

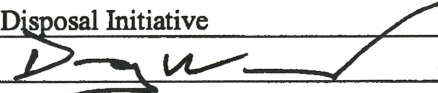
FCT Quality Assurance Program Document

Appendix E FCT Document Cover Sheet

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Assessment of Research Needs for Actinide and Brine Chemistry in Support of a HLW Repository in Salt

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Report: M3FT-12LA08180117

Work Package: FT-12LA08180117

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Assessment of Research Needs for Actinide and Brine Chemistry in Support of a HLW Repository in Salt

Executive Summary

An understanding of the relevant actinide and brine chemistry is a potentially important need for the safety case for a salt-based nuclear repository. Although a salt repository is predicted to be mostly unsaturated [WIPP Appendix SOTERM -2009] during its performance lifetime, there are brine-inundation scenarios, mostly due to human intrusion, that must be considered in the regulatory licensing process. This need is best exemplified by the ongoing recertification effort in the Waste Isolation Pilot Plant (WIPP), and the FEPs associated with this project, where brine and actinide chemistry is shown to be a critical part of the safety case.

The goal of this report is to provide an overview assessment of where we are in the WIPP project as it relates to the data/research needs and gaps for a HLW (processing and spent fuel) salt-based repository. In this context, this is a first step in the process of fully identifying research needs in this area and is built on a series of US-German workshops on this subject. The extension of the safety case from the WIPP TRU repository to an HLW nuclear repository (defense or commercial) is relatively straightforward and many aspects of the current WIPP safety case and approach will apply. There are, however, some research and data needs that are specific to the HLW case that still need to be addressed. These mainly fall into two categories: 1) research that has not been done because it does not apply to the WIPP case; 2) improvements to fill data gaps in the existing WIPP safety case to further define the conservatism in place.

Specific to the brine and actinide chemistry in a brine-inundation scenario, the following improvements to fill existing data gaps are identified:

- Expanded Pitzer model for brine chemistry – specifically to add/increase the specifics on Fe, borate, and Mg chemistry
- Increased understanding of the microbiology in salt formations
- Need for an improved analog for the +4 actinides (or use plutonium itself) to replace thorium
- Better mechanistic understanding of redox and in particular the iron chemistry associated with these redox processes

There are three important issues that are specific to a HLW repository in Salt that are not currently considered in the WIPP model:

- 1) Higher thermal loadings and associated heating of the brine
- 2) Waste form and source term differences (e.g., consideration of fission products and increased emphasis on uranium chemistry)
- 3) Radiolytic effects

These are all needed to extend the current safety case to address the brine intrusion scenarios for the HLW case. This assessment will be developed further through our US-German interactions and will be a key focus of the upcoming ABC-Salt III workshop planned in 2013.

1. Introduction

The goal of this report is to provide a top-level assessment of the strengths and weaknesses of the safety case for the development a high-level nuclear waste repository in Salt from the narrow scope/view of actinide and brine chemistry. This is an important issue that needs to be addresses as we look to evaluate the possible use of bedded or domed salt geologies for the permanent disposal of both high-level (HLW) defense and commercial nuclear waste. The benefit to the DOE/NE of this report is that insight based on the current experience in the Waste Isolation Pilot Plant (WIPP) transuranic repository and the two past ABC Salt workshops centered on this topic can help guide and prioritize the emphasis of future research and data collection activities.

The core safety case for a salt-based repository rests on the very favorable geotechnical properties of salt. The self-sealing properties of salt will, within a few hundred years, lead to the resealing of the excavated portions of the salt mine. This leads to an unsaturated site, meaning that there is no interconnected groundwater, which can remain geologically isolated for millions of years. In the presence of a redox-active barrier, e.g. reduced iron, an anoxic and highly reducing environment is also created that establishes favorable thermodynamics for the long-term immobilization of radionuclides. This self-sealing repository concept is the basis of the currently EPA-licensed and operating WIPP TRU repository.

The regulatory process, although it accepted and validated the core geotechnical safety case for a salt repository, is also the reason why it is important to address the actinide and brine chemistry issues that are the subject of this assessment report. A key driver in any regulatory process is a demonstration that acceptable performance is attained even under low-probability scenarios. In the WIPP regulatory process, for example, the potential for human intrusions that lead to brine inundation is considered as an event that could lead to dissolved brine release (DBR) release of transuranics. DOE was able to assure the EPA that, even under these inundation scenarios, the target low-release limits were attained. In fact, under the reducing conditions in the WIPP, even with very conservative assumptions with respect to actinide

concentrations, low actinide solubilities are observed and DBR release is a relatively small contributor to overall release.

In this report we first summarize the current state of the actinide and chemistry understanding in the WIPP salt repository, we then summarize and address the key differences likely in extending a salt repository to the HLW case (thermally loaded repository), and conclude with a overall summary of data gaps and research needs that will help strengthen the analysis of the brine release scenario that would be expected to extend to the HLW case. These are based on the following assumptions and observations:

- The WIPP TRU repository is a good, but not sufficient, template for a HLW nuclear waste repository in a salt geology
- The regulatory requirements to define a safety case for a HLW repository in salt will likely be more, rather than less, stringent than our experience in the WIPP case
- The regulatory process, as was the case in the WIPP, will drive the need to understand the chemistry and actinide chemistry in the scenario of brine inundation
- The brine and actinide chemistry is sufficiently and conservatively defined in the WIPP safety case, although there are some data gaps. Given this, there are a number of key differences anticipated in the thermal and higher-activity HLW case. The most important of these potentially positive and negative factors are:
 - Elevated temperature that may impact many aspects of repository performance but will certainly have an effect on the radionuclide source term
 - Significant differences in the nature of the wastefrom. Most importantly radionuclides beyond just the TRU need to be considered (e.g., fission products), uranium (particularly in spent fuel) chemistry is much more important, and there is likely to be significantly less organics and oxy-anions that have driven many aspects of the WIPP safety case

- Increased potential for radiolytic effects on the brine and actinide chemistry due to the higher activity present. Radiolytic effects are not a significant factor in the WIPP safety case due to the low activity present and the overwhelming effect of the chemistry associated with the large amount of reduced iron present

The high ionic strength brine and actinide chemistry just outlined have been the subject of a continuing series of workshops on which much of this report is based. The abstracts of the first workshop, Actinide and Brine Chemistry in a Salt Repository (ABC Salt I) which was held in September 2010 in Carlsbad NM, are included as an attachment to this report. The proceedings for the ABC Salt II workshop, held in Karlsruhe Germany in November 2011, although not yet issued are also reflected in this report.

2. Assessment of WIPP Safety Case

The Waste Isolation Pilot Plant (WIPP) project is a transuranic nuclear waste repository in bedded salt, located in Southeastern New Mexico that has operated for over ten years (See Figure 2-1). This repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. WIPP's current purpose is to permanently dispose of defense-generated transuranic waste that is a byproduct of past nuclear weapons activities. The operation of the WIPP nuclear waste repository has led to significant experience in dealing with environmental regulations, the logistics of nuclear waste transportation, and safety concerns. In this context, it provides a template for the evaluation of an expanded repository options in a salt geology.

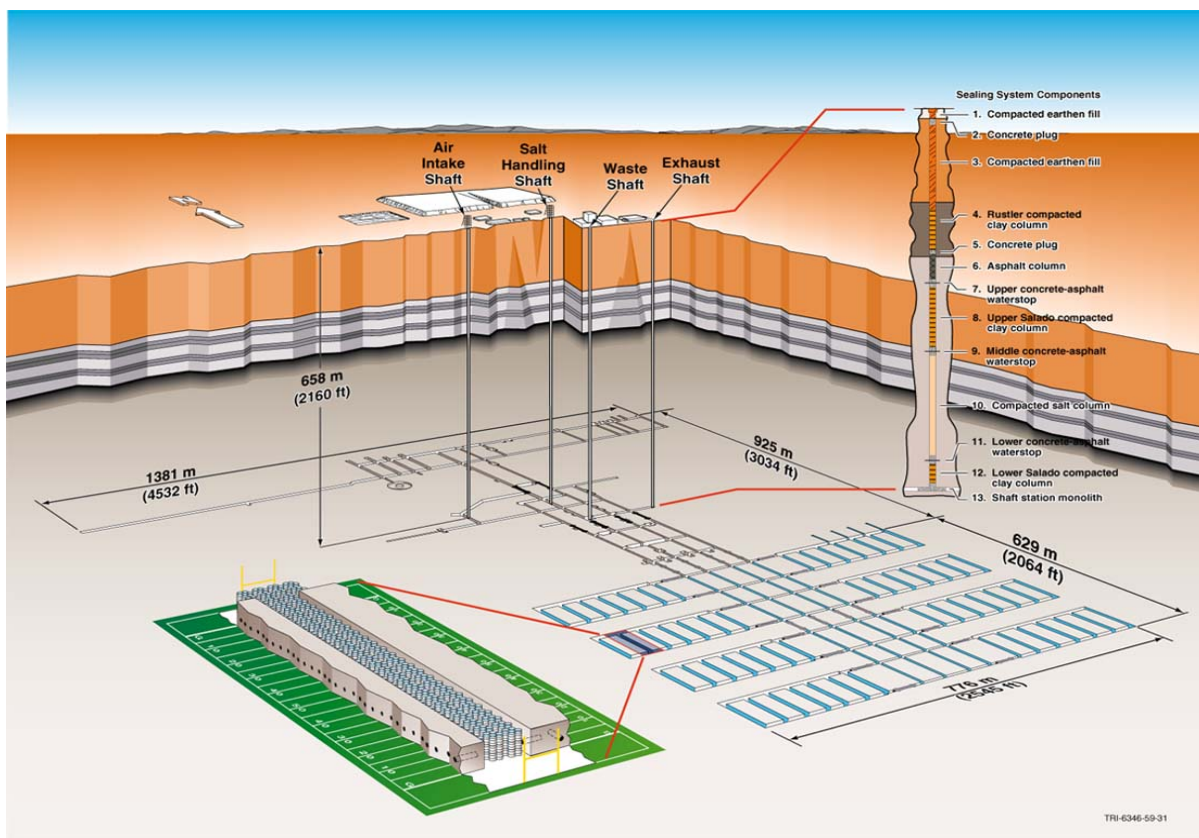


Figure 2-1. Overall Configuration of the WIPP Transuranic Repository in the Salado Salt Formation. The waste is emplaced in approved containers in rooms within each of the eight panels.

Waste disposal operations began at the WIPP on March 26, 1999 after license approval by the US Environmental Protection Agency (EPA) and the New Mexico State Environmental Department (NMED). A requirement of this license is that the WIPP needs to be recertified every 5 years for TRU disposal operations. Two re-certifications of the WIPP are now complete (April 2006 and November 2010) and efforts are already underway to prepare documentation for the third recertification application that is scheduled to be provided to the EPA regulator in March of 2014. The key accomplishments of this project to date include:

- 12+ years of safe operation
- 21 waste storage sites in the US were cleaned up
- Over 10,000 TRU shipments received and 78,000 m³ of waste emplaced
- Five panels are full, panel 6 is being filled, and panel 7 is under excavation

From a more technical viewpoint, the WIPP repository is an excellent example of a salt geological repository that our data show provides a robust, long-term, and permanent disposal site for TRU waste due to the naturally self-sealing, mostly dry, and reducing environment it provides. These panels and disposal rooms are located in Salado salt formation at an average depth of 2150 ft (~700 m). Many, but not all, aspects of the WIPP safety case extend to other repository concepts and the WIPP safety case and lessons learned in the regulatory interactions area a good starting point for the safety case for the thermally hotter and higher-activity high level waste (HLW) repository concept.

In this section, an overview of the WIPP safety case is given and evaluated as it relates to research needs for a HLW salt repository. The WIPP safety case continues to be strong, but includes some conservative assumptions and simplifications that could be reduced or eliminated with additional experimental or modeling results – something that may be beneficial to the HLW case.

2.1 WIPP FEPs Related to Brine and Actinide Chemistry

Features, events and processes (FEPs) are used in the WIPP PA to document the consideration of the several processes that could lead to radionuclide release from the WIPP. A number of these address brine and actinide/radionuclide chemistry although all are considered to be low in probability. It is this regulatory process that leads to the need to address significant low-probability events to assure the regulator that the repository will meet the release criteria even if these low probability events occur. The FEPs that are most relevant to brine chemistry, the radionuclide source term and release are listed in this section (WIPP appendix SCR 2009).

FEP N34 and N38: Saline intrusion and effects of dissolution on groundwater chemistry

This is excluded from PA because no natural events have been identified that lead to saline intrusions into the WIPP. Human intrusion scenarios are included in PA but are low probability.

FEP W52: Radiolysis of brine

This is eliminated from PA consideration on the basis of low consequence to WIPP performance.

FEP W56: Speciation of actinides

Chemical speciation is accounted for in PA through estimates of radionuclide solubility. Speciation will affect retardation in the Culebra (e.g., transport of radionuclides).

FEP W57: Kinetics of Speciation

Kinetic arguments are eliminated from PA on the basis of low consequence to WIPP PA. Radionuclide solubilities are controlled by thermodynamics.

FEP W58, W59, W60: Precipitation and Dissolution (of radionuclides)

Waste dissolution and release of radionuclides are accounted for in WIPP PA. These impact the available dissolved radionuclide concentrations (mobile species).

FEP W61, W62, W63: Sorption (of radionuclides)

Sorption is only accounted for in transport in the Culebra. It is eliminated from PA within the disposal rooms because it is beneficial and mitigates transport. Pseudo colloid formation is accounted for in estimating radionuclide dissolved (mobile) concentrations.

FEP W64 and W66: Reduction-Oxidation Chemistry (of radionuclides)

This is accounted for in PA in the actinide source term model. WIPP solubilities are calculated as a function of oxidation state.

FEP W65: Redox Fronts

This is eliminated from consideration in PA due to the low probability of its occurrence in the 10,000 year repository lifetime.

FEP W67: Localized redox zones

These are eliminated from PA calculations due to their low consequence to WIPP PA.

FEP W68, 69, 71: Organic Complexation (of radionuclides)

The effect of organic complexation on radionuclide solubility is accounted for in WIPP PA. The kinetics of complexation is eliminated based on the relatively fast complexation kinetics predicted.

FEP W70: Humic and Fulvic Acids

The effects of humic and fulvic acids is considered in WIPP PA and incorporated into the WIPP source term model.

FEP W77: Solute transport

Transport of dissolved actinides is accounted for in WIPP PA.

FEP W78, 79, 80, 81: Colloid formation, sorption and transport

Formation, stability and transport of colloids are accounted for in WIPP PA. This is accounted for in the radionuclide dissolved concentration source term and their transport is accounted for in the Culebra.

FEP W82, 83, 84, 85, 86: Particle formation and transport

The transport of particles (e.g., radionuclide-containing) is accounted for in WIPP PA during penetration of the repository by a borehole (intrusion scenario).

FEP W87: Microbial transport

Bio-sorbed radionuclides are accounted for in PA as part of the radionuclide source term model.

FEP W90: Transport processes: advection

Advection of radionuclides is accounted for in WIPP PA.

FEP W91, 92: Transport processes: diffusion

Diffusion of contaminants and retardation by matrix diffusion is accounted for in WIPP PA.

FEP W93: Thermo-mechanical transport

Effects of thermomechanical transport are eliminated based on low consequence to WIPP PA.

FEP W94: Electrochemical transport phenomena

Effects of electrochemical transport are eliminated based on low consequence to WIPP PA.

FEP W97: Physiochemical transport

Effects of physiochemical transport are eliminated based on low consequence to WIPP PA.

2.2 Overview of the Geology and Expected Range of Conditions in the WIPP

The ambient geochemical conditions in the WIPP are discussed in detail in the WIPP Appendix SOTERM-2009. The Salado, which is the repository horizon, is predominantly pure halite (NaCl), with interbeds (marker beds) consisting mainly of anhydrite (CaSO₄). The nearly pure halite contains accessory evaporite minerals such as anhydrite (CaSO₄), gypsum (CaSO₄·2H₂O), polyhalite (K₂MgCa₂(SO₄)₄·2H₂O), magnesite (MgCO₃), and clays. Small quantities of intergranular (grain-boundary) brines and intragranular brines (fluid inclusions) are associated with the salt at the repository horizon. These brines are highly concentrated solutions (ionic strength up to 8 moles per liter [M]) of predominantly sodium (Na⁺), magnesium (Mg²⁺), potassium (K⁺), chloride (Cl⁻), and sulfate (SO₄²⁻), with smaller amounts of calcium (Ca²⁺), carbonate (CO₃²⁻), and borate (B(OH)₄⁻ and/or B₄O₇²⁻). These brines have been in contact with the Salado evaporite minerals since their deposition (estimated to be 250 million years) and are saturated with respect to these minerals.

Underlying the Salado Formation is the Castile, composed of alternating units of interlaminated carbonate, anhydrite, and nearly pure halite. The Castile in the vicinity of the WIPP site is known to contain localized brine reservoirs with sufficient pressure to force brine to the surface if penetrated by a borehole. Castile brines are predominantly saturated NaCl solutions containing Ca²⁺ and SO₄²⁻, as well as small concentrations of other elements, and are about eight times more concentrated than seawater. Overlying the Salado in the vicinity of the WIPP site is the Culebra of the Rustler Formation, a fractured dolomite (CaMg(CO₃)₂) layer. It is significant because it is expected to be the most transmissive geologic pathway to the accessible environment. Culebra brines are generally more dilute than the Salado and Castile brines, and are predominantly NaCl with K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, and CO₃²⁻.

The expected repository conditions in the WIPP are summarized in Table 2-1 and are briefly discussed below. Key conditions that may affect radionuclide behavior include: repository pressure, repository temperature, water content and relative humidity, the minimum free volume for actinide release (effective porosity), and the extent of the disturbed rock zone (DRZ).

Repository Pressure and Brine Release

The pre-excavation lithostatic pressure (Stein 2005, CRA-2004 PABC, Section 4.1.1) in the WIPP at repository depth is about 15 MPa (148 atm). This pressure can be reestablished after repository closure due to salt creep and gas generation, but there are a number of PA vectors that predict pressure may not be fully restored even by the end of the 10,000-yr period of WIPP performance, and final pressures may range from 6 to 15 MPa (in the undisturbed scenario) and from 0.1 to 15 MPa (in the disturbed scenarios) considered in the CRA-2004 PABC. In this context, the pressure in the repository after closure cannot significantly exceed the far-field confining stress of about 15 MPa. This should not change significantly in the consideration of HLW waste.

Dissolved brine release can occur when the pressure in the repository at the time of a drilling intrusion exceeds 8 MPa and a sufficient amount of brine has already flowed into the repository (see related discussions in Section 2.2.4 and Stein 2005). Eight MPa is the pressure exerted by a column of brine-saturated drilling fluid at the depth of the repository (Stoelzel and OBrien 1996). For repository pressures less than 8 MPa, no DBRs are assumed to occur because the fluid pressure in the repository cannot eject the drilling fluid from the borehole. There is also no DBR release until the brine volume exceeds the minimum brine volume needed to fill the effective porosity present in the compacted TRU waste.

Table 2-1 Expected WIPP Repository Conditions and Current Assumptions about the environment	
Repository Condition or Parameter	Current WIPP Assumptions
Ambient Geochemistry	Predominantly halite of the Salado Formation, with anhydrite interbeds and inclusions.
Temperature	Ambient temperature is 28 °C (82 °F). An increase of up to 3 °C (5.4 °F) is possible as a result of the emplacement of TRU waste.
Humidity	~70 percent (%) relative humidity (RH) at the repository temperature.
Water Content	Host rock is groundwater-saturated with inclusions in the salt that range from 0.057% to 3% by mass. Repository is unsaturated for up to 1000 years (yr) depending on pressure and intrusion scenarios.
Pressure	A lithostatic pressure of about 15 megapascals (MPa) (148 atmospheres [atm]) at repository depth; a hydrostatic pressure of about 8 MPa (79.0 atm) at the bottom of an intrusion borehole at repository depth.
Gas Phase	Initially air/oxic at repository closure, but rapidly transitions to an anoxic atmosphere dominated by hydrogen with smaller amounts of methane and nitrogen. Trace amounts of carbon dioxide, hydrogen sulfide, and other microbially produced gases may be present.
DRZ	Upper bound of 12 meter (m) above the repository and 2 m below the repository horizon.
Minimum Brine Volume for DBR	The calculated minimum volume of brine from any source needed for DBR release is 10011 cubic meters (m ³).
WIPP Brine	High-ionic-strength brine bracketed by Generic Weep Brine (GWB) and ERDA-6 brine formulations
pH	pH of about 9 and controlled by MgO, borate, and carbonate.
MgO	Engineered barrier for the WIPP that will sequester carbon dioxide (CO ₂) and control increases and decreases in pH by the precipitation of brucite, hydromagnesite, and magnesite.
Microbial Effects	Gas generation, primarily carbon dioxide and hydrogen sulfide, resulting from the biodegradation of cellulosic, plastic, and rubber (CPR) materials and creation of reducing conditions, including bioreduction of actinide elements from higher oxidation states.
Corrosion	Container steel and metals in WIPP waste will react to remove oxygen and produce hydrogen.
Radiolysis	Localized oxidizing effects possible near high-activity actinides, but overall radiolytic processes are overwhelmed by the in-room chemistry.

Repository Temperature

The ambient pre-emplacement temperature at the WIPP repository horizon was established to be 28 °C (82 °F) (Munson et al., 1987). The emplacement of TRU waste in the WIPP is expected to increase the ambient temperature by only a few degrees Celsius at most (Sanchez and Trellue 1996, Wang and Brush 1996a). For the purposes of PA, the temperature of the WIPP underground repository is assumed to be constant with time at 300 Kelvin (K) (27 °C [80 °F]).

Actinide solubilities were calculated in WIPP PA using thermodynamic and laboratory data measured at 25 °C [77 °F]. The expected effect of the slightly elevated temperature in the WIPP on actinide concentrations is relatively small, especially when compared to other uncertainties inherent in the measurement and calculation of the actinide solubilities and colloidal concentrations. For this reason, the very small effect of temperature on actinide solubility was not considered in WIPP PA calculations. This assumption will not hold for HLW repositories where higher temperatures are expected and data at elevated temperature is a key research need for HLW.

Water Content and Relative Humidity

A key argument for the WIPP as a TRU waste repository is that the self-sealing of the salt will limit the availability and transport of water into and through the repository, and correspondingly minimize the potential release of TRU from the repository. In all the undisturbed repository scenarios considered by PA, no actinide release from the WIPP is predicted (Leigh et al. 2005). There is, however, groundwater in the WIPP, even in undisturbed scenarios, that is potentially available to interact with the TRU waste. The salt surrounding waste is groundwater-saturated with both intergranular and intragranular water. The amount of water present as inclusions in the salt was used as a random variable in PA calculations (Leigh et al. 2005) with a range of 0.057 to 3 mass % based on what was measured in pre-excavation salt. This brine can seep into the repository horizon and fill the excavated areas (TRU waste). Brine saturation of the repository is estimated to occur in less than 1000 years after repository closure.

The presence of some brine in the WIPP prior to brine saturation leads to an environment that will contain an atmosphere of up to about 70% RH, defined by the vapor pressure of saturated brine at the repository temperature. This water vapor pressure will be present, at least in part, until brine saturation occurs as a result of some human intrusions or brine seepage into the excavated area. The RH is greatly affected by temperature and will be reduced at the elevated temperatures expected for HLW.

Indigenous Microbiology

A detailed study of the microorganisms indigenous to salt formation is underway. Progress to date is given by Swanson et al., 2012, LCO-ACP-12 report entitled “Progress Report on the Microbial Characterization of Halite and Groundwater Samples from the WIPP”. Members of the three biological domains — *Bacteria*, *Archaea*, and *Eukarya* (in this case, *Fungi*) — that are associated with WIPP halite (See Figure 2-2) have been identified. Thus far, their activity has been limited to aerobic respiration; anaerobic incubations are underway.

WIPP halite constitutes the near-field microbial environment. We expect that microbial activity in this setting will proceed from aerobic respiration, through nitrate reduction to focus on sulfate reduction. This is also the current WIPP performance assessment (PA) position. Sulfate reduction can occur at extremely high ionic strengths, and sulfate is available in WIPP brines and in the anhydrite interbeds. The role of methanogenesis in the WIPP remains unclear, due to both energetic constraints imposed by a high-salt environment and substrate selectivity, and it is no longer considered in PA.

Archaea identified in WIPP halite (See Figure 2-3) thus far fall exclusively within the family *Halobacteriaceae*. These include *Halobacterium noricense*, cultivated from both low- and high-salt media, and a *Halorubrum*-like species. The former has also been detected in other salt mines worldwide; the latter likely constitutes a new species. Little is known of its function, but it was prevalent in experiments investigating the biodegradation of organic complexing agents in WIPP brines. Bacterial signatures associated with WIPP halite include members of the phylum *Proteobacteria* — *Halomonas*, *Pelomonas*, *Limnobacter*, and *Chromohalobacter* — but only the latter has been isolated. Also detected and cultivated were *Salinicoccus* and

Nesterenkonia spp. *Fungi* were also isolated from halite. Although these were most likely introduced into the WIPP as contaminants from above-ground, their survival and potential role in the WIPP (e.g., cellulose degradation) is under investigation.

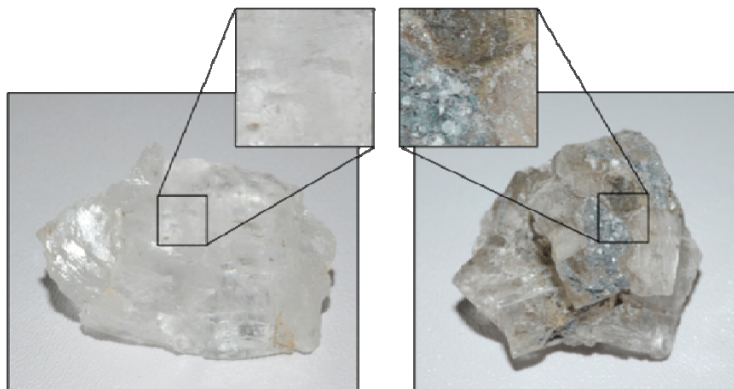


Figure 2-2 Samples of “clear” and “green/gray” halite.

WIPP groundwaters comprise the far-field microbial environment. *Bacteria* cultivated and identified (See Figure 2-4) from the overlying Culebra and nearby borehole groundwater are capable of aerobic respiration, denitrification, fermentation, metal reduction, and sulfate reduction and are distributed across many different phyla. Two of the *Bacteria* found in groundwater were also found in WIPP halite (*Chromohalobacter* sp. and *Virgibacillus* sp.). *Archaea* identified in groundwater include *Halococcus saccharolyticus*, *Haloferax* sp., and *Natrinema* sp.

The differences in the microbial communities detected thus far in halite and groundwater suggest that there will be significant differences in the associated metabolic potential of the near- and far-field environments. Whereas the near-field is dominated by *Archaea* with more limited metabolic capabilities, the far-field is dominated by *Bacteria* with extremely broad capabilities.

