DRA-38. PREDICTION OF MINERALOGICAL CHANGES OCCURING IN A ROCK PILE OVER TIME DUE TO WEATHERING

E. Trujillo, M. Niewiadomski, S. Sunkavalli, Y. Li

1. STATEMENT OF PROBLEM

Can a field model be developed to predict mineralogical changes resulting from weathering in a mine rock pile a) over a 100 year time period and b) over a 1000 year time period? The relationship of mineralogical changes to friction angle and cohesion of the rock pile will be addressed in other parts of the project evaluation.

2. PREVIOUS WORK

There have been numerous mathematical models of weathering and acid rock drainage (ARD) over the last few decades, starting with rather simple models to very complicated coupled models. The objective of most is to predict water quality after mine closure for a number of years. The problem is that ARD is a very complex process involving not only mineralogical and geochemical changes but physical and biological changes as well. Most rock piles are heterogeneous in terms of mineralogy and flow properties and the ARD process involves all three phases – solid, liquid and gas. In addition, due to heats of reaction, there is an energy component that can produce convective air currents in unsaturated, highly permeable rock piles.

The most important part of modeling ARD is to identify the dominating mechanisms that are responsible and concentrate on those mechanisms in order to produce a reasonable simulation of the rock pile. For tailings it has been found that diffusion is the dominate mechanism for oxygen transport, one of the principal components in the oxidation of pyrite, thus allowing more simple models. For rock piles with a much broader particle size distribution, not only diffusion but gas convection in unsaturated flow conditions can be important.

The properties of many rock piles are not sufficiently known to develop a detailed model of the internal characteristics of a pile but many properties can be inferred from field data collected from wellbores, lysimeter tests and laboratory testing of field samples. Although there are some common characteristics that are present in all rock piles, each rock pile should be considered unique and the reliance of a model to predict its weathering characteristics depends on how well that uniqueness is known.

One of the earliest papers on field modeling was written by Cathles and Apps (Cathles, 1975). Since then there have been numerous, more complicated geochemical field models that have been proposed and developed. Several reviews of those models are available (MEND, 1.42.1, 1995), (Mayer, 2003) (Richie, 2003) (Lichtner, 1996). Many of these models have coupled the transport and energy equation with geochemical thermodynamic programs such as PHREEQC and WATEQ4F to model the geochemical reactions, most assuming local equilibrium conditions but some using kinetic expressions. Also, many of these earlier models assumed saturated flow properties. Only in the last fifteen years or so have reactive models been developed that include three phases and unsaturated flow conditions (Alpers, 1998; Mayer, 2003).

Urlich Mayer developed a model called MIN3P which he has used on a number of occasions to model ARD both in the field and in the laboratory (Mayer, 1999; Mayer, 2002; Mayer,2007). Other models include ACIDROCK (Scharer, 1994), MINTRAN (Wunderly, 1996), MULTIFLO (Lichtner, 1996), ARDUU (Trujillo, 1997), MINTOX (Gerke, 1998), SULFIDOX (Richie, 1994) , FIDHELM (Pantelis, 1991; MEND, 2000) and RETRASO (Saaltink, 2002).

One model, developed at Lawrence Livermore Laboratories, is called TOUGH2 and was originally designed to study nonisothermal flow of multicomponent, multiphase fluids in three-dimensional porous and fractured media but did not include any chemical or geochemical reactions (Pruess, 1991; TOUGH manual, 1999). This model was subsequently modified by Lefebvre to include a limited number of geochemical reactions and was developed as part of a MEND project (1.14.2). Lefebvre refers to this model as TOUGH-AMD (Lefebvre, 1994; Lefebvre, 2001ab). Lawrence Livermore, in the meantime, developed a TOUGH-REACT model that included chemical reactions and coupled the transport code with the EQ3/6 geochemical equilibrium code (Xu, 1999; Xu, 2000; Xu, 2008). They also have a model called TOUGH2-CHEM that can be applied to ARD but uses a different solution algorithm than TOUGH-REACT and is much more convoluted computationally. There are advantages and disadvantages to all of these models and the user should be aware of the limitations of the model before applying them to a particular situation and problem.

More pertinent to this study was the work done by LeFebvre et al. in modeling several of the Questa Rock Piles using TOUGH-AMD (LeFebvre, 2001a; LeFebvre, 2001b; LeFebvre, 2002; Wels, 2003; Sracek, 2004; Sracek, 2006). One of the rock piles studied was Sugar Shack South and two 2D configurations were developed for this rock pile, a simple mostly rectangular configuration with 109 active grid blocks and a more detailed configuration with benches with 126 active grid blocks (each block 30.5 meters by 7.6 meters). A reaction core model with first order kinetics relative to oxygen was used to calculate the pyrite oxidation rate, using an oxygen volumetric rate constant of 1 x 10^{-7} sec^{-1} for the high reactive material and 1 x 10^{-10} sec^{-1} for the low reactive material. The system included two fluid phases and four components - water, air, oxygen in air, and heat, note dissolved oxygen was not a listed component. Dissolved mass transport of sulfate was calculated from the oxidation rate using a simple mass balance.

In summary, they found that the mountain slopes induce strong thermal air currents that results in the evaporation of water which can condense in areas of the pile that have lower temperatures. This redistribution of water can be important for internal water balances but is relatively insignificant (2%) when looking at an overall water balance. Due to the limited number of components, the model was not designed to be calibrated with field water quality. Other related studies have been completed using Questa rock pile material (Shaw, 2003; Shaw, 2002; Wels, 2002ab; Wels, 2003, Wels, 2001).

3. TECHNICAL APPROACH

The approach was to develop a comprehensive geochemical field model that would incorporate as many mechanisms as possible in describing weathering in the Questa rock piles, thus allowing prediction of mineralogical changes. Inclusion of these various mechanisms will give a much better prediction of weathering that could be used to determine changes in mineralogy that could be related to cohesion or friction angle. Simpler models were to be used in the development to understand various aspects of the weathering and gain insight into the dominant mechanisms. Other DRAs outlined the approaches used to understand the the geochemical mechanisms in the laboratory and how that work can be applied to the field model.

Two field modeling codes were originally to be used – TOUGHREACT and our own University of Utah software (ARDUU), but, in the interest of time and due to the delays in receiving the appropriate input to generate the models, the TOUGHREACT software was used since it has an extensive geochemical thermodynamic database that has been validated for a number of different applications, although several major revisions of the code were necessary before it could be used for ARD rock piles. Some of the more important revisions are discussed in the appendix.

One of the more important tasks that we proposed for this project was to develop a graphical user interface for the TOUGHREACT software that would help generate the rock pile configuration, set properties by layers and then visualize the output. This would save a lot of time in working with the TOUGHREACT program.

The first model to be developed would be similar to Soilvision's hydrological finite element model. The same dimensions and layering that was used for Soilvision's hydrological model would be used to develop the TOUGHREACT model that will simulate the same hydrological aspects of a hypothetical Goat Hill North pile. There were four benchmarks that were to be used to test this model against Soilvision's models to make sure both models were predicting the same results for the hydrological aspects.

1) A simple steady state GHN model assuming constant rain influx at the surface
2) After the pile reaches steady state stop the rain influx and allow the pile to drain (drain down test).
3) Add constant rain again to 2) and reach the previous steady state values.
4) Run a transient model with annual monthly rain influxes for up to 100 years, allowing some dry months with no rain, using local precipitation records to determine the monthly rain fluxes.

