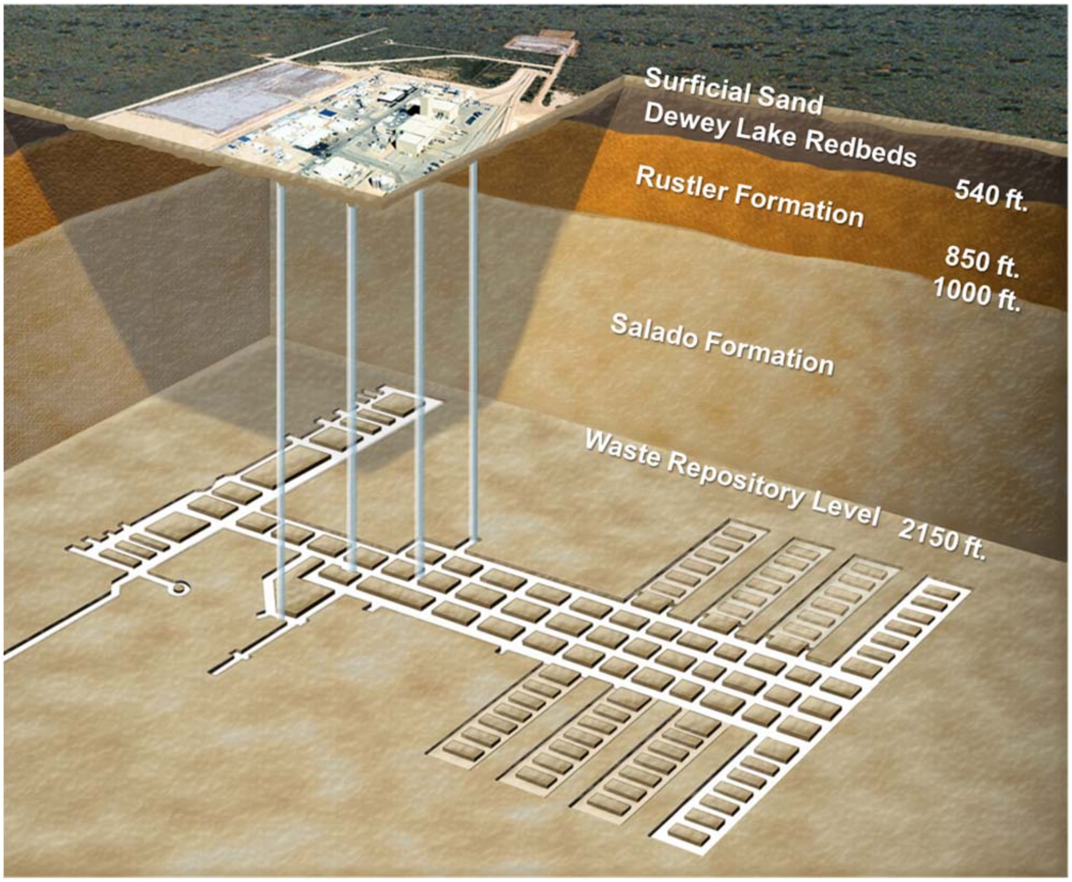
LA-UR-14-28463

Proceedings of the International Workshop on Actinide and Brine Chemistry in a Salt-Based Repository (ABC-Salt)



WIPP Facility and Stratigraphic Sequence

The funding for this document is provided by the U.S. Department of Energy, Carlsbad Field Office.

Cover illustration:
WIPP TRU Repository

Los Alamos National Laboratory, an affirmative action/ equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396.

This report was prepared as an account of work sponsored by an agency of the U.S. Government. Neither Los Alamos National Security, LLC, the U.S. Government nor any agency thereof, nor any of their employees make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Los Alamos National Security, LLC, the U.S. Government, or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of Los Alamos National Security, LLC, the U.S. Government, or any agency thereof. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Los Alamos Report LA-UR-14-28463
Issued: October 2014

Proceedings of the International Workshop on Actinide and Brine Chemistry in a Salt-Based Repository (ABC-Salt)

Edited by:

Donald Reed

Actinide Chemistry and Repository Science Team
Repository Science & Operations Program
Los Alamos National Laboratory
Carlsbad, NM, USA

Marcus Altmaier

Karlsruhe Institute for Technology
Institute for Nuclear Waste Disposal
Karlsruhe, Germany

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

Background and Observations

ABC-Salt Workshop Series

The first ABC-Salt international workshop was held in Carlsbad New Mexico (USA) on September 8/9, 2010. This was well attended with 45 scientists from 4 countries, but mostly from the United States and German repository programs. The technical agenda, extended abstracts, and attendees list are provided in this workshop proceeding. A tour of the WIPP facility was also give to the international visitors and was an important feature of the workshop.

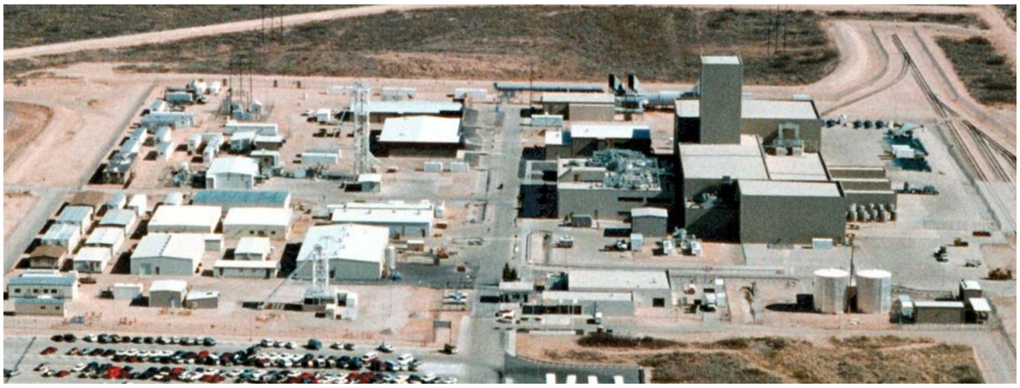
The ABC-Salt workshop evolved out of a collaborative dialog between the Los Alamos Actinide Chemistry and Repository Science team investigating actinide/brine chemistry for the U.S. Waste Isolation Pilot Plant (WIPP) and the German Karlsruhe Institute for Technology Institute for Nuclear Waste Disposal (KIT/INE) researchers investigating potential applications of a salt repository concept for nuclear waste. The goals of this workshop were to status the state-of-the-art on actinide and brine chemistry and start an international dialog to coordinate and prioritize research in the field. Further workshops are anticipated to continue this important technical exchange and dialog.

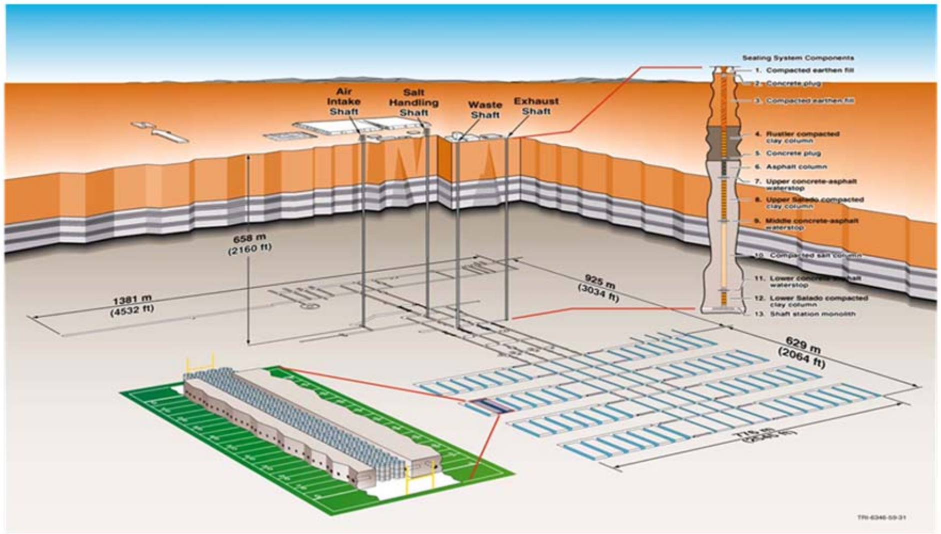
The safety case for the use of a bedded salt or salt dome for the permanent geologic isolation of nuclear waste is centered on the self-sealing properties of salt that lead to geologic isolation. This, under ideal conditions, will lead to a “dry” site that can geologically isolate the nuclear waste for millions of years. The salt formations being considered or used for geologic isolation are hundreds of millions of years old and have remained unsaturated with no interconnected groundwater for much of this time. In many respects this disposal concept is somewhat independent of the nature of the wasteform since it relies on geologic isolation and not container material and wasteform properties under the expected repository conditions. There are also significant cost advantages to a salt repository approach since the technology for the mining of salt is well established and we have a 12-year operational history and experience at the WIPP site, which is the best working example and application of this repository concept (see Figure).

It is critically important that a repository concept, and its associated safety case, has a sound scientific basis to assure the public that the repository will perform as predicted. For a salt-based nuclear repository, although primary safety reliance is on the self-sealing of its geology, there are low probability scenarios where brine intrusion leading to the solubilization of actinides/radionuclides in high ionic-strength brines and their subsequent release to the accessible environment is possible. It is this low-probability scenario that justifies the actinide and brine chemistry research that is the subject of this workshop. In this context, it is critical to show that even if the worse-case scenario of brine intrusion and release occurs, the repository will still perform and regulatory release limits are not exceeded. The dissolved actinide/ radionuclide concentration, in this low-probability scenario, is defined by the multitude of subsurface processes that impact actinide/radionuclide speciation and the associated modeling of actinide chemistry in high ionic-strength brine systems.

Figure: WIPP Salt Repository Concept and Implementation

WIPP TRU Repository Surface Site





Repository Concept in the Salado Bedded-Salt Formation

TRU Waste Transportation

TRU Waste Emplacement

Summary of Technical Results and Observation: ABC-Salt Workshop

The key result of this workshop was a reaffirmation that the salt repository concept leads to a strong safety case for the permanent disposal of nuclear waste. The self-sealing properties of the host rock, the limited availability of brine, and the strongly reducing conditions that are created should brine-inundation occur, lead to low dissolved actinide concentrations and minimal actinide/radionuclide release. These processes can be modeled using conservative assumptions which altogether strongly support the salt repository safety case.

In this workshop, updates and the scientific state of the art were presented in the following topical areas:

- US and German salt repository program status
- Brine chemistry and microbial Effects
- Actinide chemistry in brine
    - Colloids
    - Redox chemistry and processes
    - Complexation behavior
- Modeling of high ionic-strength brine and actinide systems

Detailed updates of both the German and US nuclear repository programs in salt were given. The ABC-Salt workshop took place as the German program was coming out of a 10-year moratorium on repository research and the US was looking to expand the role of salt repositories beyond the current application for TRU waste in the WIPP. Feasibility assessments for the Gorleben domed salt site in Germany were planned. The WIPP was fully operational and there were some discussions within the US program about thermal testing in salt to extend this repository concept to high-level nuclear (HLW) wasteforms.

Brine chemistry is modeled using the Pitzer approach and has been studied extensively since the early 1980's. There however remain key gaps and some initial work on iron and lead solubility, corrosion and the complexities of phase formation in MgO-dominated systems were presented. There is much less known about the indigenous microbial ecology that will persist under the highly-saline conditions expected. New programs to study this further in the US and Germany were announced and discussed. A key focus in the future plans will be the interactions between actinides and *archaeal* microorganisms in the areas of biosorption, radiotoxicity, and actinide bioreduction.

Actinide studies that show the role of colloidal species, iron reduction processes, and organic complexation were presented. Additionally, the solubility of key actinides in simulated and simplified brine systems as well as waste-impacted brine systems (e.g., cementitious systems) was described. The importance of establishing a thermodynamically-favorable reducing environment through the brine chemistry was reaffirmed for multivalent actinides such as Am, Pu, U and Np. Highly reducing systems are being established when lower-valent iron is present in brine systems. The importance of organic complexation is site and waste-dependent and initial results on the complexation of actinides with chelating agents were presented. Although a significant amount of data exists on oxidation-state invariant analogs, these are often highly conservative and additional studies are needed to extend these data to the actual actinides of interest to more realistically measure the solubilities expected. Significantly higher pH is expected in cement-dominated systems and some initial results under these conditions were presented.

The modeling of actinide and brine systems at high ionic strength was also addressed in the workshop. There are a number of modeling approaches being developed (ASCEM, THEREDA, and WIPP) and there were general discussions about the need for increased coordination. The WIPP modeling approach has been supported through the regulatory process although it relies on a number of highly conservative assumptions. There is a need to move toward more comprehensive data bases and challenge the model predictions with strategically-designed experiments.

