Predictability of the Evolution of Hydrogeological and Hydrogeochemical Systems: Geologic Disposal of Nuclear Waste in Crystalline Rocks

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Abstract: Confidence in long-term geologic isolation of high-level nuclear waste and spent nuclear fuel requires confidence in predictions of the evolution of hydrogeological and hydrogeochemical systems. Prediction of the evolution of hydrogeological and hydrogeochemical systems is based on scientific understanding of those systems in the present—an understanding that can be tested with data from the past. Crystalline rock settings that have been geologically stable for millions of years and longer offer the potential of predictable, long-term waste isolation. Confidence in predictions of geologic isolation of radioactive waste can measured by evaluating the extent to which those predictions and their underlying analyses are consistent with multiple independent lines of evidence identified in the geologic system being analyzed, as well as with evidence identified in analogs to that geologic system. The proposed nuclear waste repository at Yucca Mountain, Nevada, USA, differs in significant ways from potential repository sites being considered by other nations. Nonetheless, observations of hydrogeological and hydrogeochemical systems of Yucca Mountain and Yucca Mountain analogs present multiple independent lines of evidence that can be used in evaluating long-term predictions of the evolution of hydrogeological and hydrogeochemical systems at Yucca Mountain.

Predictability of Hydrogeological and Hydrogeochemical Systems

Predictions of future hydrogeological and hydrogeochemical conditions rely on projected uniformitarianism. That is, the assumption that those processes that have generated and controlled past and current conditions will generate and control conditions in the future. Geologic disposal of high level nuclear waste can require periods of isolation of hundreds of thousands of years and longer, and must consider processes that operate on the atomic scale over distances of tens of kilometers. The stratigraphic and mineralogic record and observations of naturally occurring isotopes provide evidence of long-term stability in some crystalline rock settings. In general, predictions of evolution of hydrogeological and hydrogeochemical systems require three components: conceptual models; analytical and numerical models; and physical and chemical properties of the systems. All three of these components must be determined for pertinent time and space scales.

Time and space scales of many natural geologic systems are amenable to analysis with respect to the capabilities of long-term nuclear waste isolation. For example, geologic and geophysical data permit credible predictions of climate, infiltration, seismicity, and volcanism over long repository (geologic) time and space scales. In contrast, experience with engineered systems in geologic settings has established confidence in the ability to predict the performance of those engineered systems over relatively brief periods of time.

Conceptual models are a fundamental component of the prediction of the evolution of hydrogeological and hydrogeochemical systems. Conceptual models are typically based on expert judgment, and form the core set of arguments about the processes that are important to the evolution of the hydrogeological and hydrogeochemical systems with respect to waste isolation. An example of expert judgment is the decision regarding representation of system dynamics. Steady-state hydrogeologic systems neglect changes in water storage over time, and thus are less burdensome to compute. At Yucca Mountain, for example, the DOE has chosen to represent the dynamics of climate change with a series of steady-state hydrologic simulations, bounded by step discontinuities. Other examples of expert judgment include: the choice of boundary conditions;

the choice of scale of feature to represent; and the choice to exclude representation of system attributes thought not significant to waste isolation.

Some hydrogeological and hydrogeochemical systems are amenable to representation by multiple conceptual models. However, the existence of multiple conceptual models does not ensure model fidelity. For example, Konikow et al. (1997) examined a model test implemented by six independent groups and found that all groups made fundamental errors in the implementation of a boundary condition. Regardless whether one or more conceptual models is invoked, it is critical that hydrogeological and hydrogeochemical system analysts explicitly describe the conceptual model(s). Conceptual models should be consistent with theory and must be tested, evaluated, and compared against field and laboratory empirical data. Inconsistency with empirical observations diminishes confidence in conceptual models.

