Status of International Activities Supporting Clay or Granite Repositories

Fuel Cycle Research & Development

Prepared for

U.S. Department of Energy

Used Fuel Disposition

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Appendix E
FCT Document Cover Sheet

Name/Title of Deliverable/Milestone	Status of International Activities Supporting Clay or Granite Repositories
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QA program which meets the requirements of

☒ DOE Order 414.1 ☐ NQA-1-2000 ☐ Other

This Deliverable was subjected to:

☐ Technical Review	☐ Peer Review
Technical Review (TR)	**Peer Review (PR)**
Review Documentation Provided	**Review Documentation Provided**
☐ Signed TR Report or,	☐ Signed PR Report or,
☐ Signed TR Concurrence Sheet or,	☐ Signed PR Concurrence Sheet or,
☐ Signature of TR Reviewer(s) below	☐ Signature of PR Reviewer(s) below

Name and Signature of Reviewers

N/A

*__NOTE__ *In some cases there may be a milestone where an item is being fabricated, maintenance is being performed on a facility, or a document is being issued through a formal document control process where it specifically calls out a formal review of the document. In these cases, documentation (e.g., inspection report, maintenance request, work planning package documentation or the documented review of the issued document through the document control process) of the completion of the activity along with the Document Cover Sheet is sufficient to demonstrate achieving the milestone. QRL for such milestones may be also be marked N/A in the work package provided the work package clearly specifies the requirement to use the Document Cover Sheet and provide supporting documentation.*

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CONTENTS

TABLES

FIGURES

ACRONYMS

CEC	Cation Exchange Capacity
DRZ	Disturbed Rock Zone
EDZ	Excavation Disturbed Zone
NBS	Natural Barrier Systems
sCMT	Synchrotron Microtomography
THMC	Thermal-Hydraulic-Mechanical-Chemical

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1. Introduction

Maximum allowable temperature is one of the most important design variables for a geological repository, because it determines waste package spacing, distance between disposal galleries, and therefore the overall size (and cost) of the repository for a given amount of waste. This is especially important for a clay repository, because clay rock has relatively low heat conductivity. However, data and knowledge gaps exist for establishing a scientific basis for determining this temperature for a clay repository. Excessive heat can result in chemical alteration—illitization and cementation—of buffer and backfill materials (bentonite) within the engineered barrier system (EBS) and clay host rock in natural barrier systems (NBS). This alteration potentially compromises (1) the function of these EBS components by reducing their plasticity and capability to swell when moisture is introduced, and (2) the function of the NBS by reducing the system's self-sealing capability within the host-rock damage zone. Note that bentonite-based buffer and backfill materials are also used in conjunction with repositories in other host rock types, such as repositories in crystalline rock.

To examine the temperature-induced changes in the physical-chemical behavior of bentonite and clay host rock, we have developed a research plan for conducting laboratory and modeling studies and have submitted a research proposal. This report summarizes the results of this planning activity. The primary objective of the proposed research is to investigate the impact of chemical alterations of buffer and backfill materials (bentonite) and clay host rock on their geomechanical and hydrological properties, and on interaction between the EBS and the natural system. Note that this interaction is critical because moisture and related chemicals needed for chemical alteration (e.g., K^+) are mainly from the host rock. The proposed laboratory experiments are planned in collaboration with the Los Alamos National Laboratory (LANL) team; in this report, however, we will describe LBNL's part of the planned research activity only. A brief review of temperature-induced processes is given in Section 2. Sections 3 and 4 discuss the planned research tasks for laboratory experiments and related modeling studies, respectively.

This planning activity directly addresses the research topic P14, Technical basis for thermal loading limits, identified in Research & Development (R&D) Plan for Used Fuel Disposition Campaign (UFDC) Natural System Evaluation and Tool Development (Wang, 2011). It also addresses key Features, Events and Processes (FEPs), which have been ranked high in importance, as listed in Table 7 and 8 of the Used Fuel Disposition Campaign Disposal Research and Development Roadmap (FCR&D-USED-2011-000065 REV0) (Nutt, 2011). Specifically, they address FEP 2.2.01, Excavation Disturbed Zone (EDZ), for shale, by investigating the impact of high temperature on the self-sealing capability within an EDZ; and FEP 2.1.04.01, buffer/backfill, by investigating chemical alteration within bentonite and its impact on mechanical and hydraulic properties.

