gives a result, one should be very careful to trust those values. Another disadvantage of combining the equations is that it is much harder to add or subtract a species if each equation is combined according to the conservation of a chemical element present in multiple chemical species. The wetted length in MacDonald’s model is predicted initially but is not recalculated as a function of time.

2.5 Literature Review Summary

The new model will be developed as an extension of the four previous models.

- The thermal hydraulic system is modeled after that of Millett. The main driving force is capillary pressure. The available superheat is used entirely to boil water. The steam formed exits the crevice deprived of impurities and the liquid water charged with impurities enters the crevice to replace the exiting steam. The wetted length will as well be calculated.
- The main equations for continuity were modeled after Dombrovski and Chun.
- The assumption that chemical reaction rates are much faster than mass transport processes (i.e. diffusion, electromigration and convection) used by Dombrovski is made. Instantaneous chemical equilibrium exists in the crevice.
- Electrochemical processes are modeled after Chun for potential gradient calculation, and as MacDonald for reference potential. Therefore, the crevice is assumed to be externally polarized and mixed potential theory evaluates the potential of the tube as the potential at the mouth of the crevice.

3

THEORETICAL APPROACH TO MODELING

The features required for the new model developed in this thesis are as follows:

- It is a transient model. The time dependent concentration and electrochemical potential profiles within the cavity region are predicted.
- Transport modes include convection induced by capillary forces and diffusion.
- Chemistry is calculated by solving chemical equilibrium
- Any number of species might be present. Any chemical or electrochemical reactions may be inserted.
- Solubility limits may be applied to any dissolved species.
- The electrochemistry is solved using an electric circuit analogy.
- Anodic and cathodic reactions occur in the crevice solution and on the wall of the tube or support plate.

The model is based on the application of energy, mass and momentum conservation laws to the porous media and pore solution.

The approach in this chapter is to describe the thermal hydraulic, chemical, and electrochemical modeling successively.

3.1 Thermal Hydraulic Modeling

The mechanical crevices (tube support plate) are packed with porous deposits of corrosion products. Corrosion deposits are there because of stagnant conditions in the flow.

In a packed crevice, the temperature gradient across the SG tube coupled with a restricted flow rate results in nucleate boiling, which is illustrated by Figure 3-1. Water is continuously evaporated by this mechanism. This causes saturated water to be drawn into the crevice to replace the exiting steam. Countercurrent flow of steam and water is due to capillary pressure at the steam-liquid interface. If insufficient liquid can be drawn into the porous media to maintain nucleate boiling, a steam-blanketed region exists below the nucleate boiling region. The actual penetration depth of liquid into the porous media is referred to as the wetted length, W_L.

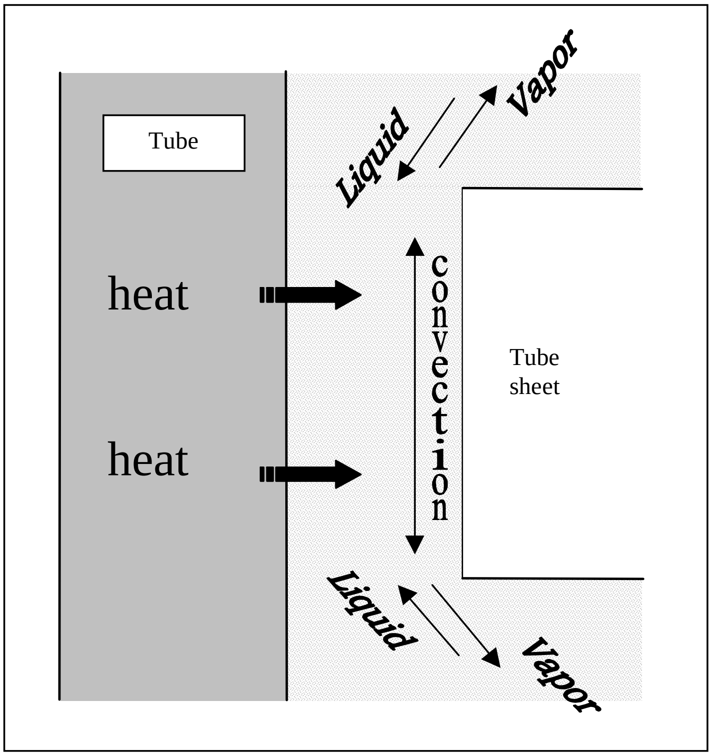


Figure 3-1
Thermal hydraulic mechanisms in the crevice

Impurities enter the crevice in solution with the liquid water. Steam exits the crevice and impurities stay trapped in the remaining liquid and they concentrate. By itself, the bulk water contains extremely low levels of impurities, however this process is efficient enough to obtain localized concentrated solutions of impurities up to several mol/L.[1]

Mass transfer processes occur within the fluid element because of the concentration gradient. Diffusion, volatilization and electromigration reduce the rate of accumulation because those fluxes oppose the liquid convection flux. Additionally, if the solubility of the impurity is exceeded, precipitation occurs. Solubility therefore can limit the concentration in the liquid phase.

Also, as the concentration of impurity increases, the boiling temperature rises. When the boiling temperature matches the primary tube temperature, the heat flux between the tube and the bulk fluid equals zero. As a result, there is no further boiling and the solution reaches a maximum concentration. Therefore, the concentration is thermodynamically limited as well.

Impurities react with each other changing the pH and electrochemical potential of the solution. With high impurity concentrations, the solution can become aggressive and the metal of the tube or the tube support plate might dissolve, introducing more ions into the solution.

In this model, it is assumed that the volatility of the impurity is negligible. This is a reasonable assumption for most species, such as sodium, since, in a packed crevice, vapor and liquid generally flow through separate channels of pores (vapor in big pores and liquid in small pores) which lessens the mixing of the two phases.

With present day computational abilities, it is impossible to solve the thermal hydraulic equations for even a single flow in a random porous structure. As a result, the overall properties of the fluid are described in a continuum sense. A differential volume is chosen that is large compared to the average pore size but small compared to the macroscopic dimensions of the porous media. The porous corrosion product is assumed to consist of a complex network of interconnected pores with an average porosity ε. The porous corrosion product is considered isotropic.

The width of the crevice (approximately 10 mils / 0.025 cm) is typically much smaller than its length dimension L shown in Figure 3-2. This small aspect ratio indicates that derivatives in the r and θ directions are small compared to the derivatives in the x direction. This approximation allows the model to be written in 1-D. The variables in the model are x for linear distance along the tube and t for time. The profiles obtained show concentration of impurity as a function of x and t. All the conservation equations are written between x = 0 and x = L. The cross sectional area is constant with x. The steam and the liquid can occupy any of the cross sectional area surface. The crevice is assumed to be symmetric in the top and bottom halves. The justification for this is provided in Section 3.1.7.

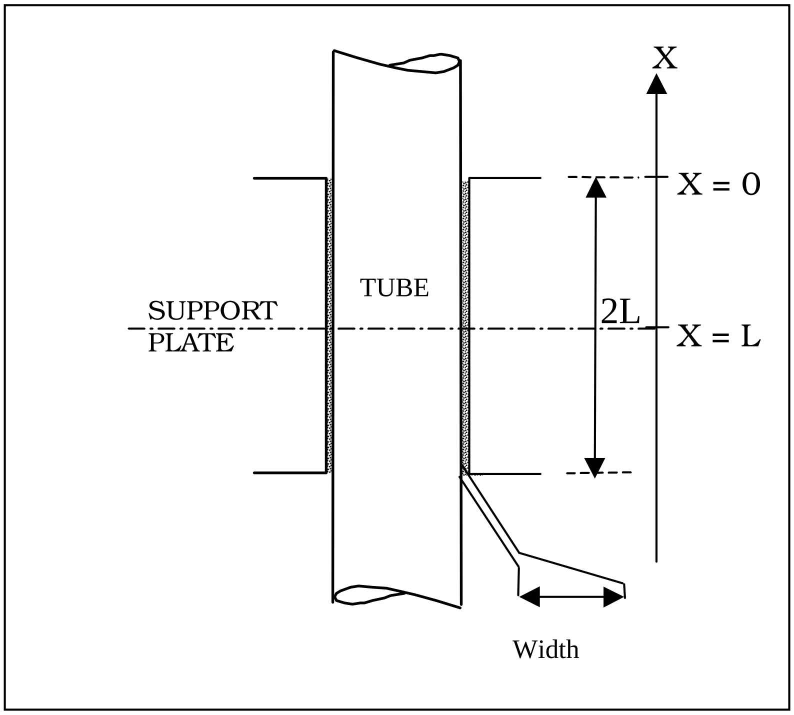


Figure 3-2
Length and width dimension of a crevice

The major objective of the model is to predict the liquid phase impurity concentrations and potential profile in the crevice as a function of time for a given bulk water chemistry. These are obtained by solving the model’s equations.

The space in the pores contains multiple components: liquid water, steam and chemical species. Each species is described by an index i. The system consists of i+2 components. For each of them a set of mass, momentum and energy equations is written. The liquid and vapor properties are subscripted l and v respectively.

The following sections, Section 3.1.1 through 3.1.8, outline the assumptions and equations used for the thermal hydraulic portion of the model. The structure of this portion of the model consists of: conservation of mass (liquid, vapor, and impurities), conservation of momentum (liquid, vapor, and impurities), conservation of energy, boiling point elevation, and capillary pressure.

3.1.1 Conservation of Mass

The general conservation of mass equation for component "A" of a multiple component mixture in a porous media with porosity ε include a generation term from either chemical reaction or phase change and is shown in Equation 3-1.

$$\varepsilon \frac{\partial \rho_A}{\partial t} + \nabla . n_A = r_A \qquad \begin{array}{l} \rho_A : \textit{mass of A per unit volume} \\ n_A : \textit{flux of A} \\ r_A : \textit{rate of reaction} \end{array}$$ **Eq. 3-1**

More specifically, the conservation of mass for the liquid phase with the fraction of liquid in the mixture (saturation) defined as S, appears as Equation 3-2.

$$\varepsilon S \frac{\partial \rho_l}{\partial t} + \nabla . \rho_l V_l = -\rho_l \rho_V \sigma_{V \to l} \qquad \rho_l \rho_V \sigma_{V \to l} : \textit{rate of production vapor}$$ **Eq. 3-2**

The mass balance for the vapor phase (steam) is described in Equation 3-3.

$$\varepsilon (1 - S) \frac{\partial \rho_V}{\partial t} + \nabla . \rho_V V_V = \rho_l \rho_V \sigma_{V \to l}$$ **Eq. 3-3**

Equation 3-4 is written for an impurity with index i present only in the liquid phase:

$$\varepsilon S \frac{\partial Ci}{\partial t} + \nabla C_i V_i = -\sum_{\substack{j=1 \\ j \neq i}}^{n} R_{ij} = -S_i \qquad \begin{array}{l} R_{ij} : \textit{rate of chemical reaction} \\ \quad \textit{between specie i and specie j} \\ S_i : \textit{sink term} \end{array}$$ **Eq. 3-4**

The sources and sink terms in Equation 3-4 consume or produce species. They include chemical reactions, precipitation that consumes species and electrochemical reactions in solution or at the wall (metal dissolution)

The model does not predict the concentration of volatile species present in the vapor phase.

3.1.2 Conservation of Momentum

Liquid and steam constitute a two-phase flow. In the porous media, capillary pressure plays an important role in determining the form of two-phase flow. The normal pattern is creeping (or viscous) flow from which there is a gradual slow departure at increasing flow rates. Macroscopic equations are used to describe two-phase flow in porous media, which are generalizations of Darcy's law for single phase flow in porous media. Darcy's law is limited to viscous flow that has a Reynolds number based on the packing particle dimension of less than 1.

Equation 3-5[12] shows the Navier-Stokes equation at steady state neglecting inertial forces:

$$\rho \frac{Du}{Dt} = -\nabla P + \mu \nabla^2 u + \rho g = 0$$

Eq. 3-5

$$k k_{rl} \nabla^2 u \approx u$$

Eq. 3-6

Equation 3-6 was proved in Darcy's experiment with single-phase flow in porous media. Combining Equation 3-5 with 3-6, and generalizing for two-phase flow, Equations 3-7 and 3-8 are derived.

$$V_l = \frac{k k_{rl}}{\mu_l} (\nabla P_l - \rho_l g)$$

μ: viscosity

ρ: density

Eq. 3-7

$$V_V = \frac{k k_{rV}}{\mu_V} (\nabla P_V - \rho_V g)$$

kk_r : permeability

Eq. 3-8

V_l and V_v are the velocities of the liquid and the vapor, respectively. Velocities are related to the gradient of pressure ∇P and the acceleration due to gravity g.

Darcy's law is generalized such that the medium is imagined to be subdivided into regions. These regions are small enough to permit the use of approximately constant values of V, P, kk_r, ρ, μ for each fluid within each region, but large enough for Darcy's law to apply macroscopically in each region. The introduction of the effect of gravity is standard procedure in hydraulics. However in this model, gravity forces can be neglected compared to pressure gradients. The gradient of pressure within a crevice 1.4 cm high is usually 30 N/cm^2 (0.03 MPa).[1]

Equation 3-9 shows an order of magnitude approximation of the pressure gradient in the crevice. Correspondingly, Equation 3-10 shows a similar approximation for the gravity forces in the crevice.

$$\nabla \mathrm{P_i} \cong \frac{30 * 10^4 \,\mathrm{Nm^{-2}}}{1.4 * 10^{-2} \,\mathrm{m}} \cong 10^6 \,\mathrm{Nm^{-3}}$$

Eq. 3-9

$$\rho g \cong 10^3 \, kgm^{-3} * 10 Nkg^{-1} \cong 10^4 \, Nm^{-3}$$

Eq. 3-10

Since the magnitude of the pressure gradient is roughly 100 times that of the gravity force, the gravity forces are not taken into account in this model.

The approximation of creeping flow can also be justified by calculating the Reynolds number of the liquid and vapor flow. The Reynolds number of a flow with kinematic viscosity ν and velocity V in a porous media with a packing particle diameter D_p is expressed by Equations 3-11 and 3-12.

$$R_e = \frac{V * D_p}{\nu}$$

Eq. 3-11

$$\nu = \frac{\mu}{\rho} = \textit{kinematic viscosity}$$

Eq. 3-12

Typical average values for density, viscosity and velocity are summarized in Table 3-1. Equations 3-13 through 3-15 show typical values for packing particle diameter and Reynolds number.

Table 3-1
Typical Values For Liquid and Vapor Properties

		Liquid Phase (l)	Vapor Phase (v)
Density, •	*(kg/m^3)*	755	32
Velocity, V	*(m/s)*	10^{-5}	10^{-3}
Viscosity, •	*(N/m^2-s)*	9.51 x 10^{-5}	1.88 x 10^{-5}

$$D_p = 200 \mu m = 2 * 10^{-4} m$$

Eq. 3-13

$$R_{el} = \frac{10^{-5} * 10^{-4}}{9.51 * 10^{-5}} * 755 = 8 * 10^{-3} < 1$$

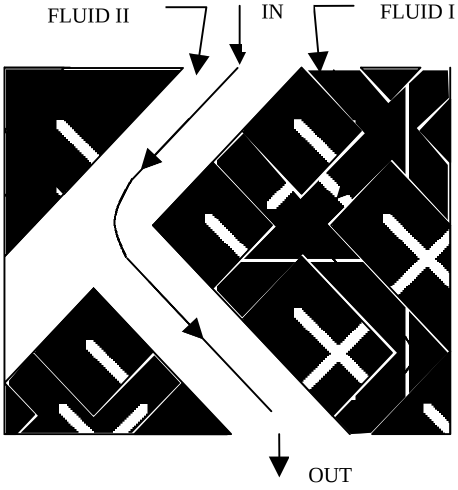
Eq. 3-14

$$R_{ev} = \frac{10^{-3} * 10^{-4}}{1.88 * 10^{-5}} * 32 = 0.17 < 1$$

Eq. 3-15

The particle packing diameter in the experiments of Lumsden and Takamatsu[5] used to benchmark this model is D_p = 200 µm. Using property values in Table 3-1 with Equation 3-11, the liquid Reynolds number is determined to be 8.0 x 10^{-3} and the vapor Reynolds number is 0.17. Both are less than 1, therefore Darcy's laws can be used for two-phase flow.

With the Reynolds numbers determined above, the flow pattern shown schematically in Figure 3-3 is predominant. The wetting fluid (liquid water) preferentially occupies the relatively small pores and the non-wetting fluid (steam) the relatively large ones. The two fluids are separated from each other by stable interfaces, which in steady state are stationary and behave like rigid partitions. Where this flow pattern dominates, the two fluids flow in separate three-dimensional networks of pore channels where the flow of each fluid can be regarded as hydrodynamically independent of the other fluid. As a result, Darcy's law of flow in porous media is applicable to each fluid and there is no mixing between steam and liquid.[13] Some species are highly volatile in a mixture of steam and liquid. Since the fluid flows are hydrodynamically independent, these chemical species' volatilization is negligible.



Two-dimensional representation of three-dimensional countercurrent steady two-phase flow in porous media. Both fluids flow in separate channels. Fluid 1 wets the uniformly wet solid surface preferentially.

Figure 3-3
Two-phase flow representation

3.1.3 Momentum of Chemical Species

It is the transport of chemical species that sets apart crevice chemistry from bulk chemistry. The three transport modes—convection, diffusion, electromigration—are formulated here.

The driving force of species i in an electrolyte solution is d_i. It is characterized in Equation 3-16.[15]

$$C_t RTd_i = C_i \nabla_{T,P} \mu_i + (\phi_i - w_i)\nabla P - (C_i F_i - w_i \sum_{j=1}^{j=n} C_j F_j)$$

C_t : *total concentration*

C_i : *concentration of species i*

$\nabla_{T,P}\mu_i$: *isothermic isobaric gradient of the molar chemical potential* **Eq. 3-16**

ϕ_i : *volume fraction of component* $i = C_i \overline{V}_i$

w_i : *mass fraction of component i*

∇P : *pressure diffusion term*

F_i : *external force applied on the species i*

In the case of the crevice, the body force per mole, F_i, acting on species i is due to the electric field as shown in Equation 3-17, where z_i is the ionic charge of the species, F is the Faraday constant and ϕ is the electrostatic potential.

$$F_i = -z_i F \nabla \phi$$ **Eq. 3-17**

The diffusion pressure term in Equation 3-16 is neglected. As a result, it simplifies to Equation 3-18.

$$C_t RTd_i = C_i \nabla_{T,P} \mu_i + (C_i z_i - w_i \sum_{j=1}^{j=n} C_j z_j) F \nabla \phi$$ **Eq. 3-18**

Except in regions close to electrode surfaces, where there is charge separation (double layer phenomena) the condition of electroneutrality in Equation 3-19 is met.

$$\sum_{j=1}^{j=n} C_j z_j = 0$$ **Eq. 3-19**

The solution is assumed to be electroneutral at all points so that there is no net electrical body force acting on the mixture as a whole. Therefore, the driving force is simply Equation 3-20.

$$d_i = \frac{x_i}{RT} \nabla_{T,P} \mu_i + \frac{x_i z_i F}{RT} \nabla \phi$$ **Eq. 3-20**

The chemical potential gradient may be expressed in terms of mole fraction and activity coefficient gradients. For non-ideal fluids the chemical potential gradient is calculated according to Equation 3-21.

$$\begin{aligned}\frac{x_i}{RT}\nabla_{T,P}\mu_i &= \frac{x_i}{RT}\sum_{j=1}^{n-1}\left.\frac{\partial\mu_i}{\partial x_j}\right|_{T,P,\Sigma}\nabla x_j = \frac{x_i}{RT}\sum_{j=1}^{n-1}\left.\frac{\partial\ln\gamma_i x_i}{\partial x_j}\right|_{T,P,\Sigma}\nabla x_j \\ &= \frac{x_i}{RT}\left(\sum_{j=1}^{n-1}\gamma_i\frac{\partial\ln x_i}{\partial x_j}+x_i\left.\frac{\partial\ln\gamma_i}{\partial x_j}\right|_{T,P,\Sigma}\nabla x_j\right) \\ &= \frac{x_i}{RT}\left(\sum_{j=1}^{n-1}\delta_{ij}+x_i\left.\frac{\partial\ln\gamma_i}{\partial x_j}\right|_{T,P,\Sigma}\nabla x_j\right)\end{aligned}$$

Eq. 3-21

To further simplify this expression, approximations are needed. By assuming infinite dilution (which is equivalent to an ideal mixture of ions in solution), the activity coefficients γ_i are equal to 1. The driving force reduces to Equation 3-22.

$$d_i = \nabla x_i + \frac{x_i z_i F}{RT}\nabla\phi$$

Eq. 3-22

With the driving force determined, the diffusion fluxes, J_i, can be determined. It is usual to define diffusion fluxes J_i with a specified reference velocity. The liquid velocity V_l is commonly used as this reference.

$$J_i^n = N_i - C_i * V_l$$

Eq. 3-23

$$N_i = C_i V_i = J_i^n + C_i * V_l$$

J_i^n : *flux of species i relative to the flux of mixture*

N_i : *molar flux velocity*

V_i : *velocity of diffusion of species i*

Eq. 3-24

The generalized Maxwell-Boltzmann equation in Equation 3-25 relates the driving force to the diffusion flux.

$$C_t d_i = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_i J_j^n}{D_{ij}} - J_i^n\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j}{D_{ij}} = -\sum_{\substack{j=1\\ j\neq i}}^{n}B_{ij}J_j^n - J_i^n B_{ii} = -\sum_{j=1}^{n}B_{ij}J_j^n$$

Eq. 3-25)

Again assuming infinite dilution with x_i approximately equal to zero, we find that:

$$B_{ii}^n = \frac{1}{D_{in}^0} \text{ and } B_{ij}^n = 0\,.$$

Eq. 3-26

Therefore: $$C_t d_i = -\frac{J_i^n}{D_{in}^0}\,.$$

Eq. 3-27

Plugging in $C_i V_i = C_i V_l - D_{in}^0 C_t d_i$ into Equation 3-25 and using 3-26 and 3-27, Equation 3-28 is finally obtained.

$$C_i V_i = C_i V_l - D_{in}^0 (\nabla C_i + \frac{C_i z_i F}{RT} \nabla \phi) \qquad \textbf{Eq. 3-28}$$

Equation 3-28 is the flux equation for infinitely dilute solutions known as the Nernst-Plank equation. Although derived assuming infinite dilution theory, this equation is often used for dilute concentrations that do not meet the strict definition of infinitely dilute solutions as in this study. The infinite dilution theory is not valid in the concentrated region. However, since the diffusion and electromigration transport terms are extremely small compared to the convection term, and since the approximation of infinite dilution does not change the convection term, this approximation is valid.

This equation implies that mass transport of chemical species occur through the mechanisms of:

- Convection: hydrodynamic transport caused by forced convection (capillary forces)
- Diffusion: movement of a species under the influence of a chemical potential gradient (i.e. concentration gradient)
- Electromigration: movement of a charged species under the influence of an electric field.

The derivation of these equations is intentionally presented in this order starting with convection to emphasize that the main driving force for mass transport is convection due to capillarity, and then forces such as potential gradient and electrochemical potential gradient slightly modify the species' velocity.

3.1.4 Conservation of Energy

The crevice being considered contains three phases (liquid, vapor, solid). There is local heat generation due to the temperature gradient across the tube, transient temperature fields and a liquid phase change. The conservation of energy equation with local volume averaging for a porous media with a porosity ε and a fraction of voids occupied by a liquid (saturation, S) is given by Equation 3-29.[14]

$$\left\langle \rho C_p \right\rangle \frac{\partial T}{\partial t} + \left[\left(\rho C_p \right)_l \left\langle V_l \right\rangle + \left(\rho C_p \right)_v \left\langle V_v \right\rangle \right] \nabla T - h_{lv} \rho_l \rho_v \sigma_{v \to l} = \nabla \left[\left\langle K_e \right\rangle \nabla T \right] + \left\langle \dot{s} \right\rangle \qquad \textbf{Eq. 3-29}$$

C_p : *heat capacity* h_{lv} : *latent heat of evaporation*

ρ : *density* $\rho_l \rho_v \sigma_{v \to l}$: *rate of evaporation*

T : *temperature* K_e : *conductivity*

V : *velocity* $\langle \dot{s} \rangle$: *source term*

The volumetric heat source term is due to heat transfer across the steam generator (SG) tube wall. The source term, $\langle \dot{s} \rangle$, may be determined using an appropriate overall heat transfer coefficient as shown in Equation 3-30.

$$\langle \dot{s} \rangle = \frac{2\pi H r_{sg}}{A_c}(T_p - T)$$

Eq. 3-30

r_{sg} is the outside radius of the SG tube. A_c is the cross sectional area of the pore matrix over which the heat flux is uniformly distributed. T_p is the fluid temperature inside the SG tube and T is the solution temperature.

The rate of evaporation of the liquid may be expressed from the continuity equation introduced earlier in Equation 3-2 for the liquid with a quasi-steady state approximation, assuming that the system is allowed to go to equilibrium after each time step, resulting in Equation 3-31.

$$\rho_l \rho_V \sigma_{V \to l} = -\frac{\partial \rho_l V_l}{\partial x}$$

Eq. 3-31

The quasi-steady state approximation method is justified since the dimensionless time constants for the conservation equations for the liquid and steam are much smaller than those for the conservation equations for the chemical species.

To further simplify the energy equation, we need to identify which term in that equation can be neglected. The three components in the system are steam, liquid water and a solid packing material. To provide a rough idea of the importance of each term, a solid packing material must be assumed. Diamond properties were used to describe this solid packing material. However, the same conclusions would be reached for other materials, such as magnetite and carbon fiber. Since magnetite and carbon fiber have lower conductivities than diamond, they can be neglected if diamond can be.

The different terms in the energy equation are evaluated as follows in Equations 3-32 through 3-35.

$$\langle K_e \rangle = k_l \varepsilon S + k_v \varepsilon (1 - S) + k_s (1 - \varepsilon)$$

Eq. 3-32

$$h_{lv} \rho_l \rho_v \sigma_{v \to l} \approx h_{lv} \rho_v \frac{V_v}{L}$$

Eq. 3-33

$$\left[(\rho C_p)_l \langle V_l \rangle + (\rho C_p)_v \langle V_v \rangle \right] \nabla T = (\rho_l C_{p_l} V_l + \rho_v C_{p_v} V_v) \frac{\Delta T}{L}$$

Eq. 3-34

$$\nabla (K_e \nabla T) \cong (k_l \varepsilon S + k_v \varepsilon (1 - S) + k_s (1 - \varepsilon)) \frac{\Delta T}{L^2}$$

Eq. 3-35

The calculations were made using the values and property data appearing in Tables 3-2 and 3-3.

Table 3-2
Properties of Liquid, Vapor, and Solid Phases

		Liquid Phase (l)	Vapor Phase (v)	Solid Phase (s)
Density, ρ	*(kg/m^3)*	755	32	—
Velocity, V	*(m/s)*	10^{-5}	10^{-3}	—
Conductivity, k	*(J/s-m-K)*	192	17.09	900
Heat Capacity, c_p	*(N/kg-K)*	23 x 10^3	27 x 10^3	—

Table 3-3
Properties of Crevice Porous Media

		Crevice porous media
Porosity, ε		0.3
Saturation, S		0.5
Heat transfer coefficient, h	*(J/s-m^2-K)*	2550
Tube radius, r_{sg}	*(cm)*	0.64
Cross sectional area, A_c	*(cm^2)*	0.255
Crevice length, L	*(cm)*	3
Latent heat of vaporisation, h_{fg}	*(J/kg)*	1557.5 x 10^3

Plugging those representative numbers into Equations 3-32 through 3-35, an order of magnitude for each contribution in the energy equation is given by Equations 3-36 through 3-39.

$$h_{lv}\rho_v\frac{V_v}{L}=1.7*10^6 \quad \textbf{Eq. 3-36)}$$

$$(\rho_l C_{p_l} V_l+\rho_v C_{p_v} V_v)\frac{\Delta T}{L}=7.0*10^4 \quad \textbf{Eq. 3-37}$$

$$(k_l\varepsilon S+k_v\varepsilon(1-S)+k_s(1-\varepsilon))\frac{\Delta T}{L^2}=7.5*10^4 \quad \textbf{Eq. 3-38}$$

$$\frac{2\pi H r_{sg}}{A_c}\Delta T=1.6*10^8 \quad \textbf{Eq. 3-39}$$

The largest two terms in the energy equation are the vaporization term and the source term. We will thus consider the temperature uniform along the x direction and keep only two terms in the energy equation as follows in Equation 3-40.

$$\frac{2\pi H r_{sg}}{A_c}(T_p - T) = h_{lv}\frac{\partial \rho_v V_v}{\partial x} \qquad \textbf{Eq. 3-40}$$

The entire heat source is used to vaporize the liquid. There are no losses. No conduction or transport of heat is taken into account. This approximation is crude. Neglecting both terms from Equation 3-37 and Equation 3-38, and keeping only Equation 3-36, introduces an error of 10% in the conservation of energy equation. This error is not very significant, since there is a greater error with the heat transfer coefficient, H.

3.1.5 Boiling point elevation

The process of concentration does not continue indefinitely. The extent of the concentration of the impurity species is limited by the elevation of the boiling point.

Initially, the fluid in the crevice is bulk water. The low level of impurities (on the order of ppb) does not significantly influence the boiling point. As the impurities concentrate, the boiling point rises. Figure 3-4 simplified for constant pressure illustrates how the boiling point rises with concentration.

Ebullition is maintained while the temperature of the fluid is still less than the temperature of the tube T_p. The temperature gradient available to drive heat transfer decreases as the concentration of impurity (and resulting boiling temperature) increases. The concentration limit is reached when the temperature of the fluid matches the temperature of the tube.

At the mouth of the crevice, the temperature of the solution equals the bulk temperature. At the center of the crevice, the temperature of the solution containing impurities equals the temperature of the tube. The temperature in the steam-blanketed region is not predicted by the model.

Figure 3-4 illustrates this process. The top of the figure represents the concentration of impurities from the mouth to the center of the crevice. The bottom of the figure represents the temperature of the solution inside the crevice associated with the concentration.

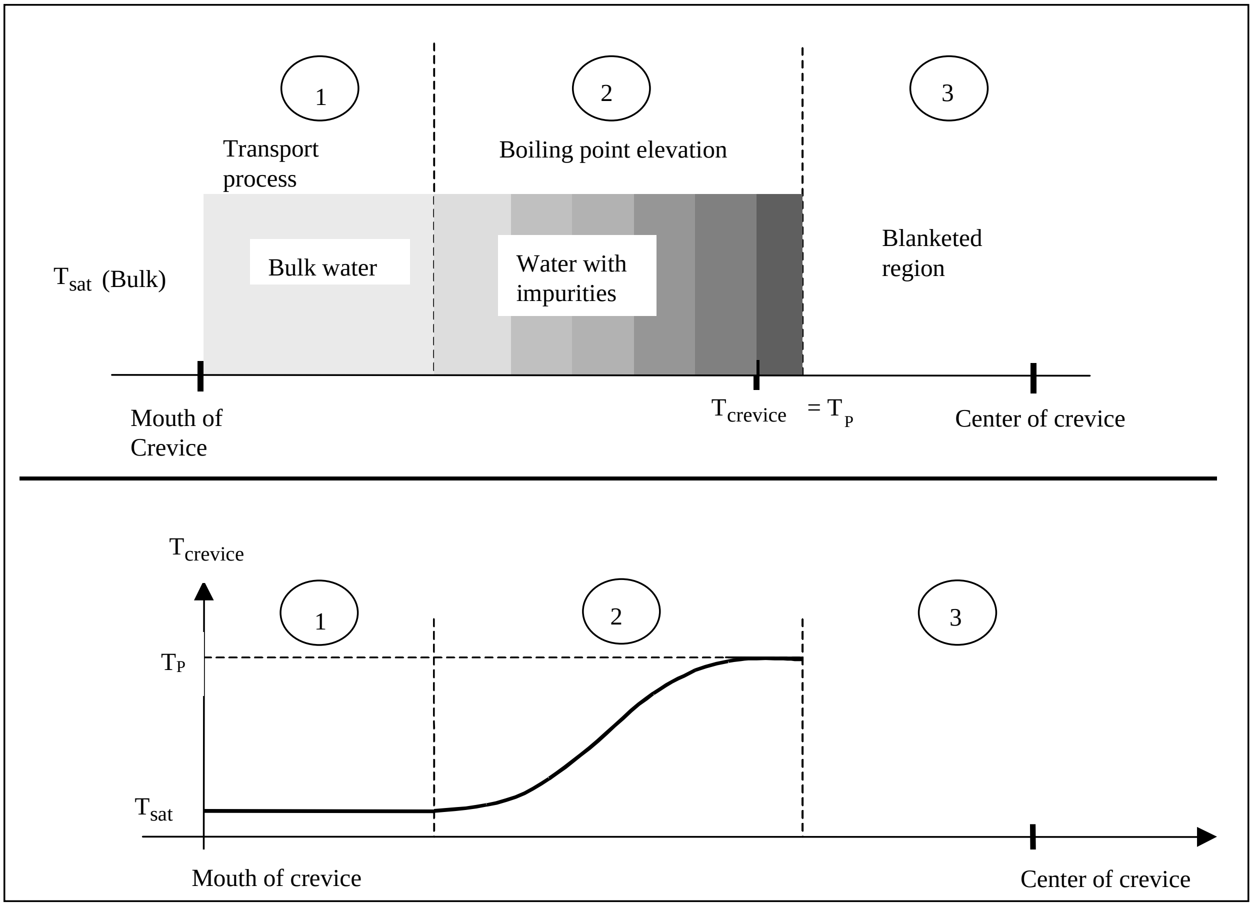


Figure 3-4
Boiling point elevation throughout the crevice due to the concentration of chemical species

In region 1, the solution is not charged with impurities. The solution inside region 1 is the bulk solution. The temperature of the solution is the saturation temperature in the bulk solution, T_{sat}.

In region 2, the impurities continue to concentrate in the direction of the center of the crevice. The grey color becomes darker. The boiling point elevates.

In region 3, the crevice is steam-blanketed, and the temperature is not predicted by the model.

At the limit between region 2 and 3, the concentration reaches a limit fixed by $T_{sat}=T_p$, the temperature of the tube. The temperature profile next to the interface between the region 2-3 interface is flat.

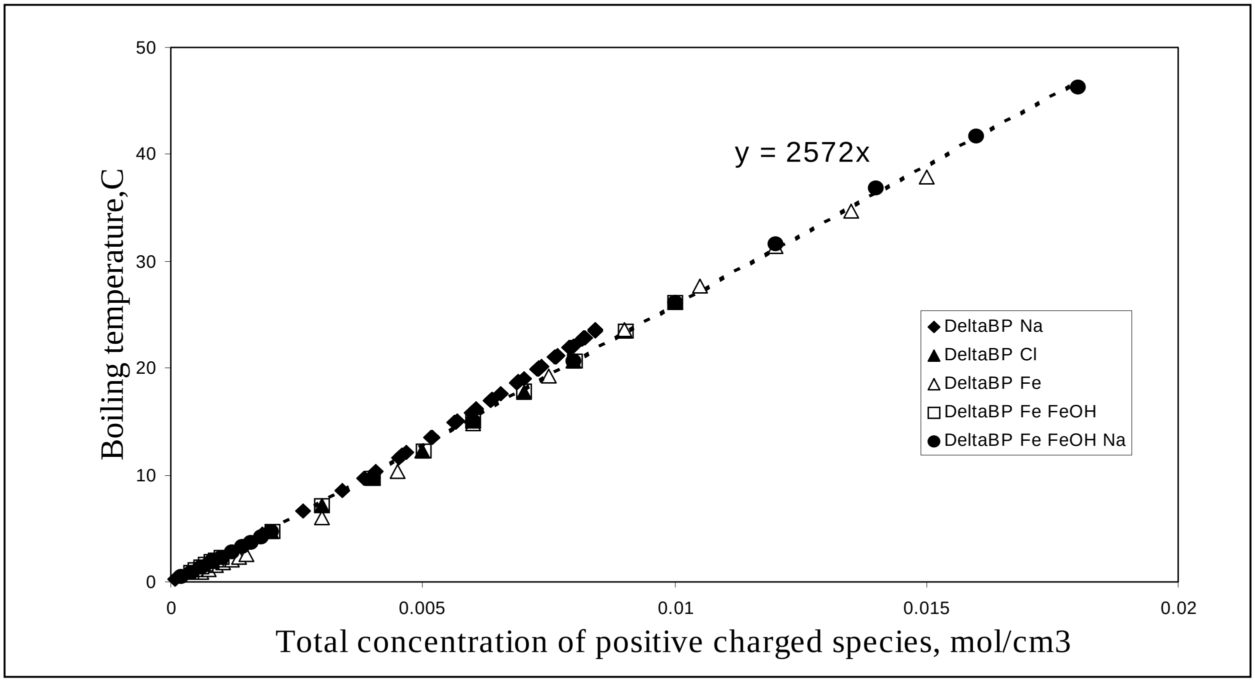


Figure 3-5
Boiling point elevation variation with the chemistry of a solution[16]

To evaluate the boiling point elevation as a function of the concentration of impurity in the solution, the MULTEQ code was used.[16] The normal default in MULTEQ is to maintain constant pressure. This is a good assumption since the pressure drop in the crevice is small. The boiling point elevation for four ions Na^+, Cl^-, Fe^{2+}, $FeOH^+$ was calculated for different concentrations. Additionally, the ionic strength was calculated for each composition. The ionic strength is defined here as Equation 3-41.

$$I = \frac{1}{2}\sum_{i=1}^{i=N} C_i \qquad \textbf{Eq. 3-41}$$

Six different studies were made using MULTEQ, each introducing different species or combinations of species. The species considered are:

- Sodium [Na^+]
- Chloride [Cl^-]
- Ferrous iron [Fe^{2+}]
- Ferrous iron [Fe^{2+}] and iron hydroxide [$FeOH^+$]
- Ferrous iron [Fe^{2+}], iron hydroxide [$FeOH^+$], and sodium [Na^+]
- Sodium [Na^+] and chloride [Cl^-]

For each case, a bulk concentration for each ion is entered. Additionally, a factor is entered which indicates the magnitude of concentration in the bulk solution. The ionic strength and the boiling point elevation are calculated. The results are plotted in Figure 3-4.

Looking at the results in Figure 3-4, it is concluded that the boiling point elevation is proportional to the ionic strength. Therefore, the temperature is a function of x as the concentration increases. This is not taken into account in the conservation of energy equation, since it was shown that the terms containing axial gradient of temperature (Equation 3-37 and 3-38) are small compared to the vaporization term (Equation 3-36) and the term containing the radial gradient of temperature (Equation 3-39).

3.1.6 Capillary Pressure

The fraction of liquid to vapor (saturation, S) still remains to be calculated. This saturation can be related to the capillary pressure.

In the crevice, the main driving force is capillarity. The capillary pressure is defined by $P_c = P_v - P_l$. The liquid and vapor pressure are determined by the conservation of momentum.

$$V_l = \frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l g) \quad \textbf{Eq. 3-42}$$

$$V_V = \frac{kk_{rV}}{\mu_V}(\nabla P_V - \rho_V g) \quad \textbf{Eq. 3-43}$$

An equivalent method of calculating capillary pressure is to relate it to the surface tension σ and the mean pore radius r as shown in Equation 3-44. At a given capillary pressure, the non-wetting fluid (vapor) tends to occupy the pore space with the radius greater than r. The wetting fluid (liquid) tends to occupy the smaller pore space (less than r).

$$P_c = \frac{2\sigma \cos\alpha}{r} \quad \textbf{Eq. 3-44}$$

Figure 3-6 shows the pressure distribution in the pore network. At the mouth of the pore network, the pressure in both the liquid and the vapor phase is equal to the steam generator pressure. The liquid phase pressure decreases towards the center since the water flows from mouth to center and the steam pressure decreases towards the center. The capillary pressure is a maximum at the center.

The countercurrent flow produces a capillary pressure, which increases from zero at the mouth of the crevice to some maximum value when the liquid has undergone complete vaporization.

The mean pore radius r occupied by the liquid decreases as capillary pressure increases. At the mouth of the crevice, r is infinite so that the liquid tends to occupy the whole region. The resulting saturation is close to one.

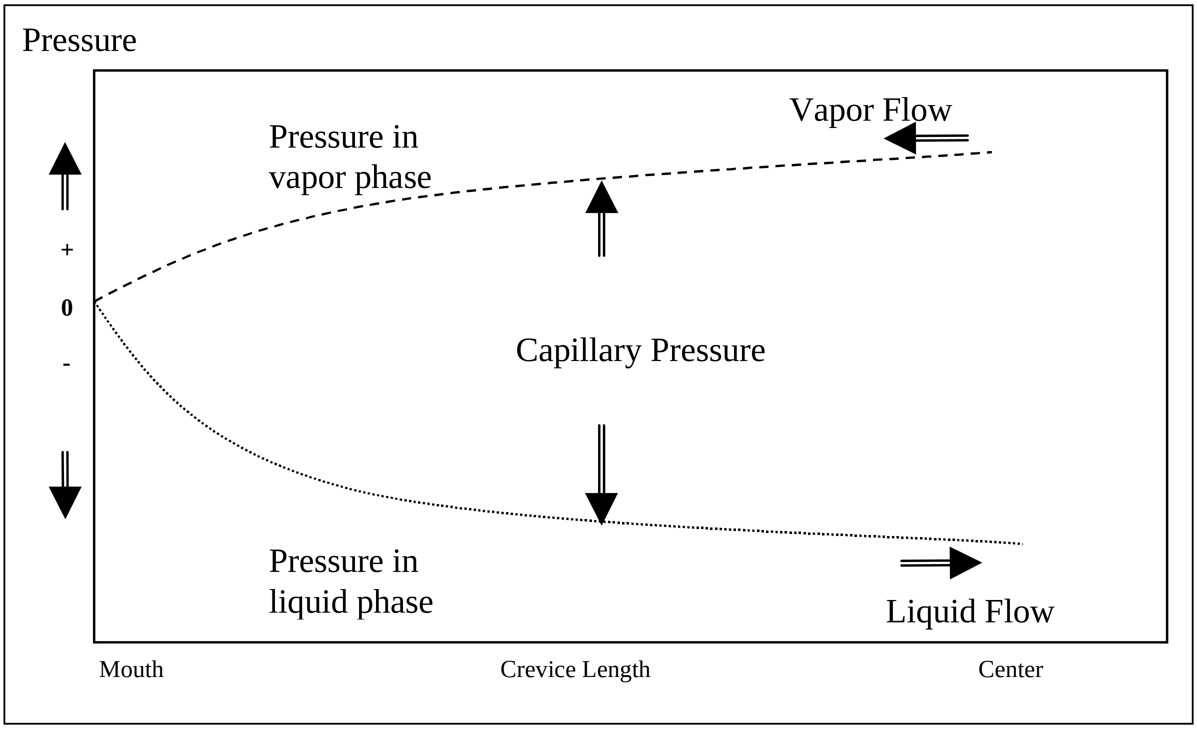


Figure 3-6
Variation of capillary pressure in the crevice

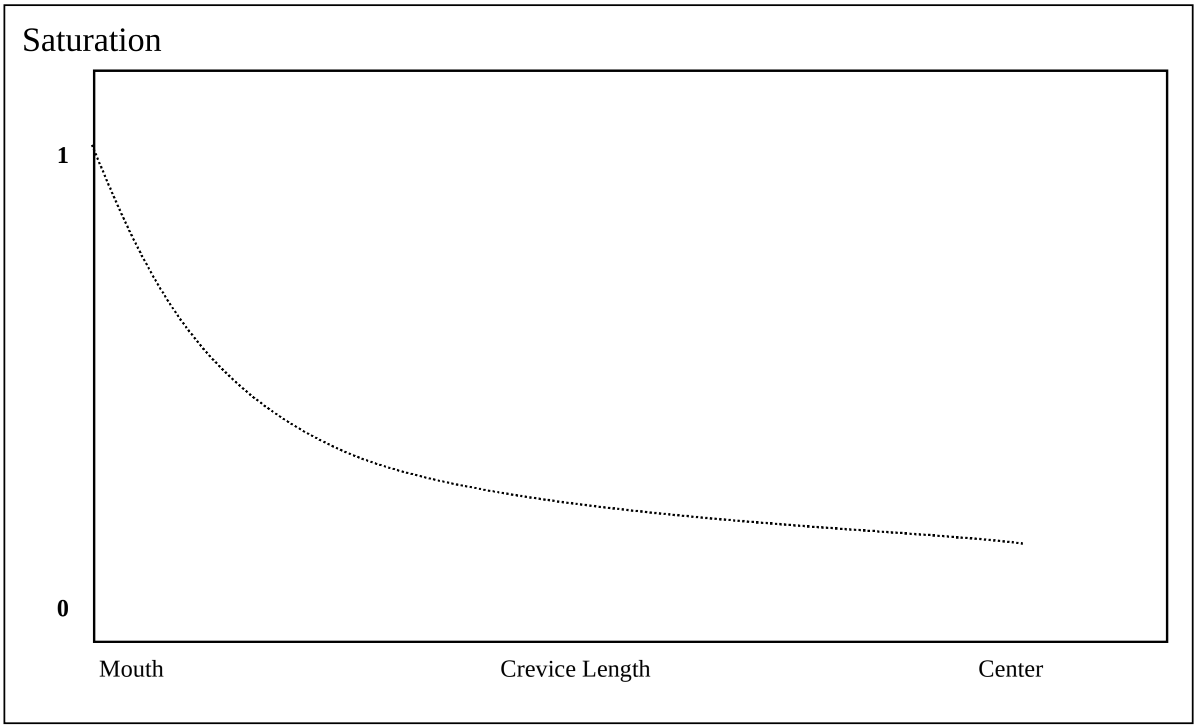


Figure 3-7
Variation of saturation in the crevice

Towards the center of the crevice as the capillary pressure gets larger and larger, r decreases, the steam occupies more and more space and S decreases as shown in Figure 3-6. Numerous studies of two-phase flow and displacement in capillary bodies have shown that the non-wetting fluid fraction increases as the capillary pressure is incremented.[17-25]

To determine what the saturation is for a given capillary pressure, no simple relationship is available, but many experimental studies have been carried out.[17-25] Transport processes within porous structures are important in many scientific disciplines. Porous structures are frequently encountered in nature (i.e. soil, rocks, etc.).[1]

Figure 3-8 shows the curve typically observed during the experiments of Dullien.[17] If the crevice is initially totally wetted (saturation close to one), there is very little displacement of the wetting fluid while the capillary pressure is increased from zero. In these experiments, the breakthrough pressure, P_b, is defined as the point where the saturation begins to decrease rapidly as capillary pressure increases. As saturation reaches the residual saturation S_r, capillary pressure increase has little effect on saturation.

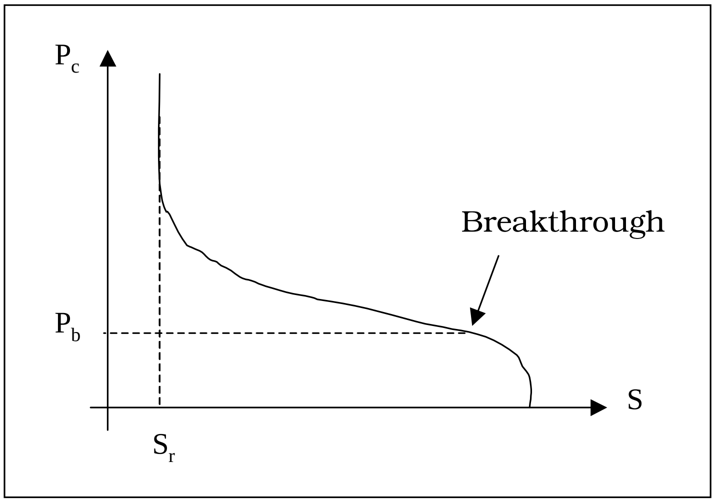


Figure 3-8
Definition of the breakthrough pressure and the residual saturation on the water retention curve

In his model, Millett used two capillary pressure–saturation curves obtained in Baum's studies of soft and hard sludge,[1] and dented crevices.[1] Baum's results presented in Figure 3-9 suggest that the capillary pressure is a linear function of the saturation. Neither residual saturation nor breakthrough pressure is observed.

The US Environmental Protection Agency (EPA) analyzes the movement of water and dissolved contaminants in the saturated and unsaturated zones of the subsurface environment. The ability to reliably characterize the hydraulic properties of various types of soils is essential. A database program for storing experimental unsaturated soil hydraulic properties named UNSODA (Unsaturated Soil Hydraulic Database) was created.[18] UNSODA serves as a repository of measured unsaturated hydraulic data, including the employed measurement methods as well as other basic soil properties (porosity, permeability, etc.).

Data from UNSODA was gathered from the literature or was obtained through personal request to scientists and engineers. The database UNSODA contains 790 different soils. For each of them different tabular data types are available: particle size distribution, mineralogy, measure of diffusivity, capillary head of water or relative permeability. The primary type of data of interest here is the water retention curve as a function of saturation. Also in order to be able to compare the soil to our porous media, porosity and permeability should be available in the properties provided by UNSODA. Only 52 soils met these criteria. These soils can be seen in Appendix A.

The water retention curves provided by UNSODA are experimental. They are determined by saturating a sample of the porous medium with the wetting fluid. The wetting fluid is then slowly replaced by a non-wetting fluid. If the pressure required to replace the wetting fluid is recorded at a succession of equilibrium states, a drying water retention curve with the pressure head on the ordinate and the water content or saturation on the abscissa can be generated. Conversely, if the non-wetting fluid is slowly replaced by the wetting fluid, then a wetting water retention curve can be generated.

At ambient temperature, a significant difference between drying and wetting curves are observed. She and Sleep concluded in their experimental study that increasing the temperature of the pore solution decreases the difference between drying and wetting water retention curves.[19] At 80°C, both drying and wetting curve are similar. Therefore in this model since the temperature inside the steam generator is around 300°C it is assumed that the drying and wetting curves are the same.

The drying and wetting water retention curves for each of the 52 different soils was obtained from UNSODA. To compare soils with different properties, a dimensionless capillary pressure was calculated as suggested by Moseley and Dhir.[20] The dimensionless capillary pressure concept was created by Leverett. It is defined in Equation 3-45.

$$J(S) = \frac{\Delta\rho g h}{\gamma}\sqrt{\frac{K}{\varepsilon}}$$ **Eq. 3-45**

The term $\frac{\Delta\rho g h}{\gamma}$ represents the mean interfacial curvature. $\Delta\rho$gh is the capillary pressure, γ the superficial tension of water, k the permeability and ε the porosity.

Results from recent experimental studies were added to the data obtained from UNSODA.[18] Demond studied the influence of octonoid acid dissolved in the aqueous phase on a capillary pressure curve.[21] Dong created a new model for immiscible deplacement in porous media.[22] His model uses a capillary pressure observed for a certain type of soil for air-water phases. Liu estimated the air-oil and oil-water capillary pressure and permeability relations.[23] Moseley studied the effect of wettability of water, ethanol and refrigerant.[20] Dury looked at the dependence of hydraulic characteristics o soils on a dissolved organic compound choosing ethanol as a model substance.[24] She and Sleep performed a parametric study on the effect of temperature on capillary pressure saturation relationships for air-water and perchloroethylene water system.[19] Van Geel simulated a LNAPL spill in variably saturated sand.[25]

In each of these experiments, an air-water retention curve was used as the reference curve. Each of these reference curves were used in this study to better characterize the relationship between capillary pressure and saturation.

The retention curves from Baum's study, UNSODA, and the other experimental studies were transformed into a J-J_b-curve with the Leverett parameter on the ordinate and the quantity S-S_r on the abscissa. J is the dimensionless capillary pressure, J_b is the dimensionless breakthrough pressure, S is the saturation, and S_r is the residual saturation. The graphs of all different soils, presented as Figures 3-9 through 3-11, show the same pattern, where J-J_b is proportional to S-S_r.

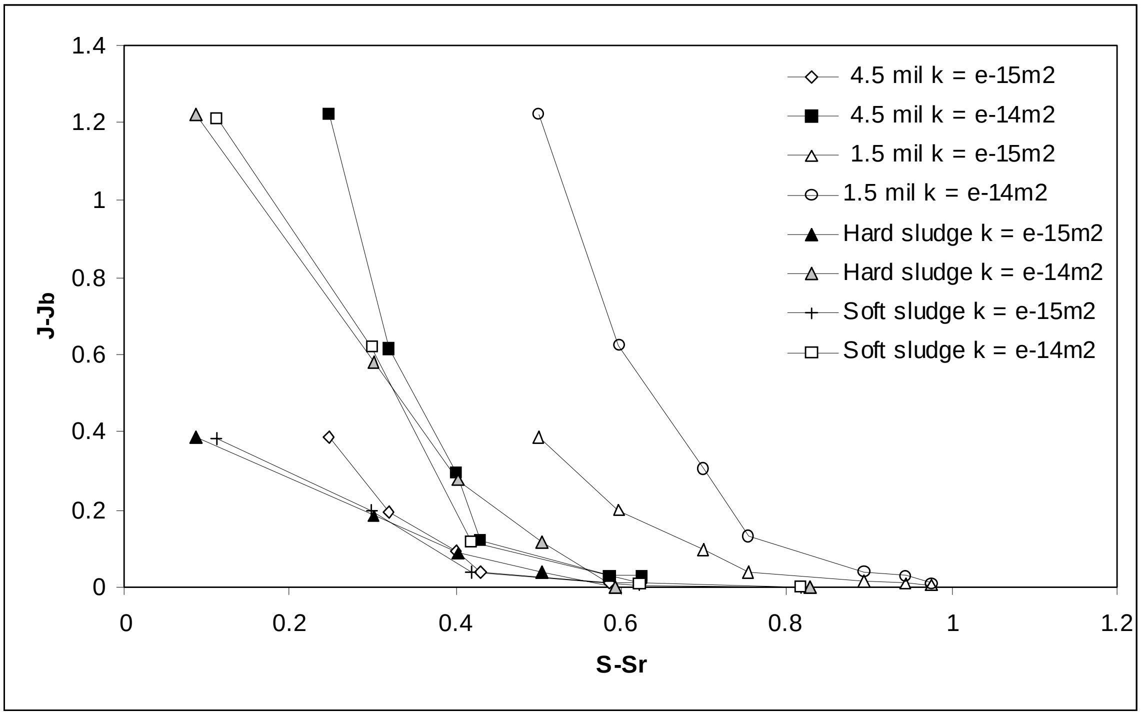


Figure 3-9
Variation of capillary pressure with saturation in 4 different porous media: 1.5 mils dented crevice, 4.5 mils dented crevice and two sludge piles. For the calculation of J, two permeabilities, k, were used: 1.0e-14m^2 and 1.0e-15m^2

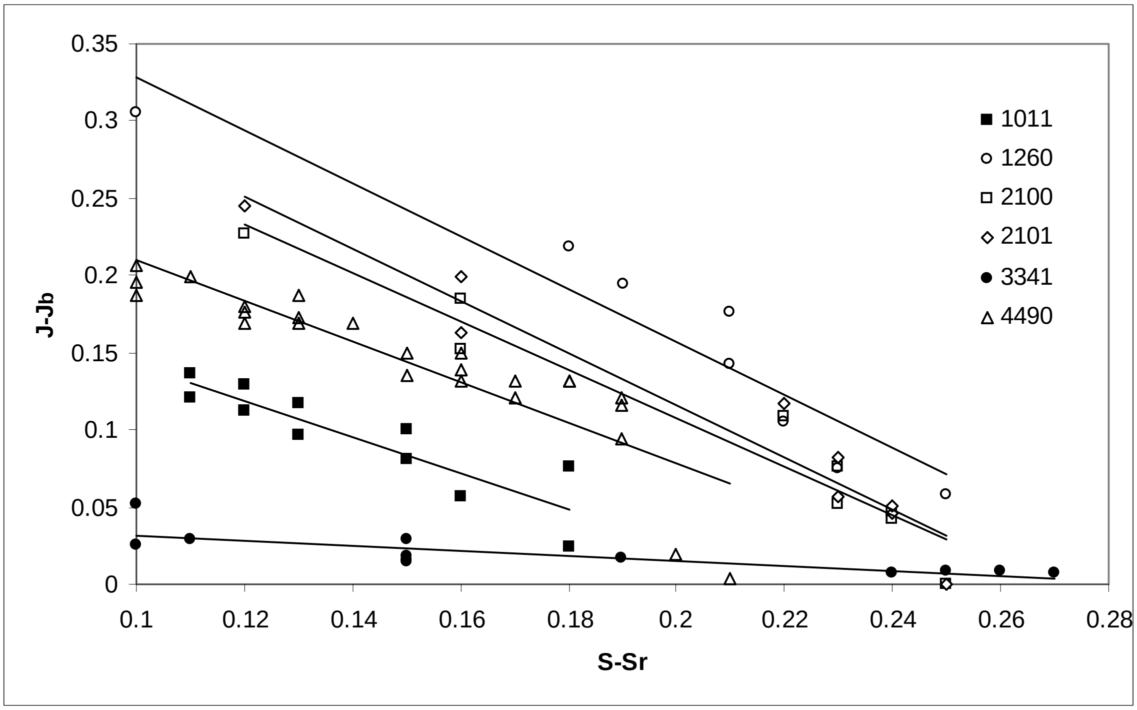


Figure 3-10
Variation of capillary pressure with saturation for 6 different soils extracted from UNSODA.[18] (Soils references: 1011, 1260, 2100, 2101, 3341, 4490)

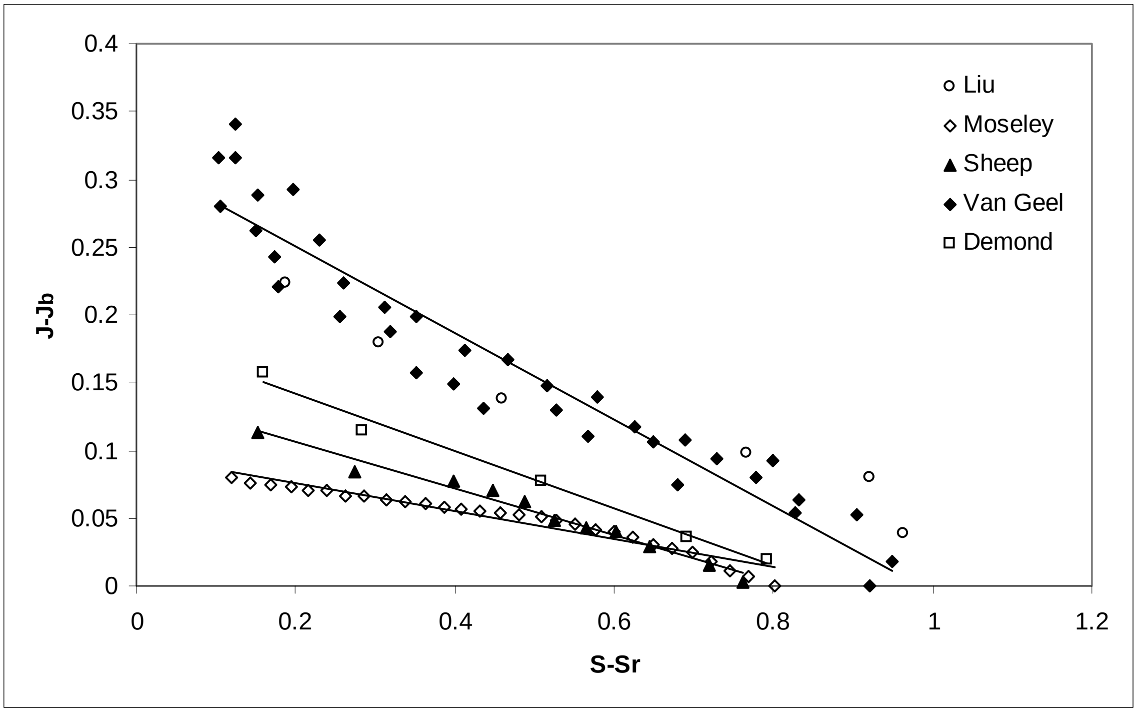


Figure 3-11
Plots for 5 variations of capillary pressure with saturation provided by Liu[23], Moseley[20], She[19], Van Geel[25], and Demond[21].

Therefore, the capillary pressure is modeled as a linear function of the saturation as shown in Equation 3-46

$$P_c = DPcDS * (S - S_0) \qquad \textbf{Eq. 3-46}$$

It is approximated that no breakthrough or residual saturation exists (as suggested by the sludge data). The slope of capillary pressure versus saturation DPcDS depends on the type of porous media.

3.1.7 Presence of a Steam-Blanketed Region

As the liquid penetrates the crevice, the capillary pressure increases. If the value of P_c reaches a high enough value, the saturation predicted by Equation 3-46 is negative. This is impossible. In fact, the capillary pressure is too high for a liquid phase to exist. As a result, a steam-blanketed region exists in the center of the crevice.

The porous media is divided in two regions: a liquid rich or wetted region having heat transfer indicative of nucleate boiling followed by a vapor-blanketed region. The liquid penetration depth from the entrance of the porous media is defined as the wetted length W_l.

In a tube support plate crevice, the solution enters the crevice from both top and bottom surfaces of the plate. Since gravity is small compared to capillary forces, the solution is drawn into the crevice from both ends. Therefore initially there are wetted zones at both ends and a dryout zone at the center portion of the crevice. The crevice is considered symmetric at the top and bottom.

The model predicts only the concentration within the wetted length. To calculate the wetted length, an estimate for it is entered and the system is then solved. If the saturation at the wetted length coordinate is negative then the next value for wetted length estimation is lower. If the saturation is more than zero the next value is larger. This way, the model predicts both wetted length and concentration profiles of impurity.

As the concentration process continues, it is expected that the dryout zone is replaced by a concentrated solution having a saturation temperature equal to the tube temperature shown in Figure 3-4. The wetted length is predicted as a function of time. After a significant amount of time, the crevice is entirely wet. The wetted length is constant and equal to L.

3.1.8 Summary of the Equations

After writing the conservation equations (continuity, momentum, energy), the system of equations for the thermal hydraulics is as follows in Equations 3-47 through 3-60.

$$\textit{Fluid water}: \quad \varepsilon S \frac{\partial \rho_l}{\partial t} + \frac{\partial \rho_l V_l}{\partial x} = -\rho_l \rho_V \sigma_{V \to l} \qquad \textbf{Eq. 3-47}$$

$$V_l = \frac{kk_{rl}}{\mu_l}\frac{\partial P_l}{\partial x}$$ **Eq. 3-48**

$$T_l = T_{saturation}$$ **Eq. 3-49**

$$-\frac{2\pi H r_{sg}}{A_c}(T_p - T_l) = h_{lv}\frac{\partial \rho_l V_l}{\partial x}$$ **Eq. 3-50**

$$Vapor: \quad \varepsilon(1-S)\frac{\partial \rho_V}{\partial t} + \frac{\partial \rho_v V_v}{\partial x} = \rho_l \rho_V \sigma_{V\to l}$$ **Eq. 3-51**

$$V_V = \frac{kk_{rV}}{\mu_V}\frac{\partial P_v}{\partial x}$$ **Eq. 3-52**

$$T_v = T_l = T_{saturation}$$ **Eq. 3-53**

$$\frac{2\pi H r_{sg}}{A_c}(T_p - T_v) = h_{lv}\frac{\partial \rho_v V_v}{\partial x}$$ **Eq. 3-54**

$$Species\ i: \quad \varepsilon S\frac{\partial Ci}{\partial t} + \nabla C_i V_i = S_i$$ **Eq. 3-55**

$$C_i V_i = C_i V_l - D_i^0(\nabla C_i + \frac{C_i z_i F}{RT}\nabla\phi)$$ **Eq. 3-56**

The saturation is related to the capillary pressure.

$$P_c = P_v - P_l = f(S)$$ **Eq. 3-57**

$$f(S) = DPcDS*(S - S_0)$$ **Eq. 3-58**

And the saturation temperature is a function of the concentration.

$$T_v = T_l = T_{saturation} = T_i = f(C_i)$$ **Eq. 3-59**

$$f(C_i) = T_{s0} + 2572.0*\frac{1}{2}\sum_{i=1}^{i=N} C_i$$ **Eq. 3-60**

To use the thermal hydraulics of this model, several parameters need to be determined. ε, ρ_v,ρ_l, k, μ_l, μ_v, r_{sg}, T_p, A_c, h_{lv}, D_i, z_i, R, F are considered constant. Typical values considering the six species H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$ are given Table 3-4.

k_{rv} and k_{rl} depend on local saturation values. The dependency has been widely studied. Wyckoff and Botset established that if the relative permeability coefficients are expressed as fractions of the absolute permeability k, the data for a number of different systems fall on two curves.[14] One curve is for the wetting phase and the other for the non-wetting phase. Correlations suggested in the literature are given below.

$$k_{rw} = kS^3 \quad \textbf{Eq. 3-61}$$

$$k_{rnw} = k(1-S) \quad \textbf{Eq. 3-62}$$

Table 3-4
Parameters value used for the thermal hydraulic modeling[1]

Parameter	Units	Default value
ε		0.3
ρ_v	g/cm^3	0.032
ρ_l	g/cm^3	0.755
K	cm^2	9.68e-9
μ_l	N*s/cm^2	9.51E-9
μ_v	N*s/cm^2	1.88E-9
r_{sg}	cm	0.94
T_p	K	603.15
T_{s0}	K	553.15
A_c	cm^2	0.166
h_{lv}	J/g	1557.49
D_{H^+}	cm^2/s	37.248E-5
D_{OH^-}	cm^2/s	21.04E-5
D_{Na^+}	cm^2/s	5.336E-5
D_{Cl^-}	cm^2/s	8.128E-5
D_{FeOH^+}	cm^2/s	2.88E-5
$D_{Fe^{2+}}$	cm^2/s	4.0E-5
z_{H^+}		1
z_{OH^-}		–1
z_{Na^+}		1
z_{Cl^-}		–1
$z_{Fe^{2+}}$		2
Z_{FeOH^+}		1
R		8.31
F	C/eq	96500
H	J/s/cm^2/K	0.255
DP_cDS	N/cm^2	–100

3.2 Chemical Modeling

Chemical reactions may generate or consume chemical species in the electrolyte. For example, iron might react with hydroxide molecules to produce positive ferrous hydroxide ($FeOH^+$). To calculate chemical concentrations during or after chemical reactions, chemical rates and chemical equilibrium constants may be used.