Analytical and numerical models are used to make estimations of future repository performance. The analytical and numerical models are based on scenarios and conditions developed in the conceptual models, and are a mathematical representation of the physical and chemical systems to be simulated. The representation of the hydrogeological and hydrogeochemical systems in the numerical models can and should be evaluated by comparison with field and laboratory observations. For example, confidence is gained in numerical models that are able to reproduce closed-form analytical results and that are able to reproduce field observations of fluid potentials or discharges or chemical concentrations. Sasowsky (2006) emphasized that for model studies to have credibility, tests that demonstrate model capabilities for the particular model application must be published. Note also that these models cannot be considered “validated” against conditions outside of the range of the experimental or observational data. Post-modeling audits have shown that hydrogeological model predictions are often incorrect. For example, Bredehoeft (2005) found that natural processes and model predictions diverged (producing model “surprises”) in seven to 10 (out of 29 reviewed) model studies. Often the failure of a numerical model to reproduce field or laboratory observations with reasonable fidelity is the result of a fundamental flaw in the underlying conceptual model. Failures of conceptual or numerical models to predict with fidelity long-term behavior of hydrogeologic and hydrogeochemical systems demonstrate the significant value of independent geologic, hydrogeologic, and hydrogeochemical observations in evaluating conceptual and numerical model predictions.

Physical and chemical properties are derived from investigations performed as a part of site characterization and from the geologic record, and provide primary information on hydrogeological and hydrogeochemical parameter values. These values can differ significantly from those posed in conceptual models developed prior to site characterization. Furthermore, site characterization provides information on past variations in hydrological and hydrochemical systems. Studies of natural analogs provide useful information on controlling processes and on potential geologic stability and variability, particularly with regard to effects of introduced materials and the unnatural hydrologic and hydrochemical perturbations due to waste disposal. Natural analog studies also yield information on hydrogeological and hydrochemical characteristics of analogous systems under potential future climatic or geologic conditions.

Characterization of hydrogeological and hydrogeochemical systems is subject to both aleatoric uncertainty due to natural variability and epistemic uncertainty due to incomplete knowledge. Variability and uncertainty lead to ranges and distributions of variables. Although there will always remain some uncertainty with regard to understanding of natural systems, data derived from site characterization and natural analog investigations can reduce epistemic uncertainty and can better constrain the natural system aleatoric uncertainty. New empirical data should be evaluated as they are collected. For example, new data sample values can be compared to statistics of previously collected sample populations. When new data values are inconsistent with previous population statistics, further investigation and explanation are required.

Introduction of engineered materials, nuclear wastes, atmospheric gases, exotic water, and sustained energy sources in a geologic repository can significantly perturb the natural stability of hydrogeological and hydrogeochemical systems and diminish the reliability of the predictability of those systems. Those perturbations are not addressed in this paper.

Prediction of Ground-Water Flow

A conceptual model of ground-water flow includes consideration of hydrogeological system dynamics, boundary conditions, and initial conditions when required. The conceptual model of ground-water flow is based on expert opinion of what phenomena operating in the hydrogeological system are relevant to answering the questions posed in the analysis. Ground-water flow is a dynamic process within a relatively static geologic domain. Ground-water system dynamics result in transient changes in storage of water in the unsaturated and saturated zones. In the unsaturated zone, ground-water flow is highly non-linear because it depends strongly on the liquid water saturation state. In some hydrogeological systems, hydraulic responses significantly lag external stresses. For example, in the Pierre Shale of South Dakota, USA, mechanical rebound to erosion occurring at varying rates over the last two million years continues to change permeability and fluid pressure (Neuzil, 1993). In the Bure argillite—a host lithology being studied by the French high-level nuclear waste program— recently observed overpressurized zones have been attributed to osmotic processes operating over geologic time spans (Neuzil, 2007). Steady-state flow occurs when there is no change in ground-water storage over time; the system is in hydrogeological equilibrium. Prediction of the long-term behavior of steady-state hydrogeological systems is attractive to investigators because it requires fewer empirical data and less computational effort. All aspects of conceptual models of hydrogeological systems should be evaluated in comparison to multiple lines of evidence in the context of the problem to be solved.

Analytical and numerical hydrogeological models can be used to predict ground-water fluid potential, flow rates, flow paths, ground-water travel time, and ground-water discharge locations and magnitudes. Those predictions can be improved by forward and inverse calibration using measured water levels and measured transient responses to applied stresses such as pumping tests. Technical credibility is evaluated by comparison of model predictions to observed data not incorporated in the modeling process.

