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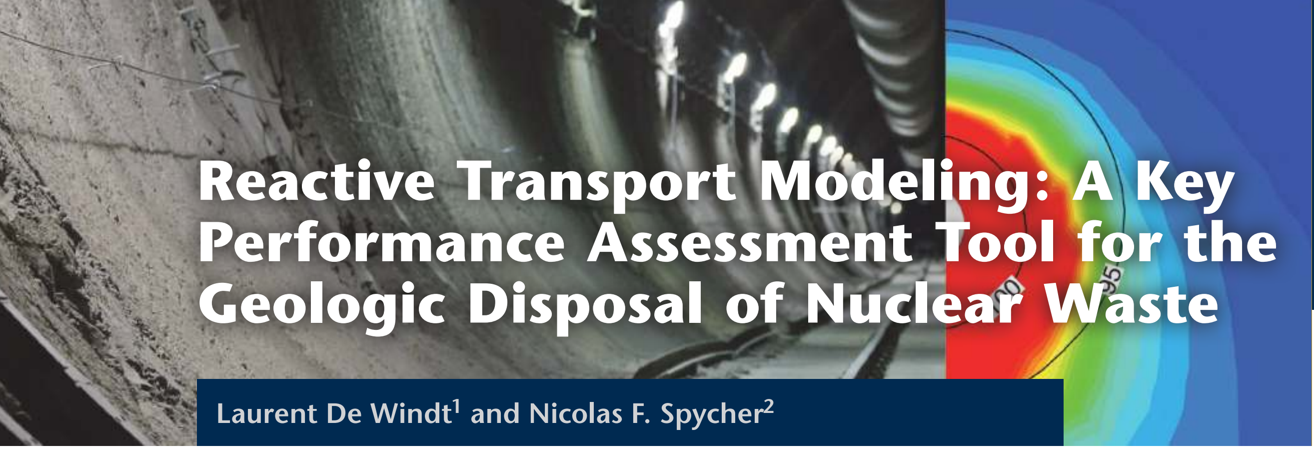

Reactive Transport Modeling: A Key Performance Assessment Tool for the Geologic Disposal of Nuclear Waste

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The disposal of spent nuclear fuel and high-level radioactive waste in the subsurface represents one of the greatest challenges for the geosciences. Most disposal strategies rely on a multiple barrier system, consisting of both natural and engineered materials, to prevent or delay the contact of groundwater with the waste and radionuclide release to the environment. Reactive transport models have been central to understanding and assessing how thermal, hydrological, and geochemical processes are coupled in these containment barriers, which are expected to experience a range of temperatures and geochemical conditions, yet, must maintain their integrity for millions of years.

KEYWORDS: bentonite, engineered barriers, geological repository, natural analogue, radioactive waste, spent nuclear fuel

SIMULATING LONG-TERM NUCLEAR WASTE DISPOSAL OPTIONS

In many countries, a geological repository for the disposal of radioactive waste is considered the best long-term solution to protect human health and the environment from possible releases of radioactive elements (Ewing et al. 2016). The containment first relies upon a series of robustly engineered barriers in close proximity to the waste (a zone referred to as the "near-field") (FIG. 1). There also needs to be a host-rock formation (referred as the "far field") that is poorly conducive to radionuclide migration. The nuclear waste is sealed into metallic canisters made of copper or iron to delay contact with groundwater. The canisters are themselves typically surrounded by bentonite and/or cementitious buffers. The surrounding geological barrier prevents transport of contaminants away from the repository should the engineered barriers fail, and it blocks ingress of elements that could be harmful to the integrity of the barrier system. The multiple barriers are designed to hydrologically contain the waste by using low-permeability materials and/or to contain it chemically by using properties that favor the immobilization of radionuclides. Immobilization can be ensured by the use of high sorption capacity materials or by chemically reduced conditions that minimize the transport of most actinides. These stringent containment measures allow radioactive isotopes to decay as much as possible before potential mobilization could occur. The characteristic lifetime of these barriers is strongly dependent on the disposal concept. Engineered barriers are typically designed for a performance lifetime on the order of thousands of years, whereas the transport through the host rock and the environment can take hundreds of thousands of years. In addition to hydrological and geochemical processes, the heat produced by the radioactive decay will also affect barrier performance. The resulting thermal pulse around the waste can vary in duration from centuries, for reprocessed glass waste, to tens of thousands of years, for spent fuel. Water saturation and gas fluxes (CO_2, H_2) are also expected to vary around disposal tunnels over time scales of centuries.

