DRA-37: COMSOL MODELS

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1. STATEMENT OF PROBLEM:

How can simple models be used to understand the mechanisms associated with pyrite oxidation and the dissolution/formation of minerals within a rock pile over time, particularly the process of the evaporation of water within the pile and the generation of air currents caused by temperature gradients within the pile?

2. PREVIOUS WORK:

There are four main mechanisms for oxygen transport within a rock pile:

1. Diffusion
2. Convection caused by temperature gradients within a rock pile
3. Barometric pumping
4. Compositional changes resulting in a difference in gas density

There are many articles that have investigated one or more of these mechanisms for various porous media [Ahn, 2004; Cairncross, 1996; Jacobs, 1997; Kannan, 1995; Lin, 1996] and several have described mathematical models that describe field data. A review of those field model articles is included in DRA-38 which describes the fully coupled geochemical transport model. Although all four transport mechanisms can be present in any given rock pile, typically only one or two are mainly responsible for the transport, the others are minor players. Every rock pile is unique however and ample field data is necessary to determine which mechanism dominates and, if the heterogeneity of the pile is extensive, the mechanism might even vary from location to location within the rock pile. Modeling plays a large role in this process.

More pertinent to this project is the study by Wels et al. [Wels, 2003] in which they gave an overview of the prediction and control of air flow in rock piles, including data from one in the Questa mining site, the Sugar Shack South rock pile. From the field data they concluded that high oxygen concentrations within the rock pile indicated strong lateral gas flows and that the high temperatures indicated high pyrite oxidation rates over the entire thickness of the pile. Using the model TOUGH-AMD they concluded that the dominate mechanism for oxygen supply was lateral convection while that for water was infiltration and vaporization. The main mechanism for heat transfer was conduction and latent heat effects. Their simulations indicated air velocities on the order of 100 meters/day, a depth of oxygen penetration greater than 30 meters and an oxidation rate of 0.33 kg O_2/m^3-yr. This was the impetus for investigating the process of evaporation from rock piles, particularly that occurring within a rock pile due to convective air currents.

Perhaps the most applicable study on evaporation from surfaces is the one done by Wilson *et al.* (1997). They were able to illustrate the effect of capillary pressure on the total drying rate using a soil water characteristic curve. They, however, did not actually model evaporation. The evaporative fluxes were simply compared to the evaporative flux from a sample in which there was no capillary pressure. Viollaz and Suarez (1985) give a short review of mass transfer correlations used to predict evaporative fluxes under various conditions. They then use numerical algorithms to find solutions to the problem of drying shrinking particles. Silva *et al.* (2000) studied porous media with very small pores (<5 nm.) in which Darcy's law was deemed invalid. They reported a method of estimating flow rates through the use of an effective diffusivity which was a function of many parameters such as porosity, tortuosity and pore size. Because waste rock piles have much larger pores (>>5 nm.) it is not reasonable to use this approach. Stacey and Udell (1997) developed analytical solutions to the problem of drying unsaturated porous media. Their solutions were compared to numerical models and experimental data with reasonable agreement. They conclude that an isothermal treatment will almost always over predict evaporation rates in porous media.

As part of this study a non-COMSOL evaporative humidity cell model was developed by Eldredge (2005). No reactions were considered in his model. His model illustrated the importance of properties of porous media such as porosity and initial saturation and used data collected from other studies as well [Klinker, 2006; Farney, 2004]. His work was continued by Evans (2007) and more complicated humidity cell models were developed as reported here.

3. TECHNICAL APPROACH

Our approach was to understand the processes involved in weathering by simulating the different mechanisms under a more controlled environment, the humidity cell. Model development would begin with a simple isothermal model describing the drying process under simplifying assumptions to one- and two-dimensional nonadiabatic models that describe humidity cell data. Thermal properties were to be obtained as a part of humidity cell testing by collecting transient temperature data and water saturation data under various repeatable conditions. These data were then used to calibrate these mathematical humidity cell models that included the drying phase. The fitted parameters, such as evaporation rate, mass transfer coefficients, effective solid thermal conductivity, and effective solid heat capacity could then be related to a particular sample and its properties to determine the effect of the various lithologies and mineralogies on those parameters.

Once the process of drying within the humidity cells was understood and the various critical parameters identified then a better understanding of the other processes could be obtained. Thus, other COMSOL models were developed that included the leaching phase and draining phase with a few geochemical reactions. Finally, all models were combined into one comprehensive model that described the weekly cycle and that could be run for any number of weeks to compare with data. Other models of the humidity cell testing program, describing the full geochemical and biological reactions, are described in DRA-36.

The simple COMSOL field models helped us understand the various mechanisms involved in pyrite oxidation and the resulting generation of heat and the formation of convective air currents which will help in the development of the more complex field-scale models of actual rock piles (DRA-38). More importantly, these simple models will help understand the temperature profiles measured in the field for these rock piles, thus providing an important link toward calibration of the more complex field model.

