

Evaluating the effects of Uranium Kd on the restoration of ISR wellfields using PHT3D

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ABSTRACT: In-situ recovery methods accounted for about 95% of the uranium produced in the U.S. in 2007. The method extracts uranium by dissolution and mobilization of uranium minerals in sandstone aquifers. Geochemical changes that are important in the successful recovery of uranium are mainly related to oxidation of reduced minerals such as uraninite. However, these changes can also influence the approach and timeframe to achieve restoration of the aquifer. Often at the end of restoration, contaminant levels increase because of re-oxidation of uranium and from slow desorption of contaminants adsorbed to various mineral phases. Successful restoration strategies must consider the whole mining cycle process including subsequent groundwater flow of water into the restored aquifer. This paper explores the advantages of using groundwater flow and reactive transport models to understand the subsequent rock-water interactions during mining and restoration. Optimization can minimize the time required to mine the uranium and minimize the time and costs required for restoration.

1 INTRODUCTION

The in-situ recovery (ISR) process for uranium differs from conventional mining techniques in that the uranium resource is not excavated. Rather, the process employs a system of injection and recovery wells to access the roll front deposits from the surface without the need for a pit. The leaching agent, which contains an oxidant such as oxygen and either CO₂(gas) or sodium bicarbonate (baking soda) is injected through wells into the ore body in a confined aquifer to dissolve the uranium. This solution is then pumped via the recovery wells to the surface for processing. The method has several advantages over conventional mining. ISR mining requires low capital costs for mine development. There is no waste rock and no tailings pond. The technique requires a smaller workforce which, combined with the lower capital costs, make it profitable on lower grade uranium deposits.

2 FLOW AND REACTIVE TRANSPORT MODELING

The models used for this paper include MODFLOW and PHT3D. MODFLOW (Harbaugh et al., 2000) was written by the U.S. Geological Survey and is widely used and accepted by the hydrogeologic community. PHT3D (Prommer and Post, 2010) combines two modeling codes for reactive transport modeling. MT3DMS (Zheng and Wang, 1999) is used to solve the advection-dispersion equation and PHREEQC Version 2 (Parkhurst and Appelo, 1999) is used to calculate the chemical conditions at each transport step. Both MT3DMS and PHREEQC are in the public domain and, like MODFLOW, are widely regarded by the scientific community. These three modeling codes are among the most widely used by hydrogeologists and geochemists today. They can be used in conjunction to solve complex three-dimensional hydrogeochemical problems. ISR restoration is such a complex problem.

The modeling data were obtained from the Agencywide Documents Access and Management System (ADAMS) database maintained by the Nuclear Regulatory Commission (NRC). Several sources from the ADAMS database were incorporated into the generic model.

The purpose was to develop a “proof of concept” model capable of implementing the surface ionization and complexation model (SICM) (Dzombak and Morel, 1990) during the restoration of the generic uranium ISR mine.

The model consisted of several steps. The first step represented the ore recovery process (in-situ recovery) and during this step uraninite and pyrite were oxidized and dissolved. Kinetic based rate laws were used to add uranium, iron and sulfur into the ore recovery solution as a function of time. For uraninite, the rate law by Posey-Dowty et al. (1987) was employed with some minor modifications. For pyrite dissolution, the well-known Williamson and Rimstidt (1994) rate law was used. Iron from the dissolving pyrite was allowed to precipitate as the ferric oxide goethite, which for these simulations provided the hydrous ferric oxide (HFO) adsorption sites. Some goethite was present in the flow field prior to the start of mining.

The second step represented the restoration treatment. The oxidant supply is halted, which stops the uraninite dissolution, and water is flushed through the zone. Rather than using a simple groundwater sweep approach, the impact of different injection solutions which resulted in different distribution coefficients were examined in two simulations. One represented a solution that produced a high distribution coefficient for the system and the other solution produced a lower distribution coefficient for the system, this second solution is effectively diluted groundwater similar to those produced using reverse osmosis.

The final step was a groundwater recovery stage where the ambient groundwater was allowed to return to the previously treated zone. To expedite this step the model used a relatively small groundwater gradient of 0.0001 feet/foot representative of field conditions.