Overall, there were some key gaps in the understanding of actinide chemistry in high ionic-strength brine systems identified. The most important of these were:

- Studies with Pu, Np and Am, rather than analogs, to establish the validity and conservatism of current modeling approaches (solubility and redox assumptions).
- Actinide Pitzer data and experiments at high pH to support cement-dominated systems
- The long-term stability of organic complexants in irradiated brine systems.
- Effects of microbes on actinide speciation in brine systems.
- Integration of models and data bases that rely on the Pitzer approach.
- Temperature-variable effects and studies for all systems discussed. This is especially needed as we look more to the possible emplacement of higher activity and thermally hot waste in a salt geology.

As a conclusion to this workshop it was decided to hold a second workshop in Germany (ABC-Salt II) in a year or so and include a special extended workshop on the measurement and modeling of actinide behavior as a function of temperature.

The organizers of the workshop wish to thank the many participants for the excellent presentation and subsequent discussions in this workshop. It is hoped that this is the start of an extended dialog on the repository chemistry of actinides/radionuclides in brine systems.

Donald T. Reed

Donald Reed

Earth and Environmental Sciences Division
Los Alamos National Laboratory

Marcus Altmaier

Institute for Nuclear Waste Disposal (INE)
Karlsruhe Institute of Technology

Table of Contents

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**
roger.nelson@cbfo.doe.gov

Russ Patterson
Russ.Patterson@wipp.ws

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

LANL-CO contact: **Don Reed**
dreed@lanl.gov

KIT contact: **Marcus Altmaier**
marcus.altmaier@kit.edu

ACKNOWLEDGEMENTS

The organizers of this workshop wish to acknowledge the following contributions:

S.M. Stoller Corporation for their generous donation to help with the costs of the workshop

Pecos River Conference Center for the use of their facilities

K&P Catering for the coffee breaks, lunches and dinners

Susan Campbell (LANL) for coordinating the clearance/security forms for the WIPP tour

WRES (Art Chavez) for the use of video equipment for the viewgraphs

CEMRC/NMSU for the use of their facilities for abstract preparations

Carlos Abeyta and Alex Roberts (LANL students) for help with many workshop preparations

ABC Salt Workshop Attendees
Outside the Pecos River Conference Center
Carlsbad NM, USA

ABC-Salt Workshop Program Overview

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 – 10:25 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 – 11:55 AM 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 AM	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 Waste 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_2O 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	**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 AM	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 Oxidation State Distributions 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 PM	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**

ABC-Salt Workshop

Abstracts

List of Abstracts

WIPP Environmental Compliance and the Chemistry Program

Russell Patterson
Department of Energy
4021 National Parks Hwy.
Carlsbad, NM 88220
Phone- 575-234-7457
russ.patterson@wipp.ws

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

Sandia National Laboratories, 4100 National Parks Hwy. Carlsbad, NM 88220, djclayt@sandia.gov

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.

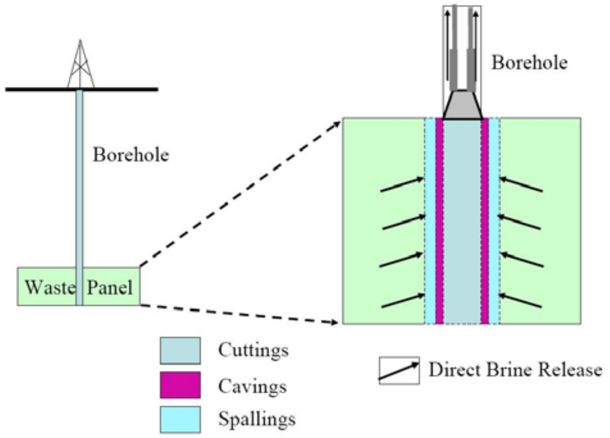


Fig. 1. Schematic of Direct Release Mechanisms Modeled in WIPP PA.

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

F. D. Hansen
Sandia National Laboratories, Albuquerque NM 87185 fdhanse@sandia.gov

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.

REFERENCES

1. http://www.sandia.gov/SALT/SALT_Home.html

2. M. Schlich. *Simulation der Bewegung von im natürlichen Steinsalz enthaltener Feuchte im Temperaturfeld*, Dissertation TH Aachen. (1986)

3. C.M. Stone, Holland, J.F., Bean J.E. and Arguello, J.G. 2010. *Coupled Thermal-Mechanical Analyses of a Generic Salt Repository for High Level Waste* . American Rock Mechanics Association. Salt Lake City Utah.

4. Hampel, A., Günther, R.M., Salzer, K., Minkley, W., Pudewills, A., Leuger, B., Zapf, D., Staudtmeister, K., Rokahr, R., Herchen, K., Wolters, R., Lux, K.-H., Schulze, O., Heemann, U., Hunsche, U. 2010. Benchmarking of Geomechanical Constitutive Models for Rock Salt. American Rock Mechanics Association. Salt Lake City Utah.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation,
a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
SAND2010-5294C.

Update on the German program on repositories and their safety assessment

Guido Bracke

GRS mbH, Schwertnergasse 1, Cologne, Germany, 50677, guido.bracke@grs.de

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 m^3 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 was 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 m^3 radioactive waste.

Gorleben is a site located in a salt dome which has been explorated 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 compentence 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.

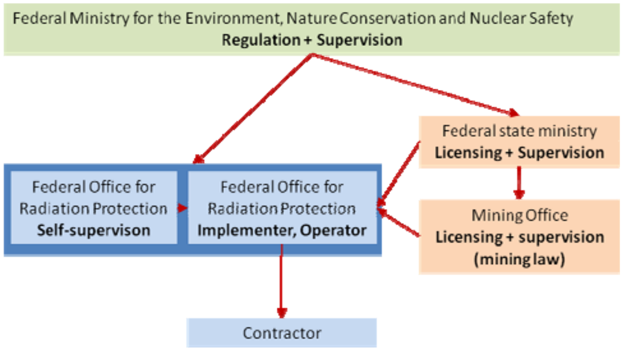


Fig. 2. Competence (atomic and mining law)

SAFETY REQUIREMENTS

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

1. only neglible 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.

REFERENCES

1. BMU, http://www.bmu.de/files/pdfs/allgemein/application/pdf/endfassung_sicherheitsanforderungen_en.pdf (2010).
2.BMU, http://www.bmu.de/atomenergie_ver_und_entsorgung/endlagerung/sicherheitsanforderungen/doc/44580.php (2009) [only in german].

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

G. Bernhard[1], W. Brewitz[2], H. Geckeis[3], K. Gompper[3], H.-J. Herbert[2], H. C. Moog[2], R. Odoj[4]

1 Forschungszentrum Dresden-Rossendorf - Institut für Radiochemie (FZD-IRC), Postfach 519119, 01314 Dresden, Germany, g.bernhard@fzd.de

2 Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Theodor-Heuss-Str. 4 38122 Braunschweig, Germany, her@grs.de

3 Karlsruher Institut für Technology - Institut für Nukleare Entsorgung (KIT-INE), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Horst.Geckeis@kit.edu

4 Forschungszentrum Jülich - Institut für Energieforschung (FZJ-IEF-6), Postfach , 52425 Jülich, Germany, r.odoj@fz-juelich.de

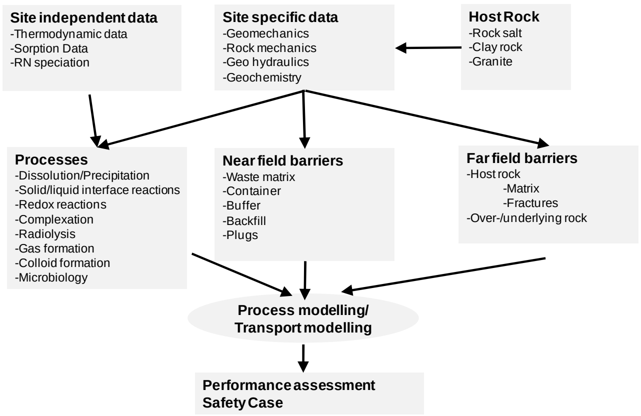
INTRODUCTION

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, $^{129}1$, $^{36}C1$, 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

Helge C. Moog*, Sven Hagemann, D. Schönwiese, T. Scharge, Barbara P. Bischofer

Gesellschaft für Anlagen- und Reaktorsicherheit (GRS), Theodor-Heuss-Str. 4, 38122 Braunschweig, Germany
**Corresponding author: helge.moog@grs.de*

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.

REFERENCES

1. HERBERT, H.-J. (1996): *Zur Geochemie und geochemischen Modellierung hochsalinarer Lösungen*. Doctorate-Thesis (Habilitationsschrift), p. 350, University of Kiel, Germany.
2. MOOG, H. C.; HAGEMANN, S.; RUMYANTSEV, A. (2004): *Isopiestic Investigation of the Systems FeCl2 - (Na, K, Mg, Ca) - Cl - H2O at 298.15 K*, Z. Physikal. Chemie 218, 1063-1087.
3. RUMYANTSEV, A.;HAGEMANN, S.; MOOG, H. C. (2004): *Isopiestic Investigation of the Systems Fe2(SO4)3 - H2SO4 - H2O, FeCl3 - H2O, and Fe(III) - (Na, K, Mg, Ca)Cln – H2O at 298.15 K*, Z. Physikal. Chemie 218, 1089-1127.
4. Moog, H. C.; Hagemann, S. (2004): *Thermodynamische Modellierung hochsalinarer Lösungen: Gewinnung von Daten für Fe(II), Fe(III) und*

S(-II) und Entwicklung eines Programms zur Modellierung des reaktiven Stofftransports im Nahfeld eines Endlagers, GRS-195, Final report to a research projekt funded by the federal ministry of economy and technology (BMWA), Contract ID 02 E 9138 4, ISBN 3-931995-63-1, p. 224.

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

Yongliang Xiong

Sandia National Laboratories, Carlsbad Programs Group, 4100 National Parks Highway, Carlsbad, New Mexico, 88220, yxiong@sandia.gov

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 CO_2 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 ($MgCO_3$).

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:

$$Mg_5(CO_3)_4(OH)_2\bullet 4H_2O + 10H^+ \leftrightarrows 5Mg^{2+} + 4CO_2(g) + 10H_2O(l)$$

Solubility experiments were conducted from undersaturation in deionized (DI) water and 0.10–4.4 m NaCl solutions at 22.5 °C at $P_{CO_2} = 10^{-3.4}$ 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 (2σ) in logarithmic unit at 22.5 °C with a corresponding value of 57.64 ± 0.40 (2σ) 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 (2σ) in logarithmic unit at 22.5 °C with a corresponding value of 58.77 ± 0.72 (2σ) 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 (2σ) in logarithmic unit at 22.5 °C with a corresponding value of 60.73 ± 0.59 (2σ) 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 ± 2 kJ mol^{-1}, -5,891 ± 4 kJ mol^{-1}, and –5,880 ± 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 (2σ).

ACKNOWLEDGEMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, 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. The author's thanks are due to Nathalia Chadwick, Kelsey Mae Davis, and Veronica Gonzales, for their laboratory assistance.

REFERENCES

1. U.S. DOE, *Title 40 CFR Part 191 Compliance Certification Application, Appendix SOTERM*, DOE/CAO 1996-2184, U.S. DOE Carlsbad Area Office, Carlsbad, NM (1996).
2. U.S. DOE, *Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant, Vols. 1-8,* DOE/WIPP 2004-3231, U.S. DOE Carlsbad Field Office, Carlsbad, NM (2004).
3. W. Schűessler, W., V. Metz, B. Kienzler, and P. Vejmelka. "Geochemically Based Source Term Assessment for the Asse Salt Mine: Comparison of Modeling and Experimental Results (abstract)," Programs and Abstracts of Materials Research Society Annual Meeting, Boston, MA, p. 713 (2002).

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

Daniela Freyer, Melanie Oestreich, Wolfgang Voigt

Institute of Inorganic Chemistry, TU Bergakademie Freiberg, Leipziger Str. 29, 09596 Freiberg,
daniela.freyer@chemie.tu-freiberg.de

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-MgCl$_2$-H$_2$O 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)$_2$ · MgCl$_2$ · 8 H$_2$O (3-1-8 phase) and 5 Mg(OH)$_2$ · MgCl$_2$ · 8 H$_2$O (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 MgCl$_2$ solution (above 1.7 mol/kg H$_2$O), 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-MgCl$_2$-H$_2$O, 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-MgCl$_2$-H$_2$O 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, super-saturated 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 MgCl$_2$ solution. Finally, after the equilibrium were reached, the solution concentrations were analysed (Mg^{2+}: 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.