The suite of physical parameters required to perform hydrogeologic modeling is determined by the conceptual model. For a transient numerical hydrogeologic model, those parameters include determination of the spatial distribution of hydrologically-distinct rock units in the model domain, and determination of the permeability, porosity, and storage characteristics of those rocks. Where significant to flow (and thus to radionuclide transport), the distribution and hydraulic character of faults, fractures, and zones of fracture concentration must be taken into consideration. Rock stratigraphy, permeability, porosity, and storage characteristics can be measured empirically. Another required parameter, ground-water recharge, can be constrained by observational data and is commonly estimated through model calibration.

The geologic record provides primary information on local variations in ground-water flow systems such as variations in the ground-water table position and in surface discharge, variations that commonly result from changes in climate and geomorphologic conditions. Evidence of past water table elevations and discharge locations is preserved in diatomite deposits, subterranean and surface silicate and carbonate mineral deposits, zones of dissolution and karstification, and zones of alteration and mineral formation, among other indicators. In addition to climate variations, natural geologic processes can lead to variations in ground-water flow systems: seismicity can affect fracture characteristics; erosion, soil formation, and sedimentation can affect topography, infiltration, rock hydraulic properties, and subsurface flow; compaction and diagenesis can alter hydraulic properties of argillaceous and other sedimentary rocks; and mineral dissolution and deposition can alter hydraulic properties of evaporite rocks, to name a few. Over geologic time, it is common for these processes to occur simultaneously or in sequence, imprinting multiple generations of altered permeability and porosity on primary rock characteristics. For example, fluid flow (and thus radionuclide transport) in crystalline rocks is commonly influenced by rock fractures and faults that create multiple interacting scales of rock heterogeneity. Representation of rock heterogeneity—including rock fractures—in computer models has improved dramatically in the decades since Warren and Root (1963) published their dual-porosity model. Nonetheless, simulating fluid flow and radionuclide transport in fractured rocks remains an active and challenging research area.

Hydrogeochemistry

Ground-water chemistry is controlled by boundary conditions, e.g., soil zone or recharge zone chemistry, by coupled chemical transport and gas-water-rock chemical reactions (i.e., reactive transport) that depend on the geologic media, and by ground-water mixing along flow paths. Predictable hydrogeochemical parameters include concentrations and speciation of dissolved constituents, ionic strength, colloid concentrations and compositions, pH, oxidation potential, temperature, and sorption parameters.

Geochemical reactions are controlled by both kinetic and equilibrium processes. Realistic predictive geochemical models must generally involve thermodynamic and kinetic constraints as well as consideration of geochemical transport (e.g., Browning et al., 2003). Many low temperature reactions between water and crystalline rock mineral constituents such as feldspar and quartz are slow and may not achieve thermodynamic equilibrium even on time scales relevant to nuclear waste isolation requirements. Other reactions including surface complexation and precipitation or dissolution of secondary phases such as calcite and amorphous silica can approach equilibrium conditions rapidly relative to repository time scales. Heterogeneity in hydrogeochemistry is influenced by gas-water-rock reaction progress, fluid mixing, bedrock heterogeneity, and aqueous diffusion and dispersion. Hydrogeochemistry evolves along hydrologic flow paths tending toward equilibrium with longer water-rock contact times and higher rock/water ratios. The spatial and temporal evolution of ground-water chemistry can sometimes be inferred from chemical and isotopic or temperature heterogeneity. Secondary mineralogy that is a product of water-rock interactions provides an important record of past hydrogeochemical conditions and variations in those conditions.

