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Sustainable Remediation in Complex Geologic Systems

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1 INTRODUCTION

Nuclear weapons production during the Cold War has led to significant radiological contamination of soil and groundwater at more than a hundred sites in the United Sates. Low-level radioactive waste solutions, for example, were often disposed of into unlined seepage basins with minimal or no engineered barriers (e.g., Refs 1,2). There have been leakages of fission products and actinides from high-level waste storage tanks (e.g., Ref. 3). Those sites pose one of the most technically challenging and complex cleanup efforts in the world.[4] Actinides—particularly uranium—have been the main species of concern at many of those sites. In addition, globally, uranium and other metal mining have resulted in soil and groundwater contamination by radionuclides.[5,6] In parallel, there have been extensive efforts to prevent future contamination, particularly to improve the designs of low-level and high-level radioactive waste storage facilities (e.g., Ref. 7). The knowledge and experiences at contaminated sites—particularly understanding the mobility of actinides in the environment—are often transferable to the waste isolation problems.

In recent years, soil and groundwater remediation has been evolving from intense soil removal and treatments towards passive remediation and monitored natural attenuation (MNA).[8] Such less intense remediation—often used within sustainable remediation—is considered more advantageous considering *net environmental impacts* including waste production, construction noise/traffic, ecological disturbance, energy use, and greenhouse gas emission. This concept is particularly critical when the site has a large plume with relatively low concentration where the residual contaminants do not pose immediate public health risk, treatments are no longer effective, and complete soil removal is not feasible. Because actinides have long half-lives, passive remediation has been targeting immobilization techniques to change the aqueous chemistry and to precipitate them in solid phase, by changing redox conditions through bioremediation (e.g., Refs 9–11) or pH (e.g., Ref. 12). Such passive remediation or natural attenuation, however, requires increased burden of proof, since a significant amount of contaminant mass remains subsurface, often in the vadose zone (i.e., above the water table). The feasibility of sustainable remediation depends on (i) understanding and predicting the fate and transport of residual contaminants as well as on (ii) monitoring technologies to ensure the stability of residual contaminants.

Recently, there have been significant advances in numerical modeling of flow, geochemical, and microbial processes, taking advantage of high-performance computing (HPC) platforms (e.g., Refs 13–15). Many codes are capable of solving subsurface and surface flow equations in three-dimensional (3D) domains, including heterogeneous features and engineering systems with sharp permeability contrasts. A variety of geochemical models can incorporate complex geochemical and biological processes to realistically represent subsurface dynamics.[14,16] In addition, advanced uncertainty quantification (UQ) techniques can accommodate Monte Carlo simulations to quantify the uncertainty in predicted values as well as global analysis methods to identify the most influential and important parameters (e.g., Refs 17–19). In particular, stochastic hydrology provides ways to incorporate the uncertain and stochastic nature of geological heterogeneity (e.g., Ref. 20).

In parallel, subsurface characterization techniques have greatly improved over the past decade to characterize flow and reactive transport properties in high resolution and over large scales. Non-invasive geophysical techniques have been used to map heterogeneous geological units in 3D, to identify the contaminant plume extent or to continuously monitor plume migration over time.[21–23] In particular, Sassen *et al*.[24] and Wainwright *et al*.[25] have developed a reactive facies concept—a concept based on the hypothesis that there are subsurface units or zones with the distinct distributions of coupled physical and chemical properties influencing reactive transport, such as effective surface area, mineralogy, and hydraulic conductivity. Because geophysical methods are sensitive to identify such geological units and interfaces, this concept allows us to take advantage of both geophysical and lithological data sets for

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estimating spatially distributed reactive transport parameters over the plume scales.

The next-generation remediation—particularly sustainable remediation—recognizes the need to integrate all these recent advances from subsurface characterization to modeling, numerical simulations and UQ. In this article, we will review the recent developments in modeling the fate and transport of actinide species under sustainable remediation, as well as techniques to characterize the complex geological environments to parameterize the reactive transport parameters. We then demonstrate the integration of all the components, using the datasets and models developed at the Savannah River Site (SRS) F-area in the United States. The SRS F-area has been the focus of many hydrological and geochemical studies in the past (e.g., Refs 1,24–27). The site has a soil and groundwater contamination from low-level radioactive waste after fuel re-processing, containing various radionuclides including uranium, tritium and other fission products. Extensive site characterization efforts have made the SRS F-area a unique site or a *testbed* to demonstrate various characterization and modeling capabilities.

2 SITE CHARACTERIZATION

The model development starts from the characterization of contaminants; particularly the source term. The discharge rate and contaminant concentration in the source needs to be quantified. Historical operation records are critical in this process (e.g., Refs 28,29). If the contamination has occurred already, the plume extent needs to be characterized through groundwater monitoring. Alternatively, geophysical methods have been used to locate and estimate the extent of the subsurface contaminant plume in a non-invasive manner.[30,31]

In parallel, the geological environment, which affects the movement of the contaminant plume in subsurface must be characterized. Without having drilling and boreholes at the site, regional-scale geological information can often be obtained through the government agencies. For example, the US Geological Survey provides the geological map of the entire US (https://www.usgs.gov/products/maps/geologic-maps). Even when the borehole data are available, regional-scale information provides insights into depositional environments and hydro-geochemical parameters relevant to the plume migration.