4. CONCEPTUAL MODELS

Although there has been a lot of effort in understanding the geochemistry of acid rock drainage (primarily water quality) and the formation of secondary minerals, not very many studies have looked at the evaporation of water within a rock pile from relatively highly permeable zones carrying convective air currents caused by temperature differences. These air currents can, under mostly arid environments, evaporate some of the water in unsaturated hot zones and redeposit that water in other parts of the pile that are cooler. This redistribution of water affects to a small degree the temperature distribution due to the heat of evaporation/condensation, but, more importantly, concentrates the aqueous ions that are in the pore spaces of the rock. In the process, this could cause the precipitation of secondary minerals that might affect the cohesion and, indirectly, the friction angle, of the rock material. This precipitated material, if water soluble, could then be redissolved by any additional water that might be flowing down the rock pile at any given time. Thus, it is important to understand the conditions that lead to in-situ evaporation and how that might affect the mineralogy over periods of wet-and-dry cycles and over the life-time of the rock pile.

Much of the ARD literature on drying typically only considers drying at the surface of a rock pile that is exposed to atmospheric weathering conditions. Even though this only affects a small part of the rock pile, a few feet from the surface, it can be very important in understanding the water balance of the overall rock pile, particularly if, in the process of drying, a cementing material is formed, sometimes called “hard-pan”, and inhibits the flow of water into the interior. Evaporation within the rock pile due to convective air currents only occurs under certain conditions and for many rock piles is probably not a significant factor in the water balance and overall water chemistry. However, in arid environments it may be important in the redistribution of water within the rock pile and thus it is necessary to understand the conditions in which it becomes important.

A. **Humidity Cell Model**

Ambient conditions were assumed to be standard temperature and pressure. The thermal conductivities of air and water as functions of temperature were given by the expressions that Eldredge (2005) used. Other thermal conductivities were assumed to change insignificantly over the temperature range of interest. The enthalpy of vaporization of water was also assumed to change very little over the temperature interval and was therefore treated as a constant. The Clausius Clapeyron equation was used to predict the saturation vapor pressure of water as a function of temperature. Water’s normal boiling point was used for the reference condition. Additionally, the solid phase was assumed to be immobile.

Several models were developed for this project:

- A 1D Isothermal model
- A 1D Adiabatic model
- A 1D Non-adiabatic model
- A 2D Non-adiabatic Homogeneous model
- A 2D Non-adiabatic Heterogeneous model
- A 1D Non-adiabatic Reactive model.

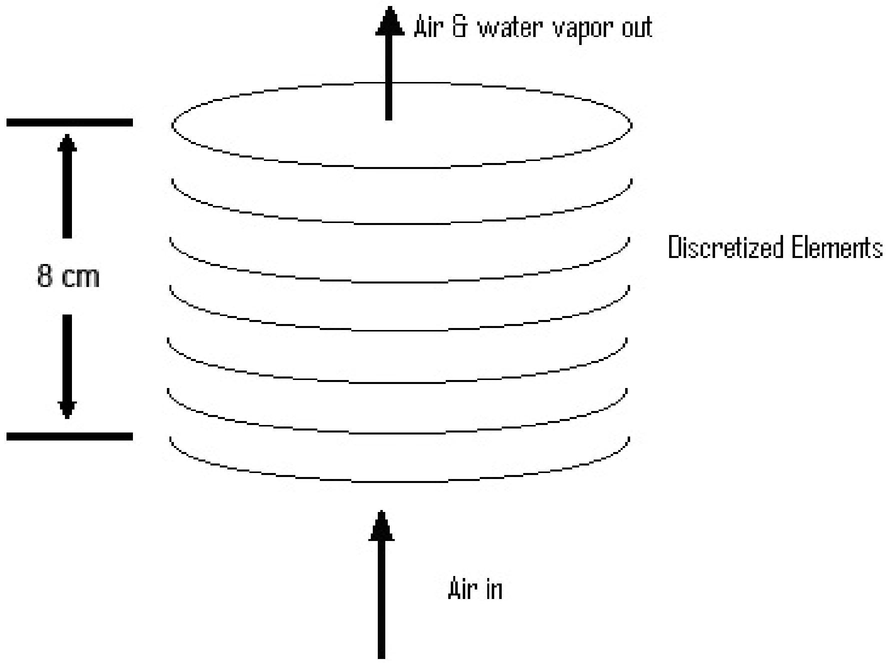

Figure 1. Conceptual diagram of the 1D evaporation model. Note, not all mesh elements have been shown.

