Reactive transport modeling at uranium *in situ* recovery sites: uncertainties in uranium sorption on iron hydroxides

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Abstract Geochemical changes that can occur down gradient from uranium *in situ* recovery (ISR) sites are important for various stakeholders to understand when evaluating potential effects on surrounding groundwater quality. If down gradient solid-phase material consists of sandstone with iron hydroxide coatings (no pyrite or organic carbon), sorption of uranium on iron hydroxides can control uranium mobility. Using one-dimensional reactive transport models with PHREEQC, two different geochemical databases, and various geochemical parameters, the uncertainties in uranium sorption on iron hydroxides are evaluated, because these oxidized zones create a greater risk for future uranium transport than fully reduced zones where uranium generally precipitates.

Keywords uranium, reactive transport, modeling, sorption

Introduction

Groundwater users proximal to uranium *in situ* recovery (ISR) sites are concerned about influences on local groundwater quality. Within a uranium deposit, the local groundwater can be elevated in uranium, radium, and radon concentrations, but surrounding groundwaters are often much lower in radionuclide concentrations and can meet drinking water standards.

Uranium ISR in the United States is generally achieved by leaching reduced uranium ore zones with water containing increased concentrations of oxygen and carbon dioxide, which makes the uranium more soluble (fig. 1). Geochemical changes that may or may not occur outside of the recovery zone are important for local groundwater users, regulatory agencies, and other stakeholders to understand when evaluating the potential effects on surrounding groundwater quality. Fig. 1 illustrates a generic uranium *in situ* recovery facility where the blue stars represent monitoring wells that are continually tested for any changes in groundwater quality. In areas with reducing conditions downgradient (where pyrite as well as organic carbon are present) uranium should be precipitated as well as strongly sorbed to the organic carbon, because this is how the original uranium ore was emplaced. However, if downgradient solid-phase materials consist of sandstone with iron hydroxide coatings (no pyrite or organic carbon), sorption of uranium on iron hydroxides is most likely the controlling factor for any future mining-related uranium in groundwater. In Fig. 1, the groundwater flow during the formation of uranium ore would have been from left to right (or oxidized to reduced). A reversal in the current groundwater flow pattern would make post-recovery groundwater contact the oxidized solid phase. Such changes in groundwater flow patterns through geologic time are common at uranium ISR sites (based on the author's experience). Using different parameters, the uncertainties in uranium sorption on iron hydroxides are evaluated, because these oxidized zones could create a greater potential

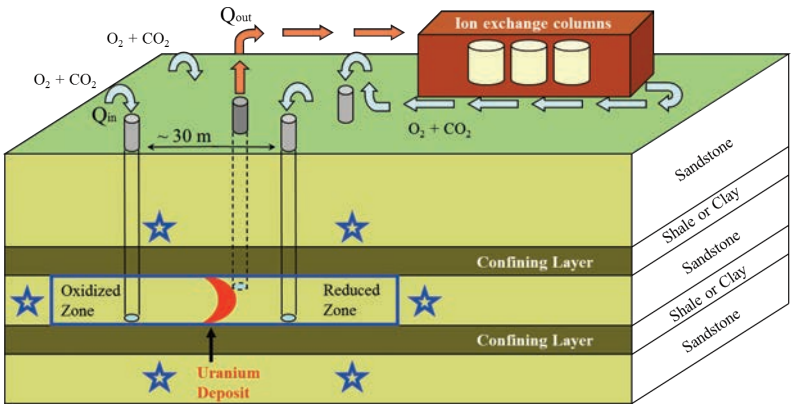

Fig. 1 *Generic uranium in situ recovery facility (not to scale). Blue box indicates main recovery zone and blue stars indicate groundwater monitoring wells.*

for future uranium transport than fully reduced zones.

