

BUFFER WORKSHOP REPORT

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Prepared by

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APPENDIX A—NRC-CNWRA BUFFER WORKSHOP—2012 AGENDA

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: None.

ANALYSES AND CODES: None.

1 BUFFER WORKSHOP SUMMARY

A one-day workshop on buffer was held June 26, 2012, at the U.S. Nuclear Regulatory Commission (NRC) in Rockville, Maryland, and the Center for Nuclear Waste Regulatory Analyses (CNWRA[®]) in San Antonio, Texas. This workshop focused on discussions of processes and characteristics of potential buffer materials proposed to be used in international high-level radioactive waste disposal programs. The objective of the workshop was to provide a higher-level understanding of the near-field barrier knowledge base that can help identify possible information needs for assessing the long-term performance of near-field barriers for isolating nuclear wastes. The workshop is part of a broader effort to prepare NRC to respond to potential changes in National high-level waste policy. Technical issues identified in this report will help NRC (i) further refine issues as they pertain to any changes in National policy and (ii) plan future staff activities.

Both NRC and CNWRA staffs participated in this, the second workshop devoted to buffer. Discussions at a buffer and backfill workshop held during the summer of 2011 were documented in Lenhard, et al. (2011). The 2011 workshop covered the spectrum of issues for buffer and backfill by identifying features and functions, and proceeded with the intention of identifying information needs, key uncertainties, and areas needing further understanding. The 2012 buffer workshop began with a summary of the 2011 workshop, providing a context for this workshop discussion. Not all knowledge gaps, uncertainties, and areas needing further understanding from the 2011 workshop were addressed in the 2012 buffer workshop. Rather, this latest workshop focused on progress over the past year in selected areas, especially those pertaining to a bentonite buffer. Specific areas discussed at the 2012 workshop were:

- Flow in bentonite buffer
- Swelling and swelling pressure
- Geochemical conditions at waste package/buffer interface
- Modeling bentonite water chemistry relevant to colloids
- Gas and microbial effects at waste package/buffer interface and buffer erosion
- Insights on sulfide corrosion of copper waste package
- Bentonite data
- Potential future work

The following sections summarize the workshop discussions. The order of the sections generally follows the agenda, which is provided in the appendix.

2 FLOW IN BENTONITE BUFFER

Understanding the state of water in clays can provide insights for thermal-hydrological-mechanical-chemical processes. Specifically, the small-range forces (see below) acting on groups of water molecules may affect the flow of water, temperature at which boiling may occur, swelling, and chemistry. The macro-structure of clays lends itself to being viewed at different scales for both porosity and the time scale of water movement. Clays, such as smectites, form aggregates.¹ Clay platelets form stacks that comprise granules (particles) at the micro-scale. The granules form a collection that comprises the mid- to macro-scale structure of the porous

¹The term aggregates as used in this instance refers to a collection of particles or granules that comprise the meso-or macro-scale structure of the porous medium. In all later usages in this document, the term aggregates refers to the granules or particles themselves, thus leading to the inter- and intra-aggregate distinction.

medium. Lempinen (2011) used the following description to link the porous medium structure to the state and movement of water: “(T)he stacks are aggregated together, so that three-level porous space is formed: the largest pores are between the aggregates; inside the aggregates there are voids between the stacks; and inside the stacks there are planar spaces between the clay platelets.” Water within and adjacent to stacks of clay platelets behaves differently than the water between aggregates (Lempinen, 2011; Kleinfelder-Domelle and Cushman, 2012) because a different set of forces predominates. Small-range forces such as van der Waals, electrostatic (ion and dipole), and osmotic forces affect intra-aggregate water molecules (specifically, groups or multiple layers of water molecules), including water molecules on the edge of aggregates (Corey, 1986; Selker, et al., 1999). Larger-range and body forces, specifically capillarity and gravity, play a more prominent role for movement of water surrounding aggregates (inter-aggregate). Capillarity and gravity typically dominate saturated and unsaturated flow in porous media. The discussion of multiple forces acting on water would appear to lend itself to application of the unifying concept of potential theory. Whereas application of total potential theory in this case may be useful qualitatively or conceptually, there is some disagreement on the validity of the approach for quantitative analysis due to the difference in applicable scales for the different forces (e.g., Corey, 1986).