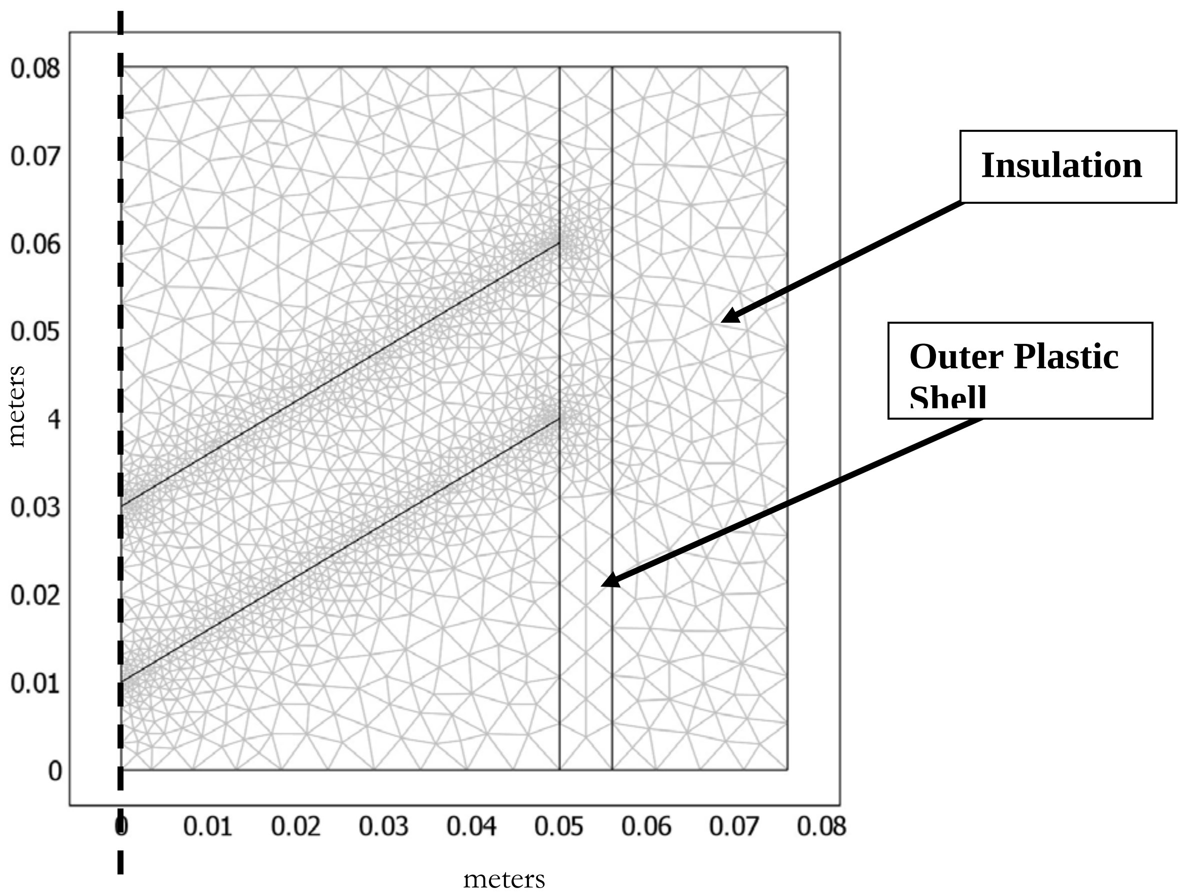

Figure 2. The finite element mesh used for the 2D heterogeneous model. Note the centerline on the left and the high density of mesh elements at the transition between zones of different permeability. The scale is in meters.

Modeling the dry-air phase helped us understand the evaporative processes within rock piles better, at least in the laboratory, which might be extrapolated to field processes. The rate of drying and the extent of drying for different rock types, mineralogy and particle size distributions is important for understanding ARD in arid environments and moisture content plays a major role in pyrite oxidation rates. Modeling results will identify which rock and fluid properties are important in determining evaporation rates and how one might extrapolate laboratory results to predict what might happen on a much larger field scale.

B. **Field Model**

There is a lot of well-bore temperature profile data from the Questa mining site from various wells drilled into the rock piles over time and these data might help calibrate the more complex field geochemical models since the temperatures observed are due primarily to the oxidation of pyrite and other reactions and the associated gas and liquid flows. However, this work will be done primarily with TOUGHREACT field models and not COMSOL field models.

5. STATUS OF INVESTIGATION

Models have been developed and calibrated with laboratory data describing the temperature drop during the dry-air phase (evaporation) of humidity cell testing of samples other than those from Questa. Modeling the Questa samples is in progress. An example is given below for the G9 control quartz cell at week 10. More plots will be included in the final report.