Methods

One-dimensional reactive transport simulations using PHREEQC (Parkhurst and Appelo 1999) were created to represent long-term groundwater flow away from a restored uranium ISR site (fig. 2). Each cell is 5 m with 8 cells characterizing the ISR zone (40 m) and 32 cells for the downgradient transport zone (160 m). Groundwater monitoring wells are often installed at a certain distance away from the ISR zone (fig. 2). No dispersion was included. No geochemical reactions were considered in the ISR zone; whereas, downgradient reactions included calcite equilibrium and sorption of uranium on iron hydroxides. The initial conditions used local background groundwater quality for the downgradient zone and groundwater quality in the ISR zone was the same as background except for higher concentrations of oxygen, sodium, chloride, carbon dioxide, and uranium (discussed below). All incoming groundwater during a simulation was of background groundwater quality. In these simulations, the dimensions and all the groundwater and solid-phase geochemistry are based on the proposed Dewey-Burdock uranium ISR site near Edgemont, South Dakota, USA (Powertech 2009). However, the procedures and results can be generically applied to any uranium ISR site.

Geochemical model testing included variations in (1) the geochemical database, (2) post-recovery ISR zone groundwater quality, (3) amount of iron in the downgradient solid phase, (4) downgradient calcium concentrations, and (5) post-recovery ISR zone carbon dioxide concentrations. Two different geochemical databases were used with the geochemical modeling: (1) the WATEQ4F database (Ball and Nordstrom 1991) that is provided upon downloading the PHREEQC program, and (2) a modified version of the PHREEQC database (herein referred to as the "updated database") with more recent thermodynamic data on uranium carbonate complexes (Guillaumont *et al.* 2003) and calcium-uranyl-carbonate/magnesium-uranyl-carbonate complexes (Dong and Brooks 2006). These updated and new complexes influence the amount of

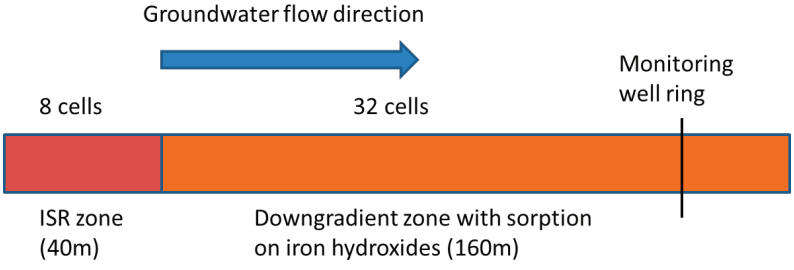

Fig. 2 *Schematic of one-dimensional model domain. ISR = in situ recovery.*

uranyl ion in solution that is available for sorption on iron hydroxides. The same thermodynamic data for uranium sorption on iron hydroxides is used for both databases and is based on Dzombak and Morel (1990). Differences in predicting uranium sorption on iron hydroxides were simulated using post-recovery restored groundwater (uranium = 200 µg/L, oxygen = 8 mg/L, all other constituents = incoming groundwater) and post-recovery groundwater that was not restored (uranium = 50 mg/L, oxygen = 500 mg/L, sodium = 0.5 mol/L, and chloride = 0.5 mol/L, all other constituents = incoming groundwater). These post-recovery groundwater constituents are approximate values for simulation only and were not measured values (the Dewey-Burdock site is only proposed at this point).

The resulting patterns of uranium concentrations were very similar in the restored and unrestored scenarios with the only difference being total uranium concentrations. As a result, only the restored scenarios are presented. Solid-phase iron concentrations of 500 ppm and 2,500 ppm were evaluated based on preliminary iron extraction results from the Dewey-Burdock site. For the simulations, these Fe amounts are converted to an equivalent hydrous ferric oxide (HFO, FeOOH). Because uranium concentrations were very sensitive to the presence of calcium with the updated database, a simulation with lower calcium concentrations in the downgradient groundwater was added. Initial simulations used a calcite saturation index of 0.0 (fully saturated) and simulations with lower calcium concentrations used a calcite saturation index of -0.5 (slightly undersaturated). Background calcium concentration is 365 mg/L. The resulting calcium concentration in the downgradient zone with a saturation index of 0.0 is 387 mg/L and a saturation index of -0.5 produces a calcium concentration of 316 mg/L. In addition, a high carbon dioxide concentration with a log pCO_2 of 0.5 was compared to the natural groundwater conditions of -1.5.