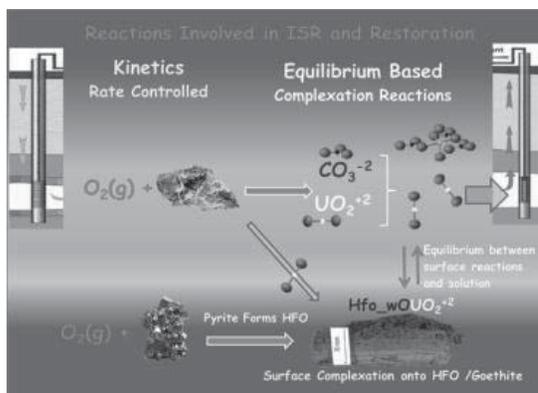


Figure 1 Surface ionization and complexation model

3 SURFACE IONIZATION AND COMPLEXATION MODEL

A simplified explanation of the SICM is illustrated in the right hand portion of Figure 1. As stated previously, oxygen (O_2) is added to an injection well along with CO_2 (gas) or $NaHCO_3$ into the roll front ore zone. The introduced O_2 dissolves uranium (coffinite or uraninite) to form uranyl ions (UO_2^{+2}). Uranyl ions complex with the carbonate ion (CO_3^{-2}) to form various uranyl carbonate complexes, such as $UO_2CO_3^0$, and $UO_2(CO_3)_3^{-4}$, these complexes are soluble and remain mobile in the groundwater. As explained above, pyrite (FeS_2) is oxidized to form the hydrous ferric oxide (HFO) substrate. Equilibrium is established between the uranyl complexes on the HFO surface and the various dissolved uranyl complexes.

3.1 The Distribution Coefficient (K_d)

The distribution coefficient (K_d) is the ratio of sorbed constituent to dissolved constituent at equilibrium and has the units L/kg. The K_d can be used to calculate the retardation coefficient (R) by the equation:

$$R = 1 + \rho K_d/n_e,$$

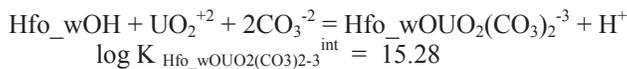
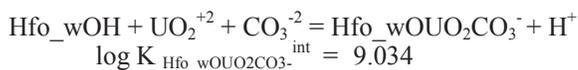
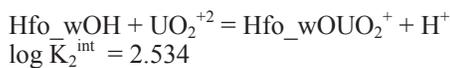
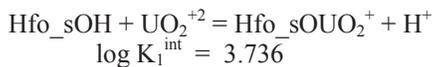
where: ρ is the bulk density, and n_e is the effective porosity of the aquifer material (Langmuir, 1997). The retardation coefficient is the velocity of the solute, in this case uranium, in relation to the groundwater velocity. A K_d of zero results in a retardation of 1, indicating the solute is moving at the same velocity as groundwater. A retardation value of 2 would result in uranium traveling at one-half the velocity of groundwater.

3.2 Sorption

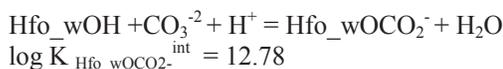
Sorption is the transfer of solutes from solution onto mineral surfaces. The sorbate, the species removed from solution, sorbs onto the sorbent, the solid onto which solution species are sorbed. In the ISR environment, sorption is the amount of uranium attached to a sorbing substrate, generally called HFO. For these calculations, the surface complexation reactions of Mahoney et al. (2009) were used, rather than the two surface complexation reactions defined by Dzombak and Morel (1990). This revised set of reactions corrects several issues related to uranium sorption that were present in the Dzombak and Morel compilation. The most significant issues with the reactions defined by Dzombak and Morel were: 1) the lack of experimental data to support the original values for the K_1^{int} and K_2^{int} surface complexation reactions and 2) failure to include any type of uranyl carbonate surface complexation reaction in the database.

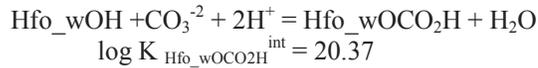
Comparisons between experimental and model results indicated that the previously defined K_1^{int} and K_2^{int} values tended to over predict the extent of adsorption in low pH or non-carbonate experimental setups. For experiments that included carbonate, particularly at pH values greater than 7.5, the original constants tended to underestimate the amount of surface complexation. Mahoney et al. (2009) refit the original $\log K_1^{int}$ and K_2^{int} values to previously published experimental data the revised $\log K_1^{int}$ and K_2^{int} values were smaller than those proposed by Dzombak and Morel; effectively correcting the low pH issue. Addition of two more surface complexation reactions that included uranyl and carbonate solved the second issue.