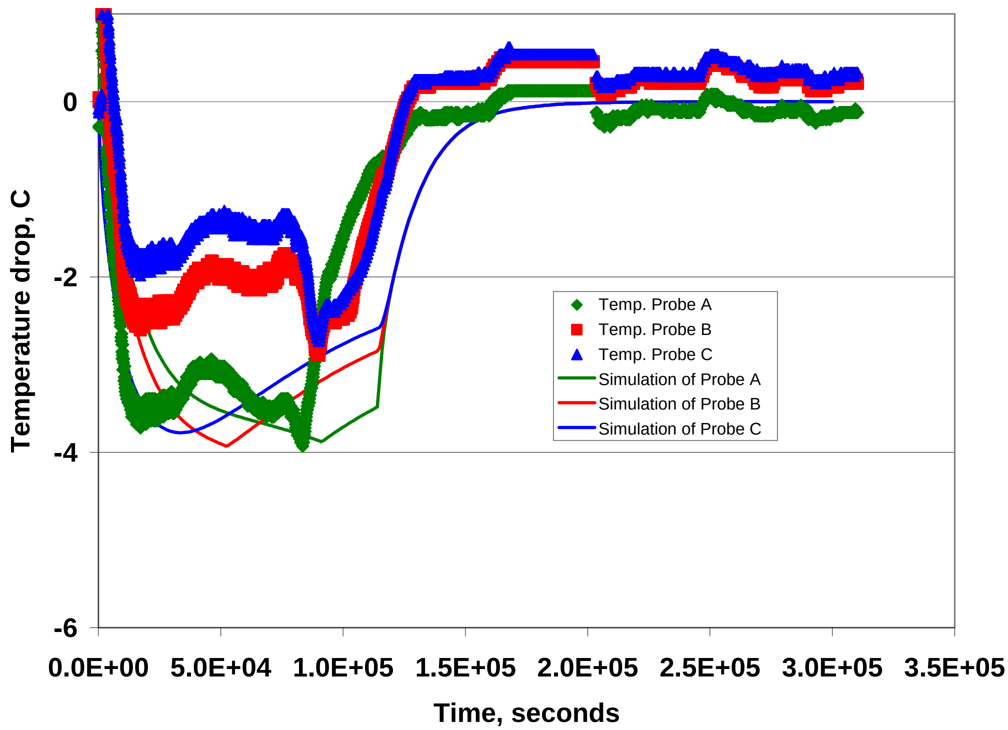

Figure 3. A comparison of the measured humidity cell temperature measurements for the drying phase in the G9 control cell (crushed quartz particles) with the simulations generated by the evaporative humidity cell model. The temperature drop is the difference between the cell temperature at the probe location and the surrounding temperature. Total air flow rate was 1.0 L/min for this run and the air was dried before it was introduced to the humidity cell and was at ambient temperature.

This shows that calibration is possible and that calibration can be used to obtain some of the thermal properties of the humidity cell samples used for the Chevron Mining project. Table 1 below shows the values of the various parameters used to model the data in Figure 1 above. Values will be obtained from all the other cells that were equipped with temperature probes.

Table 1. Parameters used in the COMSOL evaporative humidity cell model for the data shown in Figure 1 for the control cell, containing quartz particles.

PARAMETER	VALUE	UNITS
Porosity	0.3	Volume fraction
Initial Water Saturation	0.23	Fraction of pore space
Solid thermal conductivity	1.8	W/m-K
Enthalpy of Vaporization	44004	Joules/mol
Initial Temperature	295.5	Kelvin
Initial Pressure	101325	Pascals
Solid heat capacity	830	Joules/kg-K

In addition to the drying phase model, a two-dimensional COMSOL model was developed to investigate heterogeneity effects and is described in detail in Paul Evan's thesis [Evans, 2007]. An example of that work is given in the next figure. This allowed us the opportunity to investigate air flow in heterogeneous environments, which might be experienced in the field.