Typically, there are three ways to insert chemical reactions in the model:

- As a source / sink term in the conservation of mass equation within the thermal hydraulic model.
- As an equilibrium constant equation in the thermal hydraulic model.
- As an equilibrium constant system of equations outside of the thermal hydraulic model.

3.2.1 Source / Sink Term in the Thermal Hydraulic Model

We take an example to understand how to incorporate the chemical reaction in the thermal hydraulic model as a source / sink term. First, consider the equilibrium reaction for the heterogeneous reaction:

$$Fe^{2+} + 2OH^{-} \longleftrightarrow Fe(OH)_2 \qquad \textbf{Eq. 3-63}$$

This equilibrium may be broken into its forward and reverse reactions.

$$Fe^{2+} + 2OH^{-} \xrightarrow{k_f} Fe(OH)_2 \qquad \textbf{Eq. 3-64}$$

$$Fe(OH)_2 \xrightarrow{k_b} Fe^{2+} + 2OH^{-} \qquad \textbf{Eq. 3-65}$$

The source / sink term S_i for the species Fe^{2+} is the rate of creation less the rate of consumption of the species Fe^{2+}. It can be expressed as Equation 3-66 using the rate constants of the forward and reverse reactions.

$$S_i = -k_f [Fe^{2+}][OH^{-}]^2 + k_b \qquad \textbf{Eq. 3-66}$$

In most cases, the problem is that rate constants are only occasionally available, whereas equilibrium constants are readily found in standard reference sources. To deal with this difficulty, Chun makes the assumption that chemical rates of reaction are much faster than mass transport processes (i.e. diffusion, electromigration, and convection).[7]

The ratio of the rate constants equals the equilibrium constant according to Equation 3-67. Therefore, by assuming one of the rate constants and knowing the equilibrium constant, the other rate constant is determined. There are many methods used to estimate the rate constants. However, these constants must be selected so as to satisfy the assumption that these rates are much faster than those for mass transport. A lower limit on the order of unity is reasonable for k_f or k_b.

$$K_{eq} = \frac{k_f}{k_b} \qquad \textbf{Eq. 3-67}$$

3.2.2 Equilibrium Constant Equations in the Thermal Hydraulic Model

If one doesn't want to guess the chemical rate constants, then writing the conservation of chemical elements gives relations between the chemical source / sink terms. For example, consider the system of three elements: Fe, O, and H, along with the species: Fe^{2+}, $FeOH^+$, $Fe(OH)^2$, H^+, OH-, and H_2O. Using the conservation of elements for Fe, O, and H yields Equations 3-68 through 3-70.

$$\text{Conservation of Fe :} \quad S_{Fe^{2+}} + S_{FeOH} + S_{Fe(OH)2} = 0 \qquad \textbf{Eq. 3-68}$$

$$\text{Conservation of O :} \quad S_{FeOH^+} + 2S_{Fe(OH)2} + S_{OH^-} + S_{H2O} = 0 \qquad \textbf{Eq. 3-69}$$

$$\text{Conservation of H :} \quad S_{FeOH^+} + 2S_{Fe(OH)2} + S_H + S_{OH^-} + 2S_{H2O} = 0 \qquad \textbf{Eq. 3-70}$$

If the system of thermal hydraulic equations is written for the ions Fe^{2+}, OH^-, H^+, and $FeOH^+$, then combining the equations above yields Equation 3-71.

$$2S_{Fe^{2+}} + S_{FeOH^+} + S_{H^+} - S_{OH^-} = 0 \qquad \textbf{Eq. 3-71}$$

The system of mass conservation equations for the four ions becomes Equations 3-72 through 3-75, where S is the saturation. Each of source / sink terms in Equation 3-71 is replaced by the corresponding thermal hydraulic equation (Equations 3-55 and 3-56).

$$\begin{aligned} &2\varepsilon S \frac{\partial C_{Fe^{2+}}}{\partial t} + 2\nabla C_{Fe^{2+}} V_{Fe^{2+}} + \varepsilon S \frac{\partial C_{FeOH^+}}{\partial t} + \nabla C_{FeOH^+} V_{FeOH^+} + \varepsilon S \frac{\partial C_{H^+}}{\partial t} \\ &+ \nabla C_{H^+} V_{H^+} - \varepsilon S \frac{\partial C_{OH^-}}{\partial t} - \nabla C_{OH^-} V_{OH^-} = 2S_{Fe^{2+}} + S_{FeOH^+} + S_{H^+} - S_{OH^-} = 0 \end{aligned} \qquad \textbf{Eq. 3-72}$$

$$C_{H^+} \bullet C_{OH^-} = K_W \qquad \textbf{Eq. 3-73}$$

$$C_{Fe^{2+}} \bullet \left(C_{OH^-}\right)^2 = K_2 \qquad \textbf{Eq. 3-74}$$

$$\frac{C_{FeOH^+}}{C_{Fe^{2+}} \left(C_{OH^-}\right)} = K_1 \qquad \textbf{Eq. 3-75}$$

Whereas in the mass conservation equations for each of the four ions there was a source / sink term, the new system of equations, they have been eliminated using Equation 3-71.

As in the previous method, the solution is always assumed to be at equilibrium. This method runs into difficulty in the case where precipitate is not present. In this case, Equation 3-74 is no longer valid, and the number of unknowns is still the same, therefore there are more unknowns than equations and the system can not be solved.

3.2.3 Equilibrium Constant Equations Outside of the Thermodynamic Model

Since the time constants for chemical reactions are much smaller than those for transport processes, thermal hydraulics and chemistry may be solved separately in the model. This allows the thermal hydraulics to predict the concentrations of the ions: H^+, OH^-, Fe^{2+}, and $FeOH^+$ as a function of the linear depth in the crevice, x without including any chemical reaction.

The concentration of each element is determined at each value of x and the corresponding system of chemical equilibrium equations is solved. This process is illustrated by Figure 3-12.

Equations 3-76 through 3-80 describe the chemical equilibrium problem for the same system as in Section 3.1.2 in the case where $FeOH_2$ does not precipitate. The system contains five equations and five unknowns : $C_{FE}{}^{2+}$, $C_{FeOH}{}^{+}$, C_{FeOH2}, $C_{H}{}^{+}$ and $C_{OH}{}^{-}$.

Equations 3-81 through 3-84 describe the chemical equilibrium problem for the same system as in Section 3.1.2 in the case where $FeOH_2$ precipitates. The system contains four equations and four unknowns : $C_{FE}{}^{2+}$, $C_{FeOH}{}^{+}$, $C_{H}{}^{+}$ and $C_{OH}{}^{-}$. Concentrations determined by the thermal hydraulic model are denoted by the subscript “Thermo.”

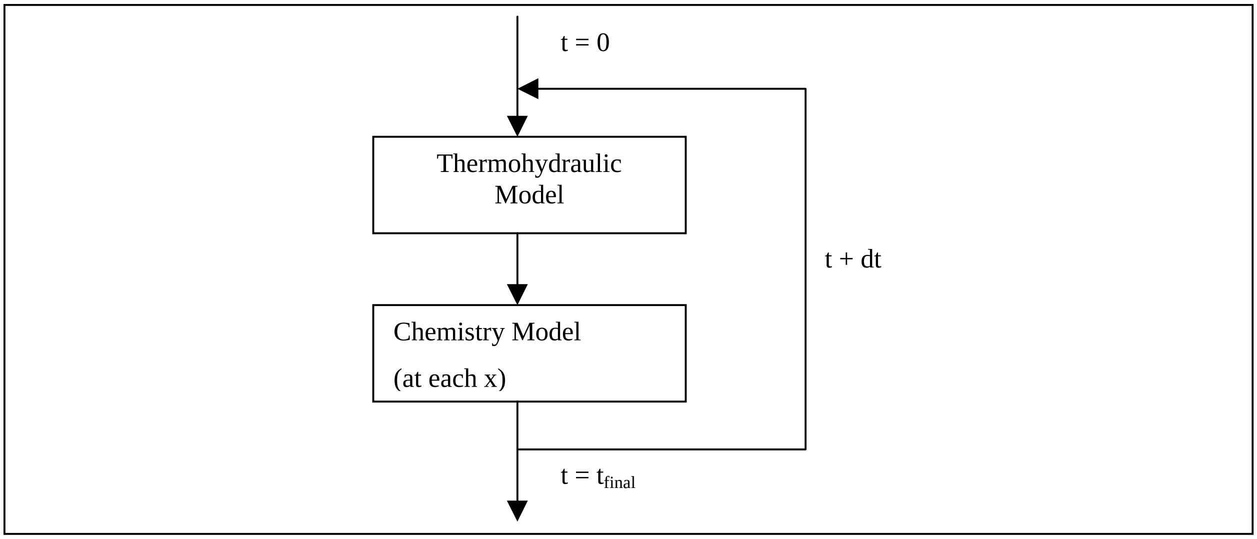


Figure 3-12
Procedure for Solving Chemical Equilibium Concentrations

$$C_{H^+} \bullet C_{OH^-} = K_W \qquad \textbf{Eq. 3-76}$$

$$\frac{C_{FeOH^+}}{C_{Fe^{2+}} \bullet C_{OH^-}} = K_1 \qquad \textbf{Eq. 3-77}$$

$$C_{Fe^{2+}} \left(C_{OH^-}\right)^2 = K_2 \qquad \textbf{Eq. 3-78}$$

$$C_{Fe^{2+}} + C_{FeOH^+} + C_{Fe(OH)_2} = C_{(Fe^{2+})Thermo} + C_{(FeOH^+)Thermo} \qquad \textbf{Eq. 3-79}$$

$$2C_{Fe^{2+}} + C_{FeOH^+} + C_{H^+} - C_{OH^-} = 0 \text{ (Electroneutrality)} \qquad \textbf{Eq. 3-80}$$

$$C_{H^+} \bullet C_{OH^-} = K_W \qquad \textbf{Eq. 3-81}$$

$$\frac{C_{FeOH^+}}{C_{Fe^{2+}} \bullet C_{OH^-}} = K_1 \qquad \textbf{Eq. 3-82}$$

$$C_{Fe^{2+}} + C_{FeOH^+} = C_{(Fe^{2+})Thermo} + C_{(FeOH^+)Thermo} \qquad \textbf{Eq. 3-83}$$

$$2C_{Fe^{2+}} + C_{FeOH^+} + C_{H^+} - C_{OH^-} = 0 \text{ (Electroneutrality)} \qquad \textbf{Eq. 3-84}$$

3.3 Electrochemical Modeling

In addition to chemical reactions occurring in the crevice solution, electrochemical reactions (i.e. dissolution of a metal) are occurring with the ions and electrons in solution. These reactions are responsible for variations in the electrochemical potential. Like the chemical reactions discussed in Section 3.2, they are assumed to proceed at much higher rates of reaction than the thermal hydraulic transport processes.

Before discussing how to calculate the electrode potential in solution, a clarification of the definition of potentials is necessary. An electrostatic or electric potential Φ, in units of Volts, is the potential commonly referred to in the study of electromagnetism. It appears as the driving force for electromigration in an electrolyte. An electrostatic potential gradient can be set up by a charge distribution of ions (Poisson’s equation) or external polarization.

The potential that is measured in practice is the electrode (electrochemical) potential, E, in Volts, measured between the corroding metals and a reference electrode. An electrode potential is a measure of the collective electrochemical potentials, μ_i, of all the ions in the electrolyte (due to chemical and electrostatic potential) and the metal.

The potential being calculated in the model is the electrochemical potential. An important assumption made in this study is that the difference between electrochemical potentials at two different locations in the electrolyte is the same but opposite in sign to the difference in electrostatic potentials. Therefore, it is easy to switch from one potential to the other, as they differ by a constant and by sign. Equation 3-85 shows the relations between the different types of potentials.

$$E = A - \Phi \qquad \textbf{Eq. 3-85}$$

There are two ways to calculate the potential. They are both based on the electroneutrality. Either the calculation is integrated in the thermal hydraulic chemistry model or it is independent.

3.3.1 Integrated Electrochemical Potential Calculation

Since the potential is dependent on the chemical composition, the calculation of potential should be integrated in the thermal hydraulic model only if the chemistry is integrated as well. The electroneutrality equation is added to the system of equations to determine the one new unknown, Φ. Additionally, the corresponding electrochemical reaction rates are added to each sink / source term.

Each electrochemical reaction is characterized by three parameters: the reversible potential E_e, the exchange current density I_o, and the Tafel slope α. Equation 3-86 gives the current density, I, in terms of these parameters. In the model, I is defined as positive for anodic reaction and negative for cathodic reaction.

$$I = I_0 \exp \frac{\alpha F}{RT}(E - E_e) \qquad \textbf{Eq. 3-86}$$

$$aA + bB \longrightarrow cC + dD \qquad \textbf{Eq. 3-87}$$

For the type of general electrochemical reaction given in Equation 3-87, the exchange current density, I_0, depends on the chemical concentrations of the reactants A and B. Once the current density is known, the flux is calculated using Faraday’s law, expressed as Equation 3-88.

$$J_e = \frac{I}{nF} \qquad \textbf{Eq. 3-88}$$

J_e: Flux for the electrochemical reaction (mol/cm^{2}s)
n: Net charge transferred for electrochemical reaction
F: Faraday constant

The net charge transferred in a reaction is readily determined by the number of electrons involved in an electrochemical reaction. If electrons appear among the reactants, n is negative (cathodic). Conversely, if electrons appear among the products, n is positive (anodic). Thus, when combined with the sign convention used for currents, J_e is always a positive quantity.

The corresponding sink / source term used in the continuity of species is expressed by Equation 3-89. In this equation, the width of the crevice is denoted by w.

$$S_i = \pm \frac{I_0 \exp\left\{ \frac{\alpha F}{RT} \left(E - E^e \right) \right\}}{nFw} \qquad \textbf{Eq. 3-89}$$

3.3.2 Separated Electrochemical Potential Calculation

It is possible to separately calculate potential since electrochemical reactions are much faster than transport processes. The problem of solving potential independently is that the potential distribution is used to calculate the sink / source term and appears in the electromigration term in the thermal hydraulic system. With this in mind, two possible methods to solve thermal hydraulics, chemistry, and electrochemistry are outlined in Figure 3-13.

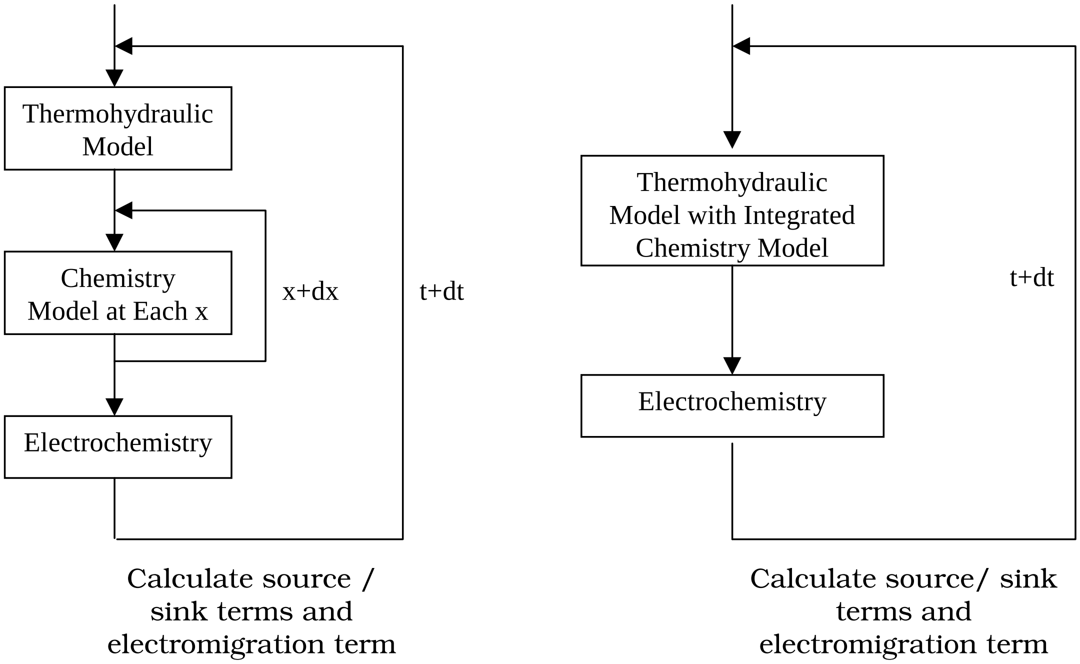


Figure 3-13
Two Alternatives for a Separated Electrochemistry Model

Initially it is assumed that the crevice is filled with the bulk solution. As a result, the initial crevice chemistry is known, and concentrations are uniform throughout the crevice. For the first time step, the potential is approximated to be uniform and equal to the mouth potential. The source / sink terms due to electrochemical reactions are calculated, and the thermal hydraulic and chemical systems are solved. For an electrochemical reaction, the rates of the reactions are known which eliminates the difficulties with chemical reactions discussed earlier.

Once the new profiles of concentration are known, the electrochemical potential is calculated for the next time step.

The calculation of electrochemical potential distribution is carried out by a method developed by Chun.[7] Chun’s model is based on electric current theory. There are several types of current in the crevice. Current, viewed as the flow of charge, can be obtained from the flux of charged species. This is illustrated in Equation 3-90.

$$I = F \sum z_i J_i$$ **Eq. 3-90**

J_i may also be expressed with Equation 3-91.

$$\varepsilon S \frac{\partial C_i}{\partial t} = -\nabla J_i + S_i$$ **Eq. 3-91**

The last term vanishes after the charge neutrality condition (Equation 3-92) and simplifies Equation 3-90 to yield Equation 3-93.

$$\sum z_i C_i = 0$$ **Eq. 3-92**

$$I = -F \sum z_i D_i \nabla C_i - F^2 \sum z_i{}^2 C_i \frac{D_i}{RT} \nabla \phi$$ **Eq. 3-93**

Therefore, current has two terms: current due to diffusion and current due to electromigration. The convection flux constitutes no current.

Another current arising from the Butler-Volmer equation is the current of an electrochemical reaction, expressed as Equation 3-94.

$$I_{BV} = I_0 \exp\left\{ \frac{\alpha I}{RT} \left(E - E^e \right) \right\}$$ **Eq. 3-94**

While electromigration current depends on electrostatic potentials, diffusion does not. Therefore, the electromigration term, $-K\nabla\phi$, with K expressed by Equation 3-95, can be simply modeled as a resistor as shown in Figure 3-14.

$$K = F^2 \sum z_i{}^2 C_i \frac{D_i}{RT}$$ **Eq. 3-95**

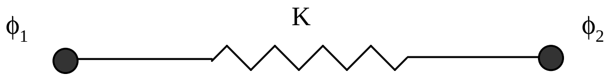


Figure 3-14
Circuit Equivalent for Electromigration Term

The diffusion term is modeled as an independent current source (Equation 3-96), whose circuit symbol is seen in Figure 3-15

$$I_{diff} = -F \sum z_i D_i \nabla C_i$$ **Eq. 3-96**

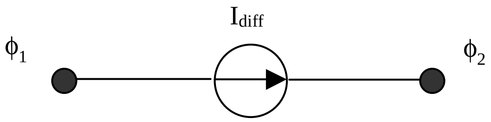


Figure 3-15
Circuit Equivalent for Diffusion Term

Putting these together, the current due to the combined transport by electromigration and diffusion is modeled as a parallel combination of a resistor and an independent current source, as illustrated in Figure 3-16.

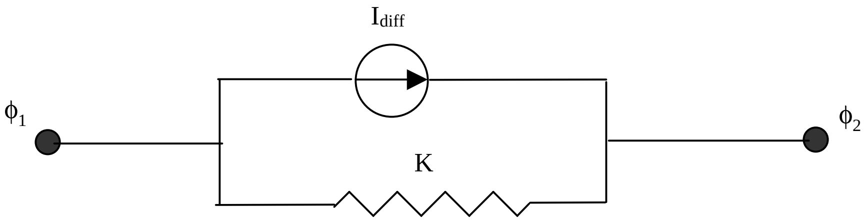


Figure 3-16
Circuit Equivalent for Combined Electromigration and Diffusion Term

The current, I_{BV}, from the Butler-Volmer equation can be modeled as a nonlinear dependent current source whose circuit equivalent is illustrated in Figure 3-17.

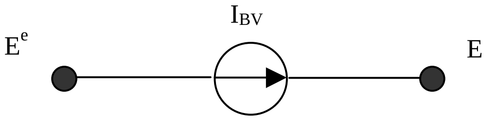


Figure 3-17
Circuit Equivalent for Butler-Volmer Current

3.3.3 Modeling Free Corrosion

With these circuit components, an equivalent circuit for any crevice chemistry condition can be constructed under free corrosion, show in Figure 3-18, or under external polarization, shown in Figure 3-19, for a crevice. Free corrosion refers to a case where the crevice is corroding independently from the external environment. The cathodic current inside the crevice determines the electrochemical potential, and there is no current flowing from the crevice to the external environment, and vice versa. External polarization refers to a case where the potential at the mouth is fixed by the external environment. As a result there is typically a current between the crevice and the external environment.

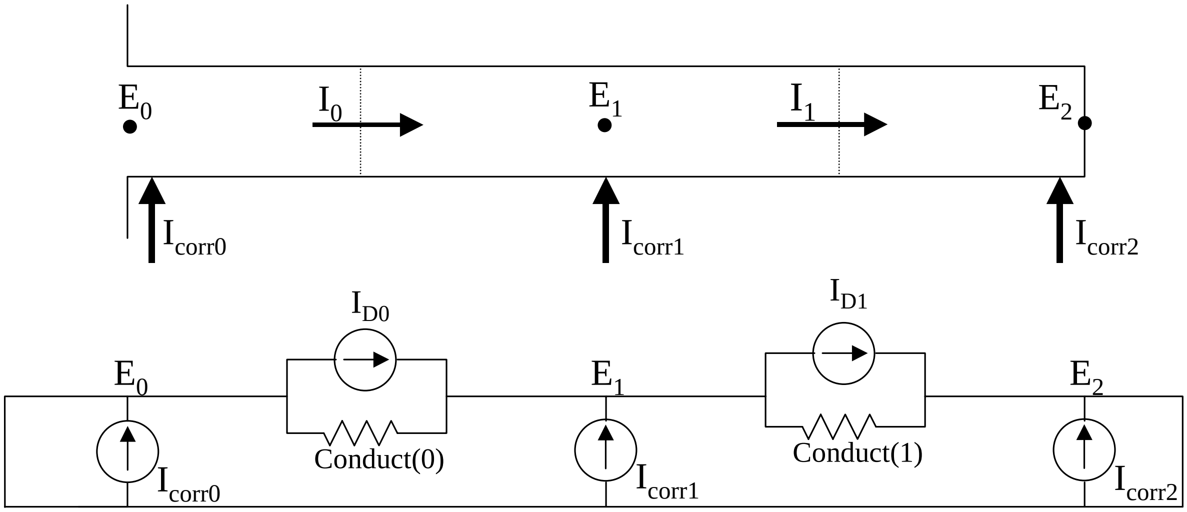


Figure 3-18
Schematic of the crevice under free corrosion

In Chun’s circuit analysis, all currents are considered positive. The crevice is divided into elementary volumes. Mesh points are at the center of each volume. Although potentials are defined at each mesh point, currents are defined at the boundary of two neighboring mesh points. The conductivity is calculated with an average of concentrations at two neighboring mesh points.

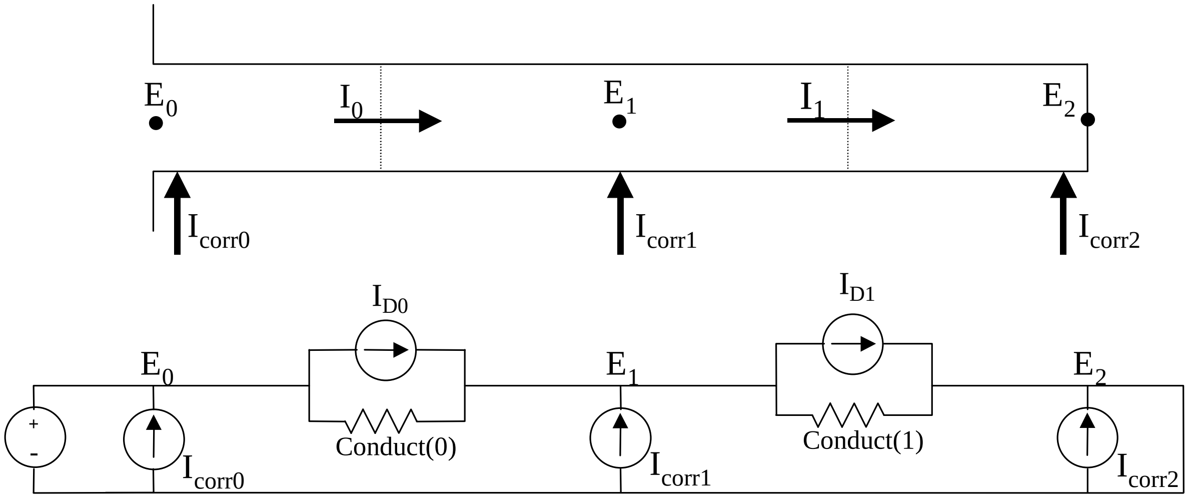
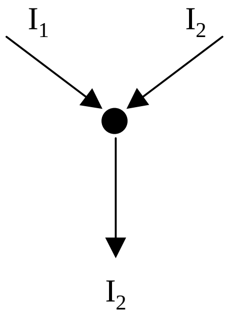


Figure 3-19
Schematic of the crevice under external polarisation E_0 at the mouth.

This circuit may be solved for the potentials at all mesh points. This is accomplished by using Kirchoff’s Current Law, which states that the sum of all currents entering or leaving a node is zero. An illustrative example of Kirchoff’s Law is shown in Figure 3-20.



$$I_1 + I_2 - I_3 = 0$$

Figure 3-20
Kirchoff's Current Law

Equations 3-97 through 3-100 give the system of current conservation equations resulting for free corrosion. Wall current, I_w, values are obtained by calculating the difference between anodic and cathodic currents resulting from reactions at the wall, illustrated in Equation 3-97.

$$I_{Wo} = \sum \text{Anodic–cathodic reactions at the wall} \qquad \textbf{Eq. 3-97}$$

$$I_{Wo} + K_0(E_0\text{-}E_1) - I_{Do} = 0 \qquad \textbf{Eq. 3-98}$$

$$I_{W1} - K_0(E_0\text{-}E_1) + K_1(E_1\text{-}E_2) + ID_0 - ID_1 = 0 \qquad \textbf{Eq. 3-99}$$

$$I_{W2} + K_1(E_1\text{-}E_2) + I_{D1} = 0 \qquad \textbf{Eq. 3-100}$$

This system consists of three equations (3-98, 3-99, and 3-100) and three unknowns (E_0, E_1, E_2). The solution of this system yields the electrochemical potential distribution in the crevice.

3.3.4 External Polarization

In the case of external polarization, the electrochemical potential at the crevice mouth is fixed by the external environment. As a result, E_0 is a known value, and the system of current conservation equations becomes Equations 3-101 and 3-102, which is equivalent to the system of equations used for free corrosion, minus Equation 3-98.

$$I_{W1} - K_0(E_0\text{-}E_1) + K_1(E_1\text{-}E_2) + ID_0 - ID_1 = 0 \qquad \textbf{Eq. 3-101}$$

$$I_{W2} + K_1(E_1\text{-}E_2) + I_{D1} = 0 \qquad \textbf{Eq. 3-102}$$

If the crevice is externally polarized, there may be a net current emanating from the crevice mouth. The external current can be found by writing the equation for Kirchoff's law at the first mesh point.

Once the chemistry is known, the diffusion currents, the conductivities, and the exchange current densities may be calculated and the system solved to get E at each mesh point. That potential profile may then be used in the next time step of the thermodynamic modeling.

With Chun's model, one must be careful to convert all current densities to currents. Currents, not current densities, are added together in his modeling.

4
COMPARISON OF MACDONALD'S AND THE NEW MODEL

In Chapter 3, the requirements for a model that would effectively describe thermal hydraulic behavior of a two-phase water solution in a porous media were discussed. This model should take into account chemical interactions between ions in solution and the electrochemical processes present in the crevice. Also, various options and methods to deal with the three different aspects of this problem were outlined.

The previous work by MacDonald mentioned in Chapter 2 resulted in one model that attempted to fulfill these requirements.[19] This model is referred to in this thesis as "MacDonald's Model".

A new model has been developed by the author in order to meet these requirements as well. The following chapter outlines the similarities and differences between both models. Additionally, it explains which of the methods described in Chapter 3 were used in each model.

4.1 MacDonald's Model

MacDonald's model calculates the concentrations of H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$, the liquid velocity, and the electrochemical potential in the crevice as a function of x and t.

MacDonald's model does not integrate all the thermal hydraulics, chemistry, and the electrochemistry in a single system of equations. Initially, it is assumed that the crevice is filled with the bulk solution. The temperature of the fluid in the crevice is uniform and equals the bulk saturation temperature. The velocity and saturation profiles are integrated based on Equations 4-1 and 4-2, with conditions $V_L = 0$ at the middle of the crevice, and $S=S_0$ at the mouth.

$$\frac{\partial V_L}{\partial x} = -\frac{2\pi H r_{sg}\left(T_p - T_{S0} - BPE * C_{Na^+}\right)}{A_c \rho_l h_{fg}} \qquad \textbf{Eq. 4-1}$$

$$\frac{\partial S}{\partial x} = -\frac{\mu_1 V_L}{(DP_c DS) * k}\left(\frac{\mu_v \rho_l}{\mu_l \rho_v} * \frac{1}{1-S} + \frac{1}{S^3}\right) \qquad \textbf{Eq. 4-2}$$

The model then solves the liquid velocity differential equation and the continuity equations of species in which the source / sink terms have been eliminated and the chemical equilibrium equations inserted and the electroneutrality added as well. Once the concentrations are known, the saturation profile is recalculated.

There are three chemical reactions included in the model, listed below as Equations 4-3 through 4-5.

$$H^+ + OH^- \longleftrightarrow H_2O$$ **Eq. 4-3**

$$Fe^{2+} + OH^- \longleftrightarrow FeOH^+$$ **Eq. 4-4**

$$Fe^{2+} + 2OH^- \longleftrightarrow Fe(OH)_2$$ **Eq. 4-5**

There are three electrochemical equations considered in MacDonald's model:

$$H_2O + e^- \longrightarrow OH^- + H^+$$ **Eq. 4-6**

$$H^+ + e^- \longrightarrow H^+$$ **Eq. 4-7**

$$Fe \longrightarrow Fe^{2+} + 2e^-$$ **Eq. 4-8**

The current densities in the model are expressed by Equations 4-9 through 4-11. The cathodic current densities are calculated with the Tafel expression. The equation for corrosion current is derived from experimental data and is only a function of the chemistry of the solution and not a function of the electrochemical potential.

The variation of corrosion current with pH is shown in Figure 4-1. Corrosion current is at a minimum when the pH is equal to 0, and increases rapidly as the solution becomes either acidic or basic.

$$I_{Cathode-H_2O} = (0.124 \times 10^7)\exp\left(-\frac{0.5F}{RT}E\right)$$ **Eq. 4-9**

$$I_{Cathode-H^+} = (0.906 \times 10^4)\exp\left(-\frac{0.5F}{RT}E\right)$$ **Eq. 4-10**

$$I_{CORR} = 10^{\left(-2.8448 + 0.4388\ pH - 0.8473\ pH^2 + 0.1977\ pH^3 - 0.0178\ pH^4 + (5.678 \times 10^{-4})\ pH^5\right)}$$ **Eq. 4-11**

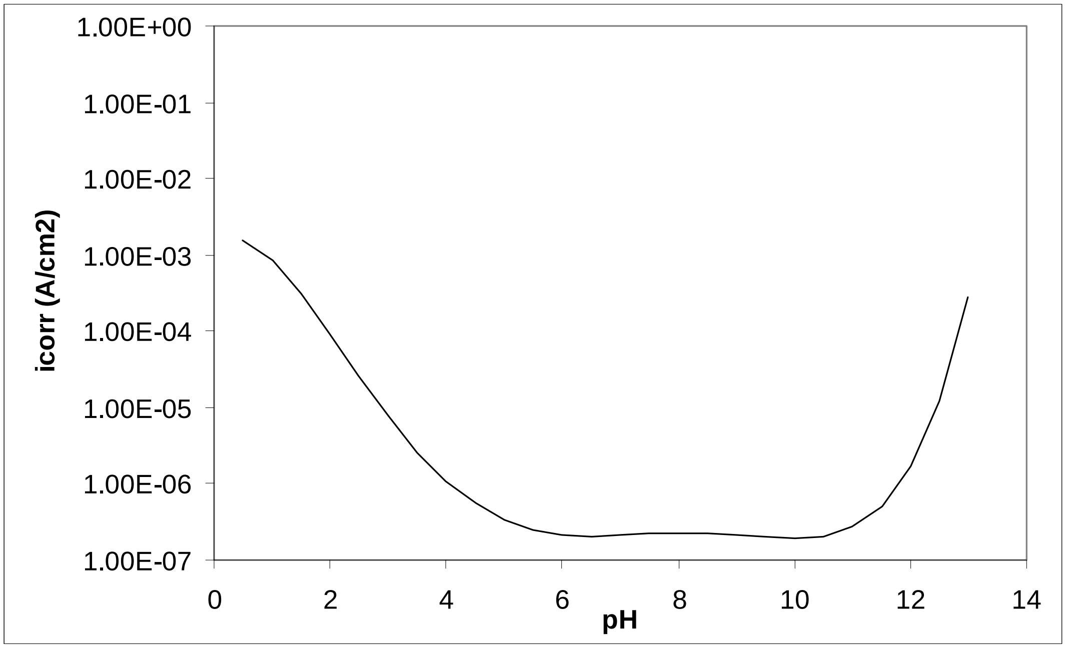


Figure 4-1
Variation of the corrosion current density as a function of the pH of the solution.

The system is solved for the concentrations of H^+, OH^-, Fe^{2+}, $FeOH^+$, Na^+ and Cl^- and appears as Equations 4-12 through 4.19.

$$
\begin{aligned}
&2\left\{-\frac{C_{Fe^{2+}}(t)S(t)-C_{Fe^{2+}}(t-1)S(t-1)}{\Delta t}+FRD_{Fe^{2+}}\frac{\partial}{\partial R}\left(C_{Fe^{2+}}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{Fe^{2+}}}{\partial x}+D_{Fe^{2+}}\frac{\partial S\frac{\partial C_{Fe^{2+}}}{\partial x}}{\partial x}\right\}\\
&+\left\{-\frac{C_{FeOH^+}(t)S(t)-C_{FeOH^+}(t-1)S(t-1)}{\Delta t}+FRD_{FeOH^+}\frac{\partial}{\partial R}\left(C_{FeOH^+}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{FeOH^+}}{\partial x}+D_{FeOH^+}\frac{\partial S\frac{\partial C_{FeOH^+}}{\partial x}}{\partial x}\right\}\\
&+\left\{-\frac{C_{H^+}(t)S(t)-C_{H^+}(t-1)S(t-1)}{\Delta t}+FRD_{H^+}\frac{\partial}{\partial R}\left(C_{H^+}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{H^+}}{\partial x}+D_{H^+}\frac{\partial S\frac{\partial C_{H^+}}{\partial x}}{\partial x}\right\}\\
&-\left\{-\frac{C_{OH^-}(t)S(t)-C_{OH^-}(t-1)S(t-1)}{\Delta t}+FRD_{OH^-}\frac{\partial}{\partial R}\left(C_{OH^-}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{OH^-}}{\partial x}+D_{OH^-}\frac{\partial S\frac{\partial C_{OH^-}}{\partial x}}{\partial x}\right\}\\
&+\frac{I_{CORR}}{w}+\frac{I_{H_2O}}{w}\exp\left\{-FRD_{H_2O}\left(E_{CORR}-\phi\right)\right\}+\frac{I_{OH^+}}{w}\exp\left\{-FRD_{H^+}\left(E_{CORR}-\phi\right)\right\}=0
\end{aligned}
$$

Eq. 4-12

$$-\frac{C_{Na^+}(t)S(t)-C_{Na^+}(t-1)S(t-1)}{\Delta t}+FRD_{Na^+}\frac{\partial}{\partial R}\left(C_{Na^+}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{Na^+}}{\partial x}+D_{Na^+}\frac{\partial S\frac{\partial C_{Na^+}}{\partial x}}{\partial x}=0$$

Eq. 4-13

$$-\frac{C_{Cl^-}(t)S(t)-C_{Cl^-}(t-1)S(t-1)}{\Delta t}+FRD_{Cl^-}\frac{\partial}{\partial R}\left(C_{Cl^-}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{Cl^-}}{\partial x}+D_{Cl^-}\frac{\partial S\frac{\partial C_{Cl^-}}{\partial x}}{\partial x}=0$$

Eq. 4-14

$$C_{Fe^{2+}}\left(C_{OH^-}\right)^2=K_s$$

Eq. 4-15

$$C_{Fe^{2+}}C_{OH^-}-K_1C_{FeOH^+}=0$$

Eq. 4-16

$$C_{H^+}C_{OH^-}-K_w=0$$

Eq. 4-17

$$2C_{Fe^{2+}}+C_{FeOH^+}+C_{Na^+}-C_{Cl^-}+C_{H^+}-C_{OH^-}=0$$

Eq. 4-18

$$\frac{\partial V_L}{\partial x}=-\frac{2\pi\mu r_{sq}\left(\Delta T-BPE*C_{Total}\right)}{\rho_L A_c h_{fg}}$$

Eq. 4-19

Initially, the model calculates the wetted length if a steam-blanketed region exists. Equation 4-20 provides a closed form expression to calculate the wetted length.

$$W_L=\sqrt{\frac{2(DP_cDS)k}{\left(\frac{2\pi Hr_{sg}\left(T_p-T_{S0}\right)}{A_c\rho_l h_{fg}}\mu\right)}\int_0^{S_0}\frac{dS}{\left(\frac{\mu_v\rho_l}{\mu_l\rho_v}*\frac{1}{1-S}+\frac{1}{S^3}\right)}}$$

Eq. 4-20

Following the initial calculation, it is assumed in the model that the wetted length is constant. This is not a good assumption since the wetted length increases as concentrated impurities diffuse towards the center of the crevice.

After the wetted length is calculated, the model solves the system of equations listed as Equations 4-12 through 4-19 for each time step. This system of equations is solved by a numerical method for boundary value problems which consist of sets of nonlinear, coupled, second-order differential equations. This numerical method, BAND(J), solves the system using Newman's method.

4.2 New Model

The MacDonald's model is facing a couple of problems. The wetted length is not recalculated as time passes. Precipitation is supposed. It is difficult to add or remove one chemical compound.

The convergence of the numerical method is rare since the system of equations is extremely inhomogeneous.

A new model has been created that solves those issues. The new model separates the thermal hydraulics, the chemical model, and the electrochemistry. At each time step, the following three tasks are carried out by the new model. First, the thermal hydraulic system is solved and the wetted length is calculated. Next, the system of chemical equations is solved independently from the thermal hydraulics at each value of x, shown in Section 3.2.3. Finally, once the chemistry is known, circuit analysis is used to calculate the electrochemical potential in Section 3.3.2.

The same chemical and electrochemical reactions than in MacDonald's model are included. The final system of equations solved in this model considers the species: Na^+, Cl^-, H^+, OH^-, Fe^{2+}, $FeOH^+$, and $Fe(OH)_2$. These equations are presented below as Equations 4-21 through 4-45.

For the first iteration, the user provides a "guess value" for the wetted length. If the saturation at the interface between the wetted region and the steam blanketed region is not negligible compared to 0.1, and calculations are converging, then the wetted length is incremented until the saturation at the interface converges within tolerance to zero.

Thermal hydraulic system:

$$\frac{\partial C_{H^+} V_{H^+}}{\partial x} = -\varepsilon S \frac{C_{H^+} - Cold_{H^+}}{TIMESTEP}$$ **Eq. 4-21**

$$\frac{\partial C_{H^+}}{\partial x} = \frac{(C_{H^+} V_l - C_{H^+} V_{H^+})}{D^0_{H^+}}$$ **Eq. 4-22**

$$\frac{\partial C_{OH^-} V_{OH^-}}{\partial x} = -\varepsilon S \frac{C_{OH^-} - Cold_{OH^-}}{TIMESTEP}$$ **Eq. 4-23**

$$\frac{\partial C_{OH^-}}{\partial x} = \frac{(C_{OH^-} V_l - C_{OH^-} V_{OH^-})}{D^0_{OH^-}}$$ **Eq. 4-24**

$$\frac{\partial C_{Na^+} V_{Na^+}}{\partial x} = -\varepsilon S \frac{C_{Na^+} - Cold_{Na^+}}{TIMESTEP}$$ **Eq. 4-25**

$$\frac{\partial C_{Na^+}}{\partial x} = \frac{(C_{Na^+} V_l - C_{Na^+} V_{Na^+})}{D^0_{Na^+}}$$ **Eq. 4-26**

$$\frac{\partial C_{Cl^-} V_{Cl^-}}{\partial x} = -\varepsilon S \frac{C_{Cl^-} - Cold_{Cl^-}}{TIMESTEP}$$ **Eq. 4-27**

$$\frac{\partial C_{Cl^-}}{\partial x} = \frac{(C_{Cl^-} V_l - C_{Cl^-} V_{Cl^-})}{D^0_{Cl^-}}$$ **Eq. 4-28**

$$\frac{\partial C_{Fe^{2+}} V_{Fe^{2+}}}{\partial x} = \frac{Icorr}{w} - \varepsilon S \frac{C_{Fe^{2+}} - Cold_{Fe^{2+}}}{TIMESTEP}$$

Eq. 4-29

$$\frac{\partial C_{Fe^{2+}}}{\partial x} = \frac{(C_{Fe^{2+}} V_l - C_{Fe^{2+}} V_{Fe^{2+}})}{D^0_{Fe^{2+}}}$$

Eq. 4-30

$$\frac{\partial C_{FeOH^+} V_{FeOH^+}}{\partial x} = -\varepsilon S \frac{C_{FeOH^+} - Cold_{FeOH^+}}{\partial t}$$

Eq. 4-31

$$\frac{\partial C_{FeOH^+}}{\partial x} = \frac{C_{FeOH^+} V_l - C_{FeOH^+} V_{FeOH^+}}{D^0_{FeOH^+}}$$

Eq. 4-32

$$\frac{\partial V_l}{\partial x} = -\frac{2\pi (H_0 + H_1 * S) r_{sg}}{h_{lv} \rho_l A_c} (T_p - T_{s0} - \sum_i ALPHA(i) * C_i)$$

Eq. 4-33

$$\frac{\partial S}{\partial x} = -\frac{1}{DPcDS} \left(\frac{\mu_V \rho_l}{kk_{rV} \rho_v} - \frac{\mu_l}{kk_{rl}} \right) V_l$$

Eq. 4-34

Chemical system:

If there is precipitation of $FeOH_2$:

$$C_{H^+} * C_{OH^-} = K_W$$

Eq. 4-35

$$2C_{Fe^{2+}} + C_{FeOH^+} + C_{H^+} + Na = C_{OH^-} + Cl$$

Eq. 4-36

$$C_{Fe^{2+}} * (C_{OH^-})^2 = K_2$$

Eq. 4-37

$$\frac{C_{FeOH^+}}{C_{Fe^{2+}} C_{OH^-}} = K_1$$

Eq. 4-38

$$C_{Fe^{2+}} + C_{FeOH^+} + C_{Fe(OH)_2} = \left(C_{Fe^{2+}} + C_{FeOH^+} \right)_{From\_Ther\,\mathrm{mod}\,ynamic\_System}$$

Eq. 4-39

If there is no precipitation of $FeOH_2$:

$$C_{H^+} * C_{OH^-} = K_W$$

Eq. 4-40

$$2C_{Fe^{2+}} + C_{FeOH^+} + C_{H^+} + Na = C_{OH^-} + Cl$$

Eq. 4-41

$$C_{Fe(OH)_2} = 10^{-42} \quad \text{(negligible)}$$

Eq. 4-42

$$\frac{C_{FeOH^+}}{C_{Fe^{2+}}C_{OH^-}} = K_1$$ **Eq. 4-43**

$$C_{Fe^{2+}} + C_{FeOH^+} = (C_{Fe^{2+}} + C_{FeOH^+})_{From\_Ther\,\mathrm{mod}\,ynamic\_System}$$ **Eq. 4-44**

Electrochemical system:

$$\frac{\partial E}{\partial x} = \frac{\dfrac{I_{CORR} - I_{Cathodic}}{wF} + 2D_{Fe^{2+}}\dfrac{\partial C_{Fe^{2+}}}{\partial x} + D_{H^+}\dfrac{\partial C_{H^+}}{\partial x} + D_{Na^+}\dfrac{\partial C_{Na^+}}{\partial x}}{4D_{Fe^{2+}} + D_{H^+} + D_{Na^+} + D_{FeOH^+} + D_{Cl^-} + D_{OH^-}} + \frac{D_{FeOH^+}\dfrac{\partial C_{FeOH^+}}{\partial x} - D_{Cl^-}\dfrac{\partial C_{Cl^-}}{\partial x} - D_{OH^-}\dfrac{\partial C_{OH^-}}{\partial x}}{4D_{Fe^{2+}} + D_{H^+} + D_{Na^+} + D_{FeOH^+} + D_{Cl^-} + D_{OH^-}}$$ **Eq. 4-45**

Numerically, each problem is solved with a different numerical method adapted to the type of equations. The thermodynamic system of equations is a set of nonlinear, first order, ordinary differential equations with boundary conditions at two points. It is solved by an IMSL method named BVPFD. The routine BVPFD is based on the subprogram PASVA3 by M. Lentini and V. Pereyra. The basic discretization is the trapezoidal rule over a nonuniform mesh. The mesh is chosen adaptively to make the local error approximately the same size everywhere. The resulting nonlinear algebraic system is solved by Newton's method with step control. The linearized system is solved by Gaussian elimination.

The chemical equilibrium equations are transformed into logarithmic equations and solved with a Newton-Rhapson method. The variables used to write the Taylor expansion and calculate the Jacobian for the Newton-Rhapson method is the logarithm of the concentration of the species. The LFTRG and LFSRG subroutines from the IMSL libraries solve the system using LU factorization.

The electrochemical system of equations is solved by the NEQNJ subroutine from the IMSL library. The subroutine solves a system of nonlinear equations. It uses a modification of M.J.D. Powell's hybrid algorithm. This algorithm is a variation of Newton's method, which takes the precaution to avoid large step sizes.

Three programs were created, each containing different parts of the new model. The first program 'Wetted length' solves the thermal hydraulic system only and calculates the wetted length. The second program 'Chemistry' solves the chemistry for a fully wetted crevice. The third program determines the potential distribution knowing the chemistry. Appendix 1 provides the reader with a fully exhaustive description of the model, the numerical method used and guide the reader through the steps from the equations in this chapter to the lines of the programs.

4.3 Similarities between the Two Models

Physically, the thermal hydraulic and chemistry equations employed in both models are the same, and shown in Equations 4-46 through 4-53. However, for the calculation of the potential, each model uses equations that look different. Although they appear different, they are actually the same, merely reformulated.

Starting from the continuity equations for the conservation of species used in MacDonald's model, Equations 4-46 through 4-48 are obtained.

$$
\begin{aligned}
&2\left\{\begin{array}{l}
-\dfrac{C_{Fe^{2+}}(t)S(t)-C_{Fe^{2+}}(t-1)S(t-1)}{\Delta t}+FRD_{Fe^{2+}}\dfrac{\partial}{\partial R}\left(C_{Fe^{2+}}S\dfrac{\partial\phi}{\partial x}\right)+\dfrac{\partial V_L C_{Fe^{2+}}}{\partial x}\\
+D_{Fe^{2+}}\dfrac{\partial S\dfrac{\partial C_{Fe^{2+}}}{\partial x}}{\partial x}
\end{array}\right\}\\
&+\left\{\begin{array}{l}
-\dfrac{C_{FeOH^{+}}(t)S(t)-C_{FeOH^{+}}(t-1)S(t-1)}{\Delta t}+FRD_{FeOH^{+}}\dfrac{\partial}{\partial R}\left(C_{FeOH^{+}}S\dfrac{\partial\phi}{\partial x}\right)\\
+\dfrac{\partial V_L C_{FeOH^{+}}}{\partial x}+D_{FeOH^{+}}\dfrac{\partial S\dfrac{\partial C_{FeOH^{+}}}{\partial x}}{\partial x}
\end{array}\right\}\\
&+\left\{\begin{array}{l}
-\dfrac{C_{H^{+}}(t)S(t)-C_{H^{+}}(t-1)S(t-1)}{\Delta t}+FRD_{H^{+}}\dfrac{\partial}{\partial R}\left(C_{H^{+}}S\dfrac{\partial\phi}{\partial x}\right)+\dfrac{\partial V_L C_{H^{+}}}{\partial x}\\
+D_{H^{+}}\dfrac{\partial S\dfrac{\partial C_{H^{+}}}{\partial x}}{\partial x}
\end{array}\right\}\\
&-\left\{\begin{array}{l}
-\dfrac{C_{OH^{-}}(t)S(t)-C_{OH^{-}}(t-1)S(t-1)}{\Delta t}+FRD_{OH^{-}}\dfrac{\partial}{\partial R}\left(C_{OH^{-}}S\dfrac{\partial\phi}{\partial x}\right)\\
+\dfrac{\partial V_L C_{OH^{-}}}{\partial x}+D_{OH^{-}}\dfrac{\partial S\dfrac{\partial C_{OH^{-}}}{\partial x}}{\partial x}
\end{array}\right\}\\
&+\frac{I_{CORR}}{w}+\frac{I_{H_2O}}{w}\exp\left\{-FRD_{H_2O}\left(E_{CORR}-\phi\right)\right\}+\frac{I_{OH^{+}}}{w}\exp\left\{-FRD_{H^{+}}\left(E_{CORR}-\phi\right)\right\}=0
\end{aligned}
$$

Eq. 4-46

$$
-\frac{C_{Na^{+}}(t)S(t)-C_{Na^{+}}(t-1)S(t-1)}{\Delta t}+FRD_{Na^{+}}\frac{\partial}{\partial R}\left(C_{Na^{+}}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{Na^{+}}}{\partial x}+D_{Na^{+}}\frac{\partial S\dfrac{\partial C_{Na^{+}}}{\partial x}}{\partial x}=0
$$

Eq. 4-47

$$
-\frac{C_{Cl^{-}}(t)S(t)-C_{Cl^{-}}(t-1)S(t-1)}{\Delta t}+FRD_{Cl^{-}}\frac{\partial}{\partial R}\left(C_{Cl^{-}}S\frac{\partial\phi}{\partial x}\right)+\frac{\partial V_L C_{Cl^{-}}}{\partial x}+D_{Cl^{-}}\frac{\partial S\dfrac{\partial C_{Cl^{-}}}{\partial x}}{\partial x}=0
$$

Eq. 4-48

Equation 4-48 is subtracted from the sum of Equations 4-46 and 4-47. This resulting expression is combined with the electroneutrality condition to yield Equation 4-51. Equations 4-49 and 4-50 define the conductivity, K, and diffusion current density, I_{diff}, in Equation 4-51.

$$K = F^2 \sum z_i^2 C_i \frac{D_i}{RT}$$ **Eq. 4-49**

$$I_{diff} = -F \sum z_i D_i \nabla C_i$$ **Eq. 4-50**

$$\frac{\partial}{\partial x}\left(K \frac{\partial \phi}{\partial x} \right) - \frac{\partial I_{DIFF}}{\partial x} + \frac{I_{CORR}}{w} - \frac{I_{H^+}}{w} = 0$$ **Eq. 4-51**

The electrostatic potential gradient is assumed to be of the same magnitude as the electrochemical potential but of opposite sign. Replacing the electrostatic potential gradient in Equation 4-51, Equation 4-52 is obtained in terms of the electrochemical potential.

$$\frac{\partial}{\partial x}\left(K \frac{\partial E}{\partial x} \right) + \frac{\partial I_{DIFF}}{\partial x} = \frac{I_{CORR} - I_{H^+}}{w}$$ **Eq. 4-52**

Equation 4-52 is equivalent to the discretized Equation 3-98 in the circuit analysis that appears in Section 3.3.2. Therefore, calculations of electrochemical potential both in MacDonald's and the new model are based on the same equations and approximations.

4.4 Conclusions

The three parts of the new model are equivalent to MacDonald's model except for:

- The thermal hydraulic part calculates the wetted length as a function of time.
- The chemical part checks whether or not there is precipitation, and then predicts the composition.
- The numerical method is adapted for each part, which makes solutions much more robust.
- Chemical species and electrochemical reactions can easily be added since the equations have not been lumped together as in MacDonald's model.

5

RESULTS AND DISCUSSION

This chapter is divided into three parts: results concerning the thermal hydraulic modeling (prediction of wetted length and concentration profiles), chemical modeling (effect of sodium to chloride on the pH), and electrochemical modeling (electrochemical potential profiles).

5.1 Thermal Hydraulic Modeling

The typical distribution of ions and the evolution of the wetted length are described in this section. Several parameter studies were performed and the program was benchmarked against experimental data.

5.1.1 Concentration profiles and evolution of the wetted length

If the crevice is highly permeable, the flow is not restricted enough to form a steam-blanketed region. The concentration profiles first become thermodynamically limited deep in the middle of the crevice. The mixture (steam/liquid water) consists of a phase rich in liquid throughout the entire crevice. The transient period is rather quick (≈ 1 day) for a high bulk water concentration of impurity (10 ppm) and rather slow (≈ 30 years) for a low bulk water concentration of impurity (1 ppb).

In operating power plants, the concentration process in crevices is always limited by shutdown of the plant. The crevice steam-blanketed region always exists. There is not enough time in continuous operation to fill the crevice. The steady state is never reached.

At steady state, the crevice is almost entirely filled with solution concentrated with impurity. The mouth of the crevice is not filled with impurities due to their diffusion into the bulk water, which contains a much lower level of impurity.

If the flow is restricted enough by the low permeability of the porous media, there is initially a steam-blanketed region in the center. The impurities concentrate at the interface between the liquid and the steam. As time passes, the concentrated solution diffuses into the steam-blanketed region towards the center, and the wetted length increases.

The liquid / steam mixture is rich in liquid at the mouth and very poor in liquid (1% liquid / 99% steam) at the interface with the steam-blanketed region (at x = wetted length). As the wetted length increases, the mixture, poor in liquid, migrates towards the center. When the liquid / steam mixture has replaced the steam-blanketed region, the fraction of the liquid in the mixture gradually increases until it is completely liquid. This liquid contains concentrated impurities. Once the center of the crevice consists of 100% rich liquid saturated with impurities, the impurities begin to accumulate closer to the mouth. This almost fills the entire crevice at steady state.

A typical series of profiles as a function of time, for a crevice with low permeability is shown in Figure 5-1 through Figure 5-3. To facilitate the visualization of what happens in the crevice over time, four diagrams were constructed from profiles at four different times. These diagrams appear in Figure 5-4.

Initially, the crevice is composed of a region rich in liquid and a steam-blanketed region. Between $t = t_1$ and $t = t_3$, the steam-blanketed region is slowly replaced by the liquid / vapor mixture containing concentrated impurities. At $t = t_3$, there is no longer a steam-blanketed region.

Between t_3 and t_5, the fraction of liquid in the liquid / vapor mixture steadily increases. At $t = t_5$, the mixture is composed almost entirely of liquid with a concentration of impurities.

Between t_5 and t_7, the impurities can not further replace the steam in the mixture in the center of the crevice, so they fill the top and bottom of it. At $t = t_7$, the entire crevice is almost filled with a liquid with a concentration of impurities.

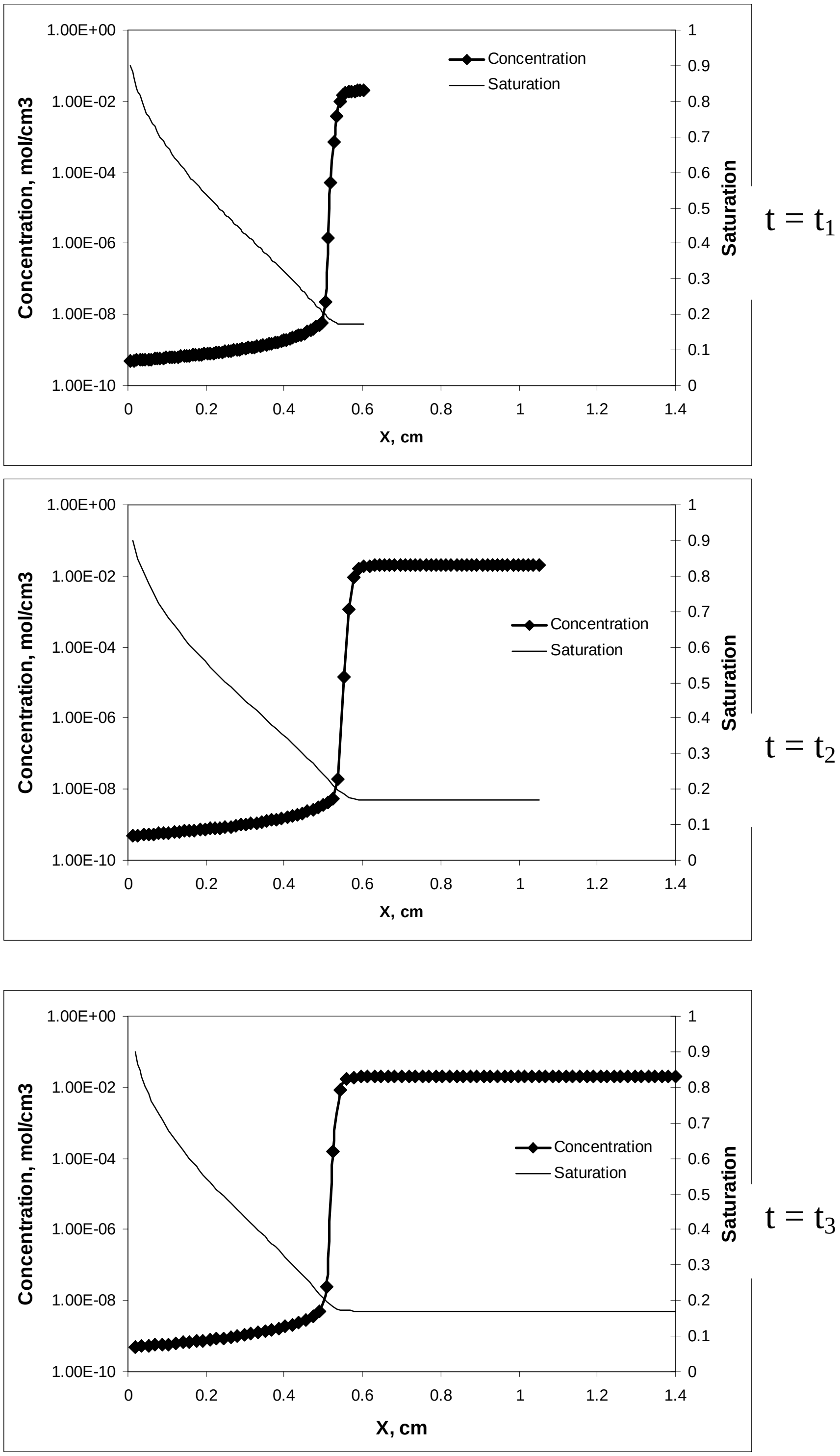


Figure 5-1
This describes phase one ($t_1 < t_2 < t_3$) of the concentration process. The wetted length increases from 0.602 cm at t_1 to 1.05 cm at t_2 to 1.40 cm at t_3 (crevice fully wetted). The concentration reaches the thermodynamic limit at the interface with the steam blanket region at t=t_1 and then slowly diffuses towards the center of the crevice. The center of the crevice is filled with a mixture of liquid and steam very poor in liquid (S~0.1).

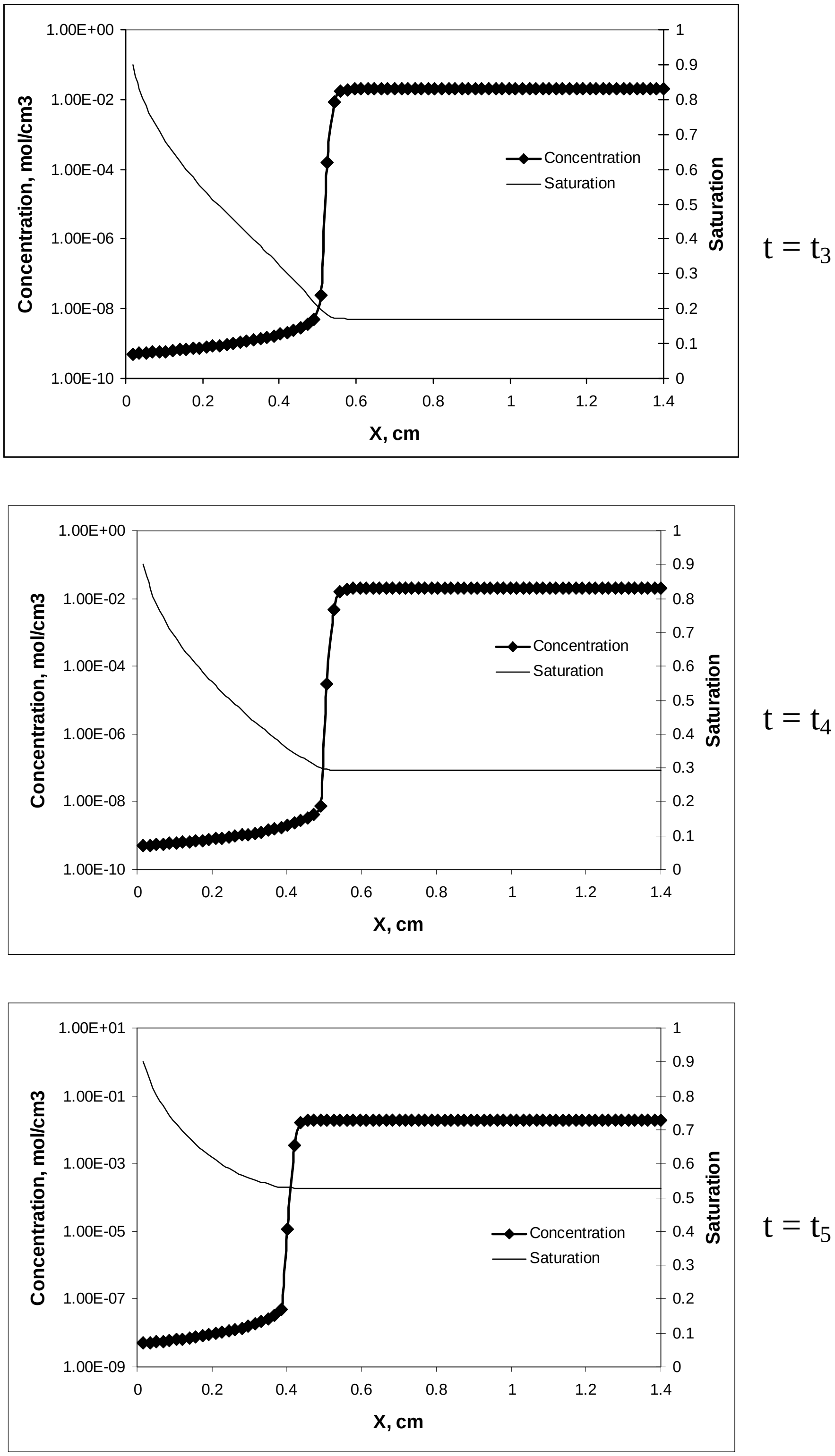


Figure 5-2
This is describing phase two ($t_3<t_4<t_5$) of the concentration process. The concentration profiles remain the same with time. The saturation increases with time from 0.15 to 0.52 at the center. The mixture becomes richer in liquid. This liquid is concentrated with impurities.