The four uranyl based surface complexation reactions were:



The surface site density for the weak sites (*Hfo_wOH*) was based upon 0.2 moles of HFO sites per mole of precipitated iron as goethite in these simulations. Their surface area was assumed to represent ferrihydrite at 600 m²/g, this effectively assumes that the HFO as defined by Dzombak and Morel (1990) is the only sorbent surface in the model. For these initial proof of concept calculations, whether the iron oxyhydroxide precipitate was goethite or ferrihydrite was not considered to be critical. For computational simplicity, strong sites (*Hfo_sOH*) were not defined in these proof of concept models. Two additional reactions have been added to the database. These reactions represent the formation of carbonate bearing surface complexes (Appelo et al., 2002):





For solution species the database defined by Guillaumont et al. (2003) was used as the primary source. Three alkaline earth uranyl tricarbonate (ternary) complexes as defined by Dong and Brooks (2006) were also included; consisting of $\text{CaUO}_2(\text{CO}_3)_3^{-2}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{\circ}$ and $\text{MgUO}_2(\text{CO}_3)_3^{-2}$.

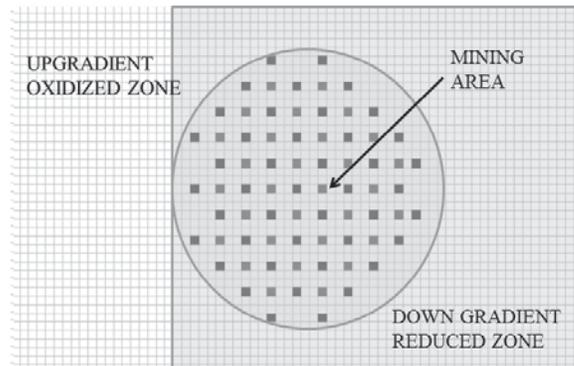


Figure 2 Theoretical ISR Mining Unit

The model we have developed is a simple theoretical model that we used to illustrate the sorption and desorption of uranium in the mining area. The mine unit is illustrated in Figure 2. To reduce the computational intensity there were several reactions, of lesser importance, that were not included in these simulations. The flow field of the theoretical mine unit is first solved using MODFLOW (hydraulic conductivity, porosity, storage terms, wells, and boundary conditions). After the MODFLOW simulation is completed, the MT3D parameters are added to solve for advection and dispersion. Simultaneously, the PHREEQC based reactions are added to distribute the uranium between the mobile groundwater system and the immobile aquifer matrix. A chemical database is used to define the various PHREEQC reactions. The parameters in the database include definitions related to the chemical components, as well as equilibrium constants for the 1) speciation reactions among the components, 2) the mineral phase solubility reactions, and 3) the surface complexation reactions. Kinetic information specific to the particular model, such as amounts of kinetic minerals and their surface area to volume terms, are also included in the PHREEQC input file. The detailed rate laws can be included in the input file or in the database.

During ISR restoration, the uranium concentration in groundwater can rebound during the post restoration phase. The purpose of the model was to determine what effect surface complexation has on uranium restoration and what efforts could be undertaken to maintain a low K_d . The low K_d should allow more uranium to be removed from the ISR mining unit during restoration and minimize the rebound effect. Since the hydrogeologic conditions and geochemistry of the ISR mining environment are complex, we wanted to determine if PHT3D could be implemented to solve these problems.

Initially, the mining phase of the ISR was simulated. For this model, the ISR mining technique was not allowed to completely remove uranium minerals from the mine unit. This step was completed to develop a mineral and sorbed uranium concentration field that was more representative of actual conditions than a uniform field. At some time the remaining mineral recovery becomes uneconomical. It is at this time that ISR restoration commences. The resulting uranium mineral field has residual uranium content in areas between recovery wells that exhibit low flow rates. Fewer pore volumes of the lixiviant have been available to dissolve all of the uranium at these locales. The resulting residual uraninite remaining in the mining unit is displayed in Figure 3. This is the modeled uraninite residual after about 3 years and was used as an input to the restoration model. It should be noted that the residual uraninite is problematic for ISR restoration.