The borehole data provide critical information to identify the boundary of hydrostratigraphic units as well as hydrological parameters. Even qualitative lithological descriptions along well bores are useful to identify key geological units (e.g., Refs 25,32). Core analysis can include soil texture analysis, visual inspection of color, classification of depositional facies, and permeability through permeameter tests. In addition, cone penetrometer testing (CPT)—an *in situ* soil exploration tool routinely used for environmental and geotechnical applications in shallow unconsolidated environments[33]—is also available for characterizing lithological variability.[32] Geostatistics is often used to interpolate between the well locations.[35–37]

In the past decade, geophysical methods have made a significant progress toward mapping complex subsurface heterogeneity (e.g., Refs 21,22). Borehole geophysical logs are useful to define the geological boundaries more accurately as well as to estimate clay content and mineral composition continuously along boreholes (e.g., Ref. 38). Surface geophysical methods are useful to visualize near-surface heterogeneity over the plume-relevant or the site scale of several hundred meters (e.g., Refs 25,30,39). Among them, electrical resistivity tomography (ERT) has enabled mapping of large contaminant plume extents,[30] vadose zone saturation and the water table,[40] and geological units.[34] ERT has been increasingly used in a time-continuous manner to monitor the contaminant concentrations and plume movements,[31,41] or to estimate hydrothermal parameters through inverse modeling (e.g., Refs 42–44). Surface seismic methods are suitable to map the heterogeneity of geological interfaces (e.g., Refs 25,45,46). In addition, the induced polarization techniques can map geochemical conditions such as redox conditions (e.g., Refs 10,34,47,48).

The site characterization often results in multi-type multiscale datasets that have different accuracy, resolution, and spatial coverages. These datasets must be integrated in a consistent manner. Datasets that provide fine-resolution information (such as borehole and core data) are typically representative of only a small spatial region. Datasets that provide good spatial coverage (such as surface geophysical data) usually provide coarse-resolution information, where each pixel in a coarse grid field represents effective or averaged properties. The challenge has been to develop effective methods for combining the multiscale data sets (e.g., wellbore, crosshole data, and surface geophysical data) in a consistent manner. Sassen *et al*.[24] and Wainwright *et al*.[25] have developed hierarchical Bayesian models to integrate multiscale geophysical and point data sets for characterizing coupled subsurface physical and chemical properties over plume-relevant scales, which is desired for parameterizing reactive transport models.

3 HYDROLOGICAL MODEL DEVELOPMENT

In most cases, contaminant sources are at the ground surface or in the vadose zone, which requires solving saturated and unsaturated flow equations. The Richards equation is often used to represent unsaturated and saturated flow in a porous medium. The non-linear nature of the Richards equation often leads to longer computational

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time or numerical stability problems. In some cases, saturated flow need only be considered with the vadose zone treated as the source term to the groundwater flow.[26,49] In addition, boundary conditions need to be carefully considered depending on the site and data locations. Natural groundwater divides such as streams and watershed boundaries constitute convenient no-flow boundary conditions without having explicit datasets.[1] However, the locations of no-flow boundaries are often uncertain, leading to unrealistic flow or water table conditions. Alternatively, fixed boundary conditions can be created if groundwater table data are available (e.g., Refs 50–52).

Many software packages are available to simulate vadose-zone and groundwater flow such as MODFLOW (water.usgs.gov/ogw/modflow/), PFLOTRAN (http://www.pflotran.org/), TOUGH2 (http://esd1.lbl.gov/research/projects/tough/), PARFLOW (https://www.parflow.org/), Amanzi (github.com/amanzi/amanzi). They typically solve the Richards equation, using the finite-difference method (PARFLOW), finite element method (TOUGH2), finite volume method (PFLOTRAN), or mimetic finite method (Amanzi; Refs 53,54). Special consideration must be made in terms of dimensionality, depending on the modeling objectives. 3D-models are the most realistic, but particularly for complex geological environments, 3D-models are often difficult to calibrate with various datasets or take a long simulation time, even using supercomputers. Often, 1D models are still useful for system understanding, and for sensitivity analysis (SA) to identify important parameters.[26,49] 2D models can be constructed along the transect following the groundwater flow line of the plume center,[1,16] which is a reasonable approach to represent the plume migration and to provide conservative estimates of contaminant concentrations. 3D models are necessary when the complex geology cannot be simplified into 1D or 2D, or when the model domains include engineering barriers that inherently create 3D flows.[55]

The hydrological parameters can be determined through laboratory experiments (i.e., permeameter data), field data (e.g., pump tests) as well as through inverse modeling (model calibration). The scale of datasets is an issue such that core permeameter tests often provide permeability (or hydraulic conductivity) values which are not representative at plume scale; particularly in coarse and unconsolidated sediments. Large-scale pumping or injection tests are a preferred approach to estimate permeability at the scale relevant to the plume migration. Alternatively, inverse modeling can be used to estimate hydraulic parameters after the hydrological models are developed (e.g., Refs 17,56). The inverse modeling can use a variety of data such as core data, borehole water table data, hydraulic tests[57] and geophysical data.[44] Inverse modeling must be carefully applied to ensure that the conceptual hydrological models are reasonably accurate and that the data have distinct information affecting each parameter.[17,58,59]

4 GEOCHEMICAL MODEL DEVELOPMENT

To describe the reactive nature of contaminants with sediment, the linear isotherm or K_d approach has been most widely used. K_d or the constant distribution coefficient describes the equilibrium partitioning of contaminants between the dissolved and sorbed phases (e.g., Refs 60,61). K_d values are often determined by batch experiments or calibration with the groundwater concentration datasets through inverse modeling.

