Dear Dr. Mote,

I was asked to contribute to the Nuclear Waste Technical Review Board’s review of the US Department of Energy (DOE) underground research laboratory (URL) collaborative activities, which are primarily undertaken in other countries. One part of your Board’s review focused on DOE’s field, laboratory, and modeling studies associated with plastic clays and bentonite. Specifically, I was asked to review materials related to DOE’s:

- Research needs on bentonite behavior particularly focused on thermal perturbations, their modeling and experimental work on high-temperature behavior from the FEBEX-DP experiment, and their proposed plans for the HotBENT (200 °C) experiment.

- Results from laboratory studies of FEBEX-DP samples that were performed to better understand the impact of early perturbations on transport properties, micro-chemistry imaging studies on FEBEX samples, and sorption experiments on those samples. High-T micro-studies and Cement–Opalinus Clay Interaction experimental work could also be presented to the Board for its review.

As part of my review I attended onsite meetings and presentations in Las Vegas, NV, on February 26, 2019, and the Workshop on Recent Advances in Repository Science and Operations from International Underground Research Laboratory Collaborations in Burlingame, CA, on April 24-26, 2019. During both of these meetings I had the opportunity to ask questions relating to the above two areas, and I provided lists of focus questions to the Board. I have evaluated all of the presentation materials provided on February 26 and on April 24-25 and background materials, including published peer-reviewed literature (list attached). I provided verbal input to several of the February and April presentations, and I was asked specifically to comment on the following two April presentations:

- DOE’s Engineered Barrier Integrity Activities: Understanding Engineered Barrier System Coupled Processes and Mineral Alterations at High Temperatures: From FEBEX-DP to HotBENT. Speaker: Liange Zheng
• DOE’s Engineered Barrier Integrity Activities:
  Thermal Implications on Transport in Bentonite: Using FEBEX-DP Samples for
  Laboratory Studies and Model Testing. Speaker: Carlos Jove-Colon

My comments can be summarized by these six bullets:

• The modeling being performed by DOE scientists is of a high level of sophistication,
  building on years of experience at the National Laboratories. However, application to the
  Underground Research Laboratories appears to involve many hidden assumptions, and
  many important aspects of mineralogy and processes are either poorly or not captured in
  the models. Fitting short-term measurements does not guarantee the accuracy of long-
  term predictions.
• Many modeled processes rely on liquid transport, but models suggest that the most
  important time period in any URL will be the early, hottest portion, when the engineered
  barrier system (EBS) is largely unsaturated. Unlike unreactive media (e.g., quartz
  sandstone) in which the medium does not interact specifically with H₂O, bentonite has
  specific chemical interactions with H₂O, and it is likely that no liquid water will be present
  in the unsaturated (<100% relative humidity conditions) period. When the temperature is
  highest, there will be no liquid water; when liquid water is present, temperatures will
  generally be low, <100°C where reaction rates are slow. The pressure in each URL is a
  major unknown, and I saw no mention of a measured pressure during the operational
  periods. Lab experiments accompanying the URLs should recognize these conditions;
  high-temperature, high-pressure, saturated experiments will not be very applicable to the
  current URLs.
• No recognition appears to have been given, for any URL, of the possible importance of
  an unsaturated, steam environment for a bentonite backfill. There are well-documented
  processes occurring with smectite in a steam environment that can eliminate some of
  the most beneficial properties of smectite in a few days. These may be particularly
  important in the HotBENT (200 °C) experiments.
• It is important to recognize that URLs provide primarily site-specific information. At the
  outset, researchers should recognize what they can and cannot learn; much can be
  learned about experimental methodology, processes, and our ability to model them from
  any URL. But researchers should also recognize at the outset that there is no “generic”
  argillite or granite or crystalline rock or “clay”, etc.
• URL studies of a bentonite backfill are likely to provide valuable, more-generic data,
  particularly in the early time period when interactions with the host rock and water (and
  possibly any sealing materials) are less significant. Thus it may be possible to do a
  largely “generic” backfill study, dependent still on geometry, the particular bentonite
  used, and the processing/compaction methods. Natural analogs may provide limited
  information, but they will still suffer from being largely site specific, and decades of
  natural analog studies illustrate the difficulties in accurately defining past conditions of
  time, temperature, pressure, and water compositions.
It became clear during the Board meeting that DOE should put increased (renewed) emphasis on training and maintenance of expertise. Many of the issues discussed at this briefing were encountered during previous DOE repository studies, but some important relevant experience seems to be either lost or not-yet rediscovered. Without a focus on training, who will do these experiments and simulations in twenty years?