Construction of the geochemical field model involved reviewing the current NMT database, developing visualization techniques for viewing GHN field data in two or three dimensions so that a representative 2D mineralogical cross-section could be obtained, reviewing pertinent technical reports and literature articles on similar models and comparing the various constructs of the GHN rock pile. Also, during the project, we will be using information gathered by previous investigators, particularly URS, SRK, Golder Co., Robertson Geoconsultants, New Mexico Tech and SoilVision Co., on the hydrological aspects including the historical environment of the pile over time (weather patterns, rainfall, seasonal temperature variations, barometric pressure, wind velocities, etc.). Our models will be constructed based somewhat on the configuration of the hydrological models. Generation of a 2D geochemical model of the Goat Hill North pile will be conducted and calibration of the model using existing laboratory and field data from the Questa mining site will be done.

After the unsaturated hydrology of the layered model has been replicated, then the thermal aspects can be added to the same model. This will be done by adding appropriate boundary conditions and a constant heat generation source in one portion of the pile and seeing how this affects air flow distribution and water distribution over time. Some sensitivity analysis will be done to see how much heat generation is needed to obtain a significant convective air flow and what effects this has on water saturation.

Once the results indicate a reasonable distribution of air and water, based on experience and published literature, then the geochemical reactions can be added to the layers. This will occur also in steps and will occur after information from the UU humidity cells is available and after previous humidity cell data has been modeled using the UU humidity cell models mentioned earlier. Some equilibrium geochemical calculations of field leachate data will be used to compare with the kinetic calculations to see if there are any discrepancies in the final results for a given period of time for some of the species. Thus, all the previous data and knowledge on the properties of the GHN pile will be used as much as possible, including the change in parameters with mineralogy and temperature and the field data collected to date.

The final geochemical configuration will be related both to the geologic conceptual model and the hydrological conceptual model. The mineralogical composition of each layer in the geological model will be provided by NMT, although, as yet, that has not been done. Some simplification of the number of layers may be necessary in order to decrease the computation time. Criteria for this simplification will be developed. It is expected that the full field-scale model will provide the spatial and temporal distribution of the change in mineralogy within the hypothetical GHN rock pile from the current time to 100 years or more. The model will also predict the change in water saturation on a yearly cycle, duplicating Soilvision's models, so that this information can be used by the geotechnical group for predicting changes in cohesion and friction angle.

The final model will be designed to be run on the University of Utah's supercomputer or in other parallel processing systems in order to obtain high resolution of the various geologic units and layering effects and make predictions for 100 to 1000 years. As the 2D model is being developed a number of tests can be conducted to determine the numerical stability of the models, the optimum number of parallel processors and the best method for visualizing the results. After the optimum computational method has been established and pertinent data have been matched, a few predictive runs can be made using the models to determine weathering products and patterns over long periods of time. The models' predictions of these geochemical data, both spatially and temporally, will then be used as input to the 2D geotechnical model to predict friction angle and cohesion and thus slope stability over time.

4. **CONCEPTUAL MODELS**

The conceptual geological model of the GHN rock pile as provided by Dr. McLemore is given in the appendix, Figure A-1. The final hydrological model from Soilvision is also given in the appendix. The current version of the geochemical model being used in TOUGHREACT is given below in Figure 1. The model has 3,125 active grid elements and is composed of the same layers and properties as the SoilVision hydrological model. Other TOUGHREACT models with greater resolution have been designed but required more computational time than this one. Thus, in the interest of time, we chose to use this model with reasonable resolution.

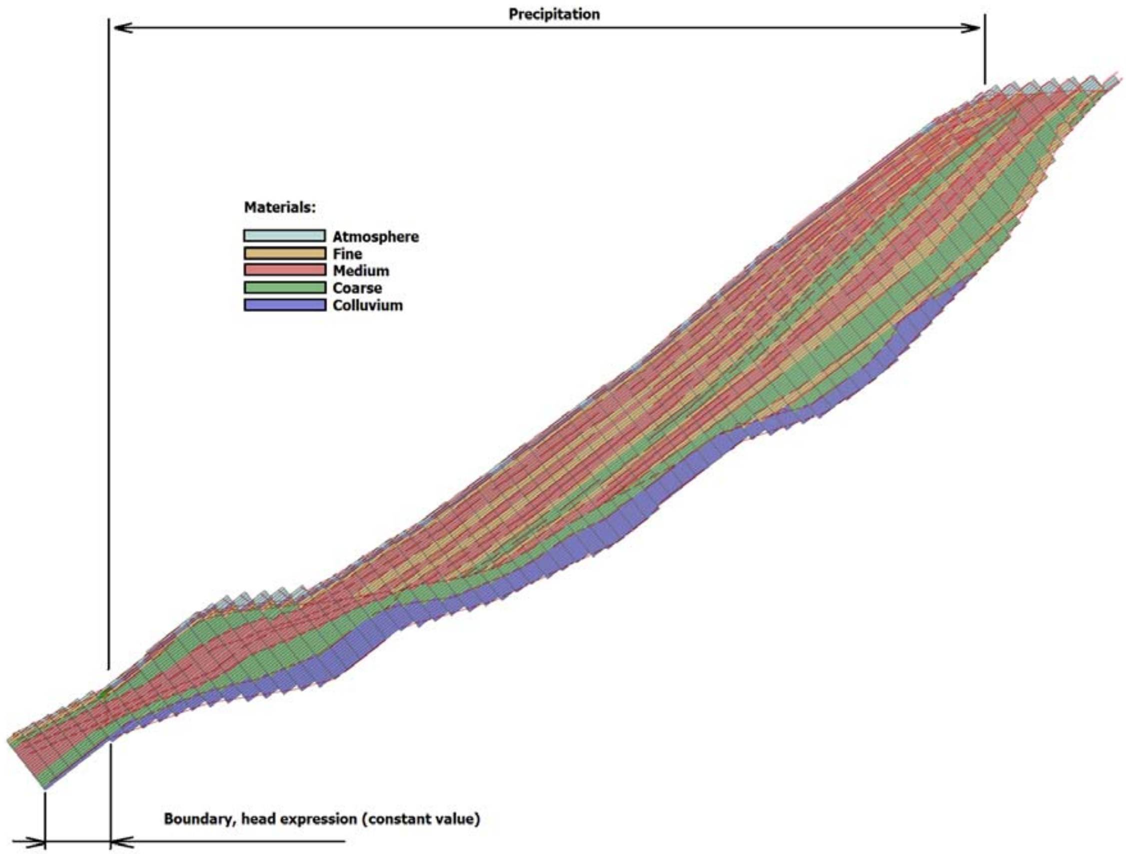

Figure 1. Conceptual model and grid being used for geochemical modeling using TOUGHREACT; 6x1 meter elements. 3,125 elements total

5. STATUS OF INVESTIGATION

Several major modifications of the TOUGHREACT code were necessary before it could be used to model the weathering mechanisms observed in the Questa mining site. Some modifications were foreseen, some were not. A summary of these modifications is included in the appendix.

The original GHN rock pile mesh for TOUGHREACT, 3x1 meter grid block element size (containing approx. 6,000 elements), turned out to have extensive calculation times when attempting to reach equilibrium flow conditions. Therefore, we built a new mesh containing 3,125 elements, including atmospheric cells, and elements were designed with a grid element size, 6x1 meters. The drawback of the new mesh is a slight compromise of the rock pile geometry when compared to the geometry presented in SVFlux mesh. The mesh was presented in Figure 1. We are considering returning to the 3x1 element size mesh when computational times using the GHN rock pile layered configuration are better known and we will be able to make faster simulation runs with our parallelized code. We are waiting for the Soilvision results for the other benchmarks. Once these are received, we will attempt to match the TOUGHREACT hydrological results with those.