The applicability of the K_d approach is, however, quite limited, particularly for actinide elements due to their complex chemical behaviors. In particular, the solid/liquid partitioning of actinides is often dependent on pH, redox and other groundwater conditions, which cannot be adequately described using a "constant" K_d approach. In addition, the K_d approach is not suitable to describe the competition between different dissolved ions for sorption to mineral phases and sediments. The use of K_d is thus considered problematic for remediation, particularly for long-term remediation and monitoring strategies.[60] For example, low K_d values are often assumed to be conservative, leading to higher plume mobility and higher peak contaminant concentrations. However, assuming low K_d often results in underestimating the persistence of the plume, failing to predict the timeframe reaching below the regulatory limit.[2] In addition, studies have found K_d to vary over several orders of magnitude particularly in environments where geochemical conditions are dynamic (such as river-groundwater interfaces[2]) or when there is a sharp gradient in pH and redox conditions.[62]

4.1 Surface Complexation Models

In the past few decades, there have been extensive efforts to model the sorption behaviors of actinides in a mechanistic manner, particularly for uranium. Surface complexation models (SCMs) have been developed to describe adsorption in geochemically dynamic environments (e.g., Refs 61,63,64). One of the commonly-used SCM approaches is a component additivity approach, which assumes that a mineral assemblage is composed of a mixture of one or more reference mineral phases and that the relative amounts of these reference minerals can be used to predict adsorption of the mixture.[62,65] SCMs are based on various parameters including surface mineral species, surface chemical reactions, equilibrium constants, mass and charge balances, and in some approaches, electrostatic potential terms.[65] These parameters are usually determined through laboratory experiments.[66]

SCMs have often had a challenge to extend the results from laboratory experimental to natural field systems with multi-mineralic assemblages. Recently, alternative methods—non-electrostatic SCMs—have been proposed to model the sorption behavior using generic surface sites

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(rather than individual phases) and no electrostatic correction terms.[26,63,65] The non-electrostatic SCMs are simple models with only a few parameters, which is an important practical consideration when coupling SCMs within larger reactive transport or risk/performance assessment models. Because non-electrostatic SCMs can still describe adsorption of contaminants as a function of variable chemical conditions in groundwater, they are preferable to the electrostatic SCMs or the constant K_d approach for remediation applications.

For reactive transport modeling of actinides, many codes are available such as TOUGHREACT,[67] PFLORTRAN,[13] and CrunchFlow.[68] While some codes (TOUGHREACT and CrunchFlow) can handle electrostatic SCMs, non-electrostatic models are relatively easily incorporated into reactive transport codes because of their mathematical simplicity and absence of electrostatic correction terms. Recently, there have been extensive efforts to benchmark different reactive transport codes and compare their conceptual models and numerical capabilities.[14,69]

4.2 Uncertainty Quantification

UQ studies—including SA and uncertainty analysis (UA)—are essential in fate and transport modeling in complex subsurface environments for risk and performance assessments.[19,70] SA quantifies the impact or importance of each input parameter on output performance measures, whereas UA quantifies the uncertainty in outputs caused by uncertainty in input parameters. In the context of risk or performance assessments, SA can be used to select the most relevant parameters to be determined in the site characterizations and/or to reduce the number of parameters to be included in the risk assessment. The UA results can be directly used in the risk assessment such that the ranges or distributions of the performance measures (e.g., well concentrations or contaminant exports from the site boundary) become input in the risk calculation models (e.g., estimating cancer risks; Ref. 71).

There are several global sensitivity methods available: Morris sensitivity[72] and Sobol'/Saltelli sensitivity.[14,73,74] The global sensitivity methods probe the entire parameter space, and thus provide more robust sensitivity measures accounting for non-linearity and interactions among parameters in system responses. Since sampling is required over the entire parameter space, global methods are often computationally intensive, although some computationally efficient alternatives are available.[19]

UA is typically based on Monte Carlo simulations to generate input parameters randomly generated from the probabilistic distributions, and to analyze the distribution of output performance measures. Although it is often computationally intensive, there are several methods available such as the Latin hypercube method to improve the convergence rate.[75] Stochastic hydrology methodology can be used to represent the uncertain and stochastic nature of subsurface heterogeneity by generating random fields of reactive transport parameters (e.g., Refs 20,25,50,76).

5 CASE STUDY IN REMEDIATION

5.1 Site Description

The SRS is located in south-central South Carolina, near Aiken, approximately 100 miles from the Atlantic Coast (Figure 1). It covers about 800 km^2 (300 mi^2) and contains facilities constructed in the early 1950s to produce special radioactive isotopes (e.g., plutonium and tritium) for the US nuclear weapons stockpile. The SRS F-area seepage basins were constructed as unlined, earthen surface impoundments that received ~7.1 billion liters of acidic, low-level waste solutions from the processing of irradiated uranium in the F-area separations facility from 1955 through 1988.[28] Currently, an acidic contaminant plume extends from the basins ~600 m downgradient to the Four Mile Branch, including various radionuclides, such as uranium isotopes, Sr-90, I-129, Tc-99, tritium, and chemical contaminants, such as nitrate.