The prominence of forces acting on water at different scales leads naturally to spatial and temporal perspectives that are important for thermal-hydrological-mechanical-chemical processes. Water in larger pores where gravity and capillarity are the dominant forces has been called bulk, interaggregate, or interparticle water. Water within aggregates has been referred to as interlayer, interlamellar, intra-aggregate, or vicinal water. Water at the two pore scales moves on different time scales in response to external forces. Exchange of water between inter- and intra-aggregate locations may add complexity to transport variables such as residence time. The view of water in clays as either interparticle or interlamellar is supported by studies of the geometry and distribution of pores (e.g., Holmboe, et al., 2012). A bimodal distribution is envisioned where smaller pores are associated with interlamellar locations and the large pores are associated with potentially interconnected large pores of the interparticle spaces. For the FEBEX-type bentonite used at underground research laboratories in Europe for waste disposal research, Lloret and Villar (2007) made measurements supporting a bimodal distribution of pore diameters. The distribution of smaller pores peaked at diameters of approximately 10 to 20 nm [4×10^{-7} to 8×10^{-7} in], and the larger pores peaked at diameters in the range from 0.01 to 0.1 mm [4×10^{-4} to 4×10^{-3} in]. The void proportion of large pores relative to small pores increased with decreases in precompacted dry density of the porous medium. Additionally, Holmboe, et al. (2012) reported values of interparticle pore space as 1 to 10 percent for MX-80 bentonite, which typically has total porosity reported as 40 to 50 percent. For MX-80 compacted to dry densities anticipated for use in waste disposal [1.6 to 2.1 g/cm³ [0.058 to 0.076 lb/in³]], the interparticle porosity values were less than 4 percent. If the effective porosity is 10 percent or less of total porosity, there will be implications for flow (conceptualization of flow) and transport (e.g., tortuosity, which is used to estimate effective diffusion). The multiple scale perspective of the state of water in bentonites affects hydraulic conductivity and boiling temperature, as described in the following paragraphs.

Hydraulic conductivity estimated for a clay would be expected to be dominated by the interconnected large pores. As the swelling pressure increases, the large pores may be “squeezed,” thus reducing the size of the interconnected pathways. As the portion of water in the small pores increases over that in the large pores, the overall effect on flow of the small-range forces (e.g., van der Waals and electrostatic) increases. The increased consequences of the small-range forces on water properties, such as the change in viscosity near liquid-solid interfaces (Liu, et al., 2012), leads to overall flow being described as

non-Newtonian, which deviates from flow predicted by Darcy's Law (i.e., flow is linearly related to the gradient of pressure).

Taking this viewpoint of processes and pore space a step further, the swelling of smectites as water is imbibed leads to an interesting question: is the swelling due to (i) a change in interparticle pore space, (ii) an increase in the small interlamellae pores, (iii) an expansion of the volume of the solid portion of the porous medium, or (iv) all the above? The discussion at the workshop revolved around the possible importance of making this distinction. Attributing the swelling to changes in porosity or the volume of the solid material may have implications for (i) numerical modeling approaches that link thermohydrological and geomechanical processes and (ii) estimates of diffusion coefficients for transport.

The forces acting on water in smectites also may have implications for estimating the boiling temperature expected in bentonite buffers surrounding emplaced waste packages. Other countries are constraining emplacement strategies to keep temperatures below 100 °C [212 °F]. It is important to determine the boiling temperature because other processes, such as two-phase flow and convection, could occur in a disposal concept with bentonite buffer surrounding a waste package. The temperature at which water boils in clay media would be expected to be higher than in coarse granular media due to the increased prominence of capillarity and small-scale forces such as van der Waals and electrostatic forces (Adamson and Gast, 1997). Capillarity and small-scale forces are attractive forces that would counter the effect of heat perturbation to boil the water. In addition, higher solute concentrations lead to higher boiling temperatures (Aiken, 1954).

The boiling temperature also will depend on whether the system is open or closed. The system would be open if gas leaks out of the buffer, or along pathways connected to access drifts. If the system is considered open, and the pressure is nominally atmospheric, the boiling temperature will nominally be 100 °C [212 °F] assuming pure water. The system would potentially be closed if the outer bentonite buffer is saturated, thus sealing the system. Assuming hydrodynamic equilibrium and a depth of 300 m [984 ft] below the water table, the water pressure would be approximately 3 MPa [30 bar]. On the phase diagram for water, this pressure would imply the temperature needed for boiling is over 200 °C [392 °F]. Also, in a closed system, the host rock will impose a water pressure on the buffer, which could be considered a minimum pressure to use on the phase diagram of water to estimate a boiling temperature. Water pressure in the swelled (outer) buffer, however, could be higher than ambient. Estimation of ambient host rock pore water pressure using the typical assumption of 9.8 kPa/m [0.03 bar/ft] is generally not valid for argillite host rock because it assumes hydrodynamic equilibrium. Particularly for argillite host rock sites, hydrodynamic disequilibrium is the norm due to the impact of clay layers on the overall flow system (e.g., Neuzil, 1995). In summary, judging whether the system is open or closed and estimating the pressure in the inner buffer are not straightforward. Evaluation of the potential for boiling is a ripe area for future work.