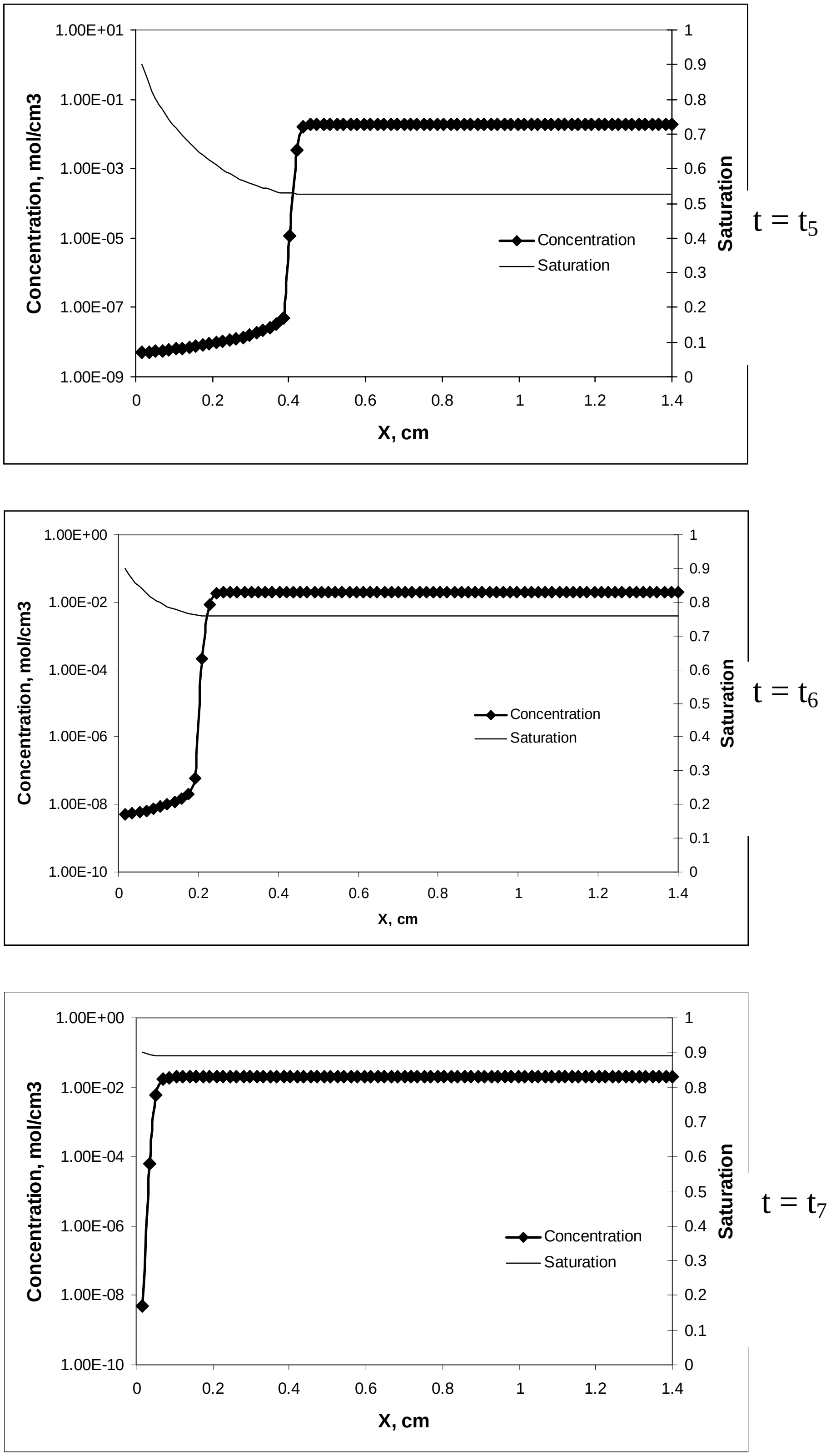
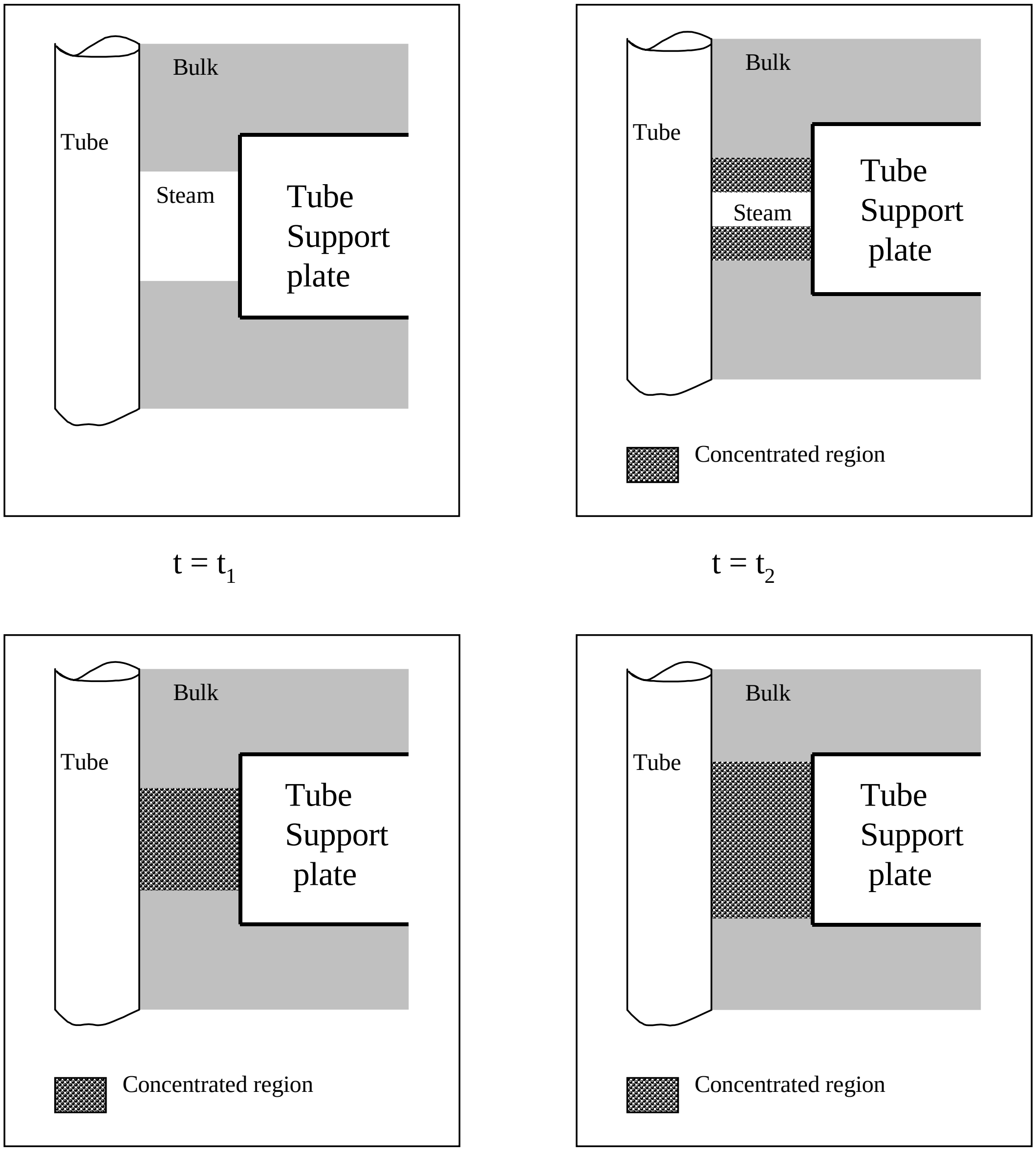


Figure 5-3
This is describing phase three (t_5<t_6<t_7). The mixture becomes richer in concentrated liquid and the concentrated solution fills the top and bottom of the crevice almost entirely.



$t = t_1$

$t = t_2$

$t = t_3$ to $t = t_5$

$t = t_7$

Figure 5-4

5.1.2 Mass of Impurity

The concentration profiles of sodium (for example) may be integrated so as to calculate the mass of sodium. The model was run at different bulk concentrations of sodium and the corresponding mass of impurity was calculated as a function of time. The mass obtained in the different runs is plotted in Figure 5-5. The mass of sodium predicted by the model is a linear function of the exposure, whether the crevice is fully wetted initially or if it has a steam-blanketed region. The exposure is defined as the product of the bulk concentration and the time of exposition. If the crevice is exposed to 0.1 ppb for 10 hours or to 1 ppb for 1 hour, the concentration distributions of the species are the same.

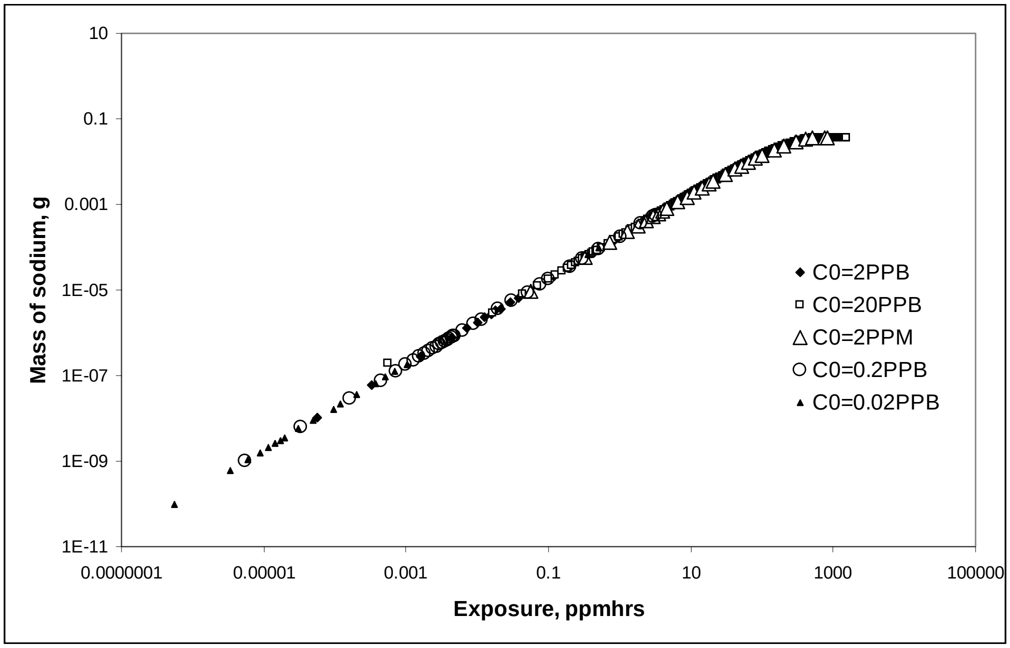


Figure 5-5
The mass of sodium predicted by the model for different bulk concentrations of sodium is plotted here. Since all the points are on the same line it is quite difficult to distinguish the five different runs.

5.1.3 Parametric studies

Millett studied the effect of several operating parameters in his thermal hydraulic modeling.[1] In this thesis, the parametric studies were done to look at the effect of poorly known physical variables such as the overall heat transfer coefficient, the intrinsic permeability of the porous media, and the slope of capillary pressure versus saturation DPcDS. This is important when the benchmarking this model to experimental results.

Since these physical constants have to be guessed, it is therefore crucial to know what their impacts on the results are. Also, the cross section area was varied to look at what happens in eccentric crevices. The values of the parameters used for the 4 case studies are summarized in Table 5-1.

Table 5-1
Values of the parameters used in the different parametric studies.

		Parametric Study			
		1	2	3	4
H, Heat Transfer Coefficient	J/(s-cm^2-K)	Between 0.05 and 1.05	0.3	0.08	0.255
K, Permeability	cm^2	0.5x10^{-11}	Between 0.5x10^{-11} and 1.0x10^{-9}	0.5x10^{-10}	0.5x10^{-11}
DPcDS, Capillary Pressure Slope	N/cm^2	–200	-50	Between –30 and –200	–200
Ac, Cross Sectional Area	cm^2	0.155	0.155	0.155	Between 0.05 and 1.05

5.1.3.1 Overall Heat Transfer Coefficient

The heat transfer coefficient is defined in the model as the ratio of the energy used to vaporize liquid to the temperature gradient between the tube wall and the solution. Heat transfer from the tube to the pore solution depends on the structure of the matrix and the thermal conductivity of each phase.

One of the most difficult aspects of the analysis of heat conduction through a porous medium is the structural modeling. H is an empirical parameter. It can not be calculated. In his previous experiment on sludge piles, Baum found an H of 0.255 J/s/cm^2/K. Therefore, H was varied around this reference, from 0.05 to 1.05 J/s/cm^2/K. The influence of H on the wetted length and the mass of sodium is plotted in Figure 5-6 and 5-7.

As H increases, the evaporation process is more significant, therefore the wetted length is initially smaller. More steam is produced, therefore more liquid containing impurities is drawn into the crevice. The process of concentration is faster, and the slope of mass versus exposure is steeper. Also the increase of wetted length is faster.

5.1.3.2 Permeability

The intrinsic permeability, k, of the porous media is difficult to calculate. It depends on more than the average pore size and porosity of the packing media. The porous media may be packed nonuniformly. During an experiment, the permeability can not be estimated unless the porous media is tested to determine its permeability for each new packing material.

Therefore the model was tested for a range of permeabilities (k) from 5 x 10^{-12} cm^2 (extremely packed) to 1 x 10^{-9} cm^2 (extremely porous). The influence of the intrinsic permeability on the evolution of the wetted length and the mass of sodium is plotted in Figure 5-8 and 5-9.

As the crevice gets less permeable, the wetted length initially is smaller. Therefore the available area where the heat is transferred to the liquid is smaller since the steam-blanketed region has a very low (assumed negligible) heat transfer coefficient. Less vaporization occurs and less liquid is drawn into the crevice. This results in a slower accumulation of impurities in the crevice and a slower evolution of the wetted length for very packed crevices with low intrinsic permeability.

Regardless of k, the crevice is fully wetted at steady state. However, the steady state mass of impurity is lower for a less permeable crevice.

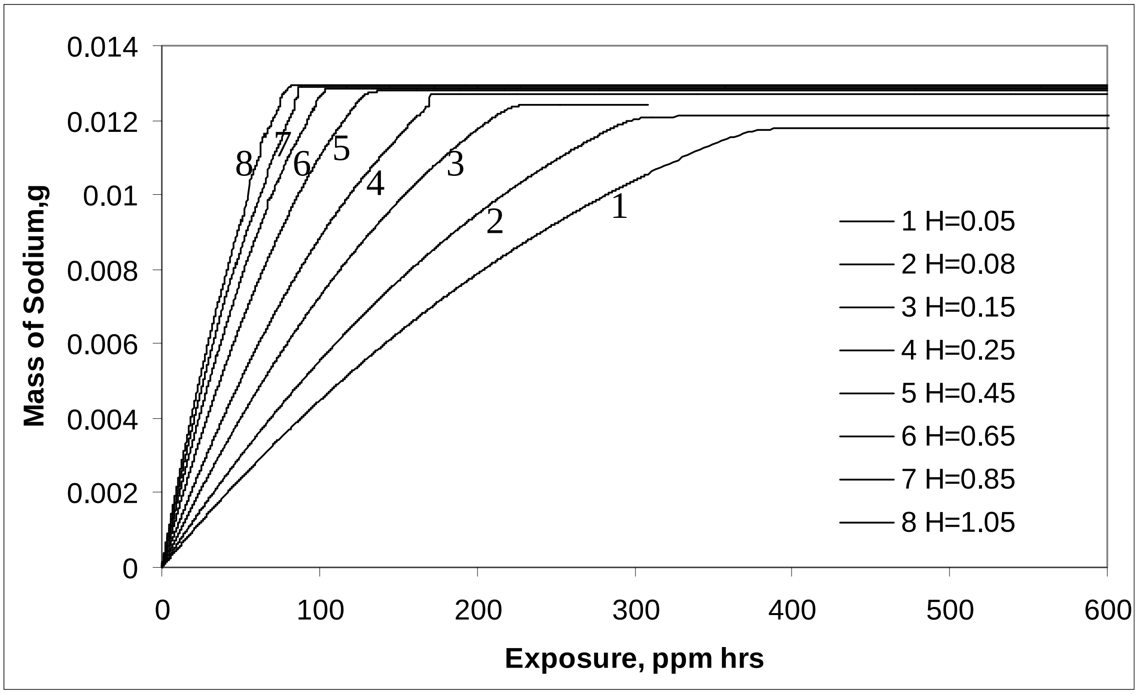


Figure 5-6
Variation of the mass of sodium with exposure for different heat transfer coefficient.

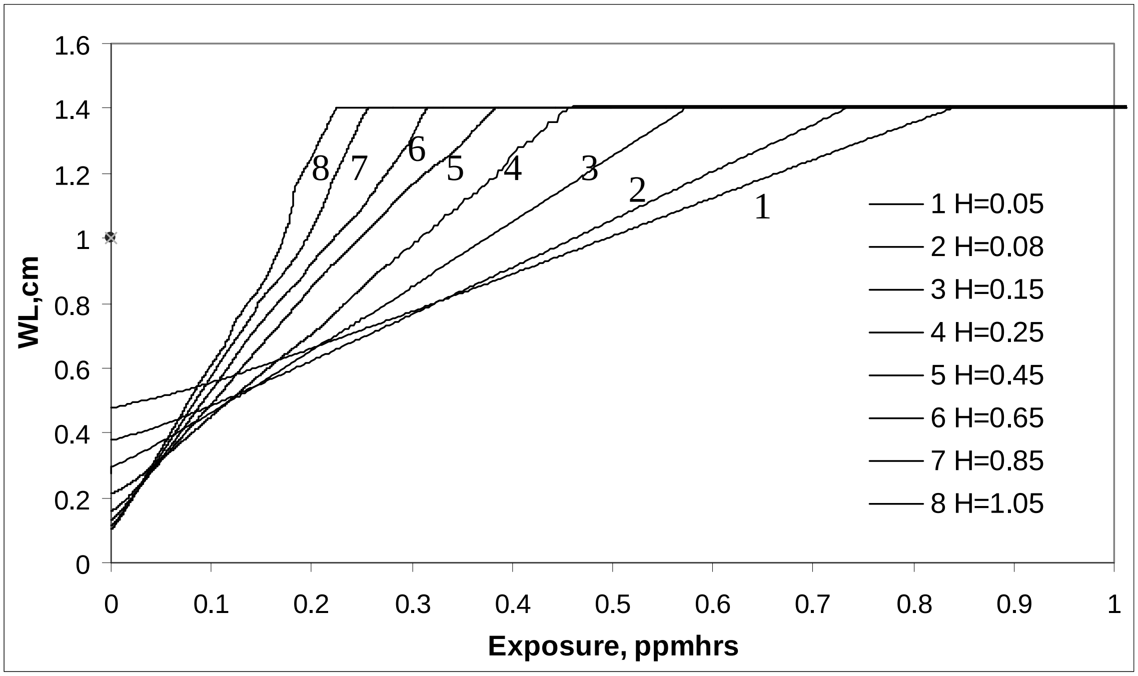


Figure 5-7
Variation of the wetted length Wl with exposure for different heat transfer coefficient.

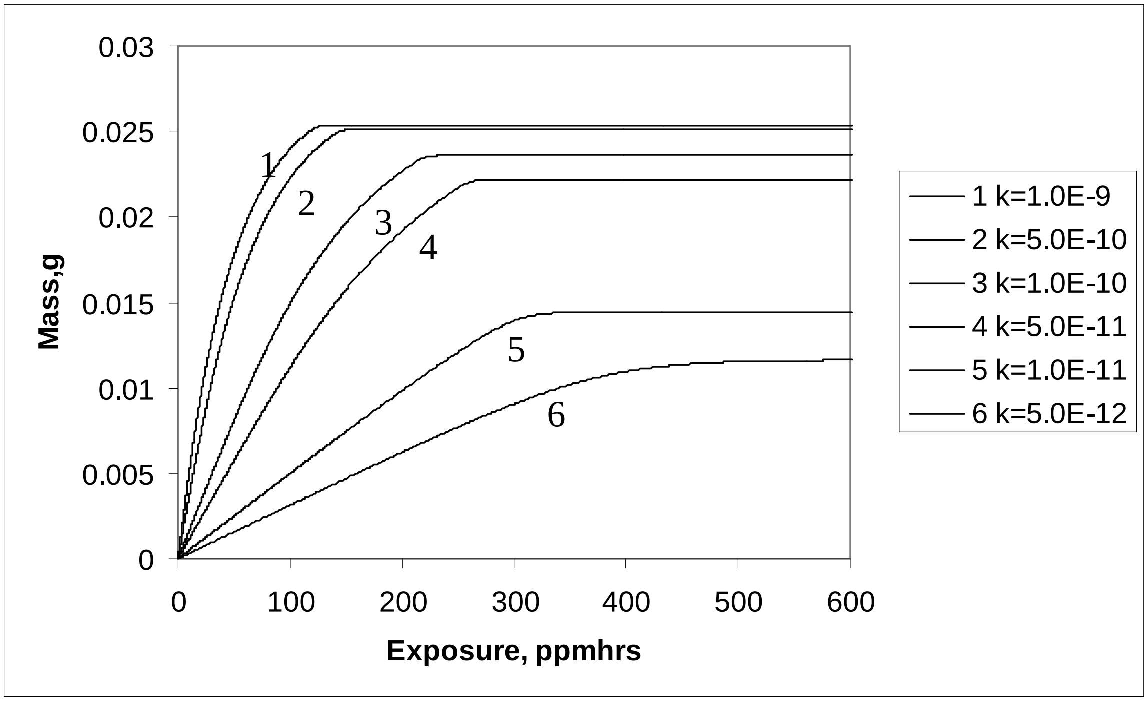


Figure 5-8
Variation of the mass of sodium as a function of exposure for different intrinsic permeabilities k.

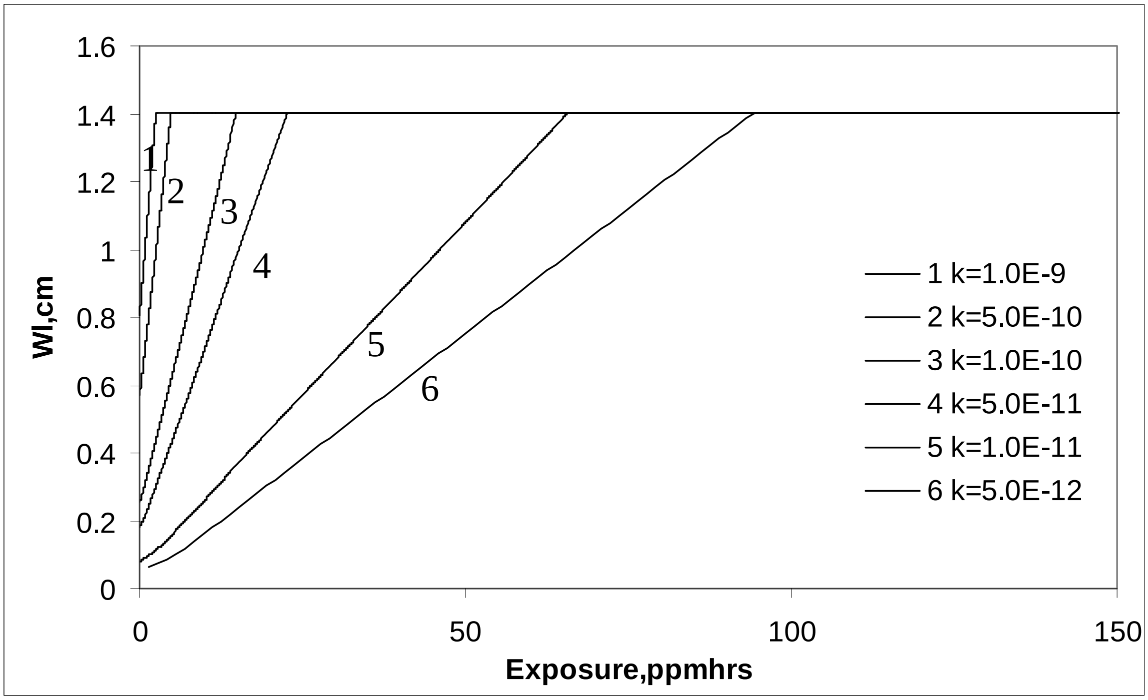


Figure 5-9
Variation of the wetted length as a function of exposure for different intrinsic permeabilities k.

The model predicts that the concentration of impurity in the crevice reaches the same thermodynamically limited maximum concentration regardless of permeability. However, at steady state, some pores are occupied by steam and are not filled by liquid for small k whereas for large k all the pores are filled with concentrated solution.

5.1.3.3 Effect of capillary pressure slope

As shown in Section 3.1.6, all the porous media from which retention curves are available in the literature or in the database UNSODA show a linear variation of the capillary pressure with saturation. Different types of porous media have different slopes DPcDS.

Based on the sludge pile results from Baum used by Millett, the slope is –100.04 N/cm^2. This gives a reference and therefore the slope will be varied between –40 and –200. The evolution of the wetted length and the mass of sodium are plotted in Figure 5-10 and 5-11.

Recall Equation 5-1, which describes the relationship between capillary pressure and saturation.

$$P_c = DPcDS * (S - S_0) \qquad \textbf{Eq. 5-1}$$

As DPcDS increases, the value of the capillary pressure at the limit of the steam-blanketed region (S approaching zero) is larger. Therefore, the wetted length is larger. Additionally, the surface area where boiling takes place is greater and more impurities are drawn into the crevice. Sodium accumulates faster and the wetted length increases faster.

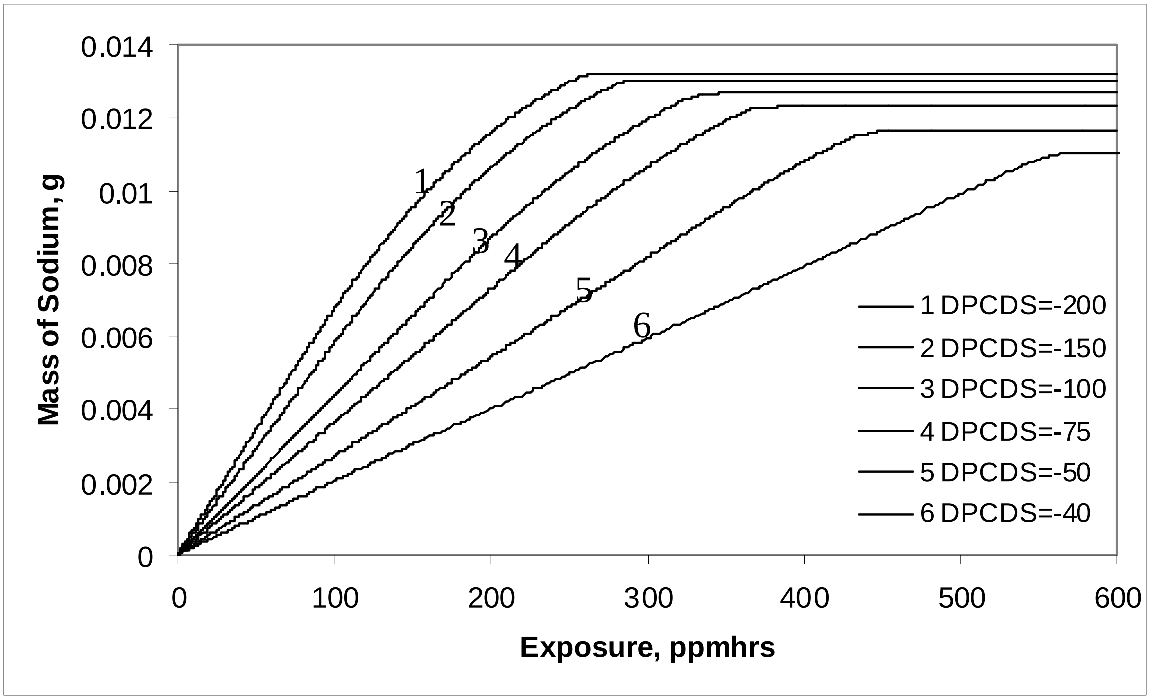


Figure 5-10
Variation of the mass of sodium as a function of the exposure for different slopes of capillary pressure DPcDS

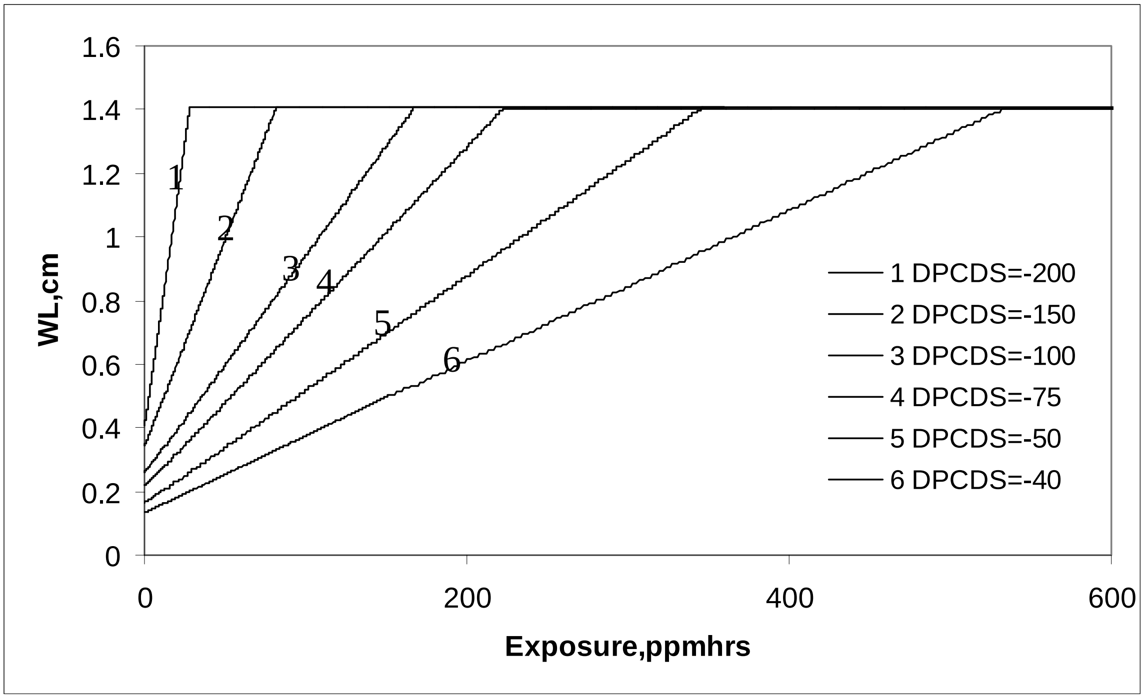


Figure 5-11
Variation of the wetted length Wl as a function of the exposure for different slopes of capillary pressure DPcDS.

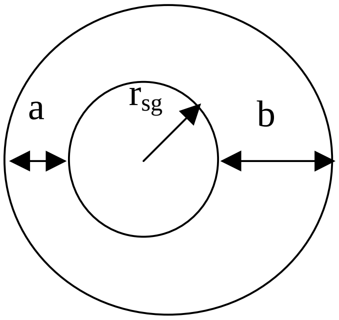
5.1.3.4 Eccentric crevice

Although the model is one dimensional, the case of an eccentric crevice can be studied by cutting it (the crevice) in small radial bands and running the model with different cross sectional areas A_c. By cutting the eccentric shape into small enough bands, their individual widths can be assumed to be constant. The resulting solutions can be combined together to obtain an understanding of the entire crevice's behavior.

In the experiment used in the next section to benchmark the model, the cross sectional area is 0.155 cm^2. This is typical of steam generator crevices. It was chosen consequently to vary A_c between 0.08 and 1.05 cm^2. The effect of the cross sectional area on the wetted length evolution and on the rate of accumulation of sodium was studied and is reported in Figures 5-13 and 5-14.

As the width of the crevice decreases, the volumetric heat source is larger. Therefore, the boiling is more intense and the steam-blanketed region is larger. However, the impurities accumulate faster and therefore the wetted length increases faster.

We take the example of the eccentric crevice illustrated in Figure 5-12 below.



R_{sg} = 0.94 cm
Width a = 0.03 cm
Width b = 0.06 cm
A_c at a = 0.177 cm^2
A_c at b = 0.354 cm^2

Figure 5-12
Schematic and dimensions of the eccentric crevice used as an example of the predictions of the model. In the schematic, the width of the crevice is greatly enlarged to define a and b.

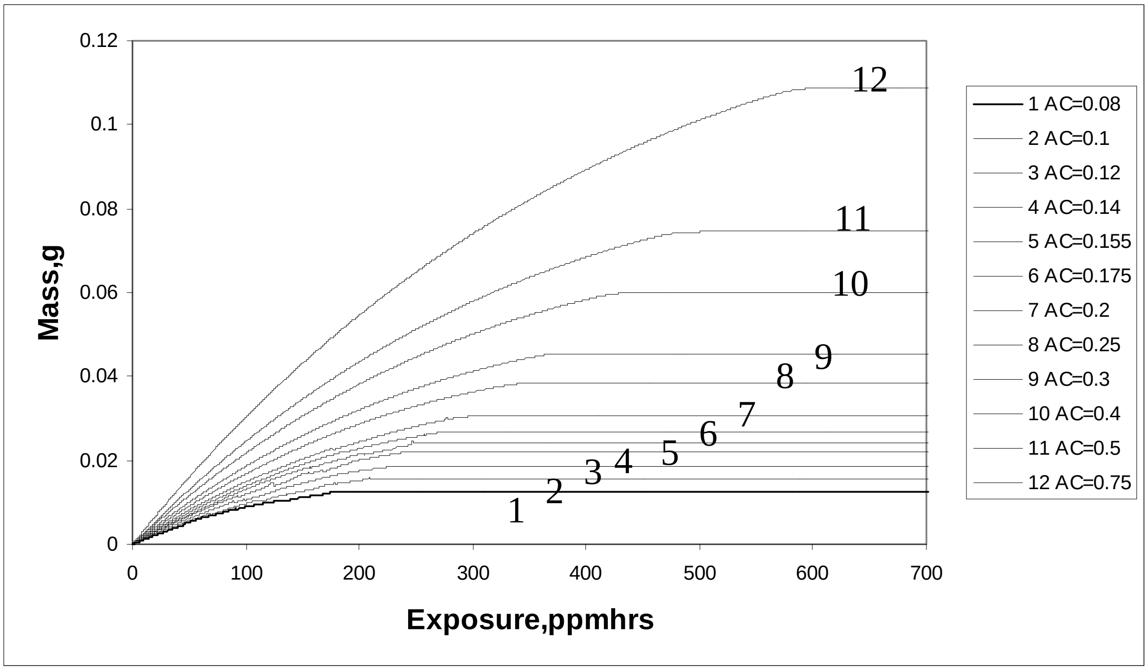


Figure 5-13
Variation of mass of sodium as a function of exposure for different cross sectional area

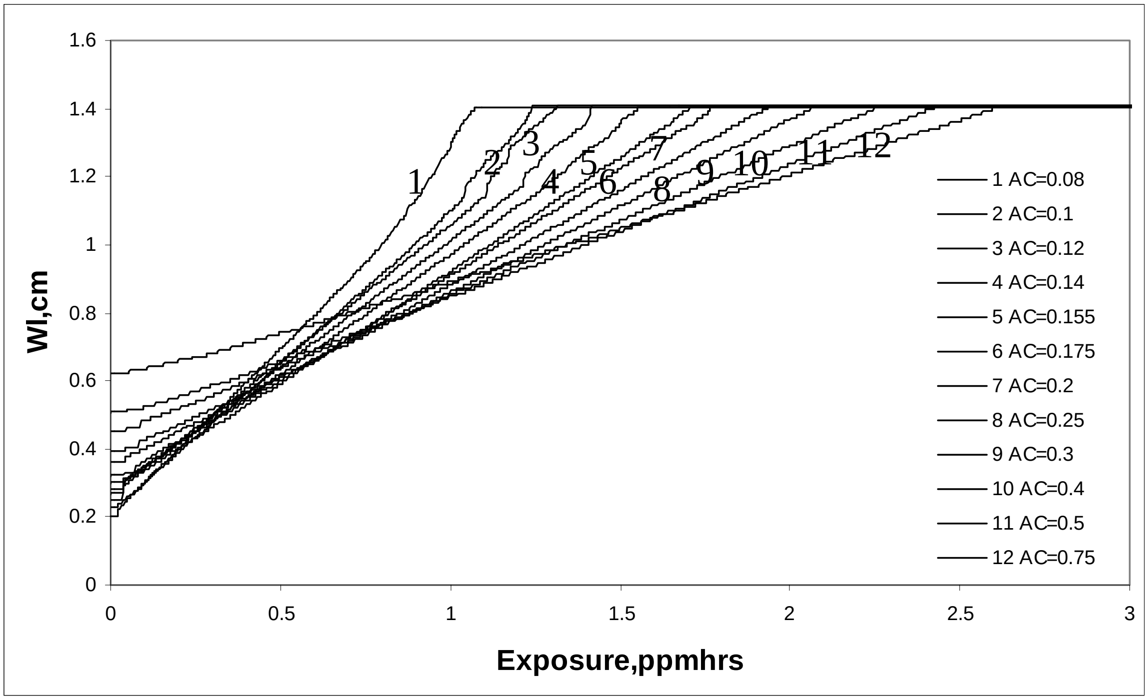


Figure 5-14
Variation of wetted length Wl as a function of exposure for different cross sectional areas, Ac, given in cm^2

After an hour of exposition at 100 ppb sodium, the wetted length at b is 0.45 cm whereas at a it is only 0.34 cm. After six hours of exposition at the same bulk chemistry, the wetted length in a and b are both equal to 0.70 cm. After 17 hours of exposition, no steam-blanket region remains on the a side whereas 15% of the crevice is still steam-blanketed in a. After 23 hours of exposition at 100 ppb sodium, the crevice is fully wetted. The center of the crevice contains a mixture of 1% liquid and 99% steam. The mixture becomes richer and richer in liquid as time passes.

5.1.4 Benchmarking the Thermodynamic Model Against Experimental Data

Three sets of experimental data are available to benchmark the thermal hydraulic model. Two come from diamond powder packed crevices at Rockwell International from Lumsden[5] and the Ohi Plant from Takamatsu.[5] The other comes from a carbon fiber packed crevice at San Jose State University.

5.1.4.1 Lumdsen / Takamatsu[5]

The model predicts that the rate at which a chemical species concentrate is proportional to the product of the rate of steam generation and the concentration of the species in the secondary water.

As steam generator's crevices are inaccessible during operation, making direct measurements of hideout is impossible. To mimic the phenomenon of a steam generator, Lumdsen has created an apparatus, which can be used as a laboratory tool for evaluating crevice chemistry and the critical variables controlling hideout. This apparatus can be used on its own, fed by a controlled chemical solution (such as is available in Rockwell's laboratories), or as a side stream boiler for a steam generator (such as the one at Ohi-2 in Japan).

The crevice formed by the intersection of the tube and ring has the dimensions of a steam generator tube support plate crevice. The radius of the tube is 0.94 cm, the crevice width is 0.0267 cm, and the crevice height is 2.84 cm. The crevice is packed with 65% diamond powder. The tube is electrically heated by an internal 600 W cartridge heater, extending 2.50 cm above and below the tube support plate so that the crevice is uniformly heated.

The autoclave is designed to incorporate sensors to monitor the crevice and bulk water environments. The ports are not located at the same elevation, allowing holes to be inserted into the crevice at different levels. Two ports contain capillary tubes. One is for solution extraction from the bulk solution, and one is for solution extraction from the crevice.

Lumsden and Takamatsu both measured the mass of sodium as a function of time using the autoclave. For each point, the procedure is as follows:

- Start the autoclave with a certain bulk concentration
- Run autoclave for a certain time
- Shut down the heater and flush the crevice
- Calculate the mass of sodium accumulated in the crevice.

Since the heater has to be shut down for each measurement, each experimental data point provided corresponds to a different experiment. For Lumsden's experiments, high bulk concentrations were used. For Takamatsu, low bulk concentrations, such as are typical in a steam generator, were fed into an autoclave. In both cases, the mass of sodium accumulated is a linear function of the exposure. The trend is very reproducible since each point corresponds to a new experiment.

The model was used with a heat transfer coefficient of 0.6 and a permeability of 8.67×10^{-10} cm^2 (~0.1 Darcy). The results are plotted in Figure 5-15 and 5-16. The agreement is very good. The model initially predicts the existence of a steam blanket region. After 150 ppm-hrs, the crevice is fully wetted (more than 100 years for a crevice exposed to 0.1 ppb sodium).

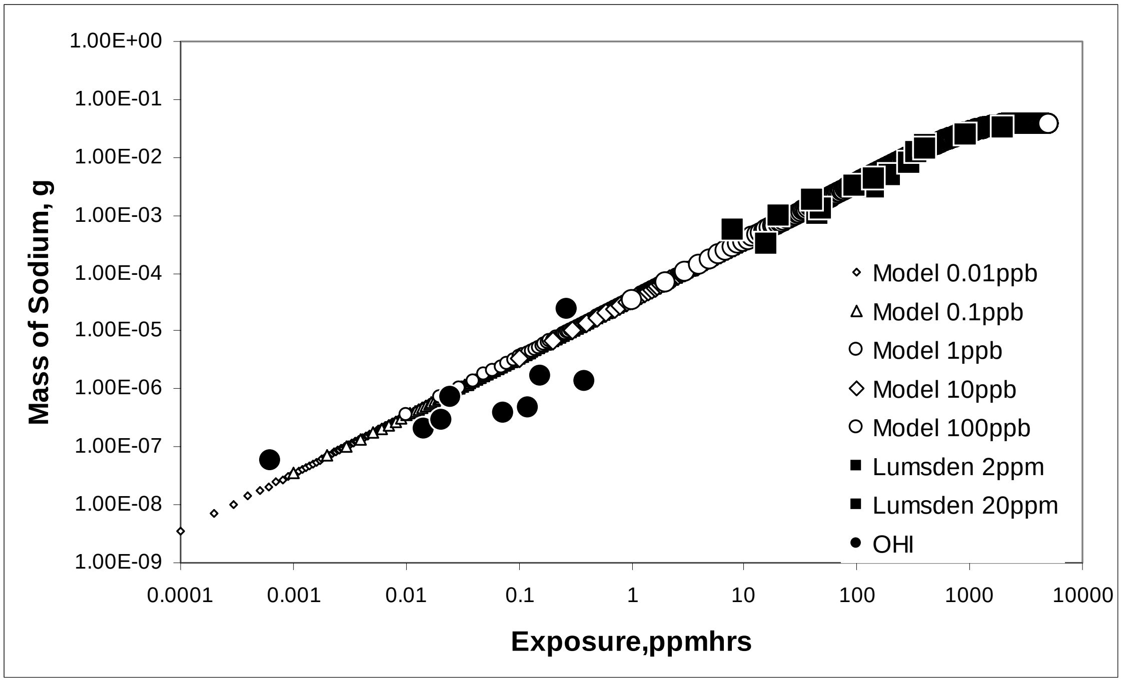


Figure 5-15
The mass of sodium as a function of exposure is plotted. The thermal hydraulic model was run with five different bulk concentrations and the parameters to mimic Ohi and Rockwell autoclaves and the experimental results from two sets of experiments from Lumsden and one set from Takamatsu were collected.[5]

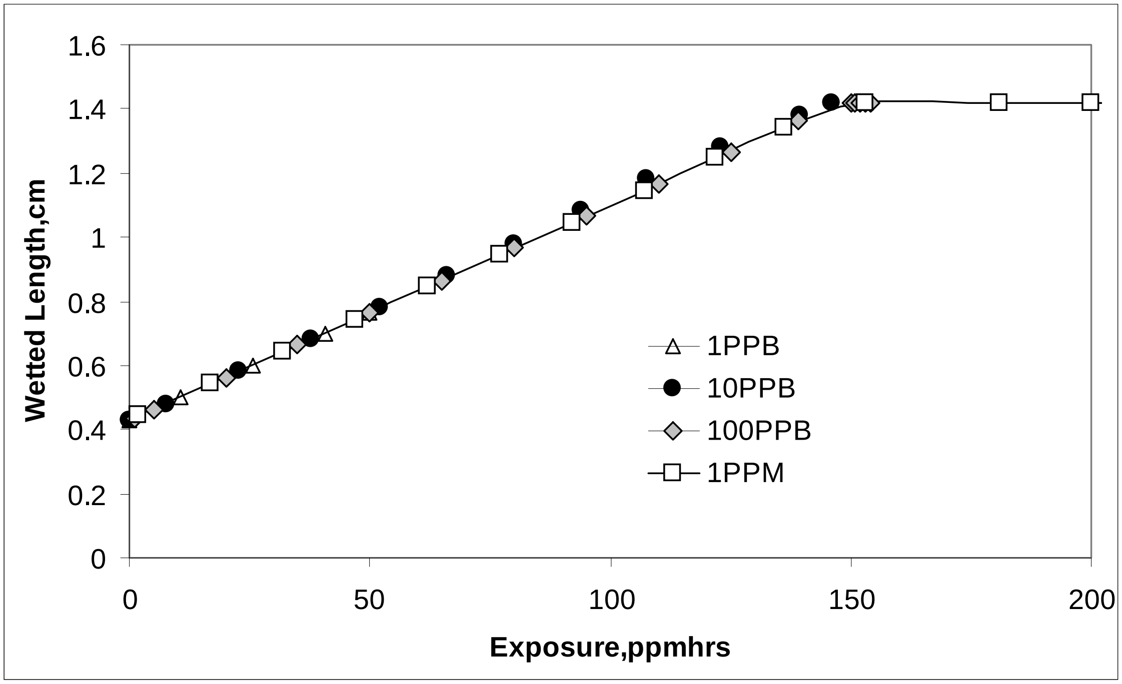


Figure 5-16
The wetted length predicted when mimicking Takamatsu's and Lumsden's results is plotted as a function of exposure.[5]

The model predicts that the steam blanket shrinks slowly during the process of concentration.

5.14.2 San Jose State University

Another recent set of experimental data is available from San Jose State University. Rockwell International has constructed an experimental tube and tube support crevice simulator to be suspended in a one liter autoclave. The choice of the packing is Thornel P.755 Carbon Filament. The exit solution of the flow loop is monitored for changes in sodium concentrations. The mass of sodium trapped in the crevice is deducted as a function of time. The runs are summarized in Table 5-2.

Table 5-2
Data obtained by San Jose State University

	Run1	**Run2**	**Run3**	**Run4**	**Run5**	**Run6**	**Run7**
Heater power(W)	85	230	85	85	230	150	150
Bulk concentration(ppm)	30	30	120	120	120	60	60
Steady state mass accumulated in the crevice(mg)	8.95	54.7	16.6	17.0	87.0	26.4	26.9

The accumulation of sodium in all the experiments is linear with time. A difference between the previous series of experiments and these is that, in one case, the crevice was packed with up to 70% diamond powder. In the other case, the crevice was packed with up to 56% carbon fiber. When the crevice is less packed, there is more mixing and carryover to the outside of the crevice. The amount of carryover is proportional to the bulk concentration. This explains why the steady state mass of sodium is a function of the bulk concentration. This carryover process was integrated in the model as follows in Equation 5-2. Γ is the mass transfer carryover constant.

$$\varepsilon S \frac{\partial C}{\partial t} = -\nabla C V_L + S_i - \Gamma (C - C_0) \qquad \textbf{Eq. 5-2}$$

This model was benchmarked against the experimental results (Figure 5-17 through 5-19). Reasonable agreement was found.

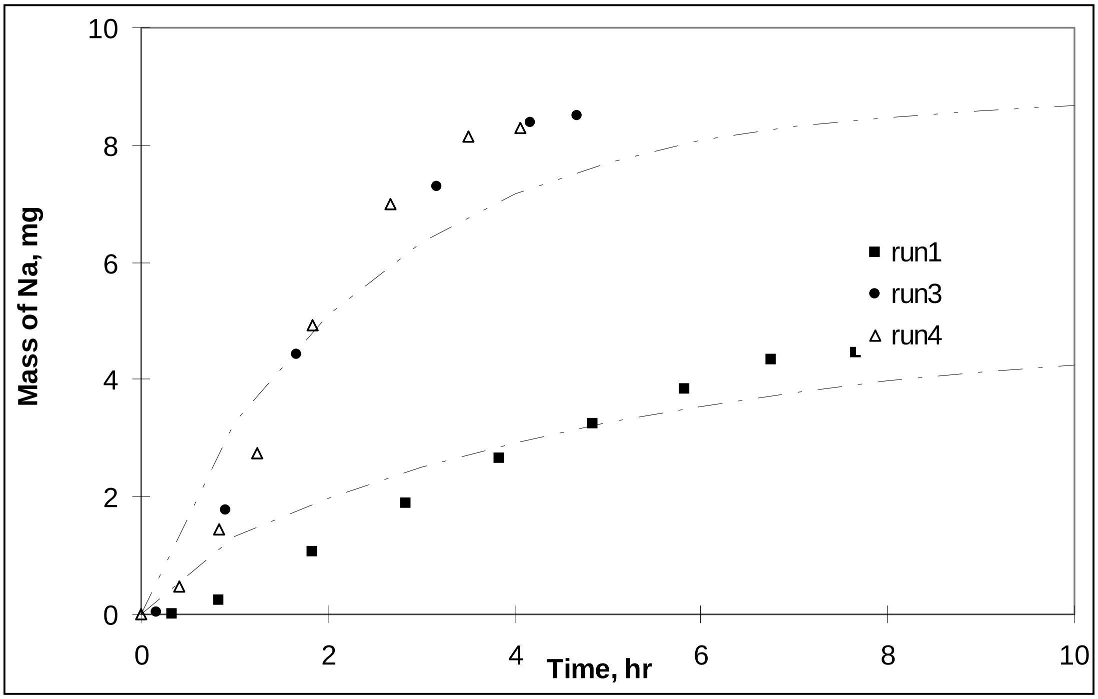


Figure 5-17
San Jose State predictions of hideout for three different bulk concentrations at a power of 85W (points) and model predictions (lines).

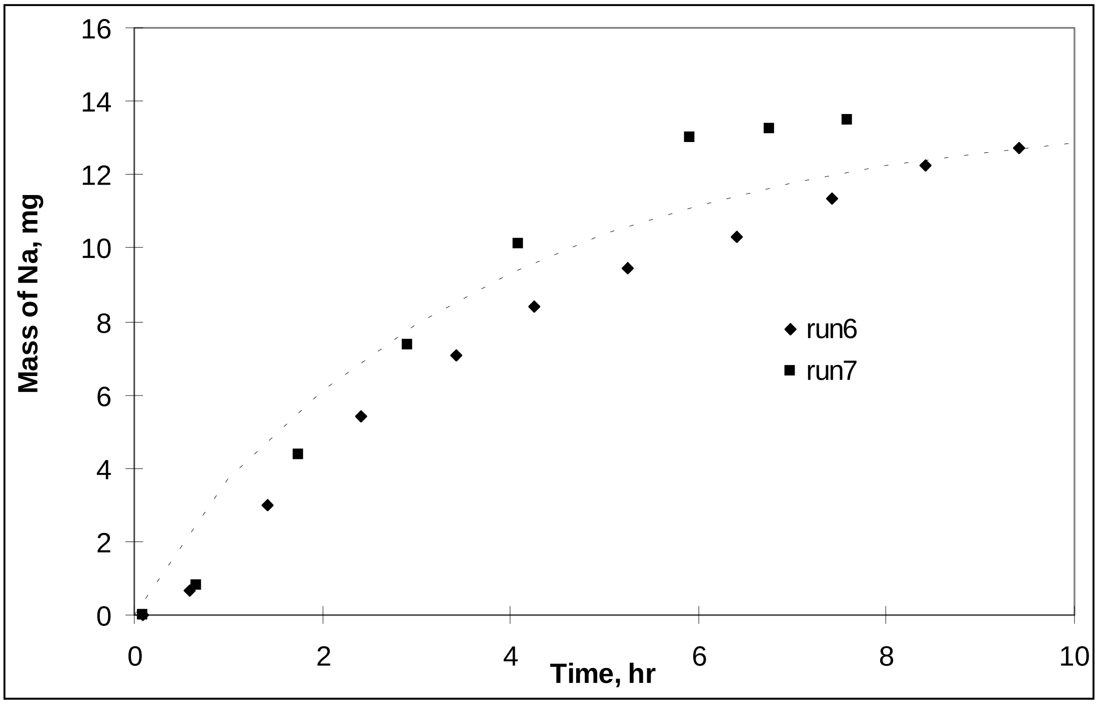


Figure 5-18
San Jose State predictions of hideout for three different bulk concentrations at a power of 150W (points) and model predictions (lines).

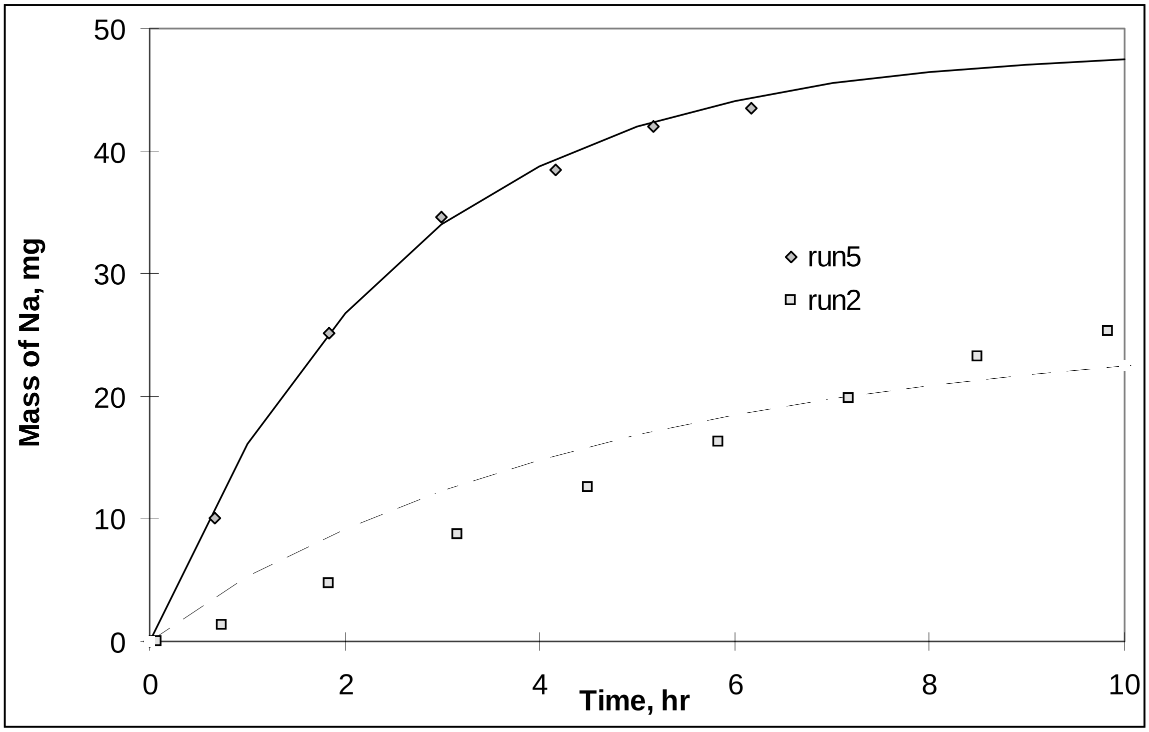


Figure 5-19
San Jose State predictions of hideout for three different bulk concentrations at a power of 230W (points) and model predictions (lines).

5.2 Chemical Modeling

In the chemical modeling, the distribution of the pH was predicted in the crevice. Two parameters were studied: the effect of the sodium chloride ratio and the effect of the corrosion current.

5.2.1 Effect of the Ratio

The ratio of sodium to chloride greatly influences the pH inside of the crevice.

Chloride is a lot more volatile than sodium. However since steam and liquid water flow through different channels, there is very little mixing in the crevice. Consequently sodium and chloride concentrate at the same rate.

Let's take an example of ratio and look at the what pH is expected in the crevice. The molar ratio chloride to sodium is 1.2. We assume the concentration of sodium and chloride in the bulk is 1.2 x 10^{-7} mol/L and 1.0 x 10^{-7} mol/L respectively. If the factor of concentration in the crevice is a billion, then the concentration in the crevice is 0.12 mol/L for sodium and 0.10 mol/L for chloride.This provided the factor of concentration of sodium and chloride are the same, In other terms, this neglects the high volatility of chloride.

Therefore in the bulk, the pH is neutral because the bulk concentrations are very small. In the crevice the excess of positive charges has to be compensated by negative charges (OH^-) and the pH is very basic.

The model was run with a very small corrosion current with different molar ratios of chloride to sodium. The results show that for a ratio less than 1 the crevice is very basic and that for a ratio greater than 1, the crevice is very acid, which can be seen in Figure 5-20.

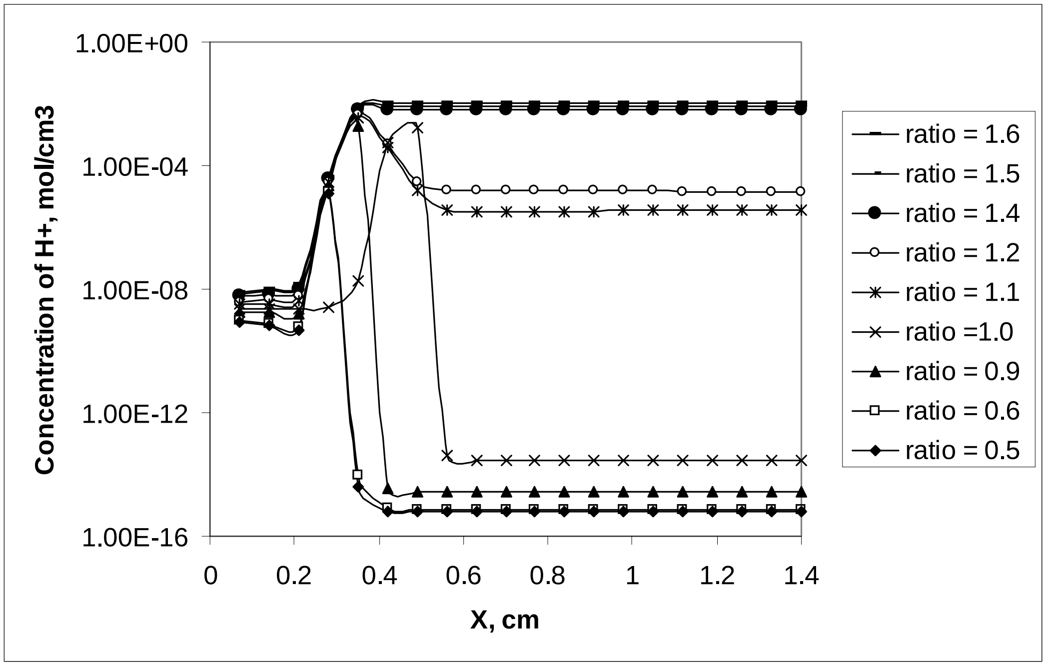


Figure 5-20
Distribution of the concentration of H+ for different ratios chloride to sodium.

When the corrosion current is high, some Fe^{2+} ions are discharged into the crevice. If the crevice is very basic (sodium dominant) then precipitation of $Fe(OH)_2$ occurs consuming the ferrous (Fe^{2+}) ions. The crevice remains basic.

If the crevice is acidic (chloride dominant) then there aren't many OH^- ions. Precipitation of $Fe(OH)_2$ doesn't occur, and the Fe^{2+} are not consumed. The positive charges of Fe^{2+} counterbalance the excess of negative charges brought by Cl^-. Therefore, H^+ doesn't have to have a high concentration to maintain electroneutrality. The crevice is less acidic than if there was no dissolution of metal. In this case, Fe^{2+} and $FeOH^+$ are highly concentrated in the crevice. As the molar ratio of chloride to sodium increases from 1 to 1.6, less precipitate is formed and more iron stays in the form Fe^{2+} /$FeOH^+$.

If the corrosion rate is very high, such as the one used in MacDonald's model, Fe^{2+} might neutralize the crevice.

The effect of the molar ratio was not compared to the predictions of MacDonald's model since the program does not converge for ratio other than 1.

5.2.2 Effect of the corrosion current

For a ratio of sodium to chloride of 1.6, the corrosion current was varied. MacDonald's model uses a corrosion current I_{CORR}. This corrosion current was divided by 10000, 100, 10 ,1 and 0.1 and the concentration of the chemical species was plotted on Figure 5-21 through 5-24. When the corrosion current is very small, H^+ is predominant. Fe^{2+} and $FeOH^+$ are small. There is no precipitation occurring.

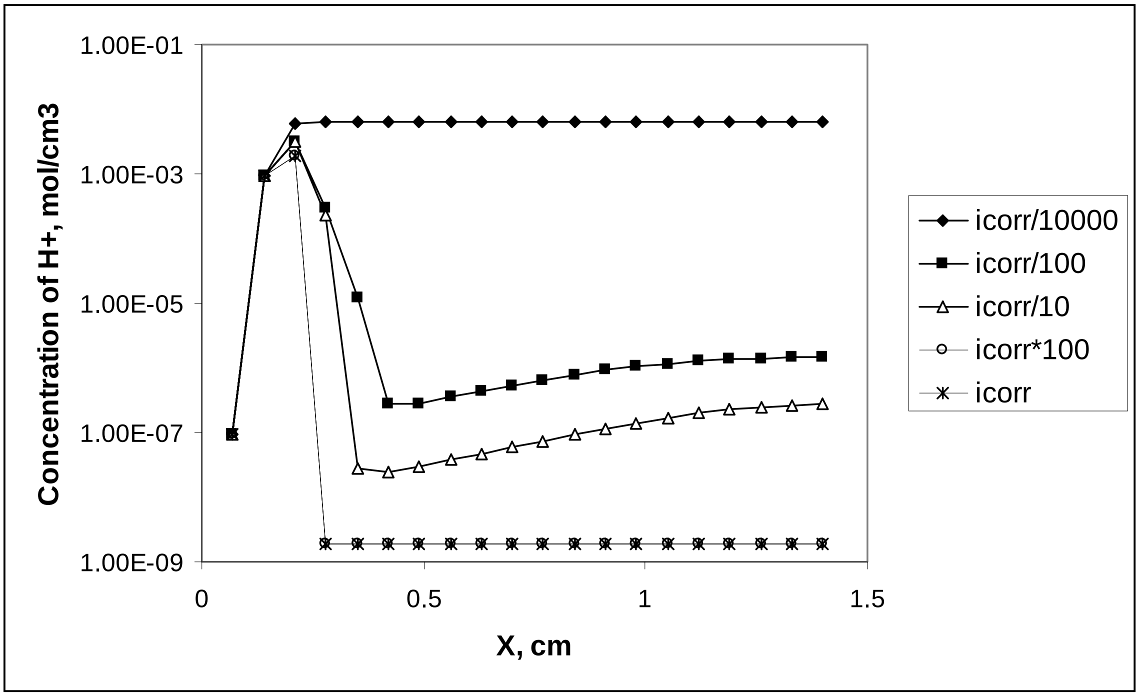


Figure 5-21
Concentration of hydrogen ion in the crevice for different corrosion current I_{CORR}/10000, I_{CORR}/100... The reference expression I_{CORR} is the one used in MacDonald's model.

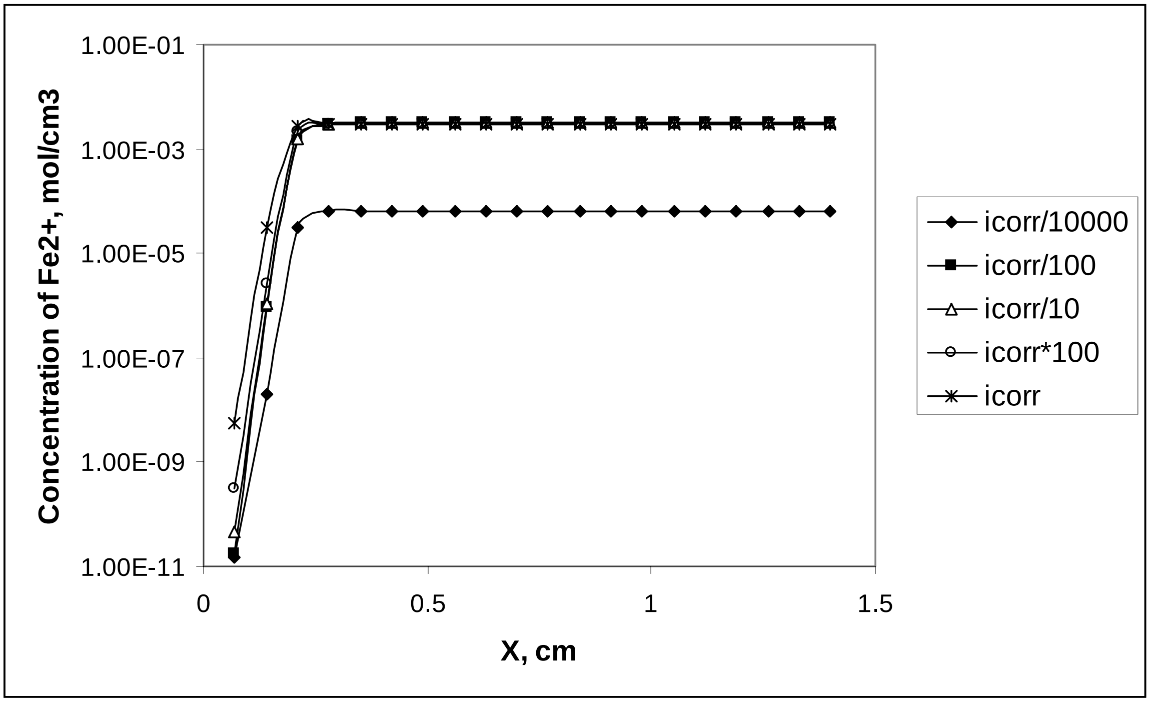


Figure 5-22
Concentration of ferrous ion in the crevice for different corrosion current I_{CORR}/10000, I_{CORR}/100... The reference expression I_{CORR} is the one used in MacDonald's model.