Various remediation activities have been conducted at the site, including capping of the basins (1991) and pump-and-treat (1997–2004). The pump-and-treat was not cost effective, producing radioactive wastes (e.g., ion exchange resins) that were difficult to handle and dispose of. In 2004, the site has transitioned to more a sustainable approach, a hybrid funnel-and-gate system, which includes low-permeability engineered flow barriers, and injection of alkaline solutions. The base injections are effective in neutralizing the acidic groundwater and in greatly increasing uranium retardation, because uranium mobility is significantly influenced by pH. At the same time, the hydraulic barriers slow down plume migration and increase decay and mixing before the plume reaches Four Mile Branch, a down-gradient stream that ultimately captures the plume. MNA is a desired closure strategy for the site, based on the expectation that infiltration of rainwater will eventually increase the pH of the plume, causing much stronger retardation and dilution of the uranium plume.

5.2 Site Characterization

Extensive efforts have been made to estimate the element compositions of the waste stream and waste discharge rate during the basin operation.[28] Process wastes were discharged into the F-area seepage basins followed by subsequent mixing processes within the basins and eventual infiltration into the subsurface.[29] Millings *et al.*[29] performed geochemical modeling to evaluate the importance of the wide variability in bulk wastewater chemistry

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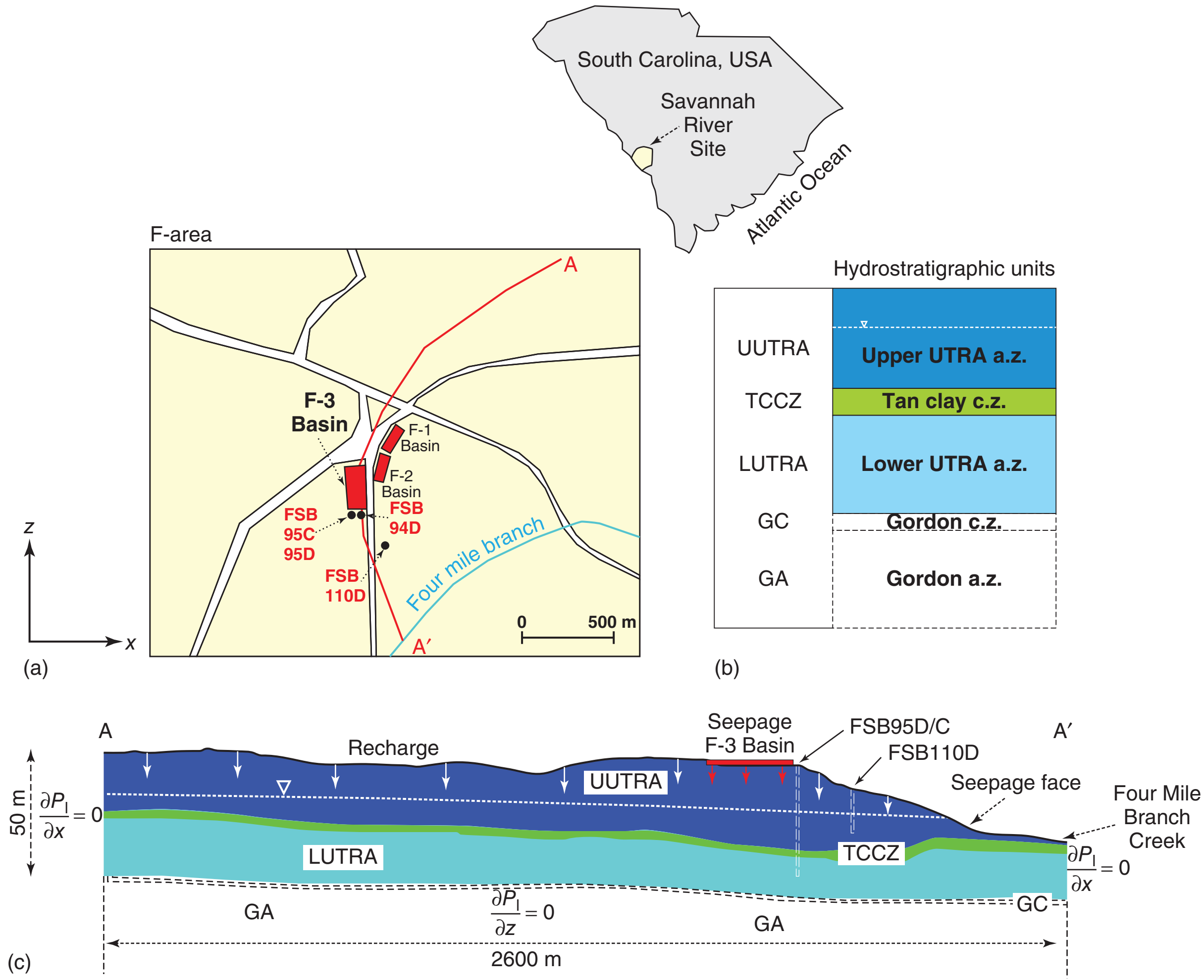

Figure 1 (a) Location of seepage basins in the F-area of the Savannah River Site (SRS). (b) Hydrostratigraphic units defined for the F-area. (c) 2D-cross section model domain [Reproduced with permission from Elsevier. © 2013]

over time as it propagated through the basins. They showed that the largest basin (Basin 3) is the primary contaminant source to the groundwater and that the fluctuation in chemistry of the waste streams is not directly representative of the source term to the vadose zone. Evapotranspiration at the basin is poorly defined and introduces uncertainty in the tritium source term. Bea *et al.*[1] included the source terms as uncertain parameters in the UQ analysis.