3 SWELLING AND SWELLING PRESSURE

The evaluation of swelling and swelling pressure due to water absorption in clay soils was discussed, focusing on an approach based on numerical geomechanics modeling.

Swelling is desirable in clay buffer designs to maintain low permeability of the buffer material and physical integrity of the buffer-canister design and to reduce independent motions during a seismic event. High swelling pressure can help prevent development of advective flow or buffer

erosion. Potential undesirable effects of high swelling could include mechanical damage to canisters and host rock fracturing. On the other hand, low swelling pressure in the buffer could favor conditions for development of advective flow or buffer erosion.

The swelling behavior of clay soils is typically characterized using indices, such as swelling pressure or swelling potential, that are defined for the assessment of swelling behavior under standardized conditions. The indices do not retain the same meaning under different loading conditions and, therefore, are not suitable for generalized geomechanics modeling. A measure of swelling behavior suitable for numerical modeling—the unit swelling potential—was identified and can be evaluated using results of a free-swell test or numerical back analysis of confined swelling tests. Examples of numerical model calculations using the unit swelling potential were discussed. The numerical model calculations will be documented in a CNWRA report that is currently under preparation. Additional verification of the modeling approach will be performed as a part of the coupled processes task.

4 GEOCHEMICAL CONDITIONS AT THE WASTE PACKAGE/BUFFER INTERFACE

Waste package corrosion will depend on the chemistry of water contacting the waste package material. The chemistry of this water and of bentonite porewater will evolve with time as host rock groundwater penetrates the buffer and interacts with the bentonite material. To understand the geochemical evolution of the bentonite and waste package–bentonite interface, reactive transport simulations were conducted using the X1t code, which is part of the Geochemist's Workbench suite (Bethke, 2008). X1t can model reactive transport, accounting for the effects of mineral dissolution/precipitation, cation exchange between aqueous solutions and clay minerals, and protonation–deprotonation reactions on clay edge sites. All model results discussed in this section are preliminary; final results will be documented in a CNWRA report that is in preparation. The simulations considered an MX-80 bentonite buffer in contact with a waste package on one end and host rock on the other end. The bentonite was assumed to be intact and fully saturated, such that diffusion is the dominant mechanism of transport through the buffer. Two waste package materials (carbon steel and copper) and three groundwater compositions were considered in the simulations. One water composition represents the chemistry of water from an argillaceous host rock [Opalinus Clay (Wersin, 2003)] and the other two compositions represent the chemistry of water from a granitic host rock [samples from Aspö and Gideå in Sweden (Bruno, et al., 1999)]. A constant temperature gradient was assumed across the bentonite, to be present—20 °C [68 °F] at the bentonite–host rock interface and 95 °C [203 °F] at the waste package–bentonite interface.

The simulation results indicate that the chemistry of water in the bentonite and at the waste package–bentonite interface is determined by the interaction of the bentonite with diffusing host rock groundwater. The bentonite composition is altered by cation exchange with the groundwater, but the swelling property of the bentonite is affected more by changes in ionic strength of the porewater than by cation exchange reactions. The bentonite porewater pH, which can affect radionuclide sorption behavior, changes due to interaction with infiltrating host rock groundwater. Bentonite porosity change due to mineral dissolution/precipitation is negligible. Montmorillonite, quartz, and calcite are persistent phases at 10,000 years.

Much of the change in water chemistry at the waste package–bentonite interface occurs within 500 to 1,000 years. To determine the effect of chemistry on the corrosion of carbon steel and copper waste package materials, the water chemistries calculated at 500 and 1,000 years using

X1t were used as input into corrosion analyses. Anodic and cathodic current densities for various reactions were calculated using OLI Analyzer Studio (OLI Systems, Inc., 2012), and diffusion-controlled currents for oxygen reduction and metal dissolution reactions were calculated using MATLAB (MATLAB, 2008). The corrosion potentials were determined where the sum of cathodic currents and anodic currents is zero. Subsequently, corrosion rates were calculated from the corrosion potential and anodic current associated with the metal dissolution reaction. The corrosion analyses were conducted at a temperature of 95 °C [203 °F] and for both oxic and anoxic conditions. The analyses indicated carbon steel corrosion rates were determined by the availability of cathodic reactions, particularly carbonic acid reduction. Based on these analyses, the calculated carbon steel corrosion rates were relatively high under both oxic and anoxic conditions. On the other hand, copper corrosion rates were determined by the availability of oxygen and activation of copper and were lower than carbon steel rates.