Results

The resulting simulations are shown at 25 years post-restoration (figs. 3–10). The key parameter changes that are evaluated are differences in the 1) database, 2) solid-phase iron hydroxide amount, 3) calcium concentrations, and 4) carbon dioxide concentrations. Differences in the databases are critical in influencing the amount of sorption of uranium on iron hydroxides. The key addition in the updated database was the inclusion of $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$ complexes based on Dong and Brooks (2006). For example, the inclusion of these calcium-uranyl-carbonate complexes makes uranium much more soluble and decreases the uranium sorption potential (figs. 3–6). A $MgUO_2(CO_3)^{2-}$ complex from Dong and Brooks (2006) was also added, but the influence of this complex in separate simulations (not presented), given the Mg concentration that was evaluated, created a minimal influence on uranium concentrations (which may not be the case at sites with higher Mg concentrations). Simulations that used only the updated uranium carbonate complexes based on Guillaumont *et al.* (2003) compared to the WATEQ4F database (Ball and Nordstrom 1991) without the added calcium-uranyl-carbonate complexes, showed no difference in uranium concentrations (not presented).

For iron, a five-fold increase in iron concentrations and the updated database show a retardation in the uranium movement (figs. 3, 5), as expected. Note that the "apparent dispersion" in uranium concentrations (fig. 3) is not dispersion included in the simulations, rather it is created by the sorption/desorption of uranium to iron hydroxides through time. For either iron concentration, the WATEQ4F database shows strong sorption of uranium (figs. 3–6).

Because the updated database relies heavily on calcium-uranyl-carbonate complexes, a lower calcium concentration was tested as described in the methods section. The results (figs. 7, 8) show how sensitive the simulations are to slight changes in calcium concentra-

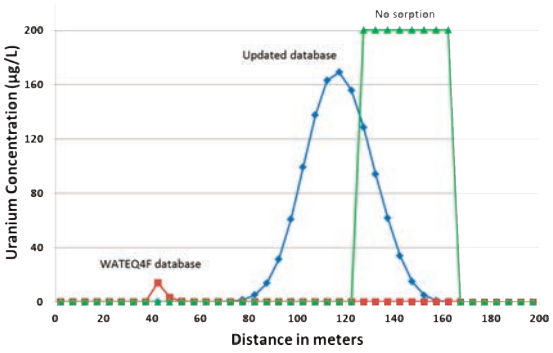

Fig. 3 *Uranium concentrations in groundwater at 25 years with 2,500 mg/L Fe. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.*

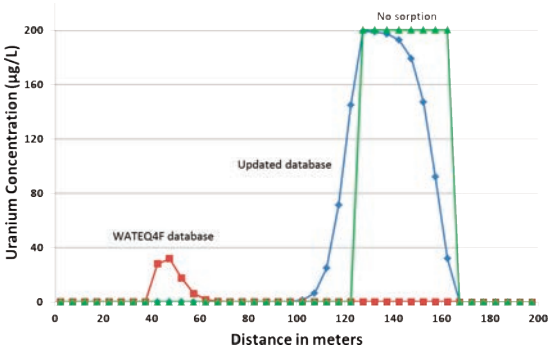

Fig. 4 *Uranium concentrations in groundwater at 25 years with 500 ppm Fe. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.*

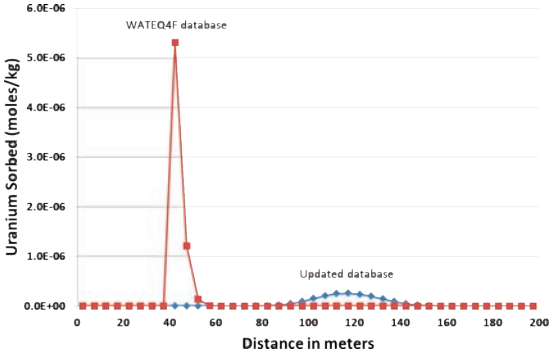

Fig. 5 *Sorbed uranium concentrations at 25 years with 2,500 ppm Fe. Blue line is sorption with updated database and red line is with WATEQ4F database .*