Reactive transport models (RTMs), by definition, can simulate the transport and chemical reactions of multiple solutes (and gases) and their chemical interaction with rocks over various time and spatial scales. Reactive transport models have, therefore, become an invaluable component in assessing the potential performance of a repository, which requires an understanding of how the various barriers evolve through space and time. Reactive transport modeling is also capable of great generality and flexibility and can be applied to a wide range of natural processes, as well as to engineering issues such as metal corrosion or bentonite alteration. Although the use of RTMs for deterministic predictive simulations is limited, these models can help constrain future repository behavior with sensitivity analyses and scenario modeling of the various disposal subsystems (e.g., the sealing of a disposal cell).

Reactive transport modeling of the geochemical evolution of nuclear waste disposal systems must be supported by laboratory experiments under well-controlled conditions (Gaucher and Blanc 2006) and by in situ experiments at various scales in underground research laboratories (Sonnenthal et al. 2005). Despite real disposal timescales being inaccessible to experimentation, scientists can partly address this limitation through RTMs of archeological analogues (De Windt et al. 2008; Verney-Carron et al. 2010) and natural analogues (Steefel and Lichtner 1998). Taking such an approach brings confidence to the modeled results when predicted long-term processes are confirmed by field observations.

TESTING MODELS OF WASTE ALTERATION

The alteration of nuclear waste is the primary process that leads to the release of radioactive species from a geologic nuclear waste disposal site. Modeling waste alteration observed in laboratory experiments and natural analogues increases confidence that such alteration can be assessed by an RTM over a wide range of time frames.

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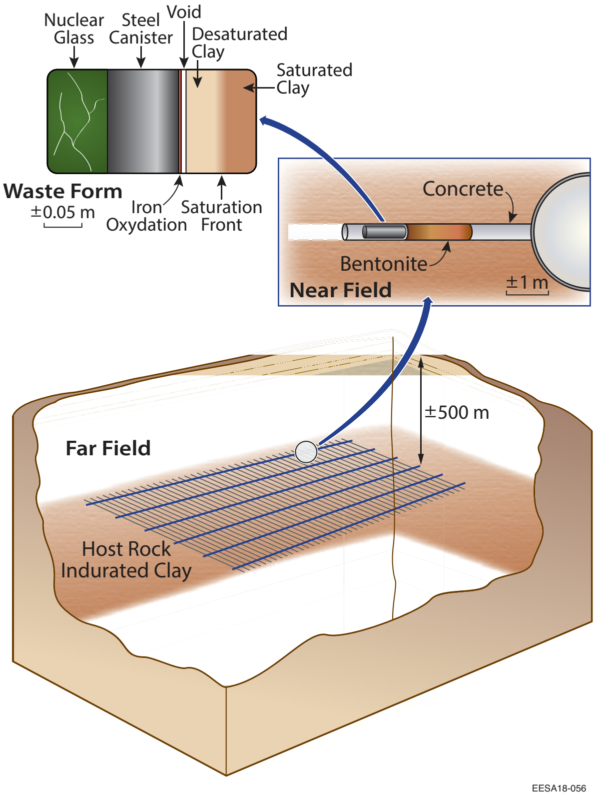

FIGURE 1 Illustration of the multiple barrier system (and terminology) that is typically adopted in geologic nuclear waste repositories, from basic canister design, to tunnel design, to overall repository design, over the multiple scales involved in performance assessment.

In spent nuclear fuel disposal, the transformation rate of the insoluble U(IV) in the UO_2 fuel to the much more soluble oxidized U(VI) compounds increases in the presence of either dissolved oxygen from groundwater or oxidants (i.e., H_2O_2) produced by the irradiation of water by radioactive waste. It is a critical issue because actinides and fission products are entrapped in the UO_2 matrix. In this context, RTM was integrated with recent laboratory experiments (Odorowski et al. 2017) to investigate the effect of Fe^{2+}, a reducing aqueous species coming from the corrosion of the iron canisters, on the oxidative dissolution of UO_2 (FIG. 2). Modeling accurately reproduced the mineralogy of the system under study and predicted the nature of the phases under observation, as well as the location of their precipitation. Inverse modeling also quantified the reaction kinetics and diffusion fluxes between the different oxidizing and reducing species. For instance, the RTM confirmed the fast consumption of H_2O_2 by Fe(II) at the uranium fuel pellet's surface, preventing UO_2 dissolution by H_2O_2 and leading to Fe(III)-(oxy)hydroxide precipitation on the UO_2 surface. Modelling also showed that a lower reaction rate would displace the Fe^{2+}/H_2O_2 redox front farther away from the pellet's surface, coinciding with the release of uranium and the formation of FeOOH colloids. However, this alternative model result disagreed with the experimental data. The knowledge gained from such modeling at laboratory scales can then serve as a basis for simulations at larger scales (FIG. 1) in the context of long-term performance assessment—such as assessing whether the steel of the waste canisters inhibits the oxidative dissolution of the UO_2 spent fuel pellets.