5 MODELING BENTONITE WATER CHEMISTRY RELEVANT TO COLLOIDS

Given certain conditions in a deep geologic repository, the use of bentonite as a buffer potentially could contribute to radionuclide release by supplying mobile colloidal material to which radionuclides can sorb. The conditions that favor colloid generation are low cation concentrations to inhibit coagulation, sodic form of montmorillonite, advection, and turbulence. International programs developing deep geologic repositories recognize the potential for colloidal effects and consider designs that may reduce or mitigate colloid formation (Moreno, et al., 2011; Missana, et al., 2011; Wold, 2010).

REACT, a reaction path program in the Geochemist's Workbench suite, was used to address the potential for low cation concentrations in bentonite porewater. The Flush model of the REACT code, in which a fluid added as a reactant displaces existing fluid in the bentonite pore space, was used. The Flush model tracks the chemical evolution of the bentonite through which the fluid migrates.

The processes considered in the model were precipitation, dissolution, and ion exchange. The minerals present in the bentonite were montmorillonite, quartz, calcite, and gypsum. Flushing solutions were dilute carbonated water (as might be found at a condensation front) and an ambient granitic host groundwater. The challenge of this modeling effort was to determine the mass of minerals contained in the bentonite that may be available for reaction with the flushing fluid. Total porosity versus effective porosity was one aspect of the modeling exercise that contributed to uncertainty.

Preliminary results suggest that over the long regulatory time periods required for the safe disposal of nuclear waste, buffer mineralogy is not likely to provide long term (permanent) changes to the cationic conditions of intruding groundwater. Therefore, these simulations suggest that concentrated flushing solutions (high cationic groundwaters) are needed to produce conditions that favor coagulation and reduced colloid generation. Future modeling can include effects of flow conditions/residence times of flushing solutions, temperature, and reactant proportions on cationic concentrations.

6 GAS AND MICROBIAL EFFECTS AT WASTE PACKAGE/BUFFER INTERFACE AND BUFFER EROSION

Waste package components are subject to a range of thermal, hydraulic, mechanical, chemical, and biological phenomena that cause environmentally induced degradation. Therefore,

interactions at the waste package/buffer interface are important for performance assessment. Three technical issues related to waste package/buffer interactions were discussed: (i) gas generation at the waste package/buffer interface, (ii) microbial-influenced corrosion, and (iii) buffer erosion.

During the construction and operation periods of a geologic repository, chemical reactions at the waste package/buffer interface involve aerobic aqueous corrosion and oxidation. After the thermal period, anaerobic conditions will be reached in a saturated environment and anaerobic corrosion of a carbon-steel waste package will lead to hydrogen gas generation at a waste package/buffer interface via the reaction: $\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2 + \text{H}_2$. Hydrogen gas generation and accumulation may affect long-term waste package performance. There are four mechanisms for hydrogen migration in and around the repository: (i) dissolution in water and diffusion, (ii) two-phase water flow, (iii) transfer along microfissures, and (iv) transfer along fractures. Both microfissures and fractures can form as a consequence of pressure build up. Microfissuring can be initiated as soon as gas pressure exceeds the swelling pressure of bentonite {~7 MPa [70 bar]}. For gas pressure greater than 12 MPa [120 bar], fracturing of bentonite could occur and facilitate gas transport. Data from a borehole measuring gas input pressure in the Callovo-Oxfordian argillites, however, suggest that the hydrogen pressures developed in a repository would never rise to such values, and transfer along fractures formed via pressure build-up does not come into play (ANDRA, 2005).

Clay-based materials in a deep geologic repository would contain a heterogeneous assemblage of microorganisms. Microbial activities have been reported in Callovo-Oxfordian argillite, Opalinus clay, and bentonite. Microbial activities in buffer may lead to the modification of electrochemistry and scale formation on waste package surfaces. Processes discussed included the effect of iron-reducing bacteria in altering the protective layer, and the effect of sulfate-reducing bacteria in transforming sulfate into hydrogen sulfide, that can result in accelerated corrosion of copper waste packages.

Buffer erosion can lead to rapid transport of groundwater and accelerated corrosion of waste package materials. There are two types of erosion: (i) chemical erosion and (ii) physical erosion. Chemical erosion of a clay buffer refers to a process in which clay minerals are suspended as colloids and transported away in flowing groundwater. Physical erosion involves the release of clay/bentonite particles at the buffer/groundwater interface by shear forces acting on the particles by flowing groundwater or, in the process of "piping," by hydraulic forces acting on the buffer during saturation (Arthur, 2011). Both chemical and physical erosion are poorly understood and conditions that may lead to erosion of buffer should be further characterized.