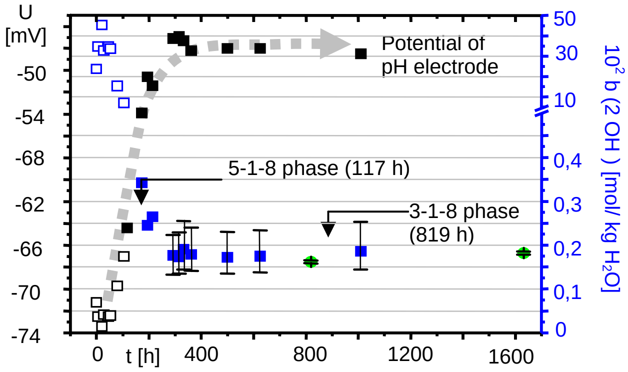


Figure 1: Monitoring of OH$^-$ decrease by pH electrode and solid phase determination with time in a 2.5 molal MgCl$_2$ solution at 25°C

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-MgCl$_2$-H$_2$O 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.

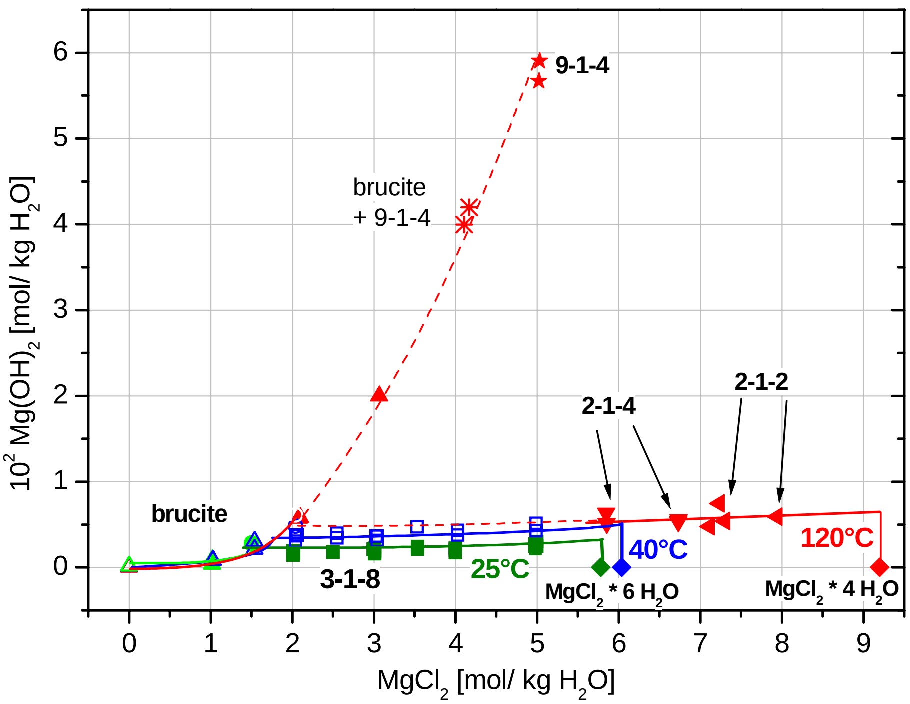


Figure 2: System $MgO-MgCl_2-H_2O$ at 25°C, 40°C and 120°C, experimental data from this work.

FUTURE DIRECTIONS

The first results of this work will be published in 3 papers: 1. “9 $Mg(OH)_2 \cdot MgCl_2 \cdot 4\ H_2O$, a High Temperature Phase of the Magnesia Binder System” *Inorg. Chem.* 2010, in print; 2. “2 $Mg(OH)_2 \cdot MgCl_2 \cdot 4\ H_2O$ and 2 $Mg(OH)_2 \cdot MgCl_2 \cdot 2\ H_2O$, High Temperature Phases of the Magnesia Binder System”. *Acta Cryst. B*, in preparation; 3. “Solubilities of Magnesia Binder Phases in the System $MgO-MgCl_2-H_2O$ and there importance as barrier construction material for radioactive waste disposals in salt formations”. *Geochim. Cosmochim. Acta*,, in preparation.

Solubility data in the system $MgO-MgCl_2-H_2O$ will be completed at 60°C, 80°C and 100°C. The influence of Ca^{2+} and SO_4^{2-} 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).

REFERENCES

1. E. S. NEWMAN, J. V. GILFRICH, L. S.WELLS, *J. Res. Nat. Bur. Stand.* **49** (6), 377 (1952).
2. F. C. HARPER *J. Appl. Chem.* **17** (1), 5 (1967).
3. E. S. SOLOVJEVA, B. I. SMIRNOV, E. E. SEGALOVA, P. A. REBINDER, *Kolloidn. Zh.* **30** (5), 754 (1968).
4. B. I. SMIRNOV, E. S. SOLOVJEVA, E. E. SEGALOVA, P. A. REBINDER, *Kolloidn. Zh.* **31** (3), 440 (1969).
5. J. J. BEAUDOIN, V. S. RAMACHANDRAN, *Cem. Concr. Res.* **5** (6), 617 (1975).
6. C. A. SORRELL, C. R. ARMSTRONG, *J. Am. Ceram. Soc.* **59** (1-2), 51 (1976).
7. B. MATKOVIC, S. POPOVIC, V. ROGIC, T. B. ZUNIC, J. F. YOUNG, *J. Am. Ceram. Soc.* **60,** 504 (1977).
8. L. URWONGSE, C. A. SORRELL, *J. Am. Ceram. Soc.* **63** (9-10), 501 (1980).
9. W. O. ROBINSON, W. H. WAGGAMAN, *J. Phys. Chem.* **13,** 673 (1909).
10. J. K. GJALDBAEK, *Z. Anorg. Allg. Chem.* **144,** 269 (1941).
11. J. D’ANS; W. KATZ, *Kali u. Steinsalz* **35** (1941) 37.
12. J. D’ANS, W. BUSSE, H.-E. FREUND, *Kali u. Steinsalz* **8,** 3 (1955).
13. C. MAZURANIC, H. BILINSKI, B. MATKOVIC, *J. Am. Ceram. Soc.* **65** (10), 523 (1982).
14. M. Altmaier, V. Metz, V. Neck, R. Müller, Th. Fanghänel, *Geochim. Cosmochim. Acta* 67 (19), 3595 (2003).

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

G. T. Roselle

Sandia National Laboratories, 4100 National Parks Hwy. Carlsbad, NM 88220, gtrosel@sandia.gov

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 CO_2 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_{CO2} and pH within ranges favoring lower actinide solubilities. Large quantities of low-C steel and Pb present in the WIPP may also consume CO_2.

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 CO_2 via the formation of carbonates or other phases, potentially supporting MgO in CO_2 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: $pO_2 < 5$ ppm; temperature of 26 °C; relative humidity at 78 ± 10%; and a range of pCO_2 values (0, 350, 1500 and 3500 ppm, balance N_2). 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 pCO_2. Scanning Electron Microscope (SEM) analysis with Energy Dispersive Spectroscopy (EDS) shows the presence of a green Fe (±Mg)-chlori-hydroxide phase at pCO_2 values <1500 ppm. At higher pCO_2 the dominant corrosion product is a Fe-Mg-Ca hydroxy-carbonate phase. Lead coupons show no corrosion products at lower pCO_2 values but significant formation of a Pb-Ca hydroxycarbonate phase at $pCO_2 > 350$ 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 pCO_2 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 μm/yr at 0 ppm CO_2 to 1.20 ± 0.25 μm/yr at 3500 ppm CO_2 (Figure 1).

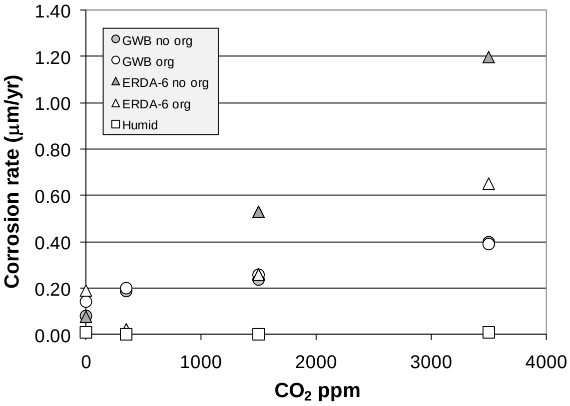


Figure 1. Steel corrosion rates (six-month) as a function of pCO_2 (ppm).

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 μm/yr (Figure 2).

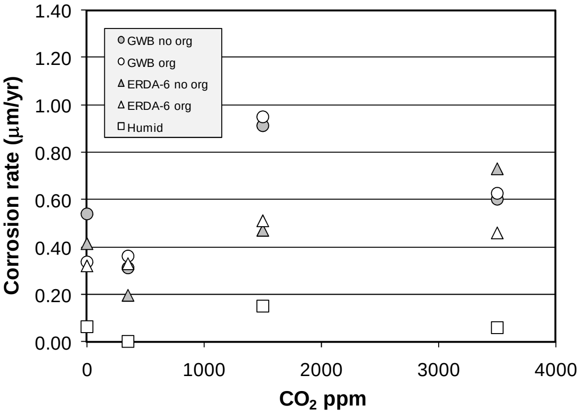


Figure 2. Lead corrosion rates (six-month) as a function of pCO_2 (ppm).

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.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Solubility of Ferrous Oxalate Dihydrate and Lead Oxalate in Magnesium Chloride and Sodium Chloride Solutions [1]

Je-Hun Jang, Yong-Liang Xiong, and Martin B. Nemer

Sandia National Laboratories,[2] 4100 National Parks Hwy. Carlsbad, NM 88220, jjang@sandia.gov

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), $CaC_2O_4{\cdot}2H_2O$ (weddellite), $MgC_2O_4{\cdot}2H_2O$ (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.

REFERENCES

1. J. Peisach and F. Brescia, “The Mechanism of the Precipitation of Magnesium Oxalate from Supersaturated Solutions,” *Journal of the American Chemical Society*, Vol. 76, pp. 5946-5948 (1954).
2. M.J. Wilson, D. Jones, D., and J.D. Russell, “Glushinskite, a Naturally Occurring Magnesium Oxalate,” *Mineralogical Magazine*, Vol.43, pp.837–840 (1980).

---

[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.

LA-UR 10-06081

Microbiology in the WIPP

Julie S. Swanson
D.A. Ams, M. Borkowski, H. Khaing, J.-F. Lucchini, M.K. Richmann, D.T. Reed

Los Alamos National Laboratory—Carlsbad Operations, Actinide Chemistry & Repository Science Program
1400 University Drive, Carlsbad, NM, 88220, jsswanson@lanl.gov

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 performance[1]. 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 England[2-6].

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 formulations[7] (~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.

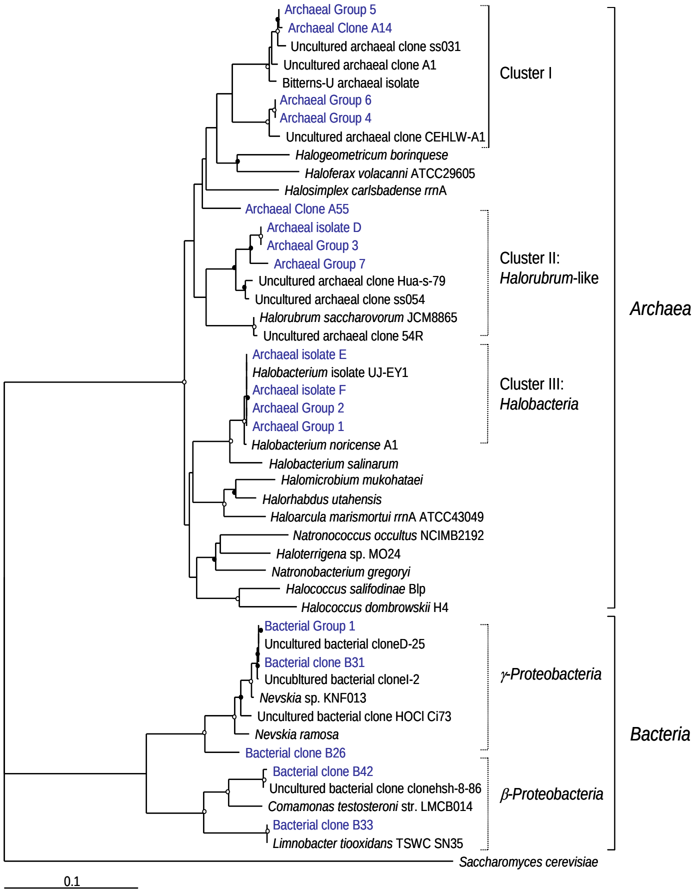


Figure 1. Phylogenetic tree of archaeal and bacterial 16S rRNA gene libraries. Tree is rooted to *Saccharomyces cerevisiae*. Solid circles denote bootstrap values greater than 50%; open circles greater than 95%. Sequences in blue are from enrichment culture.

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.

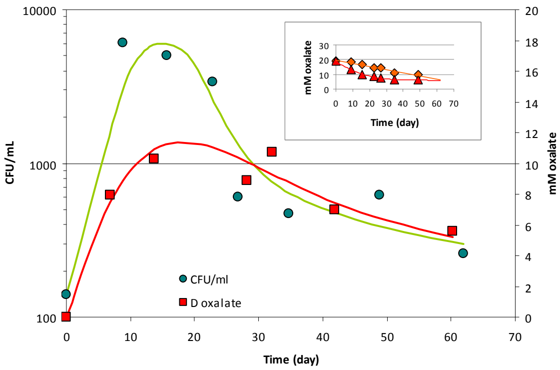


Figure 2. Growth of *Halosimplex carlsbadense* correlated with oxalate disappearance in ERDA-6. Inset provides original data used to generate differential curve shown in red.