At the same time, this site is among a small percentage of sites with extensive subsurface characterization. The SRS F-area is located within the Atlantic Coastal Plain physiographic province, which is characterized by a marine depositional environment.[27,35,36] The sedimentary layers are expected to be horizontal to sub-horizontal with smaller spatial heterogeneity within each unit compared to the alluvial environment.[35,36] Several decades of intensive site characterization have resulted in the accumulation of rich historical borehole data sets, including core sample analysis, and CPT.[77] The analysis of cores (every 0.3048 m) along more than 10 wells includes soil texture analysis, visual inspection of color, and classification of depositional facies.[35,36] Jean *et al.*[35,36] have characterized the geological units based on geostatistical approaches.

The geophysical datasets have been used to map the subsurface heterogeneity and to construct the 3D map of reactive transport parameters. Sassen *et al.*[24] and Wainwright *et al.*[25] used the "reactive facies" concept to characterize subsurface units having distinct and linked reactive transport properties, by using multiscale geophysical methods (e.g., crosshole, seismic) and core datasets. This method could parameterize the 2D transect domain in terms of parameters including permeability, clay content, and mineral ratio. Sassen *et al.*[24] showed that the coupled and corrected properties created non-additive and emergent effects in the plume migration.

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5.3 Hydrological Model Development

Groundwater flow models have been continuously developed and improved over the last 15 years.[1,27] Flach[27] developed a numerical model to simulate groundwater flow in the larger site-scale over the SRS. The steady-state flow model was solved to compute the 3D hydraulic head field with the average infiltration rate, calibrated by the water table datasets. The hydraulic head field was used to create the groundwater streamlines, along which the contaminant transport was simulated.

Bea *et al.*[1] solved the Richards' equation in the 2D transect within the F-area, following one of the flow lines calculated by Flach.[27] The no-flow boundary conditions were defined at the groundwater divide and creek at downgradient. The 3D hydrogeological model was developed including the heterogeneous hydrostratigraphic interfaces characterized by geophysical and borehole data. There are three layers units within the Upper Three Runs Aquifer: an upper aquifer zone (UUTRA), a Tan Clay Confining Zone (TCCZ), and a lower aquifer zone (LUTRA). Hydraulic parameters are determined through a series of pumping and parameter tests as well as the calibration of the 2D model.[1,27]

In the recent 3D model,[55] the domain also includes low-permeability engineered barriers, which are part of the funnel-and-gate system (Figure 2). In addition, the interfaces were updated based on recently acquired CPT datasets and surface seismic datasets,[25] which capture the detail heterogeneity of the TCCZ top (or the lower boundary of UUTRA). The top of the TCCZ is known to be quite important for plume migration, since its depressions (or troughs) accumulate the contaminants. The unstructured 3D prismatic mesh was created using the Los Alamos Grid Toolbox (LaGriT; http://lagrit.lanl.gov). The mesh is refined around the barriers and basins, where we expect a sharp gradient in pressure and concentrations. Mesh edge lengths were smallest (highest resolution) at the barrier locations with edge lengths near 0.2 m. The regions with no small features to capture have larger spacing with edge lengths between 20 and 50 m.

5.4 Geochemical Model Development

The geochemical conditions have been extensively characterized through many field and laboratory experiments, particularly for uranium geochemistry.[62] Both electrostatic and non-electrostatic models have been developed to describe its sorption and pH-dependent behaviors.[1,26] The natural attenuation of the acidic-U(VI) plume in the F-area is likely to be affected mainly by a combination of the following processes: (i) adsorption/desorption of U(VI) onto/from the surface of different minerals (mainly kaolinite and goethite at this site) under different mechanisms (i.e., electrostatic surface complexation and/or ion exchange); (ii) pH effects related to H^+ sorption and/or Al mineral dissolution and precipitation; (iii) mixing of the plume groundwater with clean (and higher pH) background groundwater.

Reactive transport models were assembled by combining the flow and transport model and the geochemical