<u>Geochemical Modeling</u>

We are moving ahead in building our geochemical model of the Goat Hill North rock pile despite the delays in receiving the field mineralogical results from NMT and the hydrological results from Soilvision. Mineralogies of the various layers are being estimated using the data available in the current Questa database for GHN including the samples used in the humidity cell experiments. We are using the VOXLER software to plot the field data in three dimensions to see how the minerals are distributed on a three-dimensional basis. We will then use VOXLER krigging techniques to determine the mineralogical composition of each layer in a two-dimensional system as much as possible. Figures 4-6 below give a preliminary view of some of the pyrite data in the database. The actual plot is three-dimensional, but we can only show a few views here. We will develop similar plots for all the other minerals and from those data determine the mineralogies of the various layers in our geochemical model.

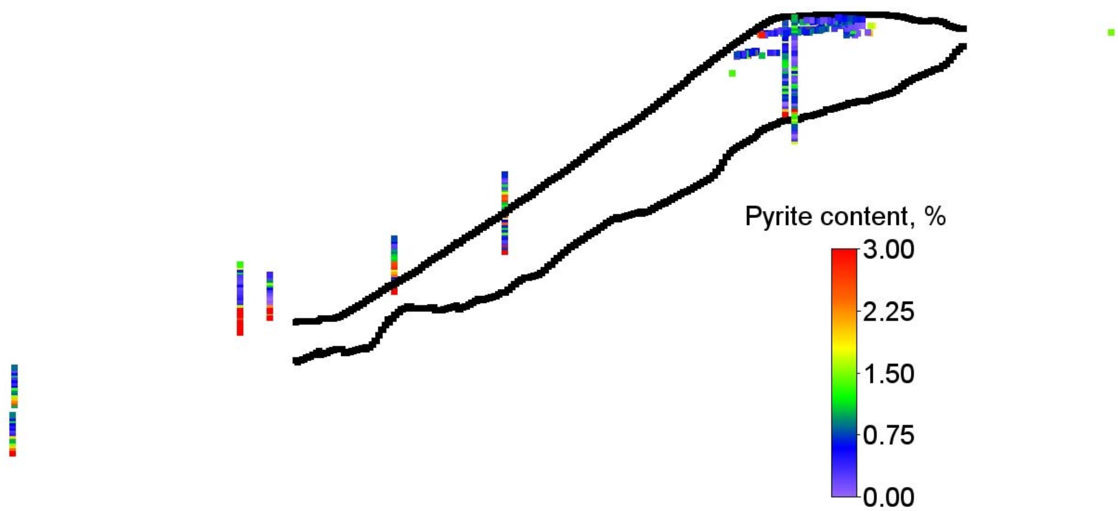

Figure 4. Distribution of pyrite concentration in 3D for the GHN rock pile as seen from the side. The cross-sectional plane used for the 2D model is shown for comparison. This is most of the pyrite data found in the database and not all the points are in the plane of the cross-section. There was one point that was 13.45% pyrite, but we are only showing points 3% or less so that the distribution can be seen better.

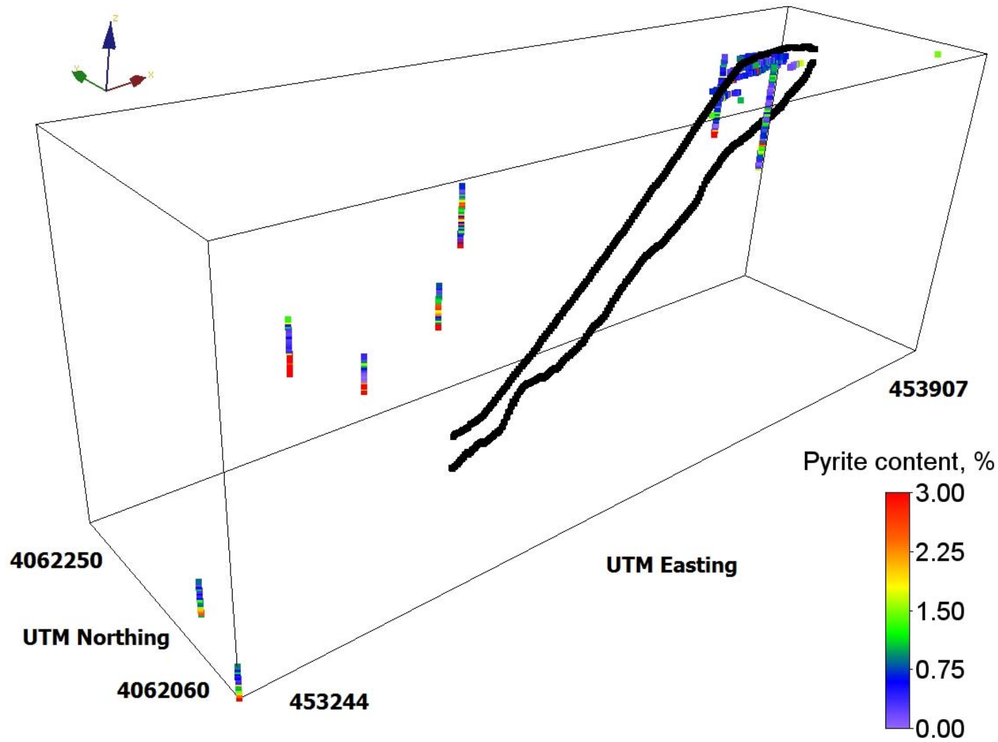

Figure 5. GHN pyrite content, view from perspective. Bounding box of sampling data location limits is included.

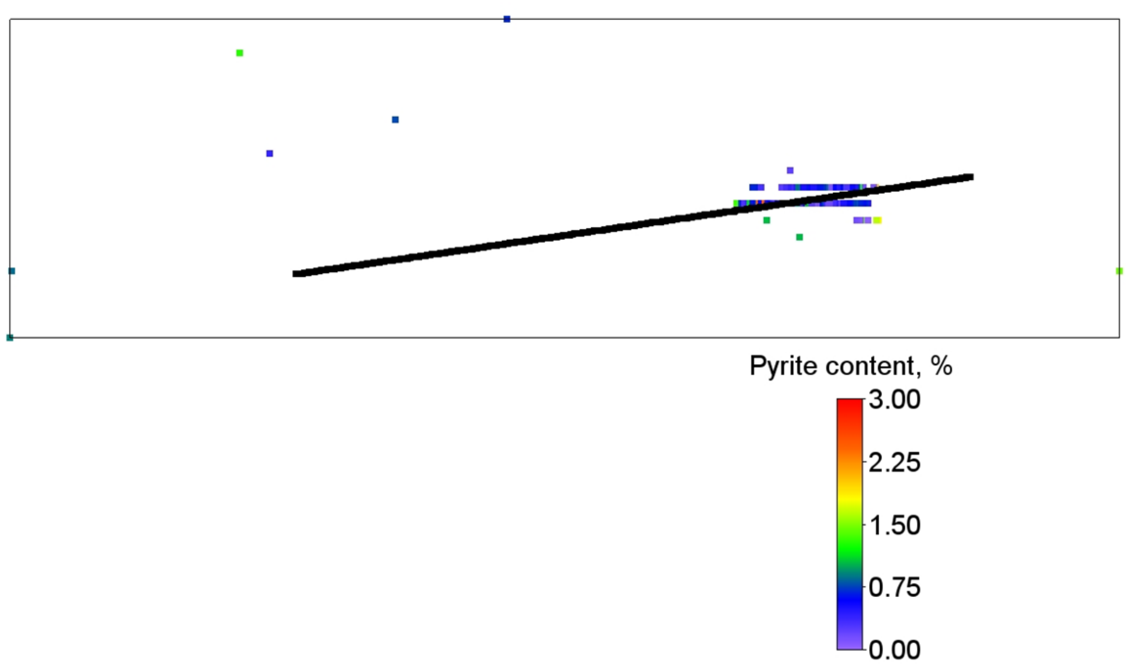

Figure 6. GHN pyrite content in 3D, view from top, including a bounding box of sampling data location limits. Position of sampling locations relative to the two-dimensional model cross-section (shown as a solid black line). Note the close proximity of the trench work to the two-dimensional cross-section.