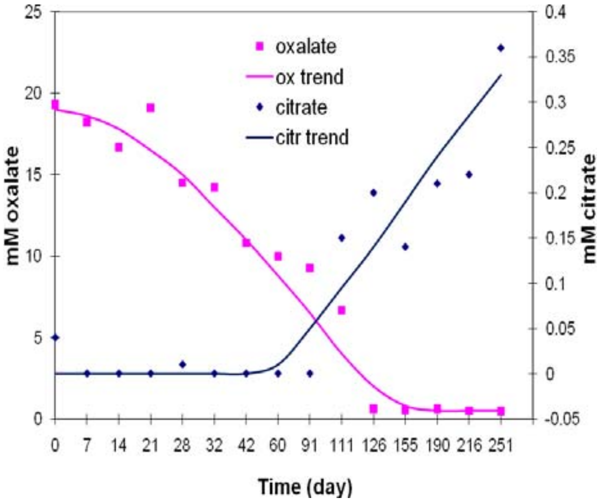


Figure 3. Oxalate and citrate levels in abiotic GWB incubations over time.

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.

REFERENCES

1. M. KEITH-ROACH, “The speciation, stability, solubility and biodegradation of organic co-contaminant radionuclide complexes: A Review”, *Sci. Total Environ.* 396, 1 (2008).
2. NORTON, C.F., McGenity, T.J., Grant, W.D. “Archaeal halophiles (halobacteria) from two British salt mines,” *J. Gen. Microbiol* 139, 1077 (1993).
3. DENNER, E.B., McGenity, T.J., Busse, H.-J., Grant, W.D., Wanner, G., Stan-Lotter, H. “Halococcus salifodinae sp. nov., an Archaeal Isolate from an Austrian Salt Mine”, *Int. J. Syst. Bacteriol*. 44, 774 (1994).
4. STAN-LOTTER, H., Pfaffenhuemer, M., Legat, A., Busse, H.-J., Radax, C., Gruber, C. “Halococcus dombrowskii sp. nov., an archaeal isolate from a Permian alpine salt deposit”, *Int. J. Syst. Evol. Microbiol*. 52, 1807 (2002).
5. GRUBER, C., Legat, A., Pfaffenhuemer, M., Radax, C., Weidler, G., Busse, H.-J., Stan-Lotter, H. “Halobacterium noricense sp. nov., an archaeal isolate from a bore core of an alpine Permian salt deposit, classification of Halobacterium sp. NRC-1 as a strain of H. salinarum and emended description of H. salinarum”, *Extremophiles* 8, 431 (2004).
6. VREELAND, R.H., Piselli, Jr., A.F., McDonnough, S., Meyers, S.S. “Distribution and diversity of halophilic bacteria in a subsurface salt formation,” *Extremophiles* 2, 321 (1998).
7. A.C. SNIDER, “Verification of the Definition of Generic Weep Brine and the Development of a Recipe for this Brine”, ERMS 527505, Sandia National Laboratories.

Actinide Interactions with Bacteria

Henry Moll, Gert Bernhard

Affiliation Information: Forschungszentrum Dresden-Rossendorf e.V., Institute of Radiochemistry, P.O. Box: 510119, 01314 Dresden, Germany, h.moll@fzd.de

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 $1x10^3$ to $5x10^6$ cells ml^{-1}, whereas the number of sulfate reducing bacteria (SRB) was between $1x10^1$ to $2x10^4$ 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: Cm > U > Pu >> 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.

REFERENCES

1. K. PEDERSEN et al., *FEMS Microbiol. Ecol.*, **19**, 249 (1996).
2. S. POULAIN et al., *Geomicrobiol. J.*, **25**, 240 (2008).
3. A. J. FRANCIS et al., *Radiochim. Acta*, **82**, 347 (1998).
4. H. MOLL et al., *Environ. Sci. Technol.*, **38**, 1455 (2004).
5. M. MOTAMEDI, K PEDERSEN, *Int. Syst. Bacteriol.*, **48**, 311 (1998).
6. H. MOLL et al., *Radiochim. Acta*, **94**, 815 (2006).
7. H. MOLL et al., *Biometals*, **21**, 219 (2008).
8. H. MOLL et al., *Radiochim. Acta*, in press (2010).

LA-UR 10-06080

Bioreduction of Actinides in Low and High Ionic Strength Environments

David A. Ams
M. Borkowski, H. Khaing, M.K. Richmann, J.S. Swanson, J-F. Lucchini, D.T. Reed

Los Alamos National Laboratory—Carlsbad Operations, Actinide Chemistry & Repository Science Program
1400 University Drive, Carlsbad, NM, 88220, dams@lanl.gov

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), it's 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.

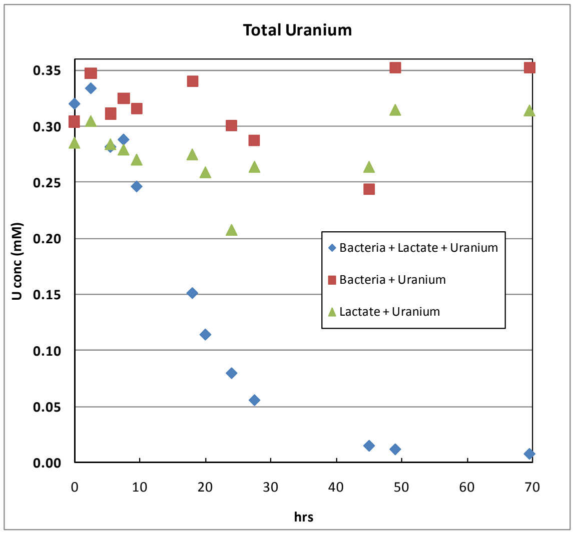


Fig. 1 Total uranium in solution with time in bioreduction experiment with *Shewanella* sp.

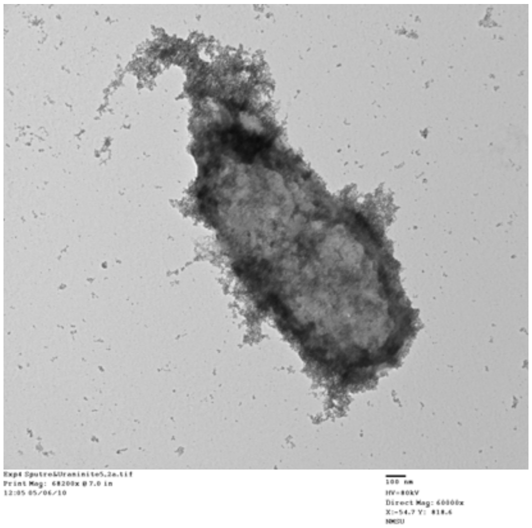


Fig. 2 Transmission electron micrograph of *Shewanella* sp. encrusted with uranium precipitate at the conclusion of bioreduction experiment.

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.

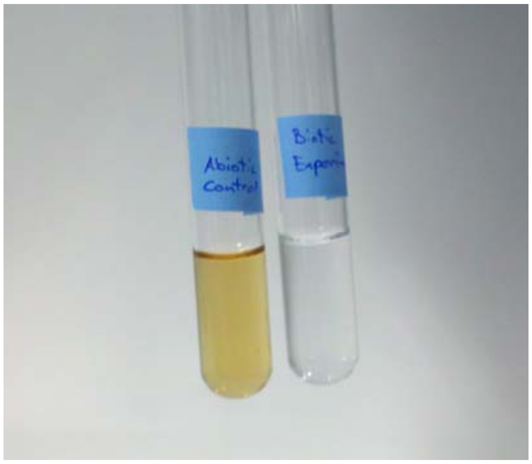


Fig. 3 Abiotic control (colored) and inoculated (clear) batch reaction vessels indicating Fe(III) reduction from a colored solution to a clear solution of Fe(II).

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 spectophotometry, 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.

REFERENCES

1. LOVLEY D.R., PHILLIPS E.J.P, GORBY Y.A., LANDA E.R., “Microbial Reduction of Uranium,” *Science*, **350**, 413-416 (1991).
2. RITTMAN B.E., BANASZAK J.E., REED D.T., “Reduction of Np(V) and precipitation and of Np(IV) by an anaerobic microbial consortium,” *Biodeg*, **13**, 329-342 (2002).
3. ICOPINI G.A., LACK J.G., HERSMAN L.E., NEU M.P., BOUKHALFA H., “Plutonium (V/VI) Reduction by the Metal Reducing Bacteria *Geobacter metallireducens* GS-15 and *Shewanella oneidensis* MR-1,” App. Env. Microbio. **75**, 3641-3647 (2009).

LA-UR-10-06088

X-Ray Diffraction and Laser Photoacoustic Absorbance Spectroscopy of Actinides

Michael K. Richmann
M. Borkowski, H. Khaing, J-F. Lucchini, J.S. Swanson, D.A. Ams, D.T. Reed

Los Alamos National Laboratory—Carlsbad Operations, Actinide Chemistry & Repository Science Program
1400 University Drive, Carlsbad, NM, 88220, richmann@lanl.gov

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 6x10^{-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.

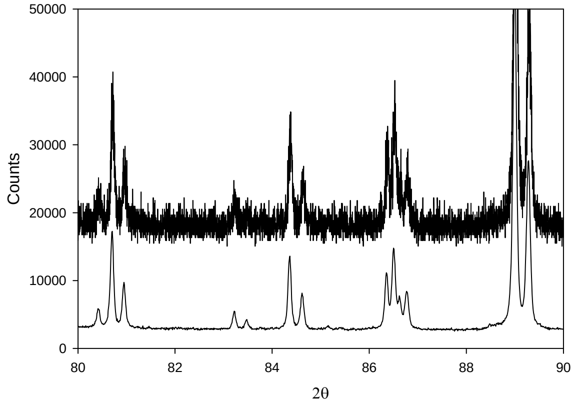


Fig. 1 Comparison of scintillation counter versus Lynx Eye sensitivity for equivalent count times, slit setting using the NIST corundum standard.

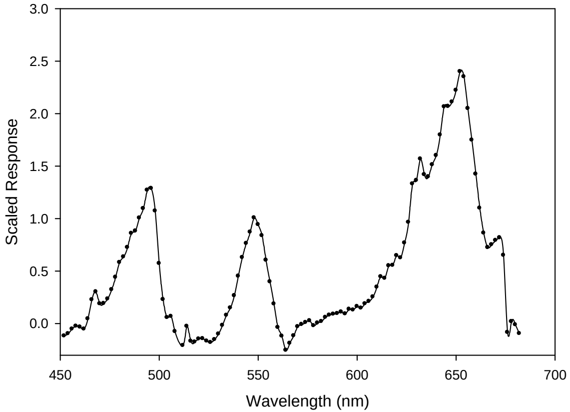


Fig.2 Uranium (IV) aqueous solution at 1x10^{-4} M in 1 M perchloric acid, baselined against 1 M perchloric acid.

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

[1]Daniel Olive, [2]Michael Richmann, [2]Donald Reed, [1]Hasitha Ganegoda, [1]Yuila Trenikhina, [1]Tim McNamee, [1]Daniel Velazquez, and [1]Jeff Terry

[1]Illinois Institute of Technology, 3101 S Dearborn St, Chicago, IL, 60616, terryj@iit.edu
[2]Los Alamos National Laboratory, 1400 University Dr, Carlsbad, NM, 88220

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.

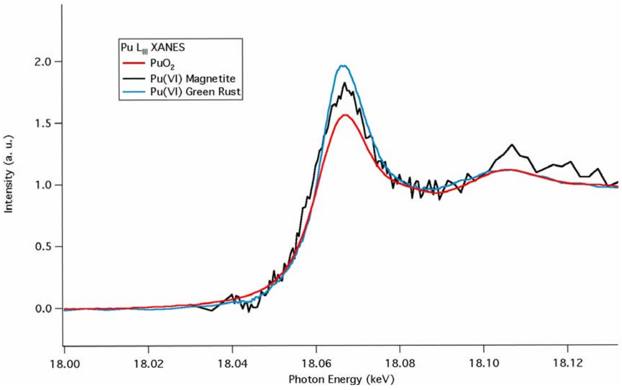


Fig. 1. XANES of precipitates from Pu(VI) reduction study. Plutonium was reduced to Pu(IV), as indicated by agreement with a PuO_2 standard. Taken from [2].

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 L_3 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 PuO_2 and PuF_3 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).