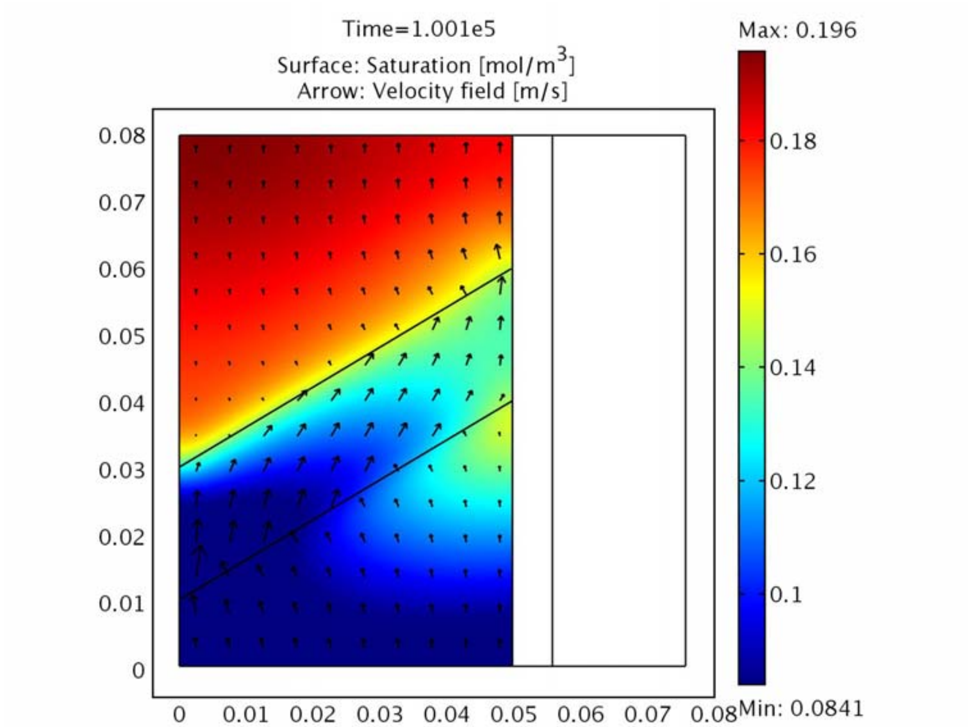

Figure 4. Saturation (color scale) and flow field (arrows) in the humidity cell with a high permeability layer after 100,100 seconds

Finally, a preliminary model of the complete humidity cell cycle was developed with five geochemical reactions and ten species. The results of that model are given in the thesis, but, it was found that the model took tens of hours to model the 52 week period and would take longer if more reactions were included. Nevertheless, a reasonable match of the leachate chemistry was obtained (see Figures A-2 to A-5 in the appendix).

Simple COMSOL models of a rock pile have been developed to understand the mechanism of forming convective air currents within a rock pile and the temperature gradients that might develop. Figure 3 below is one of the earlier models that show how temperature gradients develop when a constant heat generation term in included in the energy balance. While the temperature gradients may approximate those experienced in the field at the end of the simulation time, 31.7 years, the temperatures keep rising after that to unreasonable temperatures if the simulation is continued, thus indicating that there must be additional mechanisms for limiting the temperature. In the interest of time, this work is temporarily on hold in favor of the development of the TOUGHREACT field model that would include all known processes.

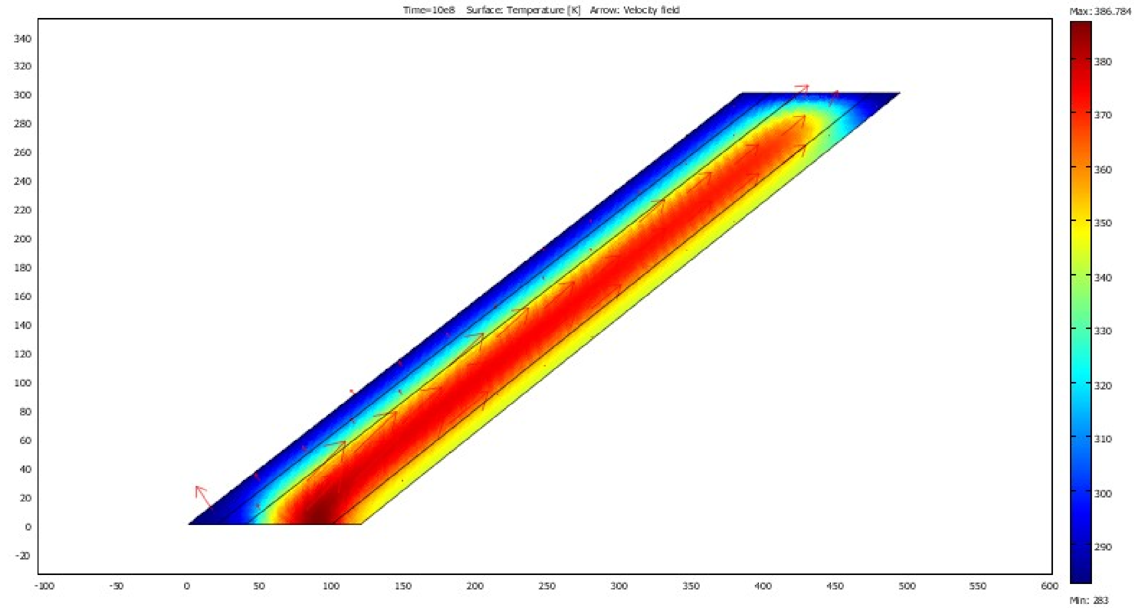

Figure 5. Simple 2D representation of a hypothetical Goat Hill North Rock pile with a few layers showing temperature profiles with a constant heat generation only in the high permeable zone equivalent to a constant rate of pyrite oxidation after 31.7 years. Initially the rock pile was at a uniform temperature of 10C.

6. **RELIABILITY ANALYSIS**

As with most models, reliability depends on validation and verification; validation meaning that the model predicts results that are reasonable and consistent with current theories while verification means that the model is able to describe experimental data adequately under varying conditions. The one-dimensional laboratory model of the drying process was verified with an analytical solution for a simplified isothermal case (see Figure A-1 in the appendix) and the results were very good. Calibration or verification is proceeding with data collected from the University of Utah humidity cell experiments and the resulting thermal properties are being compared with available literature values. Verification of our humidity cell models will be confirmed once the model has been used in a number of cases to simulate experimental humidity cell results.