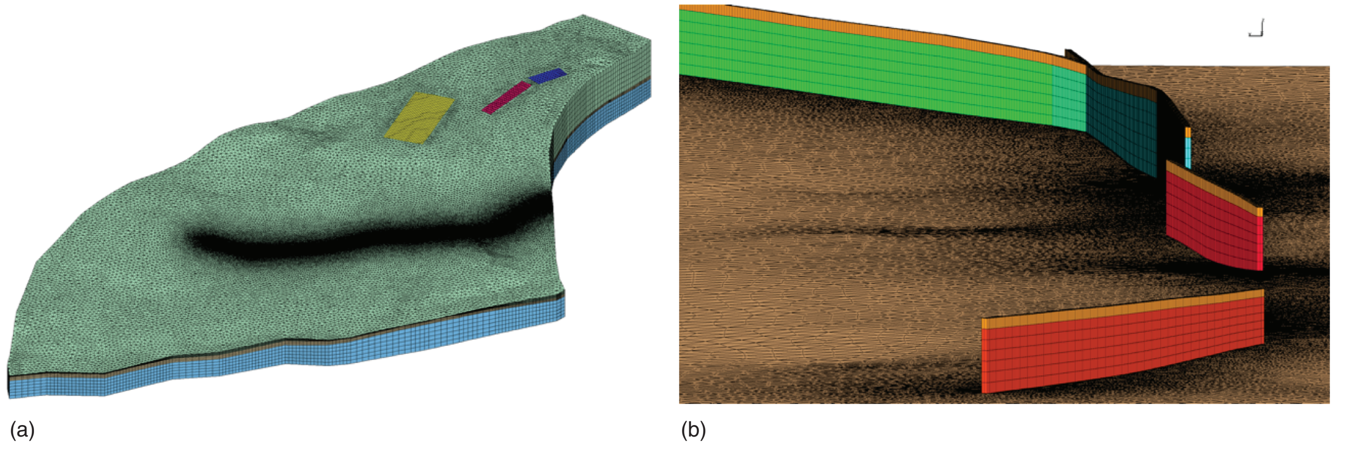

Figure 2 (a) 3D prismatic mesh generated by LaGriT is shown using an exaggerated vertical scaling to highlight the three stratigraphic layers, and (b) the barrier wall representation. In (a), the green region is the upper aquifer, the middle brown layer is the Tan Clay confining zone, and the blue region is the lower aquifer. The yellow, red, and blue surface areas are the three basin locations. The mesh used in this study has 1 849 039 cells and 982 998 vertices [Reproduced with permission from Wainwright, H. M., Faybishenko, B. Molins, S., Davis, J. A., Arora, B., Pau, G., Johnson, J., Flach, G., Denham, M., & Eddy-Dilek, C., Moulton, J. D., Lipnikov, K., Gable, C., Miller, T., & Freshley, M. (2017). Coupling Big Data Analytics and Reactive Transport Modeling for Costeffective Groundwater Monitoring. Proceedings of Waste Management 2017, March 5–9, 2017, Phoenix, Arizona, USA]

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model. The combination of the flow and transport portion of the model and the geochemical model was performed by several codes (TOUGHREACT, Amanzi). In particular, the Alquimia interface in Amanzi made it possible to use existing geochemical codes (e.g., PFLOTRAN, Crunch-Flow) within the Amanzi HPC infrastructure through a generic coupling.

5.5 Results and Applications

In the SRS F-area, the reactive transport models have provided various types of valuable information to improve our understanding of the system, to identify important parameters and processes for remediation, and to support the long-term monitoring under sustainable remediation.

5.5.1 Identifying Key Controls on Uranium Plume Migration

Bea *et al.*[1] used the reactive transport model and global SA to understand the long-term pH and U(VI) adsorption behavior at the site, which is critical to assess feasibility of MNA along with the *in situ* remediation treatments. Their analysis identified key controls on the U(VI)-plume evolution and long-term mobility at this site. Two-dimensional numerical RT simulations are run including the saturated and unsaturated (vadose) zones, U(VI) and H^+ adsorption (surface complexation) onto sediments, and dissolution and precipitation of Al and Fe minerals; key hydrodynamic processes are considered.

In addition, UQ aimed to (i) identify the complex physical and geochemical processes that control the U(VI) plume migration in the pH range where the plume is highly mobile, (ii) evaluate those physical and geochemical parameters that are most controlling, and (iii) predict the future plume evolution constrained by historical, chemical, and hydrological data. The global SA method was used to account for non-linearity and interactions among parameters.

The results show good agreement with the observed historical pH and concentrations of U(VI), nitrates and Al concentrations at multiple locations. In addition, this study identified the importance of mineral dissolution and precipitation combined with adsorption reactions on goethite and kaolinite (the main minerals present with quartz), since this combined mechanism could buffer pH at the site for long periods of time. Uranium concentrations are found to be most sensitive to the pH of the waste solution, discharge rates, and the reactive surface area available for adsorption. This model (and parameters) sensitivity evolves in space and time, and its understanding could be crucial to assess the temporal efficiency of a remediation strategy in contaminated sites.

5.5.2 Comparison of Electrostatic and Non-Electrostatic SCMs

Arora *et al.*[26] compared non-electrostatic SCMs with electrostatic SCMs to investigate if a simpler, semi-empirical, non-electrostatic U(VI) sorption model could achieve the same predictive performance as a model with electrostatic correction terms. This comparison has an impact not only at SRS but also for other sites that have sharp pH or redox gradients. In particular, such comparisons can motivate other sites to transition from using a constant K_d approach to the more accurate non-electrostatic SCMs, since the non-electrostatic SCMs are easier to develop and calibrate compared to the full electrostatic SCMs.

Arora *et al*. demonstrated that a non-electrostatic SCM is a powerful alternative for describing U plume evolution at the SRS F-area because it can describe U(VI) sorption much more accurately than a constant K_d approach, while being more numerically efficient than a model with electrostatic correction terms. Another advantage they found was that the non-electrostatic models can be easily developed with a minimal number of parameters (Table 1), while retaining the important linkage between sorbed and dissolved species through the coupling of mass action equations. With only two optimized parameters, the final non-electrostatic SCM was able to describe the long-term evolution of H^+ and uranium within the SRS; these variations are equivalent to almost four order of magnitude range in K_d values. This suggests that such an approach, without explicit correction for electrostatic attraction or repulsion, can be used efficiently to support environmental remediation as well as risk/performance assessment models.

5.5.3 Modeling Support for Long-Term Monitoring Strategies

Reactive transport modeling has been used to investigate the efficacy of *in situ* monitoring strategies at the SRS F-area. Recently, this monitoring strategy has been proposed by Eddy-Dilek et al.,[78] aiming to replace groundwater sampling by *in situ* automated sensors. Recent advances in *in situ* sensors allow us to continuously measure groundwater, and to stream data through wireless or phone networks. Although *in situ* measurable properties—such as pH, redox potential, groundwater level, and electrical conductivity—may not be of the contaminant concentrations of interest, many of them are the key properties that control plume mobility and its spatial and temporal distributions. Since these *in situ* variables are also leading indicators of the plume mobility, the *in situ* sensors can serve as an early warning system so that actions can be taken before the contamination migrates.