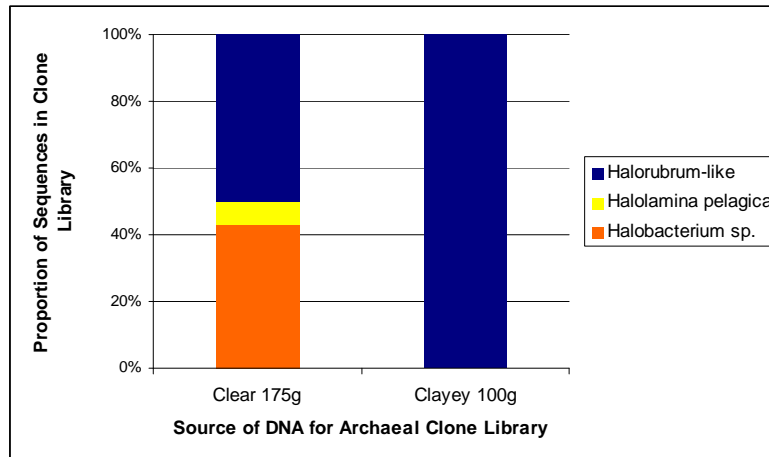


Figure 2-3 Archaeal clone libraries from enrichment cultures of clear halite with 175g NaCl and clayey halite with 100g NaCl. Note lack of diversity in clayey halite incubation, possibly due to low salt concentration.

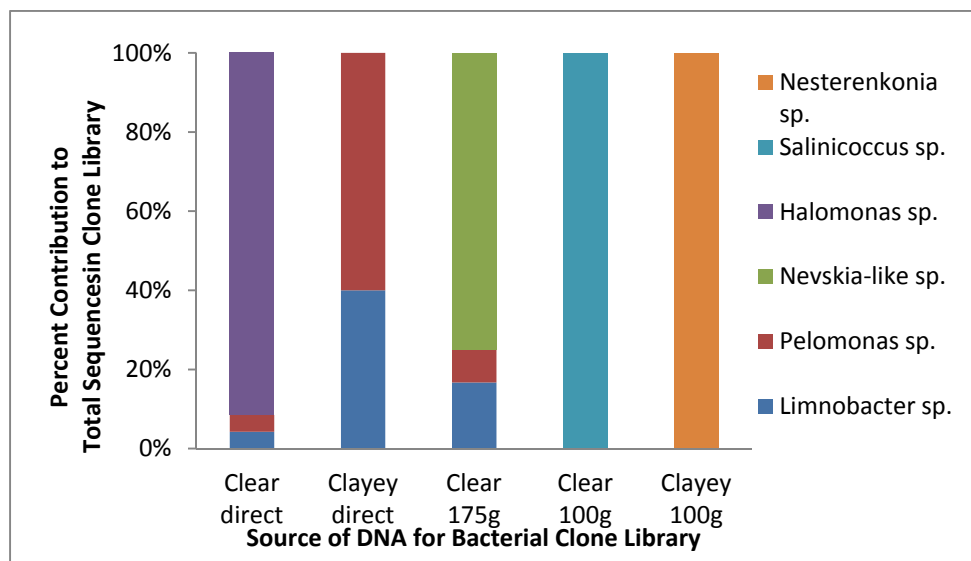


Figure 2-4 Bacterial clone libraries from direct DNA extracts of both halites and the clone library from the clear halite-175g NaCl enrichment culture. Note loss of diversity in low-salt incubations of both halites, including loss of *Halomonas* species from clear and absence from clayey. Note also the difference between culture-independent and cultivated results.

Assessment: Geology and Expected Range of Conditions

There are clearly a number of limitations in extending the WIPP case to the HLW case and there will always be a need for site-specific data once a site is selected. There are some general observations that can be made:

- WIPP geology and geochemical data used in PA pertain to temperature conditions at ~ 25°C. This is a clear limitation of the current safety case since elevated temperatures will likely be present in a HLW repository and a re-assessment of existing higher-temperature data and the collection of new higher-temperature data is likely needed.
- The lack of a good understanding of the microbiology associated with salt formations was a critical limitation in the safety case that forced very conservative assumptions and engineering decisions that were relatively costly for the WIPP project. It is critical to develop a robust understanding of microbial effects in salt so that these effects can be accounted for in the HLW safety case and, in many cases, shown to be insignificant and therefore eliminated from consideration.
- The phases found in salt are relatively well understood and are somewhat ubiquitous among the many salt formations that have been studied worldwide. The effects of temperature on the stability of these phases and their potential towards alteration are an added data need that is specific to the HLW case.
- The presence of water in salt and the humidity associated with this water is well understood in the absence of thermal effects - as is the case in WIPP. The potential effect of temperature on inclusions, water availability and relative humidity are needed to understand what happens in the absence of brine intrusion and are needed inputs to predict microbial behavior.

2.3 WIPP Brine Chemistry

Brine present in the WIPP will react with emplaced TRU waste, waste components, and engineered barrier materials to establish the brine chemistry that will define actinide solubilities and colloid formation. In this context, the composition of the brine in the repository horizon will be defined by a combination of factors, including the initial composition of the in-flow brine; reactions that control pH; and the extent to which this brine is altered by equilibration with the waste components, emplaced container materials, and the waste-derived organic chelating agents that can dissolve in the brine.

The composition of brine in and around the WIPP site prior to waste emplacement was established by sampling the groundwater and intergranular inclusions in the Salado and Castile. The stability of these brines have been investigated extensively and are the subject of a WIPP report: Lucchini et al., LCO-ACP-15, entitled “WIPP Actinide-Relevant Brine Chemistry.” A summary of the brine compositions used in the WIPP project over time and those predicted based on modeling studies is given in Table 2-2.

Salado brine will enter the repository after closure, and can be supplemented by Castile brine in some human intrusion scenarios. It is also possible that groundwater from the Rustler and Dewey Lake Formation could flow down the borehole into the repository, mix with the waste, and then be forced back up a borehole. The majority of WIPP-specific solubility studies were performed using GWB or ERDA-6 brines, since these brines bracket the expected range in brine composition. Including brine mixing in PA has been considered and rejected because using the end member brines (i.e., GWB or ERDA-6 brines) brackets the median values and uncertainties for the solubility calculations.

The overall stability of the brines and an experimental assessment to evaluate the ability of current Pitzer modeling was completed. These results are shown in Figures 2-5 and 2-6. Good agreement between model and experiment was obtained across a broad pH range with the exception of borate (which is not in our current model) and magnesium at high pH.

Table 2-2. Compositions of historical brines (Brine A, G-Seep), and GWB and ERDA-6 brines prior to and after equilibration with MgO [references in footnotes].

Ion or property^a	Brine A^b	G-Seep^b	GWB before reaction with MgO, halite, and anhydrite^c	GWB after reaction with MgO (phase 5), halite, and anhydrite^d	ERDA-6 before reaction with MgO, halite, and anhydrite^e	ERDA-6 after reaction with MgO (phase 5), halite, and anhydrite^d
B(OH) _x ^{3-x} (see footnote f)	20 mM	144 mM	158 mM	180 mM	63 mM	62.4 mM
Na ⁺	1.83 M	4.11 M	3.53 M	4.52 M	4.87 M	5.28 M
Mg ²⁺	1.44 M	0.630 M	1.02 M	0.463 M	19 mM	136 mM
K ⁺	770 mM	350 mM	0.467 M	0.532M	97 mM	96.1 mM
Ca ²⁺	20 mM	7.68 mM	14 mM	10 mM	12 mM	11.2 mM
SO ₄ ²⁻	40 mM	303 mM	177 mM	214 mM	170 mM	176 mM
Cl ⁻	5.35 M	5.10 M	5.86 M	5.37 M	4.8 M	5.23 M
Br ⁻	10 mM	17.1 mM	26.6 mM	28.3 mM	11 mM	10.9 mM
Total Inorganic C (as HCO ₃ ⁻)	10 mM	11.5 mM	Not reported	0.358 mM	16 mM	0.448 mM
pH	6.5	6.1	Not reported	8.74	6.17	8.98
Relative Density	Not reported	Not reported	1.2	1.233	1.22	1.22
Ionic Strength (m)	Not reported	Not reported	7.56	7.64	6.05	6.77

^a Ions listed represent the total of all species with this ion.

^b From [Molecke 1979]

^c From [Snider 2003]

^d From [Brush 2009]

^e From [Popielak 1983]

^f Boron species will be present in brine as boric acid, hydroxy polynuclear forms (B₃O₃(OH)₄⁻, and/or borate forms (e.g., B₄O₇²⁻)

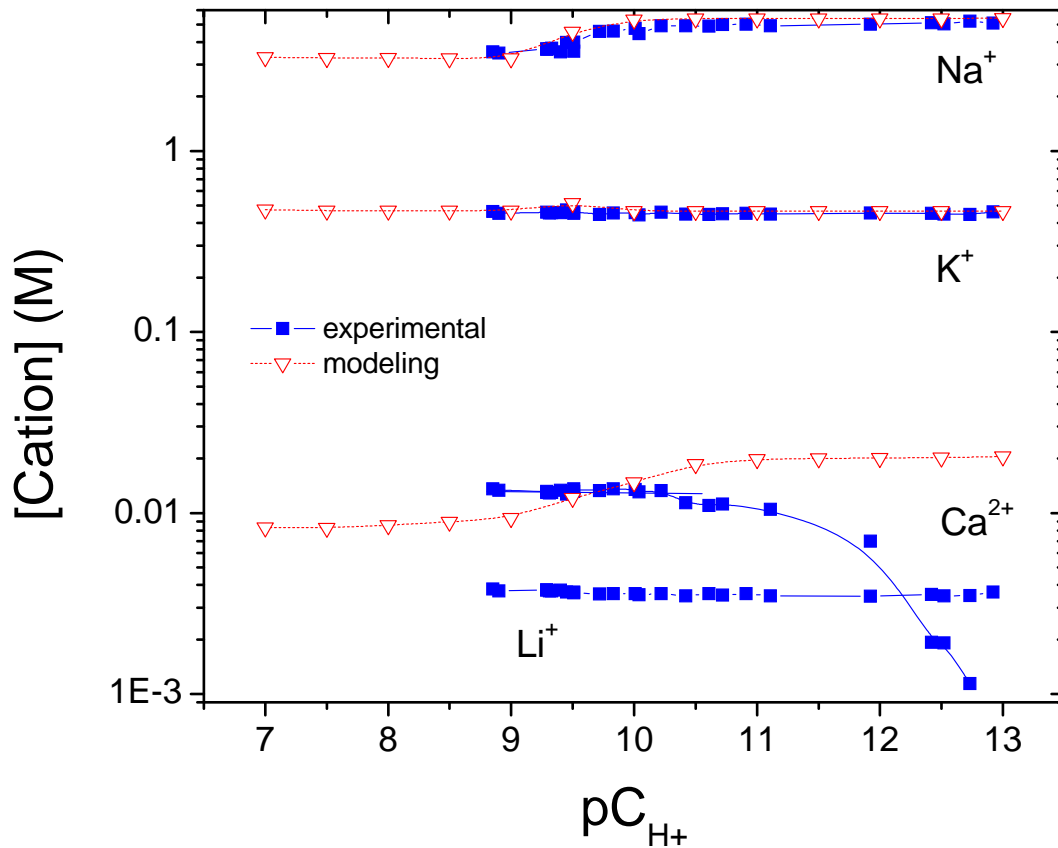


Figure 2-5. Concentrations of Na⁺, K⁺, Ca²⁺ and Li⁺ in GWB 100% saturated brine (respectively from the top to the bottom of the graph) as a function of pC_{H+}. Blue square symbols represent data measured experimentally by titration of the brine stepwise [this work]. Red triangular symbols are data obtained by modeling [Brush 2011].

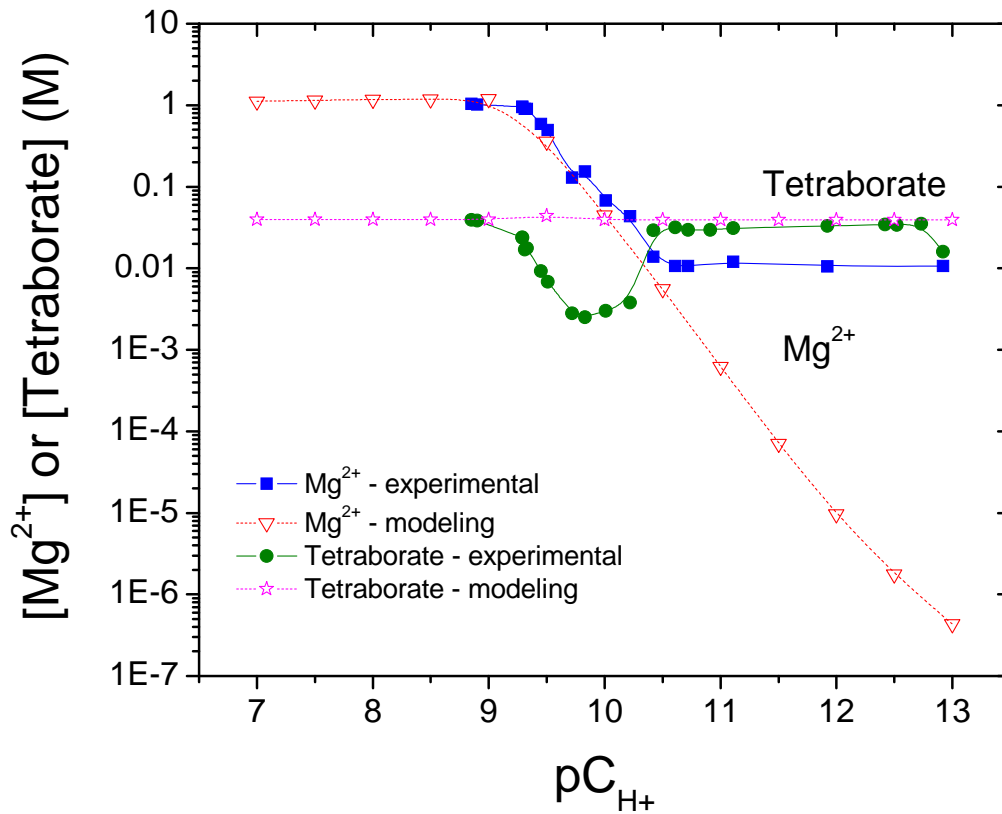


Figure 2-6 Concentrations of tetraborate and Mg²⁺ in GWB 100% saturated brine as a function of pC_{H+}. Blue square symbols and green round symbols represent data on Mg²⁺ and tetraborate respectively that were measured experimentally by titration of the brine stepwise [this work]. Red triangular symbols and pink star symbols are data on Mg²⁺ and tetraborate respectively that were obtained by modeling [Brush 2011].

Assessment of Brine Chemistry: HLW Safety Case

Brine composition is important to the calculation of actinide concentrations. The inorganic complexants, ionic strength, and pH are direct inputs needed to calculate actinide solubilities for a given brine composition. These species and properties are also important in defining the potential for colloid formation in a salt repository. Although current models sufficiently support the WIPP safety case, there are some research needs specific to the HLW case:

- The Pitzer model needs to be made more robust to fill in existing gaps in the description of magnesium and iron chemistry – two components of the repository that will likely have important impacts on the overall chemistry.
- There is little/no data on the effect of temperature on Pitzer formulations in high ionic strength systems. Selected experiments coupled with strategic extrapolation from existing room temperature data are needed to extend the Pitzer model to the higher temperatures expected in the HLW case.

2.4 Description of Dissolved Actinide Concentrations: Source Term

The WIPP repository is focused on the transuranics in TRU waste. The overall ranking of actinides, from the perspective of potential contribution to release from the WIPP, is: Pu ~ Am > U >> Th and Np. In effect, plutonium in the III/IV oxidation state and americium in the III oxidation state dominate release calculations from the WIPP. Demonstrating acceptably low actinide migration and release from the WIPP is the key performance criterion for meeting the regulations that govern the WIPP license. The overall strategy involved the following key elements:

- Conservative assumptions regarding oxidation state distribution of key actinides.
- Oxidation state-specific approach to determine the solubility of the actinides that includes organic complexation effects, carbonate effects and colloid enhancement.
- Reducing conditions that are imposed by the reactivity of the zero-valent iron present as container material.

- Relatively few, but defensibly conservative, set of complexation reactions to calculate solubilities
- Pitzer model for the high ionic strength systems expected.

The current WIPP oxidation state distribution for the actinides and oxidation-state-specific solubilities are summarized in Tables 2-3 and 2-4.

Table 2-3. Oxidation States of the Actinides in the WIPP as Used in the CRA-2004 PABC					
Actinide Element	Oxidation States, Abundance (%), and Analog Used (If Any)				
	Oxidation State^{a,b}				FMT Speciation Data Used
	III	IV	V	VI	
Thorium	—	100 %	—	—	Thorium
Uranium	—	50 %	—	50 %	1 mM assumed for VI, Th for IV
Neptunium	—	50%	50 %	—	Np for V Th for IV
Plutonium	50 %	50 %	—	—	Am for III Th for IV
Americium	100 %	—	—	—	Americium
Curium	100 %	—	—	—	Americium

^a Oxidation state distributions (percentages) refer to the percent of PA vectors that have 100% of the specified oxidation state.

^b In PA calculations the distribution of oxidation states is correlated for U, Np, and Pu such that the states for all three element are simultaneously either in the lower oxidation state (U(IV), Np(IV), and Pu(III)) or in the higher oxidation state (U(VI), Np(V), and Pu(IV)).

Table 2-4. Solubilities of the Oxidation-State Analogs (M) with MgO Backfill Calculated for the CRA-2004 PABC (Brush 2005)					
Brine	FMT Name	Solubilities of the Actinide Oxidation States from the FMT Calculations for PABC			
		(III)	(IV)	(V)	(VI)^a
GWB	Run 7 (hydromagnesite with organics [hmag. w orgs.])	3.87×10^{-7}	5.64×10^{-8}	3.55×10^{-7}	1×10^{-3}
ERDA-6	Run 11 (hmag. w orgs)	2.88×10^{-7}	6.79×10^{-8}	8.24×10^{-7}	1×10^{-3}
GWB	Run 5 (mag. w orgs)	3.87×10^{-7}	4.57×10^{-8}	6.59×10^{-6}	1×10^{-3}
ERDA-6	Run 9 (mag. w orgs)	2.87×10^{-7}	4.84×10^{-8}	1.08×10^{-5}	1×10^{-3}

hmag. – hydromagnesite

mag. – magnesite

^a Not calculated with the FMT model

Assessment of Data Needs: Radionuclide Solubility in Brine

The following are the key data needs for the HLW repository in salt in the area of radionuclide chemistry as compared to the WIPP safety case:

- Extension of the oxidation state approach to radionuclides beyond the TRU considered extensively in the WIPP case – most importantly Tc, U, Cs, Sr and lesser fission products.
- Effect of temperature on all radionuclide solubilities. Increased temperature is expected to result in lower solubilities. This however needs to be demonstrated experimentally and supported by modeling.
- Extension of the Pitzer formations for actinide species to the higher temperatures needed for HLW.
- Investigations to show that the redox mechanisms in place in the WIPP, primarily reactions with Fe, extend to the higher temperatures expected in the HLW case.
- Inclusion of radiolytic effects on radionuclide solubility and oxidation state distribution. This is excluded from consideration in the WIPP due to the low background activity and overwhelming effects of the iron chemistry.

- Greater emphasis on uranium as its chemistry will affect the other radionuclides – especially for spent fuel.
- Improved oxidation state analogs for the An(IV) oxidation state. Thorium, which is the analog currently used by the WIPP, although conservatively high is a very poor analog for the An(IV) oxidation state in many respects. Using plutonium(IV), or neptunium(IV) would greatly improve the accuracy of the results and better define the conservatisms present.

3.0 Summary of Recommendation Made for the HLW Case

The WIPP safety case has been extensively reviewed and defended to EPA which is the regulator for the WIPP repository. This safety case properly addresses the brine and actinide chemistry important for the TRU repository since there are low-probability brine intrusion scenarios that the regulator has required the WIPP project to address. In this context, many of these same arguments extend to the HLW case and it is critical to address these to assure compliance should a decision go forward to license a HLW repository in Salt.

There are however a number of aspects of this safety case that could be improved to remove or define conservatisms and there are a number of issues that are properly ignored by the WIPP safety case, that are important for the HLW case, because they do not apply. These were described in more detail in section 2, and are summarized below:

WIPP Geology and Repository Environment

- WIPP geology and geochemical data used in PA pertain to temperature conditions at ~ 25°C. This is a clear limitation of the current safety case since elevated temperatures will likely be present in a HLW repository and a re-assessment of existing higher-temperature data and the collection of new higher-temperature data is likely needed.
- The lack of a good understanding of the microbiology associated with salt formations was a critical limitation in the safety case that forced very conservative assumptions and engineering decisions that were relatively costly for the WIPP project. It is critical to develop a robust understanding of microbial effects in salt so that these effects can be accounted for in the HLW safety case and, in many cases, shown to be insignificant and therefore eliminated from consideration.
- The phases found in salt are relatively well understood and are somewhat ubiquitous among the many salt formations that have been studied worldwide. The effects of temperature on the stability of these phases and their potential towards alteration are an added data need that is specific to the HLW case.

- The presence of water in salt and the humidity associated with this water is well understood in the absence of thermal effects - as is the case in WIPP. The potential effect of temperature on inclusions, water availability and relative humidity are needed to understand what happens in the absence of brine intrusion and are needed inputs to predict microbial behavior.

Brine Chemistry

- The Pitzer model needs to be made more robust to fill in existing gaps in the description of magnesium and iron chemistry – two components of the repository that will likely have important impacts on the overall chemistry.
- There is little/no data on the effect of temperature on Pitzer formulations in high ionic strength systems. Selected experiments coupled with strategic extrapolation from existing room temperature data are needed to extend the Pitzer model to the higher temperatures expected in the HLW case.

Radionuclide Chemistry

- Extension of the oxidation state approach to radionuclides beyond the TRU considered extensively in the WIPP case – most importantly Tc, U, Cs, Sr and lesser fission products.
- Effect of temperature on all radionuclide solubilities. Increased temperature is expected to result in lower solubilities. This however needs to be demonstrated experimentally and supported by modeling.
- Extension of the Pitzer formations for actinide species to the higher temperatures needed for HLW.
- Investigations to show that the redox mechanisms in place in the WIPP, primarily reactions with Fe, extend to the higher temperatures expected in the HLW case.
- Inclusion of radiolytic effects on radionuclide solubility and oxidation state distribution. This is excluded from consideration in the WIPP due to the low background activity and overwhelming effects of the iron chemistry.

- Greater emphasis on uranium as its chemistry will affect the other radionuclides – especially for spent fuel.
- Improved oxidation state analogs for the An(IV) oxidation state. Thorium, which is the analog currently used by the WIPP, although conservatively high is a very poor analog for the An(IV) oxidation state in many respects. Using plutonium(IV), or neptunium(IV) would greatly improve the accuracy of the results and better define the conservatisms present.



Actinide and Brine Chemistry in a Salt-Based Repository (ABC-SALT)

International Workshop September 15-17, 2010 Carlsbad, NM, USA

Sponsor: US Department of Energy - Carlsbad Field Office

DOE Contact: Roger Nelson
rnelson@wipp.ws

Technical Organizers: Los Alamos- Carlsbad Operations (LANL-CO)
Karlsruhe Institute of Technology (KIT)

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Conference Fee: \$150 US

Actinide and Brine Chemistry in a Salt-Based Repository

September 15-17, 2010, Carlsbad NM, USA

Program Overview

Wednesday 9/15	Thursday 9/16	Friday 9/17
9:15 – 10:15 AM Welcome and WIPP Overview	9:00 – 10:15 AM Actinide Chemistry in Brine Systems: Colloids	8:00 AM – 2:00 PM WIPP tour in AM Optional attendance Clearances needed
10:25 AM Coffee Break	10:15 AM Coffee Break	
10:45 – 12:00 Noon International Program Updates	10:40 AM – 12:00 Noon Actinide Chemistry in Brine Systems: Redox	
12:00 Noon - 1:15 PM Technical Discussions/Lunch Conference Center	11:55 – 1:10 PM Technical Discussions/Lunch Conference Center	
1:15 -3:20 PM Brine Chemistry	1:10 -2:50 PM Actinide Chemistry in Brine Systems: Sorption and Complexation	
3:20 PM Coffee Break	2:50 PM Coffee Break	
3:40 – 4:55 PM Microbial Effects	3:15 – 4:55 PM TDB Modeling	
4:55 – 5:40 PM Experimental Techniques	4:55 – 5:30 PM Closeout/Wrapup	
Stock Exchange Restaurant Presentation/Dinner 7:00 PM	Stock Exchange Restaurant Presentation/Dinner 7:00 PM	

Wednesday, September 15, Pecos River Conference Center Detailed Program

Time	Speaker	Organization	Subject / Title
Pecos River Conference Center open at 8:00 AM			
9:15	Don Reed	LANL, US	Conference Organization Comments
9:20	Roger Nelson	DOE, US	Welcome to the Conference
9:15	Overview / Introductory talks, Ned Elkins and Russ Patterson session co-chairs		
9:35	Russ Patterson	DOE, US	WIPP Environmental Compliance and the Chemistry Program
10:00	Daniel Clayton	SNL, US	WIPP Performance Assessment Approach and Results
10:25	Coffee break		
10:45	Frank Hansen	SNL, US	Salt Disposal of HLW: Path Forward for US and German Collaborations
11:10	Guido Bracke	GRS, Ger	Update on the German program on Repositories and their Safety Assessment
11:35	Horst-Juergen Herbert	GRS, Ger	Geochemical Research Fields for the Safety of a Final Repository for Heat Producing Radioactive Wastes in Germany
12:00	Lunch (at the Pecos River Conference Center)		
1:15 PM	Brine chemistry, Yong-Liang Xiong and Volker Metz co-chairs		
1:15	Helge Moog	GRS, Ger	Pitzer Modeling in Brines: Experiments and Evaluation
1:40	Yong-Liang Xiong	SNL, US	Experimental Determination of the Solubility Constant of Hydromagnesite (5424) in NaCl Solutions up to 4.4m at Room Temperature
2:05	Daniela Freyer	UF, Ger	Solubilities of Basic Magnesium Salt Hydrates in the System MgO-MgCl ₂ -H ₂ O with respect to their Use as Building Materiel (Sorel Cement) in Salt Formations
2:30	Gregory Roselle	SNL, US	Anoxic Corrosion of Steel and Lead in Na-Cl±Mg-Dominated Brines in Atmospheres Containing CO ₂
2:55	Je-Hun Jang	SNL, US	Solubility of Ferrous Oxalate Dihydrate and Lead Oxalate in Magnesium Chloride and Sodium Chloride Solution
3:20	Coffee Break		
3:40	Microbial Effects, Don Reed chair		
3:40	Julie Swanson	LANL, US	Microbiology in the WIPP
4:05	Henry Moll	FZD, Ger	Actinide Interactions with Bacteria
4:30	David Ams	LANL, US	Bioreduction of Actinides in Low and High Ionic Strength Environments
4:55	Experimental Techniques 5 minute mini-presentations		
	Helge Moog	GRS, Ger	Redox Measurement in Saline Systems
	Michael Richmann	LANL, US	X-Ray Diffraction and Laser Photoacoustic Absorbance Spectroscopy of Actinides
	Jeff Terry	IIT, US	XANES and EXAFS of Actinides at the APS/SRL
	Clemens Walther	INE, Ger	TRLFS, LIBD and ESI-TOF-MS
5:40 PM	End of Technical Sessions		
7:00 PM	Dinner, at the Stock Exchange Restaurant	Jim Conca NMSU, US	The GeoPolitics of Energy: Achieving a Just and Sustainable Energy Distribution in The U.S., Germany and the World

Thursday, September 16, Pecos River Conference Center Detailed Program

Time	Speaker	Organization	Subject / Title
Pecos River Conference Center open at 8:00 AM			
9:00	Actinide chemistry in brines, Marcus Altmaier and Marian Borkowski session co-chairs		
9:00	Xavi Gaona	INE, Ger	Chemistry of An(III/IV)/Ln(III) Eigencolloids: Complexation Reactions with Inorganic and Organic Ligands
9:25	Clemens Walther	INE, Ger	Formation of Actinide(IV) Colloids in Saline Solutions
9:50	Jean-Francois Lucchini	LANL, US	Solubility of Uranium and Thorium in Carbonate-free WIPP Brine
10:15	Coffee break		
10:40	Don Reed	LANL, US	Plutonium Redox in High Ionic-Strength Systems
11:05	David Fellhauer	ITU, EC	Plutonium Redox Processes in Aqueous Systems
11:30	Marian Borkowski	LANL, US	Complexation of Actinides by Organic Ligands and Borate Ions
11:55	Lunch (at the Pecos River Conference Center)		
1:10	Marcus Altmaier	INE, Ger	Actinide Carbonate Complexation and Solid Phase Stability in reducing MgCl ₂ Brine Systems
1:35	Punam Thakur	NMSU, US	EDTA and Mixed –Ligands Complexes of Trivalent Am, Cm and Eu at High Ionic Strength and Temperature
2:00	Jan Tits	PSI, Ch	Experimental Sorption Studies on Cement Systems
2:25	Volker Metz	INE, Ger	Interactions of Americium and Uranium with Cement Alteration Products under Saline Conditions
2:50	Coffee break		
3:15	Thermodynamic Data Base (TDB) Modeling, Larry Brush and Vinzenz Brendler session co-chairs		
3:15	Laurence H. Brush	SNL, US	Overview of WIPP Geochemical Modeling
3:40	Bruce Robinson	LANL, US	ASCEM: Advance Simulation Capability for Environmental Management
4:05	Christian Marquardt	INE, Ger	THEREDA: Thermodynamic Data for Waste Management Assessment - Focus on Actinide Data
4:30	Vinzenz Brendler	FZD, Ger	Actinide Sorption Database
4:55	Wrap-up discussion, Don Reed and Marcus Altmaier		
5:30 PM	End of Technical Sessions		
7:00 PM	Dinner, at the Stock Exchange Restaurant	Bernhard Kienzler (INE)	Safety Research for Nuclear Waste Disposal: Contributions by the EURATOM Programm

WIPP Environmental Compliance and the Chemistry Program

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The Department of Energy/Carlsbad Field Office (DOE/CBFO) is responsible for managing, planning, integrating and implementing the National Transuranic Waste Program (NTWP) activities. CBFO directs all activities related to the disposal of Transuranic (TRU) and TRU-mixed waste at the Waste Isolation Pilot Plant (WIPP). The WIPP, a deep geologic repository, is mined 655m below the land surface in a deep underground salt formation, and is a government-owned and contractor-operated facility that is constructed on DOE property near Carlsbad, New Mexico.