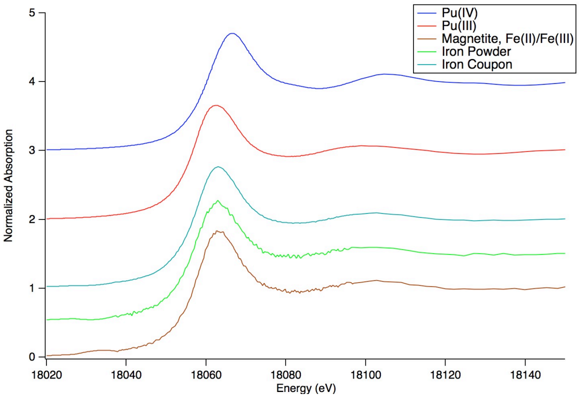


Fig. 2. XANES of precipitates/corrosion products from extended equilibration study. Analysis indicated reduction of initial Pu(VI) in solution to Pu(III), as shown by comparison with Pu(III) and Pu(IV) standards.

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.

REFERENCES

1. D. REED, J. F. LUCCHINI, M. BORKOWSKI, M. RICHMANN, "Reduction of Higer-Valent Plutonium by Iron Under Waste Isolation Pilot Plant (WIPP)-Relevant Conditions: Data Summary and Recommendations" LA-UR 10-01254, Los Alamos National Laboratory (2010).
2. D. REED, J. F. LUCCHINI, S. AASE, A. KROPF, "Reduction of plutonium(VI) in brine under subsurface conditions," Radiochim. Acta, **94**, 591 (2006).
3. B. RAVEL, M. NEWVILLE, "ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT," Journal of Synchrotron Radiation, **12**, 537 (2005).
4. M. ALTMAIER, V. NECK, J. LÜTZENKIRCHEN, TH. FANGHÄNEL, "Solubility of plutonium in $MgCl_2$ and $CaCl_2$ solutions in contact with metallic iron," Radiochim. Acta, **87**, 187 (2009).

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

J. L. Conca and J. V. Wright*

Carlsbad Environmental Monitoring & Research Center, 1400 University Drive,
Carlsbad, New Mexico 88220; jconca@cemrc.org

**UFA Ventures, Inc., 1110 Maple Place, Richland, WA 99354 judith@ufaventures.com*

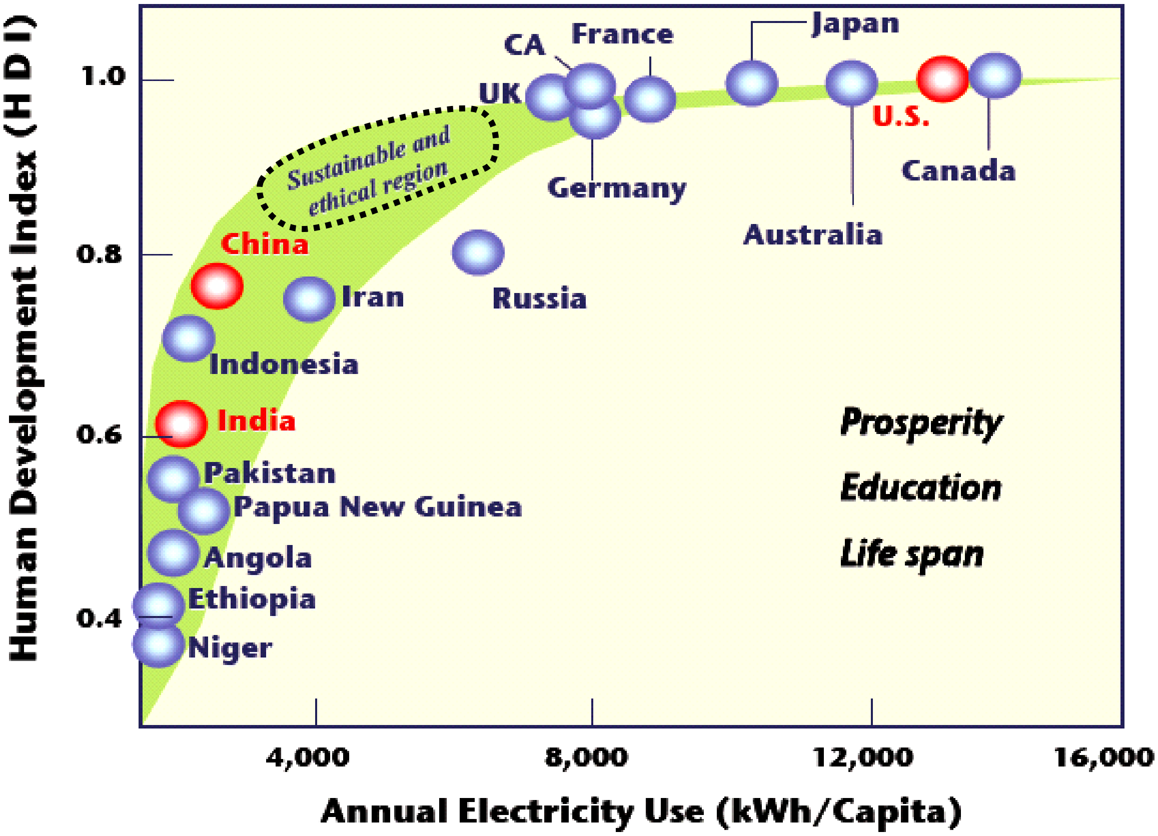
The U.S. and the EU are at a crossroads in their economic and national security that will determine the strength and leadership at home and in the world for the next century. This critical point involves our sources of energy, both their quantity and quality. As has happened throughout history, great 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, CO_2 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 ($^1/_3$–fossil fuel, $^1/_3$–renewables and $^1/_3$–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 $^1/_3$-$^1/_3$-$^1/_3$ 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

X. Gaona[1,2], M. Altmaier[1], M. Grivé[2], V. Montoya[2], E. Colàs[2], L. Duro[2]

[1]*Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[2]*Amphos 21, Passeig de García i Fària 49-51, 08019 Barcelona, Spain*

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]).

eq.1. $AnO_2(am,hyd) = 1/m An_m(OH)_{4m}(col,hyd)$
eq.2. $An(III)/Ln(OH)_3(am) = 1/m An(III)/Ln_m(OH)_{3m}(col,hyd)$

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.

eq.3. $PuO_2(am,hyd) = 1/m Pu_m(OH)_{4m}(col,hyd)$
eq.4. $PuO_2(am,hyd) + ISA^- = 1/m Pu_m(OH)_{4m}(ISA)_m^{m-}$
eq.5. $PuO_2(am,hyd) + 2ISA^- = 1/m Pu_m(OH)_{4m}(ISA)_{2m}^{2m-}$

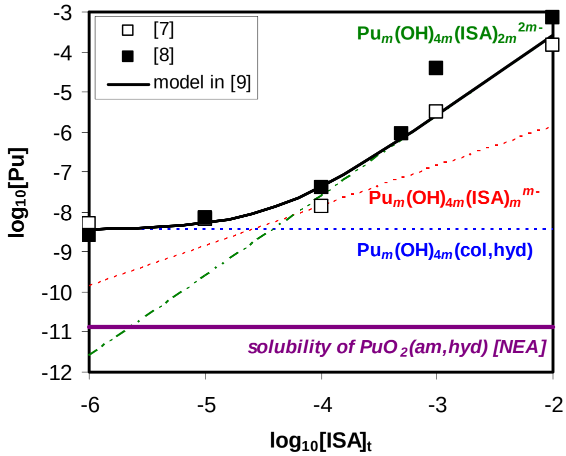


Fig. 1. Effect of ISA on colloidal Pu(IV) at pH=12.

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. LogK(eq.6) reported in [2] (in absence of carbonate) was satisfactorily used in these calculations.

eq.6. $ThO_2(am,hyd) = 1/m Th_m(OH)_{4m}(col,hyd)$
eq.7. $ThO_2(am,hyd) + CO_3^{2-} = 1/m Th_m(OH)_{3m}(CO_3)_m^{m-} + OH^-$

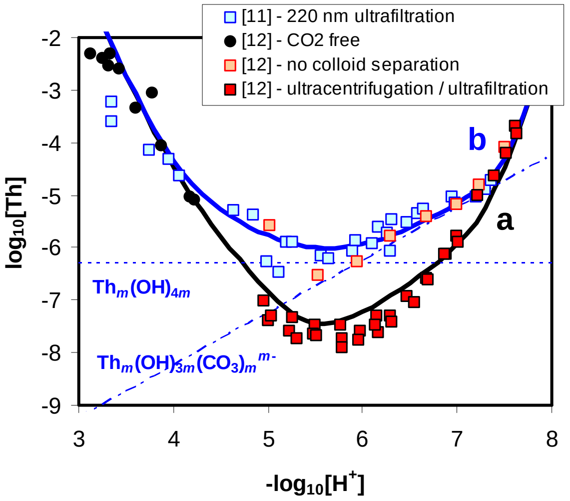


Fig. 2. Effect of carbonate on the solubility of ThO_2(am,hyd) as reported in [11,12]. $pCO_2 = 0.1$ bar. **a.** solubility curve calculated with NEA TDB [13]; **b.** solubility curve calculated including colloidal species described in eq.6-7.

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

A21 acknowledges ANDRA for partial funding of the work through the Thermochimie project. This work was enormously benefited from fruitful discussions with Volker Neck†.

REFERENCES

1. V. NECK et al., “Solubility of plutonium hydroxides/hydrous oxides under reducing conditions and in the presence of oxygen”, *Comptes Rendus Chimie*, **10**, 959 (2007).
2. M. ALTMAIER et al., “Solubility and colloid formation of Th(IV) in concentrated NaCl and $MgCl_2$ solution”, *Radiochimica Acta*, **92**, 537 (2004).
3. V. NECK et al., “An(IV) oxyhydroxide colloids / polymers in aqueous solid-liquid equilibrium systems”, Proceedings of the Russian-German Symposium on Actinide Nano-Particles (2009).
4. B.V. DERJAGUIN et al., “Therory of the stability of strongly charged sols and of the adhesion of strongly charged particles in solutions of electrolytes”, *Acta Physicochim. U.S.S.R.*, **14**, 633 (1941).
5. E.J.W. VERWEY et al., “Theory of the stability of lyophobic colloids”, Elsevier, Amsterdam (1948).
6. V. NECK et al., “Thermodynamics of trivalent actinides and neodymium in NaCl, MgCl2, and CaCl2 solutions: Solubility hydrolysis, and ternary Ca-M(III)-OH complexes”, *Pure and Applied Chemistry*, **81**, 1555-1568 (2009).
7. A.D. MORETON, “Thermodynamic modeling of the effect of hydroxycarboxylic acids on the solubility of plutonium at high pH”, *Materials Research Society Symposium Proceedings*, **294**, 753 (1993).
8. B.F. GREENFIELD et al., “The identification and degradation of isosaccharinic acid, a cellulose degradation product”, *Materials Research Society Symposium Proceedings*, **353**, 1151 (1995).
9. X. GAONA et al., “Review of the complexation of tetravalent actinides by ISA and gluconate under alkaline to hyperalkaline conditions”, *Journal of Contaminant Hydrology*, **102**, 217 (2008).
10. R. GUILLAUMONT et al., *Chemical Thermodynamics 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, F.J. MOMPEAN, Ed., NEA OECD, Elsevier (2003).
11. E. ÖSTHOLS et al., “On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO_2 in CO_2-H_2O media”, *Geochim. Cosmochim. Acta*, **58**, 613 (1994).
12. M. ALTMAIER et al., “Solubility of $ThO_2 \cdot xH_2O$(am) in carbonate solution and the formation of ternary Th(IV) hydroxide-carbonate complexes”, *Radiochim. Acta*, **93**, 83 (2005).
13. M.H. RAND et al., *Chemical Thermodynamics 11: Chemical Thermodynamics of Thorium*. NEA OECD. Elsevier (2009).

Formation of Actinide (IV) colloids in saline solutions

Clemens Walther

Institute for Nuclear Waste Disposal, Karlsruhe Institute for Technology, PO 3640, D 76021 Karlsruhe, Germany
Clemens.walther@kit.edu

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 $Th(NO_3)_4$. $5H_2O$ (p.a.), NaCl (p.a.) and HCl(ultrapure) are purchased from Merck. For further purification, NaCl is recristallized 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/(I-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

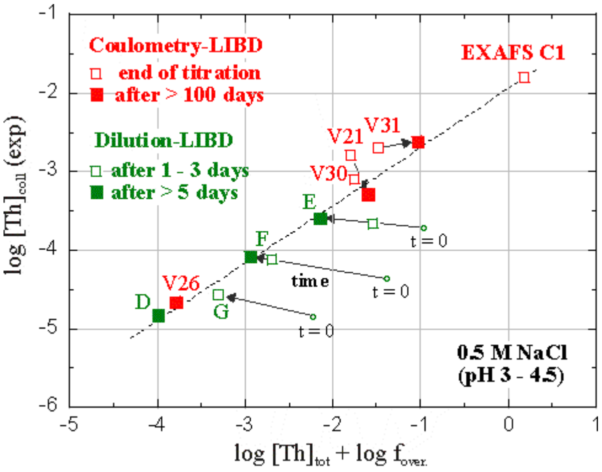


Fig. 1. The colloid content of Th(IV) solutions approaches equilibrium values defined only by the total Th concentration in solution and the degree of oversaturation, but not on the way the sample was prepared. pH drift is observed due to colloid formation and dissolution processes.

