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Title: Status of LANL investigations of temperature constraints on clay in repository environments

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Status of LANL investigations of temperature constraints on clay in repository environments

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INTRODUCTION

The Used Fuel Disposition (UFD) Campaign is presently evaluating various generic options for disposal of used fuel. The focus of this experimental work is to characterize and bound Engineered Barrier Systems (EBS) conditions in high heat load repositories. The UFD now has the ability to evaluate multiple EBS materials, waste containers, and rock types at higher heat loads and pressures (including deep boreholes). The geologic conditions now available to the U.S.A. and the international community for repositories include saturated and reduced water conditions, along with higher pressure and temperature (P, T) regimes.

Chemical and structural changes to the clays, in either backfill/buffer or clay-rich host rock, may have significant effects on repository evolution. Reduction of smectite expansion capacity and rehydration potential due to heating could affect the isolation provided by EBS. Processes such as cementation by silica precipitation and authigenic illite could change the hydraulic and mechanical properties of clay-rich materials.

Experimental studies of these repository conditions at high P,T have not been performed in the U.S. for decades and little has been done by the international community at high P,T. The experiments to be performed by LANL will focus on the importance of repository chemical and mineralogical conditions at elevated P,Tconditions. This will provide input to the assessment of scientific basis for elevating the temperature limits in clay barriers.

BACKGROUND

Clay minerals – as backfill, buffer materials, or host-rock constituents – are critical to the performance of the EBS. The relevant factors of clay mineral performance include chemical interactions, radionuclide retention, and physical and mechanical behavior. This section summarizes previous foreign studies of chemical changes in smectite clay at elevated temperatures and/or pressures. The potential application of smectites and the smectite-rich rock (i.e., bentonite) in geologic disposal of radioactive-waste have been recognized for decades, however most studies have been devoted to issues of smectite stability under low temperature repository conditions.

Altaner and Ylagan (1997) provided a good introduction to the concepts of smectite alteration. Smectite illitization proceeds through mixed-layer illite/smectite (I/S) intermediates as the percentage of illite interlayer increases. Important factors controlling these changes include increasing temperature, potassium (K) concentration, time, and water/rock ratio. Possible reaction mechanisms for smectite illitization include solid-state transformation, dissolution and crystallization, and Oswald ripening.

Meunier et al. (1998) and Wersin et al. (2007) summarize how smectites heated in the range of 110-150 °C and above, change mineralogically altering the bentonite properties relevant to backfill/buffer performance. Potential changes include silica precipitation above 130 °C, illite formation above ~150 °C, and chlorite formation in the presence of Fe at higher temperatures. Additionally, loss of structural silicon may retard rehydration as the smectite cools. Imaging evidence supports the idea of dissolution and precipitation processes during illitization, although additional solid-state changes cannot be ruled out. Simultaneous nucleation and growth mechanisms proposed by Eberl et al. (2011) require further investigation.

EXPERIMENTAL FACILITIES

Experiments simulating EBS components reacting at repository conditions will be conducted at LANL's high pressure, hydrothermal laboratory. The Dickson reaction cells that presently contain the experimental mixtures are either gold (see Figure 1) or titanium bags and were sealed within steel pressure vessels (Figure 2). The assembled reaction vessel was then placed within autoclave furnaces (Figure 3) and brought up to pressure and temperature. As noted in the figure captions, maximum experimental conditions for these vessels are 400 ^{o}C and 600 bar. The advantages of Dickson type cells are large volume (up to 250 milliliter) and the ability to extract liquid/gas samples during the experimental run.

Figure 1

Figure 2

Figure 1. Gold reaction cells: **Left:** 120 ml cell, **Right:** 240 ml cell with cap, thrust ring, and head disassembled.

Figure 2. Left: HiP (thrust ring seal type) pressure vessel, for 400 ^{o}C/600 bar furnaces.