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Table 1 Development of the non-electrostatic SCM with minimum number of fitted parameters

Simulation description	Calibration parameter	Parameter range
Non-electrostatic SCM for H^+ sorption/desorption only[(a)]	—	—
Non-electrostatic SCM for non-competitive U(VI) sorption/desorption	Effective surface area for U(VI) sorption	2.36×10^{-4} to $2.36 \times 10^{4}\ m^2\ g^{-1}$
Non-electrostatic SCM for competitive H^+ and U(VI) sorption/desorption	Surface complexation constant for U(VI) sorption	−0.5 to −2.2

[(a)]No calibration was required because transport of the pH front in the field was satisfactorily described by reactive transport simulations using the laboratory-based SCM

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In Wainwright *et al.*,[55] the authors first simulate the plume of H^+, nitrate, and uranium in the 3D domain (Figure 3). The plumes initially move straight down vertically until they hit the water table, and then migrate laterally mainly within the upper aquifer (Figure 3a and d). The low-pH plume moves more quickly downgradient (Figure 3a and b), increasing the mobility of uranium and creating a path for the uranium plume to follow (Figure 3d and e). As the plume migrates downgradient toward the creek, the plume goes through the troughs in the bottom of the upper aquifer (Figure 3b). The model predicts that a significant amount of uranium is expected to be retained in the vadose zone (Figure 3f) in 2050 even though pH would be neutralized (Figure 3c), which suggests the long-term effect of capping the basin.

Their results showed that the predicted correlations are linear between nitrate and uranium as well as between pH and uranium, which is consistent with the observations at the same wells. In addition, modeling also allows one to extrapolate the correlations into the future.

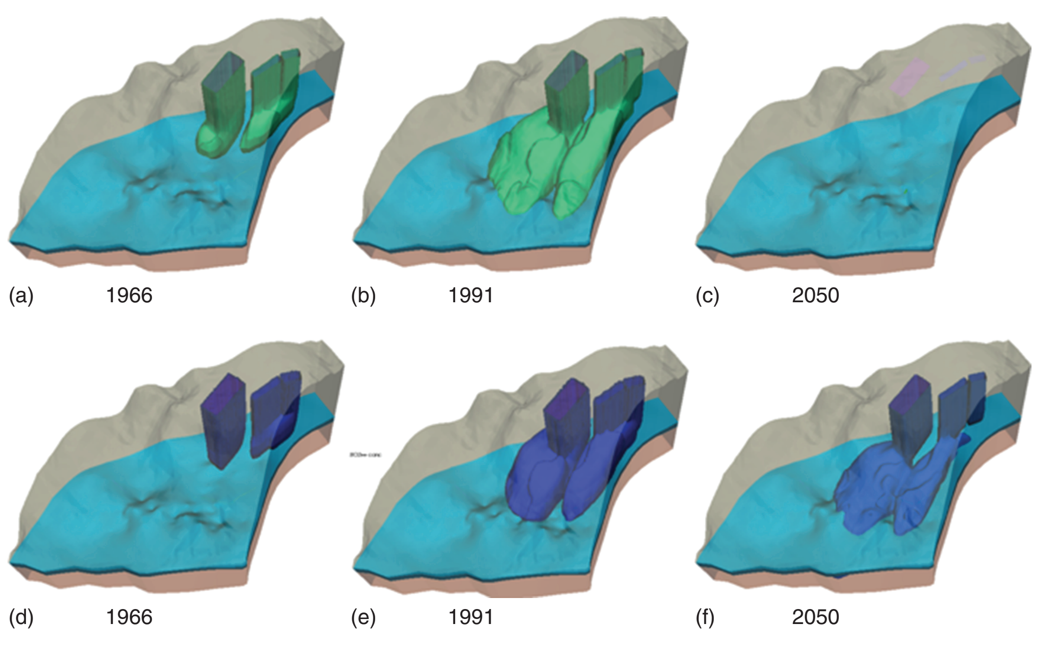

Figure 3 Upper figures (a–c) simulated evolution of low-pH plume (pH > 4); lower figures (d–f) uranium plume (concentration $> 1 \times 10^{-6}$ mol L^{-1}). The sky-blue region is the low permeable TCCZ, which separates the upper and lower aquifers. Vertical exaggeration = 15X