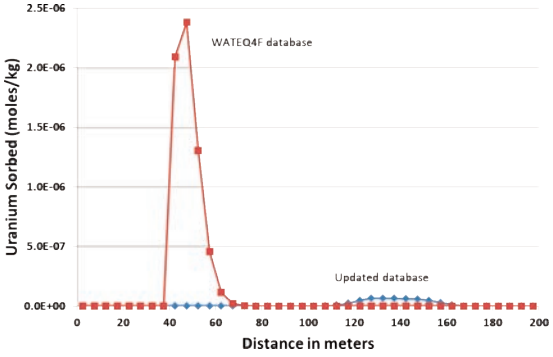

Fig. 6 *Sorbed uranium concentrations at 25 years with 500 ppm Fe. Blue line is sorption with updated database and red line is with WATEQ4F database.*

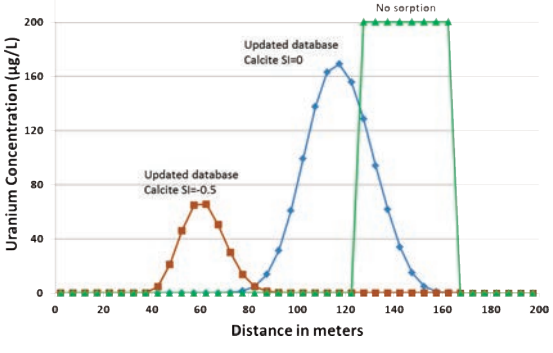

Fig. 7 *Uranium concentrations in groundwater at 25 years with 2,500 ppm Fe. Green line is with no sorption, blue line is with updated database and calcite saturation index (SI) set to 0.0. Brown line is with updated database and calcite saturation index set to -0.5.*

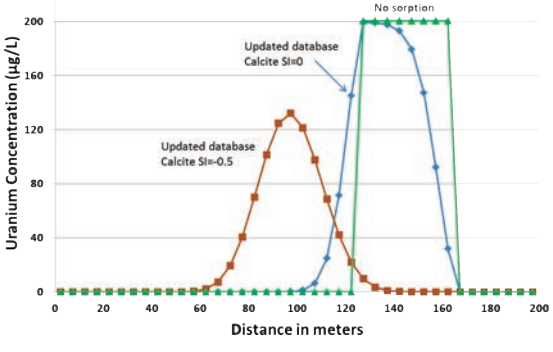

Fig. 8 *Uranium concentrations in groundwater at 25 years with 500 ppm Fe. Green line is with no sorption, blue line is with updated database and calcite saturation index (SI) set to 0.0. Brown line is with updated database and calcite saturation index set to -0.5.*

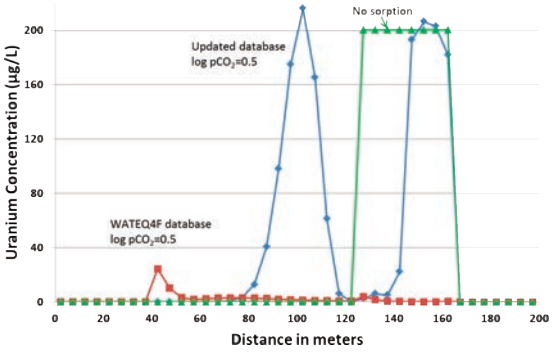

Fig. 9 *Uranium concentrations in groundwater at 25 years with 500 ppm Fe and CO2 in recovery zone of log pCO2 equal to 0.5 and downgradient calcite equal to 0.15 weight percent. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.*

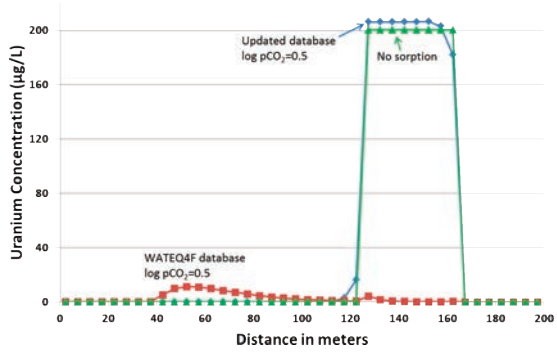

Fig. 10 *Uranium concentrations in groundwater at 25 years with 500 ppm Fe and CO2 in recovery zone of log pCO2 equal to 0.5 and infinite calcite. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.*