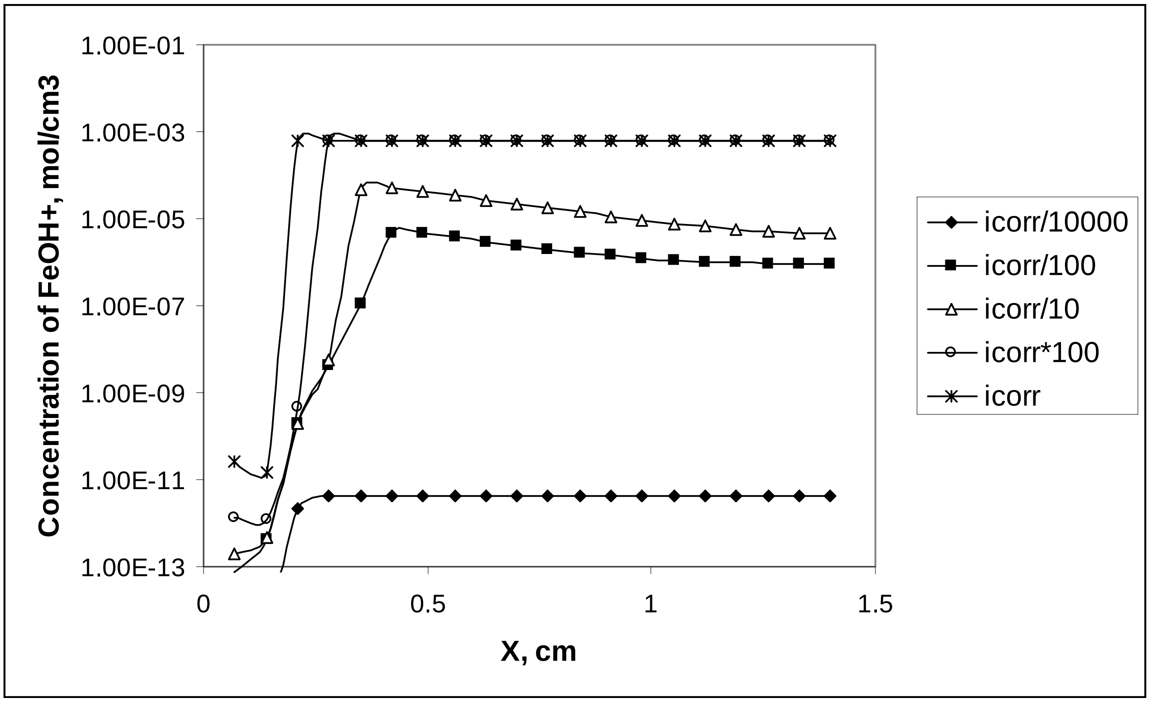


Figure 5-23
Concentration of ferrous hydroxide ion in the crevice for different corrosion current I_{CORR}/10000, I_{CORR}/100... The reference expression I_{CORR} is the one used in MacDonald's model.

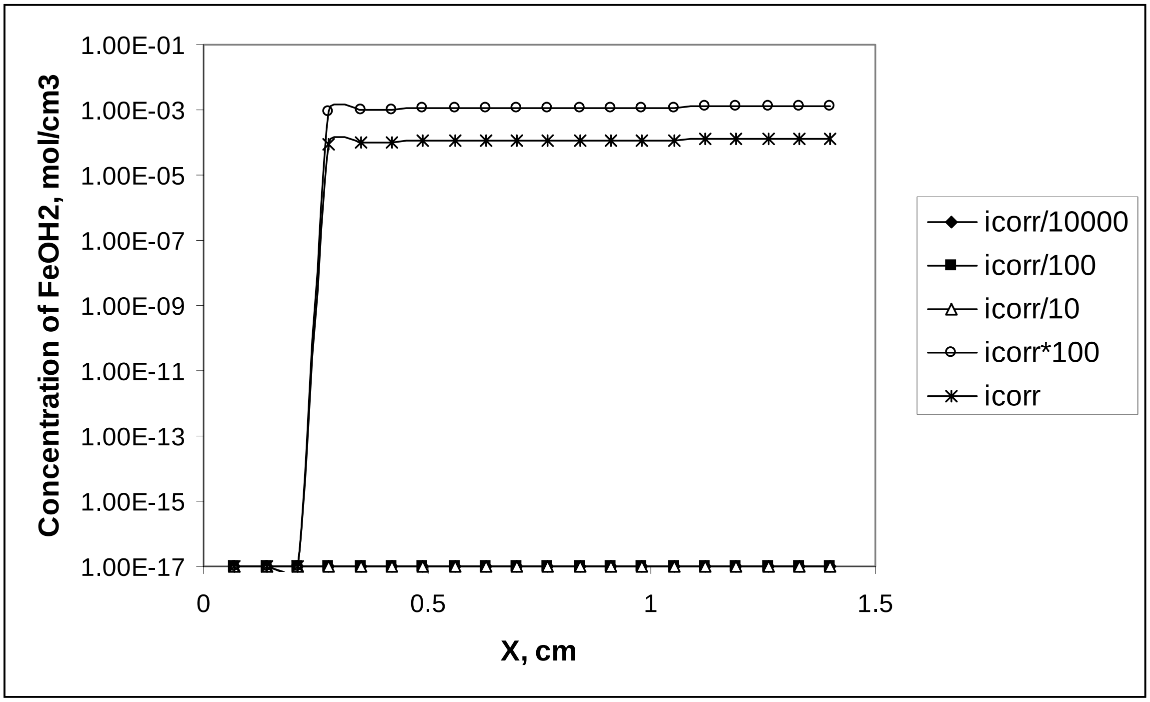


Figure 5-24
Concentration of precipitate $FeOH_2$ in the crevice for different corrosion current I_{CORR}/10000, I_{CORR}/100... The reference expression I_{CORR} is the one used in the MacDonald's model.

As the corrosion current increases, more Fe^{2+} are in solution, the iron species Fe^{2+} and $FeOH^+$ counterbalance Cl^- and H^+ decreases. If the corrosion current is increased more, at some point, Fe^{2+} reaches a maximum and more $FeOH^+$ are formed. When the solubility is exceeded $FeOH_2$ precipitates.

The approximation in MacDonald's model that there is always precipitation, is justified with the corrosion current used in that model. However, the new model predicts that if the corrosion current is smaller then precipitation does not always occur. Instead, Fe^{2+} and $FeOH^+$ are predominant.

5.3 Electrochemical Modeling

The model created to calculate potential knowing the chemistry is tested here. First the model is compared to MacDonald's model, then several parameters are tested to figure out if the predictions are reliable.

5.3.1 Predicted Electrochemical Potential Profile

Two electrochemical potential profiles are shown in Figure 5-26. The chemistry associated with the potential is shown as well in Figure 5-25. To explain these profiles it is easier to divide them into three regions.

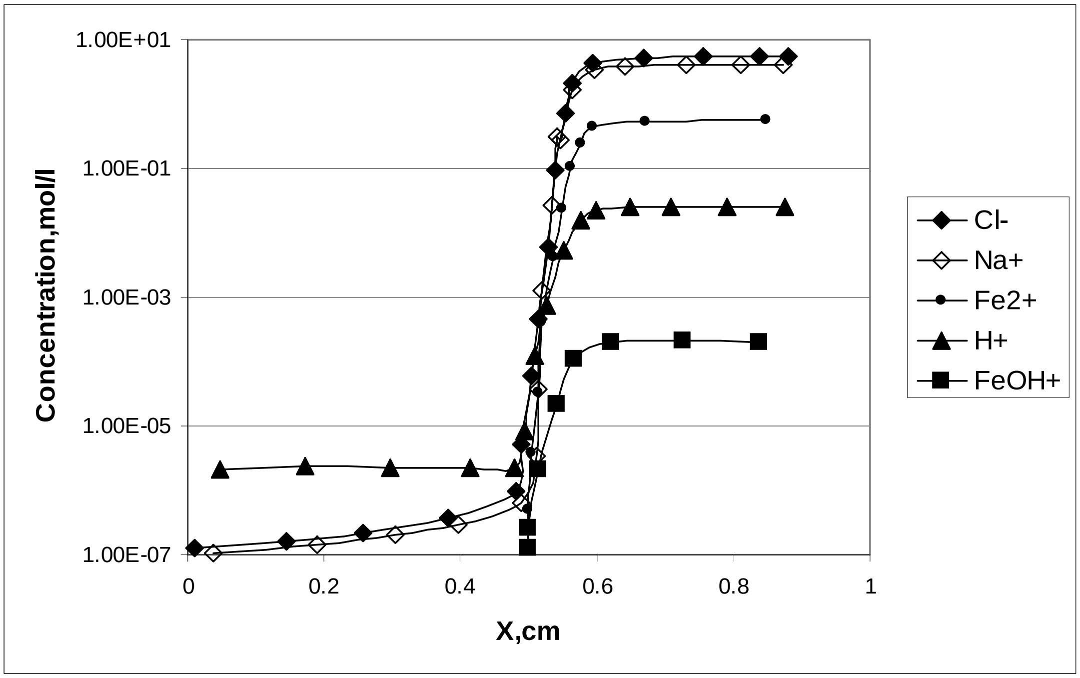


Figure 5-25
Concentration profiles for the species Cl$^-$, Na$^+$, Fe^{2+}, H$^+$, FeOH$^+$ in the crevice used in the calculation of the electrochemical potential.

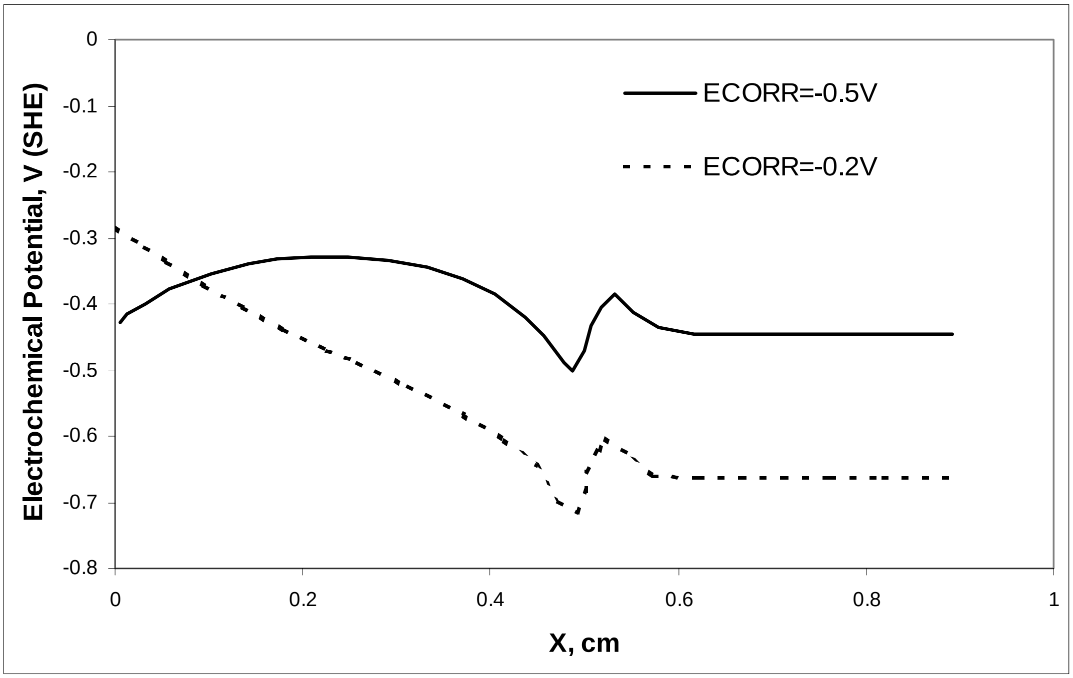


Figure 5-26
Distribution of the electrochemical potential in the crevice for two different mouth polarisations (–0.28V and –0.42) corresponding to two different metal corrosion potentials Ecorr = –0.2V and Ecorr = –0.5V respectively.

In region 1, the solution is almost pure water, therefore the conductivity is low. The potential gradient is dictated by the sum total of the cathodic and corrosion currents.

If the potential at the mouth is very low, then the cathodic current (H_2O reaction) is very high. Remember that:

$$I = I_0 \exp\left\{\frac{\alpha F}{RT}\left(E - E^e\right)\right\} \qquad \textbf{Eq. 5-3}$$

With $E^e = 0$ and $\alpha = -0.5$, if E is very negative then the cathodic current is high. As E moves closer to zero, the cathodic current decreases.

It is interesting to note that for a sufficiently negative outside polarization, the electrons are migrating from the outside of the crevice to the inside of the crevice. The corrosion potential of the metal is greater than the potential at the mouth. The cathodic reduction takes place in the middle of the crevice. The total cathodic current in the cavity is larger than the total anodic current.

If the crevice is not externally polarized enough then electrons migrate from the inside of the crevice to the outside. The corrosion potential of the metal is smaller than the potential at the mouth. The cathodic reaction takes place partially at the outside of the crevice. The total cathodic current is smaller than the total anodic current.

In region 2, the variations of the electrochemical potential are due to the diffusion current, expressed in Equation 5-4.

$$I_D = \sum z_{in} \frac{\partial C_i}{\partial x} \qquad \textbf{Eq. 5-4}$$

The corresponding plot of the diffusion current is shown in Figure 5-27.

Due to the steep concentration gradient between the concentrated and nonconcentrated region in the crevice, the diffusion current is higher than any anodic or cathodic current. If the diffusion current is positive, then positive ions tend to migrate towards the mouth whereas negative ions tend to migrate towards the center. Conversely, a negative diffusion current causes negative ions to move towards the mouth and positive ions towards the center.

In the region of the crevice where this steep concentration gradient exists, the diffusion current changes rapidly from a positive value to a negative one. If the diffusion current was the only force acting on the ions in this region, positive ions would tend to migrate away from this transition region towards the mouth on one side and the center on the other. However, if this were allowed to occur there would be a depletion of ions in the transition region. To counterbalance the diffusion current, an electrochemical potential gradient exists in region 2 to preserve electroneutrality.

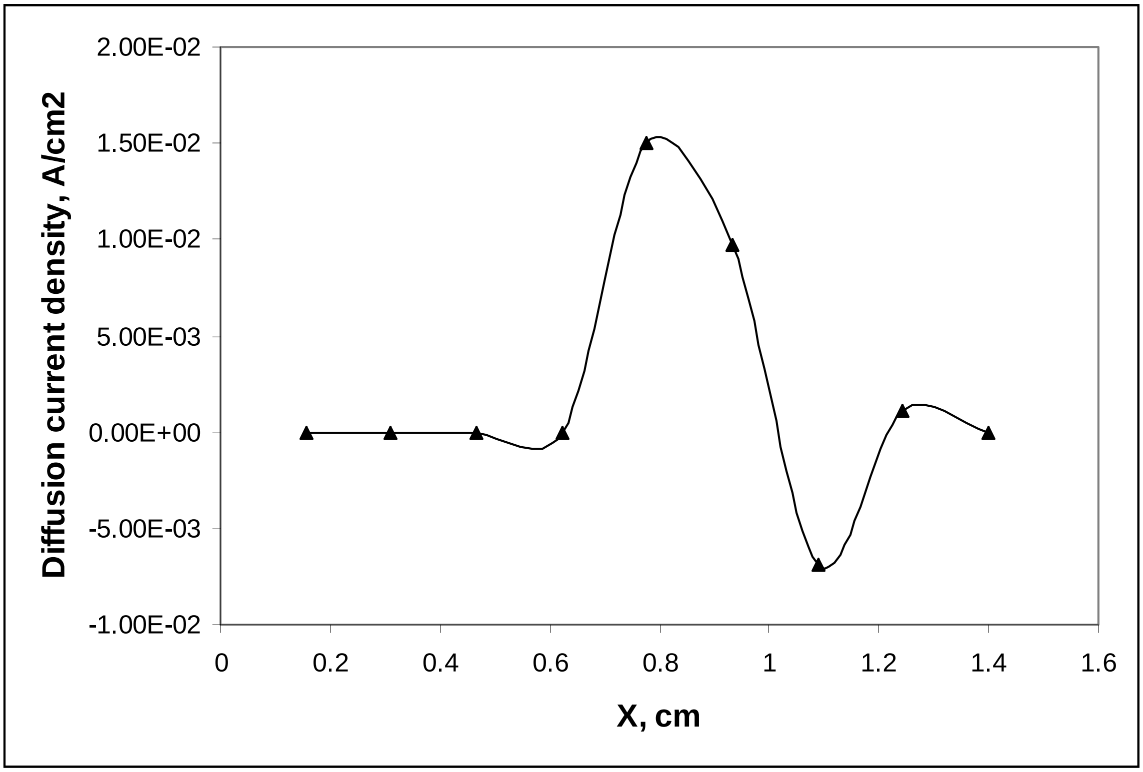


Figure 5-27
Distribution of diffusion current densities in the crevice for the corrosion metal potentials Ecorr = –0.2V and Ecorr = –0.5V (Identical).

In region 3, there is no concentration gradient. Therefore, the diffusion current equals zero. The solution is highly concentrated therefore the conductivity is high and the gradient of electrochemical potential is negligible.

5.3.2 Comparison of the New Model and MacDonald's Model

The predictions were compared for the two profiles published in MacDonald's thesis.[9] The profiles show excellent agreement in the case where E_{CORR} = –0.5 V, shown in Figure 5-28, and good agreement in the case where E_{CORR} = –0.2 V, illustrated in Figure 5-29.

It is extremely difficult to explain why the agreement is not perfect for E_{CORR} = –0.2 V. First, MacDonald's results found in his thesis could not be verified by running his program because the program does not converge.

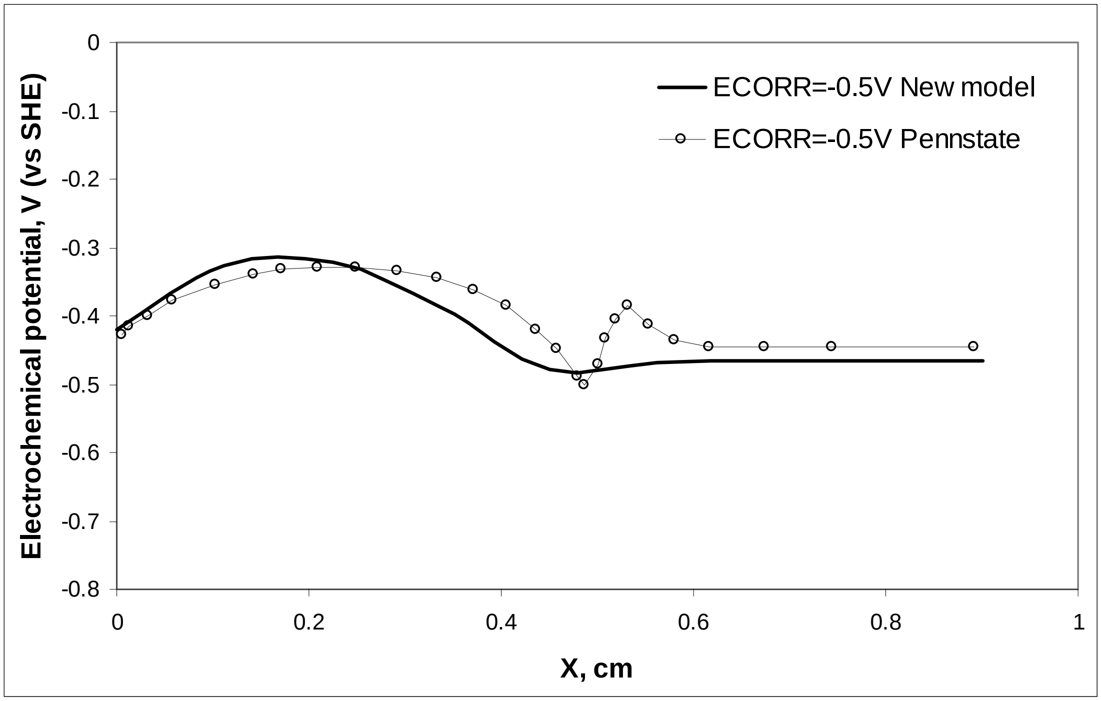


Figure 5-28
Distributions of the electrochemical potential in the crevice for a corrosion metal potential E_{corr} = –0.5V predicted by the new model and by MacDonald's model.

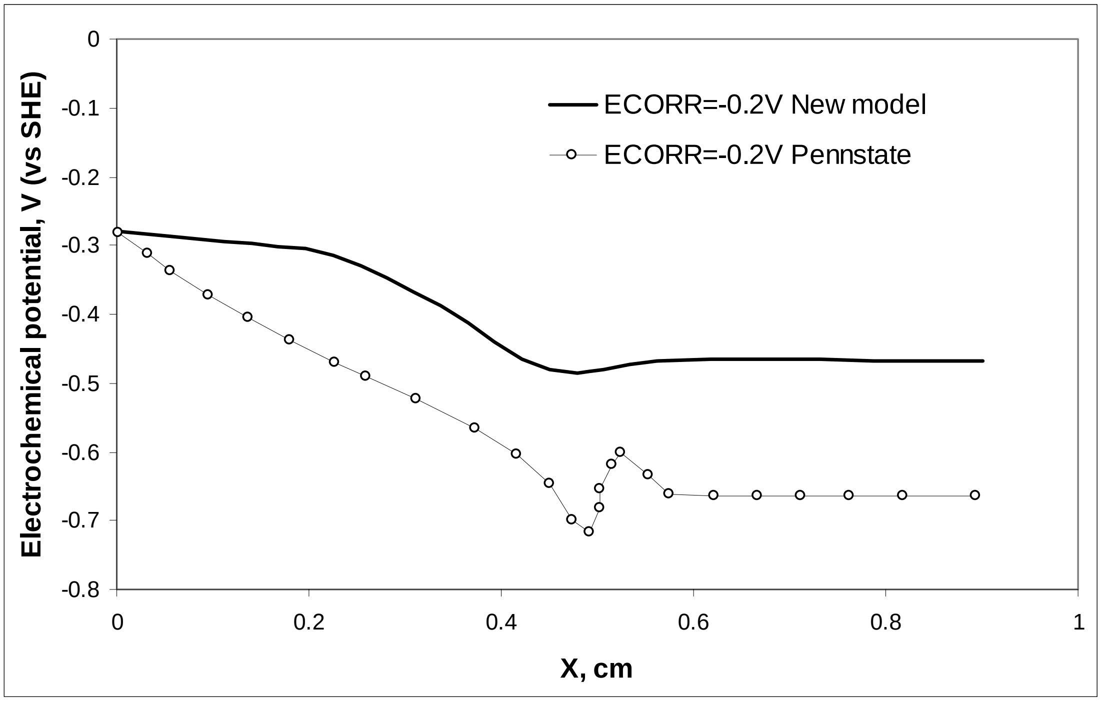


Figure 5-29
Distributions of the electrochemical potential in the crevice for a corrosion metal potential E_{corr} = –0.2V predicted by the new model and by MacDonald's model.

Also, it is believed that there is a mistake in one of the electrochemical potential curves published by MacDonald.[9] The electrochemical potential distributions predicted by MacDonald are different for E_{CORR} = –0.5V and E_{CORR} = –0.2 V. However, the cathodic current distributions predicted are the same in both cases, shown in Figures 5-30 and 5-31. Since the cathodic current is directly related to the electrochemical potential, this is impossible.

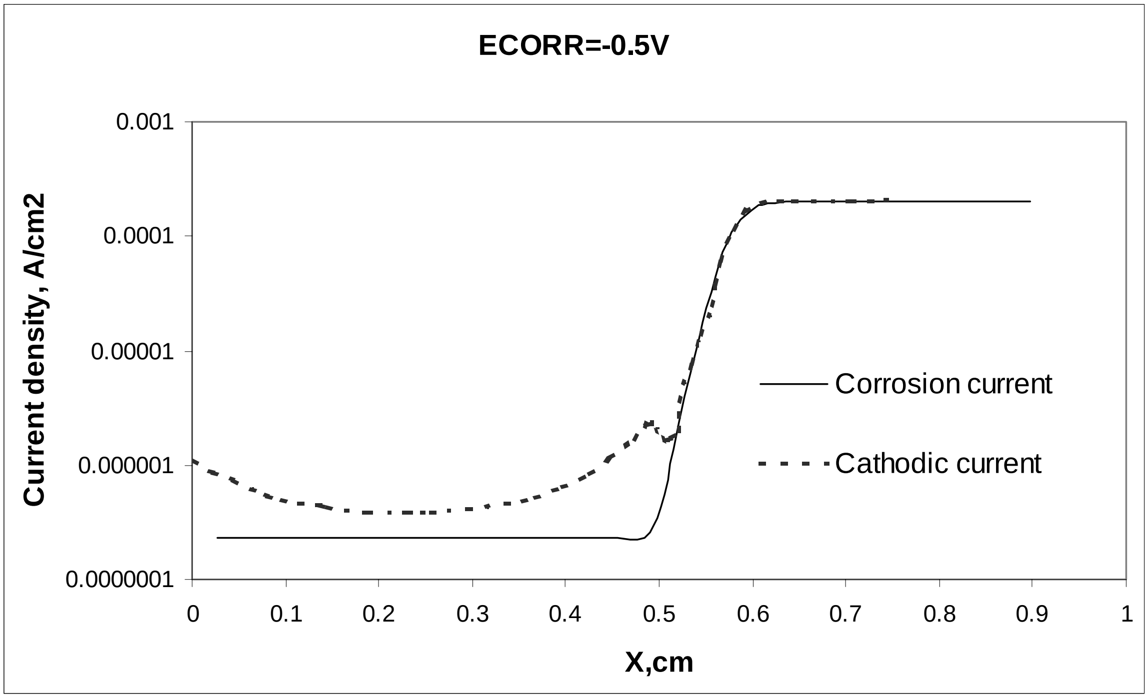


Figure 5-30
Distribution of cathodic and corrosion current densities in the crevice for the corrosion metal potential E_{corr} = –0.5V.

Therefore, the electrochemical potential distribution published in MacDonald's report corresponding to ECORR = –0.2 V is probably wrong and this explains the difference observed with the new model. For ECORR = –0.5V, the predictions of both models agree perfectly.

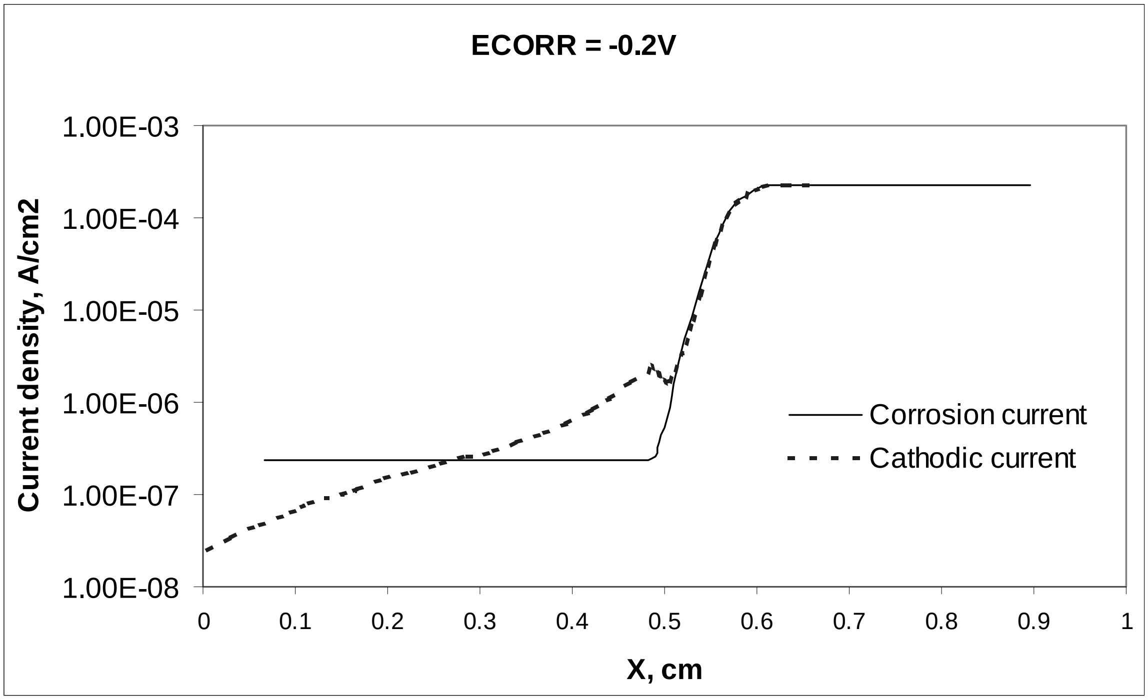


Figure 5-31
Distribution of cathodic and corrosion current densities in the crevice for the corrosion metal potential E_{corr} = –0.2V.

5.3.3 Effect of External Polarization

MacDonald's model predicts the potential at the mouth of the crevice as a function of the chemistry. More precisely, it gives the potential of the metal as a function of the hydrogen and the oxygen content. As shown in Figure 5-32, adding oxygen increases the potential at the mouth, while adding hydrogen decreases this potential.

The potential at the mouth is varied between –0.1 V and –0.5 V. The resulting potential profiles are calculated with both MacDonald's and the new model. In both cases, the potential predicted in the concentrated region is independent from the external polarization (Figures 5-33 and 5-34).

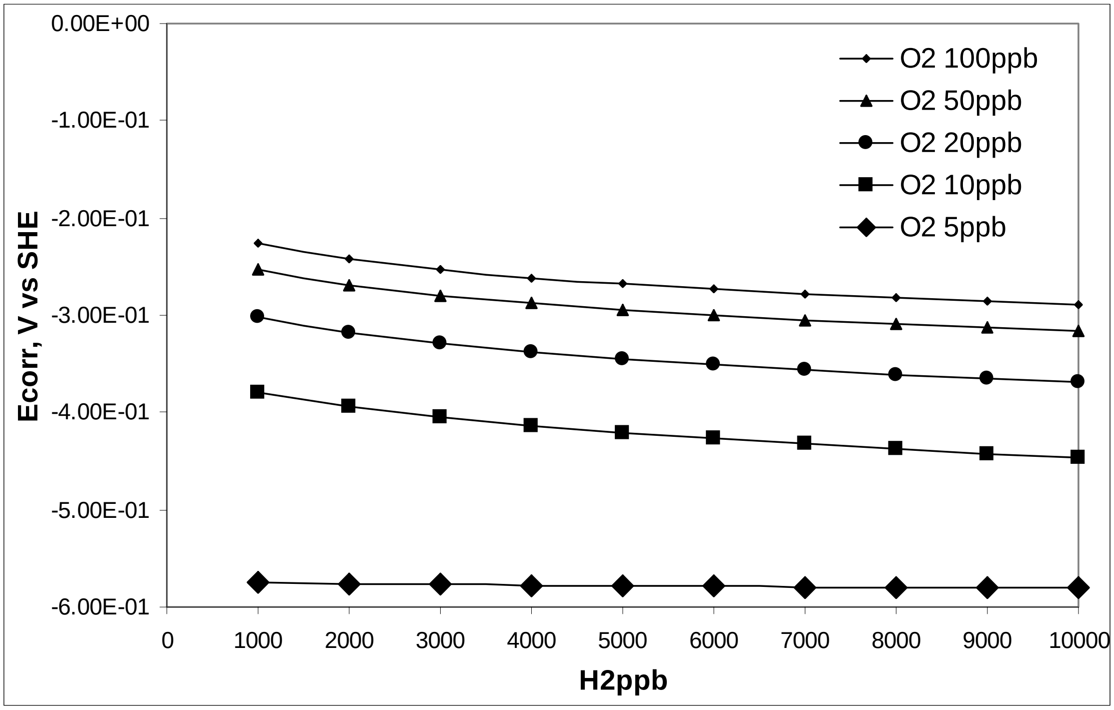


Figure 5-32
Corrosion potential predicted by MacDonald’s model as a function of the hydrogen concentration and for five different oxygen concentrations in the bulk.

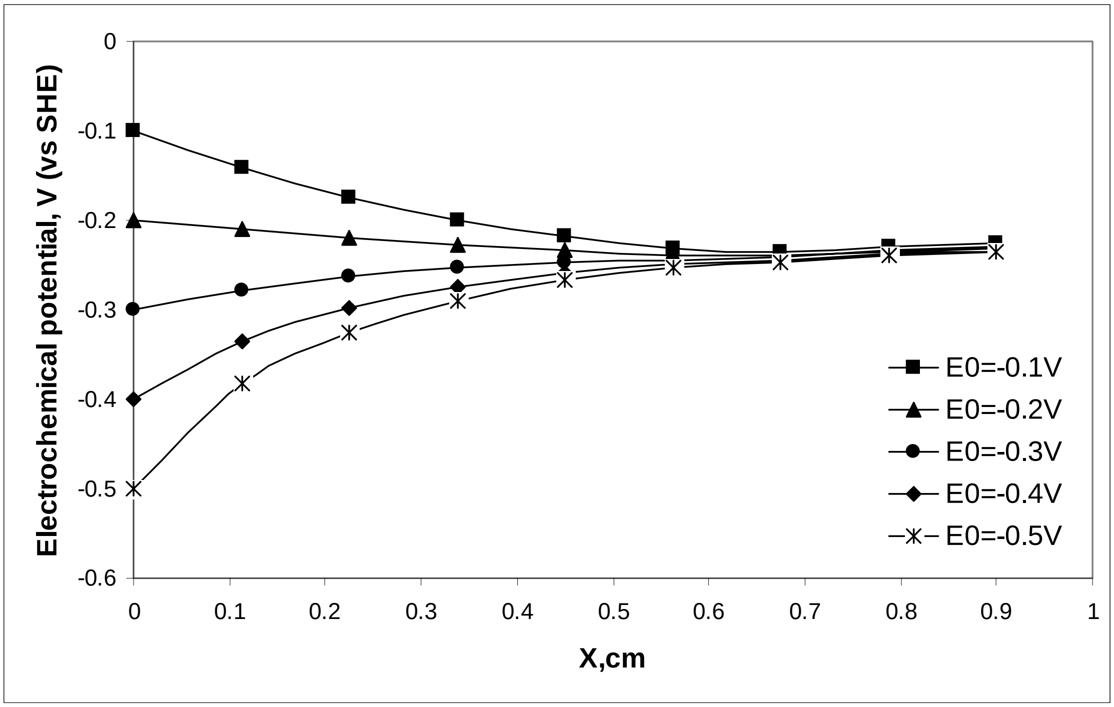


Figure 5-33
Distribution of the electrochemical potential predicted by the new model when the crevice is polarized at –0.1V, –0.2V, –0.3V, –0.4V and –0.5V at the mouth.

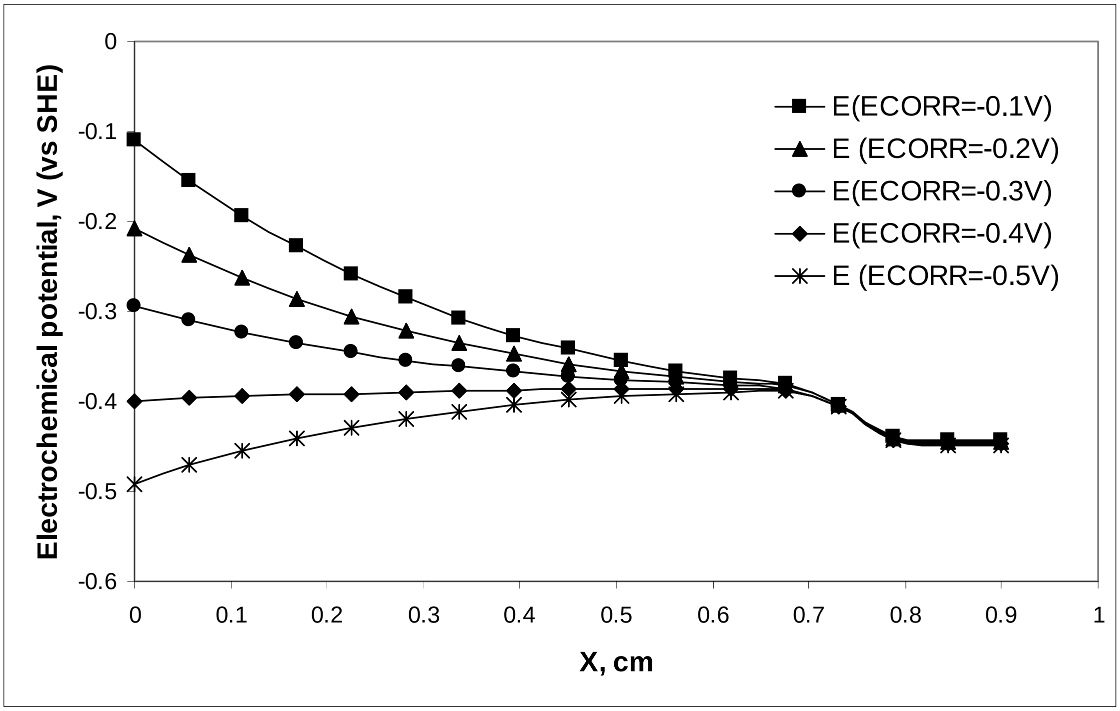


Figure 5-34
Distribution of the electrochemical potential predicted by MacDonald's model when the corrosion potential of the tube is –0.1V, –0.2V, –0.3V, –0.4V and –0.5V. The potential of the tube is very close to the potential at the mouth.

As explained in the MacDonald's thesis, the cathodic current density depends on the electrochemical potential, but only in the entry region. In the concentrated region, the cathodic current density compensates for the corrosion current density and correspondingly becomes constant since the chemistry is uniform (Figure 5-35). Therefore, $I_{cathodic}(E) = I_{CORR}$ in the concentrated region. This fixes the electrochemical potential. Recall that the electrochemical potential is an exponential term, therefore a small variation of E results in a large variation of I. Fixing $I_{cathodic}$ fixes E tightly.

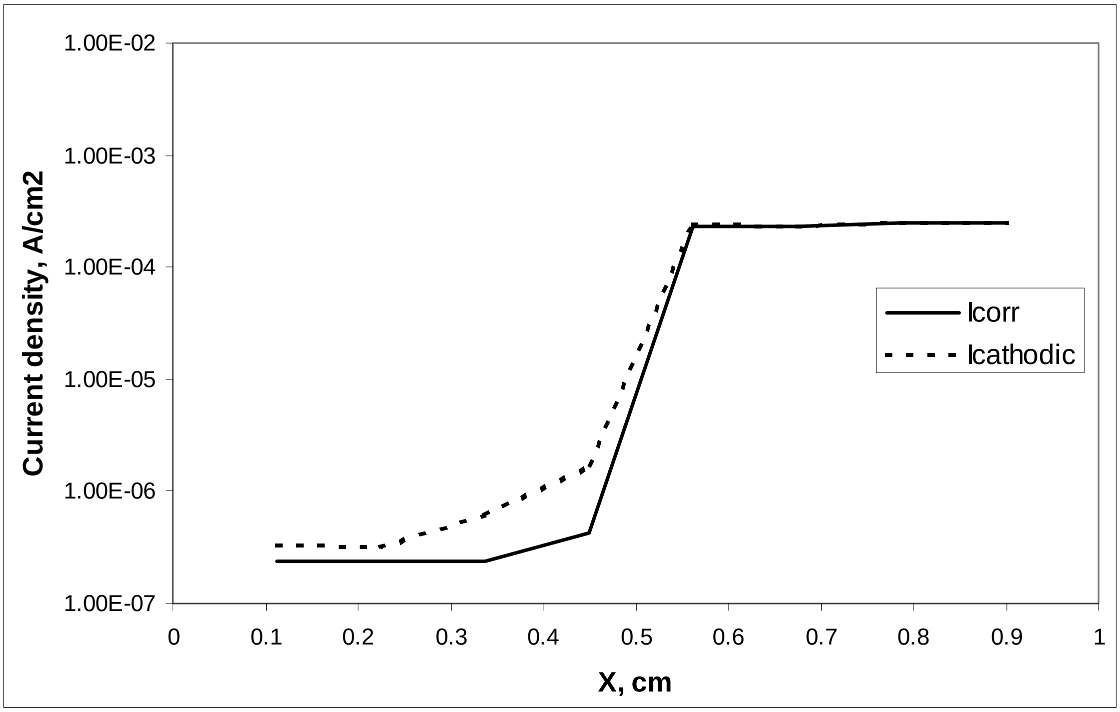


Figure 5-35
Distribution of the cathodic and the corrosion currents in the crevice predicted by the new model. The crevice is externally polarized at –0.42V at the mouth.

5.3.4 Effect of the Na/Cl Ratio on the Electrochemical Potential

The effect of the chemistry on the potential was examined. The ratios of sodium to chloride were varied from 0.8 to 1.2 and the potential distribution was calculated. These results appear as Figures 5-36 through 5-37. The transition between the nonconcentrated region and the concentrated region occurs around x=1.1 cm.

For a ratio of 1.1 and 1.2, the pH is acidic, therefore the corrosion current is quite high (Table 5-3) and the electrochemical potential is determined to match the corrosion current, and is low. For a ratio of 0.8 or 0.9, the corrosion current is small. Therefore the electrochemical potential is higher.

Varying the ratio of sodium to chloride varies the pH, therefore the corrosion current, and determines the electrochemical potential in the crevice. For a neutral crevice, the corrosion current is almost nonexistent. Therefore, the electrochemical potential is even higher than the other cases.

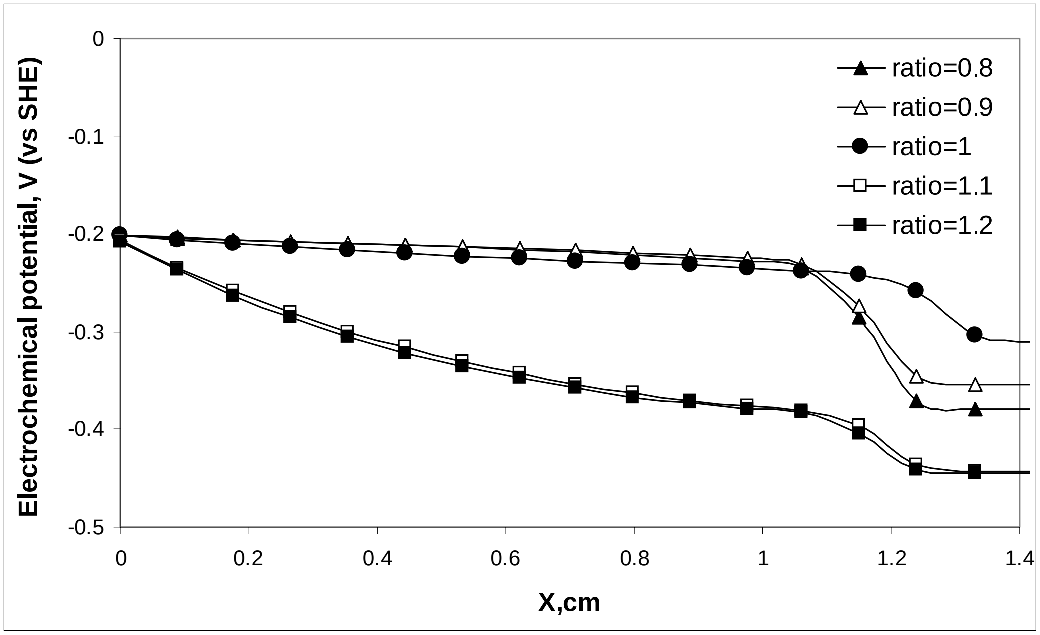


Figure 5-36
Distribution of the electrochemical potential in the crevice for different ratio chloride to sodium.

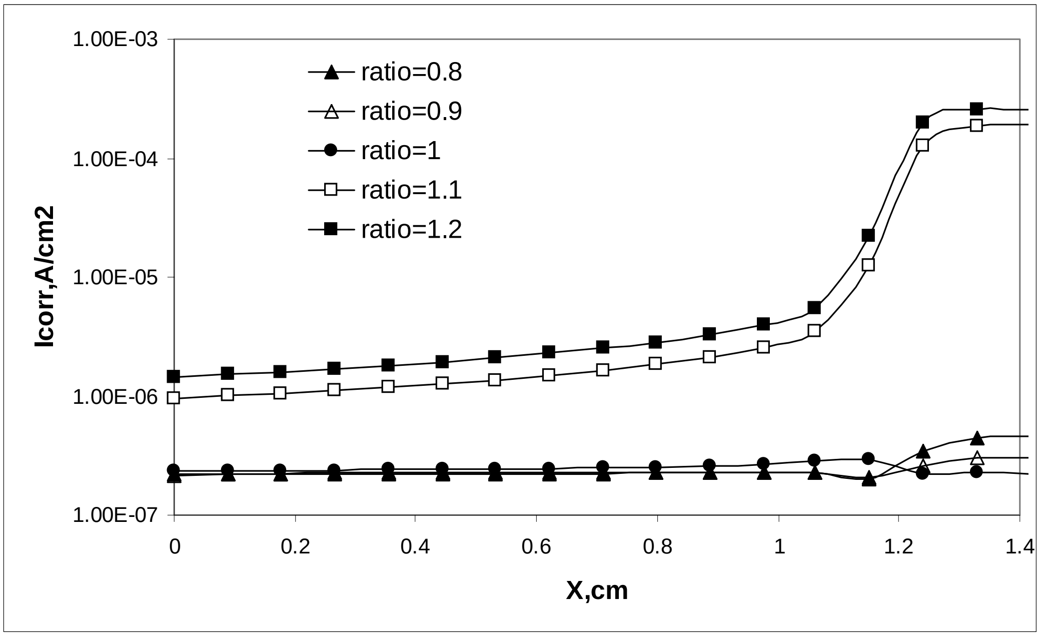


Figure 5-37
Distribution of the corrosion current density Icorr in the crevice for different ratio chloride to sodium.

Table 5-3
Effect of Varying Sodium / Chloride Ratio

Ratio of Sodium to Chloride	0.8	0.9	1.0	1.1	1.2
Corrosion Current *(A)*	4.56×10^{-7}	3.05×10^{-7}	2.23×10^{-7}	1.89×10^{-4}	2.59×10^{-4}

5.3.5 Effect of the electrochemical currents

As could be noticed before, the currents in the crevice determine the electrochemical potential. Since the currents are hardly known due to the lack of experimental data, their influence was studied in this thesis.

5.3.5.1 Effect of Cathodic Current

The exchange current density for oxygen reactions is known to be between 10^{-12} and 10^{-6} A/cm^2. This is a large variation. The exchange current density parameter A_H was varied with a factor of 10^6 and the potential was predicted, which is illustrated in Figure 5-38.

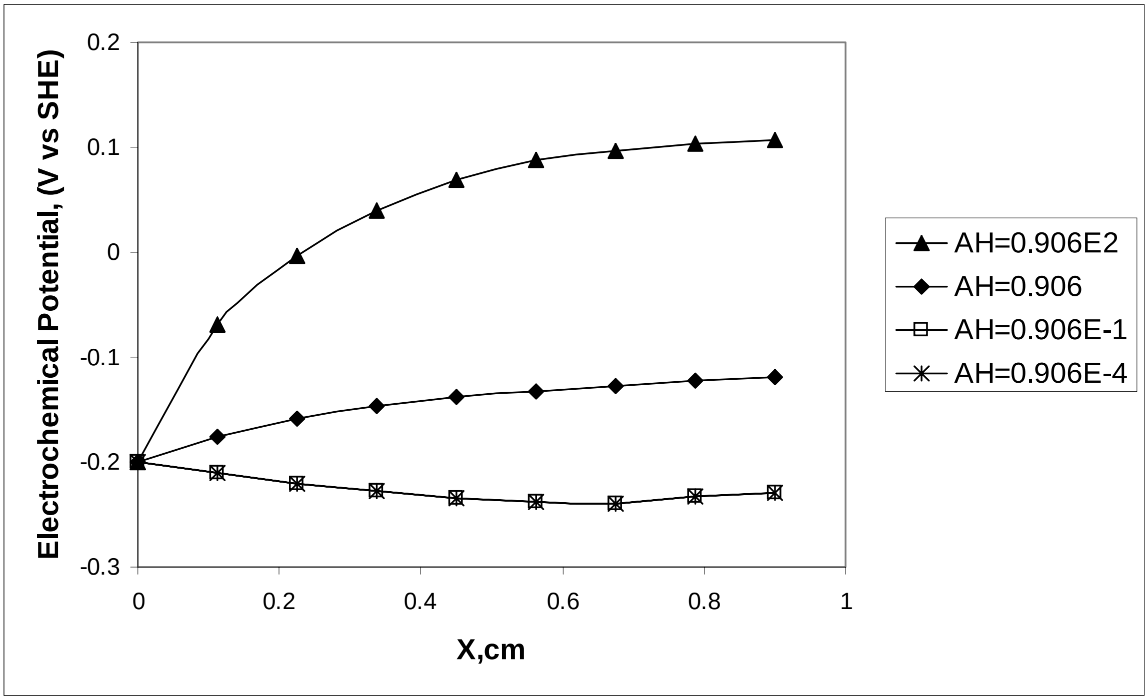


Figure 5-38
Distribution of the electrochemical potential in the crevice for different cathodic exchange current densities

$$I_{cath} = AH * C_{H^+} * \exp\left\{\frac{\alpha F}{RT}(E - E^e)\right\}$$

As expected, this shows that the greater the cathodic current, the higher the electrochemical potential. With a variation of the exchange current density by a factor of 10^6, the electrochemical potential varies by as much as ±0.35 V.

5.3.5.2 Effect of The Corrosion Current

The corrosion current was also varied from 10^{-2} I_{CORR} to 1000 I_{CORR} with I_{CORR} being the value used by MacDonald. This is shown in Figure 5-39. As expected, the electrochemical potential is lower as the corrosion current is increased. With a variation of the corrosion current density by a factor of 10^5, the electrochemical potential varies as much as 0.3 V.

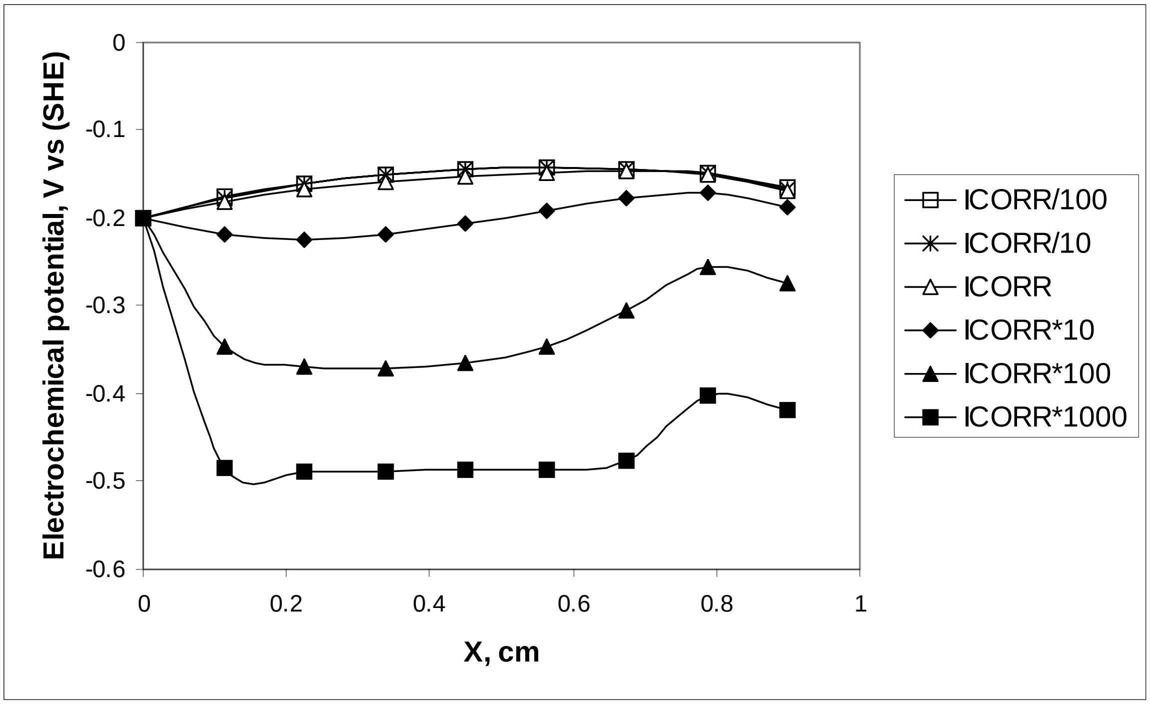


Figure 5-39
Distribution of the electrochemical potential in the crevice for different corrosion current densities. I_{CORR} corresponds to the expression used by MacDonald.

In MacDonald's thesis, the expression of the corrosion is only a function of the chemistry. However, it is probable that it is also a function of the electrochemical potential. The model was run with a corrosion current expressed as a Butler-Volmer equation with different exchange current densities. The results can be compared to the predictions with the expression of corrosion current as a function of the pH. The shapes of the curves are completely different, and shown in Figures 5-40 and 5-41.

The expressions and intensities of the current have a large effect on the prediction of the electrochemical potential. Therefore, until we have better experimental data available to determine what the currents are in a crevice, such modeling can predict qualitative variations, but can not give a good quantitative evaluation of the potential in the crevice.

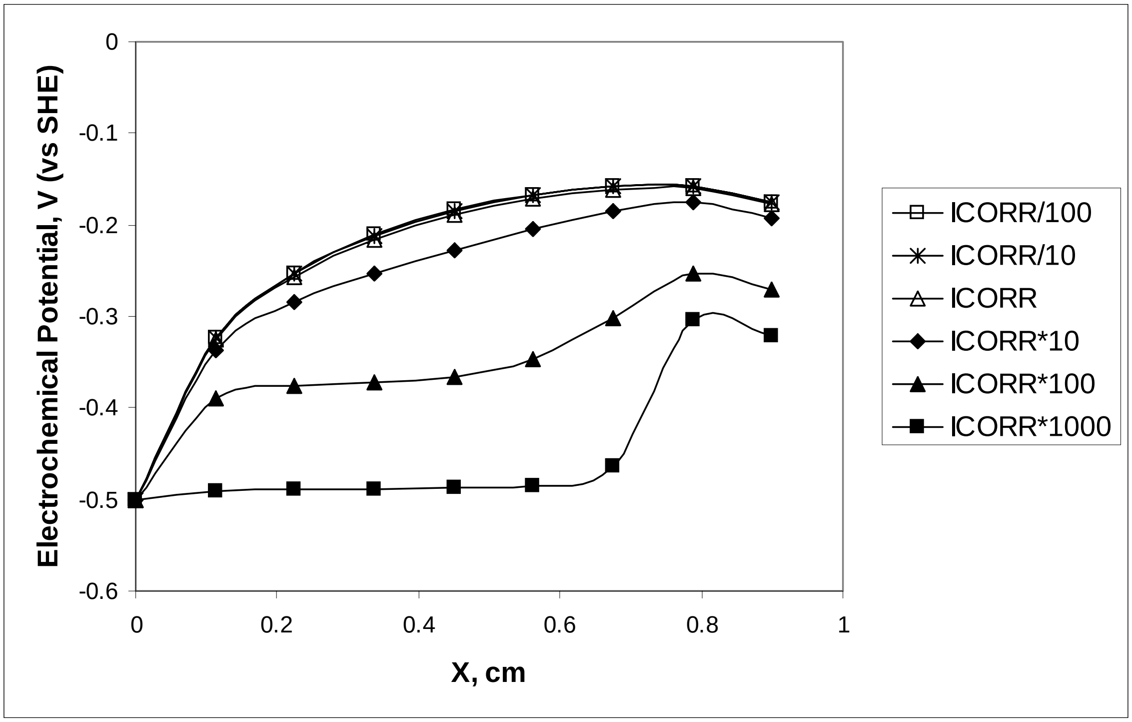


Figure 5-40
Distribution of electrochemical potential for different corrosion current. The corrosion current is a function of pH only. This is the corrosion current used by MacDonald's model.

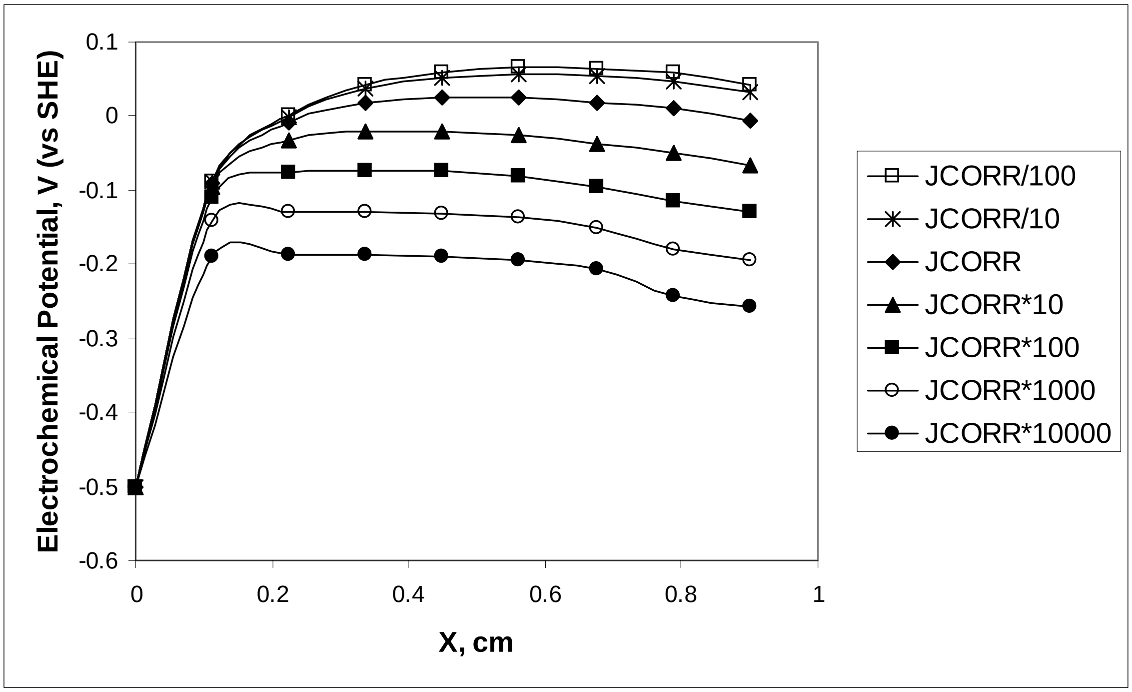


Figure 5-41
Distribution of electrochemical potential for different corrosion current. The corrosion current is a function of the electrochemical and the pH.

6

CONCLUSIONS

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1. A localized electrochemical model has been developed to study PWR steam generator crevice environments.

2. The new model predicts that if the crevice is very packed, the middle is initially steam-blanketed. As the concentration of impurities increases at the interface between the steam-blanketed region and the liquid rich region, the impurities diffuse towards the center, wetting the crevice. At steady state, the crevice is completely filled with impurities.

3. The model was benchmarked against three series of experimental results. In each case, the model predictions and the experimental data were in excellent agreement.

4. The mass of non-volatile impurities obtained experimentally and predicted by the model is **LINEAR** with exposure. Exposure is defined as the bulk concentration times the time of exposition. A crevice exposed to 1 ppb bulk sodium for 10 hours or exposed to 10 ppb bulk sodium for 1 hour contains the same amount of sodium.

5. In the case of a plant-heated crevice, it is predicted that the crevice initially is 60% steam blanketed. After roughly 150 ppmhrs of exposure, the crevice is fully wetted. Steady state is reached at around 1000 ppmhrs. Therefore, for a crevice exposed to 0.1 ppb, the crevice is fully wetted after a 170 years of continuous operation and steady state is reached after 1140 years.

6. In operating power plants, the concentration process in crevices is always limited by shutdown of the plant. The crevice steam-blanketed region always exists. There is not enough time in continuous operation to fill the crevice. The steady state is never reached and the accumulation is therefore always linear during operation.

7. In the case of Lumsden and Takamatsu's diamond packed (65%) crevices, it is predicted that when crevices are very packed, there is no mixing between steam and liquid water. Therefore, no process of carryover of impurities takes place in the crevice.

8. In the case of San Jose State University's carbon fiber packed crevices (50%), it is predicted that mixing between steam and liquid water exists. The carryover is predicted to be proportional to the bulk concentration. This carryover reduces the rate of concentration as well as the steady state mass of impurities in the crevice.

9. Several parametric studies were performed with the new model. The steam-blanketed region is predicted to be larger for high heat transfer coefficients and /or lower permeabilities.

10. The slope of capillary pressure versus saturation magnitude enhances the wetting process (initially and transient).

11. The new model was compared to previous models such as MacDonald’s model, developed in the case of a high corrosion current and a fully wetted crevice. The agreement is very good.

12. MacDonald’s model assumes a very high corrosion current and therefore assumes that there is precipitation of $FeOH_2$ in the crevice. These assumptions are valid but limiting. The model assumes as well that the wetted length is constant with time and the steam-blanketed region does not get wetted as concentration proceeds. This assumption is incorrect.

13. It was found that the system of equations obtained and solved by MacDonald is appropriate but too stiff for the numerical method to converge.

14. The new model is based on the same equations than MacDonald’s but is solved with different numerical methods. The new model does not assume that the corrosion current is high and that therefore precipitation of $FeOH_2$ always occurs.

15. According to both models, there is a very large diffusion current at the interface between the non-concentrated and the concentrated regions in the crevice, which determines the electrochemical potential behavior between the two regions.

16. According to both models, there is no effect of the external polarization on the electrochemical potential observed in the crevice.

17. Expressing the corrosion current as a function of pH only or as a function of the pH and the electrochemical potential results in very different profiles of potential in the crevice. Therefore, one should be careful on the choice of the current densities.

7

FUTURE WORK

7.1 Thermal hydraulic modeling

1. The heat transfer coefficient is an average heat transfer coefficient. It does not take into account the fact that the mixture contains more or less steam. Since the heat transfer coefficient for steam is a lot less than the heat transfer coefficient for liquid water, the heat transfer coefficient should be a function of the saturation S.

2. In the new model, H is programmed to be a linear function of the saturation as described in equation 7-1

   $$H = H_0 + H_1 * S \qquad \textbf{Eq. 7-1}$$

   However, the value of H_1 was not studied and therefore H_1 was set to zero waiting for a better value to be found in the literature. This study should be carried out and the value of H_1 entered in the model and a parametric study should be done.

3. The infinite dilution approximation is not valid in the concentrated region. Although it is believed that the diffusion coefficients have very little impact on the thermal hydraulic processes, it might be worth integrating activity coefficient.

4. In order to better model the experimental data, it would be useful during the experiment to characterize the porous media used in the experiment with a water retention curve. This way, DPCDS and the permeability would not have to be estimated. AS well, the heat transfer should be provided with the experimental data.

7.2 Chemical Modeling

5. The chemical modeling was not benchmarked. Experimental measurements of the pH in the crevice are necessary to continue the chemical modeling.

7.3 Electrochemical modeling

6. As well, it is worthless to go on modeling the electrochemistry in the crevice as long as there is no experimental data available. The corrosion current behavior should be determined. Special focus should be given to whether or not it depends on the pH and/or electrochemical potential of the solution for 600SS at high temperature.

7. The electrochemical model should be solved with a better numerical method that can divide the crevice in smaller elementary volumes.

8. The crevice should be studied under free corrosion as well as under external polarization.

9. Currents should be measured at the mouth of crevices to determine whether or not the crevice is under external polarization.

10. The effect of the external polarization should be studied in the case where the corrosion current is not high.

11. Once each part of the model is benchmarked, thermal hydraulic chemistry and electrochemistry should be integrated into one model.

8
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A

APPENDIX A CAPILLARY PRESSURE DATA FROM UNSODA

This annex provides with all the information from different soils: caracteristics, capillary pressure etc. It is divided in two parts: information from literature search and information from database UNSODA. For each soil, the saturation, corresponding capillary pressure and adimensional capillary pressure is reported in the table.