Illustrations from the Proposed Yucca Mountain Repository

Yucca Mountain is located in the arid Mojave Desert, approximately 150 kilometers northwest of Las Vegas, Nevada. It is composed of rhyolitic volcanic rocks of Miocene age (approximately 12 million years old; Ma) which have been rotated and block-faulted in response to extensional tectonic stresses. The proposed nuclear waste repository horizon is in hydrologically unsaturated, fractured volcanic rocks, about 200-300 meters above the water table and about 200-300 meters below the ground surface. Precipitation as rain or snow infiltrates through a thick sequence of variably welded, non-welded, bedded, and fractured tuffs. In non-welded rocks, ground water flows as in other porous media, while in strongly welded rocks flow occurs almost exclusively in fractures. Present-day net infiltration is estimated to average about 3.6 mm/yr over the infiltration model domain, based on calculated differences between precipitation and evapotranspiration plus runoff (BSC, 2001). Those estimates are consistent with measurements of moisture content, temperature, and chloride concentrations in the unsaturated zone (Houseworth, 2007). Localized, fast unsaturated zone flow is indicated by bomb-pulse Cl-36 and other radionuclides at depth (e.g., Fabryka-Martin et al., 2006). At the water table, ground-water flow changes from generally vertical to nearly horizontal and follows the unconfined potentiometric surface (water table) gradient toward the south. The water table is relatively flat east and south of Yucca Mountain. However, on the western boundary of Yucca Mountain the water table drops approximately 50 meters from west to east as it crosses the Solitario Canyon Fault. Also, an upward gradient of approximately 20 meters has been measured between water in deep confined Paleozoic carbonate rocks and overlying volcanic rocks (Bredehoeft et al., 2005). Shallow flow paths in the saturated ground-water zone traverse gently dipping silicic tuffs and eventually encounter heterogeneous alluvial deposits before exiting the site boundary. Ground-water discharges in some areas of the Amargosa River Valley including Franklin Lake Playa approximately 60 kilometers south of Yucca Mountain.

The gas phase in the unsaturated zone at Yucca Mountain is air at saturation with liquid water and with elevated CO_2 partial pressure (Thorstensen et al., 1998). The ambient unsaturated zone gas-water-rock system is pervasively oxidizing. Precipitation of amorphous silica, calcite, and smectite occurs in fractures and in lithophysal cavities in the welded tuffs of the repository emplacement horizon (e.g., Whelan et al., 2002). These precipitates may be a consequence of slight evaporation associated with warming gas flow. Some formerly vitric (glassy) volcanic tuffs are partially or wholly altered to zeolite minerals, possibly due to hydrothermal activity in the geologic past.

Ground-water chemistry in the unsaturated zone is dilute, oxidizing, intermediate to slightly alkaline in pH, and rich in aqueous silica. Ratios of major cations and anions in the unsaturated zone are heterogeneous (e.g., Yang et al., 1996), in part due to differences in ground-water flow paths in fractures and in the rock matrix. Fracture water chemistry shows less effect of water-rock interactions and evaporation, suggesting that water in fractures has a shorter residence time than water in the rock matrix. Fracture water chemistry is dominated by sodium bicarbonate, relative to matrix water chemistry, which is dominated to a greater extent by calcium chloride and calcium sulfate. Infiltrating water collected in the Exploratory Studies Facility within tens of meters of the ground surface exhibits much of the same variation in hydrochemistry as observed throughout the unsaturated zone. These data indicate that near surface reactions play an important role in controlling water chemistry throughout the unsaturated zone at Yucca Mountain. Aqueous calcium concentrations tend to decrease with depth in the unsaturated zone of the mountain, probably because of calcite precipitation and exchange of calcium for sodium in secondary minerals, particularly zeolites. The chemistry of ground water extracted from boreholes in the volcanic rocks of the saturated zone tends to resemble the chemistry of the water in fractures and perched lenses in the volcanic rocks of the unsaturated zone at Yucca Mountain.

Some Lines of Evidence from the Geologic Record that Can Be Used to Evaluate Predictions of Evolution of Hydrogeological and Hydrogeochemical Systems at Yucca Mountain

<u>Water table rise and long-term hydrologic stability in the unsaturated zone</u>

Secondary mineral deposits in tuffs provide evidence of the maximum rise in the water table. Extensive alteration of originally vitric tuffs to zeolites, primarily clinoptilolite, occurred by water-rock interactions at elevations up to 100 meters above the present water table at Yucca Mountain (e.g., Vaniman et al., 2001). Extensive zeolitization has been attributed to chemical alteration near or below the paleo-groundwater table (e.g., Levy, 1991; Bish et al., 2006). Major zeolitization may have occurred shortly after deposition of the 12-Ma Miocene tuffs, even as they were cooling (Levy, 1991), although vitric tuffs may slowly weather to form zeolites even at the lower ambient temperatures of the present (e.g., Carlos et al., 1995).