The two-dimensional field model of the thermal gradients in rock piles will be compared to other models published in the literature and will be calibrated with whatever field data is available. Again, reliability for this model will depend on how well the model is able to predict the temperature profiles measured in various wellbores in several Questa rock piles. This work will not be completed until next year.

7. **CURRENT CONCLUSIONS RELATED TO COHESION AND FRICTION ANGLE**

This work is related to the development of cohesion in the rock pile. As pore waters evaporate, the precipitation of secondary minerals can occur, depending on the concentrations of the various ions. It is important to understand the process of evaporation in porous media so that a better model of the overall weathering process can be developed. It has been shown in this study that the evaporation rate is insensitive to the mass transfer coefficient and the specific surface area above a threshold surface area. The model is also relatively insensitive to the thermal conductivity of the composite rock material. This indicates that, because the pore spaces are so small, the water vapor is able to come to equilibrium almost instantly. Therefore, for the purposes of modeling evaporation, it is not important to determine the mass transfer coefficient or the surface area of the porous medium with a high degree of accuracy.

Simple COMSOL field models can be developed and can be used to understand one or two of the mechanisms involved, but a complete model of all the pertinent mechanisms must be used for predictive purposes since all the different mechanisms – biological cell growth, geochemical reactions, heat generation, gas flow, liquid flow, etc. are coupled. In the interest of time most of our efforts will be directed toward the latter and the COMSOL field models will be postponed for the time being.

8. REFERENCES

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9. TECHNICAL APPENDICES

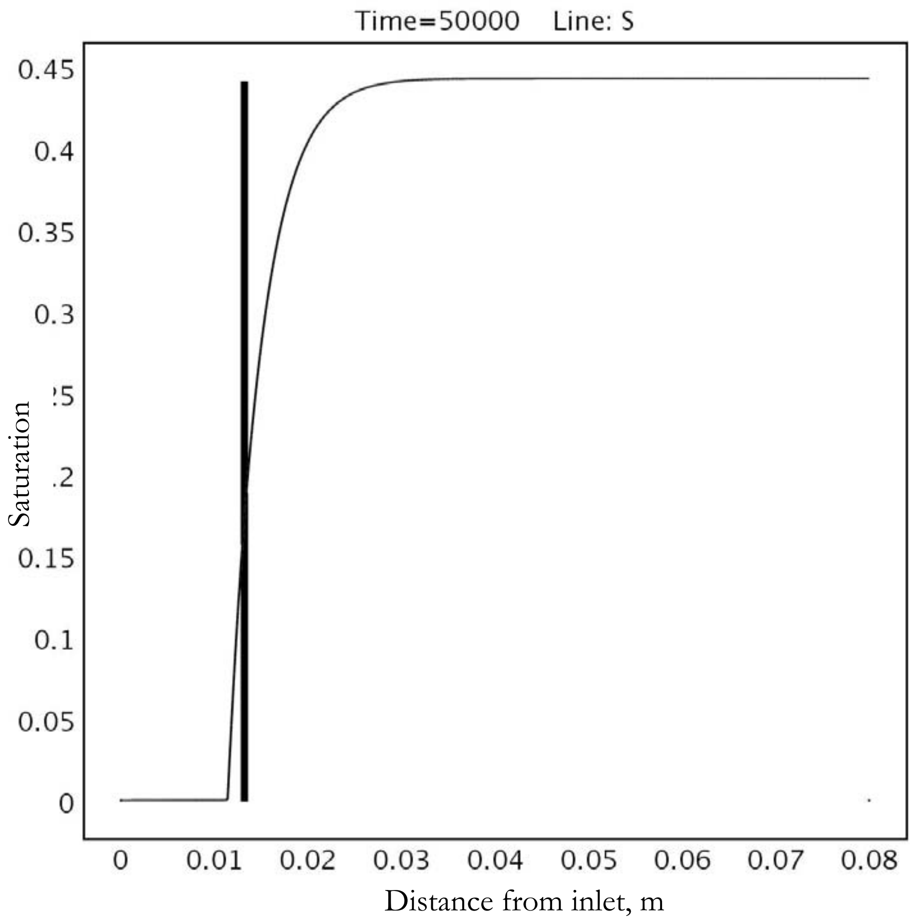

Figure A-1. Saturation (Y axis) as a function of distance from inlet in meters (X axis) after 50,000 seconds as predicted by the COMSOL 1D isothermal model. The vertical line indicates the position of the evaporation front according to a simplified analytic solution.