7 INSIGHTS ON SULFIDE CORROSION OF COPPER WASTE PACKAGE

Calculations were conducted using the Scoping of Options and Analyzing Risk (SOAR) GoldSim code to simulate performance of the buffer in limiting transport of potential corroding agents from the host rock to the waste package. Use of the SOAR code also advanced the application of a methodology developed by the NRC and CNWRA staffs for rapidly developing insights into disposal of radioactive waste in various geologic systems. Sulfide corrosion of copper waste packages was selected as a demonstration test case for this analysis. The results reported here are preliminary. Details of the SOAR adaptations and insights developed for this analysis will be documented in a CNWRA report being developed as a deliverable under the task System Analysis of Disposition Options for Spent Nuclear Fuel.

Potential sulfide corrosion in repository systems that include a buffer surrounding copper waste packages will depend on the mass flux of hydrogen sulfide through the buffer. SOAR calculations assumed an intact and fully saturated buffer, thus supporting predominantly diffusive transport. To maximize the concentration gradient for diffusive transport, hydrogen sulfide concentrations were conservatively assumed constant at the buffer/host rock interface and zero at the waste package/buffer interface. Values for this constant sulfide concentration were based on predicted chemical concentrations in the groundwater at repository depth in the Oskarshamn and Forsmark-North Uppland areas (King, et al., 2001). The performance metric for this insights analysis was the waste package failure time, determined when the estimated depth of corrosion exceeded the specified waste package thickness of 2.5 cm [1.0 in]. Staff noted that the corrosion rates may be different in other chemical environments, but that consideration was beyond the scope of these analyses.

Several minor adaptations were made to the SOAR code to enable simulation of hydrogen sulfide transport and evaluate waste package corrosion. These adaptations included adding (i) hydrogen sulfide ion to the list of chemical species, (ii) a function to calculate waste package corrosion rate and depth, and (iii) a trigger element to capture and record the waste package failure time.

Results of Monte Carlo simulations showed the majority of the realizations did not produce waste package failure in less than a million years. In realizations that resulted in breached waste packages, the groundwater hydrogen sulfide concentration or the buffer diffusion coefficient (or both) were near the upper end of their respective sampling distributions. This indicated that very high diffusive fluxes of hydrogen sulfide were needed to breach the waste packages. Furthermore, benchmarking with international performance assessments indicated that the failure-producing buffer diffusion coefficients were at least an order of magnitude greater than the worst-case values used in the SKB SR-Site safety assessments (SKB, 2010a,b). Discussions centered on the initial (installed) condition and long-term integrity of the buffer. Concerns included the buffer not performing as designed at the onset or eventually cracking due to thermally induced shrinkage, pressure from gas accumulation, or deformations producing tensile stresses. These scenarios could result in predominantly advective transport through the buffer. Future SOAR analyses may examine the effect of the nature and extent of cracking and its potential to impart flow and possibly a dominance of advective over diffusive transport.

8 BENTONITE DATA

Several bentonites have been considered for use in deep geologic disposal and have been used for *in-situ* tests at underground research laboratories. Examples are MX-80 (Na-smectite, Wyoming), FEBEX-type (Ca-Mg-Na mixed smectite-illite, Almeria, Spain), IBECO RWC (also called Deponit-CaN, Ca-smectite, Greek Island of Milos), and Kunigel (Na-smectite, Japan). Bentonite buffers are selected for repository designs for their performance capability in preventing advective flow, minimizing damage to waste packages, and retarding the migration of radionuclides. Some of the factors that affect bentonite buffer performance are (i) clay mineralogy and interlayer cations; (ii) percent smectite clay; (iii) pore water chemistry, such as ionic strength and dominant cations; (iv) dry density, compacted or granular; (v) water content; and (vi) temperature. Several compilations of bentonite properties and characteristics have been completed in the past few years:

- Man and Mantino (2009) categorizes bentonite properties and synthesizes relations of properties to bentonites and associated pore water chemistry

- Wilson, et al. (2011) contains a summary of bentonite processes and properties
- Laine and Karttunen (2010) contains a compilation of bentonite properties relating to long-term behavior
- Karnland (2010) summarizes properties of MX-80 and IBECO RWC bentonites
- Lloret and Villar (2007) summarizes FEBEX-type bentonite properties
- JAEA (2012) provides an online database for the Kunigel bentonite

Discussions during the workshop focused on hydraulic (permeability, unsaturated zone characteristic curves, affect of temperature), thermal (thermal conductivity and heat capacity combined into thermal diffusivity), and mechanical (swelling) properties. Much of the mechanical data on swelling is geared towards supporting models similar to the Barcelona Basic or Barcelona Expansive Models (e.g., Zheng, et al., 2011), as opposed to the data needed for use with effective stress approaches as implied with the generalized geomechanical modeling approach and unit swelling potential parameter mentioned in Section 3. Besides the potential use of the Man and Mantino (2009) relationships for generating inputs for performance assessment abstractions, discussions during the workshop highlighted the need for further evaluations of unsaturated zone hysteresis, heat capacity as a function of water content, and swelling potential of different bentonites in contact with different pore water chemistries.