In addition, I attach more-detailed comments, some of them focusing on the two presentations mentioned above, and a list of references that I consulted.

Sincerely yours,

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Attachments: 1) Detailed Comments
2) List of references consulted (in addition to presentation materials)

These detailed comments are arranged into five categories:

1) General points;
2) Modeling details;
3) Process/environment details;
4) Mineralogical aspects;
5) Generic vs. site-specific URLs.

**General points:**

1) Birkholzer's slide 8 (Figure 1) in his presentation to the Board provided a good summary of priorities. Some of these questions have been answered, probably many remain unanswered, and a few are missing. For example, one presenter asked “How long does bentonite need to work”? This is a seemingly simple question, but this, and why we are considering bentonite, should be the prelude to any studies and modeling efforts on EBS performance that involve bentonite backfill.

![Cross-Cutting Priority R&D Topics](image.jpg)

**Figure 1. Birkholzer presentation, slide 8**

2) It would be useful for all research groups to provide a reasonably detailed introduction to their work that discusses the purposes of their studies. For example, why we are considering an engineered barrier/backfill, what are the components (e.g., bentonite, cementitious materials) what properties are important, and what properties of bentonite are we exploiting? This could help re-focus some of the studies onto the important issues, namely why do we use a backfill, what do we want it to do, for how long, and will it work? Is bentonite the best material to use?
Modeling details:

3) There continue to be many hidden assumptions in all of the modeling and the experiments, and these are not always laid out well, explained, or perhaps recognized. For example, most of the models appear to be so complex that simply coming close to reproducing the experimental results is not an adequate test. Indeed, some modelers opined that they had “many knobs” to use to fit the data. As John von Neumann famously said, “With four parameters I can fit an elephant…” One presenter suggested that they often try simpler models first to ensure that they have the physics correct (although he did not do this). The community should consider the best ways to validate the models rather than simply by fitting the data because it seems clear that a good fit does not confidently indicate that accuracy of the models. One presenter insightfully opined that their models can match the data but not necessarily the process. Without correct process(s), accurate long-term prediction will be difficult.

4) An example of model shortcomings is the model result that mineral alteration, including formation of illite, occurred in the hottest, driest portions of the EBS, near the heater. In this region, and indeed in most of the backfill over the experimental lifetimes, conditions were not saturated, a situation that makes dissolution and precipitation (the commonly accepted method of illite formation from smectite) of silicates unlikely. In addition, this modeling result is counter to all measurements of FEBEX materials. The researchers suggested that the lack of an illite detection may be a result of insufficient detection limits by the analytical methods, rather than considering that the models were insufficient or inaccurate. In the end, more confidence in the models is necessary; they cannot just be fitting exercises.

5) It is easy to obtain the impression that only the modeled processes are those that are believed to occur, i.e., if it’s not in the model, it will not occur. Several important processes are either inadequately treated or are not treated at all (see below). For example, there are extensive literature data published by several groups showing that very important changes occur to smectite in an unsaturated, elevated-temperature environment. These processes have not been considered and are not included in any models, even though they have the potential to eliminate one of the most beneficial aspects of a bentonite backfill, namely osmotic swelling, which gives rise to smectite’s very low saturated permeability.

6) The Discrete Fracture Network and Fractured Continuum models are physically based, and we saw no confirmation that bentonite backfill will rewet and then erode under reasonable EBS flow-rate conditions. It would be useful to see experimental confirmation under realistic flow rates that any “erosion” will occur. Are the experiments or simulations that have fluid velocities sufficiently high to cause erosion reasonable? What are anticipated flow rates in the EBS?

7) It would be useful to incorporate H₂O-mineral interactions in the conceptual model for the GDSA Model. Given the importance of bentonite (and cement/concrete) in the EBS, and the fact that the mechanisms for changing EBS mineralogy involve mineral-water or mineral-vapor interactions, this appears to be important.
Process/environment details:

8) Many simulations illustrate the occurrence of significant processes and mineral reactions, e.g., precipitation of "illite", near the heater (Figure 2). However, this region of the EBS is the area of lowest saturation (lowest RH) and highest temperature, potentially at or approaching a steam environment with little or no liquid water (Figures 3 & 4). Rates of mineral reaction that involve liquid water, such as dissolution and precipitation (e.g., crystallization of illite) will be very low. This leaves us with an important Catch-22; reactions are most likely where the temperature is highest, but in this region saturations are lowest with no liquid water, generally meaning that reactions rates (particularly dissolution/precipitation reactions) are very slow. By the time the EBS is saturated, temperatures are sufficiently low that reactions rates will be very low. The result is that the most important changes to the EBS may occur in the unsaturated environment at elevated temperatures, e.g., a steam environment.