Radioactive waste disposal at WIPP is regulated by the Environmental Protection Agency (EPA) to meet requirements in 40 Code of Federal Regulations Parts 191(40 CFR Part 191) Subpart A (operations) and Subparts B and C (long-term performance), and 40 CFR Part 194 and the WIPP Land Withdrawal Act. WIPP is further regulated by the New Mexico Environment Department (NMED) to meet the requirements of the Resource Conservation and Recovery Act (RCRA) under the WIPP Hazardous Waste Facility Permit (HWFP) for mixed waste. Radioactive waste was first received at WIPP on March 26, 1999.

In the Compliance Certification Application (CCA), the 2004 and 2009 Compliance Recertification Applications (CRA-2004 and CRA-2009), as well as the most recent NMED permit renewal, the repository chemistry plays a role in convincing the regulators that the repository will contain waste for the next 10, 000 years and beyond. WIPP continues to study actinide chemistry to support previous

conservative assumptions used in performance assessment and to allow for potential changes in repository operations that may save taxpayer money through efficiencies.

This presentation will provide an overview of the regulatory chronology of WIPP, discuss actinide chemistry's role in compliance, and list potential future activities.

WIPP Performance Assessment Approach and Results

D.J. Clayton and R.C. Camphouse

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The Waste Isolation Pilot Plant (WIPP), located in southeastern New Mexico, has been developed by the U.S. Department of Energy (DOE) for the geologic (deep underground) disposal of transuranic waste. Containment of this waste at the WIPP is regulated by the U.S. Environmental Protection Agency (EPA). Containment requirements are stringent, requiring the DOE to demonstrate with a reasonable expectation that the probabilities of cumulative radionuclide releases from the disposal system during the 10,000 years following closure remain below specified limits. The DOE demonstrates compliance with these requirements by means of performance assessment (PA) calculations. WIPP PA is an analysis that 1) identifies the processes and events that might affect the disposal system; 2) examines the effects of these processes and events on the performance of the disposal system; 3) estimates the cumulative releases of radionuclides caused by all significant processes and events; and 4) accounts for uncertainty in the parameters of the models. These items give rise to a methodology for quantifying the probability distribution of possible radionuclide releases from the WIPP repository for the regulatory period of 10,000 years after facility closure, while characterizing the uncertainty in that distribution due to imperfect knowledge about the parameters contained in the models used to predict releases.

PA analyses supporting the determination of compliance are quantitative and consider uncertainties caused by all significant processes and events that may affect the disposal system, including future inadvertent human intrusion into the repository. PA calculations were included in the 1996 Compliance Certification Application. Based in part on the PA

calculations, the EPA certified that the WIPP met the containment criteria in the regulations and was approved for disposal of transuranic waste in 1998. Models used in WIPP PA are maintained and updated with new information as part of the repository recertification process. It is required that the WIPP is recertified at five-year intervals following receipt of the first shipment of waste at the site, which occurred in 1999. PA calculations were also an integral part of the 2004 Compliance Recertification Application, after which the EPA recertified the WIPP in 2006. For the 2009 Compliance Recertification Application, which is currently under EPA review, the DOE has also submitted PA calculations.

For PA, the effects of all significant processes and events that may impact the disposal system are determined, the associated uncertainties of the processes and events are considered, and the probable cumulative releases of radionuclides are estimated. The PA methodology accommodates both stochastic (i.e., aleatory) and subjective (i.e., epistemic) uncertainty in its constituent models. Stochastic uncertainty pertains to unknowable future events, such as intrusion times and locations that may affect repository performance. Subjective uncertainty concerns parameter values that are assumed to be constants whose true values are uncertain because of a lack of knowledge about the system.

The WIPP PA methodology includes twenty-four conceptual models that are used to represent specific features of the disposal system. Releases from the WIPP fall into two principal categories: 1) long term releases, which may take place throughout the regulatory period, and 2) direct releases, which may occur at the time of a drilling intrusion.

Long term releases include radionuclide transport in groundwater through the various geologic units to the land withdrawal boundary. The most transmissive unit is the Culebra. Radionuclides may be transported to the Culebra primarily by brine flow up boreholes. Other transport paths, such as through the shaft seals, or through the marker beds, have been demonstrated to be insignificant.

Direct releases are subdivided into three components: cuttings and cavings, spallings, and direct brine releases (see Fig. 1). Cuttings refer to the waste material actually encountered by a drill bit as it passes through the waste. Cavings include materials that are eroded from the walls of the waste and are brought to the surface by the drilling fluid. Generally, cuttings and cavings are grouped together. Spallings accounts for additional material that may be brought to the surface through venting of repository gas pressure to the lower-pressure borehole. Direct brine releases are flows of pressurized brine from the repository to the surface during the first few days before a borehole is assumed to be plugged.

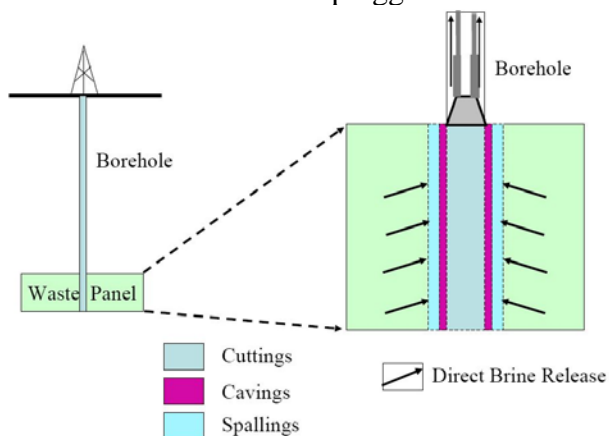


Fig. 1. Schematic of Direct Release Mechanisms Modeled in WIPP PA.

For an undisturbed repository, radionuclide transport in the groundwater is the only release mechanism considered. PA calculations for the undisturbed repository establish that the maximum annual dose and radionuclide concentration at the land withdrawal boundary

are considerably lower than the regulatory limits.

For a disturbed repository, PA analyses supporting the 2009 Compliance Recertification Application demonstrate that the WIPP continues to comply with containment requirements, with release probabilities remaining entirely below the limits specified by the EPA. No releases are predicted to occur at the ground surface in the absence of human intrusion. A sensitivity analysis of the results shows that the total releases are dominated by radionuclide releases that could occur on the surface during an inadvertent penetration of the repository by a future drilling operation.

Sandia is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.

Salt Disposal of HLW: Path Forward for US and German Collaboration

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INTRODUCTION

Recent developments in Germany and the United States have renewed efforts in salt repository investigations. Representatives of institutions in both countries conducted a workshop in Canton Mississippi USA. The workshop was hosted by Mississippi State University and Sandia National Laboratories (1). The purposes of the workshop were to coordinate a potential research agenda of mutual interest and to leverage collective efforts for the benefit of their respective programs. The following article summarizes the findings of the workshop and describes a series of investigations to advance the state-of-the art.

DESCRIPTION OF THE WORK

Invited key investigators in salt repository science and engineering presented past, present and future directions in salt research applied to heat-generating waste disposal to identify a coordinated research agenda that participants can agree in principle to pursue, with the intent of maximizing individual resources for the mutual benefit of each program. By conducting this workshop, participants intend to reinitiate collaborative research activities and bring them to the level of cooperation enjoyed in the past, create a potential joint research agenda, and renew working relationships among institutions and individuals.

Predicated on the workshop presentations (posted on the website) and other material, participants identified several potential coordinated research areas. As the German/USA salt repository programs move forward in their respective countries, the intent is to maximize individual resources for the mutual benefit of each program. This workshop basically reinitiated previous collaborative research activities that had been waning for about ten years.

An abbreviated list of research topics derived from the German/USA workshop is given in this section. A more comprehensive summary of the workshop will be published in proceedings. In some cases, the collaboration topic is less *research* than a recognition that salt repository sciences are encumbered with some lingering issues, which need to be reviewed and summarized before embarking upon a research agenda. In several instances, clear research topics for collaboration are identified.

Many of the primary attributes of salt disposal are known and have been demonstrated at an operational scale over significant periods of years. However, there remain pesky issues that perhaps have either not been substantially investigated or reviewed to the point of objective reconciliation. Some of the *issues* identified at the workshop may represent convictions or perceptions in the

absence of supporting scientific evidence. The following list identifies phenomena or processes, which might be incorporated into a performance assessment model, if warranted.

Brine Migration. Brine exists in bedded salt in three forms: fluid inclusions, hydrous minerals and grain boundary water. Owing to the characteristics and environments of the brine in salt, its transport or migration occurs via three primary mechanisms: motion of the brine inclusions in a temperature gradient, vapor-phase transport along connected porosity and liquid transport driven by the stress gradient.

Vapor Transport. One of the most important issues in a high-level-waste repository is the presence of and the fate of any brine that may be present. Schlich (2) modeled water inflow of the heater experiments conducted at the Asse mine. It appears that vapor transport processes account for moisture movement, and the often mentioned brine inclusion migration is less important.

Gas Generation and Pressure Buildup. Hydrogen gas generation from anaerobic corrosion of steel container materials might inhibit rock convergence and consolidation of crushed rock backfill. The associated hydrogen volumes and rates require further quantification.

Buoyancy. The movement of canisters containing heat-generating nuclear wastes buried in a salt formation has been questioned. The existence of buoyant forces due to thermally-produced density differences suggests the possibility of initiating convection cells in a plastic medium like salt.

Heat Effects. It is widely held that the heat load from high-level waste is detrimental to operations and long-term isolation in salt. This perception may be balanced by accounting for heat effects that are favorable to operations and long-term safety.

Hydrofracture and Dilatancy Boundary. Mechanically or hydraulically induced permeability is based on the same microphysical process of percolation flow along grain boundaries after exceeding a threshold. In both cases the induced permeability is created by removal of intergranular cohesion.

Consolidation of Hot Granular Salt. Crushed salt used as backfill may be an important element in a potential high-level-waste repository. Relatively little elevated temperature mechanical testing has been conducted for crushed salt. The accelerating effect of moisture on consolidation needs further investigation. Modeling concerned with long-term, low-porosity, two-phase flow is likely required.

Solubility and Transport. The salt repository community continues to research radionuclide solubility as if there is ample brine available within the salt to dissolve and transport the waste. There are at least two parts to this important issue: one concerns brine sources and volume and the other concerns existence of a pressure gradient capable of driving the soluble radionuclides to the biosphere.

Degradation. This research area addresses the underlying hypothesis that waste forms placed in salt will degrade sufficiently that the residue can be removed readily by a human drilling intrusion.

Radiolysis. Radiation is known to liberate hydrogen but further data are needed on the effect of combining radiation and temperature on the waste materials, waste packages, and the salt.

To be comprehensive in the pursuit of high-level waste salt repositories it is incumbent upon the salt repository advocates to objectively evaluate these issues.

FUTURE DIRECTION

Topics given above pertain to specific phenomena, several of which would be incorporated into the next generation of modeling. Thus, the future directions are likely to include evaluations of fundamental processes in the laboratory, exploration of the enormous promise of new computational tools, and possible large-scale experiments for scale effects appraisal.

Stone and coworkers (3) have taken a leading role in developing coupled process models. Recent investments in the Sandia SIERRA Mechanics code suite have supplied the basic building blocks for realizing a multi-physics capability for repository systems engineering. Several discriminating features of this highly nonlinear, thermal-mechanical analysis are being developed. Past analyses of salt creep and room closure have been constrained by the computational complexity of simulating coupled processes. Models for simulating the disposal concept have been run using the advanced code suite of SIERRA Mechanics, developed at Sandia to run on massively parallel computing hardware.

Hampel and coworkers (4) recently summarized numerical simulations for the design and stability analysis of underground openings in rock salt. Between 2004 and 2010, six project partners compared their constitutive models for rock salt. The results of specific benchmark calculations demonstrate that the models describe correctly the relevant deformation phenomena in rock salt under various influences. Their benchmark calculations and comparisons of isothermal results in joint projects showed that the constitutive models captured deformational phenomena in rock salt below and above the dilatancy boundary.

Based on the developments at Sandia Labs with SIERRA Mechanics and the developments described by several German salt researchers, it would appear that different teams have collected a comprehensive experimental data base and theoretical knowledge base for the mechanical deformation of rock salt. Several advanced constitutive models have also been developed and applied. However, the strong temperature dependence on the mechanical deformation of rock salt needs to be reevaluated today if the salt disposal option is selected. For the calculation and assessment of the tightness of the geological barrier rock salt around a repository, further effort is also to be made in the investigation and modeling of salt damage healing and the corresponding reduction of permeability.

Coupled thermo-mechanical benchmark 3-D simulations could be performed to evaluate intact salt in order to calculate the evolution of stresses, strains, dilatant volumetric strains, and damage around a potential repository for heat-generating radioactive wastes in rock salt.

The outcome of the geochemistry workshop should attempt to integrate respective research goals with those described in this paper. The ideal future would include advancing the technical baseline regarding the processes described in the German/USA salt repository workshop, and performing appropriate code benchmark calculations, ultimately leading to a reliable in situ test for model validation.

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Update on the German program on repositories and their safety assessment

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INTRODUCTION

The presentation gives an overview on the current status of existing repositories, their safety assessment and the site under investigation for disposal of heat-generating waste in Germany.

OVERVIEW ON SITES

Currently, there are four sites related to final disposal of radioactive waste in Germany:

Asse II is a former salt mine and was used as research and test site for disposal of low and medium radioactive waste. Disposal started in 1967 and was stopped in 1978.

The Asse II disposal site faces some challenges. The old mine building is instable and limits the time frame for any implementation of measures for closure. Also the knowledge of the emplaced radioactive inventory is scarce. The condition of the containers is unknown. About 12 m³ of brine enter the mine daily. The development of this inflow is not predictable although it has been quite constant since 2002. According to the present state of knowledge the proof of long-term safety required by the atomic law is uncertain. Therefore, the Federal Office for Radiation Protection (BfS) as the new operator (2009) of Asse II favours the retrieval of the radioactive waste over relocation of waste within the mine or backfilling of the mine with remaining of waste. Currently feasibility studies are underway.

Morsleben is also a former salt mine and was used for disposal of low and medium radioactive waste by the German democratic republic from 1981-1991 and Germany from 1994-1998. The approval for disposal was waived by the operator BfS in 2001. A license for closure of the repository has been applied and the public participation with display of the documents has been started (2009).

The closure concept includes the backfilling of the mine building with salt concrete and installation of technical seals (dams) to separate disposal areas from the remaining mine building. The closure concept and the long-term safety assessment are under review.

Konrad: The site is located in a iron ore deposit covered by clay rock. The site was approved for disposal of non-heat generating waste. The construction is underway. The start of disposal is planned for 2014.

The actual disposal area is located in iron ore deposit but outside of the former mining area. The former shaft

will be reused after reconstruction to allow the transportation of the containers. The license is limited to 303 000 m³ radioactive waste.

Gorleben is a site located in a salt dome which has been explored for disposal of heat-generating waste since 1977. This included the construction of galleries in the underground. There was a halt (moratorium) on exploration due to a political agreement from 2000 to 2010. Further underground investigations will start in the end of this year.



Fig. 1. Location of sites in Germany.

HISTORICAL OUTLINE SINCE 2000

A new procedure to find a final repository for all types of wastes and a phase-out of nuclear energy was initiated by the federal government (socialist-green coalition) in 2000. Fundamental questions on the suitability of Gorleben for final disposal of heat-generating waste were posed in 2002. The results showed that there is no clear or obvious advantage for any host rock type (clay, salt, granite) in Germany (2005). Furthermore, it was added that any advantage or disadvantage can be figured out only by a site-specific comparison. It was also pointed out that an updated regulation of final disposal of heat-generating waste is required for protection goals, safety analysis, safe enclosure, scenarios and retrieval of waste. Research on site-specific geochemical modelling and on parameters for evaluation and assessment of consequences of released contaminants was also proposed.

A drafting of safety requirements for disposal of heat-generating radioactive waste was subsequently

initiated (1). Reprocessing of spent fuel was prohibited in the second legislative period of the socialist-green coalition (2002-2005).

The conservative-socialist coalition (2006-2009) kept the phase-out agreement and continued drafting of safety requirements.

The present conservative-liberal coalition (2010-) is extending the lifetime of nuclear power plants (phase-out from phase-out), is restarting the exploration of Gorleben, and initiated a preliminary safety assessment of Gorleben site using existing data, information and knowledge.

PRESENT STATUS

The concept of site selection and licensing as of July 2009 foresees a stepwise process (2) for a repository of heat-generating radioactive waste. The implementer is the BfS, which may use a contractor. The safety requirements are applicable as drafted by the federal ministry (1). The site selection criteria are based on results from the AK End (2002). The public shall be included. The atomic law shall be updated to implement the stepwise process. Administrative regulations will be set accordingly.

COMPETENCE, PUBLIC PARTICIPATION

The competence of the federal ministry for environment, nature conservation and nuclear safety (federal government) includes the regulation as well as the supervision of the federal office for radiation protection (BfS) and federal states (Fig. 2).

All four repositories in Germany are operated by the BfS. BfS has to apply as implementer for license to operate or closure a repository within that federal state, where the repository is located.

The public is involved by public display of all relevant documents before a license is granted. This includes an appointment of the implementer and the public under supervision of the licensing authority to consider any objections. After granting of the license and its public display the license may be filed by court by the implementer and the public.

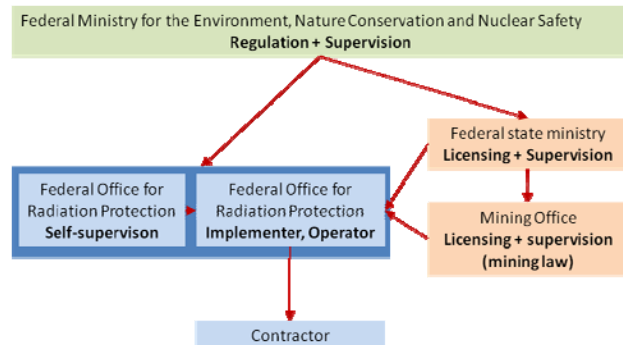


Fig. 2. Competence (atomic and mining law)

SAFETY REQUIREMENTS

The safety requirements governing the final disposal of heat generating radioactive waste (as of June 2010) foresee:

1. only negligible amounts of released pollutants within one million years
2. proof of integrity of host rock
3. presentation and assessment of risk
4. optimisation during planing and construction until closure
5. periodical safety assessments
6. multi-barrier system (redundant, independent)
7. control and documentation after closure
8. retrieval of waste has to be possible until closure of the repository

SUMMARY AND FUTURE

The federal government is cancelling the halt on exploration on Gorleben and resuming the underground exploration. An agreement on the safety requirements with the Federal States as licensing authorities is ongoing and will be published. The preliminary safety case of Gorleben site is started and will be finalized in 2012 to identify any additional exploration and research needs, to update and optimise the concept, and to assess the suitability based on available data presently.

Then, the exploration, planing and documentation shall be finalized for an application in 2017. BfS has been directed to apply for an extension of the existing license from 1983 for further exploration.

The Konrad site is under construction.

The closure concept and the long-term safety assessment of the Morsleben site are under review.

The decision about the retrieval of the radioactive waste from the Asse II site over relocation of waste within the mine or backfilling of the mine with remaining waste is made according to result of feasibility studies.

CONCLUSION

The disposal of radioactive waste, especially heat-generating waste and Asse II, remains a political issue in Germany. Due to the short-term exchange of political parties in the government and the long-term task of implementation of a repository the emphasis of the repository program and its goal is varying.

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Geochemical Research Fields for the Safety of a Final Repository for Heat Producing Radioactive Waste in Germany

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INTRODUCTION

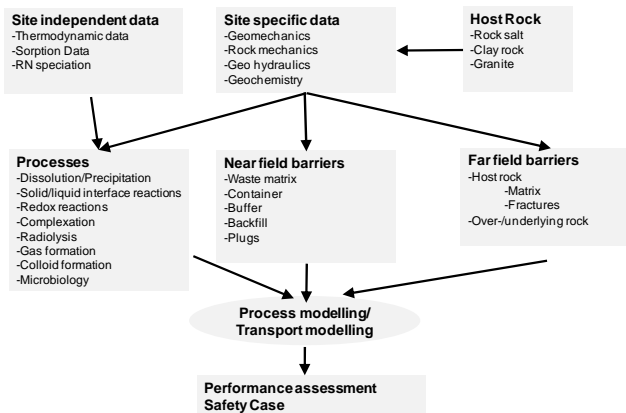
In Germany the Federal Government takes the responsibility for the safe disposal of radioactive wastes. Presently, heat producing radioactive waste consisting of spent nuclear fuel and vitrified high-level waste is intended to be disposed of in deep geological formations, either in salt or in clay formations. A safety case has to be developed to demonstrate that the repository will remain safe over a prolonged period, beyond the time when active control of the facility can be guaranteed (OECD/NEA, No. 3679, 2004). It comprises all available information and arguments that describe, quantify and substantiate the safety, and the level of confidence in the safety, of the geological disposal facility. In particular, performance assessment entails safety-analytical model calculations to quantify potential mobilization, transport, and retardation of radionuclides in the near and far field of a repository. Such calculations basically allow the quantification of consequences based on the assumption of relevant scenarios. The quality of the safety case strongly depends on the scientific understanding of the processes involved, on the quality of chemical/geochemical data base, as well as on the conceptual and mathematical development of respective models. Geochemical research furnishes the necessary thermodynamic data to describe radionuclide migration and retention along the water pathway.

GEOCHEMISTRY RESEARCH TOPICS

This presentation summarizes a technical report elaborated by German institutions contributing to chemistry and geochemistry research related to safe

nuclear waste disposal. It aims at defining present and future objectives and priorities of geochemical research for the safe disposal of heat producing waste in rock salt and clay rock in Germany

Research issues address all chemical reactions, which can lead both to the mobilization and retardation of radiotoxic substances, i.e. actinides and long-lived fission and activation products, in different regions of a repository system, the quantification of the individual processes and the collection of relevant thermodynamic data.



Scheme describing chemical and geochemical aspects of the safety case

Part A of the presentation describes fundamental research topics primarily related to chemical processes and to the generation of corresponding site independent data.

Part B describes issues concerned with specific chemical effects induced by the site specific

characteristics of host rock and the specific repository concept.

Part C focuses on the development of techniques and methods required to enhance process understanding, to generate relevant data and to develop appropriate models.

IDENTIFIED RESEARCH ISSUES

Thermodynamic data on radionuclide geochemistry have considerably evolved over the recent years. They are well documented in the famous 'blue books' of the OECD Nuclear Energy Agency. There are nevertheless open gaps in such site independent geochemical data that have to be filled. Most data are available for standard temperature conditions of 25°C only. The results are not applicable to higher temperatures, which appear in the near field of heat producing waste repositories for quite some time periods. Solubility data for solid phases and solution data might be extrapolated by applying the Helgeson-Kirkham-Flowers model. However, the general applicability of this approach has been controversially discussed and at least some experimental work appears necessary for verification. In the case of radionuclide sorption, temperature dependent data are widely missing.

The fission and activation products ^{14}C , ^{79}Se , ^{129}I , ^{36}Cl , and ^{99}Tc mostly are considered mobile in long term safety analyses for nuclear waste disposal and dominate the calculated dose exposures for selected scenarios, even though those values fall short of accepted dose limits by orders of magnitude. The assumption on no or almost no retention very often is due to missing reliable data. Therefore, a specific research focus will be laid on potential retention reactions relevant to such radionuclides.

In addition to pure surface sorption reactions, radionuclide retention under real disposal conditions over the long term is very likely influenced if not dominated by mineralization reactions. The formation of mixed solid-solution phases represents an effective retardation process for radionuclides not considered in performance assessment calculations so far. Today there are still few resilient data available and research programs on this issue have only recently been initiated and are planned to be intensified.

Colloid formation and migration is still an open issue for radionuclide transport assessment and requires more research in order to cut clearly boundary conditions where such species may form and be mobile over long distances. Similarly, the impact of microbial activities on radionuclide geochemistry is frequently discussed. Consequently, systematic investigations are required to identify the relevance and impact of microbial activities in rock salt and clay rock on radionuclide behavior.