2. Temperature-Induced Processes

As previously indicated, high temperatures can result in chemical alteration—illitization and cementation—of bentonite within an EBS and host rock in a clay repository. This section gives a brief review of these temperature-induced processes.

Smectite, a swelling 2:1 clay mineral, is responsible for the swelling capability of bentonite and clay host rock. When exposed to high temperatures, smectites are unstable and slowly transform to more stable silicate phases, such as nonswelling illite (Wersin et al., 2007). This illitization process can be schematically described by the following chemical reaction (e.g., Pusch and Karnland, 1996):

$$Na - Smectite + K^{+} + Al^{3+} \rightarrow illite + Si^{4+} \tag{1}$$

This leads to a destruction of smectite and to a release of Si, which precipitates as SiO_2 cement. The illitization (and cementation) processes reduce the swelling capability and plasticity of the bentonite materials and clay host rock. There are a number of laboratory-experiment data sets for demonstrating the effects of these temperature-induced processes (Whitney and Northrop, 1988; Horseman and McEwen, 1996; Wersin et al., 2007; Pusch et al., 2010).

Note that the detailed mechanisms involved in the chemical reactions described in (1) are still under debate. Two mechanisms have been proposed in the literature (e.g., Wersin et al., 2007): (1) solid state transformation by substitution of intracrystal cations, or (2) a dissolution-precipitation process. It is generally agreed that either transformation process may occur, depending on physical-chemical conditions.

The kinetics of the smectite-to-illite reactions strongly depend on temperature, time, and K^+ pore-water concentration (e.g., Wersin et al., 2007). Pusch and Madsen (1995) showed that the empirical kinetic model proposed by Pytte (1982) was consistent with observed mineralogical relationships and the thermal history close to the heat sources for natural analogues (such as shales exposed to hydrothermal events). That model is given by

$$-dS/dt = A\exp(E_a/RT)(K^{+}/Na^{+})mS^{n} \tag{2}$$

where S is the mole fraction of the reaction product (illite), A is the pre-exponential factor, E_a is the activation energy, R the gas constant, T the temperature and m, n are coefficients depending on the K^+/N_a^+ ratio and K^+ /N_a^+ represents the ratio of the K^+ and N_a^+ concentrations in groundwater. This reaction-rate model can be used for modeling the related processes and for identifying important parameters affecting these processes.

Note that (2) was proposed for saturated conditions. Under unsaturated conditions, the relationship given in (2) needs to be modified to consider the fact that the solid phase only partially contact with the pore water that supplies K^+ for the reaction. Most test data in the literature for chemical alteration of clay and its impact have been collected for saturated clay materials. In a clay repository, buffer, backfill, and near-field host rock are likely subject to unsaturated conditions during a certain period of heating due to decay, in particular if high temperatures are desired. In relatively dry conditions, it will be difficult for K^+ to transport from groundwater to the clay materials of concern. In other words, unsaturated conditions would significantly retard the chemical-alteration process. The time period for EBS bentonite to remain unsaturated is also highly dependent on the repository design. For example, one EBS design option proposed in the literature is to use a prefabricated EBS module enclosed in a thin steel shell (Wersin et al., 2007). In this case, essentially dry conditions (that would prevent significant chemical alteration) in the bentonite are expected to prevail for many hundreds of years, until the steel shell is compromised.

While a number of studies have been devoted to the temperature-induced mineralogical and geochemical changes in clay materials, data are rather sparse regarding the impact of chemical alteration on clay mechanical and hydraulic properties, such as swelling pressure and permeability. However, as reviewed by Wersin et al. (2007), these limited laboratory data seem to indicate that significant effects on swelling pressure and hydraulic conductivity are noted at a temperature of 150^{o}C and above. Even at such high temperature, the hydraulic properties are still rather favorable for a repository. Nevertheless, more laboratory data are needed along this line to help establish a solid scientific base for maximum allowable temperature.