Figure 2. Plot showing precipitation of illite (Fig. 6.2-7 from Birkholzer et al., 2018). Positive values indicate precipitation (note the small values on the y axis).

Figure 3. Measured and simulated RH vs. time at radial distances of 0.52 m and 1.1 m for the FEBEX test and simulated results for HotBENT (Fig. 6.2-9 from Birkholzer et al., 2018).
9) Virtually all experiments ended while much of the EBS remains partially saturated, yet simulations typically extend for thousands of years. How can we obtain assurance that the longer-term models encapsulate the physics correctly for accurate long-term predictions of behavior when the EBS is saturated, when our observations extend only over the time of partial saturation?

10) More research is needed on the behavior of a bentonite-containing EBS during the change from partially saturated to saturated conditions with time and decreasing temperature. During this period, the backfill material (bentonite) will have changed under unsaturated conditions (e.g., as a result of cation exchange and reaction in a steam environment). This unsaturated period is a crucial, and largely ignored, area of research, with little or no data during this period, although the models routinely extend beyond this period. The effects of heating in saturated and unsaturated conditions are very different and are well documented in the literature.

11) It would be useful to have a detailed discussion of how mass transport occurs in an unsaturated system. It is not clear how transport of some solutes (e.g., Mg, Ca, Na chlorides and sulfates) has occurred with relative humidities <40% and no free liquid water. Models presented suggest that there is liquid water transport in the EBS, which accounts for the Cl movement, but it is difficult to have movement of liquid water when the RH is 30% and there is no liquid phase. The experimental results appear to show evidence for small changes (Fig. 5), although the effects are much smaller than the simulations suggest. It is unclear how the results on chloride, which are presented in mol/L, apply to concentrations in the solid.
12) The FEBEX heater test ran for 18 years, evaluating the stability of bentonite in an engineered barrier, but it is not clear that even the degree of saturation reached steady state over this time period. It is highly likely that the mineralogy and perhaps chemistry did not reach equilibrium. Can we expect models to make predictions for thousands of years, when available data do not represent equilibrium? The comparatively low temperatures of the system, particularly by the time the system becomes saturated, and the geologically short time scale make incorporation of appropriate kinetic data in any THMC simulation crucial. This is an area where natural analogues may be able to make a contribution, although these analogues consistently suffer from a lack of accurate information on reaction timing, water compositions, temperature profiles, and pressures.

Mineralogical aspects:

13) The models should incorporate some recognition of the important differences between H₂O in an unsaturated non-H₂O adsorbing medium (e.g., a sandstone or granite) and a bentonite, in which the primary mineral, smectite, interacts chemically with H₂O. Partially saturated sandstone can contain liquid water in the pores whereas a bentonite in which the relative humidity is (for example) 50% will contain no liquid water (the smectite will be in equilibrium with the H₂O in the vapor phase). H₂O molecules in smectite are not liquid water and have distinct properties (thus, although common, it is incorrect to call the H₂O in smectites and in minerals in general, “water”). The thermodynamic properties of this H₂O are different from liquid water, vaporization temperatures are higher, and enthalpies of dehydration are greater, in some cases more than twice that of liquid water. All of these differences will impact the outcome and accuracy of models. In most cases these differences are not encapsulated in models, but data are readily available to allow their incorporation. Incorporation of information on the different enthalpy of dehydration of smectite will cause calculated temperatures to be lower than they are when water is assumed.
14) The above aspects emphasize that the so-called “100°C limit” is arbitrary. Although this was mentioned in the meeting, it was not related to the fact that H2O in bentonite does not evolve at 100°C in the way that liquid water boils at 100°C.

15) Given the changes in saturation as a function of time (and temperature), where the outermost portions of the backfill saturate first (and thus expand), is it possible to model the swelling stresses, originating at the outermost portions of the backfill, gradually moving inward? Do current simulations consider expansion pressures, the accompanying deformations (both expansive and tensile), and the effects of these on permeability? I saw no mention of tensile stresses, but early heating of the backfill may create tensile stresses in the dehydrating backfill unless the initial packing density is low. This is an area requiring considerable more attention.