A comprehensive quantification of possibly interacting chemical processes notably in the repository near-field requires new approaches of coupled reactive transport models and codes. Activities related to code and

model development for coupled chemistry and transport calculations will be intensified in further activities.

Future directions of geochemical research will be influenced by progress made in related research fields such as international partitioning and transmutation (P&T) or partitioning and conditioning (P&C) investigation programs. P&T or P&C are possible options for future use of nuclear fission energy within generation IV reactor concepts. The necessity for geological disposal of nuclear waste will persist even after realization of such technologies. However, waste forms may be different.

CONCLUSIONS

The time horizon for construction and operation of a repository for heat producing radioactive waste in Germany extends up to the middle of this century. Geochemically oriented research addressed in this presentation provides essential contributions to concept planning and repository site-selection activities. Notably, it contributes to various parts of a scientifically based safety case for a repository.

Pitzer Modeling in Brines: Experiments and Evaluation

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INTRODUCTION

In Germany rock salt is considered as candidate host rock for the disposal of radioactive waste. In the improbable event of intruding water the resulting solutions would be saturated with those salt minerals present in the host rock and thus are of brine type.

Within the scope of performance assessment interactions of brine with radioactive waste containments and ultimately with the waste itself have to be considered. The solubility of radio nuclides in brine is calculated employing thermodynamic equilibrium modeling. However, in brine activity coefficients of aqueous species are unequal to unity. Approaches like Extended Debye-Hückel theory cannot be used. Instead, the formalism introduced by Pitzer and co-workers is employed, which has proven to be able to reproduce even complicated diagenetic processes in brines (HERBERT 1996). The formalism contains specific parameters ("Pitzer parameters") which have to be determined for each individual ionic interaction.

GRS features a long tradition of conducting experiments to obtain such parameters. The presentation reviews the methods employed and some results for various systems.

DESCRIPTION OF THE WORK

Pitzer parameters can be derived from any kind of experiments where concentrations and activities are determined simultaneously. Methods involve

- Measurement of solubility (determination of activity product from species involved in the formation reaction of a solid phase whose solubility constant is known);
- Isopiestic measurement (determination of water activity);
- EMF measurement (direct determination of aqueous species activity).

Especially when speciation issues need to be resolved, other methods can complement the former ones, such as UV- or RAMAN-spectroscopy.

Prior to conducting own experiments, relevant literature is usually surveyed to recover suitable data.

Data processing is conducted in several steps. First, binary Pitzer parameters are determined from experimental data involving one cation and one anion (or, in the case of neutral species the species itself and a

binary salt). Second, binary Pitzer parameters are held constant and ternary Pitzer parameters determined.

During this process, different kinds of experimental data need to be taken account of. Any single datum is assigned an individual error. Upon parameter estimation, any single datum may be varied around its error. This procedure of data variation and parameter optimization may be repeated up to a thousand times to obtain a measure about the number of significant digits of Pitzer parameters. Excel sheets and a self-developed code are applied for this purpose.

In recent years, GRS has investigated numerous systems. In response to the interest of local stakeholders, GRS determined a complete set of Pitzer parameters for zinc, lead, and cadmium in the system of oceanic salts. Due to significant complex formation with chloride and sulphate, the speciation model for these heavy metals had to be adapted accordingly. Other efforts were directed on determining isopiestic data for ferrous and ferric iron (MOOG et al. 2004, RUMYANTSEV et al. 2004). For ferrous iron, these data were complemented with solubility data to help building up a complete set of Pitzer parameters (MOOG and HAGEMANN 2004).

At present work is focussed on implementing a method to perform isopiestic measurements at elevated temperatures. First measurements focus on ferrous iron, which again are complemented by solubility measurements at elevated temperatures. Other efforts are focussing on reduced sulphur, $H_2S(aq)$ and HS^- , and phosphate.

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Experimental Determination of Solubility Constant of Hydromagnesite (5424) in NaCl Solutions up to 4.4 m at Room Temperature

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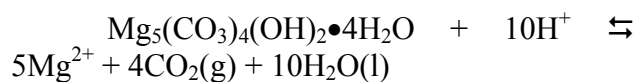
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INTRODUCTION

Industrial-grade MgO consisting mainly of the mineral periclase is the only engineered barrier certified by the Environmental Protection Agency (EPA) for emplacement in the Waste Isolation Pilot Plant (WIPP) in the U.S.^{1,2} and an Mg(OH)₂-based engineered barrier consisting mainly of the mineral brucite is to be employed in the Asse repository in Germany.³ In the WIPP, as MgO is in excess relative to CO₂ that may be produced, the brucite-hydromagnesite (5424) assemblage would buffer f_{CO_2} in the repository for considerable time before hydromagnesite (5424) converts to magnesite (MgCO₃).

DESCRIPTION OF THE WORK

This study reports the solubility constants of both synthetic and natural hydromagnesite (5424) determined in a wide range of ionic strength by using NaCl solutions as supporting electrolytes regarding the following reaction:



Solubility experiments were conducted from undersaturation in deionized (DI) water and 0.10–4.4 m NaCl solutions at 22.5 °C at $P_{\text{CO}_2} = 10^{-3.4}$ atm, and experiments lasted up to 1870 days. The weighted average solubility constant at infinite dilution calculated from the experimental results in 0.10–3.2 m NaCl solutions using the natural hydromagnesite from Staten Island, New York, with the specific interaction theory (SIT) is 58.39 ± 0.40 (2 σ) in logarithmic unit at 22.5 °C with a corresponding

value of 57.64 ± 0.40 (2 σ) at 25 °C. In weighted average calculations, weights are experimental uncertainties. Similarly, the weighted average solubility constant using the natural hydromagnesite (5424) from Gabbs, Nevada, is 59.54 ± 0.72 (2 σ) in logarithmic unit at 22.5 °C with a corresponding value of 58.77 ± 0.72 (2 σ) at 25 °C. The weighted average solubility constant of synthetic hydromagnesite (5424) determined from experiments in 0.10–4.4 m NaCl solutions is 61.53 ± 0.59 (2 σ) in logarithmic unit at 22.5 °C with a corresponding value of 60.73 ± 0.59 (2 σ) at 25 °C. The natural hydromagnesite has lower solubilities because of higher crystallinity nature. The solubility constant of synthetic hydromagnesite is about one order of magnitude lower than the literature values.

The Gibbs free energies of formation at reference state (25 °C, 1 bar) are $-5,897 \pm 2$ kJ mol⁻¹, $-5,891 \pm 4$ kJ mol⁻¹, and $-5,880 \pm 3$ kJ mol⁻¹ for the natural hydromagnesite from Staten Island, New York, from Gabbs, Nevada, and for the synthetic hydromagnesite, respectively. Based on the solubility constants of hydromagnesite determined in this study, in combination with the solubility constant of brucite determined in the literature, the log f_{CO_2} buffered by brucite-synthetic hydromagnesite is calculated as -6.13 ± 0.16 (2 σ).

ACKNOWLEDGEMENTS

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Solubilities of Basic Magnesium Salt Hydrates in the System MgO-MgCl₂-H₂O with respect to their Use as Building Material (Sorel Cement) in Salt Formations

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INTRODUCTION

Basic magnesium salt hydrates form the basis for the use of magnesium oxide as building material. The material is used for many years as barrier construction material in salt formations, since, particularly in the potash mining the magnesia cement is stable towards salts and their solutions. With the formulation development, the control of the temperature during setting and the guarantee of the desired volume development and chemical long term stability are related. In particular, temperature dependent phase formations of magnesium salt hydrates in the primary system MgO-MgCl₂-H₂O are very important, since during the setting procedure temperatures over 120°C can be reached. The formation conditions regarding the production of magnesia building materials refer on the two binder phases: 3 Mg(OH)₂ · MgCl₂ · 8 H₂O (3-1-8 phase) and 5 Mg(OH)₂ · MgCl₂ · 8 H₂O (5-1-8 phase) and were examined by different authors [1-8]. Only very few thermodynamic data exist for the system at room temperature [9-14]. Thus, in contact with MgCl₂ solution (above 1.7 mol/kg H₂O), the 3-1-8 phase is the thermodynamically stable phase. The 5-1-8 phase, with which the highest concrete strengths are reached, was never found as an equilibrium phase in contact with the solution, and can thus be regarded as metastable phase at ambient temperature.

At 100°C and 110°C the basic magnesium salt hydrates with the formulas 9-1-5, 2-1-4, 2-1-2 and 3-1-1 were found in the ternary system [14-16]. Unfortunately, from these data it is not possible to construct a phase diagram for the system MgO-MgCl₂-H₂O, because the general low concentrations of Mg(OH)₂ in the equilibrium solutions are not given.

DESCRIPTION OF THE WORK

By solubility re-investigations in the system MgO-MgCl₂-H₂O at 25°C and by the new data at 40°C the phase 3-1-8 is confirmed as the thermodynamically stable phase, the 5-1-8 phase is always metastable. This result was found by a numerous of solubility experiments with monitoring of phase formation and transformation in different concentrated magnesium chloride solutions, supersaturated by magnesium hydroxide, at 25°C and 40°C by pH electrode potential development. Fig. 1 shows as

example the monitoring in a 2.5 molal MgCl₂ solution. Finally, after the equilibrium were reached, the solution concentrations were analysed (Mg²⁺: complexometric titration, Cl⁻: potentiometric titration, OH⁻: acid-back titration), the solids identified by powder diffraction. The solubility constants of Mg(OH)₂, 3-1-8 phase at 25°C were determined according to Altmaier et al. [14] and are in agreement.

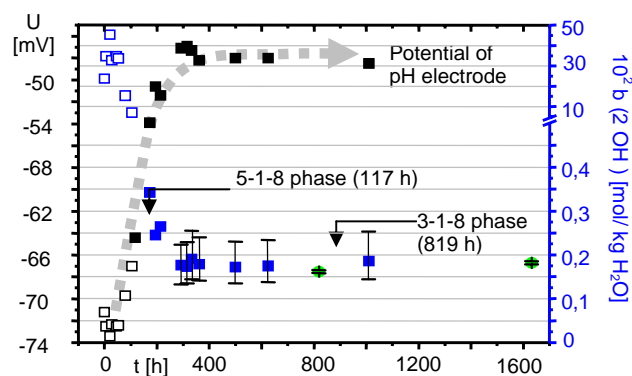


Figure 1: Monitoring of OH⁻ decrease by pH electrode and solid phase determination with time in a 2.5 molal MgCl₂ solution at 25°C

At 120°C the phase formation was investigated by hydrothermal synthesis in rotating autoclaves with reaction time up to 20 days. The subsequent separation of the solid phase from the solution phase at 120 ± 1°C took place in a special high temperature centrifuge. Afterwards the separated phases were cooled down for sampling. As result the metastable solubility curve of the 9-1-4 (from single crystal investigations the formula 9-1-4 phase result instead of 9-1-5 from literature) was found beside the stable phases 2-1-4 and 2-1-2 at 120°C.

Fig. 2 show the determined solubilities in the system MgO-MgCl₂-H₂O at 25°C, 40°C and 120°C.

In view of the construction of magnesia concrete barriers in salt formations, the 9-1-4 phase is formed in the period of increased temperature, above 80°C. To reach the long term stable binder phase the formulation must be adjusted to the 3-1-8 phase formation.

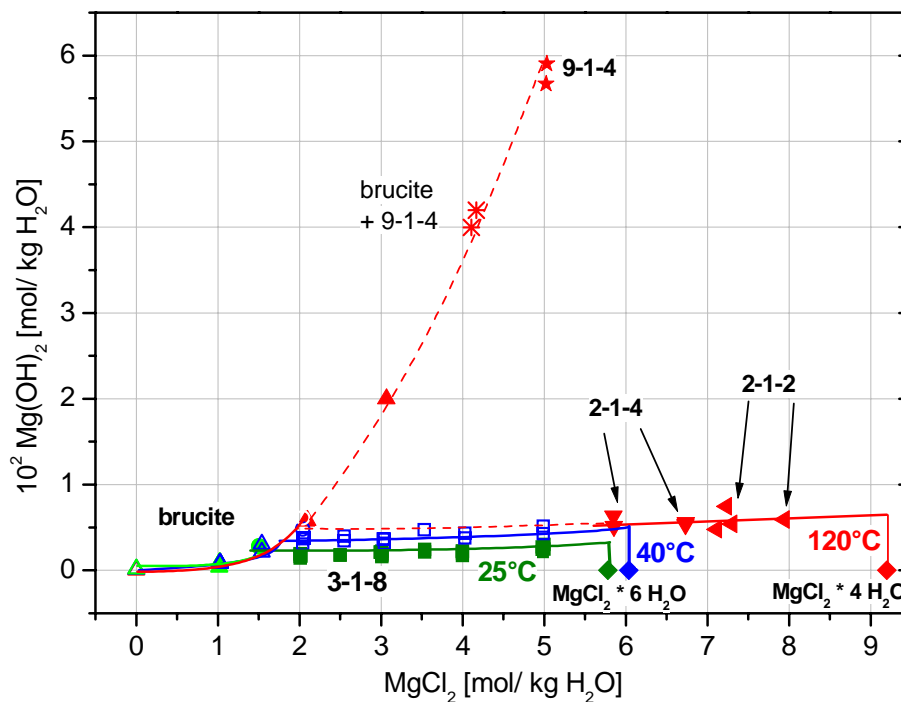


Figure 2: System MgO-MgCl₂-H₂O at 25°C, 40°C and 120°C, experimental data from this work.

FUTURE DIRECTIONS

The first results of this work will be published in 3 papers: 1. “9 Mg(OH)₂ · MgCl₂ · 4 H₂O, a High Temperature Phase of the Magnesia Binder System” *Inorg. Chem.* 2010, in print; 2. “2 Mg(OH)₂ · MgCl₂ · 4 H₂O and 2 Mg(OH)₂ · MgCl₂ · 2 H₂O, High Temperature Phases of the Magnesia Binder System”. *Acta Cryst. B*, in preparation; 3. “Solubilities of Magnesia Binder Phases in the System MgO-MgCl₂-H₂O and their importance as barrier construction material for radioactive waste disposals in salt formations”. *Geochim. Cosmochim. Acta.*, in preparation.

Solubility data in the system MgO-MgCl₂-H₂O will be completed at 60°C, 80°C and 100°C. The influence of Ca²⁺ and SO₄²⁻ on the phase formation will be investigated. The solubility constants of the metastable 5-1-8 phase and of the 3-1-8 phase at higher temperatures will be calculated.

Cement and concrete formulation are being under way for barrier engineering applications in salt rocks (waste repositories).

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Anoxic Corrosion of Steel and Lead in Na - Cl \pm Mg -Dominated Brines

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The Waste Isolation Pilot Plant (WIPP) is a deep geologic repository developed by the U.S. Department of Energy for the disposal of transuranic radioactive waste in bedded salt (Permian Salado Fm.). In order to minimize radionuclide release from the repository it is desirable to maintain actinide elements such as Pu, Am, U, and Np in their least-soluble form (i.e., low oxidation states). Post-closure conditions in the WIPP will control the speciation and solubilities of radioelements in the waste. Microbially-produced CO₂ from cellulosic, plastic and rubber materials in the waste may acidify any brine present and increase the actinide solubilities. Thus, the DOE emplaces MgO in the repository to buffer f_{CO_2} and pH within ranges favoring lower actinide solubilities. Large quantities of low-C steel and Pb present in the WIPP may also consume CO₂.

We present 6 and 12 month results from a series of multiyear experiments investigating the corrosion of steel and Pb alloys under WIPP-relevant conditions. The objective is to determine the extent to which these alloys consume CO₂ via the formation of carbonates or other phases, potentially supporting MgO in CO₂ sequestration. In these experiments steel and Pb coupons are immersed in brines under WIPP-relevant conditions using a continuous gas flow-through system. The experimental apparatus maintains the following conditions: pO₂ < 5 ppm; temperature of 26 °C; relative humidity

at 78 \pm 10%; and a range of pCO₂ values (0, 350, 1500 and 3500 ppm, balance N₂). Four high-ionic-strength-brines are used: Generic Weep Brine (GWB), a Na-Mg-Cl dominated brine associated with the Salado Fm.; Energy Research and Development Administration WIPP Well 6 (ERDA-6), a predominately Na-Cl brine; GWB with organic ligands (EDTA, acetate, citrate, and oxalate); and ERDA-6 with the same organic ligands.

Steel coupons removed after 6 months show formation of several phases dependent on the pCO₂. Scanning Electron Microscope (SEM) analysis with Energy Dispersive Spectroscopy (EDS) shows the presence of a green Fe (\pm Mg)-chloride-hydroxide phase at pCO₂ values <1500 ppm. At higher pCO₂ the dominant corrosion product is a Fe-Mg-Ca hydroxycarbonate phase. Lead coupons show no corrosion products at lower pCO₂ values but significant formation of a Pb-Ca hydroxycarbonate phase at pCO₂ > 350 ppm. Steel and lead coupons removed after 12 months of exposure show the same types of corrosion products as the six month samples.

Multiple cleaning cycles were used to remove all corrosion products from the coupons, which were then weighed to determine corrosive mass loss. These data are used to calculate average corrosion rates for each experimental condition. The 6 and 12 month data show that steel corrosion rates are a strong function of pCO₂ for all brine types. ERDA-6 brines appear to be

more corrosive than GWB brines. Steel corrosion rates in the six-month experiments vary from 0.08 ± 0.07 $\mu\text{m}/\text{yr}$ at 0 ppm CO_2 to 1.20 ± 0.25 $\mu\text{m}/\text{yr}$ at 3500 ppm CO_2 (Figure 1).

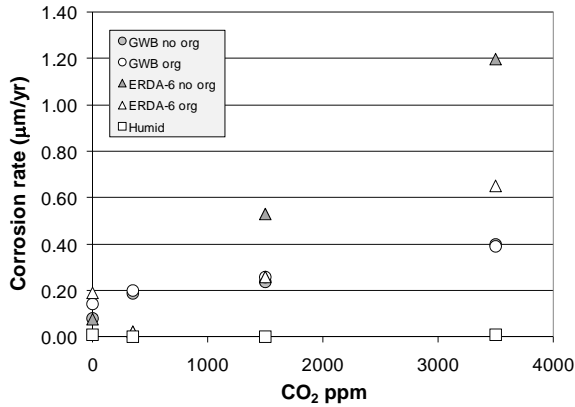


Figure 1. Steel corrosion rates (six-month) as a function of pCO_2 (ppm).

Corrosion rates for Pb coupons calculated from the six-month experimental data show no consistent trend as a function of pCO_2 or brine type. Six-month lead corrosion rates range from 0.18 ± 0.22 to 0.95 ± 0.56 $\mu\text{m}/\text{yr}$ (Figure 2).

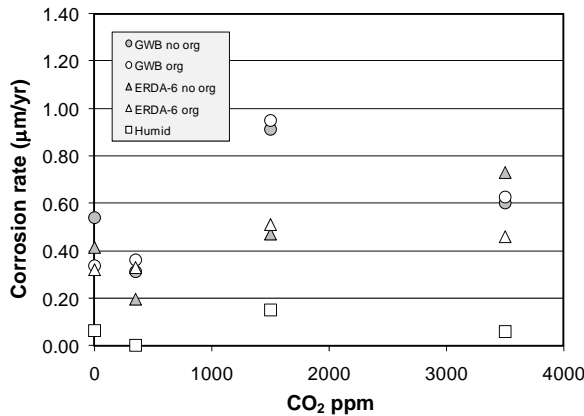


Figure 2. Lead corrosion rates (six-month) as a function of pCO_2 (ppm).

The corrosion rates calculated for both steel and lead coupons from the 12-month experiments appear to be 20 to 50% lower than the results from the six-month experiments. This may be due to the passivation of the coupon surfaces but the rates are still within the standard deviation of each other. More data from the longer-term experiments will be needed in order to determine if passivation is occurring.

This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S Department of Energy.

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Solubility of Ferrous Oxalate Dihydrate and Lead Oxalate in Magnesium Chloride and Sodium Chloride Solutions¹

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Oxalate ($C_2O_4^{2-}$) forms aqueous complexes with various divalent metal ions to form sparingly soluble minerals such as $CaC_2O_4 \cdot H_2O$ (whewellite), $CaC_2O_4 \cdot 2H_2O$ (weddelite), $MgC_2O_4 \cdot 2H_2O$ (glushinskite), $MnC_2O_4 \cdot 2H_2O$ (lindbergite), $PbC_2O_4(s)$, $PbC_2O_4 \cdot 2H_2O(s)$, and $FeC_2O_4 \cdot 2H_2O$ (humboldtine). At the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, U.S.A., iron, lead, and oxalate are present as a waste component. In addition, a significant amount of iron is present in the packaging material, and use of lead for shielded containers is highly plausible. Oxalate can solubilize actinides by forming aqueous complexes, increasing their mobility. A favorable removal mechanism for oxalate is its precipitation with benign cations. Under the chemical conditions expected in the WIPP after closure, it is possible that ferrous oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$, humboldtine), PbC_2O_4 , and $PbC_2O_4 \cdot 2H_2O$ could form if oxalate is available after the formation of whewellite. A limited number of literature articles have dealt with the solubility products for $FeC_2O_4 \cdot 2H_2O$, PbC_2O_4 , and $PbC_2O_4 \cdot 2H_2O$ [1, 2]. To determine the solubility products for $FeC_2O_4 \cdot 2H_2O$ and PbC_2O_4 and relevant Pitzer ion-interaction parameters, we examined the dissolution of $FeC_2O_4 \cdot 2H_2O$ and PbC_2O_4 by measuring the concentration of dissolved Fe(II) ($[Fe(II)]_{diss}$) and Pb(II) ($[Pb(II)]_{diss}$) in $MgCl_2$ and $NaCl$ solutions of incremental concentrations. Higher $[Fe(II)]_{diss}$ was observed in $MgCl_2$ and $NaCl$ solutions of higher concentrations. At comparable ionic strengths, the $[Fe(II)]_{diss}$ in $MgCl_2$ solutions were higher than in $NaCl$ solutions. In $MgCl_2$ solution, phenomena such as (i) a color change of $FeC_2O_4 \cdot 2H_2O$ in reactors of lower solid-to-

liquid ratio and (ii) a higher $[Fe(II)]_{diss}$ in reactors of higher solid-to-liquid ratio were observed, which could indicate the presence of reaction(s) other than simple dissolution of $FeC_2O_4 \cdot 2H_2O$. The lambda parameters of $PbC_2O_4(aq)-Mg^{2+}$ and $PbC_2O_4(aq)-Cl^-$ are -0.675 and -0.560, respectively. The zeta parameter of $PbC_2O_4(aq)-Mg^{2+}-Cl^-$ is -0.0856.

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1. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S Department of Energy.
 2. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Microbiology in the WIPP

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INTRODUCTION

Studies on the microbiology of WIPP are needed in order to contribute to the larger body of chemical, physical, hydrological, and geological knowledge that is consulted when evaluating repository performance¹. Salt-based repository microbiology has not been well studied since such repositories are rare, and there is often the misconception that organisms cannot survive in this type of environment. Although not teeming with life, the WIPP is far from sterile. The goal of this research is to characterize the microorganisms in this environment and investigate their potential interactions with the emplaced waste.

DESCRIPTION OF THE WORK

This work has focused on three key areas: microbial characterization of the WIPP halite and surrounding groundwaters, biodegradation of organic waste components, and the interaction of microorganisms with metals and actinides.

Microorganisms were enriched from WIPP halite samples in a medium designed for the growth of halophilic organisms. The results of DNA-based characterization of this enrichment culture are shown in Figure 1. Many of these sequences match to isolates and sequences obtained from other Permo-triassic rock salts in Austria and England²⁻⁶.

Archaeal isolates are initially being characterized by DNA sequence analysis in order to narrow the set for phenotypic characterization. No bacterial isolates were obtained from this culture, likely due to the restrictive growth medium. However, molecular-based characterization of the raw, uncultured halite revealed a predominance of *Bacteria* (*Halomonas* sp., *Limnobacter thiooxidans*, *Pseudomonas* sp.).

Incubations were set up in media using GWB and ERDA-6 formulations⁷ (~1M Mg and 5M NaCl, respectively) as the basal salt composition and amended with N and P. Acetate, oxalate, citrate, and EDTA were added as carbon sources at concentrations predicted by the WIPP inventory. A bacterial (*Halomonas halodenitrificans*) and archaeal (*Halosimplex carlsbadense*) isolate were used as inocula in separate incubations, as was the enrichment culture mentioned above.

With the exception of EDTA, the organics show poor solubility in the brines and precipitate over time.

However, in some incubations, the rate and extent of organic disappearance exceeded losses in abiotic controls, indicating biodegradation of certain organics. Acetate is easily degraded. Oxalate disappearance in a *Halosimplex* incubation appears to correlate with organism growth (see Figure 2). However, the competition for solubility between oxalate and citrate in some incubations masks the apparent loss of citrate (see Figure 3). No EDTA degradation has been observed during the incubation period; however, it is not toxic to microorganisms at levels predicted in the WIPP.

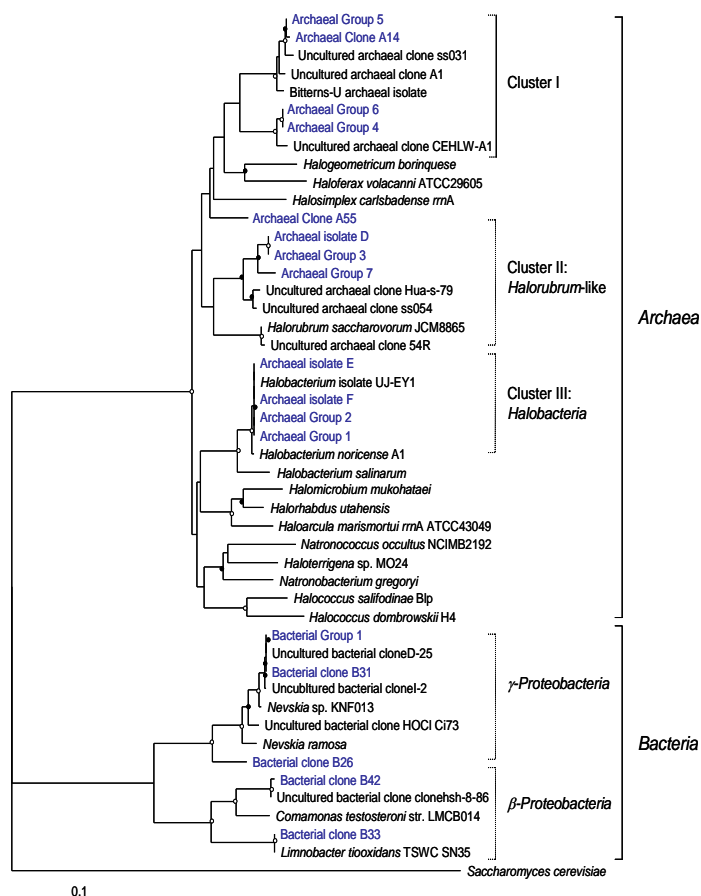


Figure 1. Phylogenetic tree of archaeal and bacterial 16S rRNA gene libraries. Tree is rooted to *Saccharomyces cerevisiae*. Solid circles denote bootstrap values greater than 50%; open circles greater than 95%. Sequences in blue are from enrichment culture.