Table 2 below shows the number of species we have incorporated into the TOUGHREACT geochemical model so far and we may consider other minerals in the future. We have made some preliminary runs with our geochemical field model with these 15 minerals and 85 species using the EOS4 module, however, as mentioned earlier, we found that we need to further work on appropriate selection of primary and secondary species to get more reasonable results. Presently, the chemical reactions are being tested using the TOUGHREACT humidity cell model before we continue with the GHN field model.

In addition to the improvements we have made to the TOUGHREACT code mentioned in the appendix, the following modifications to TOUGHREACT have also recently been made:

- Fe^{2+}/Fe^{3+} disequilibrium. This feature uses mineral kinetics in Toughreact, so no extensive code changes were needed. Feature is tested.
- Two mass-balanced pyrite oxidation reactions, oxygen and ferric, were added. Previously, the second reaction could only influence the rate of the first reaction. Feature is tested.
- Kinetically controlled bacterial growth and death rate, for Fe^{2+} to Fe^{3+} oxidation additional mechanism. Feature is tested.
- Shrinking-core mineral dissolution. The coding of the feature is nearing completion and will be tested soon.

We also attempted to develop gas flow patterns within the pile that would show the effect of convection in the existing GHN model, using Toughreact with reactions turned off. The heat of reaction was introduced to rock layers as a constant heat generation term with maximum values set to 0.4 Watt/m^3 and later 0.2 Watt/m^3. At these rates of heating, the upper part of the GHN rock pile reached temperatures above 100 C within 30 to 60 years. However, the temperature profiles that would create the desired convective flow of gas were not achieved. We will continue to make these preliminary runs until we understand how convective air currents develop over time. For these preliminary runs we also did not have heat exchange with the underlying bedrock.

Future work in geochemical modeling will now concentrate on testing all new reaction features mentioned above in humidity cell modeling. We will also complete the hydrological benchmarks in Toughreact in cooperation with Soilvision, after which we will perform GHN field model runs with reactions and their heat generation.
We also further optimize Toughreact code, where possible.

Table 2. Species incorporated into the TOUGHREACT geochemical model – 85 different species

'PRIMARY AQUEOUS SPECIES'	'AQUEOUS COMPLEXES'		'MINERALS'	'GASES'
'h2o'	'oh-'	'fef2+'	'fe(oh)3(s)'	'co2(g)'

'h+' 'ca+2' 'mg+2' 'na+' 'k+' 'fe+2' 'sio2(aq)' 'hco3-' 'so4-2' 'alo2-' 'f-' 'o2(aq)'	'al+3' 'aloh+2' 'al(oh)2+' 'al(oh)3(aq)' 'al(oh)4-' 'al(so4)2-' 'alf+2' 'alf2+' 'alf3(aq)' 'alf4-' 'also4+' 'caso4(aq)' 'cahco3+' 'caco3(aq)' 'caoh+' 'caf+' 'fe+3' 'fehco3+' 'feco3(aq)' 'fe(oh)2(aq)' 'fe(oh)2+' 'fe(oh)3(aq)' 'fe(oh)3-' 'fe(oh)4-' 'feco3+' 'fef+' 'fef+2'	'fehso4+2' 'feoh+' 'feoh+2' 'feso4(aq)' 'feso4+' 'nahco3(aq)' 'naalo2(aq)' 'naoh(aq)' 'naco3-' 'nahsio3(aq)' 'naf(aq)' 'naso4-' 'co2(aq)' 'co3-2' 'mgso4(aq)' 'mgco3(aq)' 'mgf+' 'mghco3+' 'mgoh+' 'kso4-' 'khso4(aq)' 'koh(aq)' 'hso4-' 'hf(aq)' 'hf2-' 'halo2(aq)' 'h3sio4-'	'calcite' 'pyrite-2' 'gypsum' 'kaolinite' 'illite' 'k-feldspar' 'chlorite' 'smectite-ca' 'albite~low' 'anorthite-a1' 'fluorite' 'goethite' 'epidote' 'jarosite'	'o2(g)'

6. RELIABILITY ANALYSIS

The reliability of the model will be tested, at least for the hydrological aspects, using the four benchmarks mentioned earlier, comparing Soilvision's results with ours. The geochemical portion will initially be tested by comparing the results obtained with our version of TOUGHREACT with other models published in the literature for rather simple, well-defined systems. As with all models, true validation can only be accomplished with accurate field data and we will use all available GHN field data for this purpose. Unfortunately, there is not an extensive amount of field data available for the GHN rock pile, particularly water chemistry data and temperature profile data.

In addition, predictions depend on how well the model simulates the dominant mechanisms involved in the process or processes and, while we have incorporated more mechanisms and reactions than any previous model, there is a certain degree of uncertainty in the resulting predictions. One of the least understood mechanisms is the growth of bacteria and its effect on pyrite oxidation. Humidity cell results indicate that this can occur sporatically and non-uniformly. Results also depend on the initial mineralogical composition of the rock pile, which, as we know, is not exactly known and difficult to reconstruct. Nonetheless, modeling can still be a powerful tool for understanding what might be possible under certain defined conditions.

7. CURRENT CONCLUSIONS

It is difficult to draw any final conclusions at this time, since a lot of this work is still on-going. Nevertheless, we are making great progress and should have at least a preliminary mineralogical field model working in a month or so. In any case, based on the humidity cell results and modeling completed to date, it is clear that dissolution of clay minerals is evident, and that there is significant pyrite oxidation causing the pH to fall to below 4 in various parts of the rock pile. The pH distribution and the formation of cementing material in a rock pile is probably uneven and very heterogeneous within the rock pile. This is caused by flow and mineralogical heterogeneities within the pile as well as variable wetting/drying cycles.

There may be significant amounts of secondary minerals, such as jarosite and gypsum that form throughout the pile over time and these minerals may be involved in the development of cementation together with the fine grained material identified as certain minerals and quartz particles. It is unclear which secondary minerals may form at various locations within the rock pile over time and their duration, but, it is clear that the formation of stable aqueous complexes with aluminum prevents some of those from forming. The duration of the cementing material, if it involves jarosite, gypsum, iron oxyhydroxdes and/or silica particles appears to be long-lasting, at least for 100 years and possibly 1000 years. Final modeling simulations will confirm this.