Under ambient temperature conditions, reactions among secondary zeolites and groundwater have an influence on hydrochemistry. Infiltrating groundwater exchanges divalent cations, such as strontium and calcium for sodium and potassium in the zeolites (e.g., Vaniman et al., 2001). Mass balance calculations for strontium accumulations in zeolites suggest that zeolitic units are transmissive to fluid flow—despite the observation of perched water zones above these units—and that zeolites have concentrated strontium from percolating ground waters over geologic time (Vaniman et al., 2001). Saturated zone ground water appears to be at equilibrium with analcime (Murphy et al., 1996), which occurs as a secondary mineral at depth in Yucca Mountain.

Uranium-series and uranium-lead dates on opals in the unsaturated zone at Yucca Mountain have shown a general pattern of constant growth rates over geologic time (Paces et al., 2001; Neymark et al., 2002; Paces et al., 2004). Dates have been obtained on silica phases from microstratigraphic positions approximately 25 μm in size across millimeter- to centimeter-thick layers of secondary mineral coatings on fracture and cavity surfaces. Although the temporal resolution of these data is not sufficient to record hydrologic transients of a few thousand years or less, these data indicate average deposition rates of one to five millimeters per million years consistently among all samples measured. "These data imply that the deeper parts of the unsaturated zone at Yucca Mountain maintained long-term hydrologic stability throughout periods of significant climate variations over the past 10 million years" (Neymark et al., 2002).

Hydrothermal activity in the unsaturated zone

Petrography and microchemistry of secondary minerals in unsaturated zone fractures provides a record of long-term stable unsaturated fluid flow and geochemical conditions. Secondary mineral precipitates are found on less than ten percent of fracture and cavity surfaces of tuffs of the proposed repository emplacement zone. Calcite and silica deposits on footwalls and floors of lithophysal cavities—and not on the tops of cavities—indicate that those rocks never became fully liquid saturated and that flow was always percolating downward in those rock cavities dominantly under gravitational forces (Whelan et al., 2002). Secondary mineral paragenesis in the devitrified tuffs of the repository emplacement horizon is consistently seen to evolve as follows: 1) calcite with quartz and other silica phases with occasional fluorite or zeolites; 2) calcite with opal and chalcedony; and 3) calcite containing magnesium-rich zones with clear opal (Whelan et al., 2002; Wilson and Cline, 2006). Uranium decay series dating of opals of the last stage of secondary mineral precipitation indicates that this stage began at least two to three million years ago (Wilson et al., 2003). Two-phase fluid inclusions in calcite, which may have formed at elevated (hydrothermal) temperatures, were shown to have been trapped only in the earlier (older) stages of secondary mineral precipitation. No data indicate repeated periods of two-phase fluid inclusion formation (Wilson et al., 2003).

Alteration of clay minerals can provide evidence of hydrothermal activity in the geologic past. Smectite precipitation in small quantities occurs throughout unsaturated zone and saturated zone rocks at Yucca Mountain. In the unsaturated zone smectites are found on some fracture surfaces and in lithophysal cavities, indicating the presence of water. A clay mineral transition from smectite to illite occurs over a fairly short depth interval in borehole USW-G2, drilled north of the proposed waste emplacement zone to depths far below the water table. This transition has been interpreted to reflect the upper limits of a hydrothermal system that altered the rocks about 10 million years ago (Bish and Aronson, 1993). Estimated temperatures based on clay mineralogy approached 235°C in this system. Hypotheses of more recent hydrothermal activity in the unsaturated zone are inconsistent with extensive independent investigations, which found no evidence of hydrothermal activity at Yucca Mountain in the past five million years (e.g., National Research Council, 1992; Wilson and Cline, 2006).