Understanding glass alteration is another example of how RTMs can be applied to the study of nuclear waste degradation. Vitrified wastes are produced when spent fuel is reprocessed to recover Pu and U. Simulating the kinetics of glass alteration is difficult because reactions that occur at the glass–water interface control the development of the altered layers. The chemical and physical properties of these altered layers depend upon the chemistry of the local environment. In this context, Verney-Carron et al. (2010) studied archaeological glass blocks altered for 1,800 years in a shipwreck in the Mediterranean Sea. Reactive transport modeling allowed these authors to quantify the long-term waste corrosion rate and to specify the local geochemical conditions within the crack network that led to the observed alteration products (hydrated glass, smectites, and carbonates).

DISSOLUTION, PRECIPITATION, AND ARMOURING: MODELING THE MULTIPLE BARRIERS

The multiple barriers in the near-field of a repository are often very different in nature. Steep chemical and hydrological gradients occur between the barrier materials. Therefore, the propensity for geochemical reactions is high at these interfaces (Bildstein and Claret 2015). The thermal, hydrological, and chemical interactions between cement-based and clay-based (bentonite, argillaceous rock) barriers have been investigated by RTMs for more than two decades (Mon et al. 2017). The hydrated cement phases [portlandite, calcium silicate hydrate (C–S–H), and sulfoaluminates] buffer the pH to ~12.5. In contrast, pH in bentonite and most host rocks is in the range 7 to 8. Reactive transport modeling of such a system was used to estimate the spatial extension of the alkaline pH perturbation and resulting mineralogical changes over 100,000 years (De Windt et al. 2004). Results suggest that cement-based barriers will become decalcified and clay-based barriers will dissolve, with calcite and zeolites precipitating at the interface between these two type of barriers. The modeling assumptions have since been refined by experiments. For instance, the precipitation of zeolites such as K-phillipsite has been observed in in situ cement/clay systems, but only above 70 °C (Lalan et al. 2016). The results of the long-term RTM of De Windt et al. (2004) were then expressed in terms of the spatio-temporal evolution of key parameters for performance assessment: transport parameters (e.g., decrease in diffusion coefficient due to clogging by calcite precipitation); clay swelling capacity (e.g., swelling loss due to K^+ enrichment of the exchangeable population); and radionuclide containment properties (K_d and solubility limits as calculated from the RTM) (see Jacques et al. 2014).

At Maqarin (Jordan), geological conditions produced natural cement (mostly portlandite) that is now highly fractured allowing hyperalkaline water to seep through local fractured rocks. For this reason, this site has been investigated as a natural analogue for the long-term effect of alkaline plumes. It is also an excellent example of an early application of an RTM to the study of nuclear waste disposal. At this location, high-pH waters (pH 12.5) from clinker-like pyrometamorphic rocks flowed into fractures within a biomicrite clay. Following the pioneering work of Steefel and Lichtner (1998), several RTM studies have demonstrated that fracture sealing is favored by higher effective precipitation rates within fractures than within the rock matrix. A massive precipitation of cement-like phases, such as ettringite and C–S–H, took place in fractures at the expense of the primary silicates in the wall rock next to the fractures. For the case of a repository, such clogging process would be expected to limit contaminant transport, an important finding with implications for long-term performance.