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9. TECHNICAL APPENDICES

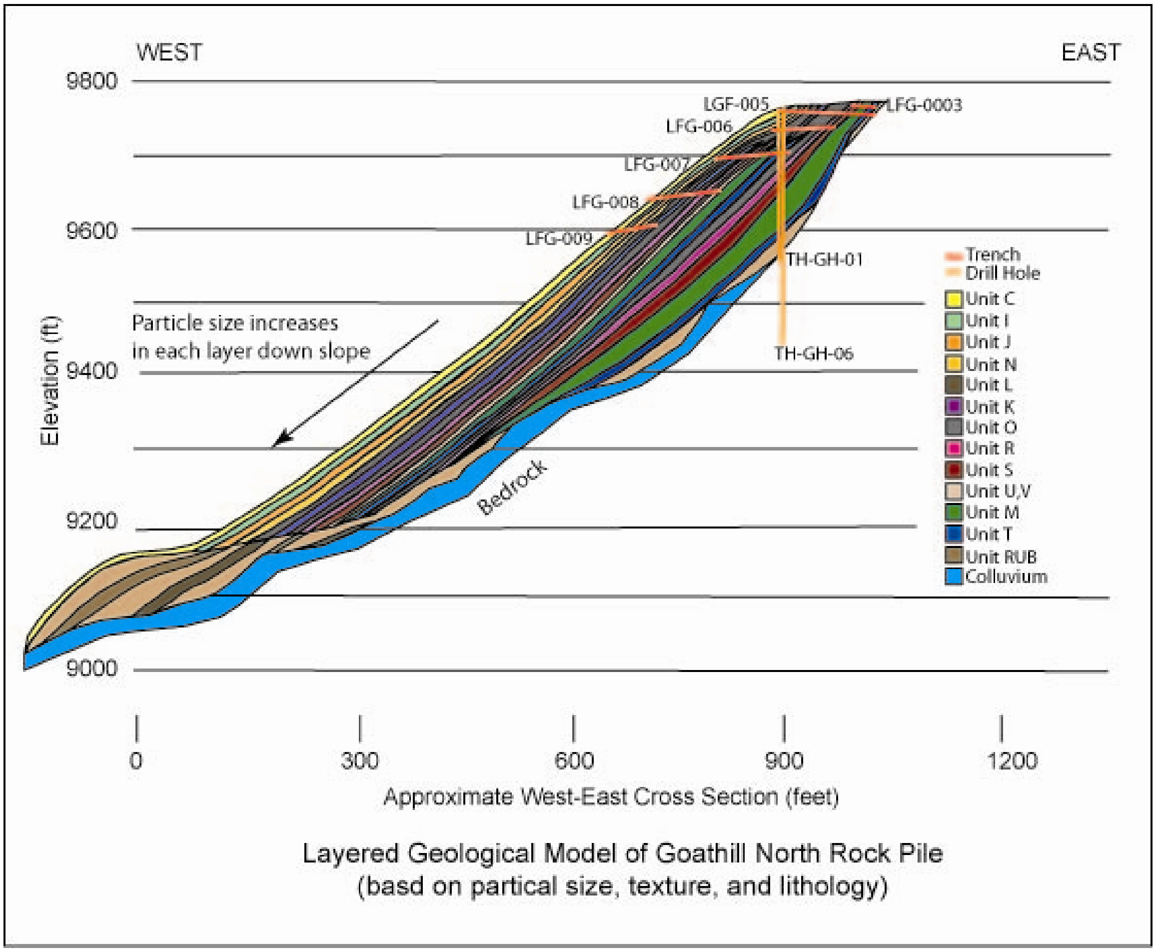

Figure A-1. Conceptual Geologic Model from New Mexico Tech (VTM)

<u>**Comparison of steady flow results between SVFlux and TOUGHREACT.**</u>

We performed flow runs in TOUGHREACT using EOS9 and EOS4 modules. The EOS9 module considers flow of water, a single component only and gas phase is a passive bystander at constant pressure. The EOS4 module includes mobile gas phase and is being used for the geochemical modeling. We declared new flux sections in the SVFlux model that were rotated by 38 degrees in order to better compare the flow in the TOUGHREACT mesh. Figure 3 presents SVFlux mesh with changed flux sections.

Soil water characteristic curves (SWCC) and relative permeability (hydraulic conductivity, HCond.) functions were needed in order to obtain agreement of the flow through the rock pile. The SVFlux model we received for comparison used the following functions:

- SWCC, 1 model:F redlund and Xing (FX) (Ebrahimi-B, et al., 2004; Vanapalli, 1998; Fredlund, 1994)
- HCond., 2 models: Fredlund and Xing, and modified Campbell (MC) (Fredlund, 2004; Thieu, 2001)

However, the functions above were not available in TOUGHREACT and the closest functions were:

- SWCC: van Genuchten (VG)
- HCond.: van Genuchten-Mualem (VGM)

As an example, we made three runs simulating GHN hydrological conditions for 100 years from initial conditions of 25% water saturation. It should be noted that equilibrium was not achieved although most of GHN rock pile appears to be very close to it. In subsequent runs we plan to use better initial conditions allowing us to reach equilibrium faster.

We initially attempted to find VG and VGM parameters that would match the SWCC and HCond curves. However these functions could not be matched with sufficient agreement and results were significantly different, as shown in Figure A-2 in the appendix. The most important difference was that SVFlux predicted the majority of flow through coarse material layers, while TOUGHREACT through fine layers.

Further, we changed both the SWCC and HCond. functions in Soilvision to VGM. We found also new VGM parameters for TOUGHREACT and compared results again. TOUGHREACT flow turned out to be significantly different with new VGM parameters and resembled more those of SVFlux, however, colluvium received majority of flow in TOUGHREACT simulations. Comparison is presented in Figure A-3

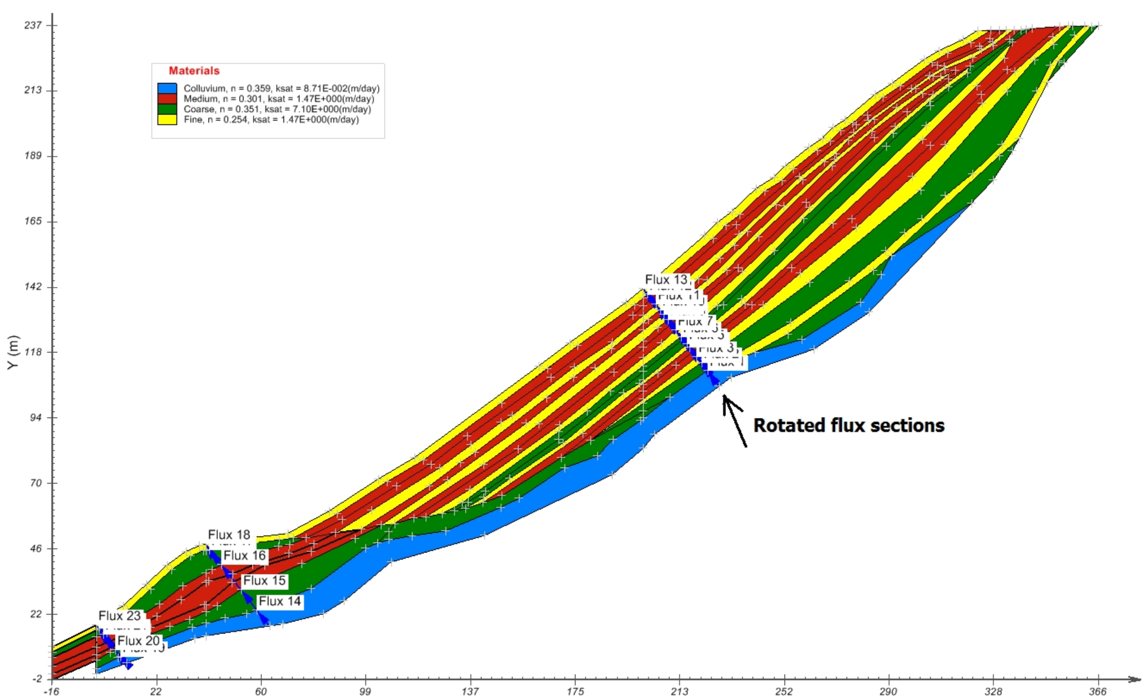

Figure A-2. SVFlux GHN rock pile mesh with rotated flux sections to compare with the TOUGHREACT model..

