RAI: Volume 3, Chapter 2.2.1.3.3, First Set, Number 8:

PTn pore water compositions and interactions with the PTn lithologic unit at elevated temperatures were not included in the NFC model. Provide additional information to demonstrate that the water compositions predicted by the NFC model adequately represent the potential range of seepage water chemistry, considering lithologic unit heterogeneity, temperature, and starting water composition.

Basis: The thickness of the TSw varies by about ±50 m from the 200-m average value used in the NFC model. In areas of the repository where the TSw is less than 200-m thick, a packet of water originating 200-m above the repository would have a PTn pore water composition and would travel through some thickness of the PTn before entering the TSw unit. SAR Figures 2.3.5-22(a) and (b) demonstrate that the PTn pore water compositions can be significantly different than those of the TSw and the chemical evolution of those PTn waters could be significantly different than that of TSw waters, which were used as input to the NFC model.

1. RESPONSE

The four starting waters used in the near-field chemistry (NFC) seepage model simulations were chosen to represent the entire range of available pore-water compositions, and include pore waters from three of the four repository-level lithologic units (Tptpmn - TSw middle non-lithophysal unit, Tptpll - TSw lower lithophysal unit, and Tptpul - the TSw upper lithophysal unit) (SNL 2007, Section 6.6). Variability in both the mineralogic and hydrologic properties of the four repository units is explicitly propagated through the model as uncertainty in the degree of water–rock interaction.

Engineered Barrier System: Physical and Chemical Environment (SNL 2007, Section 6.11) specifically considered the potential for reaction of PTn pore waters in the TSw and showed that they evolve similarly to TSw starting solutions. PTn pore water SD6-3345 was used in the alternative conceptual model because it falls in the middle of the available PTn pore-water compositions.

The model results for the PTn water and TSw waters (Groups 1 and 3) are compared in Figures 6.11-1 to 6.11-6 of *Engineered Barrier System: Physical and Chemical Environment* (SNL 2007) to show that the use of pore waters from the TSw by the model adequately bounds the chemical characteristics of a representative PTn pore water.

During the thermal pulse, reaction of waters inside the PTn will occur at lower temperatures and be relatively minor compared to reaction that occurs under the higher temperatures expected in the TSw close to the emplacement drifts. The maximum temperature calculated at the PTn boundary is approximately 40°C, and such temperature would lead to a minor increase in glass dissolution rates of 1.9 to 4.3 times the ambient glass dissolution rates. This means that temperature will result in only a minor addition of dissolution-derived mineral components to

solution. The increases in glass dissolution rates were calculated assuming activation energies for glass dissolution of 31 and 69 kJ/mol (BSC 2004). These activation energies, measured for waste glasses, are consistent with the range of activation energies observed for basalt glass dissolution (41 to 65 kJ/mol). In the TSw, higher temperatures, up to 96°C, would cause more dramatic increases in fluid rock interaction than the smaller temperature rise in the PTn. Feldspar dissolution rates in the TSw are calculated to increase by a factor of 49.8 with a temperature shift from ambient to 96°C (assuming a feldspar dissolution activation energy of 49 kJ/mol). This means that fluid-rock interaction will cause the most substantial changes in the chemistry of fluids closest to the repository. Because only minor changes in fluid chemistry will be seen in waters near the top of the rock column where the magnitude of the thermal pulse will be less, the variability in the thickness of the TSw will have little effect on the overall extent of fluid-rock interaction.

The information presented above demonstrates that NFC model water composition predictions adequately represent the potential range of seepage water chemistry, considering lithologic unit heterogeneity, temperature, and starting water composition.

2. COMMITMENTS TO NRC

None.

3. DESCRIPTION OF PROPOSED LA CHANGE

None.

4. REFERENCES

BSC (Bechtel SAIC Company) 2004. *Defense HLW Glass Degradation Model*.
ANL-EBS-MD-000016 REV 02. Las Vegas, Nevada: Bechtel SAIC Company.
ACC: DOC.20041020.0015; DOC.20050922.0002; LLR.20080408.0271; DOC.20081021.0002.

SNL (Sandia National Laboratories) 2007. *Engineered Barrier System: Physical and Chemical Environment*. ANL-EBS-MD-000033 REV 06. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070907.0003.

RAI: Volume 3, Chapter 2.2.1.3.3, First Set, Number 11:

The NFC model predicts the occurrence of two alteration minerals (celadonite and phillipsite) that are not observed, or rarely observed, at Yucca Mountain. The unique thermodynamic properties of these minerals may impact the chemical equilibria with other minerals and chemical species in solution. Demonstrate that the NFC-model-predicted seepage water chemistry is not significantly affected when the model considers alteration minerals more commonly observed at Yucca Mountain.

Basis: SAR Section 2.3.5.3.3.5.2 compares the alteration minerals predicted by the NFC model with mineral assemblages observed at Yucca Mountain. The NFC model predicts the occurrence of two alteration minerals (celadonite and phillipsite) that are not observed, or rarely observed, at Yucca Mountain. SAR Equation 2.3.5-5 indicates that celadonite is an important product of a feldspar dissolution reaction that controls the potassium concentration in solution. The SAR states that while celadonite and phillipsite may not be the actual minerals that form at Yucca Mountain, the use of these minerals in the model would still result in the correct trends in the evolution of seepage water chemistry because the minerals mainly serve as sinks for elements like aluminum, potassium, and magnesium (celadonite) or aluminum, sodium, potassium, and calcium (phillipsite).

