

Unlikelihood of localized corrosion of nuclear waste packages caused by deliquescent brines

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The U.S. Nuclear Waste Technical Review Board and consultants for the state of Nevada have recently postulated that Ca and Mg chloride brines formed from deliquescent salts in dust on the surface of waste packages of alloy 22, would cause localized corrosion and waste package failure within a few hundred years after repository closure, thereby compromising compliance with regulatory criteria at a Yucca Mountain repository. EPRI has sponsored an independent analysis to assess the risk of such corrosion and waste package failure, and concludes that it is extremely unlikely.

First, the high sulfate content, and high nitrate/chloride ratio (1.3-6.5) of salts in the dust expected to enter the repository, preclude the formation of corrosive chloride brines, which require a nitrate/chloride ratio of <0.2. Further, if such brines could form, they would decompose leaving an alkaline residue at anticipated repository temperatures, with any acid gases released neutralized by basic minerals in the wall rock. Also, the chloride content of the dust is only 0.4% or less, whereas 60% of the dust is comprised of basic minerals, 7% of which would be sufficient to neutralize all possible corrosive acidity that might be produced by deliquescent brines.

Because the breakdown and re-passivation potentials associated with pitting are significantly more positive than the corrosion potential that could be achieved on alloy 22 waste packages, localized corrosion is only possible as crevice corrosion in occluded regions on the surface. Published experimental studies and modeling indicate that the high porosity and O₂ permeability of the dust, along with dust alkalinity, prevent the initiation of crevice corrosion. Also, conditions in crevices that might form will be such that corrosion should decrease with time and be stifled without waste package penetration.

Reactivity of heterogeneous riverine sediments to molecular oxygen

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Controls on the redox status of aqueous systems need general understanding. The redox reactivity of heterogeneous Holocene riverine deposits (in Rhine-Meuse delta) to O₂ has been investigated along with groundwater chemistry and extensive bulk geochemical analyses including Sedimentary Organic Matter (SOM) and sulphur. For this purpose, sediment and groundwater samples were taken from the five most dominant facies of the layer, classified on grain size and lithogenesis (channel deposits, eolian dunes, floodplain deposits, levee deposits, peat deposits). The sediment samples were incubated for 50 days while continuously measuring O₂ consumption and CO₂ production.

The combined geochemical and incubation data show that both pyrite and SOM were the main reductants in these sediments, and thus primarily determine the potential reactivity to O₂. Within facies, samples from reduced groundwater environment showed higher reactivity than those from (sub)oxic environment, but did not necessarily have less reductant content. Thus, no straightforward linear relation between pyrite or SOM content and the rate of oxidation existed.

For all incubations, the initial reactivity was high and then dropped to a much lower rate when a steady state was reached. The initial rates measured in the finely textured sediments (floodplain deposits, levee deposits, and peat deposits) were significantly higher than for the coarser facies (channel deposits and eolian dune deposits). This indicates that grain size is an important controlling factor on initial reactivity. However, the steady state reactivity only differed a factor 2-5 among the facies, suggesting that other factors started dominating reactivity.

The results show that the redox reactivity within a geological unit is highly variable with different lithology, redox environment, contents of the reductants, and also suggest a relation with ageing under paleohydrological conditions (i.e., oxygen exposure time). This has important implications for any solute transport modeling in which aquifer reactivity is considered.