The implementation of exactly the same functions in TOUGHREACT as those used in SVFlux appears to be necessary in order to find SWCC and HCond curves for TOUGHREACT that would yield comparable flows in the various layers in GHN rock pile. We are presently implementing at least 3 new functions. Figure A-4 shows a comparison of test results. We still observe significant differences between SVFlux and TOUGHREACT, however, we believe, that further refining the SWCC and HCond functions parameters will allow us to match the flow with sufficient precision. Figures A-5 to A-7 present visualized water flow velocities with logarithmic arrow length scaling from our TOUGHER software.

Although the flows through the individual layers from the two models (Soilvision and TOUGHREACT) are still somewhat different, the total flow at any given cross-section is rather close. Table 1 below shows the ratio of the total flow for TOUGHREACT versus Soilvision at three locations in the rock pile.

Table 1. Comparison of the total cross-sectional flow between TOUGHREACT and SVFlux at three locations in the Goat Hill North rock pile after 100 years of continuous precipitation

Flux Section (measured from toe)	Toughreact Flow/SVFlux Flow (%)
200 m	101.9
40 m	98.4
0 m	97.7

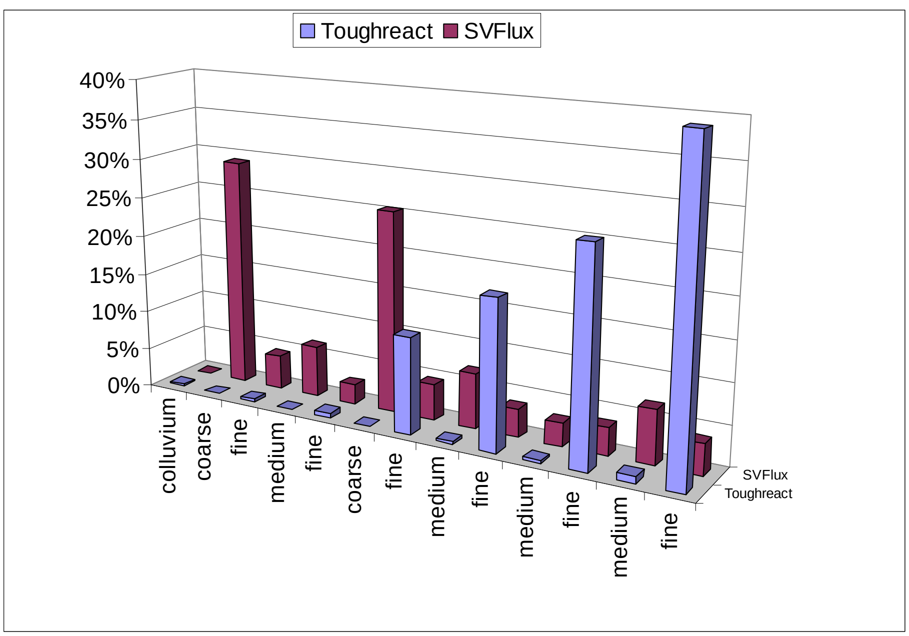

Figure. A-3. Flux sections comparison between SVFlux and Toughreact. FX and MC functions in SVFlux vs. VG and VGM functions in Toughreact.

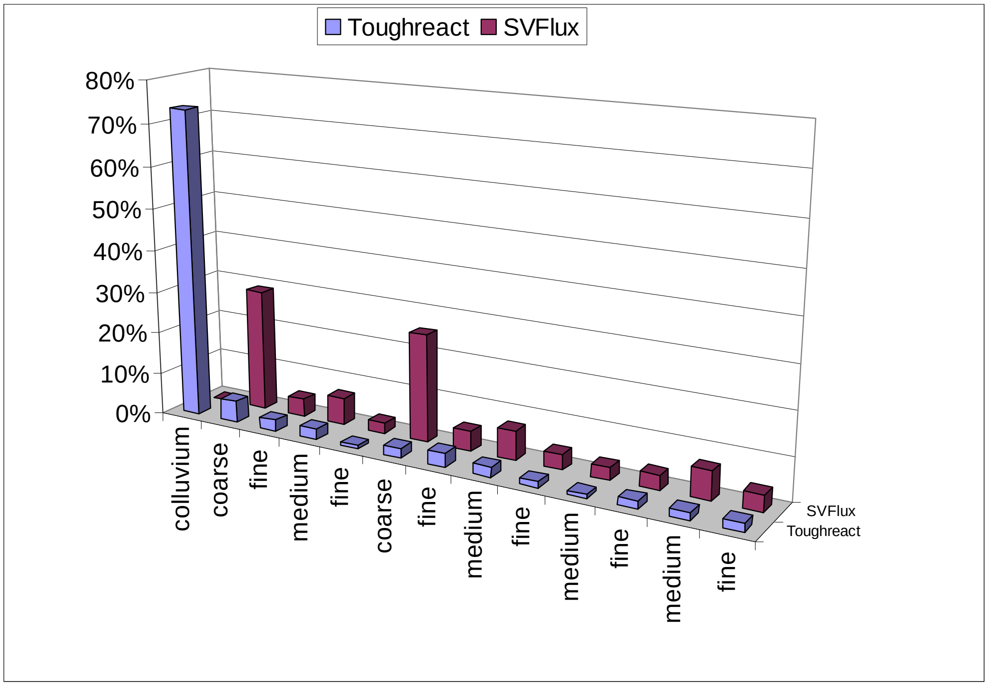

Figure A-4. Flux sections comparison between SVFlux and Toughreact. VGM functions in SVFlux and VG and VGM functions in Toughreact.