Data from literature search:

Authors		Saturation	Pc (atm)	J
Lord/Demond/ Salehzadeh/Hayes *Permeability* 1.0 E-11m2 Porosity 0.33		0.153942	0.101796407	0.780461
		0.1602	0.091566868	0.702032
		0.172716	0.083832337	0.642732
		0.209011	0.076347305	0.585346
		0.249061	0.071107789	0.545175
		0.314143	0.066117766	0.506917
		0.438048	0.060628744	0.464833
		0.663329	0.055638727	0.426575
		0.846058	0.050399204	0.386405
		0.944931	0.048153695	0.369189
		0.953692	0.045409187	0.348147
		0.98373	0.042664673	0.327105
		0.984981	0.037924156	0.29076
		0.991239	0.032684633	0.250589
		0.993742	0.024700597	0.189376
		0.997497	0.021956089	0.168335
		0.993742	0.02070859	0.15877
		0.996245	0.016966072	0.130077
		0.996245	0.014221564	0.109035
		0.996245	0.009980046	0.076516
		1	0	0

Authors		Saturation	Pc (atm)	J
Dong		0.103542	0.380833332	0.882093
Permeability		0.152589	0.324166661	0.75084
9.68E-13m2		0.201635	0.27333333	0.633099
Porosity		0.247956	0.229999989	0.53273
0.35		0.297003	0.194999996	0.451662
		0.343324	0.16249999	0.376385
		0.395095	0.137499984	0.31848
		0.446867	0.119166669	0.276016
		0.498638	0.104166669	0.241273
		0.544959	0.0942	0.218188
		0.594005	0.0875	0.202669
		0.645777	0.0817	0.189235
		0.692098	0.0775	0.179507
		0.743869	0.0742	0.171863
		0.787466	0.0692	0.160282
		0.839237	0.0625	0.144764
		0.891008	0.0533	0.123454
		0.945504	0.04	0.092649
		0.991826	0.023333328	0.054045
Authors		Saturation	Pc (atm)	J
Liu/Hopmans/Grismer/Chen		0.0455	0.686053431	1.983762
Permeability		0.127273	0.337091987	0.742325
1.16E-12m2		0.238182	0.213649891	0.617781
Porosity		0.485455	0.135311581	0.391261
0.464		0.767273	0.097329419	0.281433
		0.854545	0.080712185	0.233384
		0.929091	0.047477716	0.137284
		0.978182	0.021364983	0.061778
Authors		Saturation	Pc (atm)	J
Liu/Hopmans/Grismer/Chen		0.0363	0.190304715	1.114451
Permeability		0.0763	0.147922434	0.866254
7.00E-13		0.192748	0.09972299	0.583992
Porosity		0.307252	0.081440441	0.476926
0.362		0.46374	0.061495851	0.360128
		0.767176	0.046537423	0.27253
		0.921756	0.034072037	0.199531
		0.994275	0.008310244	0.048666

Authors		Saturation	Pc (atm)	J
Liu/Hopmans/Grismer/Chen		0.0553	0.677570095	1.959232
Permeability		0.147967	0.317757026	0.918812
1.16E-12m2		0.273171	0.198598176	0.574258
Porosity		0.520325	0.114486033	0.331043
0.464		0.788618	0.084112142	0.243215
		0.848781	0.060747671	0.175655
		0.939837	0.032710327	0.094584
Authors		Saturation	Pc (atm)	J
Liu/Hopmans/Grismer/Chen		0.0299	0.193894747	1.135474
Permeability		0.0677	0.146526325	0.858078
7.00E-13		0.187402	0.096631586	0.565888
Porosity		0.303937	0.077684214	0.454929
0.362		0.458268	0.059368433	0.34767
		0.766929	0.042315803	0.247807
		0.92126	0.034736866	0.203424
		0.962205	0.016421055	0.096164
Authors		Saturation	Pc (atm)	J
Moseley/Dhr		0.011084	0.045362192	0.300344
Permeability		0.0271	0.045232216	0.299484
9.24E-12		0.052956	0.044452348	0.29432
Porosity		0.0739	0.043672483	0.289157
0.41		0.0961	0.043152572	0.285714
		0.12069	0.042372708	0.280551
		0.144089	0.04159284	0.275387
		0.168719	0.041462863	0.274527
		0.194581	0.041202909	0.272806
		0.215517	0.040812975	0.270224
		0.238916	0.040812975	0.270224
		0.263547	0.040293064	0.266781
		0.286946	0.040163088	0.265921
		0.314039	0.039773154	0.263339
		0.337438	0.0395132	0.261618
		0.3633	0.03938322	0.260757
		0.386699	0.038993289	0.258176
		0.408867	0.038733332	0.256454
		0.432266	0.038603355	0.255594
		0.458128	0.038343401	0.253873
		0.481527	0.038213421	0.253012
		0.508621	0.03782349	0.25043
		0.528325	0.037433557	0.247849
		0.551724	0.037043623	0.245267

		0.577586	0.036523715	0.241824
		0.599754	0.036263758	0.240103
		0.623153	0.03561387	0.2358
		0.649015	0.034834006	0.230637
		0.673645	0.034444072	0.228055
		0.698276	0.033924161	0.224613
		0.722906	0.032884339	0.217728
		0.746305	0.031974498	0.211704
		0.769704	0.031324607	0.207401
		0.800493	0.030284785	0.200516
		0.821429	0.029244964	0.193632
		0.846059	0.027815211	0.184165
		0.868227	0.026385459	0.174699
		0.890394	0.024695753	0.163511
		0.912562	0.022876063	0.151463
		0.929803	0.021186357	0.140275
		0.947044	0.019366668	0.128227
		0.961823	0.017287024	0.114458
		0.970443	0.015597318	0.10327
		0.977832	0.013774301	0.0912
		0.980296	0.01208272	0.08
		0.981527	0.010391139	0.0688
		0.985222	0.008578731	0.0568
		0.992611	0.005980946	0.0396
		0.993842	0.003896677	0.0258
		0.996305	0.001812408	0.012
Authors O Dury/Fisher/Schulin Permeability 3.70E-11 Porosity 0.357 Imbibition		Saturation	Pc (atm)	J
		0.03937	0.156081079	2.19772
		0.0669	0.098648649	1.389035
		0.0827	0.058783778	0.827713
		0.114173	0.044594584	0.62792
		0.161417	0.033783782	0.475697
		0.255906	0.028378373	0.399585
		0.389764	0.02162162	0.304446
		0.543307	0.015540539	0.218821
		0.606299	0.013513506	0.190279
		0.625984	0.012162162	0.171251
		0.669291	0.012162162	0.171251
		0.700787	0.010810802	0.152223
		0.740157	0.007432425	0.104653
		0.767717	0.004729721	0.066597
		0.787402	0	0

Authors		Saturation	Pc (atm)	J
O Dury/Fisher/Schulin		0.07874	0.074324317	1.046533
Permeability		0.122047	0.053378369	0.751601
3.70E-11		0.185039	0.047297288	0.665976
Porosity		0.228346	0.043243239	0.608892
0.357		0.271654	0.039189191	0.551809
Drainage		0.299213	0.03783783	0.532781
		0.350394	0.035135126	0.494725
		0.409449	0.03310811	0.466183
		0.448819	0.030405405	0.428127
		0.480315	0.029729717	0.418613
		0.507874	0.028378373	0.399585
		0.543307	0.027027029	0.380558
		0.637795	0.025675668	0.36153
		0.700787	0.022972964	0.323474
		0.740157	0.018243243	0.256876
		0.763779	0.012162162	0.171251
		0.779528	0.008108097	0.114167

Authors		Saturation	Pc (atm)	J
She/Sleep		0.157791	0.085956417	0.203583
Permeability		0.167653	0.082808716	0.196128
1.1E-12m2		0.191321	0.080387409	0.190394
Porosity		0.207101	0.073123486	0.173189
0.37		0.246548	0.069975786	0.165734
20C Imbibition		0.284024	0.066828086	0.158279
		0.321499	0.064406779	0.152544
		0.360947	0.063196126	0.149677
		0.39645	0.059564164	0.141075
		0.508876	0.056900726	0.134766
		0.621302	0.055205811	0.130752
		0.737673	0.049636805	0.117562
		0.850099	0.047215498	0.111828
		0.998028	0.038256657	0.090609

Authors	Saturation	Pc (atm)	J
She/Sleep	0.138067	0.089104116	0.211039
Permeability	0.147929	0.076513316	0.181218
1.1E-12m2	0.17357	0.069733656	0.165161
Porosity	0.195266	0.065133171	0.154265
0.37	0.234714	0.057142855	0.13534
20C Drainage	0.272189	0.049636805	0.117562
	0.309665	0.047699757	0.112974
	0.420118	0.04261501	0.100931
	0.530572	0.036803874	0.087168
	0.648915	0.033898303	0.080286
	0.723866	0.02929782	0.06939
	0.798817	0.018886196	0.044731
	0.873767	0.011380142	0.026953
Authors	Saturation	Pc (atm)	J
She/Sleep	0.167653	0.073123486	0.181152
Permeability	0.191321	0.066828086	0.165556
1.1E-12m2	0.21499	0.060532688	0.14996
Porosity	0.242604	0.059322035	0.146961
0.37	0.35503	0.055205811	0.136764
40C Imbibition	0.469428	0.049878934	0.123567
	0.581854	0.04891041	0.121168
	0.696252	0.043583533	0.107971
	0.816568	0.041162227	0.101973
	0.923077	0.038256657	0.094775
	0.968442	0.033414044	0.082778
	0.998028	0.020823243	0.051586
	1.001972	0.007506054	0.018595
Authors	Saturation	Pc (atm)	J
She/Sleep	0.17357	0.065859565	0.163157
Permeability	0.209073	0.059079903	0.146361
1.1E-12m2	0.240631	0.049394675	0.122368
Porosity	0.360947	0.034382568	0.085177
0.37	0.475345	0.026876514	0.066582
40C Drainage	0.585799	0.025665861	0.063583
	0.684418	0.022518161	0.055785
	0.810651	0.018886196	0.046788
	0.889546	0.015496366	0.03839
	0.913215	0.010895883	0.026993
	0.919132	0.004842612	0.011997
	0.921105	0.000726388	0.0018

Authors		Saturation	Pc (atm)	J
She/Sleep		0.197239	0.057142855	0.148833
Permeability		0.254438	0.051089587	0.133067
1.1E-12m2		0.443787	0.045278451	0.117931
Porosity		0.56213	0.042857145	0.111625
0.37		0.670611	0.038498786	0.100273
60C Imbibition		0.788955	0.035593221	0.092705
		0.865878	0.031719126	0.082615
		0.90927	0.031476997	0.081984
		0.944773	0.028813561	0.075047
		0.980276	0.027845038	0.072525
		0.998028	0.024697338	0.064326

Authors		Saturation	Pc (atm)	J
She/Sleep		0.155819	0.075302663	0.196132
Permeability		0.195266	0.064406779	0.167753
1.1E-12m2		0.216963	0.054237287	0.141265
Porosity		0.274162	0.041888621	0.109102
0.37		0.34714	0.032445521	0.084507
60C Drainage		0.534517	0.025665861	0.066849
		0.658777	0.025423726	0.066218
		0.698225	0.02300242	0.059912
		0.733728	0.02276029	0.059281
		0.812623	0.019370461	0.050452
		0.850099	0.015012107	0.0391
		0.889546	0.007021789	0.018289
		0.944773	0.000242129	0.000631

Authors		Saturation	Pc (atm)	J
She/Sleep		0.242604	0.078692493	0.216402
Permeability		0.282051	0.060290556	0.165797
1.1E-12m2		0.317554	0.047941887	0.131839
Porosity		0.398422	0.041646486	0.114527
0.37		0.510848	0.040193704	0.110531
80C Imbibition		0.637081	0.035593221	0.09788
		0.745562	0.031476997	0.086561
		0.86785	0.02929782	0.080568
		0.927022	0.026634385	0.073244
		0.960552	0.024455202	0.067251
		0.984221	0.020338984	0.055932
		1.001972	0.000968518	0.002663

Authors		Saturation	Pc (atm)	J
She/Sleep		0.236686	0.084745762	0.233048
Permeability		0.280079	0.057869249	0.159139
1.1E-12m2		0.353057	0.040920098	0.112529
Porosity		0.473373	0.030508473	0.083897
0.37		0.599605	0.028087167	0.077239
80C Drainage		0.646943	0.025423726	0.069914
		0.686391	0.022518161	0.061924
		0.723866	0.017433413	0.047941
		0.765286	0.015738496	0.04328
		0.802761	0.014527843	0.039951
		0.844181	0.010653754	0.029298
		0.919132	0.005326871	0.014649
		0.960552	0.000968518	0.002663

Author		Saturation	Pc (atm)	J
Van Geel/Sykes		0.0231	0.116397749	1.026668
Permeability		0.0375	0.114146342	1.00681
1.5E-11m2		0.04611	0.109418386	0.965107
Porosity		0.0288	0.105816135	0.933334
0.374		0.048991	0.103339587	0.91149
Drainage		0.00576	0.098611632	0.869788
		0.04611	0.09816135	0.865817
		0.051873	0.095234521	0.840001
		0.048991	0.092983115	0.820143
		0.051873	0.088255158	0.778441
		0.0403	0.086228892	0.760568
		0.0865	0.083527204	0.736738
		0.0951	0.081500938	0.718866
		0.0692	0.076998126	0.67915
		0.0807	0.073846152	0.651348
		0.132565	0.074521575	0.657306
		0.175793	0.073170733	0.645391
		0.106628	0.070694182	0.623547
		0.144092	0.066866789	0.589788
		0.132565	0.065966231	0.581845
		0.184438	0.070243903	0.619575
		0.230548	0.068442776	0.603689
		0.190202	0.06348968	0.560001
		0.172911	0.061913693	0.5461
		0.224784	0.058986869	0.520284
		0.21902	0.061688554	0.544114
		0.259366	0.065515947	0.577873

0.302594	0.065065668	0.573901
0.253602	0.06078799	0.536171
0.273775	0.056735457	0.500426
0.311239	0.058086305	0.512341
0.345821	0.061913693	0.5461
0.389049	0.06078799	0.536171
0.386167	0.059662287	0.526242
0.357349	0.056060039	0.494469
0.34294	0.054934336	0.48454
0.383285	0.053133209	0.468653
0.414986	0.054484052	0.480568
0.469741	0.056510318	0.49844
0.475504	0.058986869	0.520284
0.461095	0.053358349	0.470639
0.443804	0.050881803	0.448795
0.489914	0.049756095	0.438866
0.504323	0.052682925	0.464681
0.54755	0.054709191	0.482554
0.553314	0.056960602	0.502412
0.550432	0.050656658	0.446809
0.54755	0.048180113	0.424965
0.590778	0.045928707	0.405107
0.587896	0.049080676	0.432908
0.605187	0.052232646	0.46071
0.608069	0.055159476	0.486525
0.662824	0.049305816	0.434894
0.685879	0.051106943	0.450781
0.642651	0.045478423	0.401135
0.685879	0.043677296	0.385249
0.717579	0.046829265	0.41305
0.743516	0.047504689	0.419008
0.763689	0.050431519	0.444823
0.746398	0.045253283	0.399149
0.752161	0.042776733	0.377305
0.786744	0.039849908	0.35149
0.789625	0.043902441	0.387235
0.806916	0.046829265	0.41305
0.847262	0.048855532	0.430922
0.824208	0.0387242	0.341561
0.855908	0.042551593	0.37532
0.878963	0.04412758	0.38922
0.899135	0.046604126	0.411064
0.896254	0.039624763	0.349504

	0.913545	0.041876175	0.369362
	0.925072	0.042326454	0.373334
	0.942363	0.039399624	0.347518
	0.930836	0.036923078	0.325674
	0.948127	0.044577859	0.393192
	0.982709	0.043677296	0.385249
	0.988473	0.041876175	0.369362
	0.971182	0.037373358	0.329646
	0.959654	0.034671667	0.305816
	1.008646	0.035347091	0.311773
	1.005764	0.033771104	0.297873
	0.988473	0.031519703	0.278015
	1	0.028592868	0.252199
	0.997118	0.027016881	0.238298
Author	Saturation	Pc (atm)	J
Van Geel/Sykes	0.0144	0.086454034	0.762554
Permeability	0.00865	0.090056285	0.794327
1.5E-11m2	0.0144	0.095909944	0.845958
Porosity	0.0173	0.098836772	0.871774
0.374	0.00288	0.101988744	0.899576
Imbibition	0.0202	0.081500938	0.718866
	0.0317	0.077448405	0.683121
	0.0692	0.071819885	0.633476
	0.0807	0.067992497	0.599717
	0.0865	0.064165104	0.565958
	0.123919	0.061238275	0.540142
	0.103746	0.058536584	0.516313
	0.106628	0.054484052	0.480568
	0.123919	0.058536584	0.516313
	0.152738	0.055384615	0.488511
	0.149856	0.052457785	0.462696
	0.172911	0.050206379	0.442837
	0.178674	0.047729829	0.420993
	0.195965	0.055834894	0.492483
	0.230548	0.051557222	0.454752
	0.259366	0.047954974	0.422979
	0.256484	0.045253283	0.399149
	0.311239	0.045928707	0.405107
	0.319885	0.043902441	0.387235
	0.351585	0.045253283	0.399149
	0.351585	0.040525327	0.357447
	0.397695	0.039624763	0.349504

	0.412104	0.042326454	0.373334
	0.466859	0.04165103	0.367376
	0.435158	0.037598497	0.331632
	0.527378	0.037373358	0.329646
	0.51585	0.039399624	0.347518
	0.579251	0.03849906	0.339575
	0.567723	0.035121952	0.309788
	0.62536	0.036022515	0.317731
	0.648415	0.034671667	0.305816
	0.680115	0.031069414	0.274043
	0.688761	0.034896812	0.307802
	0.729107	0.033320825	0.293901
	0.778098	0.031744843	0.28
	0.798271	0.033095685	0.291915
	0.832853	0.029943716	0.264114
	0.827089	0.028818008	0.254185
	0.904899	0.028592868	0.252199
	0.948127	0.024765475	0.21844
	0.92219	0.022739209	0.200568
	0.959654	0.018911816	0.166809
	0.959654	0.013508446	0.119149
	1.008646	0.010581611	0.093333
	1.011527	0.006754218	0.059575
Author	Saturation	Pc (atm)	J
Van Geel/Sykes	0.016621	0.114869888	1.013192
Permeability	0.016621	0.112416356	0.991551
1.5E-11m2	0.016621	0.110185873	0.971877
Porosity	0.0249	0.107063197	0.944334
0.374	0.0111	0.10527881	0.928595
	0.0249	0.103048325	0.908921
	0.0111	0.101933084	0.899085
	0.0222	0.098810408	0.871542
	0.016621	0.096579924	0.851868
	0.016621	0.094126392	0.830227
	0.0194	0.090111522	0.794814
	0.0499	0.088327137	0.779075
	0.0526	0.085873605	0.757434
	0.0277	0.084089217	0.741696
	0.0277	0.085873605	0.757434
	0.0194	0.08788104	0.775141
	0.0388	0.083197023	0.733826
	0.0471	0.07962825	0.702348
	0.0776	0.080743491	0.712185

		0.0942	0.079851297	0.704316
		0.0582	0.074944234	0.661034
		0.0831	0.074052045	0.653164
		0.0776	0.07048327	0.621686
		0.091413	0.070037175	0.617752
		0.124654	0.0664684	0.586274
		0.146814	0.066914494	0.590209
		0.157895	0.067583641	0.596111
		0.124654	0.074721187	0.659066
		0.160665	0.073159851	0.645295
		0.180055	0.07048327	0.621686
		0.229917	0.068475835	0.60398
		0.249307	0.064684012	0.570535
		0.290859	0.065130112	0.57447
		0.210526	0.061338289	0.541025
		0.213296	0.05843866	0.515449
		0.252078	0.059999995	0.52922
		0.263158	0.057546466	0.507579
		0.307479	0.057323419	0.505612
		0.3241	0.053977691	0.476102
		0.34349	0.056431225	0.497743
		0.385042	0.060669142	0.535123
		0.382271	0.061561336	0.542992
		0.33795	0.061561336	0.542992
		0.301939	0.065353159	0.576437
		0.254848	0.065576206	0.578405
		0.396122	0.05442379	0.480036
		0.379501	0.052416355	0.46233
		0.401662	0.051301114	0.452493
		0.457064	0.053754643	0.474134
		0.459834	0.056431225	0.497743
		0.468144	0.058661707	0.517416
		0.493075	0.053308549	0.4702
		0.481994	0.048401485	0.426918
		0.529086	0.047286244	0.417081
		0.531856	0.050185873	0.442657
		0.531856	0.055092937	0.485938
		0.531856	0.056431225	0.497743
		0.598338	0.054869884	0.483971
		0.578947	0.052639402	0.464297
		0.573407	0.04884758	0.430852
		0.576177	0.045724904	0.403309
		0.631579	0.04483271	0.39544
		0.65374	0.049293679	0.434787

		0.67867	0.051078062	0.450526
		0.698061	0.047063192	0.415113
		0.66482	0.043717469	0.385603
		0.731302	0.047063192	0.415113
		0.767313	0.050631967	0.446591
		0.747922	0.045501857	0.401342
		0.745152	0.04126394	0.363962
		0.783934	0.044163568	0.389538
		0.803324	0.047286244	0.417081
		0.842105	0.049962821	0.440689
		0.775623	0.040148693	0.354125
		0.825485	0.038587358	0.340354
		0.822715	0.039479552	0.348223
		0.842105	0.042825275	0.377734
		0.869806	0.044163568	0.389538
		0.886427	0.047063192	0.415113
		0.875346	0.039256505	0.346256
		0.908587	0.042156133	0.371831
		0.922438	0.042156133	0.371831
		0.955679	0.045278809	0.399375
		0.916897	0.040148693	0.354125
		0.919668	0.037472117	0.330517
		0.969529	0.043717469	0.385603
		1	0.042379181	0.373799
		0.977839	0.037472117	0.330517
		0.972299	0.034795535	0.306908
		1.00277	0.036133829	0.318713
		1.00277	0.034795535	0.306908
		0.99169	0.032565053	0.287235
		0.99169	0.029888477	0.263627
		0.99169	0.028550183	0.251822

Data collected from UNSODA:

N: Reference number in UNSODA
ε: Porosity of the porous media
κ: Hydraulic conductivty
k: Permeability
S: Saturation
H: Pressure head
J: Adimensional capillary pressure

The saturation and adimensional are given in the following first table and then the properties for each soil with reference N in UNSODA are reported in the second table.

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
1010	0.39	171.10	1.98E-03	1.98E-12	0.29	13.0	1300.0	0.041
	0.39	171.10	1.98E-03	1.98E-12	0.27	23.0	2300.0	0.072
	0.39	171.10	1.98E-03	1.98E-12	0.26	31.0	3100.0	0.097
	0.39	171.10	1.98E-03	1.98E-12	0.25	37.0	3700.0	0.116
	0.39	171.10	1.98E-03	1.98E-12	0.24	41.0	4100.0	0.129
	0.39	171.10	1.98E-03	1.98E-12	0.24	44.0	4400.0	0.138
	0.39	171.10	1.98E-03	1.98E-12	0.19	51.0	5100.0	0.160
	0.39	171.10	1.98E-03	1.98E-12	0.18	53.0	5300.0	0.166
	0.39	171.10	1.98E-03	1.98E-12	0.18	56.0	5600.0	0.176
	0.39	171.10	1.98E-03	1.98E-12	0.15	71.0	7100.0	0.223
	0.39	171.10	1.98E-03	1.98E-12	0.14	86.0	8600.0	0.270
	0.39	171.10	1.98E-03	1.98E-12	0.13	89.0	8900.0	0.279
	0.39	171.10	1.98E-03	1.98E-12	0.13	91.0	9100.0	0.286
	0.39	171.10	1.98E-03	1.98E-12	0.13	92.0	9200.0	0.289
	0.39	171.10	1.98E-03	1.98E-12	0.12	96.0	9600.0	0.301
	0.39	171.10	1.98E-03	1.98E-12	0.12	103.0	10300.0	0.323
	0.39	171.10	1.98E-03	1.98E-12	0.11	109.0	10900.0	0.342
1011								
	0.43	310.00	3.59E-03	3.59E-12	0.28	6.0	600.0	0.024
	0.43	310.00	3.59E-03	3.59E-12	0.26	14.0	1400.0	0.056
	0.43	310.00	3.59E-03	3.59E-12	0.28	19.0	1900.0	0.076
	0.43	310.00	3.59E-03	3.59E-12	0.25	20.0	2000.0	0.080
	0.43	310.00	3.59E-03	3.59E-12	0.23	24.0	2400.0	0.097
	0.43	310.00	3.59E-03	3.59E-12	0.25	25.0	2500.0	0.101
	0.43	310.00	3.59E-03	3.59E-12	0.22	28.0	2800.0	0.113
	0.43	310.00	3.59E-03	3.59E-12	0.23	29.0	2900.0	0.117
	0.43	310.00	3.59E-03	3.59E-12	0.21	30.0	3000.0	0.121
	0.43	310.00	3.59E-03	3.59E-12	0.22	32.0	3200.0	0.129
	0.43	310.00	3.59E-03	3.59E-12	0.21	34.0	3400.0	0.137
	0.43	310.00	3.59E-03	3.59E-12	0.19	37.0	3700.0	0.149
	0.43	310.00	3.59E-03	3.59E-12	0.17	39.0	3900.0	0.157
	0.43	310.00	3.59E-03	3.59E-12	0.17	40.0	4000.0	0.161
	0.43	310.00	3.59E-03	3.59E-12	0.16	41.0	4100.0	0.165

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.43	310.00	3.59E-03	3.59E-12	0.16	42.0	4200.0	0.169
	0.43	310.00	3.59E-03	3.59E-12	0.16	44.0	4400.0	0.177
	0.43	310.00	3.59E-03	3.59E-12	0.16	45.0	4500.0	0.181
	0.43	310.00	3.59E-03	3.59E-12	0.14	47.0	4700.0	0.189
	0.43	310.00	3.59E-03	3.59E-12	0.14	48.0	4800.0	0.193
	0.43	310.00	3.59E-03	3.59E-12	0.13	51.0	5100.0	0.205
	0.43	310.00	3.59E-03	3.59E-12	0.12	57.0	5700.0	0.229
	0.43	310.00	3.59E-03	3.59E-12	0.13	59.0	5900.0	0.237
	0.43	310.00	3.59E-03	3.59E-12	0.12	61.0	6100.0	0.245
	0.43	310.00	3.59E-03	3.59E-12	0.10	62.0	6200.0	0.249
	0.43	310.00	3.59E-03	3.59E-12	0.13	64.0	6400.0	0.257
	0.43	310.00	3.59E-03	3.59E-12	0.11	66.0	6600.0	0.266
	0.43	310.00	3.59E-03	3.59E-12	0.13	67.0	6700.0	0.270
	0.43	310.00	3.59E-03	3.59E-12	0.13	72.0	7200.0	0.290
	0.43	310.00	3.59E-03	3.59E-12	0.11	75.0	7500.0	0.302
	0.43	310.00	3.59E-03	3.59E-12	0.11	77.0	7700.0	0.310
1012								
	0.44	207.00	2.40E-03	2.40E-12	0.31	0.0	0.0	0.000
	0.44	207.00	2.40E-03	2.40E-12	0.25	5.0	500.0	0.016
	0.44	207.00	2.40E-03	2.40E-12	0.28	9.0	900.0	0.029
	0.44	207.00	2.40E-03	2.40E-12	0.27	12.0	1200.0	0.039
	0.44	207.00	2.40E-03	2.40E-12	0.30	26.0	2600.0	0.084
	0.44	207.00	2.40E-03	2.40E-12	0.25	23.0	2300.0	0.075
	0.44	207.00	2.40E-03	2.40E-12	0.26	28.0	2800.0	0.091
	0.44	207.00	2.40E-03	2.40E-12	0.16	30.0	3000.0	0.097
	0.44	207.00	2.40E-03	2.40E-12	0.25	31.0	3100.0	0.101
	0.44	207.00	2.40E-03	2.40E-12	0.14	32.0	3200.0	0.104
	0.44	207.00	2.40E-03	2.40E-12	0.13	33.0	3300.0	0.107
	0.44	207.00	2.40E-03	2.40E-12	0.17	34.0	3400.0	0.110
	0.44	207.00	2.40E-03	2.40E-12	0.22	35.0	3500.0	0.114
	0.44	207.00	2.40E-03	2.40E-12	0.14	38.0	3800.0	0.123
	0.44	207.00	2.40E-03	2.40E-12	0.19	39.0	3900.0	0.127
	0.44	207.00	2.40E-03	2.40E-12	0.16	40.0	4000.0	0.130
	0.44	207.00	2.40E-03	2.40E-12	0.15	42.0	4200.0	0.136
	0.44	207.00	2.40E-03	2.40E-12	0.15	43.0	4300.0	0.140
	0.44	207.00	2.40E-03	2.40E-12	0.13	44.0	4400.0	0.143
	0.44	207.00	2.40E-03	2.40E-12	0.15	45.0	4500.0	0.146
	0.44	207.00	2.40E-03	2.40E-12	0.13	49.0	4900.0	0.159
	0.44	207.00	2.40E-03	2.40E-12	0.11	52.0	5200.0	0.169
	0.44	207.00	2.40E-03	2.40E-12	0.13	53.0	5300.0	0.172
	0.44	207.00	2.40E-03	2.40E-12	0.10	54.0	5400.0	0.175
	0.44	207.00	2.40E-03	2.40E-12	0.10	57.0	5700.0	0.185
	0.44	207.00	2.40E-03	2.40E-12	0.10	60.0	6000.0	0.195
	0.44	207.00	2.40E-03	2.40E-12	0.11	62.0	6200.0	0.201
	0.44	207.00	2.40E-03	2.40E-12	0.11	63.0	6300.0	0.205
	0.44	207.00	2.40E-03	2.40E-12	0.11	66.0	6600.0	0.214

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.44	207.00	2.40E-03	2.40E-12	0.10	68.0	6800.0	0.221
1013								
	0.44	207.00	2.40E-03	2.40E-12	0.31	0.0	0.0	0.000
	0.44	207.00	2.40E-03	2.40E-12	0.28	7.0	700.0	0.023
	0.44	207.00	2.40E-03	2.40E-12	0.23	19.0	1900.0	0.062
	0.44	207.00	2.40E-03	2.40E-12	0.19	25.0	2500.0	0.081
	0.44	207.00	2.40E-03	2.40E-12	0.17	28.0	2800.0	0.091
	0.44	207.00	2.40E-03	2.40E-12	0.16	30.0	3000.0	0.097
	0.44	207.00	2.40E-03	2.40E-12	0.14	37.0	3700.0	0.120
	0.44	207.00	2.40E-03	2.40E-12	0.13	47.0	4700.0	0.153
	0.44	207.00	2.40E-03	2.40E-12	0.12	54.0	5400.0	0.175
	0.44	207.00	2.40E-03	2.40E-12	0.11	59.0	5900.0	0.192
	0.44	207.00	2.40E-03	2.40E-12	0.10	62.0	6200.0	0.201
	0.44	207.00	2.40E-03	2.40E-12	0.10	66.0	6600.0	0.214
	0.44	207.00	2.40E-03	2.40E-12	0.10	67.0	6700.0	0.218
	0.44	207.00	2.40E-03	2.40E-12	0.10	68.0	6800.0	0.221
1120								
	0.31	37.90	4.39E-04	4.39E-13	0.22	33.0	3300.0	0.054
	0.31	37.90	4.39E-04	4.39E-13	0.20	40.0	4000.0	0.066
	0.31	37.90	4.39E-04	4.39E-13	0.19	47.0	4700.0	0.078
	0.31	37.90	4.39E-04	4.39E-13	0.18	57.0	5700.0	0.094
	0.31	37.90	4.39E-04	4.39E-13	0.18	66.0	6600.0	0.109
	0.31	37.90	4.39E-04	4.39E-13	0.17	78.0	7800.0	0.129
	0.31	37.90	4.39E-04	4.39E-13	0.16	96.0	9600.0	0.159
1121								
	0.35	7.13	8.25E-05	8.25E-14	0.29	1.0	100.0	0.001
	0.35	7.13	8.25E-05	8.25E-14	0.29	9.0	900.0	0.006
	0.35	7.13	8.25E-05	8.25E-14	0.28	12.0	1200.0	0.008
	0.35	7.13	8.25E-05	8.25E-14	0.28	18.0	1800.0	0.012
	0.35	7.13	8.25E-05	8.25E-14	0.27	23.0	2300.0	0.016
	0.35	7.13	8.25E-05	8.25E-14	0.28	29.0	2900.0	0.020
	0.35	7.13	8.25E-05	8.25E-14	0.26	30.0	3000.0	0.020
	0.35	7.13	8.25E-05	8.25E-14	0.26	34.0	3400.0	0.023
	0.35	7.13	8.25E-05	8.25E-14	0.28	37.0	3700.0	0.025
	0.35	7.13	8.25E-05	8.25E-14	0.24	39.0	3900.0	0.026
	0.35	7.13	8.25E-05	8.25E-14	0.27	46.0	4600.0	0.031
	0.35	7.13	8.25E-05	8.25E-14	0.25	47.0	4700.0	0.032
	0.35	7.13	8.25E-05	8.25E-14	0.23	49.0	4900.0	0.033
	0.35	7.13	8.25E-05	8.25E-14	0.25	54.0	5400.0	0.037
	0.35	7.13	8.25E-05	8.25E-14	0.27	60.0	6000.0	0.041
	0.35	7.13	8.25E-05	8.25E-14	0.22	61.0	6100.0	0.041
	0.35	7.13	8.25E-05	8.25E-14	0.24	64.0	6400.0	0.043
	0.35	7.13	8.25E-05	8.25E-14	0.22	68.0	6800.0	0.046
	0.35	7.13	8.25E-05	8.25E-14	0.21	77.0	7700.0	0.052
	0.35	7.13	8.25E-05	8.25E-14	0.24	79.0	7900.0	0.054
	0.35	7.13	8.25E-05	8.25E-14	0.21	91.0	9100.0	0.062

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
1122								
	0.36	2.92	3.38E-05	3.38E-14	0.31	1.0	100.0	0.000
	0.36	2.92	3.38E-05	3.38E-14	0.30	7.0	700.0	0.003
	0.36	2.92	3.38E-05	3.38E-14	0.30	13.0	1300.0	0.006
	0.36	2.92	3.38E-05	3.38E-14	0.30	21.0	2100.0	0.009
	0.36	2.92	3.38E-05	3.38E-14	0.30	25.0	2500.0	0.011
	0.36	2.92	3.38E-05	3.38E-14	0.30	32.0	3200.0	0.014
	0.36	2.92	3.38E-05	3.38E-14	0.30	46.0	4600.0	0.020
1123								
	0.35	0.74	8.56E-06	8.56E-15	0.31	4.0	400.0	0.001
	0.35	0.74	8.56E-06	8.56E-15	0.31	8.0	800.0	0.002
	0.35	0.74	8.56E-06	8.56E-15	0.31	30.0	3000.0	0.007
1130								
	0.40	2.74	3.17E-05	3.17E-14	0.37	0.0	0.0	0.000
	0.40	2.74	3.17E-05	3.17E-14	0.34	6.0	600.0	0.002
	0.40	2.74	3.17E-05	3.17E-14	0.33	14.0	1400.0	0.005
	0.40	2.74	3.17E-05	3.17E-14	0.31	22.0	2200.0	0.009
	0.40	2.74	3.17E-05	3.17E-14	0.30	28.0	2800.0	0.011
	0.40	2.74	3.17E-05	3.17E-14	0.30	29.0	2900.0	0.011
	0.40	2.74	3.17E-05	3.17E-14	0.30	31.0	3100.0	0.012
	0.40	2.74	3.17E-05	3.17E-14	0.30	34.0	3400.0	0.013
	0.40	2.74	3.17E-05	3.17E-14	0.29	37.0	3700.0	0.015
	0.40	2.74	3.17E-05	3.17E-14	0.28	42.0	4200.0	0.016
	0.40	2.74	3.17E-05	3.17E-14	0.27	48.0	4800.0	0.019
	0.40	2.74	3.17E-05	3.17E-14	0.27	54.0	5400.0	0.021
	0.40	2.74	3.17E-05	3.17E-14	0.26	64.0	6400.0	0.025
1131								
	0.24	3.74	4.33E-05	4.33E-14	0.29	0.0	0.0	0.000
	0.24	3.74	4.33E-05	4.33E-14	0.29	10.0	1000.0	0.006
	0.24	3.74	4.33E-05	4.33E-14	0.28	17.0	1700.0	0.010
	0.24	3.74	4.33E-05	4.33E-14	0.27	20.0	2000.0	0.012
	0.24	3.74	4.33E-05	4.33E-14	0.24	21.0	2100.0	0.012
	0.24	3.74	4.33E-05	4.33E-14	0.24	25.0	2500.0	0.015
	0.24	3.74	4.33E-05	4.33E-14	0.23	28.0	2800.0	0.016
	0.24	3.74	4.33E-05	4.33E-14	0.23	32.0	3200.0	0.019
	0.24	3.74	4.33E-05	4.33E-14	0.22	38.0	3800.0	0.022
	0.24	3.74	4.33E-05	4.33E-14	0.22	44.0	4400.0	0.026
	0.24	3.74	4.33E-05	4.33E-14	0.22	51.0	5100.0	0.030
	0.24	3.74	4.33E-05	4.33E-14	0.21	62.0	6200.0	0.036
1132								
	0.35	0.42	4.80E-06	4.80E-15	0.37	0.0	0.0	0.000
	0.35	0.42	4.80E-06	4.80E-15	0.37	3.0	300.0	0.000
	0.35	0.42	4.80E-06	4.80E-15	0.36	12.0	1200.0	0.002
	0.35	0.42	4.80E-06	4.80E-15	0.36	14.0	1400.0	0.002
	0.35	0.42	4.80E-06	4.80E-15	0.34	15.0	1500.0	0.002
	0.35	0.42	4.80E-06	4.80E-15	0.33	16.0	1600.0	0.003

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.35	0.42	4.80E-06	4.80E-15	0.32	17.0	1700.0	0.003
	0.35	0.42	4.80E-06	4.80E-15	0.32	19.0	1900.0	0.003
	0.35	0.42	4.80E-06	4.80E-15	0.32	24.0	2400.0	0.004
	0.35	0.42	4.80E-06	4.80E-15	0.31	32.0	3200.0	0.005
	0.35	0.42	4.80E-06	4.80E-15	0.32	38.0	3800.0	0.006
	0.35	0.42	4.80E-06	4.80E-15	0.30	44.0	4400.0	0.007
	0.35	0.42	4.80E-06	4.80E-15	0.30	53.0	5300.0	0.009
1133								
	0.33	0.09	1.05E-06	1.05E-15	0.38	0.0	0.0	0.000
	0.33	0.09	1.05E-06	1.05E-15	0.38	1.0	100.0	0.000
	0.33	0.09	1.05E-06	1.05E-15	0.38	5.0	500.0	0.000
	0.33	0.09	1.05E-06	1.05E-15	0.38	6.0	600.0	0.000
	0.33	0.09	1.05E-06	1.05E-15	0.37	9.0	900.0	0.001
	0.33	0.09	1.05E-06	1.05E-15	0.37	14.0	1400.0	0.001
	0.33	0.09	1.05E-06	1.05E-15	0.37	18.0	1800.0	0.001
	0.33	0.09	1.05E-06	1.05E-15	0.37	22.0	2200.0	0.002
	0.33	0.09	1.05E-06	1.05E-15	0.36	28.0	2800.0	0.002
1240								
	0.40	389.00	4.50E-03	4.50E-12	0.31	0.0	0.0	0.000
	0.40	389.00	4.50E-03	4.50E-12	0.30	2.0	200.0	0.009
	0.40	389.00	4.50E-03	4.50E-12	0.30	7.0	700.0	0.033
	0.40	389.00	4.50E-03	4.50E-12	0.23	9.0	900.0	0.042
	0.40	389.00	4.50E-03	4.50E-12	0.16	10.0	1000.0	0.047
	0.40	389.00	4.50E-03	4.50E-12	0.21	12.0	1200.0	0.056
	0.40	389.00	4.50E-03	4.50E-12	0.19	13.0	1300.0	0.061
	0.40	389.00	4.50E-03	4.50E-12	0.20	14.0	1400.0	0.066
	0.40	389.00	4.50E-03	4.50E-12	0.16	15.0	1500.0	0.070
	0.40	389.00	4.50E-03	4.50E-12	0.14	16.0	1600.0	0.075
	0.40	389.00	4.50E-03	4.50E-12	0.14	17.0	1700.0	0.080
	0.40	389.00	4.50E-03	4.50E-12	0.14	18.0	1800.0	0.084
	0.40	389.00	4.50E-03	4.50E-12	0.13	19.0	1900.0	0.089
	0.40	389.00	4.50E-03	4.50E-12	0.13	20.0	2000.0	0.094
	0.40	389.00	4.50E-03	4.50E-12	0.13	21.0	2100.0	0.098
	0.40	389.00	4.50E-03	4.50E-12	0.12	22.0	2200.0	0.103
	0.40	389.00	4.50E-03	4.50E-12	0.11	23.0	2300.0	0.108
	0.40	389.00	4.50E-03	4.50E-12	0.12	24.0	2400.0	0.113
	0.40	389.00	4.50E-03	4.50E-12	0.11	26.0	2600.0	0.122
	0.40	389.00	4.50E-03	4.50E-12	0.10	27.0	2700.0	0.127
	0.40	389.00	4.50E-03	4.50E-12	0.11	28.0	2800.0	0.131
	0.40	389.00	4.50E-03	4.50E-12	0.11	29.0	2900.0	0.136
	0.40	389.00	4.50E-03	4.50E-12	0.11	30.0	3000.0	0.141
	0.40	389.00	4.50E-03	4.50E-12	0.10	31.0	3100.0	0.145
	0.40	389.00	4.50E-03	4.50E-12	0.10	32.0	3200.0	0.150
	0.40	389.00	4.50E-03	4.50E-12	0.10	33.0	3300.0	0.155
	0.40	389.00	4.50E-03	4.50E-12	0.10	34.0	3400.0	0.159
	0.40	389.00	4.50E-03	4.50E-12	0.10	35.0	3500.0	0.164

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.40	389.00	4.50E-03	4.50E-12	0.09	37.0	3700.0	0.174
	0.40	389.00	4.50E-03	4.50E-12	0.11	38.0	3800.0	0.178
1260								
	0.44	77.80	9.00E-04	9.00E-13	0.40	29.0	2900.0	0.058
	0.44	77.80	9.00E-04	9.00E-13	0.38	38.0	3800.0	0.075
	0.44	77.80	9.00E-04	9.00E-13	0.37	53.0	5300.0	0.105
	0.44	77.80	9.00E-04	9.00E-13	0.36	72.0	7200.0	0.143
	0.44	77.80	9.00E-04	9.00E-13	0.36	89.0	8900.0	0.177
	0.44	77.80	9.00E-04	9.00E-13	0.34	98.0	9800.0	0.194
	0.44	77.80	9.00E-04	9.00E-13	0.33	110.0	11000.0	0.218
	0.44	77.80	9.00E-04	9.00E-13	0.25	154.0	15400.0	0.305
	0.44	77.80	9.00E-04	9.00E-13	0.24	167.0	16700.0	0.331
	0.44	77.80	9.00E-04	9.00E-13	0.19	236.0	23600.0	0.468
	0.44	77.80	9.00E-04	9.00E-13	0.16	286.0	28600.0	0.567
	0.44	77.80	9.00E-04	9.00E-13	0.15	340.0	34000.0	0.674
1261								
	0.44	77.80	9.00E-04	9.00E-13	0.40	42.0	4200.0	0.083
	0.44	77.80	9.00E-04	9.00E-13	0.39	49.0	4900.0	0.097
	0.44	77.80	9.00E-04	9.00E-13	0.39	58.0	5800.0	0.115
	0.44	77.80	9.00E-04	9.00E-13	0.39	71.0	7100.0	0.141
	0.44	77.80	9.00E-04	9.00E-13	0.39	83.0	8300.0	0.165
	0.44	77.80	9.00E-04	9.00E-13	0.38	91.0	9100.0	0.180
	0.44	77.80	9.00E-04	9.00E-13	0.38	100.0	10000.0	0.198
	0.44	77.80	9.00E-04	9.00E-13	0.31	143.0	14300.0	0.284
	0.44	77.80	9.00E-04	9.00E-13	0.30	153.0	15300.0	0.303
	0.44	77.80	9.00E-04	9.00E-13	0.23	217.0	21700.0	0.430
	0.44	77.80	9.00E-04	9.00E-13	0.20	269.0	26900.0	0.534
	0.44	77.80	9.00E-04	9.00E-13	0.18	323.0	32300.0	0.641
1330								
	0.45	35.00	4.05E-04	4.05E-13	0.39	63.0	6300.0	0.083
	0.45	35.00	4.05E-04	4.05E-13	0.31	74.0	7400.0	0.098
	0.45	35.00	4.05E-04	4.05E-13	0.32	92.0	9200.0	0.122
	0.45	35.00	4.05E-04	4.05E-13	0.27	114.0	11400.0	0.151
	0.45	35.00	4.05E-04	4.05E-13	0.28	141.0	14100.0	0.186
	0.45	35.00	4.05E-04	4.05E-13	0.29	156.0	15600.0	0.206
	0.45	35.00	4.05E-04	4.05E-13	0.29	160.0	16000.0	0.211
	0.45	35.00	4.05E-04	4.05E-13	0.29	162.0	16200.0	0.214
	0.45	35.00	4.05E-04	4.05E-13	0.29	175.0	17500.0	0.231
	0.45	35.00	4.05E-04	4.05E-13	0.29	181.0	18100.0	0.239
	0.45	35.00	4.05E-04	4.05E-13	0.29	186.0	18600.0	0.246
	0.45	35.00	4.05E-04	4.05E-13	0.30	193.0	19300.0	0.255
	0.45	35.00	4.05E-04	4.05E-13	0.22	210.0	21000.0	0.278
	0.45	35.00	4.05E-04	4.05E-13	0.22	218.0	21800.0	0.288
	0.45	35.00	4.05E-04	4.05E-13	0.23	233.0	23300.0	0.308
	0.45	35.00	4.05E-04	4.05E-13	0.24	246.0	24600.0	0.325
	0.45	35.00	4.05E-04	4.05E-13	0.24	261.0	26100.0	0.345

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.45	35.00	4.05E-04	4.05E-13	0.25	275.0	27500.0	0.363
	0.45	35.00	4.05E-04	4.05E-13	0.25	283.0	28300.0	0.374
	0.45	35.00	4.05E-04	4.05E-13	0.25	288.0	28800.0	0.381
	0.45	35.00	4.05E-04	4.05E-13	0.26	304.0	30400.0	0.402
	0.45	35.00	4.05E-04	4.05E-13	0.17	342.0	34200.0	0.452
	0.45	35.00	4.05E-04	4.05E-13	0.17	362.0	36200.0	0.478
	0.45	35.00	4.05E-04	4.05E-13	0.18	405.0	40500.0	0.535
	0.45	35.00	4.05E-04	4.05E-13	0.19	473.0	47300.0	0.625
	0.45	35.00	4.05E-04	4.05E-13	0.21	571.0	57100.0	0.755
	0.45	35.00	4.05E-04	4.05E-13	0.25	661.0	66100.0	0.873
	0.45	35.00	4.05E-04	4.05E-13	0.16	748.0	74800.0	0.988
	0.45	35.00	4.05E-04	4.05E-13	0.16	785.0	78500.0	1.037
	0.45	35.00	4.05E-04	4.05E-13	0.16	816.0	81600.0	1.078
	0.45	35.00	4.05E-04	4.05E-13	0.16	841.0	84100.0	1.111
	0.45	35.00	4.05E-04	4.05E-13	0.16	853.0	85300.0	1.127
1331								
	0.45	40.00	4.63E-04	4.63E-13	0.38	10.0	1000.0	0.014
	0.45	40.00	4.63E-04	4.63E-13	0.35	19.0	1900.0	0.027
	0.45	40.00	4.63E-04	4.63E-13	0.37	49.0	4900.0	0.069
	0.45	40.00	4.63E-04	4.63E-13	0.38	55.0	5500.0	0.078
	0.45	40.00	4.63E-04	4.63E-13	0.34	64.0	6400.0	0.090
	0.45	40.00	4.63E-04	4.63E-13	0.34	79.0	7900.0	0.112
	0.45	40.00	4.63E-04	4.63E-13	0.32	114.0	11400.0	0.161
	0.45	40.00	4.63E-04	4.63E-13	0.32	120.0	12000.0	0.170
	0.45	40.00	4.63E-04	4.63E-13	0.32	152.0	15200.0	0.215
	0.45	40.00	4.63E-04	4.63E-13	0.33	158.0	15800.0	0.223
	0.45	40.00	4.63E-04	4.63E-13	0.33	176.0	17600.0	0.249
	0.45	40.00	4.63E-04	4.63E-13	0.31	289.0	28900.0	0.408
	0.45	40.00	4.63E-04	4.63E-13	0.32	305.0	30500.0	0.431
	0.45	40.00	4.63E-04	4.63E-13	0.32	309.0	30900.0	0.437
	0.45	40.00	4.63E-04	4.63E-13	0.27	337.0	33700.0	0.476
	0.45	40.00	4.63E-04	4.63E-13	0.28	437.0	43700.0	0.617
	0.45	40.00	4.63E-04	4.63E-13	0.28	457.0	45700.0	0.646
	0.45	40.00	4.63E-04	4.63E-13	0.28	508.0	50800.0	0.718
	0.45	40.00	4.63E-04	4.63E-13	0.28	524.0	52400.0	0.740
	0.45	40.00	4.63E-04	4.63E-13	0.28	579.0	57900.0	0.818
	0.45	40.00	4.63E-04	4.63E-13	0.29	625.0	62500.0	0.883
2100								
	0.37	370.00	4.28E-03	4.28E-12	0.31	0.0	0.0	0.000
	0.37	370.00	4.28E-03	4.28E-12	0.30	9.0	900.0	0.043
	0.37	370.00	4.28E-03	4.28E-12	0.30	10.0	1000.0	0.047
	0.37	370.00	4.28E-03	4.28E-12	0.29	11.0	1100.0	0.052
	0.37	370.00	4.28E-03	4.28E-12	0.29	16.0	1600.0	0.076
	0.37	370.00	4.28E-03	4.28E-12	0.28	23.0	2300.0	0.109
	0.37	370.00	4.28E-03	4.28E-12	0.22	32.0	3200.0	0.152
	0.37	370.00	4.28E-03	4.28E-12	0.22	39.0	3900.0	0.185

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.37	370.00	4.28E-03	4.28E-12	0.18	48.0	4800.0	0.227
	0.37	370.00	4.28E-03	4.28E-12	0.15	50.0	5000.0	0.237
	0.37	370.00	4.28E-03	4.28E-12	0.11	61.0	6100.0	0.289
	0.37	370.00	4.28E-03	4.28E-12	0.09	64.0	6400.0	0.303
	0.37	370.00	4.28E-03	4.28E-12	0.11	66.0	6600.0	0.313
	0.37	370.00	4.28E-03	4.28E-12	0.07	78.0	7800.0	0.369
	0.37	370.00	4.28E-03	4.28E-12	0.06	91.0	9100.0	0.431
	0.37	370.00	4.28E-03	4.28E-12	0.06	109.0	10900.0	0.516
	0.37	370.00	4.28E-03	4.28E-12	0.07	115.0	11500.0	0.545
2101								
	0.41	473.00	5.47E-03	5.47E-12	0.31	0.0	0.0	0.000
	0.41	473.00	5.47E-03	5.47E-12	0.30	9.0	900.0	0.046
	0.41	473.00	5.47E-03	5.47E-12	0.30	10.0	1000.0	0.051
	0.41	473.00	5.47E-03	5.47E-12	0.29	11.0	1100.0	0.056
	0.41	473.00	5.47E-03	5.47E-12	0.29	16.0	1600.0	0.082
	0.41	473.00	5.47E-03	5.47E-12	0.28	23.0	2300.0	0.117
	0.41	473.00	5.47E-03	5.47E-12	0.22	32.0	3200.0	0.163
	0.41	473.00	5.47E-03	5.47E-12	0.22	39.0	3900.0	0.199
	0.41	473.00	5.47E-03	5.47E-12	0.18	48.0	4800.0	0.245
	0.41	473.00	5.47E-03	5.47E-12	0.15	50.0	5000.0	0.255
	0.41	473.00	5.47E-03	5.47E-12	0.11	61.0	6100.0	0.311
	0.41	473.00	5.47E-03	5.47E-12	0.09	64.0	6400.0	0.327
	0.41	473.00	5.47E-03	5.47E-12	0.11	66.0	6600.0	0.337
	0.41	473.00	5.47E-03	5.47E-12	0.07	78.0	7800.0	0.398
	0.41	473.00	5.47E-03	5.47E-12	0.06	91.0	9100.0	0.465
	0.41	473.00	5.47E-03	5.47E-12	0.06	109.0	10900.0	0.556
	0.41	473.00	5.47E-03	5.47E-12	0.07	115.0	11500.0	0.587
2140								
	0.46	540.00	6.25E-03	6.25E-12	0.43	0.0	0.0	0.000
	0.46	540.00	6.25E-03	6.25E-12	0.43	1.0	100.0	0.005
	0.46	540.00	6.25E-03	6.25E-12	0.42	4.0	400.0	0.021
	0.46	540.00	6.25E-03	6.25E-12	0.42	10.0	1000.0	0.052
2150								
	0.40	518.00	6.00E-03	6.00E-12	0.40	0.0	0.0	0.000
	0.40	518.00	6.00E-03	6.00E-12	0.39	1.0	100.0	0.005
	0.40	518.00	6.00E-03	6.00E-12	0.38	4.0	400.0	0.022
	0.40	518.00	6.00E-03	6.00E-12	0.35	10.0	1000.0	0.054
2151								
	0.30	518.00	6.00E-03	6.00E-12	0.27	0.0	0.0	0.000
	0.30	518.00	6.00E-03	6.00E-12	0.26	1.0	100.0	0.006
	0.30	518.00	6.00E-03	6.00E-12	0.25	4.0	400.0	0.025
	0.30	518.00	6.00E-03	6.00E-12	0.22	10.0	1000.0	0.062
3090								
	0.46	19.50	2.26E-04	2.26E-13	0.33	31.0	3100.0	0.030
	0.46	19.50	2.26E-04	2.26E-13	0.03	34.0	3400.0	0.033
	0.46	19.50	2.26E-04	2.26E-13	0.33	44.0	4400.0	0.043

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.46	19.50	2.26E-04	2.26E-13	0.32	50.0	5000.0	0.049
	0.46	19.50	2.26E-04	2.26E-13	0.32	61.0	6100.0	0.060
	0.46	19.50	2.26E-04	2.26E-13	0.32	66.0	6600.0	0.065
	0.46	19.50	2.26E-04	2.26E-13	0.32	97.0	9700.0	0.095
	0.46	19.50	2.26E-04	2.26E-13	0.31	116.0	11600.0	0.114
	0.46	19.50	2.26E-04	2.26E-13	0.30	171.0	17100.0	0.167
	0.46	19.50	2.26E-04	2.26E-13	0.29	202.0	20200.0	0.198
	0.46	19.50	2.26E-04	2.26E-13	0.28	226.0	22600.0	0.221
	0.46	19.50	2.26E-04	2.26E-13	0.28	270.0	27000.0	0.264
	0.46	19.50	2.26E-04	2.26E-13	0.26	401.0	40100.0	0.392
	0.46	19.50	2.26E-04	2.26E-13	0.26	430.0	43000.0	0.421
	0.46	19.50	2.26E-04	2.26E-13	0.25	493.0	49300.0	0.483
	0.46	19.50	2.26E-04	2.26E-13	0.25	498.0	49800.0	0.487
	0.46	19.50	2.26E-04	2.26E-13	0.25	509.0	50900.0	0.498
	0.46	19.50	2.26E-04	2.26E-13	0.24	590.0	59000.0	0.577
3091								
	0.45	15.40	1.78E-04	1.78E-13	0.37	29.0	2900.0	0.025
	0.45	15.40	1.78E-04	1.78E-13	0.36	44.0	4400.0	0.039
	0.45	15.40	1.78E-04	1.78E-13	0.36	63.0	6300.0	0.055
	0.45	15.40	1.78E-04	1.78E-13	0.32	74.0	7400.0	0.065
	0.45	15.40	1.78E-04	1.78E-13	0.32	92.0	9200.0	0.081
	0.45	15.40	1.78E-04	1.78E-13	0.31	96.0	9600.0	0.084
	0.45	15.40	1.78E-04	1.78E-13	0.30	140.0	14000.0	0.123
	0.45	15.40	1.78E-04	1.78E-13	0.28	195.0	19500.0	0.171
	0.45	15.40	1.78E-04	1.78E-13	0.27	262.0	26200.0	0.230
	0.45	15.40	1.78E-04	1.78E-13	0.26	384.0	38400.0	0.337
	0.45	15.40	1.78E-04	1.78E-13	0.26	404.0	40400.0	0.354
3100								
	0.55	168.00	1.94E-03	1.94E-12	0.38	13.0	1300.0	0.034
	0.55	168.00	1.94E-03	1.94E-12	0.37	33.0	3300.0	0.086
	0.55	168.00	1.94E-03	1.94E-12	0.38	37.0	3700.0	0.097
	0.55	168.00	1.94E-03	1.94E-12	0.35	49.0	4900.0	0.128
	0.55	168.00	1.94E-03	1.94E-12	0.33	66.0	6600.0	0.173
	0.55	168.00	1.94E-03	1.94E-12	0.29	102.0	10200.0	0.267
	0.55	168.00	1.94E-03	1.94E-12	0.31	122.0	12200.0	0.319
	0.55	168.00	1.94E-03	1.94E-12	0.29	184.0	18400.0	0.481
	0.55	168.00	1.94E-03	1.94E-12	0.28	198.0	19800.0	0.518
	0.55	168.00	1.94E-03	1.94E-12	0.28	224.0	22400.0	0.586
	0.55	168.00	1.94E-03	1.94E-12	0.27	285.0	28500.0	0.746
	0.55	168.00	1.94E-03	1.94E-12	0.25	308.0	30800.0	0.806
	0.55	168.00	1.94E-03	1.94E-12	0.24	402.0	40200.0	1.052
	0.55	168.00	1.94E-03	1.94E-12	0.21	576.0	57600.0	1.507
	0.55	168.00	1.94E-03	1.94E-12	0.22	588.0	58800.0	1.538

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
3101								
	0.48	55.80	6.46E-04	6.46E-13	0.42	37.0	3700.0	0.060
	0.48	55.80	6.46E-04	6.46E-13	0.41	52.0	5200.0	0.084
	0.48	55.80	6.46E-04	6.46E-13	0.39	86.0	8600.0	0.139
	0.48	55.80	6.46E-04	6.46E-13	0.37	98.0	9800.0	0.158
	0.48	55.80	6.46E-04	6.46E-13	0.36	103.0	10300.0	0.166
	0.48	55.80	6.46E-04	6.46E-13	0.35	119.0	11900.0	0.192
	0.48	55.80	6.46E-04	6.46E-13	0.33	194.0	19400.0	0.313
	0.48	55.80	6.46E-04	6.46E-13	0.32	204.0	20400.0	0.329
	0.48	55.80	6.46E-04	6.46E-13	0.31	250.0	25000.0	0.403
	0.48	55.80	6.46E-04	6.46E-13	0.29	325.0	32500.0	0.525
	0.48	55.80	6.46E-04	6.46E-13	0.29	398.0	39800.0	0.642
	0.48	55.80	6.46E-04	6.46E-13	0.29	481.0	48100.0	0.776
	0.48	55.80	6.46E-04	6.46E-13	0.27	621.0	62100.0	1.002
3102								
	0.51	109.00	1.26E-03	1.26E-12	0.39	42.0	4200.0	0.092
	0.51	109.00	1.26E-03	1.26E-12	0.38	52.0	5200.0	0.114
	0.51	109.00	1.26E-03	1.26E-12	0.35	53.0	5300.0	0.116
	0.51	109.00	1.26E-03	1.26E-12	0.34	62.0	6200.0	0.136
	0.51	109.00	1.26E-03	1.26E-12	0.33	101.0	10100.0	0.222
	0.51	109.00	1.26E-03	1.26E-12	0.33	132.0	13200.0	0.290
	0.51	109.00	1.26E-03	1.26E-12	0.32	148.0	14800.0	0.325
	0.51	109.00	1.26E-03	1.26E-12	0.30	181.0	18100.0	0.397
	0.51	109.00	1.26E-03	1.26E-12	0.30	198.0	19800.0	0.435
	0.51	109.00	1.26E-03	1.26E-12	0.29	232.0	23200.0	0.509
	0.51	109.00	1.26E-03	1.26E-12	0.29	259.0	25900.0	0.568
	0.51	109.00	1.26E-03	1.26E-12	0.29	365.0	36500.0	0.801
	0.51	109.00	1.26E-03	1.26E-12	0.28	374.0	37400.0	0.821
	0.51	109.00	1.26E-03	1.26E-12	0.28	404.0	40400.0	0.887
	0.51	109.00	1.26E-03	1.26E-12	0.28	448.0	44800.0	0.983
	0.51	109.00	1.26E-03	1.26E-12	0.27	520.0	52000.0	1.141
	0.51	109.00	1.26E-03	1.26E-12	0.27	607.0	60700.0	1.332
3110								
	0.47	91.00	1.05E-03	1.05E-12	0.40	14.0	1400.0	0.029
	0.47	91.00	1.05E-03	1.05E-12	0.39	37.0	3700.0	0.077
	0.47	91.00	1.05E-03	1.05E-12	0.38	49.0	4900.0	0.102
	0.47	91.00	1.05E-03	1.05E-12	0.38	78.0	7800.0	0.163
	0.47	91.00	1.05E-03	1.05E-12	0.38	53.0	5300.0	0.111
	0.47	91.00	1.05E-03	1.05E-12	0.37	84.0	8400.0	0.175
	0.47	91.00	1.05E-03	1.05E-12	0.36	102.0	10200.0	0.213
	0.47	91.00	1.05E-03	1.05E-12	0.36	133.0	13300.0	0.278
	0.47	91.00	1.05E-03	1.05E-12	0.35	105.0	10500.0	0.219
	0.47	91.00	1.05E-03	1.05E-12	0.33	201.0	20100.0	0.420
	0.47	91.00	1.05E-03	1.05E-12	0.33	190.0	19000.0	0.397
	0.47	91.00	1.05E-03	1.05E-12	0.33	266.0	26600.0	0.555
	0.47	91.00	1.05E-03	1.05E-12	0.32	261.0	26100.0	0.545

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.47	91.00	1.05E-03	1.05E-12	0.31	397.0	39700.0	0.829
	0.47	91.00	1.05E-03	1.05E-12	0.31	422.0	42200.0	0.881
	0.47	91.00	1.05E-03	1.05E-12	0.30	516.0	51600.0	1.077
3111								
	0.49	98.00	1.13E-03	1.13E-12	0.43	31.0	3100.0	0.066
	0.49	98.00	1.13E-03	1.13E-12	0.42	51.0	5100.0	0.108
	0.49	98.00	1.13E-03	1.13E-12	0.42	66.0	6600.0	0.140
	0.49	98.00	1.13E-03	1.13E-12	0.41	78.0	7800.0	0.165
	0.49	98.00	1.13E-03	1.13E-12	0.41	67.0	6700.0	0.142
	0.49	98.00	1.13E-03	1.13E-12	0.39	89.0	8900.0	0.189
	0.49	98.00	1.13E-03	1.13E-12	0.39	103.0	10300.0	0.218
	0.49	98.00	1.13E-03	1.13E-12	0.39	123.0	12300.0	0.261
	0.49	98.00	1.13E-03	1.13E-12	0.37	154.0	15400.0	0.326
	0.49	98.00	1.13E-03	1.13E-12	0.36	163.0	16300.0	0.345
	0.49	98.00	1.13E-03	1.13E-12	0.36	201.0	20100.0	0.426
	0.49	98.00	1.13E-03	1.13E-12	0.35	235.0	23500.0	0.498
	0.49	98.00	1.13E-03	1.13E-12	0.33	293.0	29300.0	0.621
	0.49	98.00	1.13E-03	1.13E-12	0.31	397.0	39700.0	0.841
	0.49	98.00	1.13E-03	1.13E-12	0.31	420.0	42000.0	0.890
	0.49	98.00	1.13E-03	1.13E-12	0.31	439.0	43900.0	0.930
3112								
	0.49	109.00	1.26E-03	1.26E-12	0.42	21.0	2100.0	0.047
	0.49	109.00	1.26E-03	1.26E-12	0.41	31.0	3100.0	0.069
	0.49	109.00	1.26E-03	1.26E-12	0.40	39.0	3900.0	0.087
	0.49	109.00	1.26E-03	1.26E-12	0.39	50.0	5000.0	0.111
	0.49	109.00	1.26E-03	1.26E-12	0.38	52.0	5200.0	0.116
	0.49	109.00	1.26E-03	1.26E-12	0.36	83.0	8300.0	0.185
	0.49	109.00	1.26E-03	1.26E-12	0.35	103.0	10300.0	0.229
	0.49	109.00	1.26E-03	1.26E-12	0.34	123.0	12300.0	0.274
	0.49	109.00	1.26E-03	1.26E-12	0.34	154.0	15400.0	0.343
	0.49	109.00	1.26E-03	1.26E-12	0.34	208.0	20800.0	0.463
	0.49	109.00	1.26E-03	1.26E-12	0.33	226.0	22600.0	0.503
	0.49	109.00	1.26E-03	1.26E-12	0.32	247.0	24700.0	0.550
	0.49	109.00	1.26E-03	1.26E-12	0.32	257.0	25700.0	0.572
	0.49	109.00	1.26E-03	1.26E-12	0.31	309.0	30900.0	0.688
	0.49	109.00	1.26E-03	1.26E-12	0.29	360.0	36000.0	0.801
	0.49	109.00	1.26E-03	1.26E-12	0.29	453.0	45300.0	1.008
	0.49	109.00	1.26E-03	1.26E-12	0.28	515.0	51500.0	1.146
3240								
	0.45	1.84	2.13E-05	2.13E-14	0.30	35.0	3500.0	0.011
	0.45	1.84	2.13E-05	2.13E-14	0.29	85.0	8500.0	0.026
	0.45	1.84	2.13E-05	2.13E-14	0.28	109.0	10900.0	0.033