Saturated zone flow

Demonstration of ground-water flow model fidelity is often accomplished by comparing observed and calculated water potential or hydraulic head. Where the residual difference between observed and calculated potential is small, the model is believed to be a credible representation of the natural hydrogeologic system. In a presentation to the U.S. Nuclear Waste Technical Review Board Panel on the natural system, a Center for Nuclear Waste Regulatory Analyses (CNWRA) hydrogeologist presented a model of the saturated zone at Yucca Mountain with a very small root mean square (residual) error of 1.1 m for the entire model domain (Winterle, 2004).

Confidence in the CNWRA model was further enhanced by a test comparing it with paleohydrological conditions. South of Yucca Mountain, a paleospring discharge formed a deposit known as the Horsetooth Diatomite. In simulating that past climate, the CNWRA analysts increased the ground-water recharge in the numerical model until discharge occurred from the model cell at the paleospring location (Winterle, 2004). The resulting water table rise under Yucca Mountain ranged from 50 to 100 m, consistent with geologic observations of alteration of vitric volcanic tuff to zeolites.

Using a novel thermal-perturbation technique, recent investigations in the volcanic rocks near the southern end of the Yucca Mountain saturated zone flow field identified zones of fluid velocity as high as 10 km/yr (Freifeld et al., 2006). Zones such as this were previously unknown at the Yucca Mountain site, and are not incorporated into DOE numerical ground-water models of the saturated zone at Yucca Mountain. The frequency and pervasiveness of these high-velocity zones has not been subsequently investigated, nor has the potential impact on model predictions of fluid flow and radionuclide transport been evaluated.

<u>Extent of Fracture-Matrix Water Interactions</u>

Saturated zone groundwater extracted from deep boreholes in the vicinity of Yucca Mountain is chemically undersaturated in calcite (Kerrisk, 1987; Murphy, 1995). However, core samples from the same boreholes contain calcite as a fracture filling material (Bish and Vaniman, 1985). These relations, together with information on the water producing zones in the boreholes, indicate that the ground water flowing in high permeability fracture systems is chemically isolated on a geologic time scale from water in a matrix pore system (Murphy, 1995).

<u>Waste Form Stability and Alteration on a Geologic Time Scale</u>

The Nopal I uranium deposit at Peña Blanca near Chihuahua, Mexico, is a natural analog of the proposed repository at Yucca Mountain (e.g., Murphy and Pearcy, 1992; Pearcy et al., 1994; Fayak et al., 2006). The geology (fractured silicic tuffs in an active extensional tectonic setting), semi-arid climate, and deep hydrologically unsaturated zone are closely analogous to the Yucca Mountain hydrogeological and hydrogeochemical environment. The primary uranium ore at Nopal I was uraninite, a close chemical and structural analog of spent nuclear fuel. Information from Nopal I relevant to the stability and predictability of the proposed repository at Yucca Mountain comes from studies of the geochemical alteration of primary uraninite and the formation of relatively stable secondary uranyl minerals in the oxidizing environment. Persistence of primary uraninite for millions of years at this site depends on its physical isolation from oxidizing conditions by silica cements. Stability of secondary uranyl minerals, principally uranophane, at Nopal I attests to their potential role in sequestering radionuclides at Yucca Mountain on a geologic time scale.

Conclusions

Crystalline rock systems can provide hydrogeologically- and hydrogeochemically-stable environments for geologic disposal of nuclear wastes over long time scales. Numerous lines of evidence are present in the geologic record that can support evaluation of predictions of evolution of hydrogeologic and hydrogeochemical systems at Yucca Mountain—predictions required to ascertain the ability to isolate spent nuclear fuel and high-level radioactive waste. Confidence in those predictions is increased when conceptual models, analytical and numerical models, and empirical observations are internally consistent and are consistent with all available geological, hydrogeological, and hydrogeochemical evidence.

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References

Bish, D.L., and Aronson, J.L. (1993) Paleogeothermal and paleohydrologic conditions in silicic tuff from Yucca Mountain, Nevada. Clays and Clay Minerals, v. 41, p. 148-161.

Bish, D.L., Carey, J.W., Chipera, S.J., and Vaniman, D.T. (2006) The importance of mineralogy at Yucca Mountain. In Uncertainty Underground (eds., A.M. MacFarlane and R.C. Ewing), MIT Press, Cambridge, Massachusetts, p. 217-235.