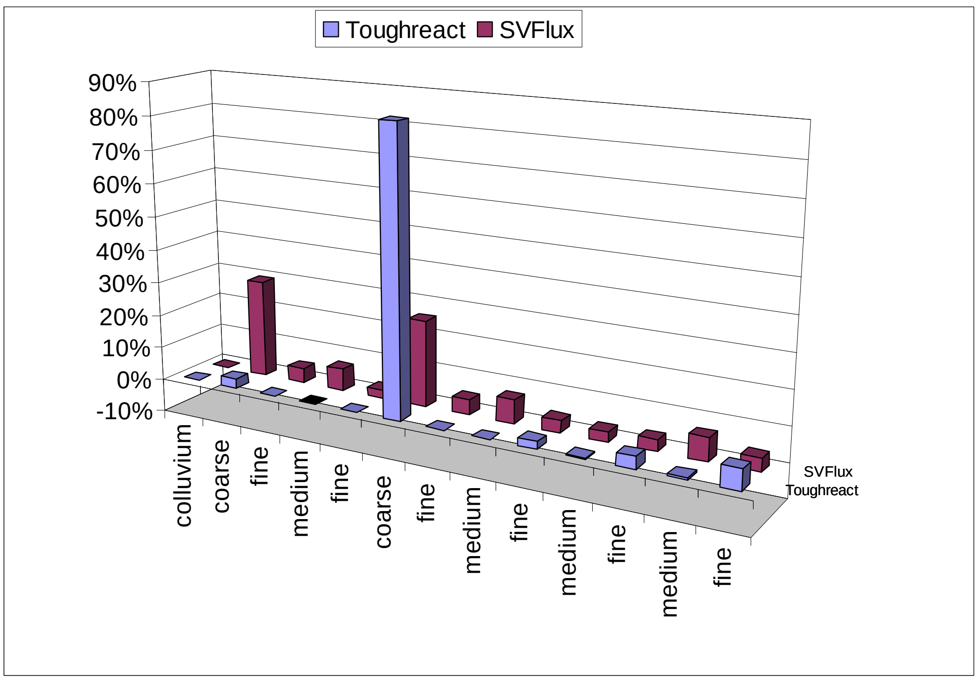

Figure A-5. Flux sections in the individual layers comparison between SVFlux and Toughreact. FX and MC functions in SVFlux vs. implemented and tested functions in Toughreact.

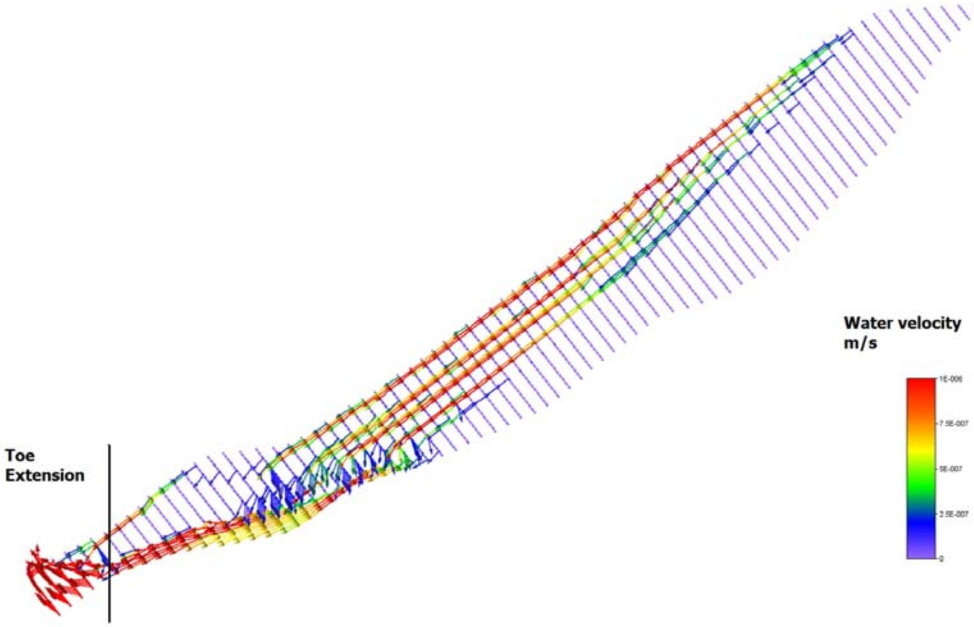

Figure A-6. Water flow velocities as shown in VOXLER. Simulation used EOS4 and VG, VGM parameters in first attempt to match GHN conditions between SVFlux and Toughreact

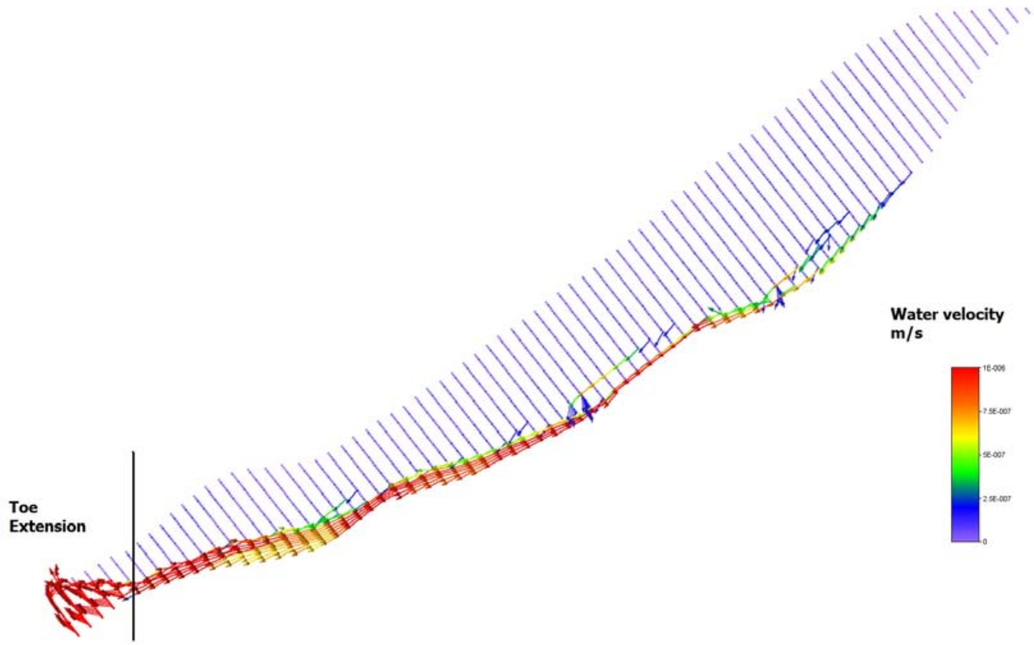

Figure A-7 . Water flow velocities. EOS9 and VG, VGM parameters with improved match of functions parameters.

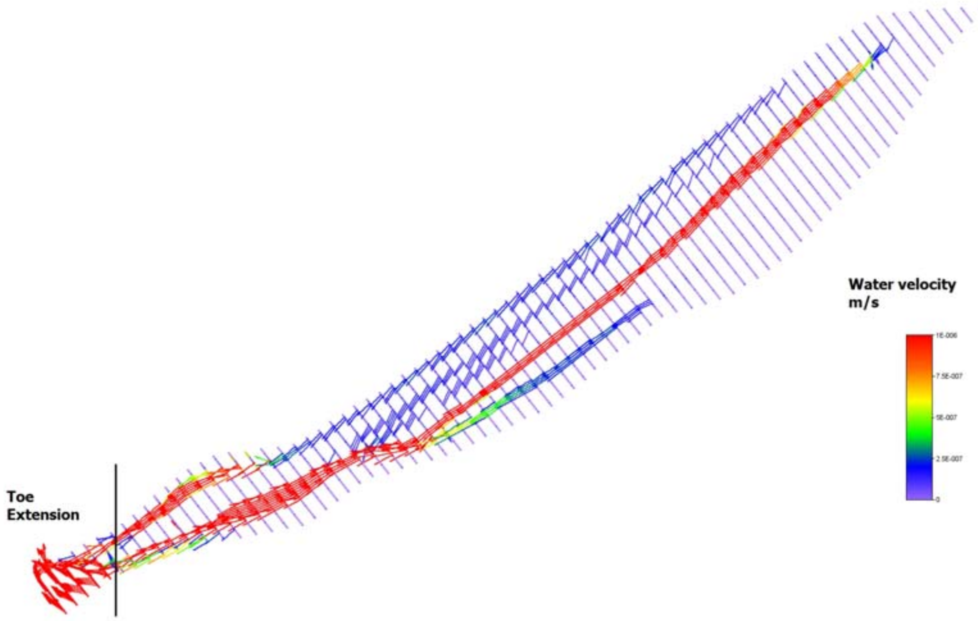

Figure A-8. Water flow velocities. EOS9 and FX and MC functions in first attempt to match GHN conditions between SVFlux and Toughreact.