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:

$$\mathrm{Th}\left(\mathrm{OH}\right)_4(\mathrm{coll}) \leftrightarrow \mathrm{Th}\left(\mathrm{OH}\right)_3^+(\mathrm{aq}) + 3\mathrm{OH}^- \quad (1)$$

$$\mathrm{Th}\left(\mathrm{OH}\right)_3^+ + (\mathrm{aq}) + 3\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Th}\left(\mathrm{OH}\right)_4(\mathrm{coll}) + 3\mathrm{H}^+ \quad (2)$$

However, the absolute colloid content $[\mathrm{Th}]_{\mathrm{coll}}$ is a function of total thorium concentration and degree of oversaturation f defined by $\log f = \log [\mathrm{Th}]_{\mathrm{tot}} - \log[\mathrm{Th}]_{\mathrm{sol}}$ 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=1m 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 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 $\mathrm{ThO_2}$ 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.

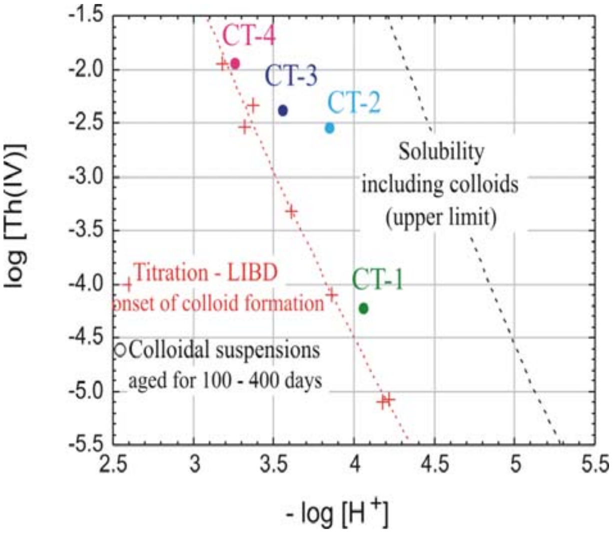


Fig. 2. Th(IV) solutions oversaturated with respect to amorphous Th(IV) hydroxide may contain considerable amounts of Th(IV) colloids. In contrast to the behavior of colloids according to DLVO theory, these colloids are stable for time periods of many years at I=0.5M NaCl.

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 $^{228}\mathrm{Th}$ and observe the enrichment of $^{228}\mathrm{Th}$ in solution after addition of these colloids. Vice versa, $^{232}\mathrm{Th}$ colloids could be introduced to a colloid free solution spiked with $^{228}\mathrm{Th}$. After varying interaction periods the colloids are to be separated from the solution and the $^{228}\mathrm{Th}$ can content be determined. Combining both results, formation and dissolution kinetics can be obtained.

REFERENCES

1. V. DURAND-VIDAL;J.P. SIMONIN;P. TURQ;O. BERNARD, Acoustophoresis of electrolyte solutions and sedimentation profiles of screened charged colloids *Prog. Coll. Polym. Sci.,* **98** 184 (1995)
2. V. NECK;R. MÜLLER;M. BOUBY;M. ALTMAIER;J. ROTHE;M.A. DENECKE;J.I. KIM, Solubility of amorphous Th(IV) hydroxide - application of LIBD to determine the solubility product and EXAFS for aqueous speciation *Radiochim. Acta,* **90** 485 (2002)
3. C. BITEA;R. MÜLLER;V. NECK;C. WALTHER;J.I. KIM, Study of the generation and stability of thorium(IV) colloids by LIBD combined with ultrafiltration *Coll. Surf. A,* **217** 63 (2003)
4. C. WALTHER;M. FUSS;S. BÜCHNER;H. GECKEIS, Stability of Th(IV) polymers measured by electrospray mass spectrometry and laser-induced breakdown detection *J. Radioanal. Nucl. Chem. ,* **282** 1003 (2009)
5. P.W. SCHINDLER, Heterogeneous Equilibria Involving Oxides, Hydroxides Carbonates, and Hydroxide Carbonates *Advances in Chemistry Series,* **67** 196 (1967)

LA-UR 10-06083

Solubility of Uranium and Thorium in Carbonate-free WIPP Brine

Jean-Francois Lucchini, Marian Borkowski, Hnin Khaing, Michael K. Richmann, Julie S. Swanson, David A. Ams, Donald T. Reed

Los Alamos National Laboratory, Carlsbad Operations, Carlsbad, NM 88220, lucchini@lanl.gov

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 ~ 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 7×10^{-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 $ThO(OH)_2$. 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 8×10^{-7}M and 5×10^{-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].

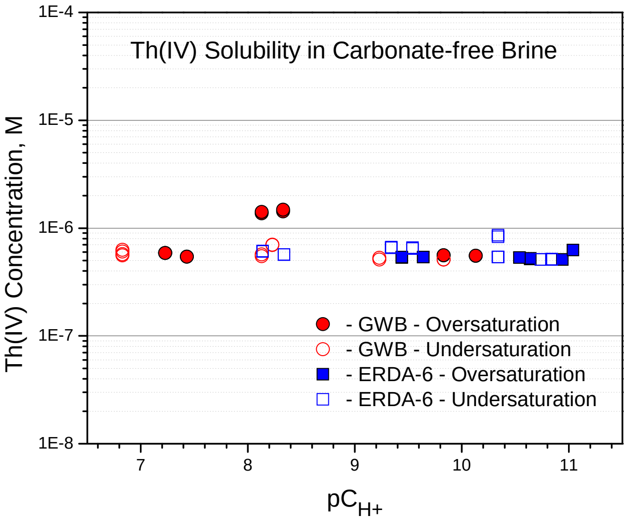


Fig. 1. Measured solubility of thorium (IV) in carbonate-free brine from under- and over-saturation versus pC_{H+}.

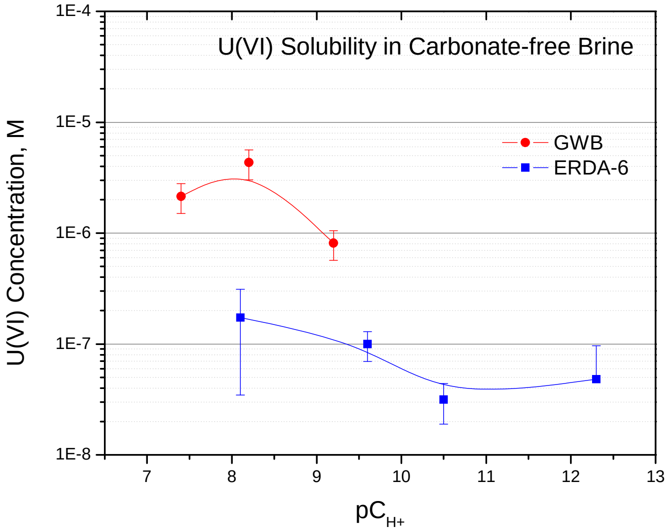


Fig. 2. Measured solubility of uranium (VI) in carbonate-free brine from under- and over-saturation versus pC_{H+}.

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 ~4.8×10^{-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.

REFERENCES

1. J.F. LUCCHINI, M. BORKOWSKI, M.K. RICHMANN, S. BALLARD, D.T. REED, *Journal of Alloys and Compounds* **444/445**, 506 (2007).
2. M. BORKOWSKI, J.F. LUCCHINI, M.K. RICHMANN, D.T. REED, Los Alamos National Laboratory Report LA-14360 (2009).
3. J.F. LUCCHINI, H. KHAING, D.T. REED, Scientific Basis for Nuclear Waste Management XXXIV, *MRS Proceedings*, Volume 1265, San-Francisco, California, April 5-9, 2010, Material Research Society.
4. J.F. LUCCHINI, H. KHAING, M. BORKOWSKI, M.K. RICHMANN, D.T. REED, Los Alamos National Laboratory Report LA-UR-10-00497 (2010).
5. M. ALTMAIER, V. NECK, Th. FANGHANEL. *Radiochimica Acta* **92**, 537 (2004)
6. P. DIAZ AROCAS, B. GRAMBOW, *Geochimica et Cosmochimica Acta* **62**, 245 (1998).

LA-UR 10-06084

Plutonium Oxidation State Distribution in High Ionic Strength Systems

Donald T. Reed
M. Borkowski, H. Khaing, J.-F. Lucchini, M.K. Richmann, J.S. Swanson, D.A. Ams

Los Alamos National Laboratory—Carlsbad Operations, Actinide Chemistry & Repository Science Program
1400 University Drive, Carlsbad, NM, 88220, dreed@lanl.gov

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 established[1-3] 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

Plutonium^{242}, as Pu^{3+} and PuO_2^{2+}, was used in the experiments performed to minimize radiolytic effects. A range of simulated or simplified groundwaters[1-3] 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 method[4] 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 Fe^{2+} and Fe^{3+} towards various plutonium oxidation states was also established. Organic interaction studies where 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 Fe^{2+}(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.

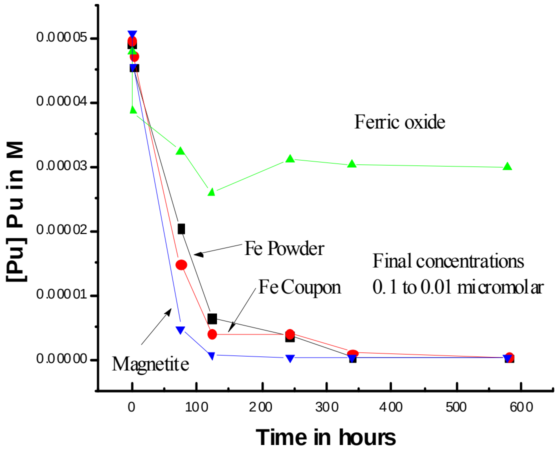


Fig. 1. Reduction of Pu(VI) by reduced iron in brine at pH ~ 9

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 plutonium[6] by stabilizing oxidation states through complexation and by direct reaction with plutonium to oxidize Pu^{3+} and reduce the higher valent PuO_2^{+} and PuO_2^{2+}. The predominant plutonium speciation in these solutions was Pu(IV) organic complexes. This effect argues for the predominance of Pu(IV) in abiotic systems.

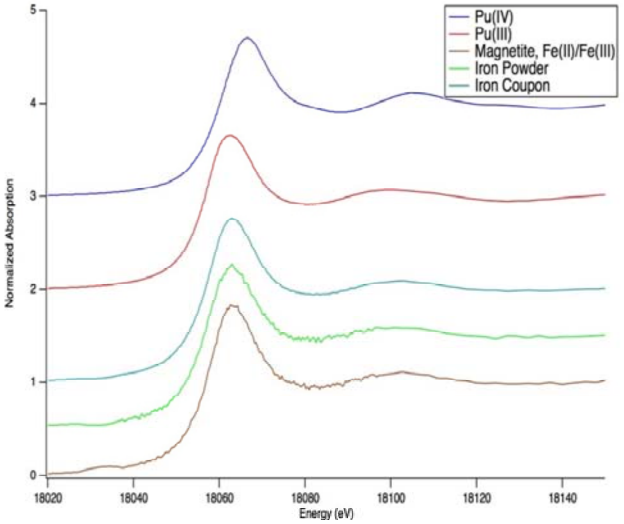


Fig. 2. XANES analysis of Fe-associated plutonium after ~ four year under anoxic conditions in WIPP brine (Argonne APS courtesy of Dr. Jeff Terry and Dan Olive – IIT)

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 Fe^{2+}(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.

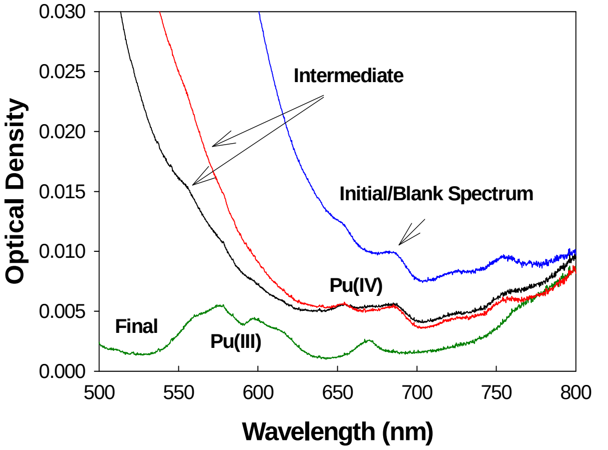


Fig. 3. The bioreduction of Pu(V/VI) to Pu(III) by *S. putrefaciens* when NTA is present as a chelating agent.