Bish, D.L., and Vaniman, D.T. (1985) Mineralogic summary of Yucca Mountain, Nevada. Los Alamos National Laboratory, Report LA-10543, 55 p.

Bredehoeft, J. (2005) The conceptual model problem—surprise, Hydrogeol. J., v. 13(1), p. 37–46.

Bredehoeft, J., Fridrich, C., and King, M. (2005) The lower carbonate aquifer as a barrier to radionuclide transport. Proceedings, WM'05 Conference, February 27 – March 3, 2005, Tucson, Arizona.

Browning, L., Murphy, W.M., Manepally, C., and Fedors, R. (2003) Reactive transport model for the ambient unsaturated hydrogeochemical system at Yucca Mountain, Nevada. Computers & Geosciences, v. 29, p. 247-263.

BSC (2001) Simulation of net infiltration for modern and potential future climates. U.S. Department of Energy Office of Civilian Radioactive Waste Management Contractor Report ANL-NBS-HS-000032 Rev 00 ICN 02.

Carlos, B.A., Chipera, S.J., and Snow, M.G. (1995) Multiple episodes of zeolite deposition in fractured silicic tuff. In Water-Rock Interaction 7 (eds. Y.K. Kharaka and A.S. Maest), Balkema, p. 67-71.

Fabryka-Martin, J., Flint, A., Meijer, A., and Bussod, G. (2006) Water and radionuclide transport in the unsaturated zone. In Uncertainty Underground (eds., A.M. MacFarlane and R.C. Ewing), MIT Press, Cambridge, Massachusetts, p. 179-197.

Fayek, M., Ren, M., Goodell, P., Dobson, P., Saucedo, A., Kelts, A., Utsunomiya, S., Ewing, R.C., Riciputi, L.R., and Reyes, I. (2006) Paragenesis and geochronology of the Nopal I uranium deposit, Mexico. International High Level Radioactive Waste Management 2006, p. 55-62.

Kerrisk, J.F. (1987) Groundwater chemistry at Yucca Mountain, Nevada, and vicinity. LA-10560-MS. Los Alamos National Laboratory, Los Alamos, NM, 118 p.

Konikow, L.F., Sanford, W.E., and Campell, P.J. (1997) Constant-concentration boundary condition: Lessons from the HYDROCOIN variable-density groundwater benchmark problem. Water Resources Research, v. 33(10), p. 2253–2261.

Houseworth, J. (2007) "Evaluation of Technical Impacts of Sandia National Laboratories Estimates of Infiltration on Unsaturated Zone Hydrology Simulation Results." Presentation to U.S. Nuclear Waste Technical Review Board Panel on Postclosure Performance, March 14, 2007, Berkeley, California. *http://www.nwtrb.gov/meetings/2007/march/houseworth.pdf*

Levy, S.S. (1991) Mineralogic alteration history and paleohydrology at Yucca Mountain, Nevada. Proceedings 2nd International Conference on High Level Radioactive Waste Management, p. 477-485.

Murphy, W.M. (1995) Contributions of thermodynamic and mass transport modeling to evaluation of groundwater flow and groundwater travel time at Yucca Mountain, Nevada. Materials Research Society Symposium Proceedings, v. 353, p. 419-426.

Murphy, W.M., Pabalan, R.T., Prikryl, J.D., and Goulet, C.J. (1996) Reaction kinetics and thermodynamics of aqueous dissolution and growth of analcime and clinoptilolite at 25°C. American Journal of Science, v. 296, p. 128-186.

Murphy, W.M., and Pearcy, E.C. (1992) Source-term constraints for the proposed repository at Yucca Mountain, Nevada, derived from the natural analog at Peña Blanca, Mexico. Materials Research Society Symposium Proceedings, v. 257, p. 521-527.

National Research Council (1992) Ground Water at Yucca Mountain: How High Can It Rise? National Academy Press, Washington, DC, 242 p.