9 POTENTIAL FUTURE WORK

Attendees had opportunities to discuss, add to, or expand on topics both during the topical discussions and at a round-table discussion at the end of the workshop. Staff also identified several potential topics and tasks that could be considered in planning for activities in the next fiscal year and beyond. The list is provided here only to capture the discussions during the workshop. In selecting items from this list, or any new topics, it is expected that the needs and priorities of the program will be considered when planning tasks in the future. These include:

- Flow in Bentonite Buffer: This discussion identified potential future work in areas related to the influence on flow conditions of (i) boiling and above-boiling temperatures and (ii) changes in porosity.
 - Boiling: Evaluate the potential for and extent of two-phase flow and convection in the near-field environment. Boiling temperature should be much higher than 100 °C [212 °F] when considering capillarity, water chemistry, higher pressure conditions (consideration of whether the system is open or closed), and how additional forces tie water molecules to clay minerals in bentonites. Understanding pressure conditions may require assumptions about the presence of open pathways to areas beyond the sealing components of the repository. This item would require technical (e.g., thermodynamic) analysis of the conditions at the waste package/buffer interface and analysis of *in-situ* field tests where the temperature at waste package/buffer interface was greater than 100 °C [212 °F] for indications of possible occurrence of boiling (e.g., FEBEX).
 - Porosity and available water: Additional forces on water in bentonite porous media can lead to the conceptualization that some portion of the liquid water is more tightly bound to the smectite minerals due to electrostatic and van der

Waals forces. In a simplified conceptualization, a bimodal distribution of pore sizes leads to some portion of water more readily moving than the other portion. Holmboe, et al. (2012), for example, suggests that the more readily transportable water comprises only a small portion of the total porosity. Besides affecting simulations of flow through bentonites, the bimodal characterization of porosity also could affect transport, both advective and diffusive, through flow area and tortuosity. If the concept of the bimodal characterization continues to be supported, the next step could be to understand the consequence for thermal-hydrological-mechanical-chemical analyses of buffers.

- Swelling and Swelling Pressure: Geomechanically verify the effective stress approach using swelling pressure data and define the nature of porosity changes associated with free swelling (i.e., change in pore space, change in porous medium volume, or some of both).
- Geochemical Conditions at Waste Package/Buffer Interface: Staff discussed potential future work related to (i) reactive transport modeling and (ii) the relationship between geochemical conditions and swelling potential.
 - Reactive transport modeling: Additional reactive transport calculations could help assess the effects of higher temperatures, advective transport, unsaturated conditions, and various host rock water compositions on the geochemistry of bentonite buffer and the waste package–buffer interface. In addition, corrosion rates derived from a review of published literature on waste package material corrosion could be compared to the corrosion rates determined from the corrosion analyses described in Section 4. Further, corrosion analyses could allow evaluation of the effect of sulfur species on carbon steel and copper corrosion. Simulations of chemical conditions at the waste package/buffer interface for selected bentonite and porewater chemistries suggest small changes in porosity due to dissolution and precipitation and the persistence of calcite, which influences corrosion of steel. Future work could consider simulations at higher temperatures, which could result in more significant changes in porosity and, possibly, in bentonite mineralogy. Simulations for above boiling conditions that would include two-phase flow may not be possible with Geochemist’s Workbench. Staff will have to consider using other software that can simulate unsaturated conditions. Implicit in these simulations is transport of species through the bentonite by diffusion only.
 - Geochemical conditions and swelling potential: Literature review indicates swelling potential varies both for different bentonites (e.g., Na-type versus Ca-type) and for different pore water chemistries. A better understanding of the relationship between pore water chemistry and bentonite type could help in numerical simulations of experiments and evaluations of performance assessment (e.g., future changes in groundwater chemistry).
- Modeling Bentonite Water Chemistry Relevant to Colloids: Develop performance insights for colloids with regard to both advective flow to the waste package (because of buffer erosion), and release and transport of radionuclides. Consider the use of Critical Coagulation Concentration for formation of colloids, and take into account unsaturated conditions, temperature effects, and porosity characterization.