In separate halite enrichments, with a single chelating agent as a carbon source, citrate was shown to degrade.

An additional microbial characterization is underway to examine the community resulting from these incubations. GWB is in progress. ERDA incubations have resulted in a narrowing of the community to a majority of *Halorubrum*-like organisms. These appear to be unique and may comprise a new haloarchaeal species.

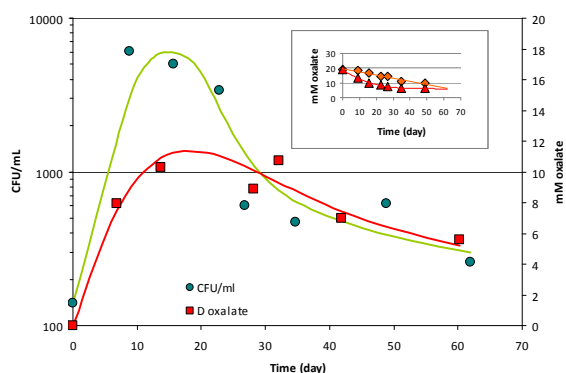


Figure 2. Growth of *Halosimplex carlsbadense* correlated with oxalate disappearance in ERDA-6. Inset provides original data used to generate differential curve shown in red.

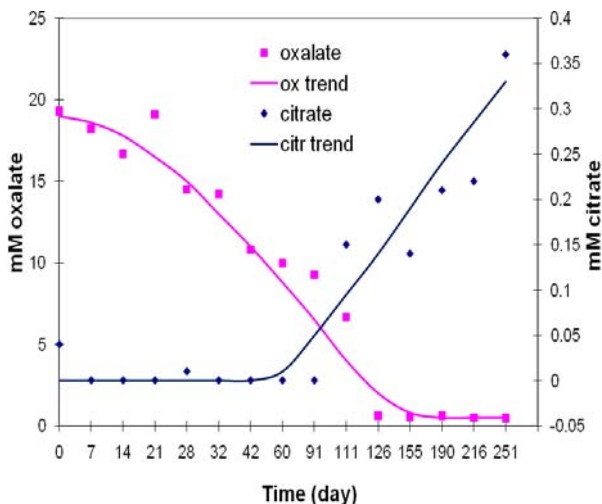


Figure 3. Oxalate and citrate levels in abiotic GWB incubations over time.

Aerobic and anaerobic incubations of three groundwaters surrounding the WIPP have been set up. Microbial characterization is ongoing. The anaerobic incubations proceed relatively quickly through sulfate reduction. Methanogenesis has not yet been demonstrated.

Microbial growth obtained in an iron-reducing incubation of high ionic strength groundwater (~3.7M NaCl) was used to inoculate a new set of iron reduction experiments. Reduction of iron has occurred, but the resulting microbial community is exclusively haloarchaea. This culture has been used to inoculate further metal/actinide reduction studies.

FUTURE DIRECTIONS

Microbial characterization is an ongoing project as new samples are available. Anaerobic enrichments from halite are currently being set up. Cellulose degradation and gas generation studies are planned.

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Actinide Interactions with Bacteria

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INTRODUCTION

Microbes are widely distributed in nature also under harsh conditions (e.g., high salinity; low permeability; high and low temperatures). They can strongly influence the migration of hazardous actinides in the environment once they have been released. This is demonstrated by an increased interest in studies exploring the interaction processes involving actinides and bacteria during the last years. However, worldwide only little detailed information is available about the biodiversity and microbial influences on radionuclide migration under the conditions of a deep nuclear repository.

There are two examples in Europe for research to test the probabilities of bedrock to store nuclear waste taking into account the occurrence of resident microbial communities: a) crystalline bedrock – the Äspö Hard Rock Laboratory (Äspö HRL; Sweden): the total number of microbes range from 1×10^3 to 5×10^6 cells ml^{-1} , whereas the number of sulfate reducing bacteria (SRB) was between 1×10^1 to 2×10^4 cells ml^{-1} [1], and b) clay bedrock – the Mont Terri Underground Rock Laboratory, Switzerland: bacterial concentration around 10^3 cells g^{-1} were observed [2]. The concentrations of naturally occurring microbes in the hyper saline environments at the Waste Isolation Pilot Plant (WIPP), New Mexico, are about 10^4 to 10^7 cells ml^{-1} [3].

DESCRIPTION OF THE WORK

The presentation covers the broad topic of actinide interactions with bacteria. A short overview about the determination of the microbial diversity giving the dominant bacterial strains will be given. In more detail, the manifold interaction process of bacteria with actinides will be highlighted based on selected examples. Microorganisms can interact with actinides directly: biosorption at the cell surface, intracellular accumulation, precipitation, and redox transformations (oxidation/reduction) and indirectly: formation of soluble complexes of actinides with various bioligands secreted by resident microorganisms. Examples of both pathways are presented.

One direct interaction process is the biosorption of the trivalent actinide curium by the SRB *Desulfovibrio aespoeensis* [4], which is indigenous to Äspö HRL groundwater [5]. Assuming that *D. aespoeensis* cells are attached to the fracture surfaces of granitic rock, Cm^{3+} released in the aquifer will become immobilized due to biosorption on bacterial cells in the neutral pH range. For the first time, the direct interaction processes between plutonium in different oxidation states (+6 and

+4) with cells of *D. aespoeensis* were determined [6]. Shortly, the reduction of Pu(VI) to Pu(V) by the bacteria leads to an increased dissolution of the cell bound plutonium. In contrast to the release of Pu(V) from the cell surface into the surrounding solution, we observed an immobilization of Pu as Pu(IV) polymers by the biomass. Our results showed that the interaction mechanism with *D. aespoeensis* depends on the nature of the actinide element. In contrast to Cm, for U, Pu, and Np the interaction mechanism is more complex and consists of various sub-processes. After contact with the cells changes in the oxidation state of the actinides U, Pu, and possibly Np, were determined affecting their migration behavior by both mobilization in case of Pu(V) and immobilization in case of U(IV) and Pu(IV). To summarize, the strength of the interaction of *D. aespoeensis* with the selected actinides at pH 5 and actinide concentrations ≥ 10 mg/L ([Cm] 0.07 mg/L) followed the pattern: $\text{Cm} > \text{U} > \text{Pu} \gg \text{Np}$.

One indirect interaction process is the formation of soluble complexes of actinides with bioligands secreted by ubiquitous Pseudomonads. Fluorescent *Pseudomonas* species secrete bioligands, the pyoverdins, under iron-deficient conditions. Due to their unique structure pyoverdins have a great potential to complex metals. In this presentation we focus on results describing the complexation between the hazardous actinide neptunium with the pyoverdins released by *Pseudomonas fluorescens* (CCUG 32456) cells isolated also from the granitic rock aquifers at the Äspö HRL [7, 8]. Our study answers the question if pyoverdins besides iron(III) also form strong species with hazardous and radiotoxic actinides. Since the answer is yes, pyoverdins have an impact of those behaviors in the vicinity of a nuclear waste disposal site.

With this presentation we want to point out the importance of actinide-microbe interactions for the disposal of nuclear waste.

FUTURE DIRECTIONS

Our future directions of work are focused on the exploration of the microbial diversity in clay formations mainly by application of culture-independent methods. Based on these results we will explore the interaction of dominant clay microbes with actinides. We plan a similar strategy for salt formations because detailed information is not available but needed.

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Bioreduction of Actinides in Low and High Ionic Strength Environments

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INTRODUCTION

Microorganisms can utilize a variety of alternative terminal electron acceptors, including actinides, in aqueous environments where the utilization of all available oxygen results in anaerobic conditions (e.g., Lovley et al., 1991; Rittmann et al., 2002; and Icopini et al., 2009). As a result microorganisms play a critical role in determining the oxidation state of actinides in such environments. Key processes controlling actinide fate and transport behavior (i.e., solubility, complexation, and adsorption) are often dependant on the oxidation state of the actinide. Thus, an understanding of microbial actinide reduction processes is critical to predicting the behavior of actinides in the environment.

The publications by the Lovley group (e.g., Lovley et al., 1991), were the earliest reports showing enzymatic reduction of U(VI) to U(IV) by a variety of common metal reducing soil bacteria. When U(VI) is reduced to U(IV), its solubility decreases, resulting in immobilization through precipitation. Based on their results and the results of others enzymatic U(VI) reduction has been proposed as one of the dominant processes controlling uranium immobilization in a variety of natural low-temperature, low-ionic strength, aqueous environments. Although there is an extensive body of research published on microbial U(VI) reduction relatively little work has been extended to include transuranic actinides such as neptunium (e.g., Rittmann et al., 2002) and plutonium (e.g., Icopini et al., 2009), which are the primary contaminants in the proposed waste streams considered for emplacement in salt-based nuclear waste repositories. The results of these studies indicate that like U(VI), higher valent neptunium (Np(V)) and plutonium (Pu(VI) and Pu(IV)) can be reduced enzymatically by some microorganisms under specific conditions resulting in potential altered subsurface mobility. However, almost all actinide microbial interaction studies performed to date have been performed with common gram-negative or gram-positive soil bacteria under chemically simplified low-ionic strength aqueous conditions which are not directly applicable to conditions present in the subsurface at salt-based repositories.

DESCRIPTION OF THE WORK

Based on the results of previous studies utilizing common soil bacteria it is likely that some microorganisms indigenous to the salt-based Waste Isolation Pilot Plant (WIPP) will exhibit a similar ability to reduce actinides under WIPP relevant conditions. As such, our research has focused on developing and performing experiments designed to elucidate the microbial effects on the oxidation state and subsequent fate and transport behavior of uranium, neptunium, and plutonium under low ionic strength and WIPP relevant high ionic-strength conditions, with an emphasis on determining mechanisms and extent of reduction.

We performed bioreduction experiments at low ionic strength with a common *Shewanella* sp. with aqueous uranium-carbonate and neptunyl species under growth and non-growth conditions. In experiments with uranium, our results were similar to other researchers showing that U(VI) was converted to U(IV) with time resulting in the formation of an insoluble uranium precipitate. Figure 1 below depicts temporal aqueous total uranium concentration trends over the course of an experiment. Total uranium with bacteria and a suitable carbon source results in rapid uranium loss. Controls with just bacteria and uranium or with just a carbon source and uranium result in negligible uranium loss from solution.

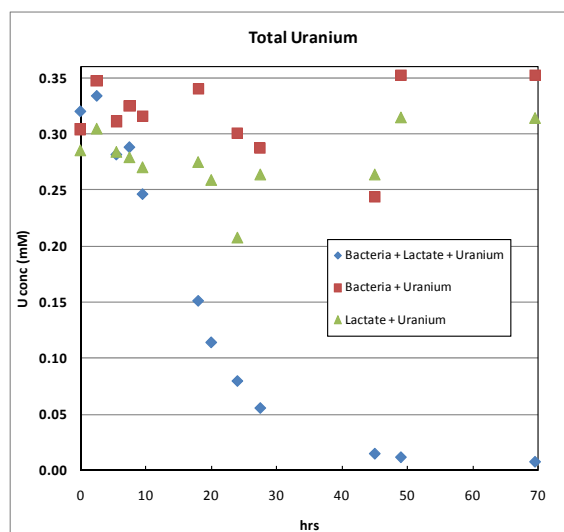


Fig. 1 Total uranium in solution with time in bioreduction experiment with *Shewanella* sp.

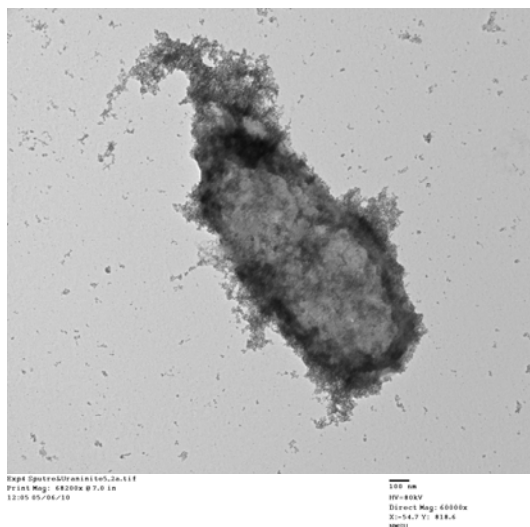


Fig. 2 Transmission electron micrograph of *Shewanella* sp. encrusted with uranium precipitate at the conclusion of bioreduction experiment.

In similar preliminary experiments with Np(V), total neptunium in solution was reduced by more than an order of magnitude in the presence of *Shewanella* sp. compared to abiotic controls. However, the oxidation state of neptunium and the presence of a reduced precipitate phase in these experiments has not yet been confirmed.

Preliminary bioreduction experiments in high ionic strength simulated brines with halophilic bacteria indigenous to the WIPP site have also been performed. A mixed culture of microorganisms cultured from a briny groundwater at the WIPP site were inoculated into a simulated brine with aqueous Fe(III) present as the only terminal electron acceptor. Over 5 months, the halophilic mixed culture reduced the majority of Fe(III) to Fe(II) demonstrating that these extremophiles exhibit the capacity for metal reduction. As a next step, aliquots from this Fe reduction experiment were spiked with Np(V) and allowed to equilibrate. Within one hour of Np(V) spiking, approximately 95% of the neptunium was removed from solution compared to the abiotic control suggesting the formation of a reduced Np(IV) precipitate. However, the oxidation state of neptunium and the identification of the precipitate phase in these experiments has not yet been confirmed either.

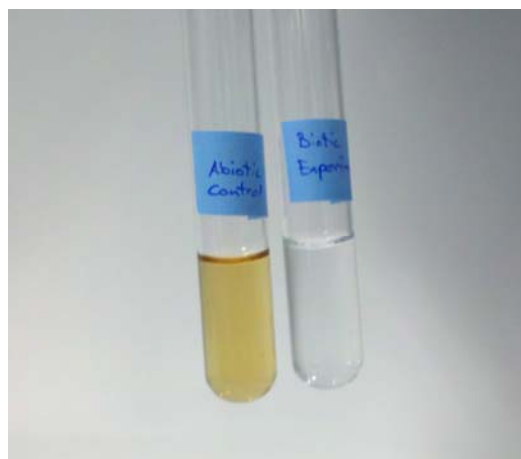


Fig. 3 Abiotic control (colored) and inoculated (clear) batch reaction vessels indicating Fe(III) reduction from a colored solution to a clear solution of Fe(II).

FUTURE DIRECTIONS

Future bioreduction research will consist of further extending the low ionic strength experiments with soil bacteria to completely characterize the process for neptunium and plutonium reduction. As a component of this work, characterization of oxidation state and precipitated solids will be performed through a variety of techniques including UV-VIS spectrophotometry, X-Ray diffraction, and X-ray adsorption spectroscopy. Further, bioreduction experiments with halophilic organisms in synthetic and natural brines will be performed in order to ascertain the effects of such systems on overall actinide mobility.

Future bioreduction research will also consist of elucidating the effects of more complex solution chemistry on bioreduction processes. For instance, varying Eh conditions through manipulations of specific redox couples such as Fe(II)/Fe(III) can provide insight into the mechanisms of bioreduction under these specific conditions.

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X-Ray Diffraction and Laser Photoacoustic Absorbance Spectroscopy of Actinides

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INTRODUCTION

Detection and characterization of actinide chemical species of interest to the WIPP, at relevant concentrations and in chloride matrices, frequently presents a technical challenge. Determination of signals from these species with acceptable signal to noise ratios is often problematic at WIPP-relevant concentrations. Herein, we will discuss two approaches to addressing this issue.

DESCRIPTION OF THE WORK

X-Ray Diffraction (XRD) spectroscopy of solids is a powerful technique for identifying phases and their relative proportions. As many of the species that are of interest to the WIPP are chlorides, hydroxides and mixed hydroxychlorides, all with actinide phases that tend to be of very minor concentration, the ability to separate out the minor phases during analysis is a key concern. Analysis of actinides such as plutonium and americium also present safety issues from a total sample concentration standpoint and require small sample sizes for acquisition.

The most direct approach to enhancing XRD utility in this regard is achieved by increasing detector sensitivity and resolution. Various approaches have been tried over the years, such as replacing Scherer powder camera techniques with direct scintillation counters, replacing scintillation counters with fluorescence detectors like the Bruker Sol-X and by the use of highly sensitive CCD detectors, as represented by the Bruker Lynx Eye. This work describes the installation of a Lynx Eye detector on a Bruker D8 Advance diffractometer, which had a scintillation counter detector prior to this installation. Detection of trace phases has been dramatically improved, as shown in Fig. 1 and for identical S/N ratios, the acquisition time is much faster.

For aqueous-phase actinides, a problem frequently encountered and in particular with plutonium, is the fact that WIPP-relevant species show poor conventional spectroscopic response, i.e. they prefer to decay from their excited states non-radiatively. Use of Laser Photoacoustic Spectroscopy (LPAS) relies on detection of the non-radiative decay photoacoustic “chirp” to detect these species.

Also presented here is progress in the setup of an LPAS system for detection of aqueous actinide species. This system, has at present, reached a limiting sensitivity (using a 1:1 S/N ratio) of approximately 6×10^{-7} absorbance units in the visible. In addition, the use of a solid-state OPO type laser allows for convenient broad spectral tuning, as demonstrated in Fig. 2.

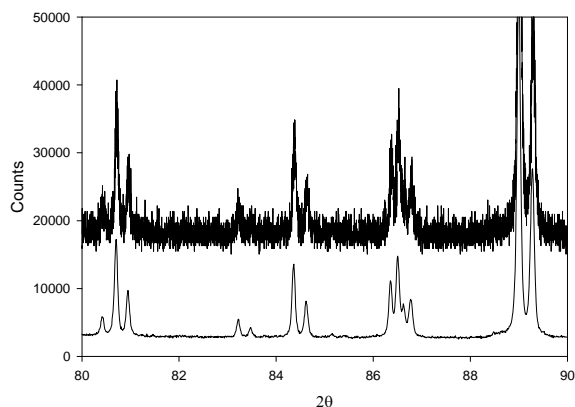


Fig. 1 Comparison of scintillation counter versus Lynx Eye sensitivity for equivalent count times, slit setting using the NIST corundum standard.

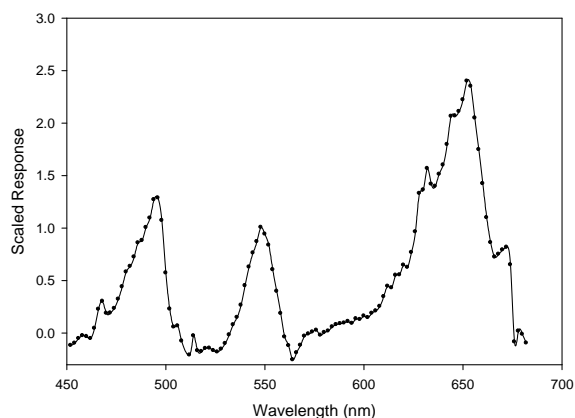


Fig.2 Uranium (IV) aqueous solution at 1×10^{-4} M in 1 M perchloric acid, baselined against 1 M perchloric acid.

FUTURE DIRECTIONS

The XRD system is being setup for capillary work to perform plutonium/americium sample acquisitions. The LPAS system is being refined to increase sensitivity in the visible spectrum and operation in the near infrared is being examined, particularly for neptunium-species characterization.

Investigation of Iron Corrosion Products from Brines Using XAFS

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INTRODUCTION

Accurate models for actinide solubility are required to understand actinide fate and transport in the environment. Understanding the influence of iron on oxidation state, and therefore solubility, of the actinides is of upmost importance with regards to waste repositories such as the Waste Isolation Pilot Plant (WIPP) where iron based packaging will far exceed the mass of the emplaced transuranic waste [1].

Efforts to study the reducing effects of reduced iron phases in repository relevant conditions have been reported previously [2]. New results, obtained from x-ray absorption spectroscopy, on long term versions of those studies indicate the possibility of reduction mechanism operating on the timescale of several years.

DESCRIPTION OF THE WORK

Reduced iron, in the form of Fe(0) coupons and powder as well as magnetite Fe(II/III) oxide powder was added to simulated WIPP brines containing Pu(VI) according to [1], replicating the experimental conditions reported in [2].

In our earlier study [2] we found rapid reduction of plutonium upon the introduction of iron, with the majority of the plutonium reduced to Pu(IV) as determined by x-ray absorption near edge spectroscopy (XANES), figure 1.

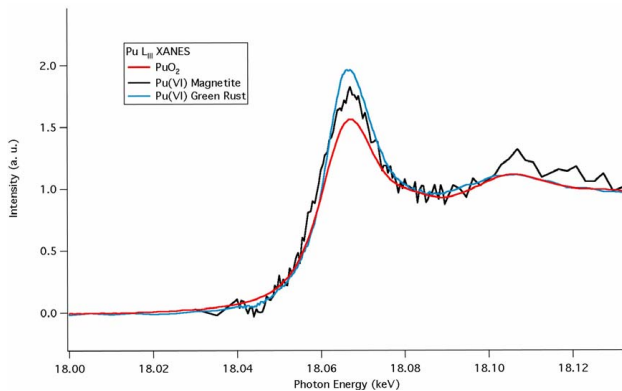


Fig. 1. XANES of precipitates from Pu(VI) reduction

study. Plutonium was reduced to Pu(IV), as indicated by agreement with a PuO₂ standard. Taken from [2].

After equilibrating for approximately 4 years sealed inside a nitrogen glovebox the plutonium/iron/brine solutions were sampled, and the precipitates/corrosion products recovered. After drying, they were mounted in Kel-F and aluminum sample holders, and triply sealed with Kapton tape before being removed from the glove box and shipped to the Advanced Photon Source (APS) at Argonne National Laboratory.

Pu L₃ XANES analyses were performed at the MRCAT undulator beamline, which uses a Si(111) double crystal monochromator and a harmonic rejection mirror for energy selection. Ion chambers were used to measure incident and transmitted flux, while fluorescence measurements were obtained with the use of a HPGe multi-element detector. Oxidation state standards, consisting of PuO₂ and PuF₃ were measured in transmission mode, while the rest of the samples were measured in fluorescence geometry. The K edge of a Zr foil was measured for energy calibration, and used along with a third ion chamber to verify energy consistency among scans.

Data processing and linear combination fitting was done with the ATHENA program [3]. Results, figure 2, indicate most of the plutonium reduced to Pu(III).

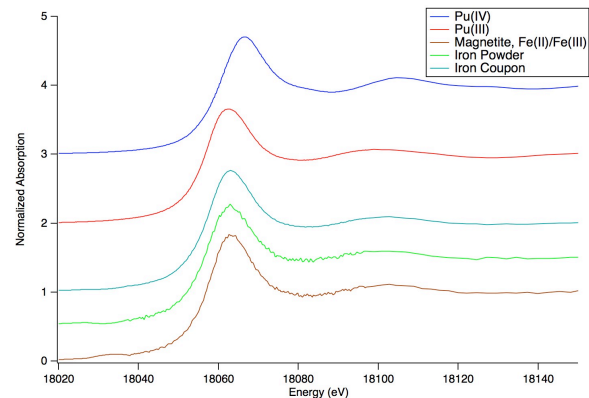


Fig. 2. XANES of precipitates/corrosion products from extended equilibration study. Analysis indicated reduction of initial Pu(VI) in solution to Pu(III), as shown by comparison with Pu(III) and Pu(IV) standards.

Experiments done from the undersaturation approach using simplified MgCl_2 and CaCl_2 brines [4] indicated solubility would be controlled by either Pu(III) or Pu(IV) depending on pH. For WIPP brine systems these new results suggest that initial plutonium present in solution will be rapidly reduced to Pu(IV), and eventually will be reduced to Pu(III) by a mechanism operating at a longer time scale.

FUTURE DIRECTIONS

The ultimate goal is to understand the underlying thermodynamics of plutonium in complex brine systems. In order to model the solubility controlling phases of these systems they must first be identified. Extended x-ray absorption fine structure (EXAFS) spectroscopy is capable of identifying the number and geometry of near neighbor atoms, however, these scans require significantly more time than XANES scans. With such long exposures, these samples begin to suffer oxidation state changes as a result of damage caused by the intense x-ray beam. The issue of how to acquire spectra on these kinds of delicate samples must first be addressed.

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The GeoPolitics of Energy: Achieving a Just and Sustainable Energy Distribution in The U.S., Germany and the World

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The U.S. and the EU are at a crossroads in their economic and national security that will determine the strength and leadership at home and in the world for the next century. This critical point involves our sources of energy, both their quantity and quality. As has happened throughout history, great nations have risen and fallen on how well they embraced new energy sources and technologies and incorporated them into their societies. The present energy dilemma is similar in nature, only this time, because of the magnitude of humanity's energy needs, we are not on a verge of another single energy source, but of a multitude of various sources and applications, all of which must be developed to their full potential if we are to attain a sustainable energy production that will allow our economy to grow without intermittent shortages, security vulnerabilities, extreme costs or environmental catastrophe.

Unfortunately, the sheer magnitude of humanity's energy consumption, presently 15 trillion kW-hrs/year growing to well over 30 trillion kW-hrs/year by 2040, is limiting this diversity and increasing our reliance even more on fossil fuels. Unless renewables and nuclear capture over two-thirds of this energy production, CO₂ emissions will not decrease at all, but will increase dramatically. And because most of this accelerating growth in energy consumption is occurring in developing countries, changes within the U.S. or Germany will have little effect unless it is to lead the world in replacing coal by the new designs for nuclear and renewable energy systems. Coupled with this growth is the ethical need to provide each person in the world with about 3,000 kW-hrs/year of energy, the amount needed to lift a person out of poverty and

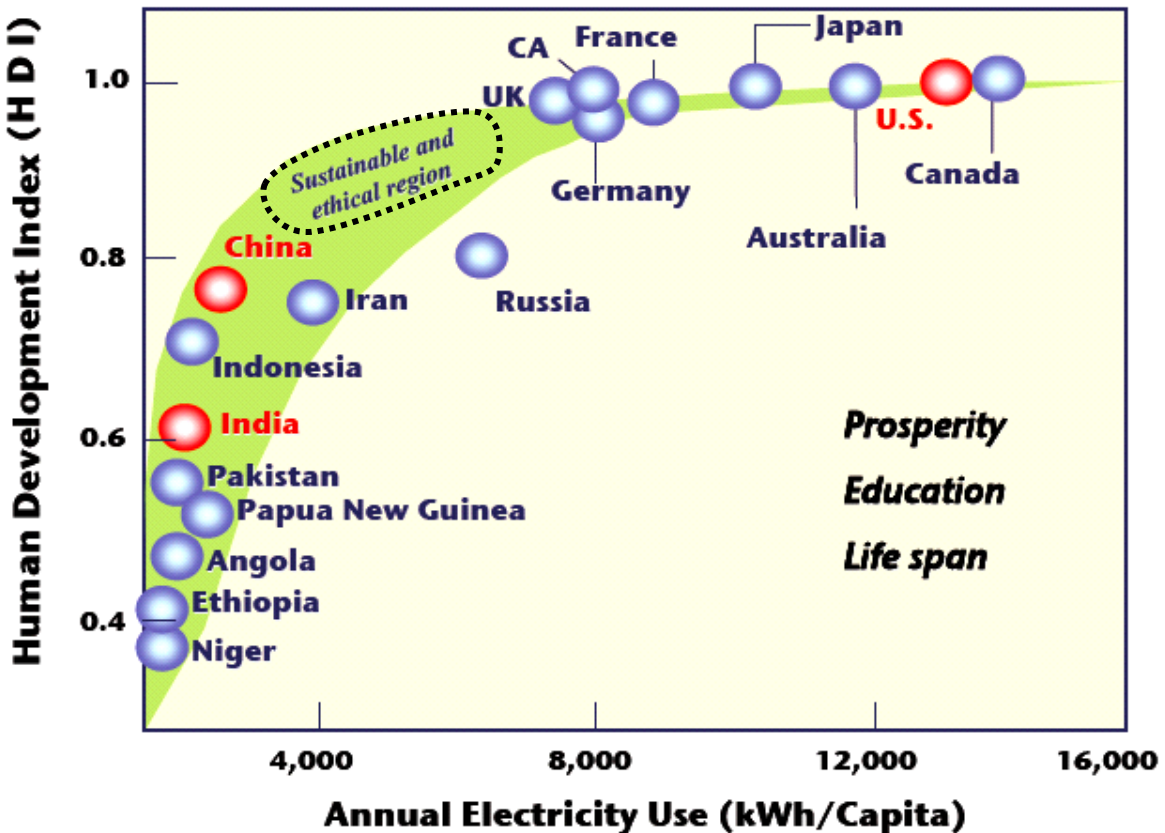
above 0.8 on the United Nations Human Development Index. Along with this change comes increased life span, decreased population growth, and decreased terrorism and war. This relationship is embodied in the Human Development Index (HDI), the United Nations' measure of quality of life, which tracks closely with a nation's per capita electricity use (Figure 1).