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
3241								
	0.48	2.29	2.65E-05	2.65E-14	0.40	21.0	2100.0	0.007
	0.48	2.29	2.65E-05	2.65E-14	0.38	42.0	4200.0	0.014
	0.48	2.29	2.65E-05	2.65E-14	0.37	65.0	6500.0	0.021
	0.48	2.29	2.65E-05	2.65E-14	0.36	84.0	8400.0	0.027
	0.48	2.29	2.65E-05	2.65E-14	0.35	98.0	9800.0	0.032
	0.48	2.29	2.65E-05	2.65E-14	0.30	128.0	12800.0	0.042
3242								
	0.47	31.30	3.62E-04	3.62E-13	0.41	16.0	1600.0	0.020
	0.47	31.30	3.62E-04	3.62E-13	0.39	32.0	3200.0	0.039
	0.47	31.30	3.62E-04	3.62E-13	0.39	50.0	5000.0	0.061
	0.47	31.30	3.62E-04	3.62E-13	0.39	65.0	6500.0	0.079
3243								
	0.44	6.99	8.09E-05	8.09E-14	0.39	9.0	900.0	0.005
	0.44	6.99	8.09E-05	8.09E-14	0.39	22.0	2200.0	0.013
	0.44	6.99	8.09E-05	8.09E-14	0.38	36.0	3600.0	0.021
3250								
	0.45	1.51	1.75E-05	1.75E-14	0.33	6.0	600.0	0.002
	0.45	1.51	1.75E-05	1.75E-14	0.34	19.0	1900.0	0.005
	0.45	1.51	1.75E-05	1.75E-14	0.32	29.0	2900.0	0.008
	0.45	1.51	1.75E-05	1.75E-14	0.35	42.0	4200.0	0.012
	0.45	1.51	1.75E-05	1.75E-14	0.31	51.0	5100.0	0.014
	0.45	1.51	1.75E-05	1.75E-14	0.33	63.0	6300.0	0.017
	0.45	1.51	1.75E-05	1.75E-14	0.33	77.0	7700.0	0.021
	0.45	1.51	1.75E-05	1.75E-14	0.32	88.0	8800.0	0.024
	0.45	1.51	1.75E-05	1.75E-14	0.33	101.0	10100.0	0.028
	0.45	1.51	1.75E-05	1.75E-14	0.33	121.0	12100.0	0.033
3251								
	0.46	2.74	3.17E-05	3.17E-14	0.39	20.0	2000.0	0.007
	0.46	2.74	3.17E-05	3.17E-14	0.39	31.0	3100.0	0.011
	0.46	2.74	3.17E-05	3.17E-14	0.39	52.0	5200.0	0.019
	0.46	2.74	3.17E-05	3.17E-14	0.39	71.0	7100.0	0.026
	0.46	2.74	3.17E-05	3.17E-14	0.38	96.0	9600.0	0.035
	0.46	2.74	3.17E-05	3.17E-14	0.38	114.0	11400.0	0.042
3252								
	0.45	1.44	1.67E-05	1.67E-14	0.38	12.0	1200.0	0.003
	0.45	1.44	1.67E-05	1.67E-14	0.37	38.0	3800.0	0.010
	0.45	1.44	1.67E-05	1.67E-14	0.37	69.0	6900.0	0.018
	0.45	1.44	1.67E-05	1.67E-14	0.37	109.0	10900.0	0.029
	0.45	1.44	1.67E-05	1.67E-14	0.36	141.0	14100.0	0.038
3253								
	0.55	1.48	1.71E-05	1.71E-14	0.37	9.0	900.0	0.002
	0.55	1.48	1.71E-05	1.71E-14	0.37	32.0	3200.0	0.008
	0.55	1.48	1.71E-05	1.71E-14	0.36	74.0	7400.0	0.018
	0.55	1.48	1.71E-05	1.71E-14	0.36	119.0	11900.0	0.029
	0.55	1.48	1.71E-05	1.71E-14	0.36	149.0	14900.0	0.037

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
3260								
	0.49	10.80	1.25E-04	1.25E-13	0.33	39.0	3900.0	0.027
	0.49	10.80	1.25E-04	1.25E-13	0.29	105.0	10500.0	0.074
	0.49	10.80	1.25E-04	1.25E-13	0.28	181.0	18100.0	0.127
	0.49	10.80	1.25E-04	1.25E-13	0.27	200.0	20000.0	0.141
3261								
	0.49	32.00	3.70E-04	3.70E-13	0.30	28.0	2800.0	0.034
	0.49	32.00	3.70E-04	3.70E-13	0.29	99.0	9900.0	0.120
	0.49	32.00	3.70E-04	3.70E-13	0.26	178.0	17800.0	0.216
	0.49	32.00	3.70E-04	3.70E-13	0.26	196.0	19600.0	0.237
3262								
	0.49	35.30	4.09E-04	4.09E-13	0.34	16.0	1600.0	0.020
	0.49	35.30	4.09E-04	4.09E-13	0.32	84.0	8400.0	0.107
	0.49	35.30	4.09E-04	4.09E-13	0.29	160.0	16000.0	0.203
	0.49	35.30	4.09E-04	4.09E-13	0.29	177.0	17700.0	0.225
3263								
	0.49	54.00	6.25E-04	6.25E-13	0.32	7.0	700.0	0.011
	0.49	54.00	6.25E-04	6.25E-13	0.30	72.0	7200.0	0.113
	0.49	54.00	6.25E-04	6.25E-13	0.30	125.0	12500.0	0.197
	0.49	54.00	6.25E-04	6.25E-13	0.28	170.0	17000.0	0.267
	0.49	54.00	6.25E-04	6.25E-13	0.28	210.0	21000.0	0.330
	0.49	54.00	6.25E-04	6.25E-13	0.28	244.0	24400.0	0.384
3264								
	0.49	58.10	6.72E-04	6.72E-13	0.33	30.0	3000.0	0.049
	0.49	58.10	6.72E-04	6.72E-13	0.31	142.0	14200.0	0.232
	0.49	58.10	6.72E-04	6.72E-13	0.31	214.0	21400.0	0.349
	0.49	58.10	6.72E-04	6.72E-13	0.30	237.0	23700.0	0.387
3280								
	0.39	13.50	1.56E-04	1.56E-13	0.32	28.0	2800.0	0.025
	0.39	13.50	1.56E-04	1.56E-13	0.31	44.0	4400.0	0.039
	0.39	13.50	1.56E-04	1.56E-13	0.30	58.0	5800.0	0.051
	0.39	13.50	1.56E-04	1.56E-13	0.30	74.0	7400.0	0.065
	0.39	13.50	1.56E-04	1.56E-13	0.29	98.0	9800.0	0.086
	0.39	13.50	1.56E-04	1.56E-13	0.28	126.0	12600.0	0.111
	0.39	13.50	1.56E-04	1.56E-13	0.28	263.0	26300.0	0.232
1								
	0.41	3.00	3.47E-05	3.47E-14	0.37	25.0	2500.0	0.010
	0.41	3.00	3.47E-05	3.47E-14	0.36	38.0	3800.0	0.015
	0.41	3.00	3.47E-05	3.47E-14	0.36	49.0	4900.0	0.020
	0.41	3.00	3.47E-05	3.47E-14	0.36	59.0	5900.0	0.024
	0.41	3.00	3.47E-05	3.47E-14	0.35	81.0	8100.0	0.033
	0.41	3.00	3.47E-05	3.47E-14	0.35	107.0	10700.0	0.044
3340								
	0.45	1.84	2.13E-05	2.13E-14	0.32	8.0	800.0	0.002
	0.45	1.84	2.13E-05	2.13E-14	0.14	19.0	1900.0	0.006
	0.45	1.84	2.13E-05	2.13E-14	0.12	19.0	1900.0	0.006

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H$_2$O	N/m2	
	0.45	1.84	2.13E-05	2.13E-14	0.12	44.0	4400.0	0.013
	0.45	1.84	2.13E-05	2.13E-14	0.10	65.0	6500.0	0.020
	0.45	1.84	2.13E-05	2.13E-14	0.11	65.0	6500.0	0.020
	0.45	1.84	2.13E-05	2.13E-14	0.10	85.0	8500.0	0.026
	0.45	1.84	2.13E-05	2.13E-14	0.09	131.0	13100.0	0.040
	0.45	1.84	2.13E-05	2.13E-14	0.09	131.0	13100.0	0.040
	0.45	1.84	2.13E-05	2.13E-14	0.09	157.0	15700.0	0.048
	0.45	1.84	2.13E-05	2.13E-14	0.06	223.0	22300.0	0.068
	0.45	1.84	2.13E-05	2.13E-14	0.06	223.0	22300.0	0.068
	0.45	1.84	2.13E-05	2.13E-14	0.05	232.0	23200.0	0.070
	0.45	1.84	2.13E-05	2.13E-14	0.06	232.0	23200.0	0.070
	0.45	1.84	2.13E-05	2.13E-14	0.06	270.0	27000.0	0.082
	0.45	1.84	2.13E-05	2.13E-14	0.05	358.0	35800.0	0.108
3341								
	0.48	2.29	2.65E-05	2.65E-14	0.31	21.0	2100.0	0.007
	0.48	2.29	2.65E-05	2.65E-14	0.34	23.0	2300.0	0.008
	0.48	2.29	2.65E-05	2.65E-14	0.32	25.0	2500.0	0.008
	0.48	2.29	2.65E-05	2.65E-14	0.33	26.0	2600.0	0.009
	0.48	2.29	2.65E-05	2.65E-14	0.22	44.0	4400.0	0.014
	0.48	2.29	2.65E-05	2.65E-14	0.22	48.0	4800.0	0.016
	0.48	2.29	2.65E-05	2.65E-14	0.26	52.0	5200.0	0.017
	0.48	2.29	2.65E-05	2.65E-14	0.22	55.0	5500.0	0.018
	0.48	2.29	2.65E-05	2.65E-14	0.16	57.0	5700.0	0.019
	0.48	2.29	2.65E-05	2.65E-14	0.17	78.0	7800.0	0.026
	0.48	2.29	2.65E-05	2.65E-14	0.22	88.0	8800.0	0.029
	0.48	2.29	2.65E-05	2.65E-14	0.18	90.0	9000.0	0.029
	0.48	2.29	2.65E-05	2.65E-14	0.14	147.0	14700.0	0.048
	0.48	2.29	2.65E-05	2.65E-14	0.13	148.0	14800.0	0.048
	0.48	2.29	2.65E-05	2.65E-14	0.17	157.0	15700.0	0.051
	0.48	2.29	2.65E-05	2.65E-14	0.14	179.0	17900.0	0.059
	0.48	2.29	2.65E-05	2.65E-14	0.08	213.0	21300.0	0.070
	0.48	2.29	2.65E-05	2.65E-14	0.09	266.0	26600.0	0.087
	0.48	2.29	2.65E-05	2.65E-14	0.11	336.0	33600.0	0.110
	0.48	2.29	2.65E-05	2.65E-14	0.08	390.0	39000.0	0.128
	0.48	2.29	2.65E-05	2.65E-14	0.07	488.0	48800.0	0.160
	0.48	2.29	2.65E-05	2.65E-14	0.07	611.0	61100.0	0.200
	0.48	2.29	2.65E-05	2.65E-14	0.07	618.0	61800.0	0.202
	0.48	2.29	2.65E-05	2.65E-14	0.09	709.0	70900.0	0.232
4460								
	0.39	367.00	4.25E-03	4.25E-12	0.28	40.0	4000.0	0.184
	0.39	367.00	4.25E-03	4.25E-12	0.28	44.0	4400.0	0.203
	0.39	367.00	4.25E-03	4.25E-12	0.28	51.0	5100.0	0.235
	0.39	367.00	4.25E-03	4.25E-12	0.28	62.0	6200.0	0.286
	0.39	367.00	4.25E-03	4.25E-12	0.27	75.0	7500.0	0.346
	0.39	367.00	4.25E-03	4.25E-12	0.27	79.0	7900.0	0.364
	0.39	367.00	4.25E-03	4.25E-12	0.27	82.0	8200.0	0.378

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.39	367.00	4.25E-03	4.25E-12	0.27	95.0	9500.0	0.438
	0.39	367.00	4.25E-03	4.25E-12	0.26	139.0	13900.0	0.641
	0.39	367.00	4.25E-03	4.25E-12	0.25	145.0	14500.0	0.668
	0.39	367.00	4.25E-03	4.25E-12	0.25	175.0	17500.0	0.806
	0.39	367.00	4.25E-03	4.25E-12	0.25	176.0	17600.0	0.811
	0.39	367.00	4.25E-03	4.25E-12	0.24	192.0	19200.0	0.885
	0.39	367.00	4.25E-03	4.25E-12	0.24	214.0	21400.0	0.986
	0.39	367.00	4.25E-03	4.25E-12	0.24	215.0	21500.0	0.991
	0.39	367.00	4.25E-03	4.25E-12	0.24	235.0	23500.0	1.083
	0.39	367.00	4.25E-03	4.25E-12	0.24	245.0	24500.0	1.129
	0.39	367.00	4.25E-03	4.25E-12	0.23	252.0	25200.0	1.161
	0.39	367.00	4.25E-03	4.25E-12	0.24	259.0	25900.0	1.194
	0.39	367.00	4.25E-03	4.25E-12	0.24	261.0	26100.0	1.203
	0.39	367.00	4.25E-03	4.25E-12	0.24	273.0	27300.0	1.258
	0.39	367.00	4.25E-03	4.25E-12	0.23	285.0	28500.0	1.313
	0.39	367.00	4.25E-03	4.25E-12	0.22	299.0	29900.0	1.378
	0.39	367.00	4.25E-03	4.25E-12	0.22	327.0	32700.0	1.507
	0.39	367.00	4.25E-03	4.25E-12	0.21	335.0	33500.0	1.544
	0.39	367.00	4.25E-03	4.25E-12	0.22	344.0	34400.0	1.585
	0.39	367.00	4.25E-03	4.25E-12	0.21	351.0	35100.0	1.617
	0.39	367.00	4.25E-03	4.25E-12	0.21	365.0	36500.0	1.682
	0.39	367.00	4.25E-03	4.25E-12	0.22	389.0	38900.0	1.793
	0.39	367.00	4.25E-03	4.25E-12	0.16	662.0	66200.0	3.051
	0.39	367.00	4.25E-03	4.25E-12	0.17	1000.	100000.	4.608
	0.39	367.00	4.25E-03	4.25E-12	0.01	15849.0	1584900.0	73.036
4470								
	0.35	430.00	4.98E-03	4.98E-12	0.20	0.0	0.0	0.000
	0.35	430.00	4.98E-03	4.98E-12	0.19	38.0	3800.0	0.200
	0.35	430.00	4.98E-03	4.98E-12	0.19	39.0	3900.0	0.205
	0.35	430.00	4.98E-03	4.98E-12	0.18	41.0	4100.0	0.215
	0.35	430.00	4.98E-03	4.98E-12	0.19	42.0	4200.0	0.221
	0.35	430.00	4.98E-03	4.98E-12	0.19	46.0	4600.0	0.242
	0.35	430.00	4.98E-03	4.98E-12	0.19	47.0	4700.0	0.247
	0.35	430.00	4.98E-03	4.98E-12	0.19	47.0	4700.0	0.247
	0.35	430.00	4.98E-03	4.98E-12	0.18	48.0	4800.0	0.252
	0.35	430.00	4.98E-03	4.98E-12	0.18	51.0	5100.0	0.268
	0.35	430.00	4.98E-03	4.98E-12	0.19	52.0	5200.0	0.273
	0.35	430.00	4.98E-03	4.98E-12	0.17	52.0	5200.0	0.273
	0.35	430.00	4.98E-03	4.98E-12	0.18	52.0	5200.0	0.273
	0.35	430.00	4.98E-03	4.98E-12	0.17	53.0	5300.0	0.278
	0.35	430.00	4.98E-03	4.98E-12	0.18	53.0	5300.0	0.278
	0.35	430.00	4.98E-03	4.98E-12	0.17	55.0	5500.0	0.289
	0.35	430.00	4.98E-03	4.98E-12	0.17	56.0	5600.0	0.294
	0.35	430.00	4.98E-03	4.98E-12	0.18	58.0	5800.0	0.305
	0.35	430.00	4.98E-03	4.98E-12	0.15	60.0	6000.0	0.315
	0.35	430.00	4.98E-03	4.98E-12	0.17	61.0	6100.0	0.320

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.35	430.00	4.98E-03	4.98E-12	0.17	61.0	6100.0	0.320
	0.35	430.00	4.98E-03	4.98E-12	0.17	61.0	6100.0	0.320
	0.35	430.00	4.98E-03	4.98E-12	0.16	64.0	6400.0	0.336
	0.35	430.00	4.98E-03	4.98E-12	0.17	67.0	6700.0	0.352
	0.35	430.00	4.98E-03	4.98E-12	0.16	68.0	6800.0	0.357
	0.35	430.00	4.98E-03	4.98E-12	0.15	68.0	6800.0	0.357
	0.35	430.00	4.98E-03	4.98E-12	0.16	68.0	6800.0	0.357
	0.35	430.00	4.98E-03	4.98E-12	0.16	71.0	7100.0	0.373
	0.35	430.00	4.98E-03	4.98E-12	0.15	72.0	7200.0	0.378
	0.35	430.00	4.98E-03	4.98E-12	0.17	73.0	7300.0	0.383
	0.35	430.00	4.98E-03	4.98E-12	0.15	73.0	7300.0	0.383
	0.35	430.00	4.98E-03	4.98E-12	0.14	75.0	7500.0	0.394
	0.35	430.00	4.98E-03	4.98E-12	0.15	76.0	7600.0	0.399
	0.35	430.00	4.98E-03	4.98E-12	0.15	76.0	7600.0	0.399
	0.35	430.00	4.98E-03	4.98E-12	0.15	81.0	8100.0	0.425
	0.35	430.00	4.98E-03	4.98E-12	0.15	86.0	8600.0	0.452
	0.35	430.00	4.98E-03	4.98E-12	0.14	105.0	10500.0	0.551
	0.35	430.00	4.98E-03	4.98E-12	0.14	105.0	10500.0	0.551
	0.35	430.00	4.98E-03	4.98E-12	0.14	119.0	11900.0	0.625
	0.35	430.00	4.98E-03	4.98E-12	0.14	121.0	12100.0	0.635
	0.35	430.00	4.98E-03	4.98E-12	0.14	187.0	18700.0	0.982
	0.35	430.00	4.98E-03	4.98E-12	0.12	265.0	26500.0	1.392
	0.35	430.00	4.98E-03	4.98E-12	0.11	349.0	34900.0	1.833
	0.35	430.00	4.98E-03	4.98E-12	0.12	425.0	42500.0	2.232
	0.35	430.00	4.98E-03	4.98E-12	0.11	469.0	46900.0	2.463
	0.35	430.00	4.98E-03	4.98E-12	0.11	740.0	74000.0	3.886
4480								
	0.40	120.00	1.39E-03	1.39E-12	0.29	5.0	500.0	0.013
	0.40	120.00	1.39E-03	1.39E-12	0.29	12.0	1200.0	0.031
	0.40	120.00	1.39E-03	1.39E-12	0.27	26.0	2600.0	0.067
	0.40	120.00	1.39E-03	1.39E-12	0.26	36.0	3600.0	0.093
	0.40	120.00	1.39E-03	1.39E-12	0.26	40.0	4000.0	0.104
	0.40	120.00	1.39E-03	1.39E-12	0.25	43.0	4300.0	0.112
	0.40	120.00	1.39E-03	1.39E-12	0.23	45.0	4500.0	0.117
	0.40	120.00	1.39E-03	1.39E-12	0.22	50.0	5000.0	0.130
	0.40	120.00	1.39E-03	1.39E-12	0.21	55.0	5500.0	0.143
	0.40	120.00	1.39E-03	1.39E-12	0.20	52.0	5200.0	0.135
	0.40	120.00	1.39E-03	1.39E-12	0.19	52.0	5200.0	0.135
	0.40	120.00	1.39E-03	1.39E-12	0.19	55.0	5500.0	0.143
	0.40	120.00	1.39E-03	1.39E-12	0.19	62.0	6200.0	0.161
	0.40	120.00	1.39E-03	1.39E-12	0.19	64.0	6400.0	0.166
	0.40	120.00	1.39E-03	1.39E-12	0.17	59.0	5900.0	0.153
	0.40	120.00	1.39E-03	1.39E-12	0.17	60.0	6000.0	0.156
	0.40	120.00	1.39E-03	1.39E-12	0.18	60.0	6000.0	0.156
	0.40	120.00	1.39E-03	1.39E-12	0.17	59.0	5900.0	0.153
	0.40	120.00	1.39E-03	1.39E-12	0.16	60.0	6000.0	0.156

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.40	120.00	1.39E-03	1.39E-12	0.16	60.0	6000.0	0.156
	0.40	120.00	1.39E-03	1.39E-12	0.16	62.0	6200.0	0.161
	0.40	120.00	1.39E-03	1.39E-12	0.12	65.0	6500.0	0.169
	0.40	120.00	1.39E-03	1.39E-12	0.17	67.0	6700.0	0.174
	0.40	120.00	1.39E-03	1.39E-12	0.18	68.0	6800.0	0.176
	0.40	120.00	1.39E-03	1.39E-12	0.15	68.0	6800.0	0.176
	0.40	120.00	1.39E-03	1.39E-12	0.16	68.0	6800.0	0.176
	0.40	120.00	1.39E-03	1.39E-12	0.16	70.0	7000.0	0.182
	0.40	120.00	1.39E-03	1.39E-12	0.17	70.0	7000.0	0.182
	0.40	120.00	1.39E-03	1.39E-12	0.15	75.0	7500.0	0.195
	0.40	120.00	1.39E-03	1.39E-12	0.15	74.0	7400.0	0.192
	0.40	120.00	1.39E-03	1.39E-12	0.12	70.0	7000.0	0.182
	0.40	120.00	1.39E-03	1.39E-12	0.12	77.0	7700.0	0.200
	0.40	120.00	1.39E-03	1.39E-12	0.13	70.0	7000.0	0.182
	0.40	120.00	1.39E-03	1.39E-12	0.14	78.0	7800.0	0.202
	0.40	120.00	1.39E-03	1.39E-12	0.14	80.0	8000.0	0.208
	0.40	120.00	1.39E-03	1.39E-12	0.11	80.0	8000.0	0.208
	0.40	120.00	1.39E-03	1.39E-12	0.11	79.0	7900.0	0.205
	0.40	120.00	1.39E-03	1.39E-12	0.10	86.0	8600.0	0.223
	0.40	120.00	1.39E-03	1.39E-12	0.09	103.0	10300.0	0.267
	0.40	120.00	1.39E-03	1.39E-12	0.07	113.0	11300.0	0.293
	0.40	120.00	1.39E-03	1.39E-12	0.07	132.0	13200.0	0.343
	0.40	120.00	1.39E-03	1.39E-12	0.06	157.0	15700.0	0.407
	0.40	120.00	1.39E-03	1.39E-12	0.04	209.0	20900.0	0.542
4490								
	0.44	276.00	3.19E-03	3.19E-12	0.23	1.0	100.0	0.004
	0.44	276.00	3.19E-03	3.19E-12	0.22	5.0	500.0	0.019
	0.44	276.00	3.19E-03	3.19E-12	0.21	25.0	2500.0	0.094
	0.44	276.00	3.19E-03	3.19E-12	0.21	31.0	3100.0	0.116
	0.44	276.00	3.19E-03	3.19E-12	0.21	32.0	3200.0	0.120
	0.44	276.00	3.19E-03	3.19E-12	0.19	32.0	3200.0	0.120
	0.44	276.00	3.19E-03	3.19E-12	0.20	35.0	3500.0	0.131
	0.44	276.00	3.19E-03	3.19E-12	0.20	35.0	3500.0	0.131
	0.44	276.00	3.19E-03	3.19E-12	0.19	35.0	3500.0	0.131
	0.44	276.00	3.19E-03	3.19E-12	0.18	35.0	3500.0	0.131
	0.44	276.00	3.19E-03	3.19E-12	0.17	36.0	3600.0	0.135
	0.44	276.00	3.19E-03	3.19E-12	0.18	37.0	3700.0	0.139
	0.44	276.00	3.19E-03	3.19E-12	0.18	40.0	4000.0	0.150
	0.44	276.00	3.19E-03	3.19E-12	0.17	40.0	4000.0	0.150
	0.44	276.00	3.19E-03	3.19E-12	0.16	45.0	4500.0	0.169
	0.44	276.00	3.19E-03	3.19E-12	0.15	45.0	4500.0	0.169
	0.44	276.00	3.19E-03	3.19E-12	0.15	46.0	4600.0	0.173
	0.44	276.00	3.19E-03	3.19E-12	0.14	45.0	4500.0	0.169
	0.44	276.00	3.19E-03	3.19E-12	0.14	47.0	4700.0	0.176
	0.44	276.00	3.19E-03	3.19E-12	0.14	48.0	4800.0	0.180
	0.44	276.00	3.19E-03	3.19E-12	0.11	48.0	4800.0	0.180

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.44	276.00	3.19E-03	3.19E-12	0.15	50.0	5000.0	0.188
	0.44	276.00	3.19E-03	3.19E-12	0.12	50.0	5000.0	0.188
	0.44	276.00	3.19E-03	3.19E-12	0.13	53.0	5300.0	0.199
	0.44	276.00	3.19E-03	3.19E-12	0.12	52.0	5200.0	0.195
	0.44	276.00	3.19E-03	3.19E-12	0.12	55.0	5500.0	0.206
	0.44	276.00	3.19E-03	3.19E-12	0.11	55.0	5500.0	0.206
	0.44	276.00	3.19E-03	3.19E-12	0.11	58.0	5800.0	0.218
	0.44	276.00	3.19E-03	3.19E-12	0.11	58.0	5800.0	0.218
	0.44	276.00	3.19E-03	3.19E-12	0.10	60.0	6000.0	0.225
	0.44	276.00	3.19E-03	3.19E-12	0.11	62.0	6200.0	0.233
	0.44	276.00	3.19E-03	3.19E-12	0.09	61.0	6100.0	0.229
	0.44	276.00	3.19E-03	3.19E-12	0.09	66.0	6600.0	0.248
	0.44	276.00	3.19E-03	3.19E-12	0.08	66.0	6600.0	0.248
	0.44	276.00	3.19E-03	3.19E-12	0.07	66.0	6600.0	0.248
	0.44	276.00	3.19E-03	3.19E-12	0.08	68.0	6800.0	0.255
	0.44	276.00	3.19E-03	3.19E-12	0.08	70.0	7000.0	0.263
	0.44	276.00	3.19E-03	3.19E-12	0.08	72.0	7200.0	0.270
	0.44	276.00	3.19E-03	3.19E-12	0.07	72.0	7200.0	0.270
	0.44	276.00	3.19E-03	3.19E-12	0.06	71.0	7100.0	0.266
	0.44	276.00	3.19E-03	3.19E-12	0.06	75.0	7500.0	0.281
	0.44	276.00	3.19E-03	3.19E-12	0.06	77.0	7700.0	0.289
	0.44	276.00	3.19E-03	3.19E-12	0.08	79.0	7900.0	0.296
	0.44	276.00	3.19E-03	3.19E-12	0.05	81.0	8100.0	0.304
	0.44	276.00	3.19E-03	3.19E-12	0.05	82.0	8200.0	0.308
	0.44	276.00	3.19E-03	3.19E-12	0.05	85.0	8500.0	0.319
	0.44	276.00	3.19E-03	3.19E-12	0.06	86.0	8600.0	0.323
	0.44	276.00	3.19E-03	3.19E-12	0.06	88.0	8800.0	0.330
	0.44	276.00	3.19E-03	3.19E-12	0.04	92.0	9200.0	0.345
	0.44	276.00	3.19E-03	3.19E-12	0.05	93.0	9300.0	0.349
	0.44	276.00	3.19E-03	3.19E-12	0.04	95.0	9500.0	0.357
	0.44	276.00	3.19E-03	3.19E-12	0.05	97.0	9700.0	0.364
	0.44	276.00	3.19E-03	3.19E-12	0.05	98.0	9800.0	0.368
	0.44	276.00	3.19E-03	3.19E-12	0.05	99.0	9900.0	0.372
	0.44	276.00	3.19E-03	3.19E-12	0.04	105.0	10500.0	0.394
	0.44	276.00	3.19E-03	3.19E-12	0.04	106.0	10600.0	0.398
	0.44	276.00	3.19E-03	3.19E-12	0.04	108.0	10800.0	0.405
	0.44	276.00	3.19E-03	3.19E-12	0.04	110.0	11000.0	0.413
	0.44	276.00	3.19E-03	3.19E-12	0.02	108.0	10800.0	0.405
	0.44	276.00	3.19E-03	3.19E-12	0.02	116.0	11600.0	0.435
4500								
	0.39	150.00	1.74E-03	1.74E-12	0.29	2.0	200.0	0.006
	0.39	150.00	1.74E-03	1.74E-12	0.27	15.0	1500.0	0.044
	0.39	150.00	1.74E-03	1.74E-12	0.26	16.0	1600.0	0.047
	0.39	150.00	1.74E-03	1.74E-12	0.29	16.0	1600.0	0.047
	0.39	150.00	1.74E-03	1.74E-12	0.27	18.0	1800.0	0.053
	0.39	150.00	1.74E-03	1.74E-12	0.28	18.0	1800.0	0.053

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.39	150.00	1.74E-03	1.74E-12	0.25	21.0	2100.0	0.062
	0.39	150.00	1.74E-03	1.74E-12	0.28	21.0	2100.0	0.062
	0.39	150.00	1.74E-03	1.74E-12	0.25	21.0	2100.0	0.062
	0.39	150.00	1.74E-03	1.74E-12	0.25	23.0	2300.0	0.068
	0.39	150.00	1.74E-03	1.74E-12	0.26	25.0	2500.0	0.074
	0.39	150.00	1.74E-03	1.74E-12	0.25	27.0	2700.0	0.079
	0.39	150.00	1.74E-03	1.74E-12	0.25	29.0	2900.0	0.085
	0.39	150.00	1.74E-03	1.74E-12	0.25	30.0	3000.0	0.088
	0.39	150.00	1.74E-03	1.74E-12	0.24	30.0	3000.0	0.088
	0.39	150.00	1.74E-03	1.74E-12	0.25	32.0	3200.0	0.094
	0.39	150.00	1.74E-03	1.74E-12	0.22	33.0	3300.0	0.097
	0.39	150.00	1.74E-03	1.74E-12	0.25	34.0	3400.0	0.100
	0.39	150.00	1.74E-03	1.74E-12	0.25	35.0	3500.0	0.103
	0.39	150.00	1.74E-03	1.74E-12	0.21	35.0	3500.0	0.103
	0.39	150.00	1.74E-03	1.74E-12	0.25	36.0	3600.0	0.106
	0.39	150.00	1.74E-03	1.74E-12	0.21	38.0	3800.0	0.112
	0.39	150.00	1.74E-03	1.74E-12	0.22	38.0	3800.0	0.112
	0.39	150.00	1.74E-03	1.74E-12	0.25	39.0	3900.0	0.115
	0.39	150.00	1.74E-03	1.74E-12	0.23	40.0	4000.0	0.118
	0.39	150.00	1.74E-03	1.74E-12	0.24	40.0	4000.0	0.118
	0.39	150.00	1.74E-03	1.74E-12	0.24	40.0	4000.0	0.118
	0.39	150.00	1.74E-03	1.74E-12	0.22	43.0	4300.0	0.127
	0.39	150.00	1.74E-03	1.74E-12	0.22	43.0	4300.0	0.127
	0.39	150.00	1.74E-03	1.74E-12	0.23	44.0	4400.0	0.129
	0.39	150.00	1.74E-03	1.74E-12	0.18	44.0	4400.0	0.129
	0.39	150.00	1.74E-03	1.74E-12	0.23	45.0	4500.0	0.132
	0.39	150.00	1.74E-03	1.74E-12	0.21	46.0	4600.0	0.135
	0.39	150.00	1.74E-03	1.74E-12	0.20	46.0	4600.0	0.135
	0.39	150.00	1.74E-03	1.74E-12	0.20	47.0	4700.0	0.138
	0.39	150.00	1.74E-03	1.74E-12	0.19	48.0	4800.0	0.141
	0.39	150.00	1.74E-03	1.74E-12	0.19	48.0	4800.0	0.141
	0.39	150.00	1.74E-03	1.74E-12	0.20	49.0	4900.0	0.144
	0.39	150.00	1.74E-03	1.74E-12	0.21	50.0	5000.0	0.147
	0.39	150.00	1.74E-03	1.74E-12	0.19	51.0	5100.0	0.150
	0.39	150.00	1.74E-03	1.74E-12	0.21	52.0	5200.0	0.153
	0.39	150.00	1.74E-03	1.74E-12	0.20	52.0	5200.0	0.153
	0.39	150.00	1.74E-03	1.74E-12	0.19	53.0	5300.0	0.156
	0.39	150.00	1.74E-03	1.74E-12	0.17	55.0	5500.0	0.162
	0.39	150.00	1.74E-03	1.74E-12	0.18	56.0	5600.0	0.165
	0.39	150.00	1.74E-03	1.74E-12	0.16	58.0	5800.0	0.171
	0.39	150.00	1.74E-03	1.74E-12	0.17	58.0	5800.0	0.171
	0.39	150.00	1.74E-03	1.74E-12	0.18	59.0	5900.0	0.174
	0.39	150.00	1.74E-03	1.74E-12	0.16	60.0	6000.0	0.177
	0.39	150.00	1.74E-03	1.74E-12	0.17	60.0	6000.0	0.177
	0.39	150.00	1.74E-03	1.74E-12	0.17	60.0	6000.0	0.177
	0.39	150.00	1.74E-03	1.74E-12	0.16	63.0	6300.0	0.185

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.39	150.00	1.74E-03	1.74E-12	0.17	65.0	6500.0	0.191
	0.39	150.00	1.74E-03	1.74E-12	0.15	67.0	6700.0	0.197
	0.39	150.00	1.74E-03	1.74E-12	0.16	67.0	6700.0	0.197
	0.39	150.00	1.74E-03	1.74E-12	0.15	69.0	6900.0	0.203
	0.39	150.00	1.74E-03	1.74E-12	0.17	69.0	6900.0	0.203
	0.39	150.00	1.74E-03	1.74E-12	0.16	72.0	7200.0	0.212
	0.39	150.00	1.74E-03	1.74E-12	0.15	72.0	7200.0	0.212
	0.39	150.00	1.74E-03	1.74E-12	0.15	73.0	7300.0	0.215
	0.39	150.00	1.74E-03	1.74E-12	0.14	73.0	7300.0	0.215
	0.39	150.00	1.74E-03	1.74E-12	0.15	73.0	7300.0	0.215
	0.39	150.00	1.74E-03	1.74E-12	0.15	73.0	7300.0	0.215
	0.39	150.00	1.74E-03	1.74E-12	0.15	76.0	7600.0	0.224
	0.39	150.00	1.74E-03	1.74E-12	0.15	78.0	7800.0	0.230
	0.39	150.00	1.74E-03	1.74E-12	0.14	79.0	7900.0	0.232
	0.39	150.00	1.74E-03	1.74E-12	0.14	81.0	8100.0	0.238
	0.39	150.00	1.74E-03	1.74E-12	0.15	83.0	8300.0	0.244
	0.39	150.00	1.74E-03	1.74E-12	0.14	83.0	8300.0	0.244
	0.39	150.00	1.74E-03	1.74E-12	0.14	84.0	8400.0	0.247
	0.39	150.00	1.74E-03	1.74E-12	0.13	84.0	8400.0	0.247
	0.39	150.00	1.74E-03	1.74E-12	0.14	85.0	8500.0	0.250
	0.39	150.00	1.74E-03	1.74E-12	0.14	87.0	8700.0	0.256
	0.39	150.00	1.74E-03	1.74E-12	0.13	88.0	8800.0	0.259
	0.39	150.00	1.74E-03	1.74E-12	0.14	89.0	8900.0	0.262
	0.39	150.00	1.74E-03	1.74E-12	0.14	91.0	9100.0	0.268
	0.39	150.00	1.74E-03	1.74E-12	0.14	93.0	9300.0	0.274
	0.39	150.00	1.74E-03	1.74E-12	0.13	93.0	9300.0	0.274
	0.39	150.00	1.74E-03	1.74E-12	0.13	97.0	9700.0	0.285
	0.39	150.00	1.74E-03	1.74E-12	0.13	98.0	9800.0	0.288
	0.39	150.00	1.74E-03	1.74E-12	0.13	101.0	10100.0	0.297
	0.39	150.00	1.74E-03	1.74E-12	0.14	10.0	1000.0	0.029
	0.39	150.00	1.74E-03	1.74E-12	0.13	103.0	10300.0	0.303
	0.39	150.00	1.74E-03	1.74E-12	0.12	107.0	10700.0	0.315
	0.39	150.00	1.74E-03	1.74E-12	0.13	111.0	11100.0	0.327
	0.39	150.00	1.74E-03	1.74E-12	0.13	112.0	11200.0	0.330
	0.39	150.00	1.74E-03	1.74E-12	0.12	113.0	11300.0	0.332
	0.39	150.00	1.74E-03	1.74E-12	0.13	113.0	11300.0	0.332
	0.39	150.00	1.74E-03	1.74E-12	0.12	117.0	11700.0	0.344
	0.39	150.00	1.74E-03	1.74E-12	0.12	119.0	11900.0	0.350
	0.39	150.00	1.74E-03	1.74E-12	0.12	122.0	12200.0	0.359
	0.39	150.00	1.74E-03	1.74E-12	0.11	126.0	12600.0	0.371
	0.39	150.00	1.74E-03	1.74E-12	0.12	130.0	13000.0	0.383
	0.39	150.00	1.74E-03	1.74E-12	0.11	133.0	13300.0	0.391
	0.39	150.00	1.74E-03	1.74E-12	0.12	133.0	13300.0	0.391
	0.39	150.00	1.74E-03	1.74E-12	0.12	133.0	13300.0	0.391
	0.39	150.00	1.74E-03	1.74E-12	0.12	137.0	13700.0	0.403
	0.39	150.00	1.74E-03	1.74E-12	0.11	139.0	13900.0	0.409

N	Pε	κ	κ	k	S	h	h	J
		cm/day	cm/s	m^2		cm H_2O	N/m2	
	0.39	150.00	1.74E-03	1.74E-12	0.12	140.0	14000.0	0.412
	0.39	150.00	1.74E-03	1.74E-12	0.11	144.0	14400.0	0.424
	0.39	150.00	1.74E-03	1.74E-12	0.11	147.0	14700.0	0.433
	0.39	150.00	1.74E-03	1.74E-12	0.12	151.0	15100.0	0.444
	0.39	150.00	1.74E-03	1.74E-12	0.12	151.0	15100.0	0.444
	0.39	150.00	1.74E-03	1.74E-12	0.11	154.0	15400.0	0.453
	0.39	150.00	1.74E-03	1.74E-12	0.11	156.0	15600.0	0.459
	0.39	150.00	1.74E-03	1.74E-12	0.12	158.0	15800.0	0.465
	0.39	150.00	1.74E-03	1.74E-12	0.11	158.0	15800.0	0.465
	0.39	150.00	1.74E-03	1.74E-12	0.10	171.0	17100.0	0.503
	0.39	150.00	1.74E-03	1.74E-12	0.10	173.0	17300.0	0.509
	0.39	150.00	1.74E-03	1.74E-12	0.10	173.0	17300.0	0.509
	0.39	150.00	1.74E-03	1.74E-12	0.11	176.0	17600.0	0.518
	0.39	150.00	1.74E-03	1.74E-12	0.10	182.0	18200.0	0.536
	0.39	150.00	1.74E-03	1.74E-12	0.11	185.0	18500.0	0.544
	0.39	150.00	1.74E-03	1.74E-12	0.10	190.0	19000.0	0.559
	0.39	150.00	1.74E-03	1.74E-12	0.10	192.0	19200.0	0.565
	0.39	150.00	1.74E-03	1.74E-12	0.10	198.0	19800.0	0.583
	0.39	150.00	1.74E-03	1.74E-12	0.10	204.0	20400.0	0.600
	0.39	150.00	1.74E-03	1.74E-12	0.10	205.0	20500.0	0.603
	0.39	150.00	1.74E-03	1.74E-12	0.10	207.0	20700.0	0.609
	0.39	150.00	1.74E-03	1.74E-12	0.10	213.0	21300.0	0.627
	0.39	150.00	1.74E-03	1.74E-12	0.10	216.0	21600.0	0.636
	0.39	150.00	1.74E-03	1.74E-12	0.08	228.0	22800.0	0.671
	0.39	150.00	1.74E-03	1.74E-12	0.09	228.0	22800.0	0.671
	0.39	150.00	1.74E-03	1.74E-12	0.09	235.0	23500.0	0.691
	0.39	150.00	1.74E-03	1.74E-12	0.10	240.0	24000.0	0.706
	0.39	150.00	1.74E-03	1.74E-12	0.10	244.0	24400.0	0.718

Properties of the UNSODA soils **L = LOAMY** **SA = SAND**
SI = SILICEOUS **MM = MIXED MESIC**

Reference number	Family	Series name	Bulk density	Particle density	Porosity	Organic matter content	Saturated conductivity	Saturated water content
1010	L-SI	TROUP	1.64	2.64	0.39		171.1	0.384
1011	L-SI	TROUP	1.52	2.68	0.43		310	
1012	L-SI	TROUP	1.4	2.66	0.44		207	
1013	L-SI	TROUP	1.4	2.66	0.44		207	
1120	FINE L SI	DOTHAN	1.63				37.9	0.312
1121	FINE L SI	DOTHAN	1.64				7.13	0.348
1122	FINE L SI	DOTHAN	1.66				2.92	0.359
1123	FINE L SI	DOTHAN	1.64				0.74	0.349
1130	FINE L SI	DOTHAN	1.56				2.74	0.4
1131	FINE L SI	DOTHAN	1.97				3.744	0.243
1132	FINE L SI	DOTHAN	1.77				0.415	0.352
1133	FINE L SI	DOTHAN	1.81				0.091	0.327
1150	FINE L SI	GLODSBORO	1.76					0.279
1151	FINE L SI	GLODSBORO	1.8					0.268
1152	FINE L SI	GLODSBORO	1.74					0.289
1240	MM	QUINCY SAND	1.7	2.82	0.3971631		389	
1241	MM	QUINCY SAND	1.7	2.82	0.3971631			
1260	MM	WARDEN SILT L	1.54	2.77	0.4440433		77.8	
1261	MM	WARDEN SILT L	1.54	2.77	0.4440433		77.8	
1330	ALBIC LUVISOL	OHLERDORF PARABRAUNERDI	1.37		0.45		35	0.44
1331	ALBIC LUVISOL	OHLERDORF PARABRAUNERDI	1.43		0.45		40	0.43
2100	SI	LABOUCHERI	1.7	2.7	0.3703704		370	0.374
2101	SI	LABOUCHERI	1.6	2.7	0.4074074		473	0.406
2140	SA MM	MANAWATU	1.44	2.65	0.4566038		540	0.41
2150	COARSE L MM	TIVYFORD	1.14				518	0.4
2151	COARSE L MM	TIVYFORD	1.45				518	0.3
2470	SI CLAY	TERRA FUSCA	0.702					0.73
2471	SI CLAY	TERRA FUSCA	0.872					0.668
2472	SI CLAY	TERRA FUSCA	0.897					0.659
2480	L-SA	VOLCANOELASTIC PSAMMENTS	1.23					0.423
2481	L-SA	VOLCANOELASTIC PSAMMENTS	1.2					0.42
2482	L-SA	VOLCANOELASTIC PSAMMENTS	1.05					0.497
2483	L-SA	VOLCANOELASTIC PSAMMENTS	1.3					0.339
3031	CHERNOZEM	ORENBURY	1.07	2.87	0.63			0.53
3032	CHERNOZEM	ORENBURY	1.21	2.76	0.56			0.55
3033	CHERNOZEM	ORENBURY	1.32	2.76	0.51			0.57
3090	CHERNOZEM	ODESSA	1.4	2.58	0.457	3.85	19.5	
3091	CHERNOZEM	ODESSA	1.43	2.6	0.45	3.02	15.4	
3092	CHERNOZEM	ODESSA						
3093	CHERNOZEM	ODESSA	1.38	2.67	0.481			
3100	CHERNOZEM	HOLDOVA	1.14	2.54	0.551	4	168	
3101	CHERNOZEM	HOLDOVA	1.33	2.56	0.481	4.3	55.8	
3102	CHERNOZEM	HOLDOVA	1.3	2.64	0.508	2.88	109	
3103	CHERNOZEM	HOLDOVA	1.37	2.64	0.481	1.8		
3110	CHERNOZEM	HOLDOVA	1.35	2.54	0.469	4.27	91	
3111	CHERNOZEM	HOLDOVA	1.31	2.57	0.49	3.84	98	
3112	CHERNOZEM	HOLDOVA	1.3	2.57	0.494	3.08	109	
3113	CHERNOZEM	HOLDOVA	1.38	2.69	0.487	2.5		
3130	SANDY MIXED	HAMAR	1.5			1.2		0.57
3131	SANDY MIXED	HAMAR	1.58			1		0.426
3132	SANDY MIXED	HAMAR	1.51			0.3		0.364
3133	SANDY MIXED	HAMAR	1.61			0.06		0.6542

3220	COARSE SILTY MIXED	GARDENA	1.33			5.2		0.691
3221	COARSE SILTY MIXED	GARDENA	1.51			1		0.5738
3222	COARSE SILTY MIXED	GARDENA	1.46			0.74		0.73
3223	COARSE SILTY MIXED	GARDENA	1.42			0.6		0.71
3224	COARSE SILTY MIXED	GARDENA	1.35			0.47		0.756
3230	SA	KOSTWIJK	1.1			2.5		0.52
3231	SA	KOSTWIJK	1.5			1		0.41
3232	SA	KOSTWIJK	1.5			1		0.41
3240	FINE SILTY MIXED	LORING	1.45		0.45		1.84	
3241	FINE SILTY MIXED	LORING	1.39		0.48		2.29	
3242	FINE SILTY MIXED	LORING	1.41		0.47		31.3	
3243	FINE SILTY MIXED	LORING	1.49		0.44		6.99	
3250	FINE SILTY MIXED	MEMPHIS	1.47		0.45		1.51	0.54
3251	FINE SILTY MIXED	MEMPHIS	1.44		0.46		2.74	0.5
3252	FINE SILTY MIXED	MEMPHIS	1.46		0.45		1.44	0.47
3253	FINE SILTY MIXED	MEMPHIS	1.48		0.55		1.476	
3260	COARSE SILTY MIXED	VICKSBURG	1.35		0.49		10.8	0.475
3261	COARSE SILTY MIXED	VICKSBURG	1.43		0.49		32	0.495
3262	COARSE SILTY MIXED	VICKSBURG	1.36		0.49		35.3	0.445
3263	COARSE SILTY MIXED	VICKSBURG	1.37		0.49		54	0.465
3264	COARSE SILTY MIXED	VICKSBURG	1.38		0.49		58.1	0.5
3270	SI CLAY L	BUNDOORA	1.44					0.443
3271	SI CLAY L	BUNDOORA	1.61					0.425
3272	SI CLAY L	BUNDOORA	1.61					0.425
3273	SI CLAY L	BUNDOORA	1.47					0.474
3274	SI CLAY L	BUNDOORA	1.54					0.463
3281	CLAY	GOULBURN	1.61	2.64	0.39		13.5	0.366
3282	CLAY	GOULBURN	1.57	2.64	0.405		3	0.409
3283	CLAY	GOULBURN	1.64	2.64	0.379			0.402
3340	FINE SILTY	LORING	1.45		0.45		1.84	
3341	SI CLAY L	LORING	1.39		0.48		2.29	
4460	SA L	MORNAY	1.652	2.7	0.388		367	0.32
4470	SA	BOUCAKE	1.7	2.65	0.35		430	0.2
4480	SA	DIOR	1.6	2.7	0.4		120	0.29
4490	SA L	DIERI	1.5	2.7	0.44		276	0.22
4500	SA CLAY L	DEK	1.65	2.7	0.389		150	0.3

B

APPENDIX B MEMO TO USE THE PROGRAM “WETTEDLENGTH”

Outline

1. Definition of the variables
2. Algorithm of the program
3. Thermohydraulic system
4. Changing the input
5. Example of output

1. Definition of the variables

The variables can be divided in two major categories: the variables used in the principal program **(bold)**, the variables used by the numerical method BVPFD *(italics)*.

The function BVPFD solves a system of differential equations with two boundary conditions. In this program it is used to solve the thermohydraulic equations.

1.1 Variables for entire program

LDYFIN : Leading dimension of YFINAL exactly as specified in The dimension
LDYINI : Leading dimension of YINIT exactly as specified in the dimension statement of the calling program
MXGRID : Maximum number of grid points allowed
NEQNS : Number of differential equations
NINIT : Number of initial grid points including the endpoints. It must be at least four
KKPRT : Integer (used as a placeholder value in the comparison statement <if K .EQ. KKPRT>. It is used since <if K .EQ. 4> is invalid syntax)
IPRT : Integer (same than KKPRT)
NCUPBC : Number of coupled boundary conditions. The number NLEFT + NCUPBC must be greater than zero and less than or equal to NEQNS
NFINAL : Number of final grid points including the endpoints
NLEFT : Number of initial conditions. the value NLEFT must be greater than or equal to zero and less than NEQNS.
I : Counter
J : Counter

KK : Counter

ISTORE : Counter to store the results in STOREPROFILES and STOREWLMASS

GRIDCOLD : Number of grid points during the previous calculation (at t-1)

NTIMESTEP : Number of time step to be calculated

ERREST : Array if size NEQNS containing the estimated error in Y(J)

PISTEP : Initial increment size for p. If this value is zero, continuation will not be used in the problem solved by BVPFD. The routines FCNPEQ and FCNPBC will not be called

TFINAL : Array of size MXGRID containing the final grid points. Only the first NFINAL points are significant

TINIT : Array of size NINIT containing the initial grid points.

TLEFT : The left endpoint

TOL : Relative error control parameter. The computation stops when Abs. value(ERROR(J,I)/MAX(ABS(Y(J,I)),1.0) less than TOL for all J=1,...,N and I=1,...,NGRID. Here, ERROR(J,I) is the estimated error in Y(J,I).

TRIGHT : The right endpoint

YFINAL : Array of size N by MXGRID containing the values of Y at the points in TFINAL

YININT : Array of size N by MXGRID containing the values of Y at the points in TINIT

DELTAWL : Increment value to calculate the wetted length Wl.(cm)

MUF : Liquid viscosity (Ns/cm^2)

H0 : Term in the calculation for the heat transfer coefficient as shown in this equation : H = H0 + H1*S ($J/s/cm^2/K$)

H1 : Term in the calculation for the heat transfer coefficient as shown in this equation : H = H0 + H1*S ($J/s/cm^2/K$)

RSG : Radius of the tube (cm)

TP : Temperature of the tube (K)

TS0 : Temperature of the bulk solution (K)

RHOF : Liquid density (g/cm^3)

AC : Cross sectional area (cm^2)

HFG : Latent heat of vaporization (J/g)

dPcdS : Term in the calculation for the capillary pressure as shown in this equation : Pc = Pc0 + dPcdS*S (N/cm^2)

MUV : Vapor viscosity (Ns/cm^2)

KV : Permeability of the porous media (cm^2)

RHOV : Vapor density (g/cm^3)

PI : Mathematical constant = 3.14

TIMESTEP : Length of time during each time step (s)

D(6) : Vector containing the diffusion coefficient of H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$. (cm^2/s)

EPS : Porosity of the porous media

ALPHA(6) : Vector containing the coefficients of for the calculation of the boiling point elevation. $\mathrm{BPE} = \sum_i \mathrm{ALPHA(i)} \times \mathrm{C(i)}$ where C(i) is the vector containing the concentrations of H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$ ($K/mol*cm^3$)

LENGTH : Half length of the crevice (the crevice is assumed to be symmetric) (cm)

SOLD(8000) : Vector containing the values of the saturation at the previous time step

COLD(6,8000) : Vector containing the values of the concentrations of H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$ at the previous time step. (mol/cm^3)

MASS : Real value used for the calculation of the integrated mass of sodium in half the crevice at a time t (g)

WL : Liquid wetted length in the crevice at a time t (cm)

WLOLD : Liquid wetted length in the crevice at the previous time (cm)

CBULK(6) : Vector containing the bulk concentration of H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$ (mol/cm^3)

SLIM : Saturation limit to ensure a liquid phase (criterion of convergence for the calculation of WL)

STOREWLMASS : Vector storing all the mass and wetted length history before writing them in the output file (This way, the program doesn't have to access the output file at each time iteration)

STOREPROFILES : Vector storing all the saturation and concentration profiles at different time before writing them in the output file

LINEAR : Logical .TRUE. if differential equations and the boundary conditions are linear

PRINT : Logical .TRUE. if intermediate output is to be printed

1.2 Local variables of FCNEQN

T : Independent variables t

Y : Array of size NEQNS containing the dependent variable values, y(t)

DYDT : Array of size NEQNS containing the derivatives y'(t)

1.3 Local variables of FCNJAC

T : Independent variables t

Y : Array of size NEQNS containing the dependent variable values, y(t)

DYPDY : Array of size NEQNS containing the partial derivatives

$$a_{ij} = \partial f_i / \partial y_j$$

evaluated at (t,y). The values aij are returned in DYPDY(i,j).

2. Program algorithm

The program has been copied at the end of this memo including line numbers. The algorithm will refer to those line numbers.

2.1 Main Program

- Definition of variables
- Wetted length WL is initialized (0.43 in this case)
- Input of variables (properties of the crevice, porous media, operating parameters)
- Setting up the output files :

1PPBMASS.out which contains the times, mass of sodium accumulated and wetted length

1PPBPROF which contains the profiles of Na^+ concentration and saturation at different times.

- Initialize TINIT with the grid of the wetted of the crevice (the grid is not over the entire half of the crevice)
- Initialize YINIT
- Initialize the concentrations in the crevice (at t=0 there is no concentrated solution in the wetted length of the crevice)
- Do from KK=1 to KK=TIMESTEP
  - IPAR = .TRUE.
  - MASS = 0
  - Label 1
  - Call subroutine **BVPFD** to solve the thermal hydraulic system of equations in the crevice

    Inputs : YINIT, TINIT, TLEFT, TRIGHT...
    Outputs : YFINAL containing
    YFINAL(1,I):Concentration of H+ at the Ith space grid with I from 1 to NFINAL
    YFINAL(2,I): Concentration of OH– at the Ith space grid with I from 1 to NFINAL
    YFINAL(3,I): Concentration of Na+ at the Ith space grid with I from 1 to NFINAL
    YFINAL(4,I): Concentration of Cl– at the Ith space grid with I from 1 to NFINAL
    YFINAL(5,I): Concentration of Fe2+ at the Ith space grid with I from 1 to NFINAL
    YFINAL(6,I): Concentration of FeOH+ at the Ith space grid with I from 1 to NFINAL
    YFINAL(7,I) : Not used, set to one
    YFINAL(8,I) : Saturation at the Ith space grid with I from 1 to NFINAL
    YFINAL(9,I) : Liquid velocity at the I^{th} space grid with I from 1 to NFINAL
  - If the saturation at X=WL is greater than SLIM, WL is less than LENGTH and IPAR is true (Which means that at the limit of the wetted length, the model predicts still a quantitative fraction of liquid so the wetted length is probably bigger.)

    THEN
    WL is increased to WL+ DELTAWL
    TRIGHT is increased to WL+DELTAWL(which is now WL)
    The gridpoints (TINIT) are recalculated with the increased wetted length.
    Return to the call of the subroutine BVPFD in 1
  - If the saturation at X=WL is less than SLIM and IPAR is true

(This condition means that at the limit of the wetted length, the model predicts a very small fraction of liquid so it is already the steam blanketed region, the wetted length is a little too big.)

THEN
WL is decreased to WL-DELTAWL (This is the wetted length +/– DELTAWL)
TRIGHT is decreased to WL-DELTAWL(which is now WL)

```
        The gridpoints (TINIT) are recalculated with the decreased wetted length
        IPAR = .FALSE. (the next iteration @WL-DELTAWL will be the last one)
        Return to the call of the subroutine BVPFD in 1
```

So typically, the calculation starts with a small WL. The saturation at the right endpoint is substantial (The limiting criterion is defined by the user: It should be greater than zero, less than 1 and as small as possible.). As WL is increased, the saturation at the right endpoint decreases until it reaches a level that is too small for a liquid phase to remain. The wetted length is then determined as the value of WL (giving this too little right endpoint saturation)—DELTAWL.

- – Store the concentrations for the next time step in COLD
- – Store the saturation for the next time step in SOLD
- – Calculate the mass of sodium MASS
- – Store in STOREPROFILE(1,ISTORE) a value of–500 to visibly indicate that this is a new time step
- – Store in STOREPROFILE(2,ISTORE) the time (KK*TIMESTEP)
- – ISTORE = ISTORE+1
- – Every 100 time step

```
        DO I from 1 to NFINAL
        Every 50 spatial points
        STOREPROFILE(1,ISTORE) = YFINAL(3,I) (Concentration of sodium)
        STOREPROFILE(2,ISTORE) = YFINAL(8,I) (Saturation)
        STOREPROFILE(3,ISTORE) = TINIT(I) (Grid point)
        ISTORE = ISTORE + 1
        END DO
```

- – STOREWLMASS(3,KK) = KK*TIMESTEP (The time is stored at each time step in STOREWLMASS(3))
- – STOREWLMASS(1,KK) = MASS
- – STOREWLMASS(2,KK) = WL

- END DO
- DO I from 1 to ISTORE-1

```
    IF STOREPROFILES less than –450

    THEN write in '1PPBPROF.out' STOREPROFILES(2,I)

    ELSE write in '1PPBPROF.out' STOREPROFILES (3,I) ,STOREPROFILES (1,I)
    STOREPROFILES (2,I) (X, Concentration of sodium at X, Saturation at X)
```

An entry of "-500" in the array STOREPROFILES(1,I) signifies the beginning of the concentration vector. Each following element of the array represents the next component of the concentration vector, until the next value of –500 is reached. This process is repeated until all the values are extracted from STOREPROFILES(1,I)

Each element of the array STOREPROFILES(1,I) has a corresponding element in the array STOREPROFILES(2,I). These are the elements from the saturation vector.

-500 corresponding element is the time at which the following saturations and concentrations were calculated at.

STOREPROFILES(1) = (-500,$C_{Na}{}^{+}$(x=0,t=0),...,$C_{Na}{}^{+}$(x=WL, t=0),
-500,$C_{Na}{}^{+}$(x=0,t=timestep),...,$C_{Na}{}^{+}$(x=WL, t=timestep),
-500,...

STOREPROFILES(2)= (time=timestep,S(x=0, t=0),...,S(x=WL, t=0),
time=2timestep,S(x=0,t=timestep),...,S(x=WL,t=timestep),
time=3timestep,.....

- END DO
- END

3. Thermal hydraulic system

3.1 Numerical method used

BVPFD (IMSL library) solves that system of ordinary differential equations with boundary conditions at two points using a variable order, variable step size finite difference method with deferred corrections.

The problem statement is abbreviated by writing it as a system of first order ODEs $y(t) = [y_1(t),..., y_N(t)]^T, f(t,y) = [f_1(t,y),..., f_N(t,y)]^T$ y is the dependent variable and t is the independent variable. First order means that the highest order any derivatives in the equation is 1.

The problem becomes $y' = \frac{dy(t)}{dt} = f(t,y)$. In the boundary value problem (BVP) for ODEs, constraints on the dependent variables are given at the endpoints of the interval of interest, [a,b]. the routine BVPFD solve the BVP for systems of the form $y' = \frac{dy(t)}{dt} = f(t,y)$, subject to the conditions $h_i[y_1(a),..., y_N(a), y_1(b),..., y_N(b)] = 0$ with i=1,...,N f and $[h_1(t),..., h_N(t)]^T$ are user supplied.

Usage

CALL BVPFD(FCNEQN, FCNJAC, FCNBC, FCNPEQ, FCNPBC, N, NLEFT, NCUPBC, TLEFT, TRIGHT, PISTEP, TOL, NINIT, TINIT, YINIT, LD YINI, LINEAR, PRINT, MXGRID, NFINAL, TFINAL, YFINAL, LDYFIN, ERREST)

Arguments

FCNEQN—User supplied SUBROUTINE to evaluate derivatives. The usage is CALL FCNEQN (N, T, Y, P, DYDT), where

N—Number of differential equations. (Input)
T—Independent variable values, y(t) (Input)
Y—Array of size N containing the dependent variable values, y(t) (Input)
P—Continuation parameter, p. If the value of PISTEP is greater than zero, then the routine BVPFD assumes that the user has embedded the problem into a one parameter family problems:
y'=y'(t,y,p)
h(yleft,yright,p)=0
such that for p=0 the problem is simple. For p=1, the original problem is recovered.
DYDT—Aray of size N containing the derivatives y'(t). (Output)

The name FCNEQN must be declared EXTERNAL in the calling program.

FCNJAC—User supplied SUBROUTINE to evaluate the Jacobian. The usage is CALL FCNJAC (N, T, Y, P, DYPDY), where

N—Number of differential equations. (Input)
T—Independent variable values, y(t) (Input)
Y—Array of size N containing the dependent variable values, y(t) (Input)
P—Continuation parameter, p.
DYPDY—N by N array containing the partial derivatives $a_{ij} = \partial f_i / \partial y_j$ evaluated at (t,y). The values a_{ij} are returned in DYPDY(i,j). (Output)

The name of FCNJAC must be declared EXTERNAL in the calling program.

FCNBC—User supplied SUBROUTINE to evaluate the boundary conditions. The usage is CALL FCNBC (N, YLEFT, YRIGHT, P, H), where

N—Number of differential equations (Input)
YLEFT—Array of size N containing the values of dependent variable at the left endpoint. (Input)
YRIGHT—Array of size N containing the values of dependent variable at the right endpoint. (Input)
P—Continuation parameter, p.
H—Array of size N containing the boundary conditions residuals. (Output)
The boundary conditions are defined by h_i= 0; For i = 1,...,N. The left endpoint conditions must defined first, then, the conditions involving both endpoints, and finally the right endpoint conditions.

The name of FCNBC must be declared EXTERNAL in the calling program.

FCNPEQ—User supplied SUBROUTINE to evaluate the partial derivatives of y' with respect to the parameter p. The usage is CALL FCNPEQ (N, T, Y, P, DYPDY), where

N—Number of differential equations. (Input)
T—Independent variable values, y(t) (Input)
Y—Array of size N containing the dependent variable values, y(t)
(Input)
P—Continuation parameter, p.
DYPDP—N by N array containing the partial derivatives $a_{ij} = \partial f_i / \partial y_j$ evaluated at (t,y).
The values a_{ij} are returned from DYPDY(i,j). (Output)

The name of FCNPEQ must be declared EXTERNAL in the calling program.

FCNBPC—User supplied SUBROUTINE to evaluate the derivatives of the boundary conditions with respect to the parameter p.

The usage is CALL FCNPBC(N, YLEFT, YRIGHT, P, H), where
N—Number of differential equations (Input)
YLEFT—Array of size N containing the values of dependent variable at
the left endpoint. (Input)
YRIGHT—Array of size N containing the values of dependent variable at the
right endpoint. (Input)
P—Continuation parameter,p.
H—Array of size N containing the derivatives of f_i with respect to p. (Output)

The name of FCNBPC must be declared EXTERNAL in the calling program.

N—Number of differential equations. (Input)

NLEFT—Number of initial conditions. (Input)

NCUPBC—Number of coupled boundary conditions. (Input)

The value NLEFT+NCUPBC must be greater than zero and less than or equal to N.

TLEFT—The left endpoint. (Input)

TRIGHT—The right endpoint (Input)

PISTEP—Initial increment size for p. (Input)

If this value is zero, continuation will not be used in this problem. The routines FCNPEQ and FCNPBC will not be called.