3. Laboratory Experiment Plans

High-temperature laboratory studies (above 100°C) of clay physical-chemical alteration, and of high temperature's impact on clay—and clay-bearing rock—with respect to mechanical and hydrological properties, are not commonly performed. Experimental data that would be obtained from such experiments could well be critical in repository selection and design of an EBS. We plan to conduct multiscale laboratory experiments to examine the impact of micro- and core-scale textural and structural changes in clay resulting from application of heat.

3.1 Core-scale experiments

The primary objectives of the core-scale experiment are to produce clay samples subject to heat under different sample conditions, and to determine their core-scale mechanical and hydrological properties. Bentonite clay with different values of (1) porosity (density), (2) water saturation, and (3) KCl concentration will be packed in miniature, sealed, spring-loaded cylindrical pressure vessels. These samples will be heated to selected temperature levels (from 100°C to 300°C) to induce smectite-to-illite transformation. (The higher temperatures [>200°C] are used to accelerate the reaction, so that the results can be achieved within several weeks.)

These core-scale experiments will employ sealed, miniature pressure vessels in which the pore pressure is provided primarily by the vapor pressure of the heated pore fluid. A schematic view of the pressure vessel is shown in Figure 1, and a currently commercially available vessel (manufactured by High Pressure Equipment Company, PA) in Figure 2. To reduce chemical reactions between the clay and the pressure vessel wall at high temperature, the vessels will be produced from a titanium alloy (grade 5). (Note that, ideally, high-corrosion-resistant alloys such as grade 29 are preferred when experiments involve high temperature and extreme pH (e.g., Thomas, 2003). However, alloys with the strength required for building pressure vessels are rarely produced and are currently not available to us.) Five to ten of these vessels will be used simultaneously for a single clay sample. Using these vessels as test tubes, we remove each of the vessels from the oven at different heating durations to examine the changes in the clay's properties over time.

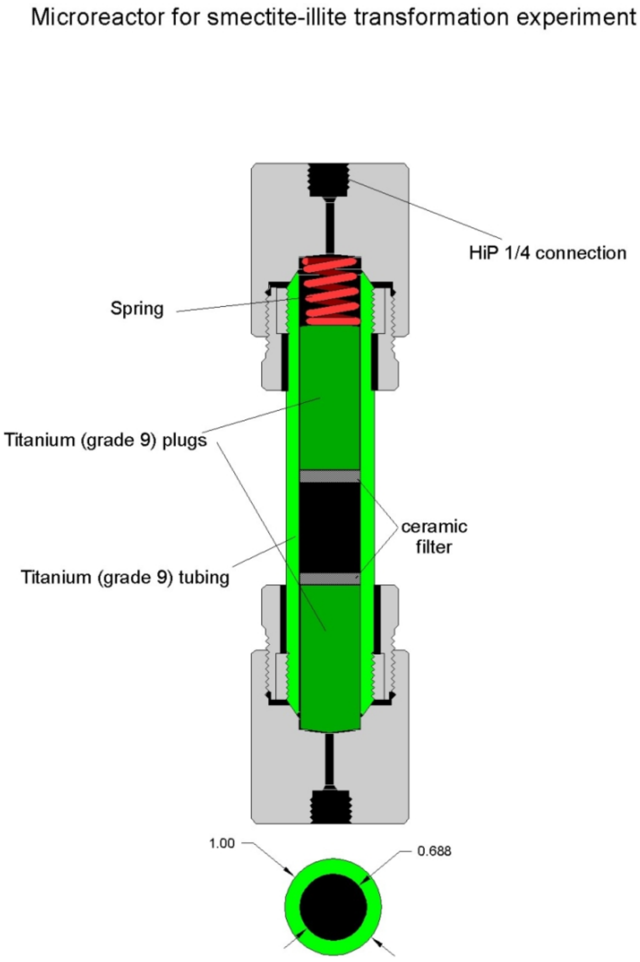

Figure 1. Micro-reactor vessel designed for core-scale experiments.