<u>Modifications made to TOUGHREACT code</u>

Several major modifications of the TOUGHREACT code were necessary before it could be used to model the weathering mechanisms observed in the Questa mining site. Some modifications were foreseen, some were not.

1. **The current TOUGHREACT code is not very user-friendly and setting up a particular simulation with a large number of grid elements and connections requires a tremendous amount of time.**

We decided to develop our own graphical interface program that would (1) generate the input files necessary and that (2) could be use to visualize the output. Although a few commercial programs could be used, we found them to be very expensive and were not flexible enough for our purposes. The graphical interface program is complete and is currently being tested, with minor modifications being made as necessary. A full description of the software with a user's manual will be included in the final report for this project. A screenshot of the software in mesh generation mode is given in Figure 2 below.

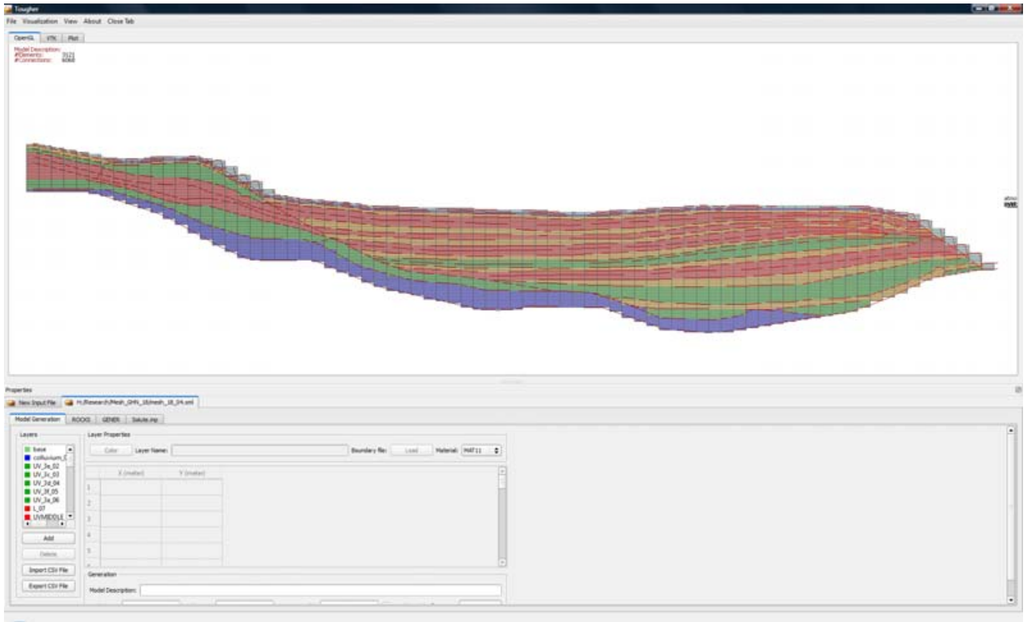

Figure 2. An example of the TOUGHER software. A screenshot in mesh generation mode with the most recent 6x1 meters mesh

2. **The current TOUGHREACT code is not designed for parallel processors.**

We developed our own version that would run on any number of parallel processors since we would be working with models that require high resolution and thus a significant number of grid elements and computation time. The parallelization using OpenMP is complete and the parallelization using MPI is also complete. However, due to the software limitation of Center of High Performance Computing (CHPC), our MPI version cannot utilize more than 4 CPUs. Therefore we decided to use the slightly more efficient OpenMP architecture to fully utilize a shared-memory system. Even before parallelization, we modified the code to run over 20% faster on a single processor by eliminating unnecessary string comparison. The TOUGHREACT code parallelized using OpenMP works on shared memory computers. Presently the chemical solver in TOUGHREACT makes use of parallelization, which takes the majority of the computational time. The flow solver is more difficult to parallelize, but it consumes much less time, thus its parallelization is not presently crucial. Parallel code works fully in TOUGHREACT version 1.0. We also upgraded TOUGHREACT to version 1.2 and we have completed the addition of parallelization to this version as well.

3. **The current TOUGHREACT code does not include heats of reaction in its energy balances**.

We modified the code to include heats of reaction.

4. **The current TOUGHREACT code is limited to a number of functions to describe the soil water characteristic curve**.

We had to include the Fredlund and Xing model (Fredlund, 1994) in order to obtain comparable hydrodynamic results with SoilVision's model. Likewise, we had to add the Fredlund and Xing model and the modified Campbell model (Fredlund, 2004; Thieu, 2001) to the TOUGHREACT code in order to match the hydraulic conductivity characteristics of the SoilVision model.

5. **The current TOUGHREACT code is limited to a structured set of geochemical reactions, allowing only those reactions with minerals to be kinetically controlled, all aqueous species are assumed to be in equilibrium. Thus, Fe^{+2} and Fe^{+3} are restricted to be in local equilibrium at all times and only one can be a primary species, typically the ferrous ion.**

This has been found to be a severe limitation of the model. For now it is better to use the Fe^{+2} ion as the primary species and the Fe^{+3} ion as the secondary species. This requires that all mineral reactions be written in terms of the primary species, often changing the chemical reaction. For example, the reaction in the TOUGHREACT database for the dissolution of K-jarosite, with Fe^{+2} as the primary species, is

$$K\,Fe_3\,(SO_4)_2\,(OH)_6 \;+\; 3H^+ \;\longrightarrow\; K^+ \;+\; 3Fe^{+2} \;+\; 2\;SO_4^{-2} \;+\; 4.5\,H_2O \;+\; 0.75\;O_{2(aq)}\;.$$

We are in the process of modifying the code to permit the disequilibrium of Fe^{+2}/Fe^{+3} so that the generation of Fe^{+3} can be kinetically controlled and the chemical reactions for the dissolution/precipitation of the minerals can be written correctly.

In summary,

- Parallelization of the TOUGHREACT code is complete using both OpenMP and MPI.
- A graphical interface program has been developed making TOUGHREACT more user friendly and is in the final stages of testing.
- We have been able to construct a hypothetical hydrological field model of GHN using TOUGHREACT that almost simulates the hydrological model developed by SOILVISION. Flow within the individual layers is being refined. We are in the process of running that model to duplicate the results from SOILVISION for several bench marks. Preliminary results indicate good agreement between our TOUGHREACT model and SOILVISION's model for the simple steady-state case benchmark. We are waiting for the other benchmark results from Soilvision so that we can compare our results.
- We have been able to construct a hypothetical geochemical field model of GHN using TOUGHREACT that includes at least 15 minerals and many aqueous complexes with several layers and mineralogical regions and we are starting to input the final mineralogical compositions of each layer.
- We are currently running the geochemical field model using the geochemical reactions defined in the humidity cell modeling work and have included even more aqueous complexes in the field model to see if the program can handle this many species. So far, it appears that we can obtain reasonable turn around times for a high resolution grid size for long periods of time, at least to 100 years. However, the geochemical reactions in the current TOUGHREACT database are not appropriate for our case and we are in the process of changing the database so that we can use our, more appropriate, reactions.