Figure 3. 400 ^{o}C /600 bar rocking autoclave rack (autoclave drums are ~24” tall)

A second extremely useful reactor type is a cold seal reaction vessel. We are presently developing this capability at LANL which has the advantage of providing much more precise analyses over a wider set of temperature / pressure conditions. When fully on line, this will provide six additional reaction vessels. The reaction vessel is depicted in Figure 4, while the furnace is pictured in Figure 5.

Figure 4. Cold seal reaction vessel, disassembled (800 ^{o}C, 2.5 kbar max.; from London 2008, Figure 14-1a).

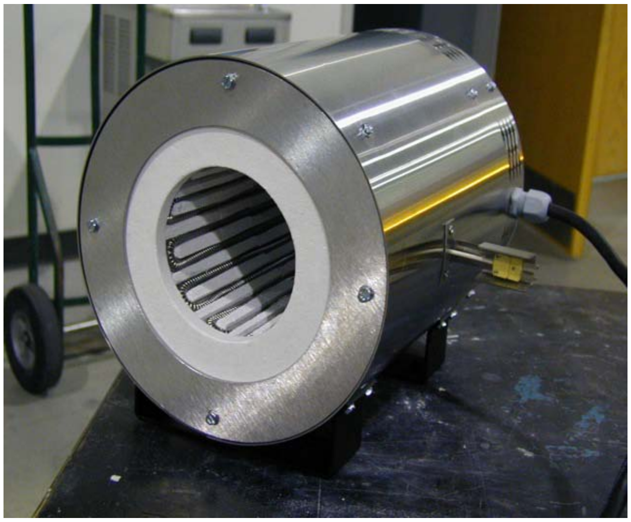

Figure 5. Furnace assembly for cold seal apparatus

RECENT RESULTS IN EBS STUDIES

During the FY12 experimental program for Engineered Barrier Systems (EBS) of the Used Fuel Campaign, six critical experiments were conducted. Experiments were performed in Dickson cells at 150 bar and sequentially stepped from 125 ^{o}C to 300 ^{o}C over a period of ~1 month. An unprocessed bentonite from Colony, Wyoming was used as the buffer material in each experiment. An K-Cl-rich brine (replicating K-enriched deep Stripa groundwater) was used at a 9:1 water:rock ratio. The baseline experiment contained brine + clay, while five other experiments contained brine, clay, and metals that could be used as waste form canisters (304SS, 316SS, Cu, and low carbon SS). All experiments were buffered at the Mt-Fe oxygen fugacity univarient line to mimic reducing conditions predicted for realistic repositories.

As experiment temperature increased and time progressed, pH and K ion concentrations dropped, while $SiO_{2(aq)}$, Na, and SO_4 concentrations increased. Silica was liberated into the fluid phase (>1000 ppm) and precipitated during the quenching of the experiment. The precipitated silica transformed to cristobalite as cooling progressed.

Potassium was mobilized and exchanged with interlayer Na, transitioning the clay from Na-montmorillonite to K-smectite. Though illitization was not observed in these experiments, its formation may be kinetically limited and longer-term experiments are underway to evaluate the equilibrium point in this reaction. Clinoptilolite present in the starting bentonite mixture is unstable above 150 ^{o}C (Smyth, 1982). Hence, the zeolite broke down at high temperatures but recrystallized as the quench event occurred. This was borne out in SEM images that showed clinoptilolite as a very late stage growth mineral (Figure 6).