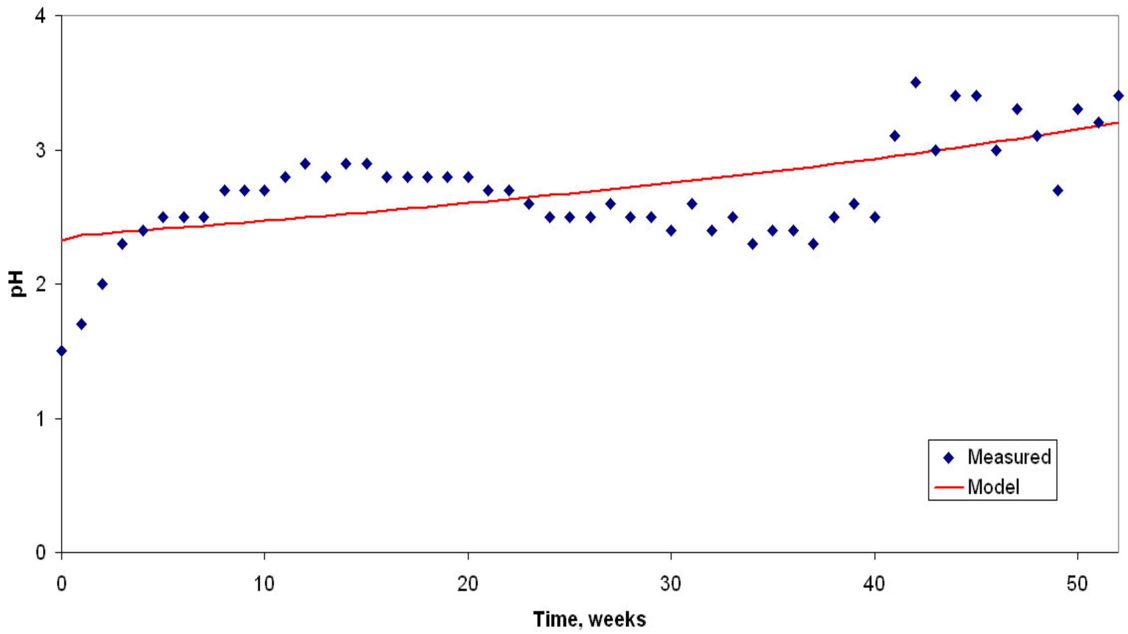

Figure A-2. Experimentally determined and model predicted pH of leachate from the COMSOL reactive model. The model appears to predict pH well over the entire one-year testing period.

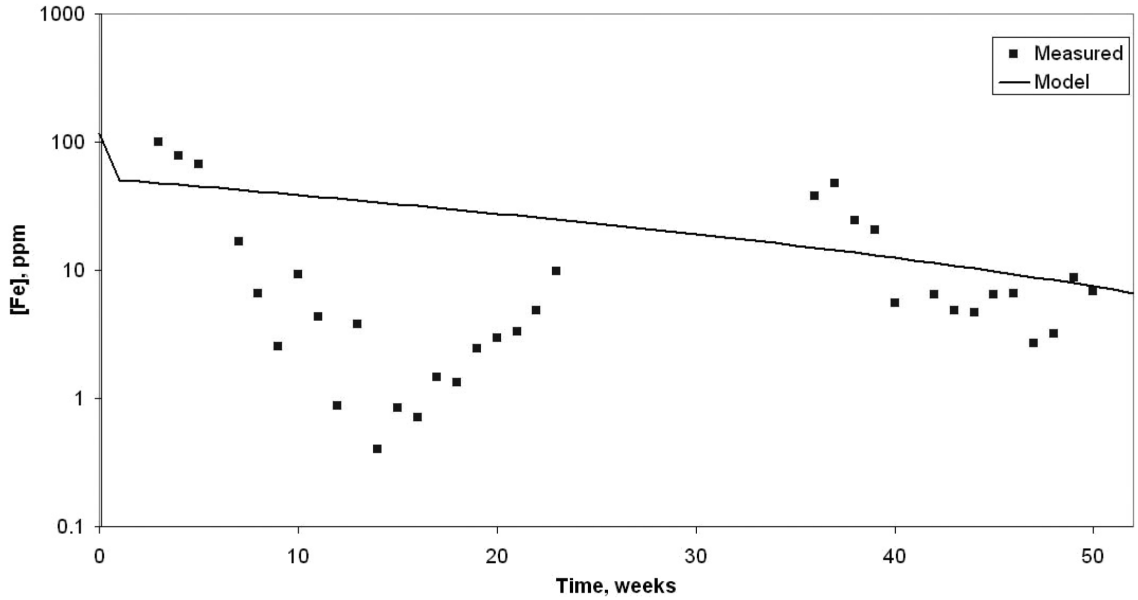

Figure A-3. Total concentration of iron in leachate as predicted by the 1D reactive COMSOL humidity cell model along with experimental data from Farney (2004). The model appears to predict the general trend, but not the flucturations in concentrations of iron in solution.