Therefore, a rational mix of energy sources needs to be achieved quickly ($\frac{1}{3}$ -fossil fuel, $\frac{1}{3}$ -renewables and $\frac{1}{3}$ -nuclear), each source generating over 10 trillion kW-hrs/year, the amount generated by all fossil fuels in the world today. The technical and distribution hurdles facing renewables may be overcome in time to generate 10 trillion kW-hrs/year by 2040 if huge resources are committed to development, as they should be. Nuclear can immediately begin replacing coal, producing over 10 trillion kW-hrs/year by 2040 with its new designs and non-proliferating strategies, but only if aggressively pursued over the next ten years. Because of false comparisons with nuclear weapons, most Americans and Germans are unaware that nuclear energy has been the cleanest, safest, most effective producer of electricity with the smallest environmental footprint of any source, even renewables. And the nuclear waste problem has quietly been solved in southeastern New Mexico with little fanfare. The thick, bedded, undisturbed Permian Salado salt formation set aside for this purpose is easily able to host all the nuclear waste that could ever be produced in the next thousand years. Other thick salt deposits occur around the world, including Germany, and these deposits must be developed as much as possible for regional and central permanent nuclear repositories.

The costs, risks, benefits and consequences of any energy path forward must be communicated to the public and to policymakers in a way that is understandable without too much simplification. We believe such a communication strategy can and has been developed, and will be presented here. Without a comprehensive push for both renewables and nuclear, humanity will not avert environmental and economic catastrophe by 2040, and we will not be able

to prevent world-wide weapons proliferation. This $\frac{1}{3}-\frac{1}{3}-\frac{1}{3}$ mix requires committed leadership amongst the nations of the world, especially the U.S. and Germany, with an understanding that failure will result in developed nations losing their high standards of living and developing nations losing the opportunity to achieve such standards, while the planetary ecosystem teeters on the brink of collapse.

Figure 1. The United Nations Human Development Index (HDI). 80% of the world's population of 6.5 billion people is below 0.8 on the HDI. It is no coincidence that this is the region of the world's greatest social problems. We will not end global poverty, terrorism, war or genocide until everyone is above 0.8 HDI or about 3,000 kWhrs per person per year. If we raise everyone in the developing world up to 3,000 kWhrs per person per year, and rein in the industrialized world to about 6,000 kWhrs per person per year, then the total sustainable energy requirement for the world will level at about 30 trillion kWhrs per year by 2040. Germany and the UK are approaching sustainability. Note that China is a combination of 500 million above 0.9 with over 5,000 kWhrs and 800 million below 0.5 with less than 1,000 kWhrs. Secondary effects from the form of government are seen in Russia and Iran who are lower on the HDI than is warranted by their energy use.



Chemistry of An(III,IV)/Ln(III) *eigencolloids*: complexation reactions with inorganic and organic ligands

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INTRODUCTION

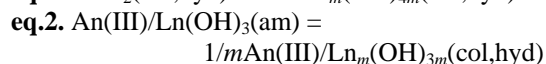
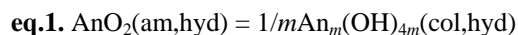
Colloids involving actinides (An) are often classified in *eigencolloids* (actinide self-aggregation) and pseudo-colloids (An-ions/complexes sorbed on Al-, Si-, Fe- ... colloids). Although widely recognized to contribute to radionuclide mobilization, the current state of knowledge on the responsible mechanisms is far from satisfactory.

Several publications have reported a significant stability of Pu(IV) and Th(IV) *eigencolloids* in neutral to alkaline solutions [1-3], which cannot be explained by classical aggregation theories like DLVO (Derjaguin-Landau-Verwey-Overbeek, [4,5]). A number of experimental evidences also indicate that An-*eigencolloids* could interact with ligands available in solution, potentially affecting An solubility/sorption behavior. In this presentation, several examples have been selected from published literature data to explore the concept of An-*eigencolloid* formation and complexation with inorganic and organic ligands.

DISCUSSION OF SELECTED EXAMPLES

Formation of neutral $An_m(OH)_{4m}(col,hyd)$ and $An(III)/Ln_m(OH)_{3m}(col,hyd)$

The solubility of $AnO_2(am,hyd)$ and $An(III)/Ln(OH)_3(am)$ in the neutral to alkaline pH range is very low ($10^{-11}M$ to $10^{-8}M$), and mostly controlled by the formation of the monomeric neutral species $An(OH)_4(aq)$ and $An(III)/Ln(OH)_3(aq)$. In the absence of appropriate separation procedures (ultrafiltration-ultracentrifugation), several authors have systematically quantified An(IV) and An(III)/Ln concentrations 1.5 to 3 orders of magnitude higher [1-3, 6]. The pH-independent character of this observation for the pH-range 7-13 suggests that, in analogy to monomeric species, neutral colloidal species coexist in the aqueous phase (eq.1 and eq.2). These colloids have been shown to be also stable at high ionic strengths (5M NaCl and 2.5M $MgCl_2$ [2]).



Complexation of ISA and CO_3^{2-} to $An_m(OH)_{4m}(col,hyd)$

The solubility of $PuO_2(am,hyd)$ at pH=12 in the presence of ISA (isosaccharinic acid) was studied in [7,8]. As discussed in [9], the solubility observed by the authors

in absence of ISA was far above that calculated for $PuO_2(am,hyd)$ when using the NEA Thermodynamic DataBase [10]. The possibility of oxidation to Pu(V) was also discussed and ruled out in [9]. Interestingly, $\log[Pu]$ reported by the authors at low [ISA] (-8.2, see Fig. 1) is virtually the same as $\log[Pu(IV)(col)]$ reported in [1] (-8.3 ± 1.0). [7,8] were looking at the effect of ISA on $Pu_m(OH)_{4m}(col,hyd)$. According to the chemistry of monomeric An(IV)-ISA complexes [9], eq.3-5 can be proposed and the corresponding logKs calculated to fit experimental data shown in Fig. 1.

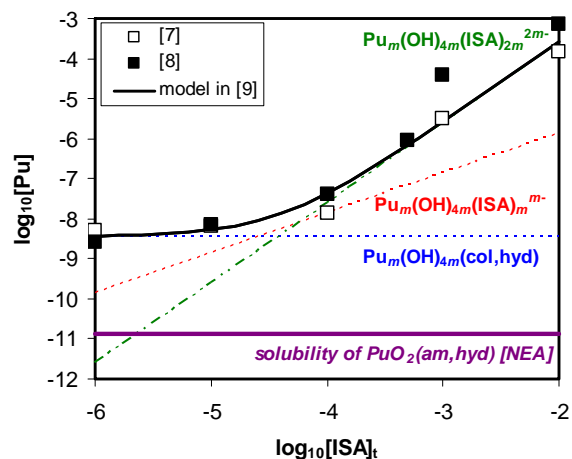
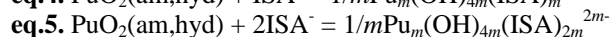
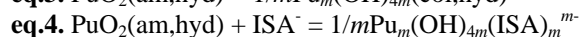
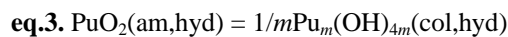
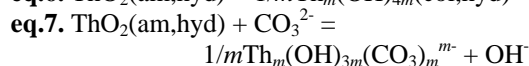
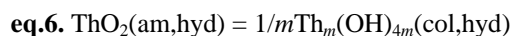


Fig. 1. Effect of ISA on colloidal Pu(IV) at pH=12.

The solubility of $ThO_2(am,hyd)$ in presence of carbonate was studied in [11] and thoroughly revisited in [12]. As shown in [12], the lack of adequate ultrafiltration/ultracentrifugation and the resulting presence of mixed Th-OH- CO_3 colloids led to overestimated solubilities in [11]. Considering the slope of the “colloidal” solubility curve (b in Fig. 2), as well as the analogous monomeric species prevailing in this pH range and $[CO_3^{2-}]$, equations eq.6-7 could be proposed and data in the “colloidal region” of Fig. 2 fitted. $\log K(eq.6)$ reported in [2] (in absence of carbonate) was satisfactorily used in these calculations.



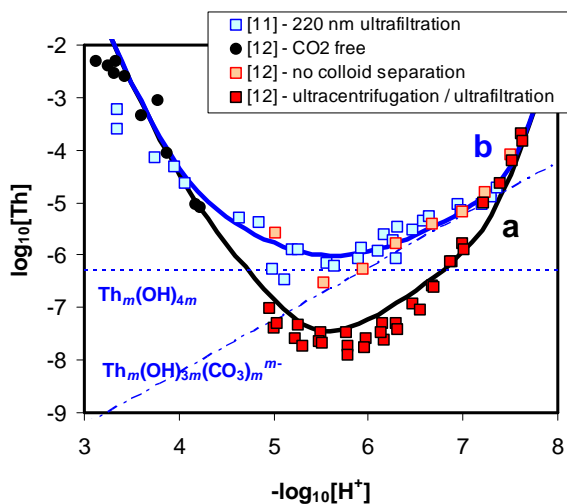


Fig. 2. Effect of carbonate on the solubility of $\text{ThO}_2(\text{am,hyd})$ as reported in [11,12]. $p\text{CO}_2 = 0.1$ bar. **a.** solubility curve calculated with NEA TDB [13]; **b.** solubility curve calculated including colloidal species described in eq.6-7.

SUMMARY

Experimental evidences from An(IV) and Ln(III) suggest that An-*eigencolloids* are not inert and respond to chemical boundary conditions. The examples shown in this contribution also indicate that these *eigencolloids* may keep strong similarities with the original monomeric species in terms of reaction stoichiometry. As the examples above can provide only a first indirect evidence of this behavior, the concept of “colloid chemistry” should at present be considered as a working hypothesis. However, being both scientifically rewarding and possibly relevant for the Safety Case, we consider this topic deserving further attention in the future.

ACKNOWLEDGEMENTS

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Formation of Actinide (IV) colloids in saline solutions

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INTRODUCTION

Colloids are known to enhance heavy metal transport in aquifers either by formation of pseudocolloids or by formation of intrinsic colloids. In solutions of high ionic strength, however, colloids are expected to be unstable. According to DLVO theory [1] charge neutralization of their surface should induce aggregation followed by precipitation of colloids. However, this is contradictory to what is observed for polymers and colloids of tetravalent actinides. A considerable colloidal fraction is stable over extended time periods even at $I=0.5M$ or higher.

DESCRIPTION OF THE WORK

Investigations of colloid stability in solutions containing up to 2.6 mol/kg NaCl are performed using thorium, representing the tetravalent actinides.

Preparation

For the stock solutions $Th(NO_3)_4 \cdot 5H_2O$ (p.a.), NaCl (p.a.) and HCl(ultrapure) are purchased from Merck. For further purification, NaCl is recrystallized twice. Colloid free thorium stock solutions are obtained by double filtrations through Amicon 10 kDa ultrafilters. All solutions are prepared with ultrapure water. The aged suspensions of Th(IV) colloids have been prepared previously [2] by coulometric titration of 10^{-2} - 10^{-5} M thorium nitrate solutions at I 0.5 M(NaCl) and initial H^+ concentrations in the rang $-\log[H^+] = 2.7$ -4.1. Fresh colloidal suspensions are prepared by dilution of thorium solutions with 0.5 M NaCl of neutral pH, leading to a simultaneous decrease of [Th] and $[H^+]$ (increase of pH). In order to avoid local over-saturation the dilution experiments are performed by adding the diluents 0.5 M NaCl very slowly to the vigorously stirred thorium solutions. The colloidal Th(IV) suspensions are stored in perfluorated alkoxy (PFA) vessels in order to prevent sorption to container walls. All experiments are performed at room temperature. It is important to note that none of the suspensions contained visible precipitates.

The total thorium concentration of the samples is determined from unfiltered aliquots. The fractions of Th(IV)colloids and ionic species is determined by performing 1, 30 and 100 kDa ultrafiltration (Filtron, pore

size ca. 1.2 nm, 3.7nm and 5.6nm) respectively. Thorium concentrations are determined by ICP MS. A combination pH electrode (type ROSS, Orion) is used to determine the H^+ concentration. Four separate calibrations for $I=0, 0.5, 1$ and 2.6 are performed using x M HCl/($1-x$) M NaCl standard solutions with x in the range 0.001_0.1. This allows us to measure $-\log[H^+]$.

Results and Discussion

In [3] we reported on experiments performed at $I=0.5M$. Samples were obtained by successive dilution and acidification of stock solution. Dilution of undersaturated samples by pH neutral NaCl solution results in simultaneous pH increase and decrease of thorium concentration. Acidification by addition of HCl/NaCl mixtures allows one to enhance the solubility at constant thorium concentration. For the final solutions, prepared by successive dilution and acidification, the colloid content of the sample does not depend on the exact sequence of dilution and acidification. I.e. the colloid concentration does not depend on the preparation but only on pH and thorium concentration (and consequently on the degree of oversaturation) of the final sample. During the course of the preparation, in particular

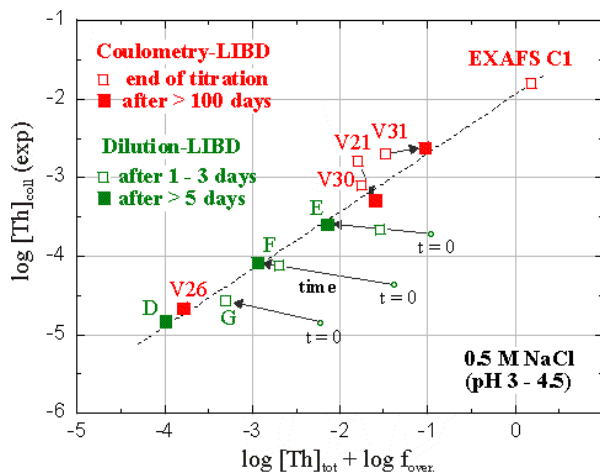
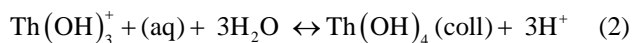
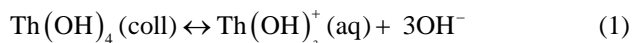


Fig. 1. The colloid content of Th(IV) solutions approaches equilibrium values defined only by the total Th concentration in solution and the degree of oversaturation, but not on the way the sample was prepared. pH drift is observed due to colloid formation and dissolution processes.

after transition from oversaturation to undersaturation, colloid dissolution may proceed very slowly. In some cases complete dissolution of colloids took more than 30 days.

Colloid formation and dissolution is accompanied by a pH change which is observed in all cases:



However, the absolute colloid content $[\text{Th}]_{\text{coll}}$ is a function of total thorium concentration and degree of oversaturation f defined by $\log f = \log [\text{Th}]_{\text{tot}} - \log [\text{Th}]_{\text{sol}}$ as depicted in Fig.1.

The second main result of this work is that Th colloids are long term stable species. Formation or dissolution processes of the colloids accompanied by a pH change according to equations (1) and (2) may proceed very slowly. However, once a steady state is achieved, the colloid content and also the mean colloid size as measured by laser-induced breakdown detection do no longer change. Some of the samples prepared by coulometric titration were proven to be stable for >400 days (Fig.2) even if they are considerable oversaturated with respect to freshly formed amorphous thorium hydroxide, which should lead to colloid aggregation and precipitation. Similar experiments at $I=1\text{m}$ and 2.6m corroborate these findings.

Electrospray mass spectrometry measurements on the stability of small thorium hydroxide polymers [4] show that these polymers grow and form up to 100nm sized colloids in an Ostwald ripening like process. From these findings we conclude that in solutions containing

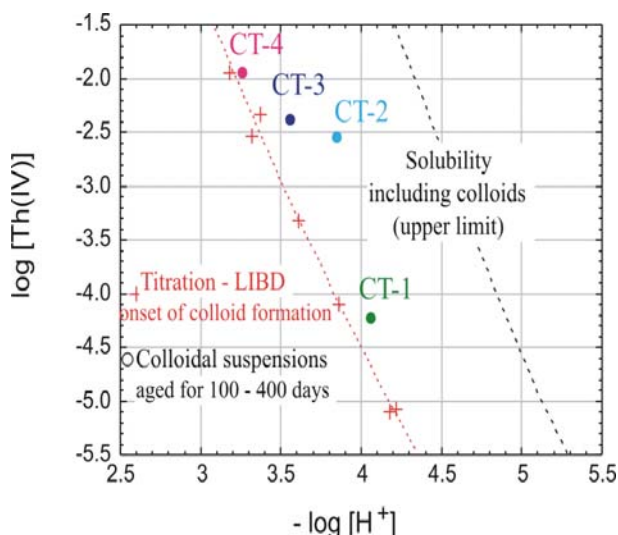


Fig. 2. Th(IV) solutions oversaturated with respect to amorphous Th(IV) hydroxide may contain considerable amounts of Th(IV) colloids. In contrast to the behavior of colloids according to DLVO theory, these colloids are stable for time periods of many years at $I=0.5\text{M}$ NaCl.

thorium colloids simultaneous formation and dissolution processes take place and that ionic species are in equilibrium with the amorphous thorium hydroxide colloids. It is, however, not clear at this point whether an ageing towards thorium oxide (so called oxolation) and formation of more crystalline ThO_2 is taking place and how a change in electrolyte (composition and concentration) may affect these reactions. Formation of (micro-)crystalline phases and also changes in particle size [5] strongly influence the solubility and as a consequence stability of colloidal phases.

FUTURE DIRECTIONS

In order to elucidate this proposed equilibrium mechanism, formation and dissolution processes should be investigated directly. One promising approach is marking Th(IV) colloids with the short lived isotope ^{228}Th and observe the enrichment of ^{228}Th in solution after addition of these colloids. Vice versa, ^{232}Th colloids could be introduced to a colloid free solution spiked with ^{228}Th . After varying interaction periods the colloids are to be separated from the solution and the ^{228}Th content be determined. Combining both results, formation and dissolution kinetics can be obtained.

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Solubility of Uranium and Thorium in Carbonate-free WIPP Brine

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INTRODUCTION

In the anoxic and strongly reducing environment expected in the Waste Isolation Pilot Plant (WIPP), uranium (IV) is predicted to be the dominant oxidation state. However, some uranium (VI) phases and aqueous species, although not expected to predominate in the WIPP, could be present due to localized oxidation effects. Consequently, in WIPP performance assessment (PA), both IV and VI oxidation states of uranium are considered. Uranium is conservatively assumed to be U(VI) in 50% of the PA vectors and U(IV) in 50% of the PA vectors. Uranium (VI) is the only VI oxidation state actinide considered in WIPP PA. Thorium (IV) is used as an oxidation-state invariant analog for IV actinides (U(IV), Pu(IV), Np(IV)). The solubility of actinides in the WIPP is expected to be defined by the combined contribution of two processes: hydrolysis with oxyhydroxide phase formation, and carbonate complexation. The focus of this paper is to estimate the contribution of hydrolysis in the solubility of the IV and VI oxidation state actinides.

DESCRIPTION OF THE WORK

Long-term experiments to establish the solubility of U(VI) and Th(IV) were performed in carbonate-free ERDA-6 and GWB brines, two simulated WIPP brines, at pC_{H^+} values between 6.5 and 12.5.

Experimental Approach

The general experimental approach was to investigate uranium (VI) and thorium (IV) solubility from over-saturation and under-saturation. The two simulated WIPP brines, GWB and ERDA-6, were prepared at 95% of initial formulations, using reagent-grade chemicals without further purification. GWB brine simulates intergranular brines from the Salado formation at or near the stratigraphic horizon of the repository. ERDA-6 brine is representative of fluids in the Castile brine reservoirs that underlie the repository horizon. The source of uranyl ion was depleted uranium (VI) nitrate hexahydrate that was converted to a nitrate-free hydrochloric complex with an oxidation-state purity of $\sim 100\%$ for UO_2^{2+} . The source of thorium (IV) was a nitrate complex, in nitric acid. For the under-saturation experiments, uranyl precipitate obtained in the over-saturation experiments and thorium hydroxide were used.

Significant care was taken to establish carbonate-free conditions. The removal of carbonate from the brines was a two-step process. The first step consisted of acidification of the brines which converted carbonate into bicarbonate, in equilibrium with carbonic acid, then into dissolved carbon dioxide gas. The second step was to use a vacuum chamber, placed in a low-flow-through high-purity-nitrogen glove box for a slow pump-down process to smoothly remove gas from the brine.

The experiments were initiated by the addition of uranyl (or thorium) into the pC_{H^+} -adjusted solutions. The solutions were kept in a nitrogen-controlled atmosphere for the duration of the experiments. Aliquots were periodically removed, centrifuged and filtered through Microcon[®] Millipore centrifugal filters with a nominal molecular weight limit of 30,000 Daltons. Filtrates were analyzed for uranium or thorium content using inductively coupled plasma mass spectrometer (ICP-MS). More details on these experiments can be found elsewhere [1- 4].

Results and Discussion

The measured solubility of Th(IV) and U(VI) in carbonate-free brines is plotted as a function of pC_{H^+} in Fig.1 and Fig.2 respectively.

The thorium solubility measurements from under- and over-saturation were similar in both brines over the investigated pC_{H^+} range (Fig.1). The average thorium concentration was equal to $7 \times 10^{-7} M$. This value depended on neither the pC_{H^+} , nor the composition of the brine. This suggests that the solubility-controlling phase is certainly a thorium hydroxyl oxide $Th(OH)_2$. The solubility of Th(IV) measured in our systems were in good agreement with the values of colloidal and dissolved species reported in the literature in similar experimental conditions [5]. At high pC_{H^+} , no effects of amphotericity were observed.

The solubility of uranium measured in carbonate-free ERDA-6 and GWB was different over the investigated pC_{H^+} range (Fig.2). At $7 \leq pC_{H^+} \leq 9.2$, the solubility of uranium (VI) in carbonate-free GWB brine was found to be approximately $10^{-6} M$ (between $8 \times 10^{-7} M$ and $5 \times 10^{-6} M$). The variation of the solubility with pC_{H^+} was small in the range of pC_{H^+} where steady state concentrations were established (7-9.2). The slight increase in the middle of this pC_{H^+} range (~ 8.1) is not significant, but may reflect a small effect of borate complexation, like it was discovered in neodymium solubility experiments [2].

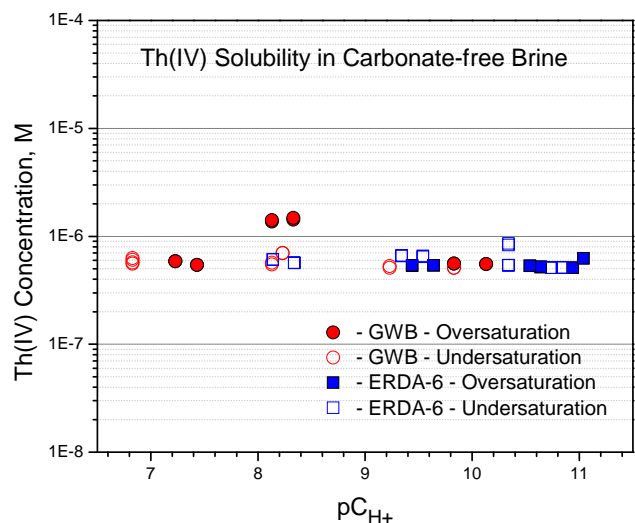


Fig. 1. Measured solubility of thorium (IV) in carbonate-free brine from under- and over-saturation versus pC_{H^+} .

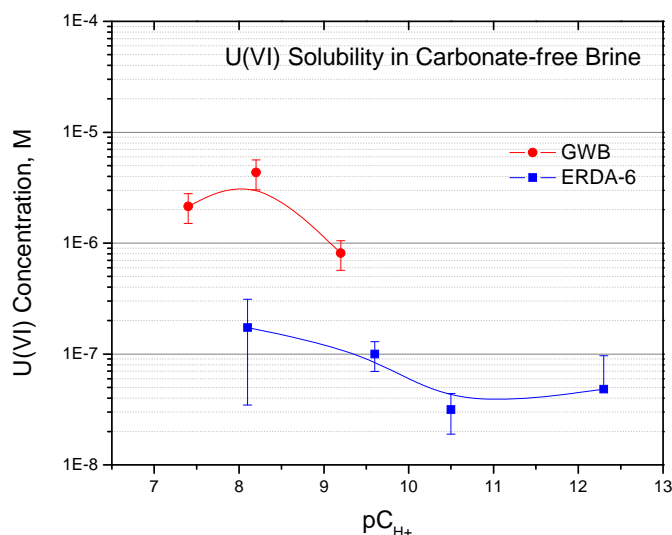


Fig. 2. Measured solubility of uranium (VI) in carbonate-free brine from under- and over-saturation versus pC_{H^+} .

From pC_{H^+} 8 to 11, the solubility of uranium (VI) in carbonate-free ERDA-6 brine was in the range 10^{-8} to 10^{-7} M, specifically this was between 3.1×10^{-8} M and 2.3×10^{-7} M. This solubility decreased slightly from $pC_{H^+} \sim 8$ to $pC_{H^+} \sim 11$.

At $pC_{H^+} \sim 12.3$, which is beyond the chemical stability of ERDA-6, the solubility of uranium (VI) in carbonate-free solution was $\sim 4.8 \times 10^{-8}$ M. This solubility was within the range of the data measured at $pC_{H^+} \geq 8$. The presence of a precipitate from the brine components prior to the beginning of the experiments did not impact the solubility of uranium (VI). Under these experimental conditions we did not see evidence for significant amphotericity and

there was no significant effect of borate complexation on the solubility trends observed.

The solubility of thorium (IV) was found superior to the solubility of uranium (VI) in carbonate-free ERDA-6 brine. This was likely due to the nature of the thorium species that form colloids in our experimental conditions. The colloidal fraction of the thorium species was included in our measurements.