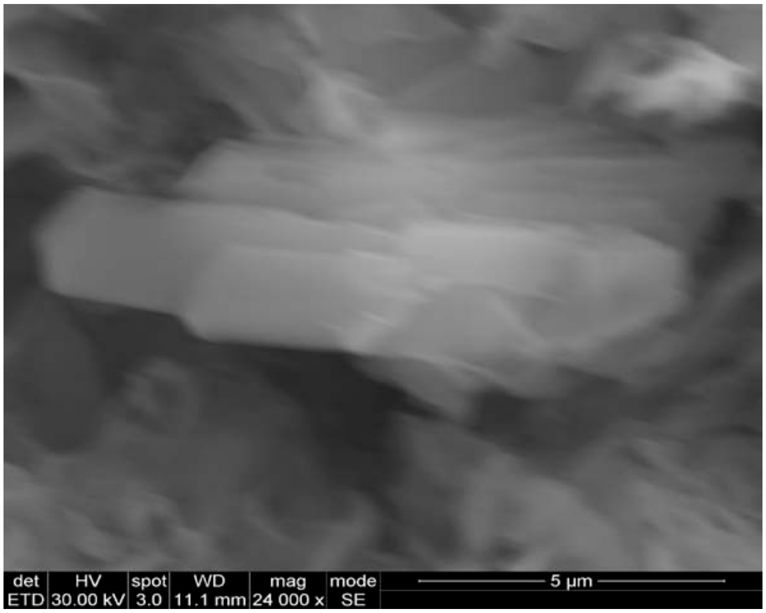

Figure 6. SEM image of late stage euhedral monoclinic clinoptilolite in EBS experiments.

All experimental runs containing steel exhibit the generation of a chlorite / Fe-saponite layer at the clay-metal boundary (Figure 7). The formation of minor amounts of pentlandite [$(Fe,Ni)_9S_8$] also occurs on 304 and 316 steel plates (Figure 8). Chalcocite (Cu_2S) (Figure 9) formed as a corrosion product on the Cu plates. The two sulfide phases have been produced by the generation of H_2S gas during the experimental runs. The H_2S is formed by the breakdown of pyrite framboids at high temperature .