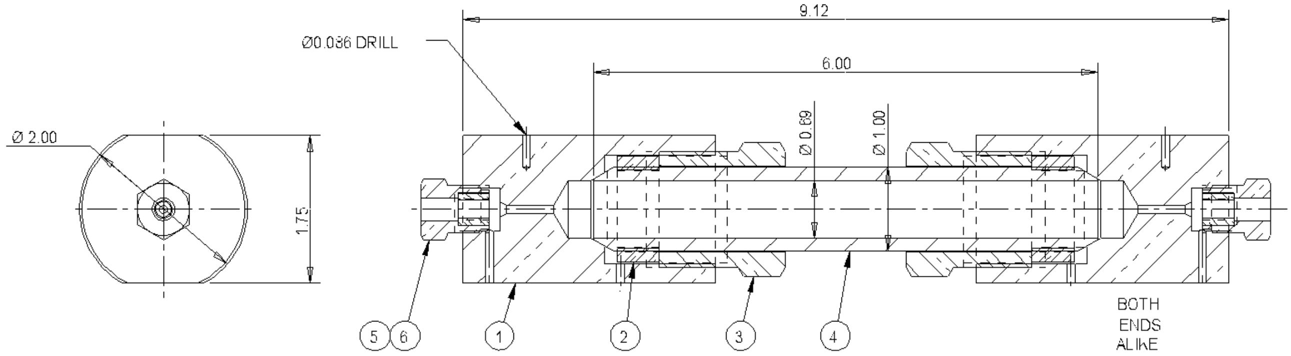

Figure 2. Titanium (grade 5) micro reactor cell readily available from High Pressure Equipment Company (PA).

After applying the heat for varying periods of time (1 day up to 30 days), each sample is removed from the oven. Once sufficiently cooled, the cell's end caps are removed, and the clay sample is tested for ultrasonic (P-wave) velocity and air permeability before being removed from the cell. The length (or volume) change of the sample is determined from the location of a piston plug within the cell. Subsequently, a smaller cylindrical core is cut out of the sample, which will be tested for unconfined uniaxial compression strength.

Reducing the temperature may cause additional microfracturing of the sample, because of the larger contraction of the metal cell wall and the differential cooling within the sample itself. To distinguish this effect, we will prepare a small number of the samples within a pressure vessel, with the endcaps fitted with a gas feedthrough, and measure changes in the gas permeability periodically *in situ*. These changes will be compared to the tests after the temperature is reduced. Experimental tasks to be performed, including activity details, are as follows (Table 1).

Table 1. Task descriptions for core-scale laboratory experiments

Task 1.1 **Preparation of experimental setup**		In this task, miniature pressure vessels containing the clay samples to be tested are fabricated at the LBNL machine shop, and an experimental setup are built for the long-duration (several weeks) heating test. The task also includes preparation of necessary safety documents and acquisition of internal work authorization.
Task 1.2 **Acquisition of clay samples and initial characterization**		Clay-based samples (bentonite and natural clay stones) will be obtained in large quantities from two sources (possibly from the Source Clay Repository and the Mont Terri URL, respectively) to avoid sample variability between experiments. These samples will be shared with the LANL team so that the experiments conducted at both labs can be easily compared and interpreted. The LANL team will conduct initial characterization of the clay for its mineral composition.
Task 1.3 **Heating experiment**		Bentonite and clay samples with a range of water content (below saturation) and KCl concentration will be packed in miniature, sealed, spring-loaded cylindrical pressure vessels. These samples will be heated to selected temperatures (from 100°C to ~300°C) to induce smectite-to-illite transformation. (The higher temperatures [>200°C] are used to accelerate the reaction, so that the results can be achieved within several weeks.) The experiment will be conducted within a sealed pressure vessel in which the pore pressure is provided primarily by the vapor pressure of the heated pore fluid. After applying the heat for a varying period of time (1 day up to 30 days), each sample will be removed from the oven and tested. Selected samples, including pre-test reference samples, will be shared with the LANL researchers for detailed chemical analysis of the samples. Preliminary tests to calibrate the testing system will be done in FY2013 Q2-Q3, followed by several tests with a range of temperatures. Because the main purpose of this task is to produce a large number of samples for material property characterizations, the activity will continue for the duration of the project. Very High Temperature Tests: Conducted at T=250-300°C range High Temperature Tests: Conducted at T~200°C Medium Temperature Tests: Conducted at T~100° Room Temperature Tests: Reference tests at ambient T
	Activity 1.3.1 ***Variable-duration heating of clay samples***	Bentonite and clay samples will be packed in miniature, sealed cylindrical pressure vessels and heated (within an oven) for several weeks at a selected temperature (from 100°C to approximately 300°C). A batch of samples with identical water content and KCl concentration will be prepared, so that the samples can be tested for a range of heating durations.