Conclusion

The solubility data presented herein were the first WIPP repository-relevant data for the IV and VI actinide oxidation states. They were the first data generated at high pC_{H^+} under conditions that we believe to be truly carbonate-free. They established uranium (VI) solubility, in the absence of carbonate that was 10-100 times lower than results published by others [6]. The uranium (VI) solubility measured in our experiments was about 10^{-8} - 10^{-7} M at $pC_{H^+} \geq 8$ in ERDA-6, and between 8×10^{-7} M and 5×10^{-6} M at $7 \leq pC_{H^+} \leq 9.2$ in GWB. The thorium (IV) solubility was higher, about 7×10^{-7} M in both brines, and was in good agreement with the literature data [5]. No amphotericity effects were found at high pC_{H^+} values for the two actinides.

FUTURE DIRECTIONS

These data in carbonate-free brine provided a baseline for carbonate effects on U(VI) and Th(IV) solubility, during the ongoing research program in actinide solubility under WIPP-relevant conditions. Future directions of this work are twofold: identify the solid phases obtained in the experiments described herein, and conduct similar experiments in the presence of carbonate.

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Plutonium Oxidation State Distribution in High Ionic Strength Systems

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INTRODUCTION

Plutonium is the most important multivalent actinide with respect to release from the WIPP repository. Under the wide range of possible conditions in the WIPP it can exist in the III, IV, V and VI oxidation state. Its solubility, and hence its mobility, is highly dependent on the distribution of these oxidation states throughout repository history. For the expected repository scenario, which is an iron-rich anoxic environment, only the lower oxidation states, Pu(III) and IV) will be predominant. Current WIPP PA assumes that Pu(III) is the plutonium oxidation state in the reduced PA vectors (50%) and as Pu(IV) in the oxidized PA vectors (50%). Although transient concentrations of Pu(V/VI) can exist due to radiolysis and localized chemical effects, these are expected to be quickly overwhelmed by the reducing conditions expected.

In the WIPP, the two most important reduction pathways for actinides are reduction by reduced iron, Fe(0/II), or bioreduction by halo-tolerant microorganisms. These pathways, to various extents, have been established¹⁻³ under WIPP-relevant conditions and there is now significant data for the reduction of Pu(V/VI) to Pu(III/IV). The remaining and key question is the relative importance of the two reduced oxidation states throughout the expected WIPP repository history. Overall, the understanding these reduction pathways, and their synergisms, is critical to establishing the release of plutonium from a salt-based repository.

PLUTONIUM REDOX EXPERIMENTS

Plutonium²⁴², as Pu³⁺ and PuO₂²⁺, was used in the experiments performed to minimize radiolytic effects. A range of simulated or simplified groundwaters¹⁻³ was also used. The initial oxidation state was determined using absorption spectrometry (CARY 5000). Liquid scintillation counting and ICP-MS were used to determine total concentration. Aqueous iron chemistry was analyzed using a combination of a FerroZine® colorimetric method⁴ and ICP-MS. XANES was used to establish the oxidation state of the precipitated or bio-associated plutonium.

Iron reduction experiments were carried out by adding iron and iron oxides to stable anoxic Pu(VI) solutions as a function of pH. The reactivity of Fe²⁺ and Fe³⁺ towards various plutonium oxidation states was also

established. Organic interaction studies were performed by equilibrating Pu(VI) or Pu(III) solutions with citrate and EDTA to establish oxidation state changes and trends. Microbial interaction studies were performed with *shewanella sp.*, which are known facultative metal reducers, according to existing procedures^{2,5}.

RESULTS

Plutonium Oxidation State Distribution in the Presence of Reduced Iron

The oxidation state distribution of plutonium in simulated brine under anoxic conditions at pH ~ 9 and in the presence of iron and iron oxides was established. Pu(VI), in the absence of reduced iron, is stable under the conditions of our experiments. The additions of reduced iron, as iron coupons, iron powder, magnetite or Fe²⁺(aq) led to the relatively rapid reduction of Pu(VI) to initially form Pu(IV) phases (see Fig. 1). This was confirmed by XANES analysis of the Fe-associated plutonium. In contrast, ferric oxide led to the formation of Pu(V).

At longer times, however, further reduction of the precipitated/associated Pu(IV) to a Pu(III) solid was observed. This was also confirmed by XANES analysis (see Fig. 2). The mechanism for this further reduction process is not yet clear. These longer-term data show greater agreement between what is predicted thermodynamically and what is experimentally observed under the strongly reducing conditions in these iron-dominated brine systems.

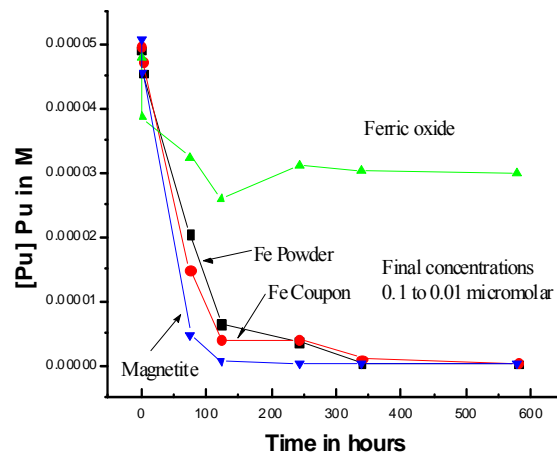


Fig. 1. Reduction of Pu(VI) by reduced iron in brine at pH ~ 9

Effect of Organic Chelating Agents on the Plutonium Oxidation State

Strong organic chelating agents such as citrate and EDTA affect the oxidation state distribution of plutonium⁶ by stabilizing oxidation states through complexation and by direct reaction with plutonium to oxidize Pu³⁺ and reduce the higher valent PuO₂⁺ and PuO₂²⁺. The predominant plutonium speciation in these solutions was Pu(IV) organic complexes. This effect argues for the predominance of Pu(IV) in abiotic systems.

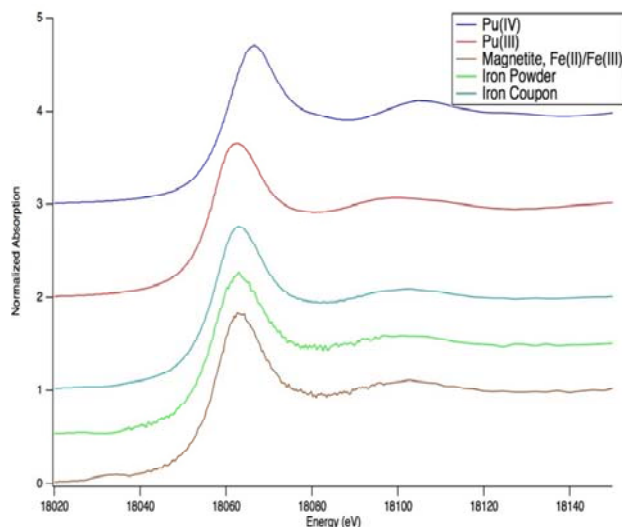


Fig. 2. XANES analysis of Fe-associated plutonium after ~ four year under anoxic conditions in WIPP brine (Argonne APS courtesy of Dr. Jeff Terry and Dan Olive – IIT)

Oxidation State Distribution in Microbiologically Active Systems

Shewanella sp., which are facultative metal reducing soil bacteria, reduced higher-valent plutonium to Pu(III) and Pu(IV) depending on the presence and absence of complexants that stabilized Pu(IV) in solution (see Fig. 3). The Pu(IV) → Pu(III) reduction step appeared to be primarily enzymatic although there was strong coupling with abiotic reduction by Fe²⁺(aq).

The combined effect of iron reduction, complexation/redox effects of organics, and anaerobic microbial activity is to establish the low-solubility Pu(III) and Pu(IV) species as the predominant mobile species in anoxic groundwater systems.

FUTURE DIRECTIONS

Future research will address the mechanistic aspects of plutonium redox control and distribution under increasingly relevant salt repository conditions. Specifically the bioreduction work will be extended to

halo-tolerant microbes and the linkages between iron and plutonium redox chemistry in more simplified systems will be explored. These will also focus on the relative stability of the Pu(III) and Pu(IV) oxidation states under abiotic and biotic conditions.

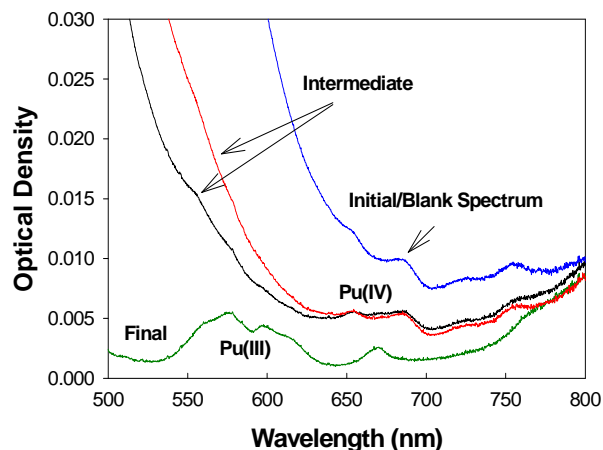


Fig. 3. The bioreduction of Pu(V/VI) to Pu(III) by *S. putrefaciens* when NTA is present as a chelating agent.

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Plutonium Redox Processes in Aqueous Systems

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INTRODUCTION

The disposal of nuclear waste in deep geological formations demands an adequate description of the redox behavior of Pu in aqueous solution. Iron minerals are widespread in the environment and can be formed inside a repository by corrosion of steel canisters or construction materials. Their interaction with actinides and impact on redox chemistry needs to be understood for reliable performance assessment calculations.

In the present study we have investigated the sorption and redox behavior of aqueous Pu(III) and Pu(V) in presence of synthetic nanocrystalline iron mineral suspensions and in homogeneous redox buffer solutions by using a combination of classical wet chemistry methods and advanced spectroscopy (XANES, EXAFS). The impact of the redox conditions (pH + E_H) in solution / suspension on the oxidation state distribution of Pu is studied by comparing the results to thermodynamic model calculations.

EXPERIMENTAL

For the Pu experiments in presence of heterogeneous iron suspensions, ten matrix solutions were prepared by equilibration of different synthetic iron minerals in 45 ml 0.1 M NaCl at pH 6 to 8 (table I). All experiments were carried out at room temperature in Ar or N₂ glove boxes (O₂ < 10 ppm).

Table I. Experimental conditions for the heterogeneous Pu samples. SSR describes the solid to solution ratio of the iron minerals in the samples.

Mineral suspension in 45 ml 0.1 M NaCl	SSR [g/l]	pH	[Pu(III)] ^o [M]	[Pu(V)] ^o [M]
Maghemite (γ -Fe ₂ O ₃)	5.6	6	1.2·10 ⁻⁵	---
Magnetite (Fe ₃ O ₄)	5.5	6	1.2·10 ⁻⁵	---
Magnetite (Fe ₃ O ₄)	5.5	8	1.2·10 ⁻⁵	---
Mackinawite (FeS)	2.0	6	1.2·10 ⁻⁵	---
Hematite (α -Fe ₂ O ₃)	11.5	8	---	1.3·10 ⁻⁵
Goethite (FeOOH)	2.0	8	---	1.3·10 ⁻⁵
Maghemite (γ -Fe ₂ O ₃)	5.6	6	---	1.3·10 ⁻⁵
Magnetite (Fe ₃ O ₄)	5.5	8	---	1.3·10 ⁻⁵
Siderite (FeCO ₃)	3.4	8	---	1.3·10 ⁻⁵
Mackinawite (FeS)	2.0	8	---	1.3·10 ⁻⁵

After addition of electrochemically prepared ²⁴²Pu(III) or ²⁴²Pu(V) stock solution (initial concentration: 1.2·10⁻⁵ M Pu(III) and 1.3·10⁻⁵ M Pu(V), respectively) the samples were analyzed for pH, redox potential E_H and Pu concentration after 10kD ultrafiltration over a period of 40 days. The Pu adsorbed on the iron solids was investigated by XANES / EXAFS at the Rossendorf Beamline at ESRF. Samples were shock-frozen in LN₂ and measured at 15 K to avoid oxygen and/or photon-induced changes of the Pu oxidation state.

In addition to the systems with solid iron phases, the redox behavior of ²⁴²PuO₂⁺(aq) (1.0·10⁻⁴ M in 10 ml 0.1 M NaCl) was studied at pH 4 – 8 in homogeneous solution with chemically different reducing systems: 1 - 3 mM Na₂S₂O₄, FeCl₂/FeCl₃ buffers (10:1), hydroquinone and sodium anthraquinone / anthrahydroquinone disulfonate redox buffers. The reduction of Pu(V) was monitored as a function of (pH + E_H) and time (up to 150 days) by analyzing the solution for Pu concentration and speciation (LSC, UV-vis, PMBP / HDEHP extraction).

NEA data were used for the thermodynamic model calculations [1]. Missing complex formation constants and SIT interaction coefficients for Pu(III), Pu(V) and Pu(VI) were estimated from data for Am(III), Np(V) and U(VI) analogues.

RESULTS

In all of the four heterogeneous samples with additions of Pu(III), sorption was the main process. Within few minutes the initial [Pu] decreased by more than 90%. The predominant Pu species on the mineral surfaces after 40 days reaction time is monomeric Pu(III) as determined by XANES and EXAFS analysis. Major contributions of higher oxidation states were only observed for the Maghemite system (60% Pu(III) / 40%Pu(IV)). The six heterogeneous samples with Pu(V) showed a more complex behavior. Besides sorption onto the mineral phases, reduction to Pu(IV) or Pu(III) occurred in all cases, even in systems containing pure Fe(III) minerals.

Both, the redox stability of Pu(III) and the reduction of Pu(V) can be understood if the redox conditions for each sample are compared to thermodynamic

calculations. The measured pH and E_H values are far away from the stability field of Pu(V) and close to the borderline calculated for the equilibrium $\text{Pu(III)} \rightleftharpoons \text{Pu(IV)}$ in the predominance diagram of Pu.

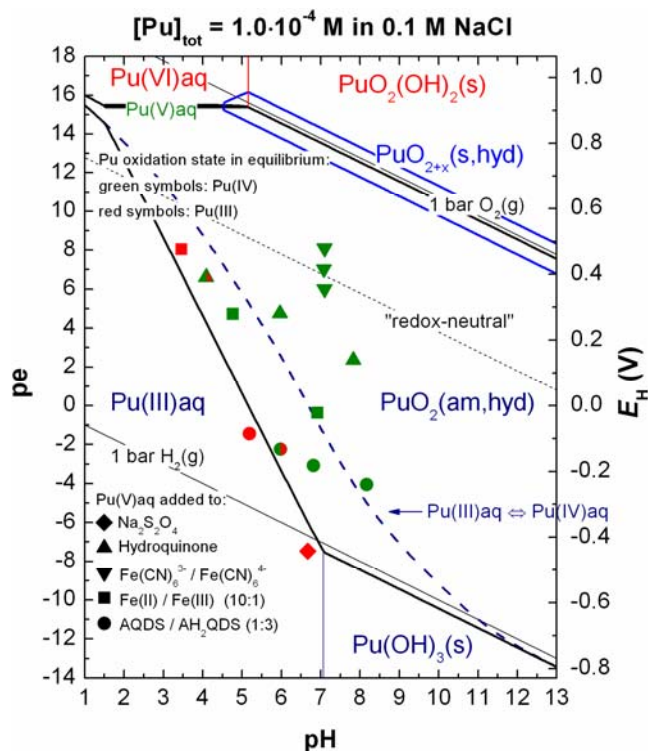


Fig. 1. Measured pH and E_H (pe) values for the Pu experiments in homogeneous redox buffer solutions plotted in the predominance diagram of Pu. Red symbols: predominant Pu oxidation state after reaction: Pu(III). Green symbols: Pu(IV).

These observations are supported by the results obtained for a series of Pu(V) redox experiments in homogeneous solution with similar redox conditions as present in the iron suspensions (figure 1): the initial Pu(V) was reduced very fast to Pu(IV) in samples where the ($E_H + \text{pH}$) values were in the stability field of Pu(IV) while mixtures of Pu(IV) / Pu(III) were obtained if the redox conditions were close to the borderline $\text{Pu(III)} \rightleftharpoons \text{Pu(IV)}$.

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Complexation of Actinides by Organic Ligands and Borate Ions

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INTRODUCTION

Organic chelating agents are used in the processing and cleanup/decontamination of actinides throughout the DOE complex. For this reason, they are often present as contaminants with the TRU component in the WIPP waste. Some of these chelating agents strongly complex actinides and could have a significant effect on their solubility in brine. In this context, four organic chelating agents – oxalate, acetate, citrate, and EDTA – are tracked as part of the WIPP inventory process, and the potential effects of these complexants on the calculated actinide solubilities are evaluated as part of the WIPP Performance Assessment (PA).

Beside of actinides other metals will be present in the brine. Transition metal ions will corrode and dissolve into the brine. These ionic species include iron (Fe) and lead (Pb). Other steel constituents, such as nickel (Ni), chromium (Cr), vanadium (V), and manganese (Mn), may also be present. Additionally, divalent cations, most importantly Mg^{2+} and Ca^{2+} , will also be present and will form complexes with organic chelating agents. The formation constants for these metals, in many respects, follow the same trends as the actinide species and, when present in high enough concentrations, will compete with the actinide to form complexes and effectively lower the effect of organic complexation on actinide solubility. Many Pitzer parameters for these species are not available and cannot be included in the PA.

DESCRIPTION OF THE WORK

The potential concentrations of the key organic ligands in the WIPP used in the CRA-2009 PABC were calculated by Brush and Xiong (2009)¹ based on the inventory provided by Crawford et al. (2009)². These concentrations are summarized in Table I, where the potential maximum organic concentration in the WIPP is defined as the inventory amount of the organic ligand divided by the minimum volume of brine needed for the direct brine release (Clayton 2008)³.

Table I. Concentrations of Organic Ligands in WIPP Brine Calculated for use in the CRA-2009 PABC (Brush and Xiong 2009)¹.

Organic Ligand	Compound	Total Potential Concentration ^a (M)
Acetate	Acetic acid Sodium acetate	1.94×10^{-2}
Oxalate	Oxalic acid Sodium oxalate	^b 1.73×10^{-2}
Citrate	Citric acid Sodium citrate	2.38×10^{-3}
EDTA	Sodium salt	6.47×10^{-5}

^a Inventory, in moles, of the organic chelating agent divided by 17,400 m³

^b Concentration of oxalate will be limited by solubility, not inventory, in ERDA-6-like brine

The effects of all four organic ligands on Nd(III) solubility (analog for An(III)) and Th(IV) (analog for An(IV)) in the range of concentrations listed in Table I were measured in two brines: GWB and ERDA-6.

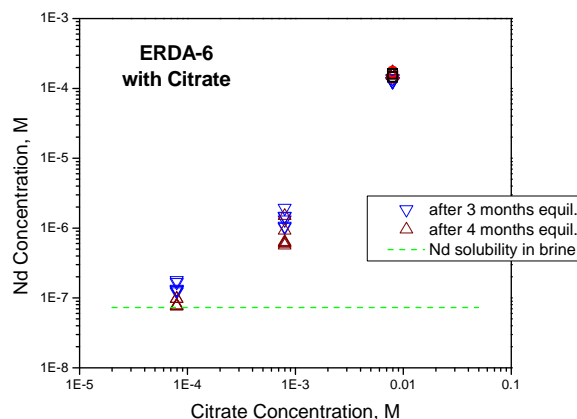


Figure 1. Effect of citrate concentration on Nd(III) solubility in ERDA-6 brine

A significant effect of EDTA and citrate (Figure 1) anions on An(III) solubility was confirmed. In GWB, the high Mg concentration effectively competes with An(III) for the organic ligands.

The oxalate is solubility-limited at a concentration that is smaller than theoretically achievable based on its inventory amount. Synergistic effect affecting mutual solubility of organics was observed. Acetate and oxalate do not affect An(III) solubility.

Thorium solubility was not affected by any of the organic ligands. An(III) complexation by tetraborate ions (brine component) was measured and a slight effect on An(III) solubility was noted. The effect of tetraborate ions on An(III) solubility was compared with those for U(VI) and are presented in Figure 2).

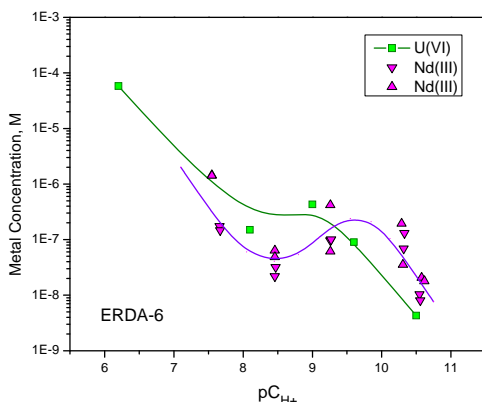


Figure 2. Effect of tetraborate on An(III) and An(VI) solubility.

CONCLUSIONS AND FUTURE WORK

There are two final, but important, observations about the organic chelating agents present in the WIPP. First, they are expected to have very different tendencies toward biodegradation, based on extensive experience with soil bacteria in the literature (Banaszak, Rittmann, and Reed 1999)⁴. This important degradation pathway is not as certain for EDTA, which tends to resist biodegradation in most groundwaters. These degradation pathways have, however, not been demonstrated for the halotolerant microorganisms typically present in the WIPP, and it

is currently assumed in the WIPP PA that no degradation pathways for these organic complexants, microbiological or chemical, exist.

The second important observation is that these chelating agents, under WIPP-relevant conditions, are expected to help establish reducing conditions in the WIPP because they tend to reduce higher-valent actinides. This has been demonstrated in WIPP brine for Np(V) and Pu(V/VI), but was not observed for U(VI) (Reed et al. 1998)⁵.

These potentially beneficial effects of organic chelating agents on actinide speciation are also currently not included in the WIPP PA and will be investigated.

Solubility and Pitzer parameters for Fe^{2+} and Pb^{2+} , the two major competitors for organic ligands, have to be measured and used in WIPP PA.

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Overview of WIPP Geochemical Modeling¹

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The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy (DOE) repository in southeast New Mexico for defense-related transuranic (TRU) waste. The repository, which opened in March 1999, is located at a subsurface depth of 655 m in the Salado Fm., a Permian bedded-salt formation. After filling the repository with TRU waste and installation of panel closures, creep closure of the salt will crush the steel waste containers in most cases and encapsulate the waste.

Anoxic corrosion of Fe-, Pb-, and Al-base metals in the waste containers and/or TRU waste; and microbial consumption of cellulosic, plastic, and rubber (CPR) materials in the waste containers and/or TRU waste could produce significant quantities of gas in the WIPP. The DOE is emplacing MgO in the WIPP to decrease the solubilities of the actinide elements in TRU waste in any brine present in the postclosure repository. MgO will decrease actinide solubilities by consuming essentially all of the CO₂ produced by microbial consumption of CPR materials (even if microbes consume all of the CPR materials in the TRU waste and/or waste containers), thereby maintaining the f_{CO_2} and pH within ranges favorable from the standpoint of actinide solubilities.

1. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.
2. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Prediction of the long-term, near-field chemical conditions in WIPP disposal rooms has included: (1) use of Generic Weep Brine (GWB)^{1,2} to simulate intergranular brines from the Salado Fm. at the stratigraphic horizon of the repository and Energy Research and Development Administration (WIPP Well) 6 (ERDA-6)³ to represent fluids in brine reservoirs in the underlying Castile Fm.; (2) the assumption that instantaneous, reversible equilibria among these brines and several of the important solids in WIPP disposal rooms such as halite (NaCl), anhydrite (CaSO₄), brucite (Mg(OH)₂), and the "5424" polymorph of hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) will control near-field chemical conditions; and (3) use of the speciation and solubility code in Fracture-Matrix Transport (FMT)^{4,5} to calculate chemical conditions. We have also used EQ3/6, versions 7.2c, 8.0, and 8.0a^{6,7} to predict near-field conditions. We expect that the brucite-hydromagnesite (5424) carbonation reaction will buffer f_{CO_2} in the repository during the first several hundred to few thousand years, but that the brucite-magnesite (MgCO₃) reaction might buffer f_{CO_2} thereafter. The calculated values of f_{CO_2} expected in the repository are 3.14×10^{-6} atm in the first several hundred to few thousand years, possibly decreasing to 1.20×10^{-7} atm after a few thousand years. The brucite dissolution-precipitation reaction will increase the pH of GWB or ERDA-6 from their mildly acidic in situ values to calculated values of 8.69 in GWB⁸ and 8.98 in ERDA-6⁸.

Predictions of actinide speciation and solubilities under the long-term chemical conditions expected in the WIPP have included: (1) solubility models based on the Pitzer activity-coefficient model for Th(IV), Np(V), and Am(III); (2) inclusion of the effects of

acetate, citrate, EDTA, and oxalate (the organic ligands in TRU waste) on Th(IV), Np(V), and Am(III) speciation and solubilities; (3) use of the speciation and solubility code in FMT to calculate the speciation and solubilities of Th(IV), Np(V), and Am(III); (4) development of solubility uncertainty ranges and probability distributions for the Th(IV) and Am(III) solubility predictions (5) redox speciation of Th, U, Np, Pu, and Am entirely as Th(IV), U(IV), Np(IV), Pu(III), and Am(III); or Th(IV), U(VI), Np(V), Pu(IV), and Am(III); (6) use of the oxidation-state analogy⁹ to apply the solubilities calculated for Th(IV) to U(IV), Np(IV), and Pu(IV); and to apply those calculated for Am(III) to Pu(III) (the model developed for Np(V) has been used only for Np(V) because Np is the only actinide expected to speciate in the +V oxidation state under the conditions predicted for the WIPP); and (7) use of a solubility estimate of 1×10^{-3} M for U(VI)¹⁰. The most recently predicted “baseline” or “nominal” solubilities (to which deviations sampled from the uncertainty ranges are added or subtracted) of Th(IV), Np(V), and Am(III) are: 5.63×10^{-8} M, 3.90×10^{-7} M, and 1.66×10^{-6} M, respectively, in GWB⁸; and 6.98×10^{-8} M, 8.75×10^{-7} M, and 1.51×10^{-6} M in ERDA-6⁸.

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ASCEM: Advanced Simulation Capability for Environmental Management

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INTRODUCTION

ASCEM, the Advanced Simulation Capability for Environmental Management, is a state-of-the-art scientific tool and approach for integrating data and scientific understanding to enable prediction of contaminant fate and transport in natural and engineered systems. The initiative supports the reduction of uncertainties and risks associated with the Department of Energy Office of Environmental Management's (DOE-EM) environmental cleanup and closure programs by better understanding and quantifying the subsurface flow and contaminant transport behavior in complex geological systems. A second aspect addresses the long-term performance of engineered components, including cementitious materials in nuclear waste disposal facilities.

The organizing methodology that drives the need for advanced computing systems is shown schematically in Figure 1. Field test or site characterization data are tightly integrated with a field test model to provide a continuously updated assessment of uncertainty in parameters and models. These uncertainties, derived from the testing analysis, are applied to predictions of system performance for the risk application of interest. Risk projections are vetted with decision makers leading to refinements of the testing program. Uncertainties and ultimately risk are systematically reduced. Major advancements in numerical model development are required to reduce the cycle time to the limit of a continuously updated assessment of uncertainty and risk.