16) Researchers should ensure that the literature data used in their models are appropriate for their systems. One researcher used kinetic data for the smectite-to-illite transformation measured on a K-bentonite and then applied the data to modelling the long-term behavior of a “normal” Na-bentonite with low K (Pusch and Madsen). This is inappropriate, particularly given the availability of appropriate kinetic data that show that reaction rates are greatly affected by the availability of K (and Al). It was suggested that K may come from dissolution of K-feldspar, but conditions likely preclude dissolution, and amounts are trivial. Any simulation of the kinetics of this reaction must also include consideration of the degree of saturation. All experimental measurements of reaction kinetics were done under saturated conditions.

17) Processes affecting bentonite backfill are obviously highly coupled, but it appears that several important aspects are not incorporated into the models, e.g., heats of reaction/hydration/dehydration, the effects of expansion/contraction (on stress, permeability), and effects of H2O desorption/adsorption (on degree of saturation, fluid availability), all of which are coupled. One of the major reasons for choosing bentonite for an EBS is that has a very low saturated permeability due to the formation of a gel structure during osmotic swelling. But simulations suggest that the EBS will not be saturated until temperatures have decreased below 100°C. The mechanisms for complete saturation from a compacted powder are not well understood, and compacted bentonite does not usually saturate uniformly, largely due to the strong relationship between permeability and saturation. In practice the saturated portion of bentonite effectively armors adjacent unsaturated portions. It would be worthwhile performing some URL experiments and/or lab experiments on the efficiency of bentonite saturation. It is also well known that smectite expands when unsaturated in a stepwise fashion Figure 6 illustrates the large change (in one dimension, providing directly a similar percentage volume change) as a function of relative humidity for a Na-smectite.
Figure 6. 001 (basal) spacing for a Na-saturated smectite as a function of relative humidity. Data for the increasing-humidity and the decreasing-humidity directions are shown (from Chipera et al., 1997, Fig. 5). These values provide information on the layer-layer spacing and can be used as a proxy for volume change as a function of relative humidity.

Although this effect may not be important in a compacted bentonite of finite porosity, existing data are sufficiently detailed that it should be possible to incorporate this into the models (it would be useful to provide the approximate porosity of the compacted bentonite used in URLs). I understand that current models assume linear expansion, and this may be sufficient. Expansion does not cease once saturation is reached, and smectite continues to expand osmotically. Fig. 7 illustrates the step-wise behavior at low H$_2$O contents and the gradual transition with increasing H$_2$O contents (C is electrolyte concentration). It also emphasizes the very large amount of expansion possible in the osmotic swelling (the linear) region. For the most part I believe we have reliable experimental data on the applicable behaviors of bentonite in these environments, but not all of the important phenomena are included in the models.
11

Figure 7. Expansion of montmorillonite (a smectite) as a function of the water content (X - in NaCl solutions; O - in Na$_2$SO$_4$ solutions). The step-wise portion below a C$^{-1/2}$ value of two represents the unsaturated portion of the curve, whereas the continuous portion above this point represents osmotic swelling. C is the concentration in g equiv per liter. (Norrish, 1954, Fig. 5).

18) It is useful to experimentally determine the nature of microporosity, but it appears that the micro-CT method has insufficient resolution to capture the important features. Resolutions are generally well above 1 $\mu$m (although 100 nm is possible). It is very possible that cracking features observed are the result of sample preparation and presentation to the instrument, and these effects should be considered.

19) Fig. 8 (Slide 5 from the L. Zheng presentation) schematically illustrates some of these phenomena occurring in the EBS, although it does not appear to treat stress correctly. The primary stress during the heating (increasing T) phase should be due to dehydration of the bentonite backfill, during which time dehydration-induced contraction will far overcome any minor thermal expansion. Thus any stresses should be tensile. As rehydration occurs, expansion stresses should occur and eventually be significantly larger than the contraction-induced stresses occurring during the heating phase, because the bentonite will ultimately be much more hydrated and expanded than it was in the emplacement/compaction phase (due to osmotic swelling in the eventually saturated environment, if steam has not destroyed this property). It is likely that the mineral alteration time phases are incorrect, as little mineral alteration will occur early due to lack of water, and little alteration will occur late due to the low temperatures.
20) What is being done to recognize the impact of time and partial saturation (i.e., heating in steam conditions) on mineral alteration, particularly smectite? There has been little or no recognition yet by DOE of the fact that portions of the EBS may experience steam conditions for at least the first several thousand years. Literature data show that steam causes drastic reductions in smectite's ability to osmotically swell, one of the most important properties of a bentonite backfill (Couture, 1985; Oscarson and Dixon, 1989, 1990; Bish et al., 1997). This is a potentially important phenomenon and should be considered. Some of the U sorption data on heated materials may show the effects of this, and the HotBENT experiment may be particularly susceptible to such reactions.