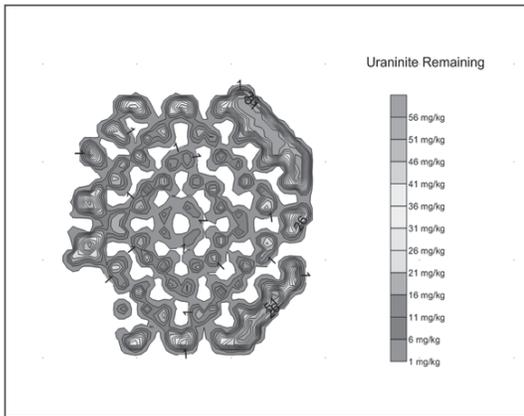


Figure 3 Remaining Uraninite after the Completion of Mining, concentrations report in units of mg/kg of water

ISR restoration typically includes injecting recovered groundwater that has undergone reverse osmosis (RO). The RO water is intended to rinse the residual metals, including uranium, from the mining unit and return the mining unit to pre-mining concentrations. Typically, fewer injection and recovery wells are employed for restoration. The reduction in the number of wells results from the quantity of RO water available and the reduced pumping and injection requirements.

9.1 Mineral Phases

In our investigation we included four mineral phases. For this proof of concept model we did not include any silicate bearing minerals in the model. The minerals we did include in the calculations and the respective concentrations are summarized in Table 1 below. Uraninite, pyrite and calcite comprise the most significant non-silicate minerals in the sandstone. Goethite and the resultant HFO surface are the products of pyrite oxidation. Uraninite and pyrite were defined as kinetic immobile phases and their dissolution was controlled by rate laws. Their concentrations varied between the mining unit and the area outside the mining unit, where they were set to zero concentrations. Calcite and goethite were assigned as equilibrium phases and their precipitation or dissolution were considered instantaneous equilibrium processes. More mineral phases are expected to be added as the model is applied to an active mining unit with time varying data.

Table 1 Mineral Phases. To accommodate the PHREEQC based calculations concentrations represent moles/L of solution

Mineral	MINIMUM PRE-RESTORATION CONCENTRATION (moles/L)	MAXIMUM PRE-RESTORATION CONCENTRATION (moles/L)
GOETHITE	1.13E-04	4.20E-04
URANINITE	0	4.90E-03
PYRITE	0	9.00E-02
CALCITE	0.1	0.1

9.2 Model Components

In our investigation we included 13 chemical components (Table 2). These components do not represent a complete list of the components present in the water contained in the aquifer and

lixiviant water. Nevertheless, they are the essential components required for the simulation of the restoration process. These components, along with the mineral phases, provide the building blocks for the myriad of components and phases potentially produced in the reactive transport model. As with the mineral phases, additional components are expected to be added as the model is applied to an active mining unit.

In addition to modeling the current restoration methods, we also modeled the effects of continuing to inject NaHCO_3 after O_2 is terminated. Our thought was that considerable money and effort had been expended to mobilize uranium, continuing to inject NaHCO_3 would continue to keep it mobile during restoration. Two models were created using different NaHCO_3 concentration in the injected water. The remaining 12 chemical components were injected at the same concentrations for both model simulations. The different NaHCO_3 concentrations are listed in Table 2. The lower concentration is indicative of the amount of NaHCO_3 remaining in the groundwater after undergoing RO. The higher NaHCO_3 concentration represents RO water augmented with NaHCO_3 to maintain a low K_d .

Table 2 Model Chemical Components

	UPGRADIENT CONCENTRATION (mg/L)	POST MINING CONCENTRATION (mg/L)	GRAMS/MOLE	UPGRADIENT CONCENTRATION (Moles/l)	POST MINING CONCENTRATION (Moles/L)	HIGH K_d INJECTION WATER (Moles/L)	LOW K_d INJECTION WATER (Moles/L)
Ca	44.10	313.40	40.078	1.10E-03	7.82E-03		
Mg	9.00	59.50	24.305	3.70E-04	2.45E-03		
Na	12.20	80.80	22.98	5.31E-04	3.52E-03	0.0001	0.01
K	8.00	13.40	39.09	2.05E-04	3.43E-04		
HCO3	215.00	720.20	61	3.52E-03	1.18E-02	0.0001	0.01
SO4	91.00	380.60	96.06	9.47E-04	3.96E-03		
Cl	4.70	212.60	35.45	1.33E-04	6.00E-03		
ALK	177.00	591.00	100.9	1.75E-03	5.86E-03		
Fe	0.05	0.05	55.84	8.95E-07	8.95E-07		
U	0.05	40.19	238.028	2.10E-07	1.69E-04		
O	7.00	0.00	16	4.38E-04	0.00E+00	0.00044	0.00044
pH	8.00	6.78		6.78E+00	8.00E+00	8.2	8.2
pe	11.00	11.00		1.10E+01	1.10E+01	11	11