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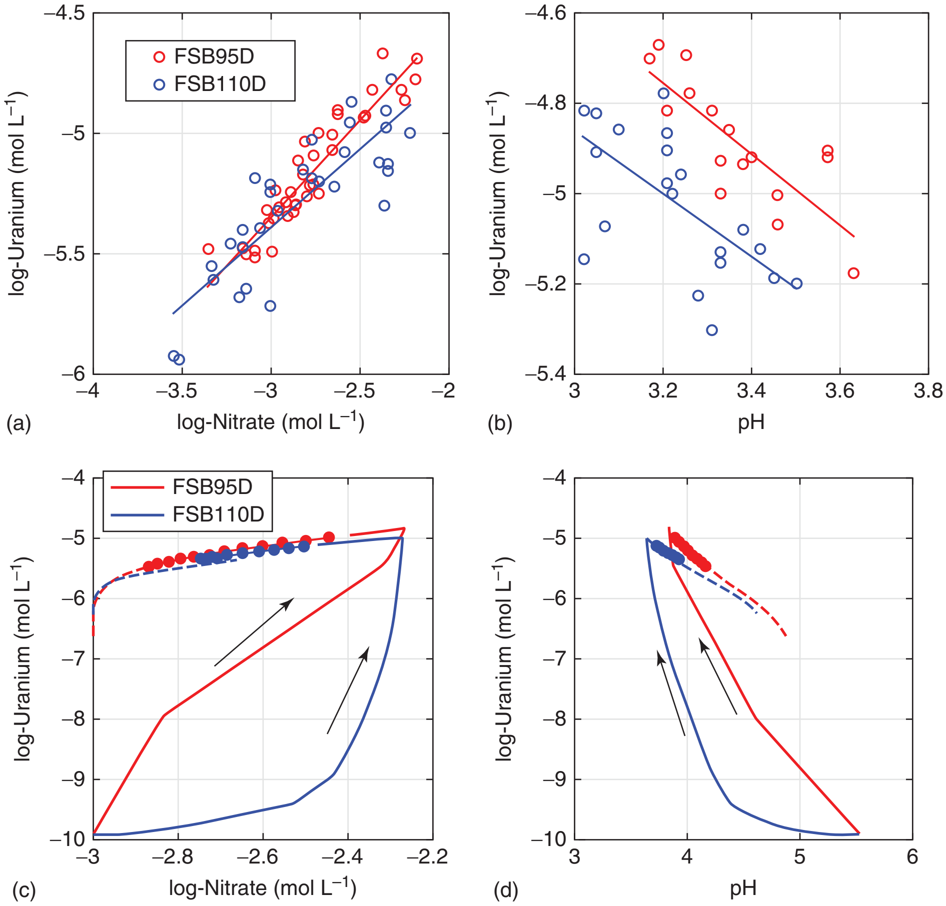

Figure 4 Observed (a, b) and simulated (c, d) correlations between uranium (U) concentration (log-transformed mol L^{-1}) and controlling variables at FSB95D and Well FSB110D: (a, c) nitrate concentration (log-transformed mol L^{-1}), and (b, d) pH. In each plot, the solid lines are between 1954 and 1993, the circles are between 1993 and 2005 (corresponding to the observation time) and the dotted lines are between 2005 and 2100. The black arrows in each plot represent the direction of the time evolution from 1954 to 2100

The simulated results show that the pH-U correlations will be linear and constant until 2100, while the EC-U correlation will become nonlinear and change over time (Figure 4). In addition, UQ coupled with the reactive transport simulations was used to simulate the correlations between the contaminant concentrations and in situ variables in the various hydrological and geochemical conditions. SA enables one to identify which parameters are influencing these correlations and creating variability. Sobol' global sensitivity indices (Figure 5) suggest that the key parameters are the upper aquifer permeability, cation exchange capacity (CEC), sorption site density, and source uranium concentrations. Precipitation has little effect on the correlations. These findings are useful for long-term monitoring. For example, the key parameters are mostly material properties and the future conditions—such as precipitation—do not have an impact on those correlation parameters.

6 ABBREVIATIONS AND ACRONYMS

CPT = cone penetrometer testing; ERT = electrical resistivity tomography; LaGriT = Los Alamos Grid Toolbox; LUTRA = Upper Three Runs Aquifer: lower aquifer zone (in Savannah River Site); MNA = Monitored Natural Attenuation; SA = sensitivity analysis; SCM = surface complexation model; SRS = Savannah River Site; TCCZ = Tan Clay Confining Zone (in Savannah River Site); UA = uncertainty analysis; UQ = uncertainty quantification; UUTRA = Upper Three Runs Aquifer: upper aquifer zone (in Savannah River Site)

7 RELATED ARTICLES

Speciation: Radionuclides; Geology, Geochemistry and Natural Abundances; Sustainable Water Remediation

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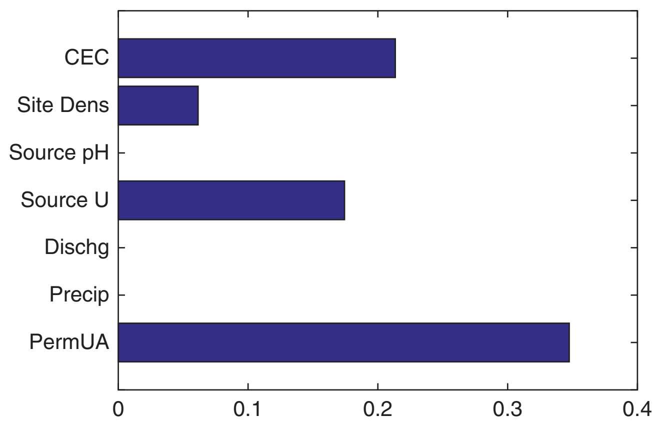

Figure 5 Sensitivity analysis results; Sobol' sensitivity index of each variable with respect to the correlations between pH and U-238 concentrations. The parameters are: CEC, cation exchange capacity; Site Dens, sorption site density; Source pH, pH in the source discharge; Source U, uranium concentrations in the source discharge; Discharge, discharge rate; Precip, precipitation; and PermUA, permeability in the upper aquifer (UUTRA)

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