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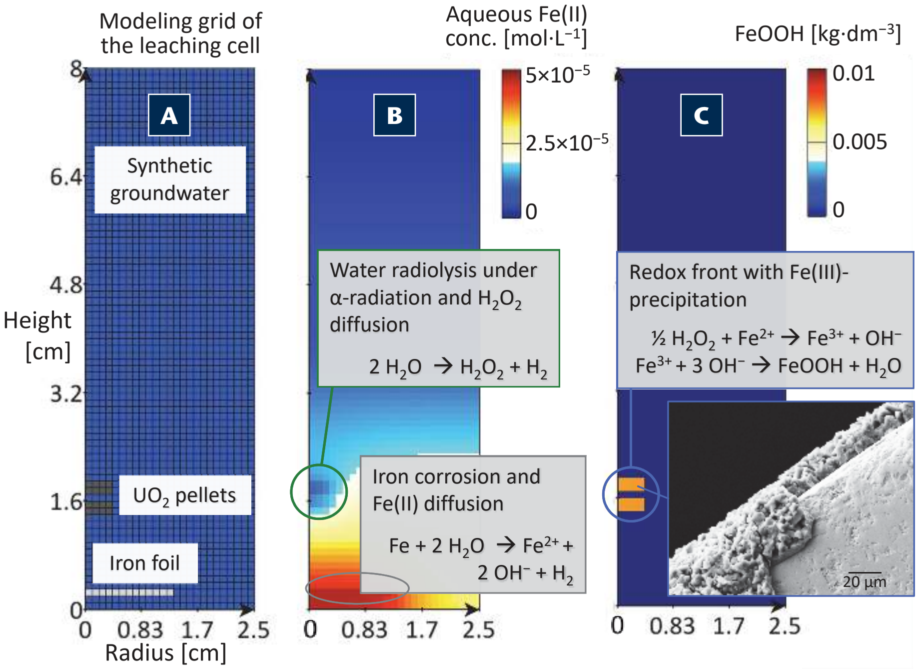

FIGURE 2 Reactive transport model of a laboratory experiment performed in a cylindrical reactor to mimic the alteration of spent nuclear fuel in the vicinity of a carbon steel canister in a deep geological repository. (**A**) Setup of the experiment, showing an iron foil and UO_2 pellets doped with an alpha emitter, both immersed in synthetic groundwater. (**B**) Fe(II) is continuously released due to the iron foil corrosion by water, whereas the oxidant H_2O_2 forms from radiolysis. The color scale is in units of mole Fe(II) per liter. (**C**) The formation of Fe(III)OOH only on the UO_2 pellets indicate that H_2O_2 readily reacts with Fe(II), thereby preventing UO_2 oxidative dissolution. The color scale is in kilograms per cubic decimeter. The scanning electron micrograph image is of FeOOH precipitates on the pellet surface. Solid characterization at the micron scale is very helpful for reactive transport model validation. The modeling of redox reactions is a key point for quantifying radionuclide release. ADAPTED FROM ODOROWSKI ET AL. (2017).

WHEN HOST ROCKS GET HOT: MODELING THERMAL PERTURBATIONS

Many different geological environments have been considered for radioactive waste disposal, including fractured crystalline rocks, volcanic tuffs, evaporite salts, and sedimentary formations containing low permeability claystones (Ewing et al. 2016). In sedimentary clays, reactive transport processes take place within a pore network. In crystalline rocks, these processes occur along multiple flow paths: primarily in fracture networks, and more slowly by matrix diffusion (MacQuarrie and Mayer 2005). Reactive transport modeling is well-suited to the study these systems, including fracture–matrix interactions and the coupled effects of mineral dissolution/precipitation on fracture permeability and flow.

A good example for such RTM applications is the assessment of the proposed spent nuclear fuel repository at Yucca Mountain (Nevada, USA). This site was unique because of its location above the water table and the fact that the host rocks were fractured volcanic tuffs, whereas most other repositories around the world are designed to be below the water table and in low permeability rock formations. Reactive transport modeling was integrated with laboratory experiments and large underground heater tests at Yucca Mountain to assess the long-term coupled thermal, hydrological, and geochemical processes that might arise from high-level radioactive waste being stored in unsaturated fractured rocks. Reactive transport modeling investigations for this site included simulating the evolution of fluid chemistry and mineral alteration around the waste emplacement tunnels for two operating temperature modes: above the boiling point of water for several hundred years, and below the boiling point for the entire life of the repository. The sealing of fractures by mineral precipitation above these tunnels was predicted to retard seepage into them. The heat released by radioactive decay was predicted to enhance the dissolution of wall rock minerals, leading to elevated dissolved silica concentrations and the precipitation of primarily amorphous silica above modeled tunnels (FIG. 3) (Spycher et al. 2003). The occurrence of this process was supported by laboratory experiments (Dobson et al. 2003). Reactive transport models also showed that, upon heating, CO_2 exsolved from the pore water in the rock matrix and then redissolved in water that had condensed in fractures further away from the modeled tunnel. This was confirmed by heater tests, the results of which could be reproduced by the RTMs (Sonnenthal et al. 2005), thereby providing confidence in model predictions. Models also suggested that calcite would precipitate from infiltration waters at a later-stage (FIG. 3), causing a further decrease in porosity and permeability in the host-rock fractures.