However, the use of these minerals in the NFC model, instead of those more commonly observed at Yucca Mountain, ignores the potential effect the unique thermodynamic properties of these minerals may have on the chemical equilibria with other minerals and species in solution. It is possible the NFC model would predict significantly different seepage water compositions if the model considered more commonly observed alteration minerals.

1. RESPONSE

The differences in thermodynamic properties of alteration minerals other than celadonite and phillipsite are bounded by the uncertainty assigned to seepage water chemistry in the total system performance assessment (TSPA). Also, the near-field chemistry (NFC) model-predicted seepage water chemistry is not significantly affected when considering alteration minerals more commonly observed at Yucca Mountain.

1.1   DEPENDENCE OF NFC RESULTS TO ALTERATION MINERAL ASSEMBLAGE

Near-field chemistry-predicted seepage water compositions depend very little on the alteration mineral assemblage used in the reaction path calculation. To examine this, a number of new parallel reaction path calculations were performed with celadonite and/or phillipsite suppressed from precipitating while tracking sodium, potassium, calcium, magnesium, and pH as a function of feldspar dissolution. The four representative waters from the NFC model were used as the input waters. Feldspar alteration must exceed 0.008 to 0.01 moles before sodium and potassium

concentrations increase above the base case by over 10%. Between 0.002 to 0.008 moles of feldspar must dissolve before calcium, magnesium, and pH deviate from cases performed with no celadonite or phillipsite suppressions. Maximum predicted pH shifts are on the order of 0.5 units. The vast bulk of NFC realizations (~99%) were performed at feldspar alterations below the range where deviations in fluid chemistry can occur, with only 1.08% of the NFC realizations performed at conditions where fluid chemistry is affected by the choice of alteration mineral in the calculation (i.e. where greater than 0.00316 moles of feldspar has dissolved). Moreover, since the TSPA primarily samples intermediate values of the range away from the high end of the WRIP (the Water Rock Interaction Parameter, the amount of feldspar dissolved), the effect of alteration mineral(s) is bounded by the uncertainty of the model. For this reason, the NFC-predicted seepage water chemistry is not significantly affected by the choice of alteration mineral(s) used in the model; hence the model is adequate for use.

1.2   COMPARISONS BETWEEN NFC AND THC MODELS

The near-field chemistry model (SNL 2007) predicts fluid compositions that are similar to those predicted by the THC seepage model. Mean predicted sodium and potassium levels are typically within 50% of each other. Predicted pH values diverge during the boiling period, but are within 0.4 units of each other in the critical post-drift wall boiling period (SNL 2007, Section 7.1.3.4). Both models predict similar trends in dissolved calcium levels except from approximately 400 to 4,000 years when the two models result in different predicted CO_2 levels (calcium and CO_2 levels are linked by calcite equilibria).

1.3   LIMITATIONS OF THERMODYNAMIC DATA

Over time the composition of clays and zeolites can change in response to changes in the cation ratios of the fluids that contact them and to the ambient temperature field. Kinetic factors may also limit growth of clays and zeolites and their subsequent re-equilibration with changing fluid chemistries. The end result of these uncertainties is that it is difficult to predict the specific identities and abundances of individual alteration phases. Reaction path calculations only provide a gross picture of the chemistries of the alteration phases and the fluids in contact with them. One of the principal approximations that most reaction path calculations rely on is the fixing of clay/zeolite mineral stoichiometries, as opposed to allowing solid solutions to form. This allows the free energies of pure phases to be relatively easily defined and applied, though it complicates the application of reaction path models to natural clays/zeolites which tend to be solid solutions, and whose free energies are not well defined. Simplified stoichiometries are instead used as proxies for the more complicated natural phases. The NFC model used celadonite as a proxy for chemically similar illite clay and phillipsite as a proxy for Na-K-Ca bearing zeolites.

Although celadonite has not been observed at Yucca Mountain, chemically similar illite has. Illite and celadonite are both potassium- and magnesium-bearing micas. Smectites are observed as common alteration products in the rock. However, they are not predicted to form in the NFC calculations because either smectite end-member compositions are fixed in the calculation or because the conditions modeled to occur in the future differ from those that originally caused smectites to form in the TSw.

Like clays, zeolites are solid solution minerals whose individual stoichiometries are difficult to predict. Phillipsite, predicted to form by the NFC model, is rare at Yucca Mountain; clinoptilolite, heulandite, mordenite, and chabazite are more common. To predict fluid chemistry, the NFC model treats zeolites as a group sink for potassium and sodium produced by feldspar dissolution. Phillipsite is predicted to form first; if it is suppressed, other sodium, potassium, ($\pm$Ca) zeolites form instead, consistent with the general presence of Na-K-Ca bearing zeolites at Yucca Mountain. Therefore, these analyses demonstrate that the NFC model-predicted seepage water chemistry is not significantly affected when the model considers alteration minerals more commonly observed at Yucca Mountain.

2. COMMITMENTS TO NRC

None.

3. DESCRIPTION OF PROPOSED LA CHANGE

None.

4. REFERENCES

SNL (Sandia National Laboratories) 2007. *Engineered Barrier System: Physical and Chemical Environment*. ANL-EBS-MD-000033 REV 06. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070907.0003.