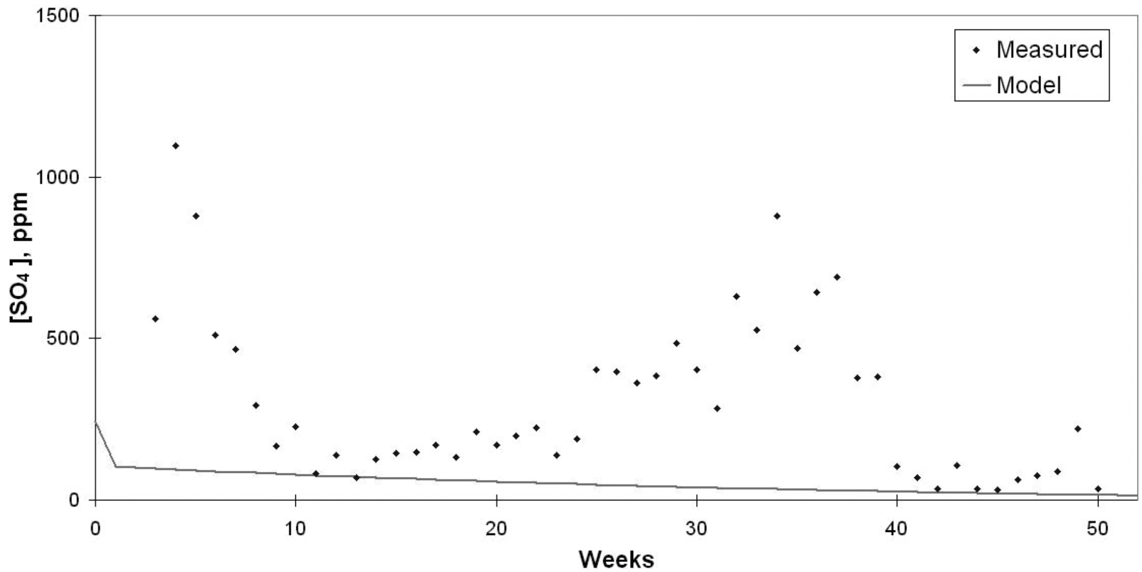

Figure A-4. Experimentally determined and model predicted concentration of sulfate ion in leachate (ppm). The model appears to under predict sulfate concentration and cannot match the periodic concentrations due to various mechanisms coming into play, such as the growth of bacteria.

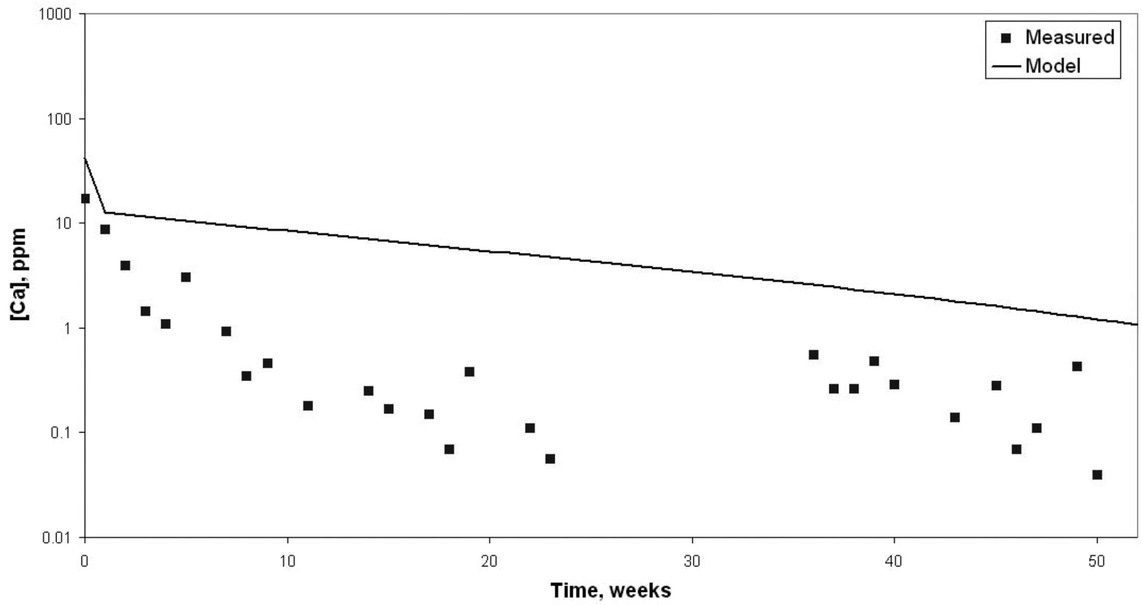

Figure A-5. Concentration of calcium ion in leachate as predicted by the 1D reactive COMSOL humidity cell model along with experimentally determined values from Farney (2004). Calcium ion is over predicted by the model. This is likely due the model's current inability to model precipitation.