FUTURE NEEDS FOR MODELING RADIOACTIVE WASTE DISPOSAL

Reactive transport models have been important tools for assessing the long-term safety of the geologic disposal of nuclear waste. The development of efficient computing methods and increased computational power will allow us to more comprehensively address uncertainty and nonuniqueness and will increase our ability to perform long-term simulations with confidence. The coupling of processes that are often modeled separately—such as chemical, mechanical, and electric/galvanic effects—together with the development of more mechanistic process models are also bound to improve long-term predictive ability and accuracy.

The implementation of swelling/shrinkage models in simulations of clay backfills (Rutqvist et al. 2014) is an example of recent developments coupling RTMs with mechanical processes. Multicomponent diffusion and electrochemical migration (Tournassat and Steefel 2015) are other important processes to consider in clay barriers. Although significant advances have been made to include microbial activity and biogeochemical reaction networks into RTMs, such advances have been much less commonly applied in long-term performance assessments of waste disposal scenarios (Nakano and Kawamura 2010). The implementation of isotopic partitioning into RTMs may be promising to trace paleohydrogeological processes through a sedimentary formation and assess the long-term hydraulic containment of such formations (Hendry et al. 2015). Reactive transport models that incorporate multiphase flow (Sin et al. 2017) will be valuable for a better assessment of the production and migration of gas, such as H_2, derived from the corrosion of iron canisters. Surprisingly, increased confidence in long-term simulations of multiple barriers may come from RTMs performed at the smallest pore scale of heterogeneous porous media. These

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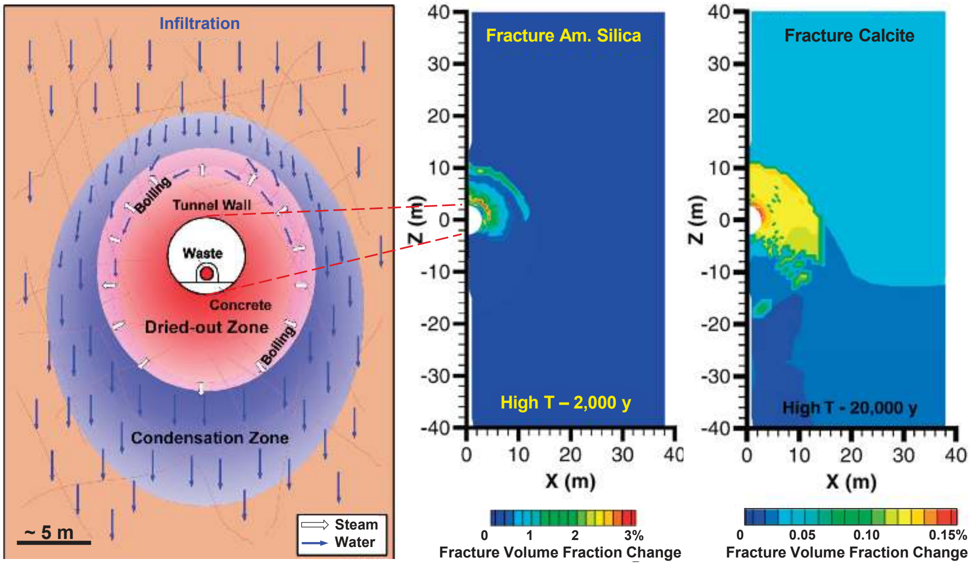

FIGURE 3 (LEFT) Conceptual model of coupled thermal and hydrological processes around a potential waste emplacement tunnel in volcanic tuffs at Yucca Mountain (Nevada, USA). Temperatures at the tunnel wall initially exceed the boiling point of water, drying out the rock in proximity of the tunnel and driving the transport of steam into fractures further away from where condensation eventually occurs. (CENTER) Reactive transport model contour plots of modeled precipitation of amorphous silica ("Am. Silica") after 2,000 years. (RIGHT) Reactive transport model contour plots of modeled precipitation of calcite after 20,000 years in fractures. ADAPTED FROM SPYCHER ET AL. (2003).

promising mechanistic models of interactions between solutes and mineral surfaces include, for example, a more detailed treatment of reactions rates (Molins et al. 2012), clogging by mineral precipitation beyond simple geometric correlations, and the explicit treatment of fractures (Deng et al. 2018).

Reactive transport models alone cannot fully assess the long-term performance of a nuclear waste disposal repository because of the wide range of length scales and intricately coupled physico-chemical processes that need to be addressed. However, RTMs have proven to be highly valuable. They will remain a unique tool by which to assess and constrain the long-term evolution of nuclear waste geologic repositories.

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