The high K_d (low NaHCO_3) baseline restoration model was pumped until uranium concentration was less than 30 micrograms per liter ($\mu\text{g/L}$), the maximum concentration limit (MCL) for uranium. The model simulation included 3 years of high K_d restoration water in the injection wells followed by 7 years of observation to determine if uranium concentration rebound occurred. Our final calculated pore volume required to reach the MCL was nine pore volumes. A 3 percent bleed (difference between pumping and injection rates) was maintained to force flow towards the well field so that no excursions would occur.

The low K_d (High NaHCO_3) restoration model used the low K_d water composition in injection wells for a period of 3 years followed by 3 years of high K_d RO water. This step was essential to remove the remaining uranyl carbonate dissolved in the mine unit after the NaHCO_3 injection was terminated. The system was then observed for 4 years to determine if uranium concentration rebound would occur. The 3 percent bleed rate was also maintained for this simulation.

10 MODEL RESULTS

The modeling results indicate that the PHT3D model is robust and can simulate the complex nature of advection-dispersion and chemical reaction of the ISR mining unit. Additional calibration may be required to better fit the parameters to site conditions.

As previously stated, the model was executed using different concentrations of injected NaHCO_3 ; one that was expected to result from the RO operations and one where the NaHCO_3 content in the injection wells was augmented. For comparison purposes, results from the two models were output to an external file that was later processed in a number of ways. First, the dissolved uranium content at a point near the center of the mining unit (model node 35, 35) was extracted to obtain a time-concentration graph at a single point. These data are presented in Figures 4 and 5. The model results clearly indicate that the addition of NaHCO_3 has had a

significant effect on the dissolved uranium in the model cell. The rebound effect is significant in the model run simulating the RO water only; whereas it is absent in the augmented water.

Additional data was extracted for the remaining sorbed uranium from both models at the termination of restoration pumping. A comparison of Figures 6 and 7 illustrate far larger amounts of sorbed uranium remain in the high K_d model. The lesser amount of sorbed uranium in the low K_d model significantly reduces the amount of uranium available for desorption after restoration pumping has terminated.

Finally, data was extracted as an average concentration over the mining unit. These data included the time and average dissolved and sorbed concentrations. Figures 8 and 9 summarize the average modeled uranium content, both dissolved and sorbed onto the HFO surfaces. The difference is obvious. Augmented injection water results in very low averaged sorbed uranium content, whereas significant amounts of uranium are present on the HFO surfaces when only RO water is injected during restoration. The resulting decrease in the uranium concentration rebound effect is also clearly observed in the augmented simulation.

The above data were used to calculate the average K_d for each output time. This was done by dividing the sorbed concentration by the dissolved concentration. The results of the calculations are shown in Figures 10 and 11. The results indicate that the low K_d injection water, water augmented with NaHCO_3 , does in fact exhibit a lower K_d in comparison to the RO injection water. The calculated augmented K_d is nearly zero for the period when rebound of the uranium concentration typically occurs.

