

**Some Issues Regarding the Measurements and Data Needed to
Characterize Repository Sites in Basalt, Tuff and Salt**

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1. General Groundwater Chemistry

Groundwater chemical compositions at all three types of sites must be known for two reasons; (1) to interpret their origin, age, and history so as to reconcile the host rock hydrology, and (2) to evaluate the impact of such groundwater compositions on radionuclide migration.

Adequate quality control over chemical sampling and analysis is critical to any such interpretation. If samples are collected from wells, definition of production zones is required as well as documentation that water has not been contaminated by drilling mud, corrosion of metal casings, or by atmospheric gases. Unstable chemical parameters such as pH, Eh, D.O, alkalinity, NH_3 , S^- and $\text{Fe}^{+2}/\text{Fe}^{+3}$ must be analyzed for in the field. Other unstable species such as organics and trace metals must be preserved by refrigeration, acidification or other techniques. All reported chemical analyses of major and minor components should include equivalent balances of cations and anions to permit assessment of the quality of the data.

The data of each site should be used to define chemical heterogeneties in the groundwater system such as (1) changes in water chemistry as a function of age, (2) changes in chemistry as

functions of flow direction, depth, and distance, (3) differences in interstitial pore chemistry and fracture water chemistry and (4) differences in water chemistry in hydrologically active and inactive parts of the groundwater system.

Such heterogeneities should be used to assess important geochemical controls on water chemistry. Such controls should include (1) source terms of dissolved species, (2) local or partial equilibrium conditions with respect to the mineral assemblage (3) ion exchange equilibrium or disequilibrium (4) kinetic rates of reaction of important solid phases. Water chemical data should be reduced using any number of computer speciation codes to identify major aqueous complexes, pH buffering controls, and chemical affinities relative to mineral phases.

2. Host Rock Mineralogy

A knowledge of host rock mineralogy is required to (1) evaluate the geologic history of the repository site, (2) interpret the evolution of groundwaters for hydrologic purposes and (3) determine the effects on radionuclide migration. Required information includes (1) identification and chemical analyses of rocks and individual minerals. (2) alteration and relic textures of mineral assemblages, (3) presence of open and healed fractures, (4) evidence of leaching or dissolution, and (5) location and presence of fluid inclusions particularly in salt. Total bulk mineralogy and chemical composition are excepted

to vary the most in salt with domal salt being almost pure halite and bedded salt containing interdigitated horizons of shale and other evaporite minerals. In this latter case, both detailed vertical and lateral changes in mineralogy will be required.

Estimates must be made as to the extent to which primary mineral phases are directly interactive with groundwater and to what extent they are isolated by alteration zones involving secondary minerals which line pore spaces and fractures. Such data are particularly important for primary highly reactive glass phases contained in both basalt and tuff.

Data must permit the determination of past and present secondary equilibrium mineral assemblages relative to groundwater conditions. The present assemblage should be compared with that predicted based on equilibrium modeling of the groundwater chemistry. Defining mineral assemblages currently in equilibrium with groundwater is complicated in extrusive volcanics such as tuff and basalt where zeolitic and clay phases may have formed under hydrothermal conditions during cooling of the flows. Also due to larger changes in paleo-water levels in the tuff at NTS, groundwater chemical conditions may have varied greatly producing sequences of secondary minerals which may not reflect current conditions.

3. Aquifer Surface Areas

The effective contact area between the repository rocks and groundwater is a critical parameter in determining chemical reactivity and sorptive capacity.

Although little surface area data is currently available and the subject poorly understood, any geochemical definition of a repository must include some estimate of such surface areas in order to model sorptive retardation of radionuclides. Possible methods include BET measurements on core, quantitative stereology, porosimetry and measurements of kinetic reaction rates of host rock minerals.

4. Radionuclide Analogues

A number of natural analogues such as U, C, Cs, I, Pb and Se are contained in measureable quantities in aquifers in basalt, tuff and salt. Their chemical distribution between the solid and groundwater phases can provide valuable information on the expected behavior of radionuclides under far field conditions. Needed information includes (1) source terms (2) concentrations and distributions in secondary minerals formed from groundwater (3) concentrations and speciation in the groundwater (4) the extent and reversibility of exchange and sorption with aquifer substrate. Trends in chemical concentrations of these analogues with changes in concentrations in other complexing species, changes in pH and Eh and changes in secondary mineralogy in the

aquifer would provide important information on solubility and transport controls of specific radionuclides.

5. Sorption on Host Rocks

Radionuclide sorption on mineral surfaces in aquifers is one of the most important mechanisms by which radionuclides are retarded. Consequently, a large body of information on the subject has been amassed for basalt, tuff, and basalt. However rigorous control of experimental conditions has often been lacking. For example, little concern has been paid until recently to the control or even the determination of redox conditions under which sorption parameters were determined. In addition many experiments failed to document whether measured sorption coefficients were reversible or whether they actually represent irreversible processes reflecting precipitation, coprecipitation or diffusion.