TOL—Relative error control parameter. The computation stops when ABS(ERROR(J,I)/MAX(ABS(Y(J,I)),1.0) .LT.TOL for all J=1,...,N and I=1,...,NGRID. Here, ERROR(J,I) is the estimated error in Y(J,I).

NINIT—Number of initial grid points, including the endpoints. (Input)

It must be at least 4.

TINIT—Array of size NINIT containing the initial grid points. (Input)

YINIT—Array of size N by NINIT containing an initial guess for the values of Y at the points in TINIT. (Input)

LDYINI—Leading dimension of YINIT exactly as specified in the dimension of the calling program. (Input)

LINEAR—Logical .TRUE. if the differential equations and the boundary conditions are linear.(Input)

PRINT—Logical .TRUE. if intermediate output is to be printed. (Input)

MXGRID—Maximum number of grid points allowed. (Input)

NFINAL—Number of final grid points, including the endpoints. (Output)

TFINAL—Array of size MXGRID containing the final grid points. (Output)

Only the first NFINAL points are significant.

YFINAL—Array of size N by MXGRID containing the values of Y at the points in

TFINAL. (Output)

LDYFIN—Leading dimension of YFINAL exactly as specified in the dimension statement of the calling program. (output)

ERREST—Array of size N. (Output)

ERREST(J) is the estimated error in Y(J)

3.2 Using BVPFD for the thermohydraulic system of equations

The thermohydraulic system solved by BVPFD is derived in this section.

It is based on the continuity of species:

$$\varepsilon \frac{\partial SCi}{\partial t} + \frac{\partial C_i V_i}{\partial x} = S_i$$

$$\mathrm{C_i V_i = C_i V_l - D_i^0 \frac{\partial C_i}{\partial x}}$$

There are six species involved : H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$. The only source term considered is the corrosion current for Fe^{2+}. For the species H^+, OH^-, Na^+, Cl and $FeOH^+$ the source term equals to zero.

Conservation of momentum and energy provides two equations for liquid velocity and saturation

$$\textit{Fluid water}:\ \varepsilon S\frac{\partial \rho_l}{\partial t}+\frac{\partial \rho_l V_l}{\partial x}=-\rho_l\,\rho_V\,\sigma_{V\rightarrow l}$$

$$V_l = \frac{kk_{rl}}{\mu_l}\frac{\partial P_l}{\partial x}$$

$$T_l = T_{saturation} \qquad -\frac{2\pi H r_{sg}}{A_c}(T_p - T_l) = h_{lv}\frac{\partial \rho_l V_l}{\partial x}$$

$$\textit{Vapor}:\quad \varepsilon(1-S)\frac{\partial \rho_V}{\partial t}+\frac{\partial \rho_v V_v}{\partial x}=\rho_l\,\rho_V\,\sigma_{V\rightarrow l}$$

$$\mathrm{V_V}=\frac{\mathrm{kk_{rV}}}{\mu_\mathrm{V}}\frac{\partial \mathrm{P_v}}{\partial \mathrm{x}}$$

$$T_v = T_l = T_{saturation} \qquad \frac{2\pi H r_{sg}}{A_c}(T_p - T_v) = h_{lv}\frac{\partial \rho_v V_v}{\partial x}$$

The saturation is related to the capillary pressure :

$$\mathrm{P_c = P_v - P_l = -DPcDS * (S - S_0)}$$

And the saturation temperature is a function of the concentration :

$$\mathrm{T_v = T_l = T_{saturation} = T_i = T_{s0} + \sum_i ALPHA(i) * C_i}$$

The heat transfer coefficient is a function of the saturation :

$$\mathrm{H = H_0 + H_1 * S}$$

Combining those equation into two :

$$\frac{\partial \mathrm{V_l}}{\partial \mathrm{x}} = -\frac{2\pi(\mathrm{H_0 + H_1 * S})\mathrm{r_{sg}}}{\mathrm{h_{lv}}\rho_\mathrm{l}\mathrm{A_c}}\left(\mathrm{T_p - T_{s0}} - \sum_\mathrm{i} \mathrm{ALPHA(i) * C_i}\right)$$

$$\frac{\partial \mathrm{S}}{\partial \mathrm{x}} = -\frac{1}{\mathrm{DPcDS}} * \frac{\partial \mathrm{P_c}}{\partial \mathrm{x}} = -\frac{1}{\mathrm{DPcDS}}\left(\frac{\mu_\mathrm{V}\mathrm{V_V}}{\mathrm{kk_{rV}}} - \frac{\mu_\mathrm{l}\mathrm{V_l}}{\mathrm{kk_{rl}}}\right) = -\frac{1}{\mathrm{DPcDS}}\left(\frac{\mu_\mathrm{V}\rho_\mathrm{l}}{\mathrm{kk_{rV}}\rho_\mathrm{v}} - \frac{\mu_\mathrm{l}}{\mathrm{kk_{rl}}}\right)\mathrm{V_l}$$

The definitive system solved is

$$\frac{\partial C_{H^+} V_{H^+}}{\partial x} = -\varepsilon \frac{SC_{H^+} - SoldCold_{H^+}}{TIMESTEP}$$

$$\frac{\partial \mathrm{C}_{\mathrm{H}^+}}{\partial \mathrm{x}} = \frac{(\mathrm{C}_{\mathrm{H}^+} \mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{H}^+} \mathrm{V}_{\mathrm{H}^+})}{\mathrm{D}^0_{\mathrm{H}^+}}$$

$$\frac{\partial C_{OH^-} V_{OH^-}}{\partial x} = -\varepsilon \frac{SC_{OH^-} - SoldCold_{OH^-}}{TIMESTEP}$$

$$\frac{\partial \mathrm{C}_{\mathrm{OH}^-}}{\partial \mathrm{x}} = \frac{(\mathrm{C}_{\mathrm{OH}^-} \mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{OH}^-} \mathrm{V}_{\mathrm{OH}^-})}{\mathrm{D}^0_{\mathrm{OH}^-}}$$

$$\frac{\partial C_{Na^+} V_{Na^+}}{\partial x} = -\varepsilon \frac{SC_{Na^+} - SoldCold_{Na^+}}{TIMESTEP}$$

$$\frac{\partial \mathrm{C}_{\mathrm{Na}^+}}{\partial \mathrm{x}} = \frac{(\mathrm{C}_{\mathrm{Na}^+} \mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{Na}^+} \mathrm{V}_{\mathrm{Na}^+})}{\mathrm{D}^0_{\mathrm{Na}^+}}$$

$$\frac{\partial C_{Cl^-} V_{Cl^-}}{\partial x} = -\varepsilon \frac{SC_{Cl^-} - SoldCold_{Cl^-}}{TIMESTEP}$$

$$\frac{\partial \mathrm{C}_{\mathrm{Cl}^-}}{\partial \mathrm{x}} = \frac{(\mathrm{C}_{\mathrm{Cl}^-} \mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{Cl}^-} \mathrm{V}_{\mathrm{Cl}^-})}{\mathrm{D}^0_{\mathrm{Cl}^-}}$$

$$\frac{\partial C_{Fe^{2+}} V_{Fe^{2+}}}{\partial x} = \frac{Icorr}{w} - \varepsilon \frac{SC_{Fe^{2+}} - SoldCold_{Fe^{2+}}}{TIMESTEP}$$

$$\frac{\partial \mathrm{C}_{\mathrm{Fe}^{2+}}}{\partial \mathrm{x}} = \frac{(\mathrm{C}_{\mathrm{Fe}^{2+}} \mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{Fe}^{2+}} \mathrm{V}_{\mathrm{Fe}^{2+}})}{\mathrm{D}^0_{\mathrm{Fe}^{2+}}}$$

$$\frac{\partial C_{FeOH^+} V_{FeOH^+}}{\partial x} = -\varepsilon \frac{SC_{FeOH^+} - SoldCold_{FeOH^+}}{\partial t}$$

$$\frac{\partial \mathrm{C}_{\mathrm{FeOH}^+}}{\partial \mathrm{x}} = \frac{\mathrm{C}_{\mathrm{FeOH}^+} \mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{FeOH}^+} \mathrm{V}_{\mathrm{FeOH}^+}}{\mathrm{D}^0_{\mathrm{FeOH}^+}}$$

$$\frac{\partial \mathrm{V}_{\mathrm{l}}}{\partial \mathrm{x}} = -\frac{2\pi(\mathrm{H}_0 + \mathrm{H}_1 * \mathrm{S})\mathrm{r}_{\mathrm{sg}}}{\mathrm{h}_{\mathrm{lv}} \rho_{\mathrm{l}} \mathrm{A}_{\mathrm{c}}} (\mathrm{T}_{\mathrm{p}} - \mathrm{T}_{\mathrm{s0}} - \sum_{\mathrm{i}} \mathrm{ALPHA(i)} * \mathrm{C}_{\mathrm{i}})$$

$$\frac{\partial S}{\partial x} = -\frac{1}{DPcDS}\left(\frac{\mu_V \rho_l}{kk_{rV}\rho_v} - \frac{\mu_l}{kk_{rl}}\right)V_l$$

In this case, compared to the chemistry program, the approximation that the saturation profile is constant with time is not valid. In the case of the presence of a steam blanketed region the saturation decreases to almost zero at the limit between the wetted region and the steam blanketed region

This system contains fourteen equations of first order. The fourteen unknowns are : C_{H^+}, C_{OH^-}, C_{Na^+}, C_{Cl^-}, $C_{Fe^{2+}}$, C_{FeOH^+}, $C_{H^+}V_{H^+}$, $C_{OH^-}V_{OH^-}$, $C_{Na^+}V_{Na^+}$, $C_{Cl^-}V_{Cl^-}$, $C_{Fe^{2+}}V_{Fe^{2+}}$, $C_{FeOH^+}V_{FeOH^+}$, V_l and S. The independent variable is not time but space (x), the time derivatives is discretized and the system is solved with a quasi steady state approximation.

The boundary conditions on those variables are the following:

At the mouth: $C_i=C_{bulk}$
$S=S_0$

At the center: $C_iV_i=0$
$V_l=0$

The initial boundary conditions (t=0) corresponds to the mouth in this case (x=0).

In the subroutine FCNBC, the left endpoint conditions (x=**0=TLEFT**, mouth of the crevice) must be defined first, followed by the conditions involving both endpoints and finally the right endpoint conditions (x=**LENGTH=TRIGHT**, center of the crevice). In this case, there is no conditions involving both endpoints (**NCUPBC=0**)

This imposes an order on the variables in the vector Y. C_i and S have to be the first part of the vector Y (because their boundary conditions are at the left endpoint) and C_iV_i and V_l should occupy the second part of Y.

Y = (C_{H^+}, C_{OH^-}, C_{Na^+}, C_{Cl^-}, $C_{Fe^{2+}}$, C_{FeOH^+}, X, S, V_l, $C_{H^+}V_{H^+}$, $C_{OH^-}V_{OH^-}$, $C_{Na^+}V_{Na^+}$, $C_{Cl^-}V_{Cl^-}$, $C_{Fe^{2+}}V_{Fe^{2+}}$, $C_{FeOH^+}V_{FeOH^+}$)

X was going to be the vapor pressure but it turns out to be useless in the thermohydraulic system therefore X is a dummy variable set to one. the system has fifteen equations (**N=5**)

Note that the parameter p is not used in this system of equation therefore the subroutines FCNPEQ and FCNPBC are not needed. Therefore in the call to BVPFD, FCNEQN and FCNBC were used in place of FCNPEQ and FCNPBC.

TOL can be set up **between 0.01 and 0.0001** (reasonable values). Generally if the program stops with an error message such as "the iteration hasn't made good progress" then increasing the tolerance might give a result (less accurate though).

NINIT should be set up **between 1000 and MXGRID** to give precise results.

TINIT contains the NINIT grid points. In the program the crevice is divided into NINIT-1 identical intervals. TINIT(I)= TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1). Make sure TINIT always contains the boundary points

YINIT should be filled with reasonable guesses on Y.

LDYINI is set to **15** (every component of Y is important in the calculation and needs to converge)

The system of equations is not linear therefore **LINEAR = .FALSE**.

MXGRID is set to 5000.

In the subroutine FCNEQN, the derivatives with respect to the independent variables x are stored in DYDT. An example for the first value of DYDT is given below:

$$\mathrm{DYDT(1)} = \frac{\partial \mathrm{Y(1)}}{\partial \mathrm{x}} = \frac{\partial \mathrm{C}_{\mathrm{H}^+}}{\partial \mathrm{x}} = \frac{(\mathrm{C}_{\mathrm{H}^+}\mathrm{V}_{\mathrm{l}} - \mathrm{C}_{\mathrm{H}^+}\mathrm{V}_{\mathrm{H}^+})}{\mathrm{D}^0_{\mathrm{H}^+}} = \frac{(\mathrm{Y(1)*Y(9)\text{ - }Y(10)})}{\mathrm{D(1)}}$$

The entire system in FCNEQN is written below:

DYDT(1) = (Y(1)*Y(9)-Y(10))/D(1)
DYDT(2) = (Y(2)*Y(9)-Y(11))/D(2)
DYDT(3) = (Y(3)*Y(9)-Y(12))/D(3)
DYDT(4) = (Y(4)*Y(9)-Y(13))/D(4)
DYDT(5) = (Y(5)*Y(9)-Y(14))/D(5)
DYDT(6) = (Y(6)*Y(9)-Y(15))/D(6)
DYDT(7) = 1.0
DYDT(8) = 1.0/dPcdS*(MUV*RHOF/KV/RHOV+MUF/KV)*Y(9)
DYDT(9) = –2.0*PI*RSG*(TP-TS0-ALPHA(3)*Y(3))
/(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYDT(10) = –EPS*(Y(8)*Y(1)-Y(8)*COLD(1,I))/TIMESTEP
DYDT(11) = –EPS*(Y(8)*Y(2)-Y(8)*COLD(2,I))/TIMESTEP
DYDT(12) = –EPS*(Y(8)*Y(3)-Y(8)*COLD(3,I))/TIMESTEP
DYDT(13) = –EPS*(Y(8)*Y(4)-Y(8)*COLD(4,I))/TIMESTEP
DYDT(14) = –EPS*(Y(8)*Y(5)-Y(8)*COLD(5,I))/TIMESTEP+ICORR(I)/0.03
DYDT(15) = –EPS*(Y(8)*Y(6)-Y(8)*COLD(6,I))/TIMESTEP

In the subroutine FCNJAC, the functions DYDT are derived with respect to Y.

DYPDY(1,1) = derivative of DYDT(1) with respect to Y(1)
DYPDY(1,1) = Y(9)/D(1)

In the subroutine FCNBC, the boundary conditions are defined. At the boundary, the function F is zero.

YLEFT contains the boundary conditions at the mouth. NLEFT equals the number of conditions at the independent variables T=0 (therefore at the mouth). NLEFT=8

YRIGHT contains the boundary conditions at the center

At the mouth: $C_{H^+} = C_{H^+}Bulk = C_{Bulk}(1)$

This boundary condition is written in the subroutine FCNBC as

F(1) = YLEFT(1)-CBULK(1).

Since the program will set F equal to zero, YLEFT(1) will be equal to CBULK(1).

YLEFT corresponds to the boundary conditions at the mouth and the index 1 in YLEFT(1) signifies that YLEFT(1) is the boundary condition of Y(1) which is C_{H^+}.

4. Changing the input

Changing the geometry of the crevice, the characteristics of the crevice or the properties of the liquid and vapor : Those properties are listed from lines 43 to lines 67

Careful! : when entering a real number, write 2.0 for 2, 4.0 for 4…
when entering an integer, write 2, 4

Changing the number of time steps : NTIMESTEP (line 60)

Changing the time of a time step : In order for the calculation to go further in time, you might want to change the time of a time step (TIMESTEP :line 59). **Careful!** If that value is too high, numerically it will predict directly the steady state.(recommended not to go above 36000s)

Changing the calculation of the Boiling point elevation : the major species in the crevice are sodium or chloride.

If sodium is predominant then enter the value in ALPHA(**3**) (line 70). Also change line 247 to :

DYDT(9) = –2.0*PI*RSG*(TP-TS0-ALPHA(**3**)*Y(**3**))/(RHOF*Ac*HFG)*(H0+H1*Y(8))
and lines 293 and 294 to :
DYPDY(9,**3**) = 2.0*PI*RSG*ALPHA(**3**)/(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYPDY(9,8) = –2.0*PI*RSG*(TP-TS0-ALPHA(**3**)*Y(**3**))/(RHOF*Ac*HFG)*H1

These two values should be the only component of the vector DYPDY(9,I)

The program default is to consider sodium predominant.

If chloride is the dominant specie then enter the value in ALPHA(**4**) (line 70), change DYDT(9) and DYPDY as follows (line 247)

DYDT(9) = –2.0*PI*RSG*(TP-TS0-ALPHA(4)*Y(4))/(RHOF*Ac*HFG)*(H0+H1*Y(8))
lines 293 and 294
DYPDY(9,4) = 2.0*PI*RSG*ALPHA(4)/(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYPDY(9,8) = –2.0*PI*RSG*(TP-TS0-ALPHA(**4**)*Y(**4**))/(RHOF*Ac*HFG)*H1

These two values should be the only component of the vector DYPDY(9,I). You should erase the expression of DYPDY(9,3) and replace it with DYPDY(9,4).

Changing the name of the output : Each time you want a new output file name you can change the name of the output file (currently 'results.out')and change status from 'OLD' to 'NEW' (lines 80 and 81).

When you are only rewritting over an OLD output file already existant, the status should be 'OLD'.

Changing the thermohydraulic system : The characteristics of the system are listed lines 5, 35 to 42, 126 to 142. The equations are fed in FCNEQN, the jacobian of the system is in FCNJAC and the boundary conditions are in FCNBC.

Changing the calculation of the wetted length : If at the first iteration to calculate the wetted length, there is not a T appearing on the running windows then decrease the initial guess of the wetted length. If the program diverges in the calculation of the wetted length then decrease DELTAWL and check the value of SLIM, it might need to be increased.

You need to make sure the value of WL is not going too far that the program stops because SLIM is too small even negative!

5. Example of output file

There are two input files : 1PPBWLMASS.out and 1PPBPROF.out. The first one has the field number **10** and the second one has the field number 11.

Therefore writing in results.out will be programmed 'WRITE(**10**,…….'

In '1PPBWLMASS', the time, mass of sodium and wetted length are listed.

In '1PPBPROF', the vectors X(spatial grid points from 0 to LENGTH), concentration of Na^+ and saturation are written at successive time step.

The program has been run with a crevice divided into 4001 parts. In the output file, the vectors are only printed every 100 components plus the endpoints every 100 time steps.

If you would like the output file to be more detailed, it is possible to change those values (lines 194 and 195).

```
IPRT =100*(I/100) +1          ! Writes only every 100 spatial steps
KKPRT =100*(KK/100) +1        ! Writes only every 100 time steps
```

It is possible to change the name of the output files. However you should change the name of status from 'OLD' to 'NEW' to run the program the first time and create the output file. Once created, if you want to rewrite the output file then the STATUS should be change back to 'OLD' (lines 80 and 81).

Example of 1PPBWLMASS.out'

```
    Time(s)          Mass(g)          Wl(cm)
  360000E+04      346757E-06      430000E+00
  720000E+04      697441E-06      430000E+00
  108000E+05      104767E-05      430000E+00
  144000E+05      139757E-05      430000E+00
  180000E+05      174718E-05      430000E+00
  216000E+05      209652E-05      430000E+00
  252000E+05      244562E-05      430000E+00
  288000E+05      279450E-05      430000E+00
  324000E+05      314316E-05      430000E+00
  360000E+05      349579E-05      431000E+00
```

'Example of 1PPBPROFILES.out'

```
       X              [Na+]          Saturation
      (cm)          (mol/cm3)

TIME = 3600.000000

  .000000E+00     .472937E-10     .900000E+00
  .107527E-01     .512832E-10     .844355E+00
  .215054E-01     .526341E-10     .803960E+00
  .322581E-01     .540581E-10     .770639E+00
  .430108E-01     .555613E-10     .741638E+00
  .537634E-01     .571505E-10     .715622E+00
  .645161E-01     .588334E-10     .691821E+00
  .752688E-01     .606184E-10     .669739E+00
  .860215E-01     .625151E-10     .649035E+00
  .967742E-01     .645345E-10     .629461E+00
  .107527E+00     .666888E-10     .610829E+00
  .118280E+00     .689919E-10     .592991E+00
  .129032E+00     .714598E-10     .575827E+00
  .139785E+00     .741110E-10     .559241E+00
  .150538E+00     .769667E-10     .543148E+00
  .161290E+00     .800514E-10     .527479E+00
  .172043E+00     .833938E-10     .512170E+00
  .182796E+00     .870278E-10     .497166E+00
  .193548E+00     .909932E-10     .482417E+00
  .204301E+00     .953375E-10     .467878E+00
  .215054E+00     .100118E-09     .453505E+00
```

```
.225806E+00    .105404E-09    .439257E+00
.236559E+00    .111279E-09    .425095E+00
.247312E+00    .117850E-09    .410982E+00
.258065E+00    .125246E-09    .396880E+00
.268817E+00    .133635E-09    .382751E+00
.279570E+00    .143231E-09    .368558E+00
.290323E+00    .154316E-09    .354262E+00
.301075E+00    .167265E-09    .339826E+00
.311828E+00    .182594E-09    .325211E+00
.322581E+00    .201030E-09    .310383E+00
.333333E+00    .223629E-09    .295308E+00
.344086E+00    .251991E-09    .279967E+00
.354839E+00    .288664E-09    .264360E+00
.365591E+00    .337985E-09    .248533E+00
.376344E+00    .408009E-09    .232618E+00
.387097E+00    .516351E-09    .216916E+00
.397849E+00    .386459E-08    .202047E+00
.408602E+00    .147357E-05    .189160E+00
.419355E+00    .577360E-04    .180067E+00
```

```
*****************************************************************************
*******************This program calculates the distribution of liquid *******************
******************* velocity and saturation and the repartition ************************
*************** of six species H+, OH-, Na+, Cl-, Fe2+, FeOH+ ***********************
*************** with the hypothesis that they can not react with each other ***************
********** This program also calculates the wetted length (Wl) at each time step ***********
*****************************************************************************
```

```
******************** MAIN PROGRAM ***********************
        USE MSIMSLMS
        CCCCCCCCC DEFINITION OF VARIABLES CCCCCCCCCCC
        INTEGER          LDYFIN, LDYINI, MXGRID, NEQNS, NINIT
        PARAMETER   (MXGRID=8000, NEQNS=15, NINIT=4000, LDYFIN=NEQNS,
        &                LDYINI=NEQNS)
        INTEGER          IPRT,KKPRT
        INTEGER          I, J, NCUPBC, NFINAL, NLEFT, GRIDCOLD,KK,ISTORE
        INTEGER          NTIMESTEP
        REAL             ERREST(NEQNS), PISTEP, TFINAL(MXGRID), TINIT(NINIT),
        &                TLEFT, TOL, TRIGHT, YFINAL(LDYFIN,MXGRID),
        &                YINIT(LDYINI,NINIT)
        REAL             DELTAWL
        REAL
            MUF,H0,H1,RSG,TP,TS0,RHOF,AC,HFG,dPcdS,MUV,KV,RHOV
        REAL             PI ,TIMESTEP,D(6),EPS,ALPHA(6),LENGTH
        REAL             SOLD(8000),COLD(6,8000)
        REAL             MASS,WL,WLOLD
        REAL             CBULK(6), SLIM
        REAL             STOREWLMASS(3,30000),STOREPROFILES(3,30000)
```

```
COMMON/ENT1/MUF,H0,H1,RSG,TP,TS0,RHOF,AC,HFG,dPcdS,MUV,
KV,RHOV
COMMON/ENT2/PI,TIMESTEP,D,EPS,ALPHA,LENGTH,WL,WLOLD
COMMON/TEMPS/COLD,GRIDCOLD,SOLD
COMMON/ENT3/CBULK
LOGICAL          LINEAR, PRINT, IPAR
INTRINSIC        FLOAT
REAL             FLOAT
EXTERNAL   FCNBC, FCNEQN, FCNJAC
CCCCCCCCCCCCC INPUTS CCCCCCCCCCCCCCCCCCCCCC
LENGTH = 1.4                           ! Half length of the
                                       crevice          (cm)
WL = 0.43          ! Estimated wetted length initially  (cm)
WLOLD = WL
         Set parameters for thermohydraulic numerical method
NLEFT            = 8
NCUPBC    = 0
TOL       = .1
TLEFT            = 0.0
TRIGHT    = WL
PISTEP           = 0.0
PRINT            = .FALSE.
LINEAR    = .FALSE.
C                Properties of the crevice
MUF       = 9.51E-9      ! Viscosity of the liquid       (Ns/cm^2)
H0        = 0.75  ! Heat transfer coefficient H = H0+H1*S
                         (J/s/cm^2/K)
H1        = 0.0   ! Heat transfer coefficient H = H0+H1*S
                         (J/s/cm^2/K)
RSG       = 0.94               ! Radius of the tube (cm)
TP        = 603.15             ! Temperature of the tube(K)
TS0       = 553.15             ! Temperature of the bulk (K)
RHOF      = 0.75               ! Density of the liquid (g/cm^3)
AC        = 0.166  ! Cross sectional area of the crevice (cm2)
HFG       = 1557.5       ! Latent heat of vaporisation (j/g)
dPcdS     = -50.0     ! Slope of the capillary pressure (N/cm^2)
MUV       = 1.88E-9      ! Viscosity of the vapor (Ns/cm^2)
KV        = 67.37E-11    ! Permeability of the porous media
(cm^2)
DELTAWL = 0.001   ! Incrementation value to calculate Wl
(cm)
RHOV      = 0.032        ! Density of the vapor (g/cm^3)
PI        = 3.1416       ! Mathematical constant
EPS       = 0.3          ! Porosity of the porous media
TIMESTEP= 3600.0               ! Time step for the time iteration (s)
```

```
64.   NTIMESTEP = 2          ! Number of time steps
65.   D(1) = 37.248E-5       ! Diffusion constant of H+  (cm^2/s)
66.   D(2) = 21.04E-5        ! Diffusion constant of OH- (cm^2/s)
67.   D(3) = 5.336E-5        ! Diffusion constant of Na+  (cm^2/s)
68.   D(4) = 8.128E-5        ! Diffusion constant of Cl- (cm^2/s)
69.   D(5) = 2.88E-5         ! Diffusion constant of Fe2+ (cm^2/s)
70.   D(6) = 4.0E-5          ! Diffusion constant of FeOH+ (cm^2/s)
71.   ! Boiling point elevation =       Alpha(1)*(concentration of H+) +
      Alpha(2)*(concentration of OH-) + ...
72.   ALPHA(1)= 0.0          ! Coefficient for H+  (K/mol*cm^3)
73.   ALPHA(2)= 0.0          ! Coefficient for OH-  (K/mol*cm^3)
74.   ALPHA(3)= 2572.0       ! Coefficient for Na+  (K/mol*cm^3)
75.   ALPHA(4)= 0.0          ! Coefficient for Cl-  (K/mol*cm^3)
76.   ALPHA(5)= 0.0          ! Coefficient for Fe2+  (K/mol*cm^3)
77.   ALPHA(6)= 0.0          ! Coefficient for FeOH+  (K/mol*cm^3)
78.   CBULK(1) = 0.5E-10     ! Bulk concentration of H+ (mol/cm^3)
79.   CBULK(2) = 0.5E-10     ! Bulk concentration of OH- (mol/cm^3)
80.   CBULK(3) = 0.5E-10     ! Bulk concentration of Na+ (mol/cm^3)
81.   CBULK(4) = 0.5E-10     ! Bulk concentration of Cl- (mol/cm^3)
82.   CBULK(5) = 0.5E-10     ! Bulk concentration of Fe2+ (mol/cm^3)
83.   CBULK(6) = 0.5E-10    ! Bulk concentration of FeOH+ (mol/cm^3)
84.   SLIM = 0.17            ! Limiting saturation to calculate Wl

85.   C OPENING THE OUTPUT FILE AND WRITING THE RATIO C
86.   CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

87.   OPEN (UNIT=10,FILE='1PPBMASS.OUT',STATUS='OLD')
88.   OPEN (UNIT=11,FILE='1PPBPROF.OUT',STATUS='OLD')

89.   C SETTING UP THE OUTPUT FILE CCCCCCCCCC
90.   CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

91.   WRITE(10,9995)
92.   FORMAT(T17,'Time(s)',T36,'Mass(g)',T54,'Wl(cm)')
93.   WRITE(11,9997)
94.   WRITE(11,9998)
95.   FORMAT(T18,'X',T36,'[Na+]',T50,'Saturation')
96.   FORMAT(T17,'(cm)',T34,'(mol/cm3)')
97.   WRITE(10,*)
98.   WRITE(11,*)

99.   CCCCCCCC INITIALISATION CCCCCCCCCCCCCCCCCCCCC
100.  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

101.  !Initialising the vectors for the thermohydraulic calculations

102.  C                      Define TINIT and YINIT
103.  DO 10  I=1, NINIT
```

```
TINIT(I)   = TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1)
YINIT(1,I) = CBULK(1)
YINIT(2,I) = CBULK(2)
YINIT(3,I) = CBULK(3)
YINIT(4,I) = CBULK(4)
YINIT(5,I) = CBULK(5)
YINIT(6,I) = CBULK(6)
YINIT(7,I) = 0.0
YINIT(8,I) = 0.9
YINIT(9,I) = 0.1
YINIT(10,I) = 0.01*CBULK(1)
YINIT(11,I) = 0.01*CBULK(2)
YINIT(12,I) = 0.01*CBULK(3)
YINIT(13,I) = 0.01*CBULK(4)
YINIT(14,I) = 0.01*CBULK(5)
YINIT(15,I) = 0.01*CBULK(6)
COLD(1,I) = 0.0
COLD(2,I) = 0.0
COLD(3,I) = 0.0
COLD(4,I) = 0.0
COLD(5,I) = 0.0
COLD(6,I) = 0.0
SOLD(I) = 0.9
10 CONTINUE
GRIDCOLD = NINIT
ISTORE = 1
KK = 0
!              Start of the time loop
100 CONTINUE
KK = KK + 1                                  ! Time counter
WRITE(*,*) KK


MASS = 0.0                                   ! units : (g)
IPAR = .TRUE.
CONTINUE
!                        Solve thermohydraulic system of equations
CALL BVPFD (FCNEQN, FCNJAC, FCNBC, FCNEQN, FCNBC, NEQNS, NLEFT,
&         NCUPBC, TLEFT, TRIGHT, PISTEP, TOL, NINIT, TINIT,
&         YINIT, LDYINI, LINEAR, PRINT, MXGRID, NFINAL,
&         TFINAL, YFINAL, LDYFIN, ERREST)
! Checking if the calculation converges and if the maximum wetted length is not
reached
IF (YFINAL(8,NFINAL) .GT. SLIM .AND.IPAR .AND. WL .LE. LENGTH)THEN
```

```
WRITE(*,*) WL
WRITE(*,*) YFINAL(8,NFINAL)
WRITE(*,*) IPAR

WL = WL + DELTAWL               ! Wetted length increased
TRIGHT = WL

DO 112  I=1, NINIT
TINIT(I)   = TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1)
CONTINUE
GOTO 111                    ! Go back to solve the system
ENDIF

! Checking if the calculation does not converge

IF    (YFINAL(8,NFINAL) .LT. SLIM .AND. IPAR ) THEN

WL = WL - DELTAWL               ! Wetted length decreased
TRIGHT = WL

DO 113  I=1, NINIT
TINIT(I)   = TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1)
CONTINUE

IPAR = .FALSE.  ! IPAR = false  (last iteration for this time)
GOTO 111                        ! Go back to solve the system

ENDIF
CCCCCCCCC RESULTS CCCCCC
CCCCCCCCCCCCCCCCCCCCCCC


DO 12 J=1, NEQNS
DO 11  I=1, NINIT
YINIT(J,I) = YFINAL(J,I)
CONTINUE
CONTINUE

! Storing the wetted length for the next time step
WLOLD = WL
DO 14 J=1, 6
DO 13  I=1, NFINAL

! Storing concentrations for next time step and calculating the integrated mass of
sodium

COLD(J,I) = YFINAL(J,I)

IPRT=3
IF (J .EQ. IPRT) THEN

! Storing saturation for next time step and calculating the integrated mass of
sodium
```

```
SOLD(I) = YFINAL(8,I)
! Calculating the integrated mass of sodium in grams
MASS = MASS + YFINAL(8,I)*YFINAL(3,I)*WL/NFINAL*AC*EPS*23.5
! Storing the profiles of saturation and sodium concentration
! every 100 spatial points and every 100 time steps into STOREPROFILES(1) and
! STOREPROFILES(2) respectively. Storing the X coordinates in STOREPROFILES(3)
! Before storing an entire distribution of concentration of sodium for a new time step
! we store -500 in storeprofile(1) (easy to trace the beginning!) and we store the
! time in storeprofile(2)
IPRT =100*(I/100) +1
KKPRT =100*(KK/100) +1
IF (I .EQ. IPRT .AND. KK .EQ. KKPRT) THEN
IF (I .EQ. 1) THEN
STOREPROFILES(1,ISTORE) = -500.0
STOREPROFILES(2,ISTORE) = KK*TIMESTEP
ISTORE = ISTORE + 1
ENDIF
STOREPROFILES(1,ISTORE) = YFINAL(3,I)
STOREPROFILES(2,ISTORE) = YFINAL(8,I)
STOREPROFILES(3,ISTORE) = TINIT(I)
ISTORE = ISTORE + 1
ENDIF
ENDIF
CONTINUE
CONTINUE
! Storing the mass and wetted length in STOREWLMASS(1) and STOREWLMASS(2)
! Storing the time in STOREPROFILES(3)
STOREWLMASS(3,KK) = KK*TIMESTEP
STOREWLMASS(1,KK)=MASS
WRITE(*,*) 'MASS=',MASS
STOREWLMASS(2,KK)=WL
GRIDCOLD = NFINAL
! Checking if the system should be solved for more time steps
IF (KK .LT. NTIMESTEP) GOTO 100
! Writing STOREPROFILES, STOREWLMASS in output file
DO 16 I=1, ISTORE-1
```

```
IF (STOREPROFILES(1,I) .LT. -450.0) THEN
WRITE(11,*)
WRITE(11,*) 'TIME = ',STOREPROFILES(2,I)
WRITE(11,*)
ELSE
WRITE(11,9992)   STOREPROFILES(3,I),STOREPROFILES(1,I)
.                ,STOREPROFILES(2,I)
ENDIF
CONTINUE
DO 17 I=1, NTIMESTEP
WRITE(10,9992)
STOREWLMASS(3,I),STOREWLMASS(1,I),STOREWLMASS(2,I)
FORMAT(10X,E15.6,2X,E15.6,2X,E15.6)
CONTINUE

CLOSE(UNIT=10)
CLOSE(UNIT=11)

END


******* END OF THE PROGRAM  PRINCIPAL ********


********** BEGINNING OF THE SUBROUTINES ***************


SUBROUTINE FCNEQN (NEQNS, T, Y, P, DYDT)
C                    SPECIFICATIONS FOR ARGUMENTS
INTEGER   NEQNS,I, GRIDCOLD
REAL      T, P, Y(NEQNS), DYDT(NEQNS),LENGTH,MUV,KV
REAL        MUF,WL,WLOLD,X
REAL COLD(6,8000), SOLD(8000)
COMMON/ENT1/MUF,H0,H1,RSG,TP,TS0,RHOF,AC,HFG,dPcdS,MUV,
KV,RHOV
COMMON/ENT2/PI,TIMESTEP,D(6),EPS,ALPHA(6),LENGTH,WL,WLOLD
COMMON/TEMPS/COLD,GRIDCOLD,SOLD
X = WL-WLOLD
IF (T  .LT. X) THEN
I=1
ENDIF
IF (T .GE. X) THEN
I = INT((T-X)*(GRIDCOLD-1)/WLOLD+0.5)+1
ENDIF
C                    Define PDE
DYDT(1)   = (Y(1)*Y(9)-Y(10))/D(1)
DYDT(2)   = (Y(2)*Y(9)-Y(11))/D(2)
DYDT(3)   = (Y(3)*Y(9)-Y(12))/D(3)
```

```
DYDT(4)    = (Y(4)*Y(9)-Y(13))/D(4)
DYDT(5)    = (Y(5)*Y(9)-Y(14))/D(5)
DYDT(6)    = (Y(6)*Y(9)-Y(15))/D(6)
DYDT(7)    = (MUV*RHOF/KV/(1.0-Y(8))/RHOV+MUF/KV/(Y(8))**3.0)*Y(9)
DYDT(8)    = 1.0/dPcdS*(MUV*RHOF/KV/(1.0-Y(8))/RHOV
.                  +MUF/KV/(Y(8))**3.0)*Y(9)
DYDT(9)    = -2.0*PI*RSG*(TP-TS0-ALPHA(3)*Y(3))
.                  /(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYDT(10)  = -EPS*(Y(8)*Y(1)-SOLD(I)*COLD(1,I))/TIMESTEP
DYDT(11)  = -EPS*(Y(8)*Y(2)-SOLD(I)*COLD(2,I))/TIMESTEP
DYDT(12)  = -EPS*(Y(8)*Y(3)-SOLD(I)*COLD(3,I))/TIMESTEP
DYDT(13)  = -EPS*(Y(8)*Y(4)-SOLD(I)*COLD(4,I))/TIMESTEP
DYDT(14)  = -EPS*(Y(8)*Y(5)-SOLD(I)*COLD(5,I))/TIMESTEP
DYDT(15)  = -EPS*(Y(8)*Y(6)-SOLD(I)*COLD(6,I))/TIMESTEP
RETURN
END


CCCCCC WRITING THE JACOBIAN OF THE SYSTEM CCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC


SUBROUTINE FCNJAC (NEQNS, T, Y, P, DYPDY)
C                        SPECIFICATIONS FOR ARGUMENTS
INTEGER            NEQNS,I,J,L,GRIDCOLD
REAL               T, P, Y(NEQNS), DYPDY(NEQNS,NEQNS),LENGTH
REAL               COLD(6,8000),SOLD(8000)
REAL               MUF,MUV,KV,WL,WLOLD,X
COMMON/ENT1/MUF,H0,H1,RSG,TP,TS0,RHOF,AC,HFG,dPcdS,MUV,KV,RHOV
COMMON/ENT2/PI,TIMESTEP,D(6),EPS,ALPHA(6),LENGTH,WL,WLOLD
COMMON/TEMPS/COLD,GRIDCOLD,SOLD
C                        Define d(DYDT)/dY
DO 11 L = 1, NEQNS
DO 12 J = 1, NEQNS
DYPDY (L,J) = 0.0
CONTINUE
CONTINUE
DYPDY(1,1)            = Y(9)/D(1)
DYPDY(1,9)            = Y(1)/D(1)
DYPDY(1,10)           = -1.0/D(1)
DYPDY(2,2)            = Y(9)/D(2)
DYPDY(2,9)            = Y(2)/D(2)
DYPDY(2,11)           = -1.0/D(2)
DYPDY(3,3)            = Y(9)/D(3)
DYPDY(3,9)            = Y(3)/D(3)
DYPDY(3,12)           = -1.0/D(3)
```

```
DYPDY(4,4)             = Y(9)/D(4)
DYPDY(4,9)             = Y(4)/D(4)
DYPDY(4,13)            = -1.0/D(4)
DYPDY(5,5)             = Y(9)/D(5)
DYPDY(5,9)             = Y(5)/D(5)
DYPDY(5,14)            = -1.0/D(5)
DYPDY(6,6)      = Y(9)/D(6)
DYPDY(6,9)      = Y(6)/D(6)
DYPDY(6,15)     = -1.0/D(6)
DYPDY(7,9)      = (MUV*RHOF/KV/(1.0-Y(8))/RHOV+MUF/KV/(Y(8))**3.0)
DYPDY(7,8)      = (MUV*RHOF/KV/(1.0-Y(8))**2.0/RHOV
.                      -3.0*MUF/KV/(Y(8))**4.0)*Y(9)
DYPDY(8,9)      = 1.0/dPcdS*(MUV*RHOF/KV/(1.0-Y(8))/RHOV
.                      +MUF/KV/(Y(8))**3.0)
DYPDY(8,8)      = 1.0/dPcdS*(MUV*RHOF/KV/(1.0-Y(8))**2.0/RHOV
.                      -3.0*MUF/KV/(Y(8))**4.0)*Y(9)
DYPDY(9,3)      = 2.0*PI*RSG*ALPHA(3)/(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYPDY(9,8)      = -2.0*PI*RSG*(TP-TS0-
ALPHA(3)*Y(3))/(RHOF*Ac*HFG)*H1
DYPDY(10,1)     = -EPS*Y(8)/TIMESTEP
DYPDY(10,8)     = -EPS*Y(1)/TIMESTEP
DYPDY(11,2)     = -EPS*Y(8)/TIMESTEP
DYPDY(11,8)     = -EPS*Y(2)/TIMESTEP
DYPDY(12,3)     = -EPS*Y(8)/TIMESTEP
DYPDY(12,8)     = -EPS*Y(3)/TIMESTEP
DYPDY(13,4)     = -EPS*Y(8)/TIMESTEP
DYPDY(13,8)     = -EPS*Y(4)/TIMESTEP
DYPDY(14,5)     = -EPS*Y(8)/TIMESTEP
DYPDY(14,8)     = -EPS*Y(5)/TIMESTEP
DYPDY(15,6)     = -EPS*Y(8)/TIMESTEP
DYPDY(15,8)     = -EPS*Y(6)/TIMESTEP
RETURN
END


CCCCCC WRITING THE BOUNDARY CONDITIONS CCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC


SUBROUTINE FCNBC (NEQNS, YLEFT, YRIGHT, P, F)
C                    SPECIFICATIONS FOR ARGUMENTS
INTEGER         NEQNS
REAL            P, YLEFT(NEQNS), YRIGHT(NEQNS), F(NEQNS)
REAL            CBULK(6)
COMMON/ENT3/CBULK
C                    Define boundary conditions
!YLEFT CONTAINS THE BOUNDARY CONDITIONS AT THE MOUTH
```

```
339.    !YRIGHT CONTAINS THE BOUNDARY CONDITIONS AT THE CENTER
        OF THE CREVICE
340.    !CONCENTRATION H+         = BULK CONCENTRATION H+
             (MOUTH)
341.    !CONCENTRATION OH- = BULK CONCENTRATION OH-
342.    !CONCENTRATION Na+ = BULK CONCENTRATION Na+
343.    !CONCENTRATION Cl-        = BULK CONCENTRATION Cl-
344.    !CONCENTRATION Fe2+       = BULK CONCENTRATION Fe2+
345.    !CONCENTRATION FeOH+      = BULK CONCENTRATION FeOH+
346.    !LIQUID PRESSURE AT THE MOUTH = 500N/cm2
347.    !SATURATION AT THE MOUTH = 0.5
348.    !LIQUID VELOCITY AT THE CENTER = 0.0
349.    !GRADIENT OF H+ CONCENTRATION AT THE CENTER = 0.0
350.    !GRADIENT OF OH- CONCENTRATION AT THE CENTER = 0.0
351.    !GRADIENT OF Na+ CONCENTRATION AT THE CENTER = 0.0
352.    !GRADIENT OF Cl- CONCENTRATION AT THE CENTER = 0.0
353.    !GRADIENT OF Fe2+ CONCENTRATION AT THE CENTER = 0.0
354.    !GRADIENT OF FeOH+ CONCENTRATION AT THE CENTER = 0.0

355.    F(1) = YLEFT(1)   -CBULK(1)
356.    F(2) = YLEFT(2)   -CBULK(2)
357.    F(3) = YLEFT(3)   -CBULK(3)
358.    F(4) = YLEFT(4)   -CBULK(4)
359.    F(5) = YLEFT(5)   -CBULK(5)
360.    F(6) = YLEFT(6)   -CBULK(6)
361.    F(7) = YLEFT(7)
362.    F(8) = YLEFT(8) - 0.9
363.    F(9) = YRIGHT(9)
364.    F(10) = YRIGHT(10)
365.    F(11) = YRIGHT(11)
366.    F(12) = YRIGHT(12)
367.    F(13) = YRIGHT(13)
368.    F(14) = YRIGHT(14)
369.    F(15) = YRIGHT(15)
370.    RETURN
371.    END


372.    ******** END OF THE SUBROUTINES **********************
```

C

MEMO TO USE THE PROGRAM “CHEMISTRY”

Outline

1. Definition of the variables
2. Algorithm of the program
3. Thermohydraulic system
4. Chemical equilibrium system
5. Changing the input
6. Example of output

1. Definition of the variables

The variables can be divided in three major categories: the variables used in the principal program **(bold)**, the variables used by the numerical method BVPFD *(italics)* and the variables used by the numerical methods LFTRG and LFSRG (underlined).

BVPFD solves a system of differential equations with boundary conditions at two points. In this program it is used to solve the thermal hydraulic equations.

LFTRG and LFSRG are used in the Newton Raphson method to solve a linear equations. In this program it solves the chemical equilibrium system.

1.1. Variables for entire program

LDYFIN : Leading dimension of YFINAL exactly as specified in The dimension
LDYFIN : Leading dimension of YFINAL exactly as specified in the dimension
LDYINI : Leading dimension of YINIT exactly as specified in the dimension statement of the calling program
MXGRID : Maximum number of grid points allowed
NEQNS : Number of differential equations
NINIT : Number of initial grid points including the endpoints. It must be at least four
KKPRT : Integer (used in if statement <if K .EQ. KKPRT> instead of <if K .EQ. 4> which is invalid at compilation)
IPRT : Integer (same than KKPRT)

NCUPBC : Number of coupled boundary conditions. The number NLEFT + NCUPBC must be greater than zero and less than or equal to NEQNS

NFINAL : Number of final grid points including the endpoints

NLEFT : Number of initial conditions. the value NLEFT must be greater than or equal to zero and less than NEQNS.

I : Counter

J : Counter

KK : Counter

GRIDCOLD : Number of grid points during the previous calculation (at t-1)

OPTION : Integer indicating whether or not precipitation should be considered. If OPTION is set to 1 then chemical equilibrium should consider no precipitation, if OPTION is set to 2 then precipitation should be included

NTIMESTEP : Number of time step to be calculated

RATIO : Ratio of the bulk concentration of chloride to the bulk concentration of sodium

ERREST : Array if size NEQNS containing the estimated error in Y(J)

PISTEP : Initial increment size for p. If this value is zero, continuation will not be used in the problem solved by BVPFD. The routines FCNPEQ and FCNPBC will not be called

TFINAL : Array if size MXGRID containing the final grid points. Only the first NFINAL points are significant

TINIT : Array of size NINIT containing the initial grid points.

TLEFT : The left endpoint

TOL : Relative error control parameter. The computation stops when ABS(ERROR(J,I)/MAX(ABS(Y(J,I)),1.0) .LT.TOL for all J=1,...,N and I=1,...,NGRID. Here, ERROR(J,I) is the estimated error in Y(J,I).

TRIGHT : The right endpoint

YFINAL : Array of size N by MXGRID containing the values of Y at the points in TFINAL

MUF : Liquid viscosity (Ns/cm2)

H0 : Term in the calculation for the heat transfer Coefficient as shown in this equation : H = H0 + H1*S (J/s/cm2/K)

H1 : Term in the calculation for the heat transfer Coefficient as shown in this equation : H = H0 + H1*S (J/s/cm2/K)

RSG : Radius of the tube (cm)

TP : Temperature of the tube (K)

TS0 : Temperature of the bulk solution (K)

RHOF : Liquid density (g/cm3)

AC : Cross sectional area (cm2)

HFG : Latent heat of vaporization (J/g)

dPcdS : Term in the calculation for the capillary pressure as shown in this equation : Pc = Pc0 + dPcdS*S (N/cm2)

MUV : Vapor viscosity (Ns/cm2)

KV : Permeability of the porous media (cm2)

RHOV : Vapor density (g/cm3)

PI : Mathematical constant = 3.14

TIMESTEP : Length of time during each time step (s)

D(6) : Vector containing the diffusion coefficient of H+, OH-, Na+, Cl-, Fe2+, FeOH+. (cm2/s)

EPS : Porosity of the porous media

ALPHA(6) : Vector containing the coefficients of for the calculation of the boiling point elevation. $\mathrm{BPE} = \sum_{\mathrm{i}} \mathrm{ALPHA(i)} \times \mathrm{C(i)}$

where C(i) is the vector containing the concentrations of H+, OH-, Na+, Cl-, Fe2+, FeOH+ (K/mol*cm3)

LENGTH : Half length of the crevice (the crevice is assumed to be symmetric) (cm)

COLD(6,5000) : Vector containing the values of the concentrations of H+, OH-, Na+, Cl-, Fe2+, FeOH+ at the previous time step. (mol/cm3)

CFe : Bulk concentration of iron (mol/cm3)

CNa : Bulk concentration of sodium (mol/cm3)

MASS : Real value used for the calculation of the integrated mass of sodium in half the crevice at a time t (g)

ICORR : Vector containing the value of the corrosion current density at each location of the half crevice (A/cm2)

pH : Value of the pH at a location of the crevice

P : Value used as an intermediate steps in ICORR calculation

K1 : Equilibrium constant FeOH+ / OH- * Fe2+ (mol-1.cm3)

KW : Equilibrium constant H+ * OH- (mol2/cm6)

K2 : Equilibrium constant Fe2+ * (OH-)2 (mol3/cm9)

CBULK(6) : Vector containing the bulk concentration of H+, OH-, Na+, Cl-, Fe2+, FeOH+ (mol/cm3)

LINEAR : Logical .TRUE. if differential equations and the boundary conditions are linear

PRINT : Logical .TRUE. if intermediate output is to be printed

X(5) : Vector containing the concentrations of H+, OH-, Fe2+, FeOH+ and FeOH2

1.2 Local variables of FCNEQN

T : Independent variables t

Y : Array of size NEQNS containing the dependent variable values, y(t)

DYDT : Array of size NEQNS containing the derivatives y'(t)

1.3 Local variables of FCNJAC

T : Independent variables t

Y : Array of size NEQNS containing the dependent variable values, y(t)

DYPDY : Array of size NEQNS containing the partial derivatives

$$a_{ij} = \partial f_i / \partial y_j$$

evaluated at (t,y). The values a_{ij} are returned in DYPDY(i,j).

1.4 Local variables of CHEMISTRY

IPATH : Path indicator
IPATH=1 means the system AX=B is solved
IPATH=2 means the system ATX=B is solved

LDA : Leading dimension of A exactly as specified in the dimension statement of the calling program

LDFAC : Leading dimension of FAC exactly as specified in the dimension statement of the calling program

N : Number of equations

IPVT : Vector of length N containing the pivoting information for the LU factorization of A as output from the routine LFTRG

A : N by N matrix containing the coefficient matrix of the linear system

B : Vector of length N containing the right hand side of the linear system
FACC : N by N matrix containing the LU factorization of the coefficient matrix A as output from routine LFCRG
X : Vector of length N containing the solution to the linear system
XNEW : Vector of length N containing the new value of X in the New Raphson iteration
XOLD : Vector of length N containing the previous value of X in the New Raphson iteration
NA : Concentration of sodium in solution
CL : Concentration of chloride in solution
FE : Concentration pf iron specie in solution

2. Algorithm of the program

The program has been copied at the end of this notice with line numbers on it. The algorithm will refer to those lines.

2.1 Principal Program

- Definition of variables
- Input of variables (properties of the crevice, porous media, operating parameters) **(4)**
- Setting up the output files : **(32)**

  results.out which contains the concentrations of H^+, OH^-, Na^+, Cl^-
  results2.out which contains the concentrations of Fe^{2+}, $FeOH^+$, $FeOH_2$ and ICORR **(78)**

- Initialize the vector X for the chemistry calculation
- CBULK(3)=Bulk concentration of sodium from inputs **(96)**
- CBULK(4)=CBULK(3)*ratio from inputs **(101)**
- CBULK(5)=Bulk concentration of iron from inputs **(102)**
- OPTION = 1 (no precipitates in the bulk) **(103)**

(104)

- Call subroutine **CHEMISTRY** to calculate the bulk chemistry **(105)**

  Inputs : Concentration of Na, Cl, Fe, presence or not of precipitates (OPTION)
  Outputs : X(1) Concentration of H^+, X(2) Concentration of OH^-, X(3) Concentration of Fe^{2+}, X(4) Concentration of $FeOH^+$, X(5) Concentration of $FeOH_2$ (Na+ and Cl- are not reacting therefore their concentrations don’t need to be an output of the subroutine)

- Fill the vector CBULK with the six concentrations

  CBULK(1) = X(1) **(106)**
  CBULK(2) = X(2) **(107)**
  CBULK(5) = X(3) **(109)**
  CBULK(6) = X(4) **(110)**
  CBULK(3) and CBULK(4) did not change

- Initialize TINIT with the grid of the crevice **(126)**
- Initialize YINIT **(127)**
- Initialize the concentrations in the crevice (at t=0 there is no concentrated solution in the crevice) **(142)**
- Initialize the current of corrosion (at t=0 there is no corrosion in the crevice) **(148)**
- Do from KK=1 to KK=TIMESTEP **(153)**
  - – Write the time every 300 time loop in both output files **(163)**
  - – Call subroutine **BVPFD** to solve the thermohydraulic system of equations in the crevice

    Inputs : YINIT, TINIT, TLEFT, TRIGHT...
    Outputs : YFINAL containing
    YFINAL(1,I):Concentration of H^+ at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(2,I): Concentration of OH^- at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(3,I): Concentration of Na^+ at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(4,I): Concentration of Cl^- at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(5,I): Concentration of Fe^{2+} at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(6,I): Concentration of $FeOH^+$ at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(7,I) : Not used, set to one
    YFINAL(8,I) : Saturation at the I^{th} space grid with I from 1 to NFINAL
    YFINAL(9,I) : Liquid velocity at the I^{th} space grid with I from 1 to NFINAL

  - – Initialize the vector X to prepare for chemistry calculations **(175)**
  - – Do from I=1 to NFINAL **(180)**
    - OPTION=1 **(181)**

- YFINAL(5,I)=YFINAL(5,I)+YFINAL(6,I) **(182)**
  (YFINAL(5,I) contains now the total amount of iron species in solution Fe^{2+} and $FeOH^{+}$)

- Call subroutine **CHEMISTRY** to calculate the bulk chemistry **(183)**

  Inputs : Concentrations of Na (YFINAL(3,I)), Cl (YFINAL(4,I)), Fe (YFINAL(5,I)+YFINAL(6,I)), no precipitates (OPTION=1)
  Outputs : X(1) Concentration of H^{+}, X(2) Concentration of OH^{-}, X(3) Concentration of Fe^{2+}, X(4) Concentration of $FeOH^{+}$, X(5) Concentration of $FeOH_{2}$ (Na^{+} and Cl^{-} are not reacting therefore their concentrations don't need to be an output of the subroutine).
  All those concentrations are at the space grid I.

- IF $X(3)*(X(2))^{2}$ greater than K2

  THEN
  OPTION=2 (there is precipitation) **(184)**
  Call subroutine **CHEMISTRY** to calculate the bulk chemistry **(185)**
    Inputs : same except OPTION=2 **(187)**
    Outputs : same
  ENDIF

- Store the value of X in YFINAL

  YFINAL(1,I) = X(1) (Concentration of H^{+})
  YFINAL(2,I) = X(2) (Concentration of OH^{-})
  YFINAL(5,I) = X(3) (Concentration of Fe^{2+}) **(189)**
  YFINAL(6,I) = X(4) (Concentration of $FeOH^{+}$) **(190)**

- Write every 50 space grids I and every 300 time **(191)**
  steps the value of the abscissa and the values of
  X(1),X(2), YFINAL(3,I) and YFINAL(4,I) in the **(192)**
  output file 'results.out'

- Write every 50 space grids I and every 300 time **(199)**
  steps the value of the abscissa from 0 to
  LENGTH of the crevice and the values of X(3),

(200)
(201)
(204)

- X(4), X(5), and ICORR(I) in the output file 'results2.out'

– END DO **(208**

  - Initialize YINIT with the values of YFINAL for better convergence for the next time step **(209)**
  - Store the values of the concentrations from YFINAL in COLD **(214)**
  - Calculate the integrated mass of sodium in the crevice (MASS) **(217)**
  - Calculate the pH at each space grid and deduce the value of the corrosion current at each space grid. Store the distribution of the corrosion current in ICORR(I) with I from 1 to NFINAL **(222)** **(223)** **(224)**

- END DO
- Close the output files
- END

3. Thermohydraulic system

3.1 Numerical method used

BVPFD (IMSL library) solves that system of ordinary differential equations with boundary conditions at tow points using a variable order, variable step size finite difference method with deferred corrections.

The problem statement is abbreviated by writing it as a system of first order ODEs $y(t) = [y_1(t), ..., y_N(t)]^T, f(t, y) = [f_1(t, y), ..., f_N(t, y)]^T$ y is the dependent variable and t is the independent variable. First order means that the highest order any derivatives in the equation is 1.

The problem becomes $y' = \frac{dy(t)}{dt} = f(t, y)$. In the boundary value problem (BVP) for ODEs, constraints on the dependent variables are given at the endpoints of the interval of interest, [a,b]. the routine BVPFD solve the BVP for systems of the form $y' = \frac{dy(t)}{dt} = f(t, y)$, subject to the conditions

$h_i[y_1(a), ..., y_N(a), y_1(b), ..., y_N(b)] = 0$ with i=1,...,N

f and $[h_1(t), ..., h_N(t)]^T$ are user supplied.

Usage

CALL BVPFD(FCNEQN, FCNJAC, FCNBC, FCNPEQ, FCNPBC, N, NLEFT, NCUPBC, TLEFT, TRIGHT, PISTEP, TOL, NINIT, TINIT, YINIT, LD YINI, LINEAR, PRINT, MXGRID, NFINAL, TFINAL, YFINAL, LDYFIN, ERREST)

Arguments

FCNEQN—User supplied SUBROUTINE to evaluate derivatives. The usage is CALL FCNEQN (N, T, Y, P, DYDT), where

N—Number of differential equations. (Input)
T—Independent variable values, y(t) (Input)
Y—Array of size N containing the dependent variable values, y(t) (Input)
P—Continuation parameter, p. If the value of PISTEP is greater than zero, then the routine BVPFD assumes that the user has embedded the problem into a one parameter family problems:
y'=y'(t,y,p)
h(yleft,yright,p)=0
such that for p=0 the problem is simple. For p=1, the original problem is recovered.
DYDT—Aray of size N containing the derivatives y'(t). (Output)

The name FCNEQN must be declared EXTERNAL in the calling program.

FCNJAC—User supplied SUBROUTINE to evaluate the Jacobian. The usage is CALL FCNJAC (N, T, Y, P, DYPDY), where

N—Number of differential equations. (Input)
T—Independent variable values, y(t) (Input)
Y—Array of size N containing the dependent variable values, y(t) (Input)
P—Continuation parameter, p.
DYPDY—N by N array containing the partial derivatives $a_{ij} = \partial f_i / \partial y_j$ evaluated at (t,y). The values a_{ij} are returned in DYPDY(i,j). (Output)

The name of FCNJAC must be declared EXTERNAL in the calling program.

FCNBC—User supplied SUBROUTINE to evaluate the boundary conditions. The usage is CALL FCNBC (N, YLEFT, YRIGHT, P, H), where

N—Number of differential equations (Input)
YLEFT—Array of size N containing the values of dependent variable at the left endpoint. (Input)
YRIGHT—Array of size N containing the values of dependent variable at the right endpoint. (Input)
P—Continuation parameter, p.
H—Array of size N containing the boundary conditions residuals. (Output)

The boundary conditions are defined by $h_i = 0$; For i = 1,...,N. The left endpoint conditions must defined first, then, the conditions involving both endpoints, and finally the right endpoint conditions.

The name of FCNBC must be declared EXTERNAL in the calling program.

FCNPEQ—User supplied SUBROUTINE to evaluate the partial derivatives of y' with respect to the parameter p. The usage is CALL FCNPEQ (N, T, Y, P, DYPDY), where

N—Number of differential equations. (Input)
T—Independent variable values, y(t) (Input)
Y—Array of size N containing the dependent variable values, y(t) (Input)
P—Continuation parameter, p.
DYPDP—N by N array containing the partial derivatives $a_{ij} = \partial f_i / \partial y_j$ evaluated at (t,y). The values a_{ij} are returned in DYPDY(i,j). (Output)

The name of FCNPEQ must be declared EXTERNAL in the calling program.

FCNBPC—User supplied SUBROUTINE to evaluate the derivatives of the boundary conditions with respect to the parameter p.

The usage is CALL FCNPBC(N, YLEFT, YRIGHT, P, H), where

N—Number of differential equations (Input)
YLEFT—Array of size N containing the values of dependent variable at the left endpoint. (Input)
YRIGHT—Array of size N containing the values of dependent variable at the right endpoint. (Input)
P—Continuation parameter,p.
H—Array of size N containing the derivatives of f_i with respect to p. (Output)

The name of FCNBPC must be declared EXTERNAL in the calling program.

N**—**Number of differential equations. (Input)

NLEFT**—**Number of initial conditions. (Input)

NCUPBC**—**Number of coupled boundary conditions. (Input)

The value NLEFT+NCUPBC must be greater than zero and less than or equal to N.

TLEFT—The left endpoint. (Input)

TRIGHT—The right endpoint (Input)

PISTEP—Initial increment size for p. (Input)

If this value is zero, continuation will not be used in this problem. The routines FCNPEQ and FCNPBC will not be called.

TOL—Relative error control parameter. The computation stop when ABS(ERROR(J,I)/MAX(ABS(Y(J,I)),1.0) .LT.TOL for all J=1,...,N and I=1,...,NGRID. Here, ERROR(J,I) is the estimated error in Y(J,I).

NINIT—Number of initial grid points, including the endpoints. (Input)

It must be at least 4.

TINIT—Array of size NINIT containing the initial grid points. (Input)

YINIT—Array of size N by NINIT containing an initial guess for the values of Y at the points in TINIT. (Input)

LDYINI—Leading dimension of YINIT exactly as specified in the dimension of the calling program. (Input)

LINEAR—Logical .TRUE. if the differential equations and the boundary conditions are linear.(Input)

PRINT—Logical .TRUE. if intermediate output is to be printed. (Input)

MXGRID—Maximum number of grid points allowed. (Input)

NFINAL—Number of final grid points, including the endpoints. (Output)

TFINAL—Array of size MXGRID containing the final grid points. (Output)

Only the first NFINAL points are significant.

YFINAL—Array of size N by MXGRID containing the values of Y at the points in

TFINAL. (Output)

LDYFIN—Leading dimension of YFINAL exactly as specified in the dimension statement of the calling program. (output)

ERREST—Array of size N. (Output)

ERREST(J) is the estimated error in Y(J)

3.2 Using BVPFD for the thermohydraulic system of equations

The thermohydraulic system solved by BVPFD is derived in this section.

It is based on the continuity of species:

$$\varepsilon \frac{\partial SCi}{\partial t} + \frac{\partial C_i V_i}{\partial x} = S_i$$

$$C_i V_i = C_i V_l - D_i^0 \frac{\partial C_i}{\partial x}$$

There are six species involved : H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$. The only source term considered is the corrosion current for Fe^{2+}. For the species H^+, OH^-, Na^+, Cl and $FeOH^+$ the source term equals to zero.