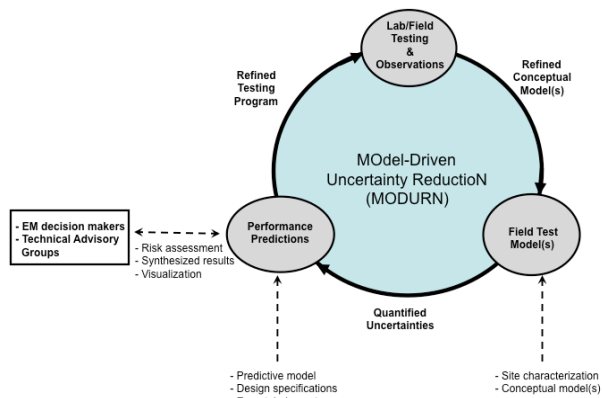


Figure 1. Schematic of the Model-Driven Uncertainty Reduction paradigm.

Within DOE Offices of Science, Nuclear Energy, and Fossil Energy there are many efforts in the development

of advanced high performance computing capabilities, as well as scientific investigations of groundwater flow and transport, source term degradation and release, and mechanical degradation of structures and barriers. By leveraging these investments, ASCEM will develop a toolset for use not only within DOE-EM, but also by the greater DOE community in the areas of geologic carbon sequestration and high-level waste repository performance. ASCEM has already established collaborative ties with each of these DOE Offices, and will strengthen these frequent interactions during the development and implementation phases of ASCEM. In addition, ASCEM staff are furthering these collaborations through investigations of new research areas.

DESCRIPTION OF THE WORK

The ASCEM modeling initiative will develop an open-source, High Performance Computing (HPC) modeling system for multiphase, multicomponent, multiscale subsurface flow and contaminant transport, and cementitious barrier and source-term degradation. The modeling tools will incorporate capabilities for predicting releases from various waste forms, identifying exposure pathways and performing dose calculations, and conducting systematic uncertainty quantification. ASCEM will demonstrate the modeling tools on selected sites and apply them in support of the next generation of performance assessments of nuclear waste disposal and decommissioning facilities across the EM complex.

A major ASCEM goal is to provide a community code for DOE-EM and the greater scientific and engineering communities. To that end, the ASCEM HPC modeling tools will be developed using an open source model, with involvement from the DOE computational science and environmental science communities. This method will allow ASCEM to leverage the considerable scientific investment that has already been made both within and outside of DOE-EM in the areas of subsurface geosciences, modeling and simulation, and environmental remediation. Through integration of these efforts, ASCEM will facilitate development of more accurate site models, allow for predictive simulation of proposed remediation methods, and prevent implementation of overly conservative and unnecessarily expensive remediation strategies. Wherever appropriate, ASCEM will use and build upon results and models developed through its associated DOE initiatives.

The ASCEM project is organized into three technical thrust areas: the Multi-Process High Performance Computing (HPC) Simulator, which constitutes the computational engine; the Platform and Integrated Toolsets, which provide the user interfaces; and Site Applications (see *Figure 2*).

The Site Applications thrust area provides the main link between ASCEM and the EM community's modeling and regulatory needs; it is vital to ensuring that ASCEM HPC modeling capabilities are widely accepted across the EM Complex. Because engaging the user community will be particularly important in the early stages of the ASCEM development, the Site Applications thrust area incorporates a "user interface" task focused on establishing contact with end users, soliciting their input about their individual sites' modeling needs, the ASCEM development plans, and conveying the feedback to members of the HPC and Platform Thrust areas responsible for the tool and code development.

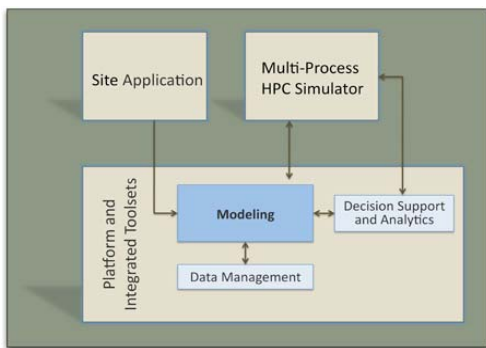


Figure 2. The 3 technical thrust areas of ASCEM: Multi-Process HPC Simulator, Platform and Integrated Toolset, and Site Applications.

The Platform and Integrated Toolset thrust will provide a standardized user interface enabling end users to create inputs, analyze outputs, and manage data associated with running simulations and performance and risk assessments. Under this thrust area, ASCEM will use a modular (or "interoperable") approach to code development, facilitating iterative and graded modeling systems that allow end-user customization for specific applications without the need for specialized computational or code development expertise. This will be accomplished by defining rigorous programming "interfaces" for each module (where an interface defines access to a module while hiding the details of its implementation). By using a common base platform available to all, this interoperable approach will support cooperation among numerous modeling groups with different methodologies and applications. This methodology has been quite successful in the past and is broadly used in similar advanced software engineering

approaches, for example, within the DOE Office of Science SciDAC program and the DOE National Nuclear Security Administration (NNSA) Advanced Simulation and Computing (ASC) program. This modular approach will also be used to develop new and complete process models that are imperative for successfully implementing performance and risk assessment approaches.

The third thrust area, the Multi-Process High Performance Computing (HPC) simulator, will provide the simulation capabilities necessary for the modeling of EM sites. The HPC Simulator will provide a flexible and extensible computational engine to simulate the coupled processes and flow scenarios described by the conceptual models developed using the ASCEM Platform. The graded and iterative approach to assessments naturally generates a suite of conceptual models that span a range of process complexity, potentially coupling hydrological, biogeochemical, geomechanical, and thermal processes. To enable this approach, ASCEM will take advantage of emerging petascale computers that handle hundreds of thousands of simultaneous process streams of information. Their use will facilitate improved uncertainty quantification and, when necessary, the use of more complex models in lieu of simplifying assumptions. These HPC-capable tools will be available on platforms from clusters to desktop computers. While there is a clear recognition that many problems will not require the highest end computing capabilities, computer architectures on today's supercomputers will be used on desktop computers in the near future (5-7 years). By developing the ASCEM modeling tools for HPC platforms, the community codes will be well positioned to run on future desktops.

FUTURE DIRECTIONS

To date, the ASCEM project has accomplished major milestones in the preparatory phases of the software development life cycle, including the development of requirements and initial design documents for the HPC simulator and platform based in the EM site end user needs. In addition, a formal process has been executed to select sites to conduct demonstration projects to evaluate and demonstrate the validity of this next-generation computational system. As the project progresses, software will be developed and tested in phases, and it will be demonstrated on increasingly complex problems that exercise its features. To engage users, the ASCEM modeling capability will be made available to EM site users through training and technology transfer. It will also be made available to the greater scientific community for use in subsurface and risk analysis research and for creating additional modules incorporating scientific advances and new research areas.

ThEREDA: Thermodynamic Data for Waste Management Assessment - Focus on Actinide Data

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INTRODUCTION

The need of reliable thermodynamic data for use in long-term safety analyses of geological waste repositories has been acknowledged internationally since decades. Excellent data collections like the NEA-TDB [1], Nagra-PSI-database [2], NBS-tables [3] or CODATA [4], have been assembled. However, as a result of high restrictions regarding data quality or limitation to country-specific repository projects, these databases are incomplete. For comprehensive modeling calculations they lack data on relevant radionuclides, chemo-toxic metals or ion interaction parameters needed for calculation in solutions with high ionic strength.

As no decision has been made on what kind of host rock will be used for a nuclear waste repository in Germany, several potential host rock candidates, e.g. crystalline rock, rock salt, and clay stone formations have to be evaluated. As a consequence, a wide range of geochemical boundary conditions has to be considered, ranging from dilute solutions to highly concentrated brines. Regarding the temperature range in the repository, geochemical modeling has to cover temperatures up to 150 °C.

DESCRIPTION OF THE WORK

FEATURES OF THEREDA

THEREDA offers evaluated thermodynamic data for all relevant elements, covering both radioactive waste and chemo-toxic substances. The database considers the geochemical conditions of crystalline rock, salt, and clay stone formations. Thus, in THEREDA, the Pitzer- and SIT-formalisms to describe activity coefficients of hydrated ions and molecules are supported.

Persistent data gaps in the database are closed via data of higher uncertainty or estimated values. The provision of uncertain or estimated data (which are, of course, marked accordingly) is important. Thermodynamic equilibrium calculations with estimated but as such well documented data is better than calculations based on incomplete parameter files, or inconsistent files to which potential users may have added missing data on their own account.

The following elements are covered in THEREDA:

- Na, K, Mg, Ca, Cl, SO₄²⁻ for temperatures up to 393 K

- The above system with CO₂/CO₃²⁻ at 298.15 K; an extension to higher temperatures is planned for the future project phase
- Radionuclides (actinides and fission products): Am, Cm, and Nd; Th, Pa, U, Np, Pu, Tc, Cs, Sm, I, Se, Sr, Ni, Ra will follow in the future.
- Toxic elements: Zn, Cr, Co, Cu, Cd, Hg, Pb, and As.
- Matrix elements: Si, Al (including a thermodynamic model for cement phases)

In the current project phase no solid solutions will be present in the database, even though this would be possible technically.

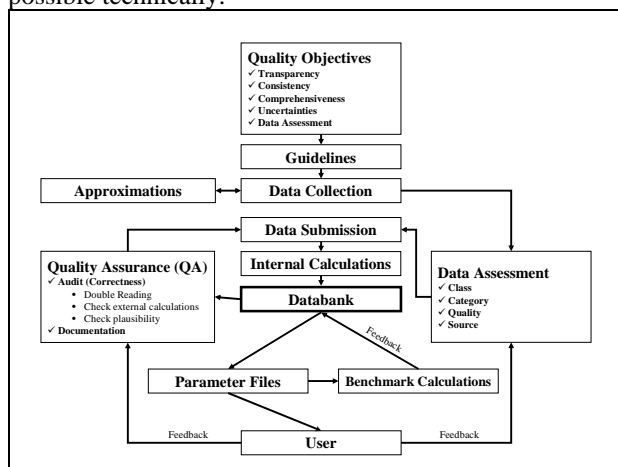


Fig. 1. Elements of Quality Assurance and their mutual relationships in THEREDA

QUALITY ASSURANCE

An essential point in the context of nuclear waste disposal is to provide quality assurance (QA) of the data. QA is accomplished in THEREDA by incorporating elements such as data categorization (review quality, original publication type, experimental category, and uncertainty level), full bibliographic tracking, formalized data evaluation procedures, internal consistency checks (coupled to the concepts of dependent data sets and alternatives), data audits, benchmark test cases, and finally external feedback enabled through free access combined with a variety of communication tools. Each part of THEREDA and its accompanying QA, as well as all technological details, are fully documented.

ACTINIDE DATA

In the first compilation, equilibrium data for Am(III), Cm(III) and Nd(III) are selected from NEA-TDB [1] and FZK-INE data basis [5] for the oceanic salt system. Protactinium, thorium, uranium, neptunium, plutonium and technetium will be handled in the future. The selected equilibrium constants are consistent with the SIT and Pitzer approach. The selected Pitzer parameters are consistent with the parameter set for the oceanic salts from Harvie and Weare [6] as well as with the extended HMW-model [7]. Due to the complexity of the Pitzer model and the numerous redundancies a lot of Pitzer parameters are not available from experiments and hence, they were estimated by well known analogies and systematic tendencies. The scope of validity of these Pitzer parameters is restricted to aqueous solutions with salt concentrations of up to 6 molal. Application of these data for modeling at higher ionic strengths is classified as very uncertain and must be proofed in further experiments. Dependencies on temperature are not known for the Pitzer parameters.

ACCESS TO THEREDA

THEREDA is providing thermodynamic data to a broad national and international community. Free access to THEREDA is available via Internet after registration (for further information please visit: www.thereda.de). THEREDA features the possibility to download data in ASCII-, Excel-tables or parameter files for specific modeling codes and includes both SIT and Pitzer parameter to calculate activity coefficients. Parameter files for PHREEQC, Geochemist's Workbench, and CHEMAPP parameter files are available end-2010.

FUTURE DIRECTIONS

Test calculations are being performed at the moment for Am(III), Cm(III), and Nd(III) in 0.1 m and 5.6 m

NaCl solution, 0.1 and 3.86 m MgCl₂ and CaCl₂ with the various codes. The results will be available end-2010. The data set for Np(V) is compiled in a next step. This data set is also used as basis for analogue values for unknown data of Pu(V) and Am(V), which cannot be determined easily by experiments due to their redox sensitivity. The release of the pentavalent actinides data is foreseen mid-2011.

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THEREDA is funded by the Federal Ministry of Economics and Technology (BWi), of Education and Research (BMBF), and by the Federal Office for Radiation Protection (BfS).

The image shows a web interface for querying thermodynamic data. It features a periodic table where elements are represented by boxes containing their symbol and a radio button. The element 'O' (Oxygen) is selected. Below the periodic table, there is a row of actinide elements (Ra, Th, Pa, U, Np, Pu, Am, Cm) with 'Np' selected. To the right of the periodic table is a control panel with the following elements:

- Datacategory / Phase type:**
 - Thermodynamic data (selected)
 - Interaction data
 - gaseous phase (checkbox)
 - aqueous species (checkbox)
 - solid phase (checkbox)
- Temperature (in °C):** from 25.00 to 25.00
- Interaction model:**
 - PITZER (selected)
 - SIT
 - Extended Debye-Hückel
- Continue** button

The periodic table includes elements from H to Xe, with a separate row for actinides (Ra, Th, Pa, U, Np, Pu, Am, Cm). Radio buttons are present for each element box.

Fig. 2: THEREDA-Internet page for querying thermodynamic data (www.thereda.de)

Actinide Sorption Database

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INTRODUCTION

Evaluation of remediation and restoration measures, as well as performance assessment for planned radwaste deposits or risk assessment for contaminated areas all require models for the migration behavior of radionuclides. Respective reactive / coupled transport codes require both realistic models for the interactions of the contaminants with their surrounding as well as an adequate parameterization.

So far, the physico-chemical processes are considered (if at all) by applying conditional distribution coefficients (K_D) in order to model the partition of a contaminant between solid and aqueous phases. Such distribution coefficients tend to have large uncertainties. They do not reveal the underlying chemical reaction mechanisms between solids and the aqueous phase and thus can not reflect changes in chemical environment. Moreover, it is extremely time-consuming to determine K_D values for the multidimensional parameter space usually to be considered in long-term risk assessment. To overcome these problems, strategies are required to “unfold” the K_D approach into more fundamental processes. This should make it possible to perform more detailed sensitivity analysis, to find the critical parameters, to reduce the parameter space and, finally, to pave the way for more reliable models for contaminant transport.

A promising approach into this direction is the application of concepts in surface chemistry that treat surface reactions as complexation reactions analogous to such reactions in homogeneous aqueous solutions. These models are called Surface Complexation Models (SCM), see e.g. Stumm [1]. They require the definition of surface sites with a finite concentration, located at the solid-aqueous interface and capable of protolysis. Many mineral surfaces, especially colloids carry a significant surface charge, creating an electrostatic potential extending into the aqueous solution. To account for this charge effect, additional terms have been introduced into adsorption models, modifying the activity of sorbate ions.

At present there are only few digital database for surface complexation equilibria existent world-wide, despite the vast amount of available data. Especially, sorption data are not part of the OECD/NEA thermochemical data base (TDB) project or of ongoing activities from CODATA, EPA, USGS or the NIST. The US EPA report by Wilhelm and Beam [2], offers at least some SCM parameters, but is still far from being complete, and as it is a printed report, it offers no facilities for user interactions and coupling to speciation software.

DESCRIPTION OF THE WORK

The lack of a comprehensive surface complexation database has triggered the development of RES³T – the Rossendorf Expert System for Surface and Sorption Thermodynamics [3], a digitized thermodynamic sorption database supporting the SCM framework. It is mineral-specific and can therefore also be used for complex models of solid phases such as rocks or soils.

Data records comprise of mineral properties, specific surface area values, characteristics of surface binding sites and their protolysis, sorption ligand information, and surface complexation reactions. An extensive bibliography is also included, providing links not only to the above listed data items, but also to background information concerning surface complexation model theories, surface species evidence, and sorption experiment techniques.

An integrated user interface helps users to access selected mineral and sorption data, to extract internally consistent data sets for sorption modeling, and to export them into formats suitable for other modeling software. It assists the identification of critical data gaps, the evaluation of existing parameter sets, consistency tests and the establishing of selected reference data sets.

Originally, the database was implemented in Microsoft Access[®] on PC and distributed to potential users via CD or e-mail. This version is still available on demand. But as the database is intended for an international use it has been converted into an Oracle-based version with a WWW user interface, thus not requiring a local installation any longer. As a side-effect every user always has automatically access to the most recent data sets. Subsequently, the portal www.fzd.de/res3t enables potential users the access to this database. An integrated user interface helps to access selected mineral and sorption data, to convert parameter units and to extract internally consistent data sets for sorption modeling.

Based on 2382 literature references, data records for 118 minerals, 1208 specific surface areas, 1325 surface site data records and 3824 surface complexation constants are stored inside RES³T (as of end of August, 2010). The actual distribution of the log K data records in terms of actinides, fission and activation products is shown in Fig. 1.

Advantages supplied by RES³T are for instance:

- It provides assistance for systematic screening and filling of data gaps.

- It shall serve as basis for accepted set of recommended values, allowing for comparisons of different sorption experiments and modeling efforts.
- Additional information enables checks which of the abundant surface complexes proposed in the literature (mostly resulting just from best-fit considerations) are actually validated by some kind of spectroscopic evidence or at least supported by theoretical (quantum-chemical) calculations.

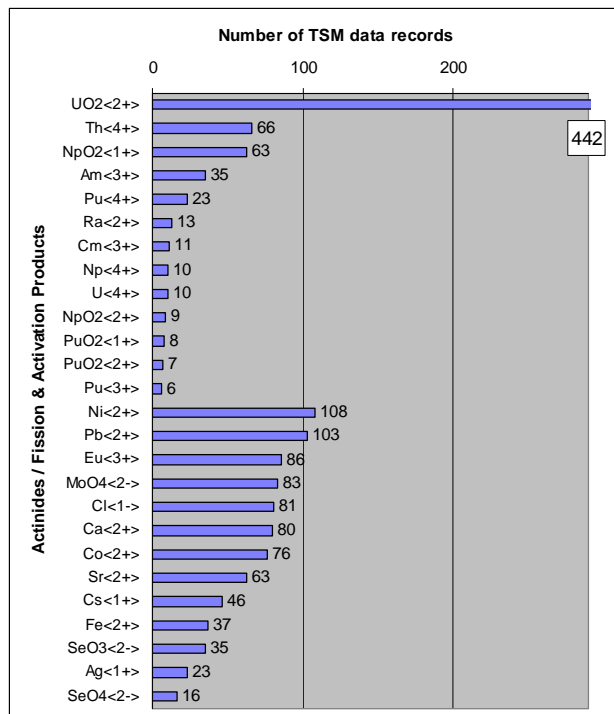


Fig. 1. Amount of surface complexation constants for actinides and relevant fission/activation products in RES³T.

As an example for data exploration the distribution of experimentally determined specific surface areas is given in Fig. 2 (taken from [4]), allowing for a surface-scaling of K_D values.

FUTURE DIRECTIONS

The most urgent task is an update of the online user manual for the WWW version. Further steps concern the data consolidation to arrive at recommended SCM data sets for all systems relevant for performance assessment in nuclear waste disposal.

In parallel, efforts are started to connect the sorption data to the German thermodynamic reference database THEREDA, see previous talk. Based on the experience with THEREDA, the long-awaited data format converters to allow data export specifically designed for geochemical speciation codes will be developed, too.

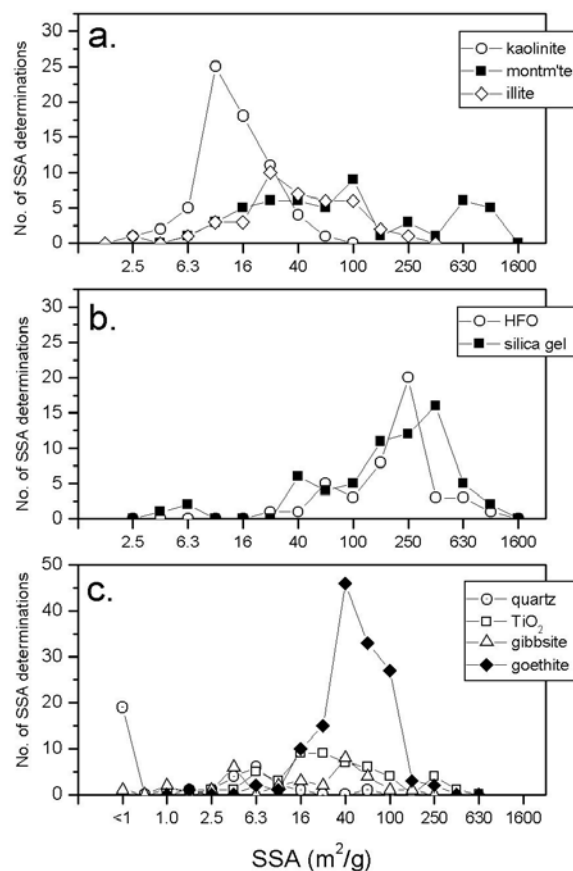


Fig. 2. Plot of experimental mineral surface areas, each point indicates the number of SSA measurements in each size range. a) Clay minerals – kaolinite, montmorillonite and illite. b) Amorphous coating minerals – ferrihydrite (HFO) and silica gel. c) Various crystalline oxides – quartz (SiO_2), gibbsite (Al oxide), goethite (Fe oxide) and titanium oxide.

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Safety Research for Nuclear Waste Disposal: Contributions by the EURATOM Programme

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European HLW repositories are planned for life-times of 50 – 80 yrs. Over this period, the Safety Case, a number of re-certifications and the license for final closure have to be delivered each on the basis of the respective current state-of-the-art. The state-of-the-art will be defined by the broad field of science which means that a continuous development and adaption of methods and ideas is required. Keeping the state-of-the-art needs education of scientists for jobs in safety research, reviewing organizations and licensing authorities. Therefore, sustainable funding for safety research for nuclear waste disposal is indispensable. One source of funding is provided by the EURATOM program. The legal basis for the EURATOM program is the corresponding treaty that has been signed by all 27 EU member states and Switzerland.

The EURATOM program is implemented through the European Commission's "framework programs" (FP) and the Joint Research Centers. The Programs cover two main topics: (I) Fusion and (II) Nuclear Fission & Radiation Protection. The program on fission is split in three sub-topics (II.1) Nuclear installations, (II.2) Nuclear waste and (II.3) Radiation protection. The overall objective of the Nuclear Fission & Radiation Protection program is to establish a sound scientific and technical basis in order to accelerate practical developments for the safe management of long-lived radioactive waste, to enhance the safety performance, resource efficiency and cost-effectiveness of nuclear energy within the EU.

Up to the mid-eighties, nuclear waste projects supported by the Commission's FPs focused on technological waste handling topics. Then the focus of the Commissions support moved to the Long-Term Safety issues of Nuclear Waste Disposal. A number of projects were launched dealing with the Migration of Radionuclides in the GEosphere (MIRAGE) including the CoCo-Club (Colloids and Complexation), geochemical modeling (Chemval) and natural analogues. Since the 1st FP, INE was involved in various projects. In the 6th FP, the EC's funding schema was changed in order to support large Integrated Projects (IP). The first 6th FP IP was NF-Pro "Understanding and physical and numerical modelling of the key processes in the near-field, and their coupling, for different hostrocks (see Fig.

1) and repository strategies" with 40 partner institutions running from 2004-2007. It was coordinated by the Belgian SCK-CEN. The total costs of this IP were 16.8 Mio € the share of EC was 8 Mio € Another example of a successful IP was FUNMIG (2005-2008) with 51 partners and an EU contribution of 8 Mio € This IP was coordinated by KIT-INE. In NF-Pro, the near-field defined by the various disposal concepts/ host rock conditions considered in Europe have been addressed. In FUNMIG the fundamental processes of radionuclide migration were investigated. In this IP, a clear distinction was chosen between the host rock systems with respect to the prevailing transport processes: In clay / argillaceous rocks, transport is controlled by diffusion, whereas in crystalline rocks advective flow along fractures and matrix diffusion influences radionuclide migration. Consequently, many of the partners involved in national disposal programs contributed to the IP FUNMIG by studies affiliated to their respective national host rock program.



Fig.1: Preferential host rocks in the EU countries. green: granite, orange: clay, blue: rocksalt

In the 6th Framework Programme, the Network of Excellence (NoE) in Actinide Sciences (ACTINET-6) was launched. The aim of this network was to make actinide research more attractive by admitting researchers from universities open access to “core” institutes where this work can be performed (pooled facilities such as synchrotron radiation, laser spectroscopy etc). The activities were directed to three scientific scopes: (1) Basic chemistry and physics on actinides, (2) chemistry of actinides in the geological environment, and (3) behaviour of actinides materials under and after irradiation. Staff of INE contributed to a wide series of joint projects within ACTINET covering mainly chemistry and thermodynamics of actinides in aqueous solution, their interactions at the water/mineral interface, structural incorporation into secondary phases, colloid formation, the dissolution of spent fuel and development and application of selective and sensitive methods for the speciation of actinides. INE is involved in ACTINET education of young scientists by giving access to the pooled facilities and by taking part in workshops, training courses and specific issues such as the annual ACTINET Theoretical User Lab (ThUL). This thematic school provides experimentalists with the opportunity to get a introduction to software and computational methods used for actinide simulation and modeling. In the 7th FP, ACTINET is continued as an integrated infrastructure Initiative (I3), see <http://www.actinet-i3.eu> .



For the 7th FP, new instruments have been defined by the EC. Smaller more targeted project were introduced again with a lower number of partners and correspondingly lower funding contribution. One example is the “Collaborative Project” ReCosy (2008-2012), coordinated by KIT-INE. Details of its work program will be presented.



<http://www.recosy.eu>

Since the beginning of Euratom’s FPs, groups/organizations/authorities have been keen on getting access to results obtained within the research programs. Starting with the IP FUNMIG, “Associated Groups”(AG) have been invited to join. AGs also from

outside of the EU (Canada, Japan, Korea, Russia and the US) have participated in different projects.

In the 7th FP, Technology Platforms (TP) are established which are expected to set priorities by defining research agendas. The main objectives of the Implementing Geological Disposal of Radioactive Waste Technology Platform (IGD-TP) are to initiate and carry out European strategic initiatives to facilitate the stepwise implementation of safe, deep geological disposal of spent fuel, high-level waste, and other long-lived radioactive waste by solving the scientific, technological and social challenges, and to support the waste management programs in the Member States. The vision of the IGD-TP is that by 2025, the first geological disposal facilities for spent fuel, high level waste, and other long-lived radioactive waste will be operating safely in Europe. Its commitment is to: (a) build confidence in the safety of geological disposal solutions among European citizens and decision-makers; (b) encourage the establishment of waste management programs that integrate geological disposal as the accepted option for the safe long-term management of long-lived and/or high-level waste; and (c) facilitate access to expertise and technology and maintain competences in the field of geological disposal for the benefit of Member States. Presently, the strategic research agenda is under development.



<http://www.igdtp.eu>

In the coming 10-15 years, until the first European HLW repository is expected to start operation, the IGD-TP and the EURATOM program are expected to support the different national programs in Europe and be instruments for international cooperation also beyond the EU.