	Activity 1.3.2 ***Characterization of thermally induced microcracks***	The reduction of temperature may cause additional microfracturing of the sample because of larger contraction of the metal cell wall and differential cooling of the sample itself. To distinguish this effect, a small number of the samples will be prepared within a pressure vessel with the endcaps fitted with a gas feedthrough. Resulting changes in the gas permeability will be measured periodically *in situ*, which will be compared to the tests after the temperature is reduced.
	Activity 1.3.3 ***Post-experiment clay characterization***	After heating, the smectite content of the samples will be determined via XRD analysis. The results will be compared to the pre-test results, and the degree of smectite-illite transformation will be determined.
	Activity 1.3.4 ***Mechanical and hydrological property measurements***	After the samples are removed from the oven and sufficiently cooled, ultrasonic (P-wave) velocity will be first measured across the pressure vessel. Water-coupled ultrasonic transducers will be used to propagate the wave across the vessel's wall. Subsequently, the vessel's end caps will be removed, and the air permeability through the sample will be measured. The length (or volume) change of the clay sample will be determined from the location of a piston plug within the cell, which will be used to determine the swelling and contraction of the clay. Finally, smaller cylindrical samples will be subcored and tested for uniaxial (unconfined) compression strength.
	Activity 1.3.5 ***Swelling property characterization***	A subset of the samples will be injected with water at room temperature and the resulting swelling of the clay will be monitored. The swelling will be determined either by measuring the sample length (volume) change under unconfined conditions, or by measuring the swelling pressure under confined condition.

3.2 Micro-scale experiments/characterizations

Transformation of the clay mineral phases is expected to occur heterogeneously within a sample in which the initial distribution of illite and smectite is also heterogeneous. This will lead to heterogeneous distribution of enlarged macroporosity (including microcracks) resulting from transformation-induced contraction of clay minerals. Also, as mentioned in Section 3.1, reducing the temperature after the experiment may lead to additional fracturing of the sample.

Since changes in the mechanical and transport properties of clays are controlled primarily by the changes in their "micro-architecture" (e.g., connected fractures and macroporosity), we will examine a selected set of samples using synchrotron microtomography (sCMT). The obtained images will be used to characterize fracture attributes, including architecture, connectivity, mean aperture, and macroporosity distribution. If possible, these attributes will be incorporated into an available analytical model to predict changes in the permeability during clay phase transformation.

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Table 2. Task descriptions for microscale laboratory experiments

Task 2.1 **Modification of micro CT imaging station at ALS-Beamline 8.3.1**		The sCMT imaging stage at the Advanced Light Source (Beamline 8.3.2) will be modified so that the miniature pressure vessels used to produce heated clay can be imaged *in situ* without disturbing the sample. A stage attachment will be developed and constructed to allow repeatable positioning of the miniature vessels, thus enabling time-lapse monitoring of micro-fracture evolution and comparison to baseline structure.
Task 2.3 **Synchrotron x-ray micro CT imaging of clay samples**	***Activity 2.2.1*** ***X-ray Data collection***	Samples produced in the Task 1.1-1.3 will be used to conduct x-ray CT imaging at ALS BL 8.3.2. Depending on the sample dimension selected, image resolution may range from 0.7 to 4.4 microns. A limited number of samples from each test sequence will be scanned consistent with available beam-time.
	Activity 2.2.2 Synchrotron x-ray micro CT imaging of clay samples: Data processing	Data collected at the beamline will be processed to reconstruct CT images of the sample microarchitecture. The resulting image volumes will be segmented to isolate the fracture network and changes induced during the heating process.
	Activity 2.2.3 Modeling of transport properties from CT image volumes	Transport properties, primarily single-phase permeability and effective gas diffusivity, will be calculated using the segmented image volume of cores where alteration was observed. The resulting values will be compared to gas-permeability measurements determined in Activity 1.3.2, as well as traditional porosity/effective diffusivity relationships.