Conservation of momentum and energy provides two equations for liquid velocity and saturation

Fluid water: $\varepsilon S \frac{\partial \rho_l}{\partial t} + \frac{\partial \rho_l V_l}{\partial x} = -\rho_l \rho_V \sigma_{V \to l}$

$$V_l = \frac{k k_{rl}}{\mu_l} \frac{\partial P_l}{\partial x}$$

$$T_l = T_{saturation} \qquad -\frac{2\pi H r_{sg}}{A_c}(T_p - T_l) = h_{lv} \frac{\partial \rho_l V_l}{\partial x}$$

Vapor: $\varepsilon (1-S) \frac{\partial \rho_V}{\partial t} + \frac{\partial \rho_v V_v}{\partial x} = \rho_l \rho_V \sigma_{V \to l}$

$$V_V = \frac{k k_{rV}}{\mu_V} \frac{\partial P_v}{\partial x}$$

$$T_v = T_l = T_{saturation} \qquad \frac{2\pi H r_{sg}}{A_c}(T_p - T_v) = h_{lv} \frac{\partial \rho_v V_v}{\partial x}$$

The saturation is related to the capillary pressure :

$$P_c = P_v - P_l = -DPcDS * (S - S_0)$$

And the saturation temperature is a function of the concentration :

$$T_v = T_l = T_{saturation} = T_i = T_{s0} + \sum_i ALPHA(i) * C_i$$

The heat transfer coefficient is a function of the saturation :

$$H = H_0 + H_1 * S$$

Combining those equation into two :

$$\frac{\partial V_l}{\partial x} = -\frac{2\pi(H_0 + H_1 * S)r_{sg}}{h_{lv}\rho_l A_c}(T_p - T_{s0} - \sum_i ALPHA(i) * C_i)$$

$$\frac{\partial S}{\partial x} = -\frac{1}{DPcDS} * \frac{\partial P_c}{\partial x} = -\frac{1}{DPcDS}(\frac{\mu_V V_V}{kk_{rV}} - \frac{\mu_l V_l}{kk_{rl}}) = -\frac{1}{DPcDS}(\frac{\mu_V \rho_l}{kk_{rV}\rho_v} - \frac{\mu_l}{kk_{rl}})V_l$$

At that point, an approximation is made : the saturation profile is constant with time. This si reasonable for a permeable porous media

The definitive system solved is

$$\frac{\partial C_{H^+} V_{H^+}}{\partial x} = -\varepsilon S \frac{C_{H^+} - Cold_{H^+}}{TIMESTEP}$$

$$\frac{\partial C_{H^+}}{\partial x} = \frac{(C_{H^+} V_l - C_{H^+} V_{H^+})}{D^0_{H^+}}$$

$$\frac{\partial C_{OH^-} V_{OH^-}}{\partial x} = -\varepsilon S \frac{C_{OH^-} - Cold_{OH^-}}{TIMESTEP}$$

$$\frac{\partial C_{OH^-}}{\partial x} = \frac{(C_{OH^-} V_l - C_{OH^-} V_{OH^-})}{D^0_{OH^-}}$$

$$\frac{\partial C_{Na^+} V_{Na^+}}{\partial x} = -\varepsilon S \frac{C_{Na^+} - Cold_{Na^+}}{TIMESTEP}$$

$$\frac{\partial C_{Na^+}}{\partial x} = \frac{(C_{Na^+} V_l - C_{Na^+} V_{Na^+})}{D^0_{Na^+}}$$

$$\frac{\partial C_{Cl^-} V_{Cl^-}}{\partial x} = -\varepsilon S \frac{C_{Cl^-} - Cold_{Cl^-}}{TIMESTEP}$$

$$\frac{\partial C_{Cl^-}}{\partial x} = \frac{(C_{Cl^-} V_l - C_{Cl^-} V_{Cl^-})}{D^0_{Cl^-}}$$

$$\frac{\partial C_{Fe^{2+}} V_{Fe^{2+}}}{\partial x} = \frac{Icorr}{w} - \varepsilon S \frac{C_{Fe^{2+}} - Cold_{Fe^{2+}}}{TIMESTEP}$$

$$\frac{\partial C_{Fe^{2+}}}{\partial x} = \frac{(C_{Fe^{2+}} V_l - C_{Fe^{2+}} V_{Fe^{2+}})}{D^0_{Fe^{2+}}}$$

$$\frac{\partial C_{FeOH^+} V_{FeOH^+}}{\partial x} = -\varepsilon S \frac{C_{FeOH^+} - Cold_{FeOH^+}}{\partial t}$$

$$\frac{\partial C_{FeOH^+}}{\partial x} = \frac{C_{FeOH^+} V_l - C_{FeOH^+} V_{FeOH^+}}{D^0_{FeOH^+}}$$

$$\frac{\partial V_l}{\partial x} = -\frac{2\pi(H_0 + H_1 * S) r_{sg}}{h_{lv} \rho_l A_c} (T_p - T_{s0} - \sum_i ALPHA(i) * C_i)$$

$$\frac{\partial S}{\partial x} = -\frac{1}{DPcDS} \left(\frac{\mu_V \rho_l}{kk_{rV} \rho_v} - \frac{\mu_l}{kk_{rl}}\right) V_l$$

This system contains fourteen equations of first order. The fourteen unknowns are : C_{H^+}, C_{OH^-}, C_{Na^+}, C_{Cl^-}, $C_{Fe^{2+}}$, C_{FeOH^+}, $C_{H^+}V_{H^+}$, $C_{OH^-}V_{OH^-}$, $C_{Na^+}V_{Na^+}$, $C_{Cl^-}V_{Cl^-}$, $C_{Fe^{2+}}V_{Fe^{2+}}$, $C_{FeOH^+}V_{FeOH^+}$, V_l and S. The independent variable is not time but space (x), the time derivatives is discretized and the system is solved in a quasi steady state approximation.

The boundary conditions on those variables are the following:

At the mouth: $C_i = C_{bulk}$
$S = S_0$

At the center: $C_i V_i = 0$
$V_l = 0$

The initial boundary conditions (t=0) corresponds to the mouth in this case (x=0).

In the subroutine FCNBC, the left endpoint conditions (x=**0=TLEFT**, mouth of the crevice) must be defined first then the conditions involving both endpoints and finally the right endpoint conditions (x=**LENGTH=TRIGHT**, center of the crevice). In this case, there is no conditions involving both endpoints (**NCUPBC=0**)

This impose an order on the variables in the vector Y. C_i and S have to be the first part of the vector Y (because their boundary conditions are at the left endpoint) and C_iV_i and V_l should occupy the second part of Y.

Y = (C_{H^+}, C_{OH^-}, C_{Na^+}, C_{Cl^-}, $C_{Fe^{2+}}$, C_{FeOH^+}, X, S, V_l, $C_{H^+}V_{H^+}$, $C_{OH^-}V_{OH^-}$, $C_{Na^+}V_{Na^+}$, $C_{Cl^-}V_{Cl^-}$, $C_{Fe^{2+}}V_{Fe^{2+}}$, $C_{FeOH^+}V_{FeOH^+}$)

X was going to be the vapor pressure but it appears useless in the thermohydraulic system therefore X is a dummy variable set to one. the system has fifteen equations (**N=5**)

Note that the parameter p is not used in this system of equation therefore the subroutines FCNPEQ and FCNPBC are not needed. Therefore in the call to BVPFD, FCNEQN and FCNBC were used in place of FCNPEQ and FCNPBC.

TOL can be set up **between 0.01 and 0.0001** (reasonable values). Generally if the program stops with an error message such as "the iteration hasn't made good progress" then reducing the tolerance might give a result (less accurate though).

NINIT should be set up **between 1000 and MXGRID** to give precise results.

TINIT contains the NINIT grid points. In the program the crevice is divided into NINIT-1 identical intervals. TINIT(I)= TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1). Make sure TINIT always contains the boundary points

YINIT should be filled with reasonable guesses on Y.

LDYINI is set to **15** (every component of Y is important in the calculation and needs to converge)

The system of equations is not linear therefore **LINEAR = .FALSE**.

MXGRID is set to 5000.

<u>In the subroutine FCNEQN</u>, the derivatives with respect to the independent variables x are stored in DYDT. An example for the first value of DYDT is given below:

$$\mathrm{DYDT(1)} = \frac{\partial \mathrm{Y(1)}}{\partial x} = \frac{\partial C_{H^+}}{\partial x} = \frac{(C_{H^+} V_l - C_{H^+} V_{H^+})}{D^0_{H^+}} = \frac{(\mathrm{Y(1)} * \mathrm{Y(9)} - \mathrm{Y(10)})}{\mathrm{D(1)}}$$

The entire system in FCNEQN is written below:

```
DYDT(1)      = (Y(1)*Y(9)-Y(10))/D(1)
DYDT(2)      = (Y(2)*Y(9)-Y(11))/D(2)
DYDT(3)      = (Y(3)*Y(9)-Y(12))/D(3)
DYDT(4)      = (Y(4)*Y(9)-Y(13))/D(4)
DYDT(5)      = (Y(5)*Y(9)-Y(14))/D(5)
DYDT(6)      = (Y(6)*Y(9)-Y(15))/D(6)
DYDT(7)      = 1.0
DYDT(8)      = 1.0/dPcdS*(MUV*RHOF/KV/RHOV+MUF/KV)*Y(9)
DYDT(9)      = –2.0*PI*RSG*(TP-TS0-ALPHA(3)*Y(3))
                     /(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYDT(10)     = –EPS*(Y(8)*Y(1)-Y(8)*COLD(1,I))/TIMESTEP
DYDT(11)     = –EPS*(Y(8)*Y(2)-Y(8)*COLD(2,I))/TIMESTEP
DYDT(12)     = –EPS*(Y(8)*Y(3)-Y(8)*COLD(3,I))/TIMESTEP
DYDT(13)     = –EPS*(Y(8)*Y(4)-Y(8)*COLD(4,I))/TIMESTEP
```

```
DYDT(14)      = –EPS*(Y(8)*Y(5)-Y(8)*COLD(5,I))/TIMESTEP+ICORR(I)/0.03
DYDT(15)      = –EPS*(Y(8)*Y(6)-Y(8)*COLD(6,I))/TIMESTEP
```

In the subroutine FCNJAC, the functions DYDT are derived with respect to Y.

DYPDY(1,1) = derivative of DYDT(1) with respect to Y(1)

DYPDY(1,1) = Y(9)/D(1)

In the subroutine FCNBC, the boundary conditions are defined. At the boundary, the function F is zero.

YLEFT contains the boundary conditions at the mouth. NLEFT equals the number of conditions at the independent variables T=0 (therefore at the mouth). NLEFT=8

YRIGHT contains the boundary conditions at the center

At the mouth: $C_{H^+} = C_{H^+}\text{Bulk} = C_{Bulk}(1)$

This boundary condition is written in the subroutine FCNBC as

F(1) = YLEFT(1)-CBULK(1).

Since the program will set F equal to zero, YLEFT(1) will be equal to CBULK(1).

YLEFT corresponds to the boundary conditions at the mouth and the index 1 in YLEFT(1) signifies that YLEFT(1) is the boundary condition of Y(1) which is C_{H^+}.

4. Chemistry system

4.1 Objective of the subroutine CHEMISTRY

The subroutine is not an IMSL subroutine

Usage

CALL CHEMISTRY (NA,CL,FE,XOLD,OPTION)

NA : Concentration of sodium	(Input)
CL : Concentration of chloride	(Input)
FE : Concentration of iron	(Input)

XOLD(5) : Vector containing the concentrations of H^+, OH^-, Fe^{2+}, $FeOH^+$, $FeOH_2$ (Input/Ouput). As an input, XOLD contains the guess for the solution. As an output, XOLD contains the concentration solution of the chemical equilibrium system.

OPTION : integer indicating whether or not there is precipitation of $FeOH_2$.

General algorithm

Input the chemical equilibrium constants K_1, K_2, K_W
IF OPTION = 2 (there is precipitation)
THEN set A and B to solve the system of equations :

$$\begin{cases} \mathrm{XOLD(1) * XOLD(2)} = \mathrm{K_w} \\ \mathrm{2.0XOLD(3) + XOLD(4) + XOLD(1) + NA = XOLD(2) + CL} \\ \mathrm{XOLD(3) * XOLD(2)^2} = \mathrm{K_2} \\ \dfrac{\mathrm{XOLD(4)}}{\mathrm{XOLD(3)XOLD(2)}} = \mathrm{K1} \\ \mathrm{XOLD(3) + XOLD(4) + XOLD(5) = FE} \end{cases}$$

ENDIF
IF OPTION = 1 (there is not precipitation)
THEN set A and B to solve the system of equations :

$$\begin{cases} \mathrm{XOLD(1) * XOLD(2)} = \mathrm{K_w} \\ \mathrm{2.0XOLD(3) + XOLD(4) + XOLD(1) + NA = XOLD(2) + CL} \\ \mathrm{XOLD(5)} = 10^{-42}\ \text{(negligeable)} \\ \dfrac{\mathrm{XOLD(4)}}{\mathrm{XOLD(3)XOLD(2)}} = \mathrm{K1} \\ \mathrm{XOLD(3) + XOLD(4) = FE} \end{cases}$$

ENDIF

4.2 Numerical method-What are A and B?

The method used to solve the system of equilibrium equation is the Newton Raphson method with logarithmic variables. The method was partially programmed and some tasks were carried out by available subroutines from IMSL library (LFTRG and LFSRG).

Newton Raphson method

The equations to be solved are those :

$$\begin{cases} f_1(x_1, x_2, ..., x_n) = 0 \\ f_2(x_1, x_2, ..., x_n) = 0 \\ . \\ . \\ f_n(x_1, x_2, ..., x_n) = \end{cases} \qquad (*)$$

involving n real functions of the n real variables $x_{1,...,}x_n$.

Classic Newton Raphson method

Let’s denote X the entire vector of values x_i, then, in the neighborhood of X, each of the functions f_i can be expanded in Taylor series

$$f_i(X + DX) = f_i(X) + \sum_{i=1}^{i=n} \frac{\partial f_i}{\partial x_j} \delta x_j + O(\delta X^2)$$

By neglecting terms of order •X^2 and higher, a set of linear equations for the corrections •X that move each function closer to zero simultaneously can be obtained, namely

$$\sum_{j=1}^{j=n} \alpha_{ij} \delta x_j = \beta_i \qquad \text{where} \qquad \alpha_{ij} = \frac{\partial f_i}{\partial x_j} \qquad \beta_i = -f_i$$

The equation above can be solved by inverting the matrix containing the α_{ij} by LU decomposition.

The corrections are then added to the solution vector,

$$x_i^{new} = x_i^{old} + \delta x_i \qquad i = 1,...,n$$

and the process is iterated to convergence.

Logarithmic Newton Raphson method

With chemical equilibrium, the solution varies by several orders of magnitude therefore it is a good idea to calculate variation of LOG(X) instead of variation of X.

The method is the same than the one above but the Taylor expansion is with LOG(X):

$$f_i(X + D(LOGX)) = f_i(X) + \sum_{i=1}^{i=n} \frac{\partial f_i}{\partial \log x_j} \delta \log x_j + O(\delta LOGX^2)$$

By neglecting terms of order •LOGX^2 and higher, a set of linear equations for the corrections •LOGX that move each function closer to zero simultaneously can be obtained, namely

$$\sum_{j=1}^{j=n} \alpha_{ij} \delta \log x_j = \beta_i \qquad \text{where} \qquad \alpha_{ij} = \frac{\partial f_i}{\partial \log x_j} \qquad \beta_i = -f_i$$

The equation above can be solved by inverting the matrix containing the α_{ij} by LU decomposition.

The corrections are then combined to the solution vector,

$$x_i^{new} = x_i^{old} \exp(\delta \log x_i) \ i = 1,...,n$$

and the process is iterated to convergence. Since the corrections are in an exponential term, the magnitude should be controlled and should make sure the changes are not too dramatic.

Calculating the corrections for the next iteration

The system $\sum_{j=1}^{j=n} \alpha_{ij} \delta \log x_j = \beta_i$ needs to be solved. If A is the matrix containing the α_{ij} coefficients and X is the matrix containing the $\delta \log x_j$ coefficients and B is the matrix containing the β_i coefficients then the system can be written AX=B with A and B known and X wanted.

The SUBROUTINES LFTRG and LFSRG used successively solve AX=B.

4.3 Subroutine LFTRG

It computes the LU factorization of a real general matrix.

Usage

CALL LFTRG (N, A, LDA, FAC, LDFAC, IPVT)

Arguments

N—Order of the matrix (Input)
A—N by N matrix to be factored
LDA—Leading dimension of A exactly as specified in the dimension statement of the calling program. (Input)
FAC—N by N matrix containing the LU factorization of the matrix A (Output)
LDFAC—Leading dimension of FAC exactly as specified in the dimension statement of the calling program. (Input)

IPVT—Vector of length N containing the pivoting information for the LU factorization. (Output)

4.4 Subroutine LFSRG

It solves a real general system of linear equation given the LU factorization of the coefficient matrix.

Usage

CALL LFSRG (N, FAC, LDFAC, IPVT, B, IPATH, X)

Arguments

N—Order of the matrix (Input)
FAC—N by N matrix containing the LU factorization of the matrix A (Output)
LDFAC—Leading dimension of FAC exactly as specified in the dimension statement of the calling program. (Input)
IPVT—Vector of length N containing the pivoting information for the LU factorization. as output from SUBROUTINE LFTRG. (Input)
B—Vector of length N containing the right-hand side of the linear system. (Input)
IPATH—Path indicator. (Input)
    IPATH=1 means the system AX=B is solved
    IPATH=2 means the system $A^TX=B$ is solved
X—Vector of length N containing the solution to the linear system. (Output)

4.5 Detailed algorithm of CHEMISTRY

System solved for OPTION 2

$$\begin{cases} F(1) = LOG(X(1) * X(2)) - LOG(K_w) = 0 \\ F(2) = LOG(2.0X(3) + X(4) + X(1) + NA) - LOG(X(2) + CL) = 0 \\ F(3) = LOG(X(3) * X(2)^2) - LOG(K_2) = 0 \\ F(4) = LOG(\dfrac{X(4)}{X(3)X(2)}) - LOG(K1) = 0 \\ F(5) = LOG(X(3) + X(4) + X(5)) - LOG(FE) = 0 \end{cases}$$

The system is slightly changed compared to A, the logarithmic of the equations is taken.

To apply the Newton Raphson method, this system is written as (*).

A and B needs to be calculated.

A is the matrix containing the α_{ij} and $\alpha_{ij} = \frac{\partial f_i}{\partial \log x_j}$

A(1,1) = derivative of F(1) with respect to log(X(1)) = 1.0
A(1,2) = derivative of F(2) with respect to log(X(2)) = 1.0
....
A(5,5) = derivative of F(5) with respect to log(X(5)) = X(5)/FE

B is the matrix containing the β_i coefficients and $\beta_i = -f_i$

B(1) = –F(1)
...
B(5) = F(5)

System solved for OPTION 1

$$\begin{cases} \mathrm{F(1) = LOG(X(1) * X(2)) - LOG(K_w) = 0} \\ \mathrm{F(2) = LOG(2.0X(3) + X(4) + X(1) + NA) - LOG(X(2) + CL) = 0} \\ \mathrm{F(3) = LOG(X(5)) + 42 = 0} \\ \mathrm{F(4) = LOG(\frac{X(4)}{X(3)X(2)}) - LOG(K1) = 0} \\ \mathrm{F(5) = LOG(X(3) + X(4)) - LOG(FE) = 0} \end{cases}$$

A and B are calculated the same way than OPTION 2.

In both options, N is 5, LDA is 5 and IPATH is 1

Detailed algorithm

Input the chemical equilibrium constants K_1, K_2, K_W

1 Calculate B and A with X = XOLD (input of subroutine at the first iteration)

```
CALL LFTRG (N,A,LDA,FACC,LDFAC,IPVT)
CALL LFSRG (N,FACC,LDFAC,IPVT,B,IPATH,X) (The correction is in vector X)
If the X(J) (correction) is greater than 0.1 then X(J) equals 0.1
If the X(J) (correction) is less than –0.1 then X(J) equals –0.1
XNEW(J) = XOLD(J)*exp(X(J))
IF abs(XNEW(J)-XOLD(J))/XOLD(J) greater than 1% (Not close enough to solution)
THEN            XOLD(J)=XNEW(J)
        GO BACK TO 1
ENDIF
IF abs(XNEW(J)-XOLD(J))/XOLD(J) greater than 1%
THEN XOLD(J)=XNEW(J
RETURN
```

5. Changing the input

<u>Changing the geometry of the crevice, the characteristics of the crevice or the properties of the liquid and vapor</u> : Those properties are listed from lines 43 to lines 67

Careful! : when entering a real number, write 2.0 for 2, 4.0 for 4…
When entering an integer, write 2, 4

<u>Changing the number of time steps</u> : NTIMESTEP (line 60)

<u>Changing the time of a time step</u> : In order for the calculation to go further in time, you might want to change the time of a time step (TIMESTEP :line 59). **Careful!** If that value is too high, numerically it will predict directly the steady state.(recommended not to go above 36000s)

<u>Changing the chemistry of the bulk solution</u> : The bulk concentration and ratio properties are lines 74 to 76

<u>Changing the calculation of the Boiling point elevation</u> : the major species in the crevice are sodium or chloride.

If sodium is predominant then enter the value in ALPHA(**3**) (line 70), make sure that (line 247)

DYDT(9) = –2.0*PI*RSG*(TP-TS0-ALPHA(**3**)*Y(**3**))/(RHOF*Ac*HFG)*(H0+H1*Y(8))

and that (line 293 to 294)

DYPDY(9,**3**) = 2.0*PI*RSG*ALPHA(**3**)/(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYPDY(9,8) = –2.0*PI*RSG*(TP-TS0-ALPHA(**3**)*Y(**3**))/(RHOF*Ac*HFG)*H1

Those two values should be the only component of the vector DYPDY(9,I)

The program default is to consider sodium predominant.

If chloride is predominant then enter the value in ALPHA(**4**) (line 70), change DYDT(9) and DYPDY as follow (line 247)

DYDT(9) = –2.0*PI*RSG*(TP-TS0-ALPHA(**4**)*Y(**4**))/(RHOF*Ac*HFG)*(H0+H1*Y(8))

and that (line 293 to 294)

DYPDY(9,**4**) = 2.0*PI*RSG*ALPHA(**4**)/(RHOF*Ac*HFG)*(H0+H1*Y(8))
DYPDY(9,8) = –2.0*PI*RSG*(TP-TS0-ALPHA(**4**)*Y(**4**))/(RHOF*Ac*HFG)*H1

Those two values should be the only component of the vector DYPDY(9,I). You should erase the expression of DYPDY(9,3) and replace it with DYPDY(9,4).

<u>Changing the name of the output</u> : Each time you want a new output file name you can change the name of the output file (currently 'results.out')and change status from 'OLD' to 'NEW' (lines 80 and 81).

When you are only rewritting over an OLD output file already existant, the status should be 'OLD'.

<u>Changing the chemical equilibrium contants</u> : Those properties are listed (lines 77, 360 to 362)

<u>Changing the value of the corrosion current</u> : the value is calculated between lines 212 and 219.

<u>Changing the thermohydraulic system</u> : The characteristics of the system are listed lines 5, 35 to 42, 126 to 142. The equations are fed in FCNEQN, the jacobian of the system is in FCNJAC and the boundary conditions are in FCNBC.

<u>Changing the chemical equilibrium system</u> : the characteristics of the system are listed line 354. The equations are used to calculate B (with a negative sign), A contains the jacobian.

6. Example of output file

There are two input files : results.out and results2.out. The first one has the field number **10** and the second one has the filed number 11.

Therefore writing in results.out will be programmed 'WRITE(**10**,…….'

Each input file indicates at the beginning the ratio chloride to sodium (line82) and the bulk concentrations (line 114).

In 'results.out', the vectors X(spatial grid points from 0 to LENGTH), concentration of H^+, concentration of OH^-, concentration of Na^+, concentration of Cl^- are written at successiv time step.

In 'results2.out', the vectors X(spatial grid points from 0 to LENGTH), concentration of Fe^{2+}, concentration of $FeOH^+$, concentration of $FeOH_2$, corrosion current are written at successiv time step.

The program has been run with a crevice divided into 1001 parts. In the output file, the vectors are only printed every 50 components plus the endpoints every 300 time steps.

If you would like the output file to be more detailed, it is possible to change those values (lines 194 and 195).

IPRT =**50***(I/**50**) +1 **! Writes only every 50 spatial steps**
KKPRT =**300***(KK/**300**) +1 **! Writes only every 300 time steps**

It is possible to change the name of the output files. However you should change the name of status from 'OLD' to 'NEW' to run the program the first time and create the output file. Once created, if you want to rewrite the output file then the STATUS should be change back to 'OLD' (lines 80 and 81).

'Example of results.out'

```
RATIO= 1.200000

X H+ OH- Na+ Cl-

  (cm)     (mol/cm3)     (mol/cm3)     (mol/cm3)     (mol/cm3)
  BULK    .432554E-09   .135706E-07   .100000E-07   .120000E-07
  (X=0)

TIME= .100000E+04s

   .00    .432689E-09   .135663E-07   .999717E-08   .119981E-07
   .07    .415230E-09   .141368E-07   .105262E-07   .126316E-07
   .14    .397670E-09   .147610E-07   .111109E-07   .133334E-07
   .21    .379863E-09   .154529E-07   .117644E-07   .141178E-07
   .28    .361798E-09   .162245E-07   .124996E-07   .150005E-07
   .35    .343460E-09   .170908E-07   .133331E-07   .160010E-07
   .42    .324834E-09   .180708E-07   .142857E-07   .171448E-07
   .49    .305900E-09   .191892E-07   .153851E-07   .184649E-07
   .56    .286635E-09   .204790E-07   .166680E-07   .200055E-07
   .63    .267010E-09   .219842E-07   .181847E-07   .218272E-07
   .70    .246989E-09   .237662E-07   .200056E-07   .240146E-07
   .77    .226530E-09   .259127E-07   .222323E-07   .266904E-07
   .84    .205576E-09   .285539E-07   .250180E-07   .300390E-07
   .91    .184056E-09   .318925E-07   .286038E-07   .343518E-07
   .98    .161874E-09   .362627E-07   .333932E-07   .401169E-07
  1.05    .138903E-09   .422598E-07   .401173E-07   .482216E-07
  1.12    .114960E-09   .510613E-07   .502534E-07   .604685E-07
  1.19    .897864E-10   .653773E-07   .673183E-07   .811933E-07
  1.26    .630901E-10   .930415E-07   .102379E-06   .124505E-06
  1.33    .769066E-05   .763263E-12   .151598E-05   .984727E-05
  1.40    .177028E-11   .331586E-05   .460886E-03   .458138E-03

TIME= .200000E+04s

   .00    .432833E-09   .135618E-07   .999717E-08   .119981E-07
   .07    .414677E-09   .141556E-07   .105270E-07   .126326E-07
   .14    .396606E-09   .148006E-07   .111128E-07   .133357E-07
   .21    .378333E-09   .155154E-07   .117675E-07   .141216E-07
   .28    .359846E-09   .163125E-07   .125043E-07   .150061E-07
   .35    .341134E-09   .172073E-07   .133395E-07   .160087E-07
   .42    .322181E-09   .182196E-07   .142943E-07   .171551E-07
   .49    .302969E-09   .193749E-07   .153964E-07   .184785E-07
```

```
  .56      .283476E-09   .207072E-07   .166828E-07   .200233E-07
  .63      .263676E-09   .222621E-07   .182039E-07   .218503E-07
  .70      .243536E-09   .241033E-07   .200305E-07   .240446E-07
  .77      .223012E-09   .263214E-07   .222649E-07   .267296E-07
  .84      .202053E-09   .290518E-07   .250612E-07   .300910E-07
  .91      .180590E-09   .325046E-07   .286621E-07   .344220E-07
  .98      .158532E-09   .370273E-07   .334743E-07   .402146E-07
 1.05      .135756E-09   .432395E-07   .402352E-07   .483638E-07
 1.12      .112089E-09   .523689E-07   .504368E-07   .606903E-07
 1.19      .872863E-10   .672499E-07   .676383E-07   .815826E-07
 1.26      .611170E-10   .960453E-07   .103081E-06   .125459E-06
 1.33      .161411E-04   .363668E-12   .287761E-05   .197615E-04
 1.40      .233317E-12   .251590E-04   .943633E-03   .918548E-03
```

‘Example of results2.out’

```
RATIO = 1.200000

    X          Fe2+          FeOH+         FeOH2          ICORR
  (cm)     (mol/cm3)     (mol/cm3)     (mol/cm3)        (A/cm2)
  BULK     .513802E-08   .486198E-08   .100000E-16   .000000E+00
 (X=0)

TIME= .100000E+04s

  .00      .513735E-08   .485982E-08   .100000E-16   .000000E+00
  .07      .530081E-08   .522530E-08   .100000E-16   .000000E+00
  .14      .547517E-08   .563551E-08   .100000E-16   .000000E+00
  .21      .566251E-08   .610154E-08   .100000E-16   .000000E+00
  .28      .586446E-08   .663468E-08   .100000E-16   .000000E+00
  .35      .608298E-08   .724933E-08   .100000E-16   .000000E+00
  .42      .632041E-08   .796419E-08   .100000E-16   .000000E+00
  .49      .657960E-08   .880394E-08   .100000E-16   .000000E+00
  .56      .686402E-08   .980183E-08   .100000E-16   .000000E+00
  .63      .717803E-08   .110036E-07   .100000E-16   .000000E+00
  .70      .752711E-08   .124740E-07   .100000E-16   .000000E+00
  .77      .791833E-08   .143075E-07   .100000E-16   .000000E+00
  .84      .836102E-08   .166473E-07   .100000E-16   .000000E+00
  .91      .886782E-08   .197208E-07   .100000E-16   .000000E+00
  .98      .945648E-08   .239116E-07   .100000E-16   .000000E+00
 1.05      .101532E-07   .299191E-07   .100000E-16   .000000E+00
 1.12      .109993E-07   .391631E-07   .100000E-16   .000000E+00
 1.19      .120698E-07   .550235E-07   .100000E-16   .000000E+00
 1.26      .135612E-07   .879823E-07   .100000E-16   .000000E+00
 1.33      .320304E-06   .170473E-10   .100000E-16   .000000E+00
 1.40      .243749E-08   .563583E-06   .798783E-03   .000000E+00
```

```
TIME= .200000E+04s

   .00      .513632E-08    .485724E-08    .100000E-16    .107723E-11
   .07      .530503E-08    .523644E-08    .100000E-16    .107641E-11
   .14      .548372E-08    .565944E-08    .100000E-16    .107566E-11
   .21      .567548E-08    .614026E-08    .100000E-16    .107499E-11
   .28      .588195E-08    .669056E-08    .100000E-16    .107442E-11
   .35      .610509E-08    .732529E-08    .100000E-16    .107395E-11
   .42      .634721E-08    .806382E-08    .100000E-16    .107359E-11
   .49      .661114E-08    .893174E-08    .100000E-16    .107341E-11
   .56      .690035E-08    .996350E-08    .100000E-16    .107340E-11
   .63      .721913E-08    .112065E-07    .100000E-16    .107363E-11
   .70      .757292E-08    .127280E-07    .100000E-16    .107415E-11
   .77      .796869E-08    .146257E-07    .100000E-16    .107503E-11
   .84      .841563E-08    .170482E-07    .100000E-16    .107638E-11
   .91      .892616E-08    .202316E-07    .100000E-16    .107837E-11
   .98      .951766E-08    .245738E-07    .100000E-16    .108122E-11
  1.05      .102157E-07    .308011E-07    .100000E-16    .108529E-11
  1.12      .110605E-07    .403895E-07    .100000E-16    .109122E-11
  1.19      .121249E-07    .568578E-07    .100000E-16    .110016E-11
  1.26      .136092E-07    .911439E-07    .100000E-16    .111455E-11
  1.33      .371397E-06    .941811E-11    .100000E-16    .352274E-09
  1.40      .423399E-10    .742783E-07    .134294E-02    .115838E-11
```

D

MEMO TO USE THE PROGRAM “POTENTIAL”

Outline

1. Definition of the variables
2. Algorithm of the program
3. Thermohydraulic system
4. Changing the input
5. Example of output
6. The subroutine POTMETAL

1. Definition of the variables

The variables can be divided in two major categories: the variables used by the numerical method NEQNJ *(italics)* and the variables used for the electrochemical equations (**Bold**).

NEQNJ solves a system of nonlinear equations using a modified hybrid algorithm with a user supplied Jacobian.

1.1 Variables for principal program

ITMAX : The maximum allowable number of iterations
N : The number of equations to be solved
ERRREL : Relative error between two successive iterations
FNORM : Norm of the vector F
E : Vector containing the value of the electrochemical potential at the grid points of the crevice
EGUESS : Vector containing the initial guess of the value E
F : Function values at point x containing the system of equations
FCN : Subroutine to evaluate the system of equations to be solved
LSJAC : Subroutine to evaluate the jacobian at a point x
$\mathbf{E_0}$: potential at the mouth
$\mathbf{E_m}$: potential of the tube
CONC : Vector containing the concentrations of H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$ at different location in the crevice

JCORR	: Vector containing the corrosion current density repartition in the crevice
JH	: Vector containing the cathodic current density repartition in the crevice
JDIFF	: Vector containing the diffusion current density repartition in the crevice
ITOTAL	: Vector containing the total current repartition in the crevice
FPH	: Logical indicating whether or not the expression employed to calculate the corrosion current should be from pH expression or Tafel expression (.TRUE. = from pH expression)
CORRECTION	: Logical indicating whether or not the corrosion current should exist under –0.447V and the cathodic current (Hydrogen above 0V)

1.2 Local variables for subroutine FCN

Ah	: Exchange current density coefficient of the cathodic reaction
Alphah	: Tafel slope for the cathodic reaction
D	: Diffusion coefficients vector (H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$)
Z	: Charges vector (H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$)
RGAZ	: Gas constant
LENGTH	: Half length of the crevice
TEMP	: Average temperature of the crevice
FARADAY	: Faraday constant
CONDUCT	: Vector containing the conductivity repartition in the crevice
Ac	: Cross sectional area of the crevice
Rsg	: Radius of the tube
Pi	: Mathematical constant
pH	: Value of the pH at a location of the crevice
P	: Value used as an intermediate steps in ICORR calculation

2. Algorithm of the program

The program has been copied at the end of this notice with line numbers on it. The algorithm will refer to those lines.

- Declare the variables
- Set up the output file 'potential.out'
- Input the concentration repartition in the crevice for H^+, OH^-, Na^+, Cl^-, Fe^{2+}, $FeOH^+$
- Input the potential at the mouth
- Input the method to calculate Icorr
- Input the guessed value for the electrochemical potential
- Input the parameters for the numerical method (relative error, maximum number of iterations)
- Call the subroutine NEQNJ that solves the system of equations

- Call the subroutine FCN that gives the residuals of F once the electrochemical potential E is known. (If the residuals are too high then the precision on the calculation of E is poor)
- Write the residuals on the screen
- Write the current densities (corrosion, cathodic,diffusion) and the electrochemical potential in the output file

3. Potential calculation : subroutines NEQNJ, FCN and LSJAC

3.1 Numerical method NEQNJ

The method solved a system of equations using a modified Powell hybrid algorithm with a user supplied Jacobian.

Usage

CALL NEQNJ(FCN, LSJAC, ERRREL, N, ITMAX, XGUESS, X, FNORM)

Arguments

FCN—User supplied SUBROUTINE to evaluate the system of equations to be solved.

The usage is CALL FCN (X, F, N) where

X—The point at which the functions are evaluated. (Input)
X should not be changed by FCN.
F—The computed function values at the point X. (Output)
N—Length of X, F. (Input)

FCN must be declared external in the calling program.

LSJAC—User supplied SUBROUTINE to evaluate the Jacobian at a point X.

The usage is call LSJAC (N, X, FJAC), where

N—Length of X. (Input)
X—The point at which the function is evaluated. (Input)
X should not be changed by LSJAC.
FJAC—The computed N by N Jacobian at the point X. (Output)

LSJAC must be declared external in the calling program

ERRREL –Stopping criterion. (Input)
The root is accepted if the relative error between two successive approximations to this root is less than ERRREL.
N—The number of equations to be solved and the number of unknowns.
ITMAX—The maximum allowable number of iterations. (Input)

Suggested value : 1000.
XGUESS—A vector of length N. (Input)
XGUESS contains the initial estimate of the root
X—A vector of length N. (Output)
X contains the best estimate of the root found by NEQNJ.
FNORM –A scalar that has the value $F(1)^2+F(2)^2+\ldots+F(N)^2$ at the point X. (Output)

3.2 From equations to numerical method

The method used to calculate the distribution of electrochemical potential in the crevice are based on the electrical analogy (Figure D-1) and the resulting equations below:

Figure D-1
Electrical analogy of the electrochemistry in the crevice

The diffusion current and conductivity are known once the chemistry is inputted. The last part missing to solve this system is the corrosion and the cathodic currents. The cathodic current density is expressed with a Tafel law.

$$J = A_{H^+}C_{H^+}\exp\quad ALPHAH\frac{F}{RT}(E_{corr}\quad j)$$

The corrosion current density can be expressed either by a Tafel law (fph=.FALSE.) or as a function of the pH (fph=.TRUE.). The Tafel law is similar to the one above except that the coefficient A and ALPHA are different. The function of pH is the following:

$$J = 10^{-2.8448 + 0.4388 * pH - 0.8473 * pH **2 + 0.1977 * pH **3 - 0.0178 * pH **4 + 5.678\varepsilon - 4 * pH **5}$$

Finally once the densities of current have been transformed to currents and the equations rearranged, the system for a crevice divided into N-1 elements with N potentials to determine is the following :

$$F(1) = E(1) - E_0$$

$$F(2) = E(2) - \frac{\kappa(2) * E(3) + \kappa(1) * E(1) - JDIFF(2) + JDIFF(1) - (JCORR(2) - JH(2)) * ((LENGTH / N) **2) * \frac{2\pi R_{SG}}{A_C}}{\kappa(2) + \kappa(1)}$$

$$\dots$$

$$F(J) = E(J) - \frac{\kappa(J) * E(J+1) + \kappa(J-1) * E(J-1) - JDIFF(J) + JDIFF(J-1) - (JCORR(J) - JH(J)) * ((LENGTH / N) **2) * \frac{2\pi R_{SG}}{A_C}}{\kappa(J) + \kappa(J-1)}$$

$$\dots$$

$$F(N-1) = E(N-1) - \frac{\kappa(N-1) * E(N) + \kappa(N-2) * E(N-2) - JDIFF(N-1) + JDIFF(N-2) - (JCORR(N-1) - JH(N-1)) * ((LENGTH / N) **2) * \frac{2\pi R_{SG}}{A_C}}{\kappa(N-1) + \kappa(N-2)}$$

$$F(N) = E(N) - \frac{\kappa(N-1) * E(N-1) + JDIFF(N-1) - (JCORR(N) - JH(N)) * ((LENGTH / N) **2) * \frac{2\pi R_{SG}}{A_C}}{\kappa(N-1)}$$

Since the current densities are a non linear function of the electrochemical potential, this a system of N non linear equations with N unknowns :$E_{1<i<n}$

These equations are in the subroutine FCN and the derivatives of those equations with respect to E are written in LSJAC.

Once those two subroutines are filled, E_0, EGUESS, ERRREL AND ITMAX set then the program is ready to calculate E.

After solving the system and getting the vector E, the function FCN is called again and the value of the F is checked to see how close to zero the F are. This is a good way to check if NEQNJ solved correctly the system of equations.

4. Changing the input

Changing the potential at the mouth: Change the value of E_0 (line 85)

Changing the chemistry of the crevice: Change the values in CONC (lines 30 to 83)

Changing the geometry of the crevice: The geometry parameters are the length, the radius of the tube and the cross sectional area (lines 143 to 145 and lines 267 to 269)

Changing the electrochemical parameters: Directly in the subroutines FCN and LSJAC.

Calculating the potential of the metal as a function of the external chemistry : remove the C(comment) in front of call potmetal(EM) (line 84). If you would like this value to be the boundary condition at the mouth then write E_0=Em below line 84 and remove line 85.

If there is some problem of convergence, please increase the ERRREL, change the EGUESS to a closer value and make sure that the residuals of F printed on the screen at the end of the run are extremely small compared to zero.

5. Example of 'potential.out'

The output file contains the values of the abscissa in the crevice and the corresponding values of the corrosion current, the cathodic current, the diffusion current and the electrochemical potential.

```
     X          Corrosion       Cathodic       Diffusion          E
                 current         current        current         vs SHE
    (cm)         (A/cm2)         (A/cm2)        (A/cm2)           (V)

 .0000E+00    .000000E+00   .000000E+00  –.213281E-06     –.200000E+00
 .0000E+00    .159593E-05   .461057E-06  –.259516E-06     –.279869E+00
 .0000E+00    .177889E-05   .950927E-06  –.278359E-06     –.344203E+00
 .0000E+00    .204535E-05   .174455E-05  –.237520E-06     –.394166E+00
 .0000E+00    .245167E-05   .291151E-05   .782174E-07     –.430961E+00
 .0000E+00    .319759E-05   .462742E-05   .433091E-05     –.455345E+00
 .0000E+00    .523891E-05   .786364E-05   .811951E-02     –.465973E+00
 .0000E+00    .185315E-03   .173398E-03   .981371E-02     –.458972E+00
 .1420E+01    .248728E-03   .222222E-03  .000000E+00      –.455705E+00
```

6. Subroutine POTMETAL

This subroutine calculates the potential of the metal based on the concentration of oxygen and hydrogen in solutions. It is based on the mixed potential theory. E is the potential such the sum of the currents cathodic and anodic is zero. A maximum value is given to E and then the value is decreased until the total current equals zero.

Usage

CALL POTMETAL(EM)

Algorithm of the subroutine :

- Input oxygen concentration
- Input hydrogen concentration
- Input average velocity of the fluid, average temperature of the solution, Faraday

- constant…
- pH=neutral
- Calculate the exchange current densities and the limiting currents.
- Calculate the reversible potentials.
- E= maximum value between reversible potential of hydrogen and oxygen
- Reactions
- DO until Itotal less than zero
    - Calculate the cathodic currents(hydrogen and oxygen) based of the equation below:

$$i_{R/O} = \frac{\exp\left(\frac{E-E^{e}_{R/O}}{b_a}\right)-\exp\left(-\frac{E-E^{e}_{R/O}}{b_c}\right)}{\frac{1}{i_{0,R/O}}+\frac{1}{i_{l,f}}\exp\left(\frac{E-E^{e}_{R/O}}{b_a}\right)-\frac{1}{i_{l,r}}\exp\left(-\frac{E-E^{e}_{R/O}}{b_c}\right)}$$

    - Calculate the corrosion current based on:
    - Itotal = Icorr + $I_{H^+/H2}$ + I_{O2/OH^-}
    - E = E-0.0001
- END DO
- EM = E + 0.0001/2.0 (The subroutine gives back this value as potential of the metal)
- END

```
********************************************************************************
************************This program calculates the repartition *********************
********************* of electrochemical potential in the crevice *********************
*************************** knowing the chemistry *****************************
*******************************************************************************
USE MSIMSLMS
C                         Declare variables
INTEGER       ITMAX, N
REAL  ERRREL
PARAMETER (N=9)
C
INTEGER                 K
REAL            FNORM, E(N), EGUESS(N)
REAL            F(N)
EXTERNAL   FCN, LSJAC

REAL            E0,EM
REAL            CONC(6,5000)
REAL            JCORR(5000),JH(5000),JDIFF(5000),ITOTAL(5000)
LOGICAL      FPH,CORRECTION

COMMON/CONCENTRATION/CONC,EM,E0
COMMON/COURANT/JCORR,JH,JDIFF,ITOTAL
COMMON/ENTREE/FPH,CORRECTION

C                                         Setting up the output file
OPEN (UNIT=10,FILE='Potential.OUT',STATUS='old')

WRITE (10,9996)
WRITE (10,9998)
WRITE (10,*)
WRITE (10,9997)
FORMAT (T17,'Corrosion',T35,'Cathodic',T51,'Diffusion', T70,'E')
FORMAT (T17,'current',T35,'current',T51,'current', T70,'vs SHE')
FORMAT (T17,'(A/cm2)',T35,'(A/cm2)',T51,'(A/cm2)', T70,'(V)')
WRITE (10,*)
CONTINUE

C                         Input the concentration profiles

CONC(5,1)=   2.26E-08
CONC(5,2)=   2.85E-08
CONC(5,3)=   3.79E-08                  !          H+
CONC(5,4)=   5.36E-08
CONC(5,5)=   8.35E-08
CONC(5,6)=   1.54E-07
CONC(5,7)=   4.49E-07
CONC(5,8)=   3.56E-04
CONC(5,9)=   6.25E-04
CONC(6,1)=   1.24E-09
CONC(6,2)=   1.39E-09
```

```
CONC(6,3)=   1.60E-09                  !          OH-
CONC(6,4)=   1.91E-09
CONC(6,5)=   2.38E-09
CONC(6,6)=   3.23E-09
CONC(6,7)=   5.52E-09
CONC(6,8)=   1.55E-07
CONC(6,9)=   2.06E-07
CONC(3,1)=   1.00E-06
CONC(3,2)=   1.17E-06
CONC(3,3)=   1.40E-06                  !          Na+
CONC(3,4)=   1.76E-06
CONC(3,5)=   2.36E-06
CONC(3,6)=   3.60E-06
CONC(3,7)=   7.67E-06
CONC(3,8)=   4.38E-03
CONC(3,9)=   6.32E-03
CONC(4,1)=   1.20E-06
CONC(4,2)=   1.40E-06
CONC(4,3)=   1.68E-06                  !          Cl-
CONC(4,4)=   2.11E-06
CONC(4,5)=   2.83E-06
CONC(4,6)=   4.32E-06
CONC(4,7)=   9.25E-06
CONC(4,8)=   5.11E-03
CONC(4,9)=   7.60E-03
CONC(1,1)=   1.54E-07
CONC(1,2)=   1.73E-07
CONC(1,3)=   1.99E-07                  !          Fe2+
CONC(1,4)=   2.37E-07
CONC(1,5)=   2.95E-07
CONC(1,6)=   4.01E-07
CONC(1,7)=   6.85E-07
CONC(1,8)=   1.93E-05
CONC(1,9)=   2.56E-05
CONC(2,1)=   3.16E-11
CONC(2,2)=   2.81E-11
CONC(2,3)=   2.44E-11                  !          FeOH+
CONC(2,4)=   2.05E-11
CONC(2,5)=   1.64E-11
CONC(2,6)=   1.21E-11
CONC(2,7)=   7.08E-12
CONC(2,8)=   2.51E-13
CONC(2,9)=   1.90E-13
C         CALL POTMETAL(EM)
E0 = –0.2                     !          Potential at the mouth
FPH= .TRUE.            ! Icorr function of pH or not(function of E)
          ! If correction = .TRUE.
```

```
CORRECTION = .FALSE.    ! Below E=-0.447 no corrosion current
C
DO 1 J=1,N
EGUESS(J) = –0.35            !Guessing value for the electrochemical
                         !        potential


CONTINUE
C
ERRREL = 0.001       ! Relative error
ITMAX = 10000        ! Maximum allowable number of iterations

C                    Find the solution of the system

CALL NEQNJ (FCN, LSJAC, ERRREL, N, ITMAX, EGUESS, E, FNORM)

C            Calculate the residuals of the systems
CALL FCN(E,F,N)
DO 34 K=1,N
WRITE (*,*) F(K)     ! Printing the residuals on the screen

C            Writing the results in the output file

WRITE (10,9995) JCORR(K),JH(K),JDIFF(K),E(K)
9995 FORMAT(10X, E15.6, 3X, E15.6, 3X, E15.6, 3X, E15.6)
CONTINUE
CLOSE(UNIT=10)
C
END

*********** END OF PRINCIPAL PROGRAM **************


************** BEGINNING OF SBUROUTINES ***********

C                    User-supplied subroutine
SUBROUTINE FCN (E, F, N)
INTEGER      N
REAL  E(N), F(N)
REAL         E0,EM
REAL         AH,ALPHAH
REAL         CONC(6,5000)
REAL         D(6),Z(6)
REAL         RGAZ,LENGTH,TEMP,FARADAY
REAL         JDIFF(5000),CONDUCT(N)

REAL         Ac,Rsg,pi
REAL         P,pH(N),JCORR(5000),JH(5000),ITOTAL(5000)
LOGICAL      FPH,CORRECTION
COMMON/CONCENTRATION/CONC,EM,E0
COMMON/COURANT/JCORR,JH,JDIFF,ITOTAL
COMMON/ENTREE/FPH,CORRECTION
```

```
C
REAL EXP
INTRINSIC EXP

D(1) = 4.0*0.72E-5                ! Diffusion coefficient of H+
D(2) = 4.0*1.E-5                  ! Diffusion coefficient of OH-
D(3) = 4.0*1.334E-5               ! Diffusion coefficient of Na+
D(4) = 4.0*2.032E-5               ! Diffusion coefficient of Cl-
D(5) = 4.0*9.312E-5               ! Diffusion coefficient of Fe2+
D(6) = 4.0*5.26E-5                ! Diffusion coefficient of FeOH+

Z(1)   = 1.0              ! Charge of H+
Z(2)   = –1.0             ! Charge of OH-
Z(3)   = 1.0              ! Charge of Na+
Z(4)   = –1.0             ! Charge of Cl-
Z(5)   = 2.0              ! Charge of Fe2+
Z(6)   = 1.0              ! Charge of FeOH+

LENGTH      = 1.42                ! Half length of the crevice
Ac          = 0.166       ! Cross sectional area of the crevice
Rsg         = 0.94                ! Radius of the tube
pi          = 3.1416      ! Mathematical constant = 3.1416

FARADAY = 96480.0                 ! faraday constant
RGAZ = 8.31                       ! Gaz constant
TEMP  = 573.15            ! Temperature

AH          = 1.0E-6      ! Exchange current coefficient(H cath. react.)
ALPHAH      = –0.5        ! Tafel slope (H cath. react.)

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCC MOUTH CCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC


C

F(1) = (E(1) – E0)                ! Mouth function to set to zero

DO 31 J=1,N-1

C       Calculating the diffusion current and the conductivity

JDIFF(J) = 0.0
CONDUCT(J) = 0.0
DO 32 I=1,6
JDIFF(J) = JDIFF(J) + FARADAY*Z(I)*D(I)*
.                 ((CONC(I,J+1)-CONC(I,J)))
CONDUCT(J) = CONDUCT(J) + (FARADAY**2)/RGAZ/TEMP*(Z(I)**2)
.                 *D(I)*(CONC(I,J)+CONC(I,J+1))/2.0
CONTINUE

CONTINUE
```

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CC BETWEEN MOUTH AND CENTER OF THE CREVICE CC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

DO 41 J=2,N-1

C Calculating the corrosion current and the cathodic current

IF (FPH) THEN                    ! corrosion current function of pH
pH(J) = –LOG10(1000*CONC(1,J))
P = –2.8448 + 0.4388*pH(J) – 0.8473*pH(J)**2 + 0.1977*pH(J)**3
–0.0178*pH(J)**4 +5.678e-4*pH(J)**5
JCORR(J) = 10**P
JH(J) = (0.124E-7+0.906E-1*CONC(1,J))*EXP(-(E(J))/0.1)
IF (CORRECTION) THEN
IF (E(J) .GT. 0.0) THEN          ! Cathodic current = 0 when E is above 0.0
JH(J) = 0.0
ENDIF
ENDIF
ENDIF

IF (.NOT. FPH) THEN              ! corrosion current function of E
JCORR(J) = 1.0e-10*exp((E(J)+0.447)/0.05)
JH(J) = (0.124E-7+0.906E-1*CONC(1,J)**0.5)*EXP(-(E(J))/0.05)
IF (CORRECTION) THEN                     ! applying correction
IF (E(J) .GT. 0.0) THEN          ! Cathodic current = 0 when E is above 0.0
JH(J) = 0.0
ENDIF
IF (E(J) .LT. –0.447) THEN       ! Corrosion current = 0 when E is below –0.447
JCORR(J) = 0.0
ENDIF
ENDIF
ENDIF
ITOTAL(J) = (JCORR(J)-JH(J))*((LENGTH/N)**2)*2*pi*Rsg/Ac

! Function to set to zero from J=2 to J=N-1
F(J) = E(J) –(CONDUCT(J)*E(J+1)+CONDUCT(J-1)*E(J-1)
.                    -JDIFF(J)+JDIFF(J-1)-ITOTAL(J))/(CONDUCT(J)+CONDUCT(J-1))
CONTINUE


CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC CENTER OF THE CREVICE CCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

C Calculating the corrosion current and the cathodic current

IF (FPH) THEN                    ! corrosion current function of pH
pH(N) = –LOG10(1000*CONC(1,N))
P = –2.8448 + 0.4388*pH(N) – 0.8473*pH(N)**2 + 0.1977*pH(N)**3
–0.0178*pH(N)**4 +5.678e-4*pH(N)**5
JCORR(N) = 10**P
```

```
JH(N) = (0.124E-7+0.906E-1*CONC(1,N))*EXP(-(E(N))/0.1)
IF (CORRECTION) THEN
IF (E(N) .GT. 0.0) THEN       ! Cathodic current = 0 when E
is above 0.0
JH(N) = 0.0
ENDIF
ENDIF
ENDIF

IF (.NOT. FPH) THEN           ! corrosion current function of E
JCORR(N) = 1.0e-10*exp((E(N)+0.447)/0.05)
JH(N) = (0.124E-7+0.906E-1*CONC(1,N)**0.5)*EXP(-(E(N))/0.05)
IF (CORRECTION) THEN                  ! applying correction
IF (E(N) .GT. 0.0) THEN       ! Cathodic current = 0 when E is above 0.0
JH(N) = 0.0
ENDIF
IF (E(N) .LT. –0.447) THEN ! Corrosion current = 0 when E is below –
0.447
JCORR(N) = 0.0
ENDIF
ENDIF
ENDIF
ITOTAL(N) = (JCORR(N)-JH(N))*((LENGTH/N)**2)*2*pi*Rsg/Ac
! Function to set to zero at J=N
F(N) = E(N) –(CONDUCT(N-1)*E(N-1)
.                 +JDIFF(N-1)-ITOTAL(N))/CONDUCT(N-1)
END
C                         User-supplied subroutine to
C                         compute Jacobian
SUBROUTINE LSJAC (N, E, FJAC)
INTEGER       N
REAL  E(N), FJAC(N,N)

REAL          EM
REAL          AH,ALPHAH
REAL          CONC(6,5000)
REAL          D(6),Z(6)
REAL          RGAZ,LENGTH,TEMP,FARADAY
REAL          CONDUCT(N)
REAL          Ac,Rsg,pi
REAL          DITOTAL(5000)
LOGICAL               FPH,CORRECTION
COMMON/CONCENTRATION/CONC,EM,E0
COMMON/ENTREE/ FPH,CORRECTION
C
REAL EXP
INTRINSIC EXP
```

```
D(1) = 4.0*0.72E-5                    ! Diffusion coefficient of H+
D(2) = 4.0*1.E-5                      ! Diffusion coefficient of OH-
D(3) = 4.0*1.334E-5                   ! Diffusion coefficient of Na+
D(4) = 4.0*2.032E-5                   ! Diffusion coefficient of Cl-
D(5) = 4.0*9.312E-5                   ! Diffusion coefficient of Fe2+
D(6) = 4.0*5.26E-5                    ! Diffusion coefficient of FeOH+

Z(1)    = 1.0                 ! Charge of H+
Z(2)    = –1.0                ! Charge of OH-
Z(3)    = 1.0                 ! Charge of Na+
Z(4)    = –1.0                ! Charge of Cl-
Z(5)    = 2.0                 ! Charge of Fe2+
Z(6)    = 1.0                 ! Charge of FeOH+

LENGTH      = 1.42                    ! Half length of the crevice
Ac          = 0.166           ! Cross sectional area of the crevice
Rsg         = 0.94                    ! Radius of the tube
pi          = 3.1416          ! Mathematical constant = 3.1416

FARADAY = 96480.0             ! faraday constant
RGAZ = 8.31                           ! Gaz constant
TEMP = 573.15                 ! Temperature

AH          = 1.0E-6          ! Exchange current coefficient(H cath. react.)
ALPHAH      = –0.5            ! Tafel slope (H cath. react.)

DO 33 J=1,N-1

CONDUCT(J) = 0.0
DO 34 I=1,6
CONDUCT(J) = CONDUCT(J) + (FARADAY**2)/RGAZ/TEMP*(Z(I)**2)
.           *D(I)*(CONC(I,J)+CONC(I,J+1))/2.0 ! Conductivity
CONTINUE

CONTINUE


C
DO 121 J=1, N
DO 111 I=1, N
FJAC(J,I) = 0.0
CONTINUE
121 CONTINUE

! Computing the jacobian at the mouth

FJAC(1,1) = 1.0


! taking the derivative of ITOTAL with respect to E between the mouth and the center of the
crevice
DO 52 J=2,N-1
```

```
IF (FPH) THEN
DITOTAL(J) =(1/0.1*(0.124E-7+0.906E-1*CONC(1,J))
.                              *EXP(-(E(J))/0.1))
.                              *((LENGTH/N)**2)*2*pi*Rsg/Ac
IF (CORRECTION) THEN
IF (E(J) .GT. 0.0) THEN
DITOTAL(J) = 0.0
ENDIF
ENDIF
ENDIF

IF (.NOT. FPH) THEN
DITOTAL(J) = (1/0.05* 1.0e-10*exp((E(J)+0.447)/0.05)
.                              +1/0.05*(0.124E-7+0.906E-1*CONC(1,J)**0.5)
.                              *EXP(-(E(J))/0.05))
.                              *((LENGTH/N)**2)*2*pi*Rsg/Ac
IF (CORRECTION) THEN
IF (E(J) .GT. 0.0) THEN
DITOTAL(J) = (1/0.05* 1.0e-10*exp((E(J)+0.447)/0.05))
.                              *((LENGTH/N)**2)*2*pi*Rsg/Ac
ENDIF
IF (E(J) .LT. –0.447) THEN
DITOTAL(J) =(1/0.05*(0.124E-7+0.906E-1*CONC(1,J)**0.5)
.                              *EXP(-(E(J))/0.05))
.                              *((LENGTH/N)**2)*2*pi*Rsg/Ac
ENDIF
ENDIF
ENDIF

! Computing the jacobian between the mouth and the center of the crevice

FJAC(J,J-1) = –CONDUCT(J-1)/(CONDUCT(J)+CONDUCT(J-1))
FJAC(J,J) = 1.0 + DITOTAL(J)/(CONDUCT(J)+CONDUCT(J-1))
FJAC(J,J+1) = –CONDUCT(J)/(CONDUCT(J)+CONDUCT(J-1))

CONTINUE

! Calculating the derivative of ITOTAL with respect to E at the center of the crevice
IF (FPH) THEN
DITOTAL(N) =(1/0.1*(0.124E-7+0.906E-1*CONC(1,N))
.                              *EXP(-(E(N))/0.1))
.                              *((LENGTH/N)**2)*2*pi*Rsg/Ac
IF (CORRECTION) THEN
IF (E(N) .GT. 0.0) THEN
DITOTAL(N) = 0.0
ENDIF
ENDIF
ENDIF

IF (.NOT. FPH) THEN
DITOTAL(N) = (1/0.05 *1.0e-10*exp((E(N)+0.447)/0.05)
```

```
.                               +1/0.05*(0.124E-7+0.906E-1*CONC(1,N)**0.5)
.                               *EXP(-(E(N))/0.05))
.                               *((LENGTH/N)**2)*2*pi*Rsg/Ac
IF (CORRECTION) THEN
IF (E(N) .GT. 0.0) THEN
DITOTAL(N) = (1/0.05 *1.0e-10*exp((E(N)+0.447)/0.05))
.                               *((LENGTH/N)**2)*2*pi*Rsg/Ac
ENDIF
IF (E(N) .LT. –0.447) THEN
DITOTAL(N) =(1/0.05*(0.124E-7+0.906E-1*CONC(1,N)**0.5)
.                               *EXP(-(E(N))/0.05))
.                               *((LENGTH/N)**2)*2*pi*Rsg/Ac
ENDIF
ENDIF
ENDIF

! Computing the jacobian at the center of the crevice
FJAC(N,N) = 1.0+DITOTAL(N)/CONDUCT(N-1)
FJAC(N,N-1) = –1.0
RETURN
END

! Calculating the potential of the metal as a function of the chemistry (PENNSTATE)
SUBROUTINE POTMETAL(ECPx)
REAL IOh2,IOo2, IpO,Icorx,Iit,Khh2,Kho2,Ilh2f,Ilh2r,Ilo2f,Ilo2r
REAL  Co2ppb,Ch2ppb,TxC,Tx,Co2,Ch2
REAL  Vf,ChD,WDX
REAL  pKW,pH,EOo2,EOh2,Xx,Eeo2,Eeh2,Cco2,Cch2
REAL  Dh2,Do2,Xv,Kv,Rnd,Sch2,Sco2
REAL  CHplus,COHmin
REAL  F,Ff,Rg,SHa,SHb,SHc
REAL  Bfh2,Brh2,Bfo2,Bro2,Bfss,Brss,EO,Ee,EeTemp
REAL  Eh2f,Eh2r,Eo2f,Eo2r,Essf,Essr,Xh2,Xo2,Xss,ECPx



C
C Input oxigen concentration
C

C Co2ppb = 5.             ! Concentration of O2 ppb

write(*,*)
write(*,*) 'Input oxygen concentration, Co2ppb, in ppb'
write(*,*) 'If Co2ppb = 5 is OK, simply input 0'
read (*,*) aa
IF(aa.ne.0.) Co2ppb = aa
write(*,*)
```

```
C Ch2ppb= 1000.

C
C Input hydrogen concentration
C

C Ch2ppb = 1000.      ! Concentration of H2 ppb

write(*,*)
write(*,*) 'Input hydrogen concentation, Ch2ppb, in ppb'
write(*,*) 'If Ch2ppb = 1000 is OK, simply input 0'
read (*,*) aa
IF(aa.ne.0.) Ch2ppb = aa
write(*,*)

TxC = 280.
c Co2ppb= 5.
c Ch2ppb= 1000.
Vf=10.                ! Liquid flow velocity (cm/sec)
ChD=10.               ! Channel hydrodynamic diameter (cm)
WDX = 0.755

Tx=TxC+273.15         ! Temperature (Degree K)

Co2=Co2ppb
Ch2=Ch2ppb

Co2=Co2*WDx/32.0E6        ! mol/L
Ch2=Ch2*WDx/2.0E6         ! mol/L
pKW=4466.2/Tx-5.941+0.016638*Tx
CHplus=10**(-pKw/2.0)
COHmin=CHplus

C—Start Calculation Loop –-------------------------------------------
50 CONTINUE

C—Calculate Equilibrium Potential –----------------------------------
F=23060.9
Ff=96487.0
Rg=1.98717
SHa=0.0165
SHb=0.86
SHc=0.33
IF (CHplus.LE.0.0) CHplus=1.0E-12
IF (Ch2.LE.0.0) Ch2=1.0E-12
IF (Co2.LE.0.0) Co2=1.0E-12
pH=-LOG10(CHplus)
EOo2=1.518489-0.001121*Tx+6.024e-7*Tx*Tx-3.2733E-10*Tx**3
Xx=2.303*Rg*Tx/F
Khh2=-1321/Tx+10.702-0.010468*Tx
Kho2=-1202/Tx+9.622-0.009049*Tx
Eeh2=-(Xx/2.0)*(LOG10(Ch2*2.0E3/WDx)+Khh2-3.301)-Xx*pH
```

```
Eeo2=EOo2+(Xx/4.0)*(LOG10(Co2*32.0E3/WDx)+Kho2-4.5051)-Xx*pH

C—Calculate Concentrations in Unit of Mol/cm**3 –---------------------
Cch2=Ch2/1.0E3
Cco2=Co2/1.0E3
C—Calculate Species Diffusivities –-----------------------------------
Dh2=EXP(-5.700267-296.7439/Tx-288379.2/(Tx*Tx))
Do2=8.03E-3*EXP(-3490.0/(Rg*Tx))
C—Calculate Kinematic Viscosity –-------------------------------------
Xv=-6.140834-1103.164/Tx+457155.3/(Tx*Tx)
Kv=EXP(Xv)
C—Calculate Reynolds and Schmidt Numbers –----------------------------
Rnd=Vf*ChD/Kv
Sch2=Kv/Dh2
Sco2=Kv/Do2
C—Calculate Limiting Currents –---------------------------------------
Ilh2f=SHa*2*Ff*Dh2*Cch2*(Rnd**SHb)*(Sch2**SHc)/ChD
Ilh2r=-1.0
Ilo2f=1.0
Ilo2r=-SHa*4*Ff*Do2*Cco2*(Rnd**SHb)*(Sco2**SHc)/ChD

C—Calculate ECP –-----------------------------------------------------
Bfh2=0.065
Brh2=0.065
Bfo2=0.071
Bro2=0.071
Bfss=0.060
Brss=0.060
IOh2= 0.01*((Ch2*2.0E3/WDx)**0.5)*EXP(-14244/Rg/Tx)*0.05
IOo2= 0.0114841*((Co2*32.0E3/WDx)**0.48633)*EXP(-14244/Rg/Tx)*.44
EO=0.200-1.5286E-3*Tx
IpO=2.6E-3*EXP(-4416.0/Tx)

Ee=Eeh2
IF (Eeo2.GT.Ee) Ee=Eeo2
Ee=Ee+0.1
400 EeTemp=Ee
Eh2f=EXP((EeTemp-Eeh2)/Bfh2)
Eh2r=EXP(-(EeTemp-Eeh2)/Brh2)
Eo2f=EXP((EeTemp-Eeo2)/Bfo2)
Eo2r=EXP(-(EeTemp-Eeo2)/Bro2)
Essf=EXP((EeTemp-EO)/Bfss)
Essr=EXP(-(EeTemp-EO)/Brss)
Xh2=(Eh2f-Eh2r)/(1/IOh2+Eh2f/Ilh2f-Eh2r/Ilh2r)
Xo2=(Eo2f-Eo2r)/(1/IOo2+Eo2f/Ilo2f-Eo2r/Ilo2r)
Xss=Essf/(IpO*EXP(0.523*((EeTemp-EO)**5)))
Icorx=(Essf-Essr)/(1/IpO+Xss)
IF (EeTemp.LT.EO) Icorx=0.0
```

```
Iit=Xh2 + Xo2 + Icorx
IF (Iit.LT.0.0) GO TO 401
Ee=EeTemp-0.0001
GO TO 400
401 ECPx=Ee +.0001/2.
END
```

Target:
Nuclear Power

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