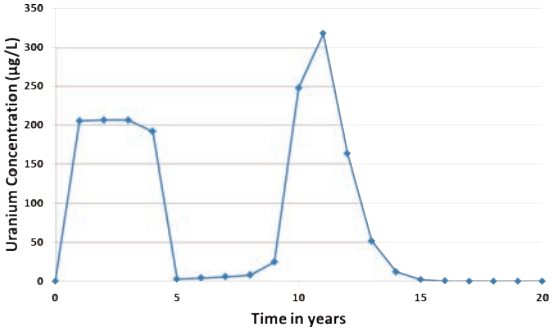

Fig. 11 *Uranium concentrations in groundwater at cell 9, the first cell downgradient from the uranium recovery zone. Simulation uses the updated database and the parameters are 500 ppm Fe, a log pCO2 in the recovery zone of 0.5, and downgradient calcite equal to 0.15 weight percent.*

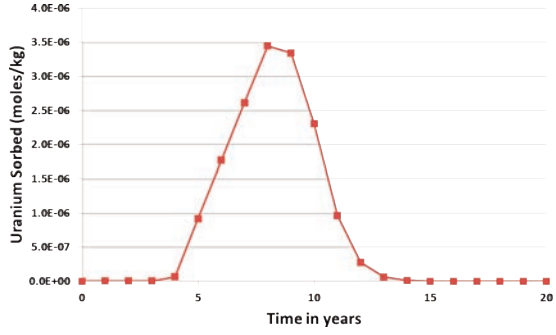

Fig. 12 *Sorbed uranium concentrations at cell 9, the first cell downgradient from the uranium recovery zone. Same simulation database and parameters as Fig. 11.*

tions. The lower Ca concentrations produce more sorption of uranium and thus slower movement and lower of uranium concentrations in the downgradient groundwater (figs. 7, 8).

Higher carbon dioxide concentrations in the recovery zone are quite likely as CO_2 is often used in the uranium ISR process. For Fe=500 ppm and the updated database, the increased CO_2 (log pCO_2 = 0.5) dissolves downgradient calcite (saturation index, SI=0), keeps Ca and alkalinity in solution, and makes uranium mobile in the groundwater (fig. 9). The large decrease in uranium concentrations at approximately 120 to 140 m was unexpected (fig. 9). Because the calcite concentration at the Dewey-Burdock site is low (0.15 weight percent), the lowered pH created by the higher CO_2 concentration consumed all of the calcite in the first downgradient cell (cell 9). Adding an infinite amount of calcite created conservative transport conditions for uranium using the higher CO_2 scenario (fig. 10). Output from the higher CO_2 and lower calcite scenario was examined further by examining the uranium in solution and the sorbed uranium in cell 9

through time (figs. 11, 12). The abrupt decrease of uranium concentrations in cell 9 at 5 years corresponds to the time when all the calcite in that cell has been dissolved, due to the acidity produced by the additional CO_2. The resulting drop in pH increases the sorption of uranium to the iron hydroxides (fig. 12). Through time, as the background groundwater begins to enter cell 9 and the ISR zone groundwater moves downgradient, the subsequent increase in pH decreases the uranium sorption and releases uranium back into the groundwater (figs. 11, 12). It is noteworthy that as desorption occurs, uranium can reach concentrations in groundwater that are actually higher than the original post-restoration uranium concentration of 200 µg/L (fig. 11).

Conclusions

These simulations provide insight for predicting likely downgradient uranium concentrations based on ultimate restoration goals at uranium ISR sites. However, this procedure relies on assumed amounts of iron hydroxides (based on preliminary site data) and their assumed sorption strengths (based on literature values and new information on calcium-uranyl-carbonate complexes). At actual uranium ISR sites, site predictions could be improved using 1) actual groundwater quality from the post-restoration ISR zone, 2) actual downgradient mineralogy (*i.e.* amount of Fe and calcite), and 3) batch or column studies of true sorption potential in the downgradient zone. Without these data, the resulting uncertainty in uranium sorption is quite high, which could produce very different predictions in future mine-related uranium concentrations (figs. 3–10). In any case, the results from one-dimensional reactive transport modeling provide a powerful tool for determining controlling parameters and assisting scientists in evaluating current and future site conditions. The unexpected "split plume" shown in Fig. 9 is a case where the amount of solid-phase calcite along with the updated database created unusual results. However, these results can be explained based upon further evaluation of the geochemical processes (figs. 11, 12).

Acknowledgements

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