4. Numerical Modeling Plans

The primary objectives of the numerical modeling are (1) to develop a reliable modeling capability for evaluating the impact of high temperature, by incorporating data from literature and the planned laboratory experiments, and (2) to recommend an optimized repository design from determining the maximum allowable temperature. The related coupled thermal, hydrological, mechanical, and chemical (THMC) processes are also investigated, because they are highly relevant to the determination of maximum allowable temperature for a clay repository. The modeling studies will be based on the coupled TOUGHREACT-FLAC3D simulator being developed at LBNL. TOUGHREACT is a simulator for multiphase flow, heat transfer, and reactive transport, and FLAC3D is a geomechanics simulator. Specific modeling tasks are listed in Table 3.

Table 3. Task descriptions for numerical modeling

Task 3.1 **Model Analysis of Laboratory**	Results of core-scale laboratory experiments conducted in Task 1 will be analyzed and matched using the TOUGHREACT-FLAC3D simulator to determine values for model parameters to be incorporated into the THMC model used in Task 3.2. These parameter values are important for accurately modeling impacts of high-temperature-induced chemical alteration, especially for unsaturated conditions. Observations from Task 2 will also be used to improve our understanding of interplay among chemical, mechanical, and hydraulic processes, and consequently refine formulations to relate model parameters for these coupled processes in the THMC model.
Task 3.2 **Determination of Maximum Allowable Temperature**	To determine the maximum allowable temperature, we will develop a THMC model based on the coupled TOUGHREACT-FLAC3D simulator that is being developed at LBNL. Typical EBS design concepts to be used in the simulations will be identified by working with Jove-Colon Carlos (SNL). The best available information from literature on chemical alteration and related changed properties will be used in the initial modeling studies, and laboratory test data from this study will be incorporated when they are available (Section 3). Modeling results for the interplay between evolutions of moisture flow, temperature, chemical transport and alteration, and mechanical deformation (including swelling pressure changes) will be documented for different scenarios of interest. The developed THMC model will also be employed to develop guidance for optimizing repository design such that impacts of temperature-induced processes are acceptable even for a relatively high temperature in the repository. Guidance and associated supporting materials will be documented for different EBS designs.

5. Interlaboratory collaborations

The laboratory experiments conducted by LBNL will use the sample clays provided by the LANL team. The LANL team will also conduct chemical analysis of the clays after the heating experiment described in Section 3. The planned research tasks for LANL can be found in Caporuscio et al. (2012). The obtained data from both LBNL and LANL will be integrated to interpret the thermally induced changes in clay and clay-bearing rocks from nanoscale (clay mineral alternation and composition) to microscale (micropore structure and microfractures) to core scale (macroscopic flow and mechanical properties).

6. Concluding Remarks

The maximum allowable temperature is one of the most important design variables for a geological repository. This is especially true for a clay repository, because clay has relatively small values for heat conductivity. This report documents a laboratory and modeling study plan for investigating the maximum allowable temperature in a clay repository. Specifically, the laboratory tests intend to provide data sets that are largely lacking in the literature and highly needed for establishing the scientific basis for determining the maximum allowable temperature, including temperature-induced chemical alteration and its impact on mechanical and hydraulic properties as a function of water saturation. The modeling study intends to develop a modeling capability for determining the maximum allowable temperature based on the data collected in the laboratory study and to provide guidance for optimizing repository design—such that the impacts of temperature-induced processes are acceptable even for a relatively high temperature in the repository. The potential collaboration on the laboratory study between LBNL and LANL has been discussed among the teams from the two laboratories. As a result of this work, a research proposal to study the temperature limits in a clay repository was submitted to UFD management through Jens Birkholzer.

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