- Gas and Microbial Effects at Waste Package/Buffer Interface: Hydrogen gas generation at the waste package/buffer interface is the result of waste package corrosion under anaerobic conditions. Hydrogen gas generated from the waste package could be quantified. Gas transport mechanisms through buffer by advection, two-phase flow, microfissures, and fractures need further understanding. In addition, the consequences of microbial activities in buffer need further evaluation.
- Insights on Sulfide Corrosion of Copper Waste Package: Identify (i) initial and transient conditions that could elevate hydrogen sulfide flux in the buffer and (ii) conditions that could elevate hydrogen sulfide concentrations in the groundwater.
- Bentonite Data: Hysteresis for unsaturated zone retention curve and heat capacity as a function of saturation are properties of bentonite that may not have been adequately considered in staff analyses. Also, for argillite host rock, anisotropy of thermal conductivity may need to be addressed.

In addition, staff also identified potential performance assessment tasks related to representation of the buffer. In the current implementation in SOAR, the buffer performs as designed at the start of the postclosure period, followed by long-term degradation conceptualized as advective flow through a fracture. Changes in pore water chemistry may lead to formation of colloids or mineral alteration, either of which may degrade buffer performance. However, in the expected evolution of the buffer, it may not perform as designed during the thermal period. After the thermal period, the buffer is expected to perform as designed for a long period until erosion or mineral alteration may influence the performance. The degraded performance affects transport after release of radionuclides. There is no linkage of buffer performance to environmental conditions at the waste package in SOAR. Addressing the current assumptions in SOAR, the staff identified three tasks:

- Degraded buffer performance during the thermal period could be incorporated into SOAR through the adjustment of waste package corrosion input parameters. Because SOAR does not link buffer performance to waste package environment or corrosion, this work would likely involve offline calculations using either (i) conservative corrosion parameters reflecting consequences of a degraded buffer performance throughout the entire performance period or (ii) modifications to SOAR by making the corrosion parameters time-dependent. This item will be discussed further at the Container Corrosion and Chemical Environment Workshop in September 2012.
- Scenarios for flow through a degraded buffer need to be defined. Current insights are based on a small area of a waste package connected to sparse preferential flow paths. If flow rates through a “degraded” buffer are set to a rate such that advective transport is comparable to diffusive transport, then both need to be combined in SOAR simulations. This item entails identification of the range of flow patterns in a degraded buffer (i.e., pervasive versus sparse preferential). For the area of waste package corrosion connected to preferential flow paths, the preference for flow along interfaces (i.e., waste package-buffer interface) needs to be considered.
- Evaluate the idea of considering buffer failure as a disruptive event, thus incorporating probability of failure into consequence.

10 REFERENCES

- Adamson, A.W. and A.P. Gast. *Physical Chemistry of Surfaces*. 6th Edition. New York City, New York: John Wiley & Sons, Inc. 1997.
- Aiken, P.W. "Physical Chemistry." 4th Edition. Oxford, United Kingdom: Oxford University Press. 1954.
- ANDRA. "Dossier 2005 Argile—Phenomenological Evolution of a Geological Disposal System." Chatenay-Malabry, France: ANDRA. 2005.
- Arthur, R. "Handling of Hydrogeochemical Relations in Erosion and Swelling Pressure Models for the Buffer and Backfill." Part I. A Review of Surface-Chemical Concepts Used in Models of Buffer Erosion." STUK-TR 10. Helsinki, Finland: Radiation and Nuclear Safety Authority. 2011
- Bethke, C.M. "Geochemical and Biogeochemical Reaction Modeling." New York City, New York: Cambridge University Press. 2008.
- Bruno, J., D. Arcos, and L. Duro. "Processes and Features Affecting the Near Field Hydrochemistry: Groundwater-Bentonite Interactions." Technical Report TR-99-29. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co. 1999.
- Corey, A. *Mechanics of Immiscible Fluids in Porous Media*." Littleton, Colorado: Water Resources Publications, LLC. 1986.
- Holmboe, M., S. Wold, and M. Jonsson. "Porosity Investigation of Compacted Bentonite Using XRD Profile Modeling." *Journal of Contaminant Hydrology*. Vol. 129. pp. 19-32. 2012.
- JAEA. online "Buffer Material Database." Ibaraki, Japan: Japan Atomic Energy Agency <https://bufferdb.jaea.go.jp/bmdb/index_e.jsp> 2012.
- Karnland, O. "Chemical and Mineralogical Characterization of the Bentonite Buffer for the Acceptance Control Procedure in a KBS-3 Repository." SKB Technical Report TR-10-60. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company. 2010.
- King, F., L. Ahonen, C. Taxén, U. Vuorinen, and L. Werme. "Copper Corrosion Under Expected Conditions in a Deep Geologic Repository." Technical Report TR-01-23. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co. 2001.
- Kleinfelder-Domelle, N. and J.H. Cushman. "The Role of Connectivity in the Theory of Saturated/Unsaturated Flow Through Swelling Media." *Water Resources Research*. Vol. 48, No. W01543. 2012.
- Laine, H. and P. Karttunen. "Long-Term Stability of Bentonite—A Literature Review." Working Report 2010-53. Eurajoki, Finland: Posiva Oy. 2010.
- Lempinen, A. "Coupling Swelling and Water Retention Processes in Compacted Bentonite." *Chemical Product and Process Modeling*. Vol. 6, Issue 1, Article 4. 2011.