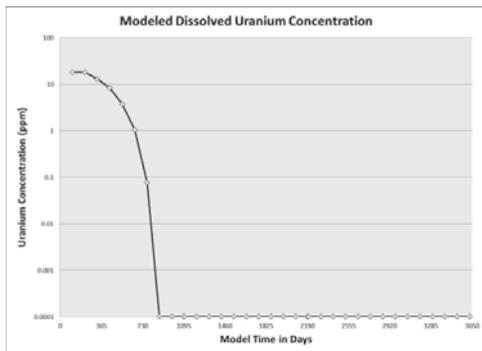


Figure 4 Low K_d (High NaHCO_3) Model Results at Model Node 35, 35

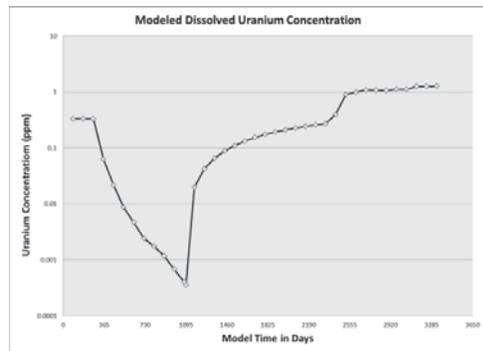


Figure 5 High K_d (Low NaHCO_3) Model Results at Model Cell 35, 35



Figure 6. High K_d Residual Sorbed Uranium at the End of Restoration Pumping

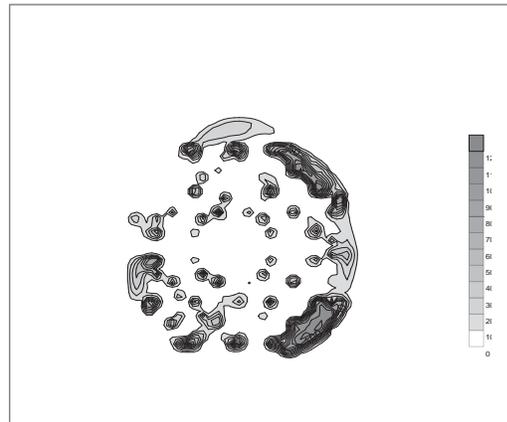


Figure 7. Residual Sorbed Uranium at the End of Restoration Pumping

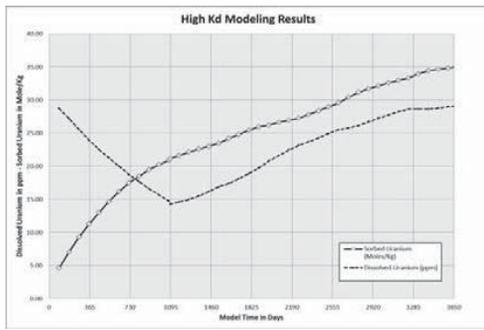


Figure 8. Average Dissolved and Sorbed Uranium Content in Mining Area

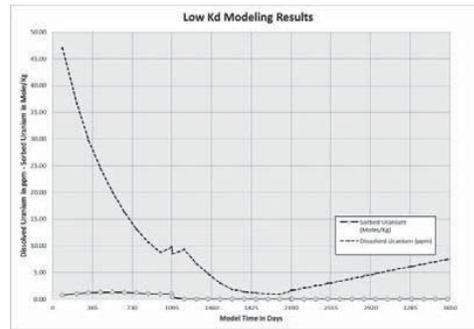


Figure 9. Average Dissolved and Sorbed Uranium Content in Mining Area

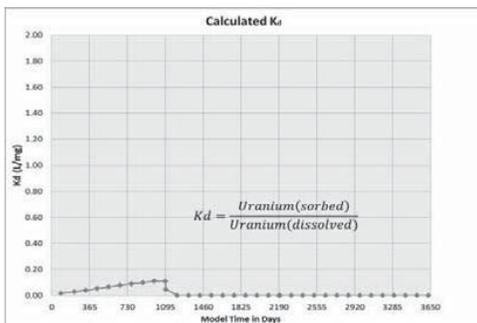


Figure 10. Calculated Kd for Low Kd Injection Water

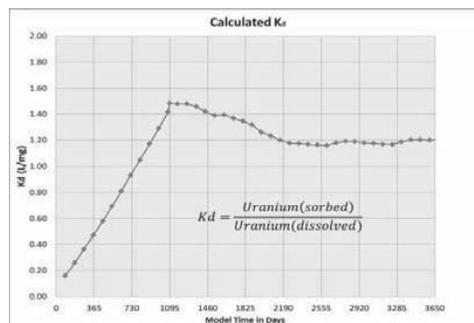


Figure 11. Calculated Kd for High Kd Injection Water

CONCLUSIONS

Based on the reactive transport modeling results, the model PHT3D is capable of simulating the basic physical and chemical processes that occur in ISR mining conditions. The model was used to simulate the mining process and the resulting conditions were implemented as initial conditions for the restoration model. During restoration, when the SICM processes become important, the model was able to produce reasonable results the matched the observed data, at least on the conceptual level.

The next logical step in the process is to obtain data required for a calibrated transient model and include additional mineral phases and chemical components. The additional data will allow a more robust simulation of the processes that occur in the ISR environment.

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