Neuzil, C.E. (2007) The Link Between Anomalous Fluid Pressures and Geologic Forcing. Geological Society of America Abstracts with Programs, v. 39(6), p. 187.

Neuzil, C.E. (1993) Low fluid pressure within the Pierre Shale: A transient response to erosion. Water Resources Research, v. 29(7), p. 2007-2020.

Neymark, L.A., Amelin, Y., Paces, J.B., and Peterman, Z.E. (2002) U-Pb ages of secondary silica at Yucca Mountain, Nevada: Implications for the paleohydrology of the unsaturated zone. Applied Geochemistry, v. 17, p. 709-734.

Paces, J.B., Neymark, L.A., Marshall, B.D., Whelan, J.F., Peterman, Z.E. (2001) Ages and origins of calcite and opal in the Exploratory Studies Facility tunnel, Yucca Mountain, Nevada. U.S. Geological Survey Water-Resources Investigations Report 01-4049, 95 p.

Paces, J.B., Neymark, L.A., Wooden, J.L., and Persing, H.M. (2004) Improved spatial resolution for U-series dating of opal at Yucca Mountain,Nevada, USA, using ion-microprobe and microdigestion methods. Geochimica et Cosmochimica Acta, v. 68, p. 1591-1606.

Pearcy, E.C., Prikryl, J.D., Murphy, W.M., and Leslie, B.W. (1994) Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. Applied Geochemistry, v. 9, p. 713-732.

Freifeld, B., Doughty, C., and Finsterle, S. (2006) Preliminary estimates of specific discharge and transport velocities near borehole NC-EWDP-24PB. LBNL-60740, Earth Sciences Division, Lawrence Berkeley National Laboratory, 43 p. *http://www-esd.lbl.gov/ESD_staff/freifeld/pdfs/LBNL_60740.pdf*

Sasowsky, I. (2006) Model verification and documentation are needed. EOS, Transactions of the American Geophysical Union, v. 87:25, p. 248.

Thorstensen, D.C., Weeks, E.P., Haas, H., Busenberg, E., Pummer, L.N., and Peters, C. (1998) Chemistry of unsaturated zone gases sampled in open boreholes at the crest of Yucca Mountain, Nevada: Data and basic concepts of chemical and physical processes in the Mountain. Water Resources Research, v. 34, p. 1507-1529.

Vaniman, D.T., Chipera, S.J., Bish, D.L., Carey, J.W., and Levy, S.S. (2001) Quantification of unsaturated-zone alteration and cation exchange in zeolitized tuffs at Yucca Mountain, Nevada, USA. Geochimica et Cosmochimica Acta, v. 65, p. 3409-3433.

Warren, J.E., and Root, P.J. (1963) The behavior of naturally fractured reservoirs. Society of Petroleum Engineers Journal, September 1963, p. 245-255.

Whelan, J.F., Paces, J.B., and Peterman, Z.E. (2002) Physical and stable-isotope evidence for formation of secondary calcite and silica in the unsaturated zone, Yucca Mountain, Nevada. Applied Geochemistry, 17, p. 735-750.

Wilson, N.S.F., and Cline, J.S. (2006) Hot upwelling water: Did it really invade Yucca Mountain? In Uncertainty Underground (eds., A.M. MacFarlane and R.C. Ewing), MIT Press, Cambridge, Massachusetts, p. 165-178.

Wilson, N.S.F., Cline, J.S., and Amelin, Y.V. (2003) Origin, timing, and temperature of secondary calcite-silica mineral formation at Yucca Mountain, Nevada. Geochimica et Cosmochimica Acta, v. 67, p. 1145-1176.

Winterle, J. (2004) "CNWRA Modeling of Site-Scale Saturated Zone Flow at Yucca Mountain." Presentation to U.S. Nuclear Waste Technical Review Board Panel on the Natural System, March 10, 2004, Las Vegas, Nevada. *http://www.nwtrb.gov/meetings/2004/march%202004/winterle.pdf*

Yang, I.C., Rattray, G.W., Yu, P. (1996) Interpretation of chemical and isotopic data from boreholes in the unsaturated zone at Yucca Mountain, Nevada. USGS Water Resources Investigations Report 96-4058.