Lenhard, R., R. Fedors, C. Manepally, R. Pabalan, G. Ofoegbu, K. Chiang, J. Bradbury, and C. Markley. "Buffer and Backfill Workshop Report." ML113410009. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2011.

Liu, H.-H., L. Li, and J. Birkholzer. "Unsaturated Properties for Non-Darcian Water Flow in Clay." *Journal of Hydrology*. Vols. 430–431. pp. 173–178. 2012.

Lloret, A. and M.V. Villar. "Advances on the Knowledge of the Thermo-Hydro-Mechanical Behaviour of Heavily Compacted "FEBEX" Bentonite." *Physics and Chemistry of the Earth*. Vol. 32. pp. 701–715. 2007.

MATLAB. "MATLAB User's Guide." Natick, Massachusetts : The MathWorks, Inc. 2008.

Man, A. and J.B. Mantino. "Thermal, Hydraulic, and Mechanical Properties of Sealing Materials." NWMO TR–2009–20. Toronto, Canada: Nuclear Waste Management Organization. 2009.

Missana, T., U. Alonso, N. Albarran, M. García-Gutiérrez, and J. Cormenzana. "Analysis of Colloids Erosion From the Bentonite Barrier of a High-Level Radioactive Waste Repository and Implications in Safety Assessment." *Physics and Chemistry of the Earth*. Vol. 36. pp. 1,607–1,615. 2011.

Moreno, L., L. Liu, and I. Neretnieks. "Erosion of Sodium Bentonite by Flow and Colloid Diffusion." *Physics and Chemistry of the Earth*. Vol. 36. pp. 1,600–1,606. 2011.

Neuzil, C.E. "Abnormal Pressures as Hydrodynamic Phenomena." *American Journal of Science*. Vol. 295. pp. 742–786. 1995.

OLI Systems, Inc. "A Guide to Using OLI Analyzer Studio Version 3.2." Morris Plains, New Jersey: OLI Systems, Inc. 2012.

Selker, J., C.K. Keller, and J.T. McCord. *Vadose Zone Processes*. Washington, DC: Lewis Publishers. 1999.

SKB. "Corrosion Calculations Report for the Safety Assessment SR-Sites." TR–10–66. ISSN 1404-0344. Stockholm, Sweden: Svensk Kärnbränslehantering AB. 2010a.

SKB. "Data Report for the Safety Assessment SR-Site." Technical Report TR–10–52. Stockholm, Sweden: Svensk Kärnbränslehantering AB. 2010b.

Wersin, P. "Geochemical Modelling of Bentonite Porewater in High-Level Waste Repositories." *Journal of Contaminant Hydrology*. Vol. 61. pp. 405–422. 2003.

Wilson, J., D. Savage, A. Bond, S. Watson, R. Pusch, and D. Bennett. "Bentonite, A Review of Key Properties, Processes, and Issues for Consideration in the UK Context." Quintessa Report for Nuclear Decommission Authority (NDA) QRS–1378ZG–1.1. Oxfordshire, United Kingdom: Qunitessa. 2011.

Wold, S. "Sorption of Prioritized Elements on Montmorillonite Colloids and Their Potential to Transport Radionuclides." Technical Report TR–10–20. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co. 2010.

Zheng. L., J. Samper, and L. Montenegro. "A Couple THC Model of the FEBEX *In-Situ* Test With Bentonite Swelling and Chemical and Thermal Osmosis." *Journal of Contaminant Hydrology*. Vol. 126. pp. 45–60. 2011.

APPENDIX A

NRC-CNWRA BUFFER WORKSHOP 2012 AGENDA

NRC-CNWRA Buffer Workshop—2012

June 26, 2012

9:30 am to 4:30 pm EDT

Location: EBB 2C19 at NRC; A237 at CNWRA (Videocon - link)

Time in EDT

9:30 Introduction

9:50 Flow in Bentonite Buffer

10:20 Swelling & Swelling Pressure

11:00 Geochemical Conditions at Waste Package/Buffer Interface

11:50 Lunch

1:00 Modeling Bentonite in Geologic Repository Using Geochemist's Workbench

1:40 Gas and Microbial Effects at Waste Package/Buffer Interface

2:20 Break

2:30 Insights on Sulfide Corrosion of Copper Waste Package

3:00 Bentonite Data

3:20 Discussion/Summary/Conclusions

4:30 Break