REFERENCES

1. D. T. REED, J. F. LUCCHINI, S. B. AASE and A. J. KROPF, "Reduction of Plutonium (VI) in Brine under Subsurface Conditions," Radiochim. Acta., 94 (2006) 591-597.

2. D. T. REED, S. E. PEPPER, B. E. RITTMANN "Subsurface bio-mediated reduction of higher-valent uranium and plutonium," Journal of Alloys and Compounds, Volumes 444-445 (2007) 376-382.

3. D.T. REED, M. K. RICHMANN, J-F. LUCCHINI and M. BORKOWSKI, "Reduction of Higher-Valent Plutonium by Iron Under Waste Isolation Pilot Plant (WIPP)-Relevant Conditions: Data Summary and Recommendations," LANL\ACRSP Report. Los Alamos, NM: Los Alamos National Laboratory, LA-UR-10-01254.

4. S. E. PEPPER, M. BORKOWSKI, M. K. RICHMANN, D. T. REED, "Determination of ferrous and ferric iron in aqueous biological solutions," Analytica Chimica Acta 663 (2010) 172–177.

5. R.P. DEO, W. SONGKASIRI, B. E. RITTMANN, and D. T. REED, "Surface Complexation of Neptunium (V) onto Whole Cells and Cell Components of *Shewanella alga*: Modeling and Experimental Study," Env. Sci. and Tech., 44 (2010) 4930-4935.

6. D. T. REED, S. B. AASE, D. WYGMANS and J. E. BANASZAK. "The Reduction of Np(VI) and Pu(VI) by Organic Chelating Agents." Radiochimica Acta 82(1998) 109-114.

Plutonium Redox Processes in Aqueous Systems

D. Fellhauer[1,2], R. Kirsch[3,4], M. Altmaier[5], V. Neck[5], A. C. Scheinost[3], T. Wiss[1], L. Charlet[4], Th. Fanghänel[1,2]

[1]European Commission – JRC – Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany
email: David.Fellhauer@ec.europa.eu
[2]University of Heidelberg, Institute of Physical Chemistry, Heidelberg, Germany
[3]Inst. of Radiochemistry, FZD, Dresden, Germany, AND Rossendorf Beamline at ESRF, BP220, 38043 Grenoble, France
[4]LGIT, UJF, BP 53, 38041 Grenoble, France
[5]Karlsruhe Institute of Technology – Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany

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 N_2 glove boxes (O_2 < 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)]° [M]	[Pu(V)]° [M]
Maghemite (γ-Fe_2O_3)	5.6	6	$1.2\cdot10^{-5}$	---
Magnetite (Fe_3O_4)	5.5	6	$1.2\cdot10^{-5}$	---
Magnetite (Fe_3O_4)	5.5	8	$1.2\cdot10^{-5}$	---
Mackinawite (FeS)	2.0	6	$1.2\cdot10^{-5}$	---
Hematite (α-Fe_2O_3)	11.5	8	---	$1.3\cdot10^{-5}$
Goethite (FeOOH)	2.0	8	---	$1.3\cdot10^{-5}$
Maghemite (γ-Fe_2O_3)	5.6	6	---	$1.3\cdot10^{-5}$
Magnetite (Fe_3O_4)	5.5	8	---	$1.3\cdot10^{-5}$
Siderite ($FeCO_3$)	3.4	8	---	$1.3\cdot10^{-5}$
Mackinawite (FeS)	2.0	8	---	$1.3\cdot10^{-5}$

After addition of electrochemically prepared ^{242}Pu(III) or ^{242}Pu(V) stock solution (initial concentration: $1.2\cdot10^{-5}$ M Pu(III) and $1.3\cdot10^{-5}$ 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 LN_2 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 $^{242}PuO_2^+$(aq) ($1.0\cdot10^{-4}$ 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 $Na_2S_2O_4$, $FeCl_2/FeCl_3$ 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 Pu(III) ⇔ Pu(IV) in the predominance diagram of Pu.

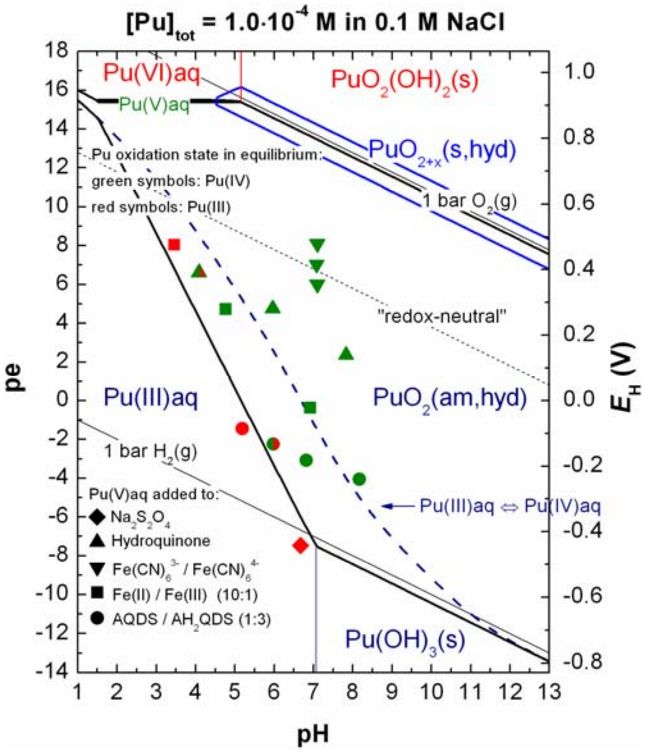


Fig. 1. Measured pH and E_H (pe) values for the Pu experiments in homogeneous redox buffer solutions plotted in the predominance diagram of Pu. Red symbols: predominant Pu oxidation state after reaction: Pu(III). Green symbols: Pu(IV).

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 + 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 Pu(III) ⇔ Pu(IV).

REFERENCES

1. R. GUILLAUMONT et al., *Chemical Thermodynamics 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, F.J. MOMPEAN, Ed., NEA OECD, Elsevier (2003).

LA-UR 10-06015

Complexation of Actinides by Organic Ligands and Borate Ions

Marian Borkowski

D.A. Ams, H. Khaing, J-F. Lucchini, D.T. Reed, M.K. Richmann, J.S. Swanson

Los Alamos National Laboratory—Carlsbad Operations, Actinide Chemistry & Repository Science Program
1400 University Drive, Carlsbad, NM, 88220, marian@lanl.gov

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 m^3

[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.

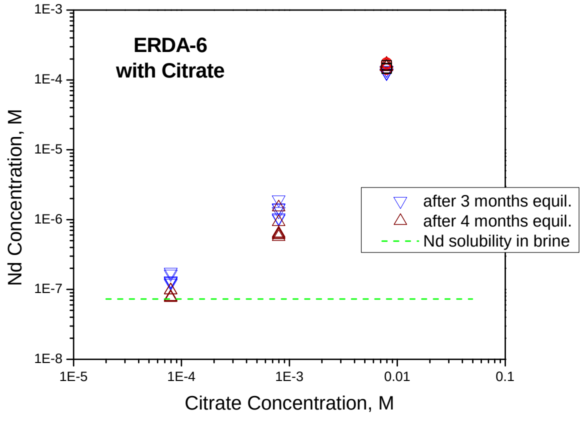


Figure 1. Effect of citrate concentration on Nd(III) solubility in ERDA-6 brine

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).

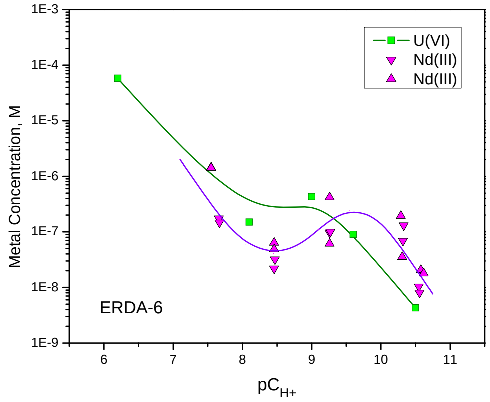


Figure 2. Effect of tetraborate on An(III) and An(VI) solubility.

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.

REFERENCES

1. Brush, L.H., and Y.-L. Xiong, 2009. “Calculation of Organic-Ligand Concentrations for the WIPP CRA-2009 PABC. Analysis Report, June 16, 2009. Carlsbad, NM: Sandia National Laboratories. ERMS 551481.

2. Crawford, B.A., D. Guerin, S. Lott, B. McInroy, J. McTaggart, and G. Van Soest. 2009. “Performance Assessment Inventory Report – 2008.” INV-PA-08, Rev 0. Carlsbad, NM: Los Alamos National laboratory – Carlsbad Operations.

3. Clayton, D.J. 2008. “Update to the Calculation of the Minimum Brine Volume for a Direct Brine Release.” Memorandum to L.H. Brush, April 2, 2008. Carlsbad, NM: Sandia National Laboratories. ERMS 548522.

4. Banaszak, J.E., B.E. Rittmann, and D.T. Reed. 1998. Subsurface Interactions of Actinide Species and Microorganisms: Implications for the Bioremediation of Actinide-Organic Mixtures. ANL-98/26. Argonne, IL: Argonne National Laboratory.

5. Reed, D.T., S.B. Aase, D. Wygmans, and J. E. Banaszak. 1998. “The Reduction of Np(VI) and Pu(VI) by Organic Chelating Agents.” *Radiochimica Acta*, vol. 82: 109-14.

Actinide Carbonate Complexation and Solid Phase Stability in reducing $MgCl_2$ Brine Systems

M. Altmaier[1], V. Neck[1], B. Brendebach[1,2], Th. Fanghänel[3,4]

[1]*Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, PO 3640, D-76021 Karlsruhe, Germany,*
email: marcus.altmaier@kit.edu
[2]*Gesellschaft für Anlagen- und Reaktorsicherheit (GRS mbH), Cologne, Germany*
[3]*Institute for Transuranium Elements, European Commission, Joint Research Centre, Karlsruhe, Germany*
[4]*Institut für Physikalische Chemie, Universität Heidelberg, Heidelberg, Germany*

INTRODUCTION

The storage of nuclear waste in underground salt deposits like the salt formations under discussion in Germany or the Waste Isolation Pilot Plant (WIPP) in the USA requires a description of the solubility of plutonium in chloride brines. In order to reliably predict the long term safety of a repository, the solubility and (redox) speciation of plutonium in NaCl or $MgCl_2$ brines under reducing conditions has to be understood.

It is known that carbonate ligands form strong complexes with actinides, thus leading to enhanced radionuclide solubility. Mg^{2+} has the ability to scavenge carbonate by formation of solid Mg-carbonate phases, but the formation of the thermodynamically stable magnesite $Mg(CO_3)(s)$ is kinetically hindered. Instead, the formation of magnesium-hydroxo-carbonate phases controlling both pH and the free carbonate concentration is observed. Under these conditions, the carbonate concentration in solution cannot be neglected and actinide-carbonate interactions need to be considered.

In this work we have investigated the solubility, solid phase stability and redox speciation of plutonium in 3.5 M (and 0.25 M) $MgCl_2$ solution under strongly reducing conditions (presence of Fe powder, (pe + pH) ~ 2) in systems with and without carbonate. Additional experiments complementing the plutonium studies were performed in dilute to concentrated $MgCl_2$ brines with Nd(III) and Am(III). Experimental results are compared to thermodynamic calculations based upon data from literature [1,2,3].

EXPERIMENTAL

The solubility experiments and sample preparation for X-ray absorption near edge structure (XANES) investigations were preformed in a glove box under inert Ar atmosphere. In a first step, 3.5 M $MgCl_2$ solutions were spiked with Na_2CO_3 solution, leading to precipitation of Mg-OH-CO_3 phases. After a pre-equilibration time with Fe powder of about two months, ^{242}Pu was added to the systems. Experiments were performed both from undersaturation (addition of $PuO_{2+x}(s)$) and oversaturation (addition of electrochemically prepared Pu(III) stock solution). The samples were analyzed over a period of 582 days and pH, redox potential pe and Pu concentration monitored as a function of time. Pu experiments in 0.25 M $MgCl_2$ solutions and solubility batch samples with Nd(III) and Am(III) in dilute to concentrated $MgCl_2$ solutions were prepared, handled and analyzed in a similar way.

Following the termination of the Pu experiments, the solid phases were separated from solution and prepared for XANES analysis. Pu L3 XANES spectra were measured at the INE-Beamline for Actinide Research at the Ångströmquelle Karlsruhe (ANKA), Karlsruhe Institute of Technology, Germany.

RESULTS

The sample in 3.5 M $MgCl_2$ under carbonate free conditions (series 1 in Fig. 1) with initial $PuO_{2+x}(s)$ solid phase, shows constant Pu solubility and concentrations scattering around $10^{-8.0\pm0.3}$ M. As discussed in [3] this can be explained by Pu(III) solution species in equilibrium with a Pu(IV)-oxyhydroxide solid phase. Note that the Pu concentrations are clearly above the expected Pu(IV) concentration level.