21) Laboratory measurements of FEBEX-DP samples (and future HotBENT samples) should recognize the factors controlling the expandability of smectite in bentonite. Researchers assumed that the difference in expansion between post-heating bentonite in air and in an ethylene glycol atmosphere could be used as a measure of expandability. However, expansion in these two environments (H₂O vs. ethylene glycol) is due to very different phenomena and cannot be used to indicate “expandability”. It is critical when comparing “before” and “after” materials to analyze the bentonite samples at a constant relative humidity; only then can a first step be taken to evaluate differences, because even small changes in relative humidity cause changes in the expansion state of smectites (and room relative humidity is insufficiently constant). If the minor differences in interlayer spacings in post-test samples are real, it is likely that they are due to differences in the interlayer chemistry, which should be evaluated. URL data appear to show small changes in alkali and alkaline earth cation compositions at early times in the hottest portions of the EBS. Such changes will directly affect how the smectite expands in air (e.g., Chipera et al., 1997).
22) Several laboratory hydrothermal experiments were done to evaluate the types of reactions occurring at elevated T and P in a saturated environment. Although these are useful, particularly to evaluate waste package-backfill reactions, it should be recognized at the outset that these are not applicable to the current URL experiments (or perhaps in realistic EBS scenarios), where the highest-temperature portions are unsaturated and simulations suggest that saturation is not reached until considerably lower temperatures are reached, well below 100°C. The pressures in these laboratory experiments ranged up to 150 bars. Formation of zeolites is likely due to the presence of volcanic glass in the bentonite; glass dissolution will keep the silica activity high, which stabilizes clinoptilolite and smectite (relative to illite). There is a substantial literature on this subject, much of it from studies relating to Yucca Mountain.

23) Discussions of the HotBENT experiment mention evolution of bentonite from partial to full saturation at 200°C. The vapor pressure of H₂O at 200°C is 1554.9 kPa, i.e., over 15 bars (well below the pressures used in the hydrothermal experiments). The repository may well self seal with time to allow saturation, but temperatures by this time may have evolved to below 100°C. Researchers should consider the possibility of a significant steam-dominant period, which could have significant adverse effects on a bentonite backfill.

**Generic vs. site-specific URLs**

24) Continued emphasis should be given to the recognition that all URLs are site specific. At the outset, researchers should emphasize what they can and cannot learn. It is apparent that much can be learned about experimental methodology, processes, and our ability to model them from any URL. But researchers should also recognize at the outset that there is no “generic” argillite or granite or crystalline rock or “clay”, etc. Some granites are largely unfractured and have low permeabilities, whereas others are more highly fractured. Some clay-rich rocks are relatively homogeneous, others are quite textured, with very directional properties (e.g., the Opalinus), and the amounts of clay minerals can vary significantly. Some “clay” rocks contain <20% smectite. Even bentonites are quite variable in mineralogy, texture, and exchangeable-cation composition. In addition, it would be useful to see some description for each URL of the effects on the system of emplacing probes, which have the potential to change conditions. It would also be useful to see some discussion about expected pressures. I saw or heard no mention of pressures, and it appears that all simulations assume one bar total P. Given the importance of H₂O and water, this is crucial.

25) The performance of a bentonite backfill may be less site specific (i.e., approaching generic), at least in the early time period when interactions with the host rock and water (and possibly any sealing materials) are less significant. Thus it may be possible to do a largely “generic” backfill study, dependent still on geometry, the particular bentonite used, the processing/compaction methods, and waste type and loading.
Bish, May 1, 2019, References Used
Underground Research Laboratory (URL) Collaborative Activities
(Provided presentation materials were also used and are not listed here.)


I. Blechschmidt (2016) Grimsel Test Site: Activities in the URLs International cooperation (Short overview). Presentation to the NWTRB.


J.-M. Hoorelbeke (2013) The Cigéo project. Presentation to the NWTRB.