The sorption mechanisms and capacities in actual repository rocks will also be affected by precipitation and dissolution reactions involving the mineral substrates. Such reactions may both contribute competing chemical species and change the sorption substrate itself. Most sorption experiments have been made on freshly prepared basalt and tuff surfaces. In the actual aquifer, these surfaces may become coated with thin films of iron and aluminum oxyhydroxides or clay minerals whose sorption characteristics bear little resemblance to the bulk host rock.

Also incongruent dissolution of weathered silicate surfaces in tuff and basalt may strongly affect the apparent sorption capacity. Clearly depletion of cations in the surfaces of silicate rocks during weathering will result in progressive changes in both surface structure and charge distribution both of which will affect sorption relative to experimentally prepared surfaces.

Some of these problems can be partially overcome by more detailed data on changes in mineral substrates during concurrent sorption and weathering by using natural surfaces of weathered basalt and tuff obtained from cores. Analytical surface techniques such as XPS, AES, and SIMS are ideally suited for such characterization. However ultimately, experimentally measured sorption capacities should be compared and verified by using tracer tests under actual groundwater and aquifer substrate conditions.

Diffusion Processes

One potentially important mechanism for removal of radionuclides from groundwater is diffusion across the water-aquifer interface. If such mechanisms are operable over long time periods in the far field, in situ K_d values would be larger than those based on short term sorption phenomena.

Solid state diffusion into the structure of crystalline silicates or salt minerals is too slow to be important at ambient temperatures. However one phase in which solid state radio-

nuclide diffusion may occur is in volcanic glasses common to both tuff and basalt. Such diffusion may result from an expanded structure during hydration by groundwater.

Diffusion can also occur along boundaries between individual mineral grains or along defect structures within grains caused by dislocations or twinning planes. Diffusion can also proceed along interlayers of sheet silicates. Such types of diffusion would be very site-specific and would reflect the crystallization and possibly tectonic history of the repository rocks. In all cases, quantitative measurements of diffusion rates should be made on site specific rocks, diffusion coefficients and activation energies calculated, and the relative importance to radionuclide retardation assessed.

Colloids

Most studies of radionuclide migration in basalt, tuff and salt have focused on the transport of dissolved radionuclides by flowing groundwater. It is possible however that significant quantities of some nuclides could be absorbed onto the surfaces of colloids in the aquifer. Chemically, colloids behave quite differently from dissolved species and would not be expected to be retarded by the same mechanisms during migration.

A fairly substantial body of information exists on the theoretical behavior of colloids but little detailed information is available on colloids in actual aquifers. Silica gels and colloids may be expected in basalt and tuff due to rapid

dissolution of natural glasses. Indeed silica gels have been observed in fracture fillings and spring discharges at NTS. Ferric and aluminum hydroxides have also been observed in unrelated groundwaters.

The concentrations of specific types of colloids, their affinity in sorbing radionuclides and their ability to be transported in site specific cases must be documented.

Redox Conditions

Concentrations levels and rates of radionuclide transport are dependent on solubilities and complexation which in turn are functions of their valency state and redox conditions of the groundwater. The few direct downhole measurements of Eh that have been made in repository aquifers using Pt electrodes are subject to many errors. Recent data indicate that free electrons can not exist in solution at concentrations in excess of 10^{-32} molar. Additional oxidation-reduction components in solution that buffer or poise the Eh of the solution are often very dilute and may not be in internal equilibrium within the system. Also interaction of groundwater components with Pt sensing electrodes and the presence of contaminating sorbed oxygen may affect direct measurements of Eh. For example the formation of oxide or sulfide coating on a Pt electrode surface can lead to Eh measurements reflecting Pt-PtO or Pt-PtS complexes as a function of pH rather than the Eh of the groundwater being sampled.

Additional data on specific redox couples such as $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{SO}_4^{2-}/\text{S}^{-2}$, $\text{As}^{+3}/\text{As}^{+5}$ and dissolved oxygen concentrations are required. In addition, other redox defining species, including radionuclides, could be added to groundwater tracer tests and their speciation and effect on overall buffering of redox system defined.

Also information is required on the effect of mineral reaction kinetics on aqueous redox conditions. In the case of basalt host rocks, redox may be controlled and buffered by the abundance of iron silicates and oxides. Recent NRC research suggests that such minerals can contribute electrons directly to solution during weathering reactions. This suggests that aqueous redox may not be controlled by aqueous redox equilibrium but by kinetic rates of surface oxidation of the minerals. Redox controls on tuff aquifers are probably the least well defined due to low concentrations of iron both in the groundwater and in the host rock. Such a redox system would be expected to be poorly buffered as is apparently suggested by the presence of dissolved O_2 in Pleistocene-age groundwater. Salt repository rocks may have redox conditions dependent on sulfur components as well as interbedded organics. In all three cases comprehensive data on individual redox species as well as mechanisms and reaction rates of electrochemically active solids are required in addition to electrode methods.