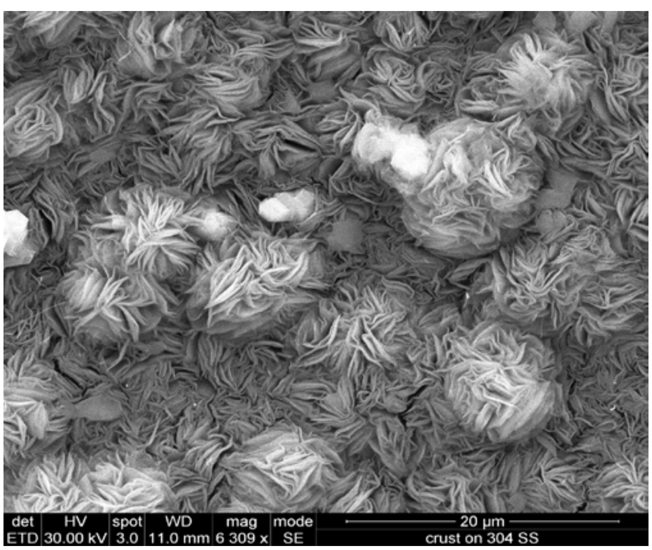

Figure 7. Chlorite layer on 304 SS coupon – EBS-2

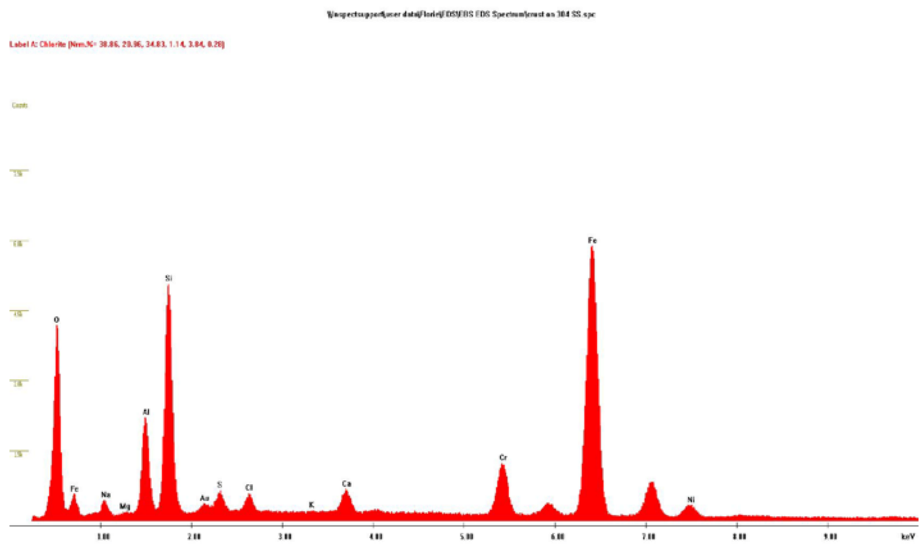

Figure 8. EDX spectra of chlorite layer on 304 SS coupon. A portion of the Fe peak and both Cr, Ni minor peaks are likely due to formation of pentlandite on the 304SS surface.

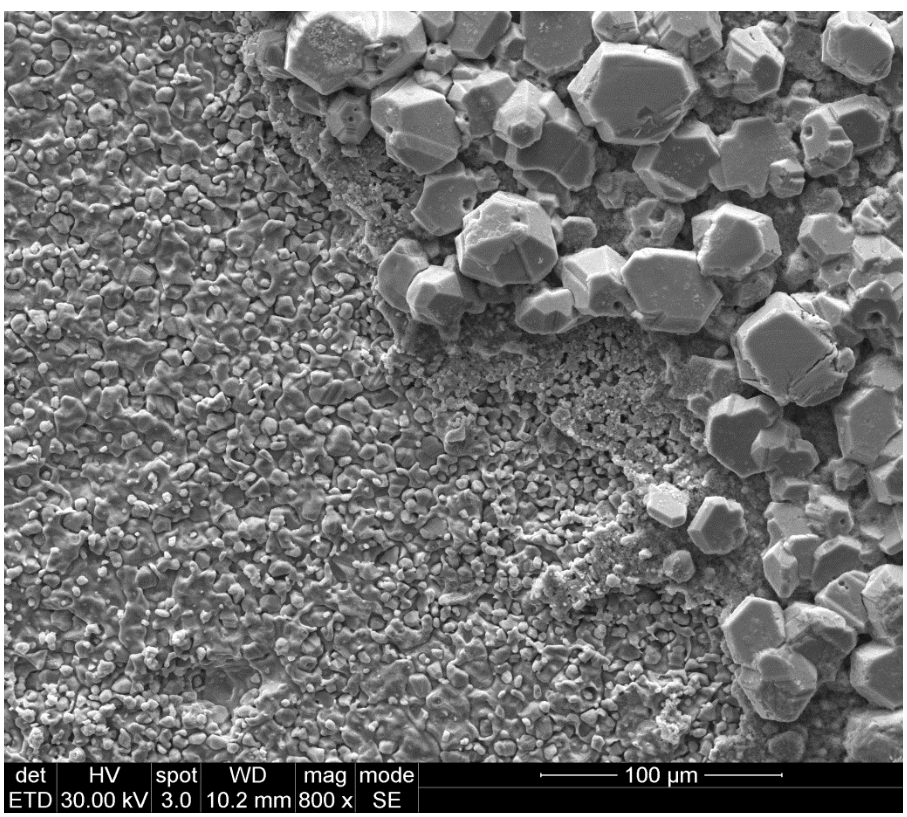

Figure 9. Image of corroded copper substrate (lower left) and newly formed chalcocite (upper right) developed during EBS experiment.

Experiments on representative EBS materials at repository P,T conditions are providing useful information for generic repository studies. Lack of illite formation is common in clay experiments and may be related to kinetics or K concentration. Precipitated SiO_2 may potentially seal heating cracks in the clay backfill. The chlorite layer generated on steel may act as a passivation material and prevent corrosion of the steel canister wall. Finally, even if zeolites break down during the high temperature thermal pulse they may form again as the repository inventory cools and perform as radionuclide sorbing phases.

LIASON WITH LAWRENCE BERKLEY NATIONAL LABORATORY (LBNL)

We propose to coordinate with LBNL to investigate how mineral phase changes influence bulk mechanical properties. Recent experiments for EBS investigations have revealed results which indicate that there was substantial cation transfer between phases, an increase in K-smectite (but no phase transformation to illite), dissolution of silicate minerals, and precipitation of opal-CT which then crystallized to cristobalite and sanidine along with late-stage feldspar and clinoptilolite formation. All these factors point toward very reactive conditions (when saturated with water) and a potential inhibitor of illite formation due to kinetic factors. Additionally, H_2S gas occurred in the brine aliquots obtained during sampling. The sulfide gas may have been produced from the decomposition of pyrite with increasing temperature. Under certain conditions, the generation of H_2S gas may have corrosive effects on canister walls.

As part of this collaboration, we will coordinate our samples used in the experimental studies. The smectite backfill used in all experiments will be drawn from a common, large, well characterized sample. Likewise, we will request large volume samples of Opalinous Clay from our international partners. Both laboratories will discuss and decide on a synthetic Mont Terri brine composition for use in experiments.

As part of this integrated research program, LANL can supply relatively large volumes (200 ml) of clay heated to 300 ^{o}C under controlled pressure and other variables for use by LBNL in their thermal mechanical studies.

PROPOSED EXPERIMENTAL STUDIES AT LANL

For the LANL experimental program we will use both hydrothermal autoclaves and cold seal vessels at our laboratory. . The advantages of the hydrothermal autoclaves are 1) fluid phases can be sampled during the experiments and 2) the reaction cells can contain large a large sample volume (75-250 ml), while the cold seal system provides much more precise results due to smaller sample size. Furthermore, Parr reaction vessels may be employed to study SiO_2 precipitation and aluminosilicate reactions in clay at lower temperatures. Lastly, dry experiments will mimic the highest temperatures of the expected heat pulse. Therefore, experiments will be conducted at both dry and saturated conditions and we will also investigate the variations in clay composition because this is a critical parameter in clay alteration processes.

We propose experiments in FY13 to investigate how physical and chemical characteristics of a clay buffer (with steel) are altered in a dry system. These experiments would more closely duplicate mined repository conditions (i.e., pressures up to 0.3 kbar) at the thermal peak. All experiments will be conducted at very low oxygen fugacities using magnetite / iron as a buffering agent. These sets of experiments, along with 100 ºC and 200 ºC quenching experiments should allow us to gather information to unravel the nuances of SiO_2 precipitation and aluminosilicate formation in clay buffer / backfill scenarios. The information will **1)** shed light on the ability for SiO_2 to close fractures and/or prop open clay structures, and **2)** give insight on cation transfer and exchange between the aqueous geochemistry and aluminosilcate matrix. If all experiments are successful, we would propose to then replicate the experiments in saturated conditions. Additionally, we plan to add host rock (shale) components to the experiments thereby fully duplicating a repository setting. Since shale host rocks contain abundant pyrite framboids, we will also investigate the effect of H_2S gas generation and the potential for canister corrosion.

We will investigate alternative characterization methods for the solid phase reaction products, e.g., TEM, Raman spectroscopy, neutron scattering techniques (LANSCE facility), Zeta potential measurements, and various synchrotron techniques.

Due to potential budget restrictions in FY-13, experiments may be extremely limited. At present funding levels we would propose to provide the following experiments:

1) Heat a large volume smectite sample at 300 ºC and provide material to LBNL as reactants for their thermo-mechanical studies.
2) Initiate a series of experimental runs involving mixed buffer material (bentonite-sand, bentonite-graphite) which is predicted to have beneficial thermal capacity characteristics. We will focus on chemical alteration trends and mineral phase mobilization and deposition products. SiO_2 dissolution, release from phyllosilicates, and mobilization will be studied in detail.

Data extracted from these experiments concerning phase stability, aqueous geochemistry, cation exchange, mineral growth and potential passivating materials will be passed on to appropriate PIs involved in Mont Terri and the DECOVALEX project. This transfer of data will be facilitated with the help of Jens Birkholzer at LBNL.

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