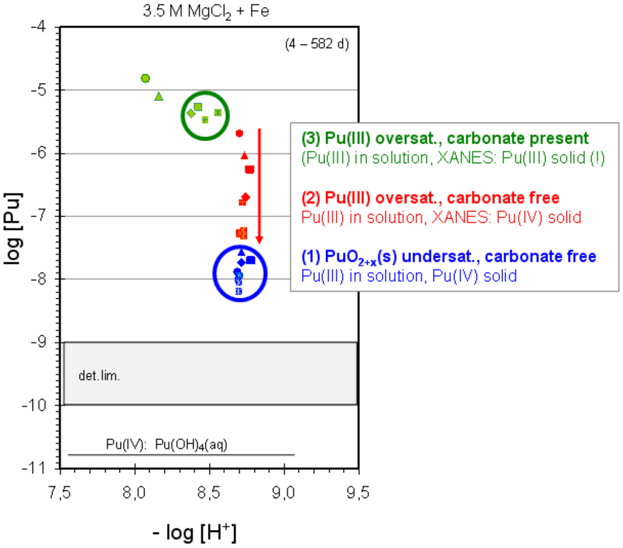


Fig. 1: Solubility of plutonium in 3.5 M $MgCl_2$ under presence and absence of carbonate. Main sample characteristics are indicated.

The carbonate free system with initial Pu(III) solution added (series 2 in Fig. 1) is characterized by a pronounced decrease of the Pu concentration (from [Pu] = $10^{-5.7}$ M to $10^{-7.3}$ M) with time. The high [Pu] measured after short equilibration times can be explained by a trivalent $Pu(OH)_3$(am) solid phase in equilibrium with Pu(III) solution species. This is supported by thermodynamic calculations based upon the data given in [2,3]. The decrease of the Pu concentration to $10^{-7.3}$ M is correlated with a solid phase transformation into Pu(IV)-oxy-hydroxide. This is evidenced by XANES and comparison of the position of the relative white line maxima of the sample with Pu L3 XANES reference spectra. Studies in 0.25 M $MgCl_2$ solution show the same phase stability and XANES characteristics. The experimentally observed instability of the $Pu(OH)_3$(am) phase relative to $Pu(OH)_4$(am) is in agreement with thermodynamic calculations [2].

The sample in equilibrium with the magnesium-hydroxo-carbonate phase with initial Pu(III) solution added (series 3 in Fig. 1), shows a pronounced different behavior. Even after 582 d equilibration the Pu concentration in solution is still about $10^{-5.4}$ M. The shift in pH over time is due to ripening effects of the Mg-OH-CO_3 solid. Contrary to the observation in series (1) and (2), Pu L3 XANES of (3) clearly shows that Pu in the solid phase is in the trivalent oxidation state. The unexpected stability of a Pu(III) solid phase under these conditions can be explained by the stabilization of Pu(III) due to coordinated carbonate ligands in the solid.

Solubility studies with redox stable Nd(III) and Am(III) in concentrated $MgCl_2$ brines equilibrated with Mg-OH-CO_3 solids indicate the transformation of the initial Nd(III)- or Am(III)- hydroxide solid phases. The solubility in the concentrated brine samples under presence of carbonate is reduced relative to the carbonate-free system at comparable pH. Further investigations are indicating solubility control by an (presumably carbonate containing) amorphous alteration phase or surface coating.

It has been confirmed by our studies that tetravalent Pu-hydroxide/oxyhydroxide is controlling Pu solubility in $MgCl_2$ brines under carbonate free conditions. It also raises the question to which extend Pu(III) solid phases are controlling the plutonium solubility in related systems containing free carbonate. This is directly related to repository safety and predictions of radionuclide solubility in salt based repositories. We will extend research activities on Pu(III) solid phase stability and aqueous speciation under strongly reducing conditions in salt brines.

REFERENCES

1. R. GUILLAUMONT et al., *Chemical Thermodynamics 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, F.J. MOMPEAN, Ed., NEA OECD, Elsevier (2003).

2. V. NECK et al., “Solubility of plutonium hydroxides/hydrous oxides under reducing conditions and in the presence of oxygen” *C.R. Chimie*, **10**, 959 (2007).

3. M. ALTMAIER et al., “Solubility of plutonium in $MgCl_2$ and $CaCl_2$ solutions in contact with metallic iron” *Radiochim. Acta*, **97**, 187 (2009).

EDTA and Mixed –Ligands Complexes of Trivalent Am, Cm and Eu at High Ionic Strength and Temperature.

P. Thakur, J. L. Conca and G.R. Choppin*

Carlsbad Environmental Monitoring & Research Center, 1400 University Drive,
Carlsbad, New Mexico-88220, pthakur@cemrc.org; Jconca@cemrc.org

**Department of Chemistry & Biochemistry, Florida State University, Tallahassee,*
Florida-32306-4390, choppin@fsu.edu

INTRODUCTION

Large quantities of hazardous and radioactive waste generated during over forty years of manufacturing and testing of nuclear weapons are stored in several U.S. Department of Energy (DOE) generator sites. The chemical nature of the waste is quite varied as it consists of radionuclides, metals, organic complexing agents and organic solvents. Organic ligands such as EDTA (ethylenediaminetetraacetic acid), Ox (oxalic acid), Cit (citric acid), etc., that are present in significant amounts in mixed radioactive/hazardous chemical waste tanks, can form stable complexes with actinides. The interaction of organic ligands with radionuclides can affect the solubility of actinides and, hence, their migration from a radioactive waste repository to the environment. The WIPP (Waste Isolation Pilot Plant) inventory contains ca. 7.5 metric tons of Cit, 6.4 metric tons of Ox and ~270 kg of EDTA. Given the high stability of the mixed complexes, it is likely that some fraction of the actinides in the storage tanks may be present as mixed complexes. Consequently, a more complete understanding of the effects of organic ligands on the aqueous speciation, including mixed complexation, is necessary in developing effective waste processing strategies.

In this article, the complexation thermodynamics of trivalent Am, Cm and Eu with Cit and EDTA alone and their mixed ligands complexation with EDTA+Cit at I = 5.0 M ($NaClO_4$) have been measured by solvent extraction in the temperature range of 0-60°C. Temperature dependence of stability constants have been used to evaluate the thermodynamic parameters of these complexes. Stochiometry of the complex species has been established by Eu/Cm-luminescence lifetime measurement studies.

DESCRIPTION OF THE WORK

Cit forms 1:1 and 1:2 complexes with these cations, while EDTA forms only the 1:1 complex. The increase in temperature greatly enhances the formation of these complexes (Table 1). The complexation enthalpy is endothermic at I = 5.0 M $NaClO_4$, in contrast to the exothermic enthalpy values usually observed for these complexes at lower ionic strength. The formation of a mixed ligand complex, $M(EDTA)(Cit)^{4-}$ (M^{3+} = Am, Cm and Eu) has been observed in the presence of EDTA+Cit, which have higher stability constants than the corresponding binary complexes. The stability constant of the mixed complexes are in the range 20.67 to 24.86 and increases with increasing temperature.

The number of coordination sites, CN_C of Cit, EDTA and EDTA+Cit bound with Eu^{3+} were calculated using the correlation, $CN_C = 0.237\ \Delta\nu + 0.628$ [1], where $\Delta\nu$ is the shift in the excitation spectra peak of Eu^{3+} (aq) upon complexation, and the number of water molecules in the primary coordination sphere of the complexes were evaluated from the luminescence decay constants (k_{obs}) using equation $N_{H2O} = 1.05\ k_{obs} – 0.70$ [2]. For Cm^{3+} the equation $N_{H2O} = 0.65k_{obs} -0.88$ was used to calculate the number of water molecules in the complex. Cit behaves as a tridentate ligand in the 1:1 and 1:2 complexes at lower pH (<7.0), but at pH 7.0-9.0, the 1:2 complex becomes predominant in which Cit binds via either tetradentatation or a combination of tri and tetradentatation. Similar spectral patterns are observed for Eu^{3+} with Cit. The $Eu(Cit)(H_2O)_6$ and $Eu(Cit)_2(H_2O)_3^{3-}$ are formed at lower pH (<7.0) in which Cit is tridentate. The complexes (a) $Eu(Cit)_2(H_2O)_2^{3-}$ and (b) $Eu(Cit)_2(H_2O)^{3-}$ form at pH 7.0 with one Cit molecule tridentate and the other, tetradentate (via the OH group of Cit) in (a) and with both Cit molecules tetradentate in (b). At pH ~9.0, the Cit has tetradentate coordination. The excitation spectra of both Cm-EDTA and Eu-EDTA indicate the formation of M(EDTA)$^-$ in the pcH range 3.6 to 9.0. At pcH >9.0, the hydration value decreases, indicating the formation of a mixed hydroxyl complex M(EDTA)(OH)$^{2-}$. The mixed complex M (EDTA)(Cit)$^{3-}$ forms at pH ~9.0. The hydration data of 1.1±0.5 for Cm^{3+} and 0.6±0.5 for Eu^{3+} indicate that EDTA is hexadentate, while Cit binds via three carboxylates groups for a CN_T of 9.0 with no water of hydration.

FUTURE DIRECTION

The stability constants of Cit and EDTA at different ionic strength (0.1 to 4.0 M) have been measured. It has been planned to measure the stability of the mixed complexes at these ionic strengths. The SIT and PITZER ionic interaction parameters will be calculated to estimate the thermodynamic stability constants at I= 0.

Table 1. Stability constants of Am^{3+}, Cm^{3+} and Eu^{3+} with Cit at 5.0 M ($NaClO_4$); T= 0-60^{o}C.

Am-Cit	**0^{o}C**	**25^{o}C**	**45^{o}C**	**60^{o}C**
log β_{101}	5.69±0.07	6.14±0.05	6.26±0.09	6.75±0.10
log β_{102}	9.79±0.09	10.55±0.09	11.07±0.11	11.71±0.12
Cm-Cit				
log β_{101}	5.68±0.08	5.93±0.06	6.38±0.07	6.70±0.09
log β_{102}	9.82±0.08	10.30±0.10	11.05±0.11	11.53±0.11
Eu-Cit				
log β_{101}	5.80±0.07	6.17±0.09	6.47±0.09	6.81±0.08
log β_{102}	9.77±0.08	10.18±0.10	10.95±0.11	11.37±0.11

REFERENCES

1. G.R. Choppin, Z.M. Wang, Correlation between Ligand Coordination Number and the Shift of the $^7F_0 – ^5D_0$ Transition Frequency in Europium (III) Complex, *Inorg. Chem*. **36**, 249 (1997).
2. T. Kimura, G.R. Choppin, Luminescence study on determination of the hydration number of Cm(III), J. Alloys & Compd. **213/214**, 313-317(1994)

ACKNOWLEDGMENT

This research was supported by a grant from the USDOE-EMSP contract.

Experimental sorption studies on cement systems

Jan Tits[1], X. Gaona[1,2], N. Macé[1], D. Kulik, T. Stumpf[2], C. Walther[2], E. Wieland[1]

[1]Paul Scherrer Institute, Laboratory for Nuclear Waste Management, CH-5232 Villigen-PSI, Switzerland
[2]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, D-76021, Karlsruhe, Germany
Email: jan.tits@psi.ch

INTRODUCTION

Cementitious materials are an important component in the multi-barrier concept used in many countries for the safe storage of intermediate level radioactive waste in deep geological repositories. They have properties making them well suited for the retention of radionuclides: These are: 1) a strong capacity to buffer the pH in the near field to values >12.5, where most radionuclides have very low solubilities. 2) High sorption potential of the calcium silicate hydrates (C-S-H phases), a major component of hydrated cements, towards many radionuclides, and 3) excellent long term stability of the C-S-H phases during cement degradation and thus preservation of the retention capacity of the cement.

In order to account for radionuclide retention in performance assessment (PA) studies, state-of-the-art sorption databases (SDB's) for the far field as well as for cementitious near-field have been developed and are regularly updated (e.g. Wieland & Van Loon, 2003). The studies carried out at PSI/LES aim at 1) providing sorption data for these SDB's and 2) providing a justification for the selected sorption data through a sufficient understanding of the sorption mechanisms and processes governing radionuclides sorption. The approach adopted combines macroscopic studies (batch sorption and diffusion experiments), with spectroscopic investigations and thermodynamic modeling and allows quantitative and structural information on the sorption processes to be obtained.

Sorption studies on cementitious near field materials are carried out both on entire hardened cement paste (HCP) and on single cement components (e.g. C-S-H phases). Key radionuclides are chosen based on their relevance for the PA studies and include activation productes (e.g., Sr, Ni), actinides and appropriate analogues, such as Am, Eu, Nd, Th, U, and Np, as well as anions and oxyanions, such as I, Cl and Se species and C-14 containing species originating from the corrosion of activated steel. The experimental approach described above will be illustrated with the help of a study on the retention of U(VI) by cementitious materials.

U(VI) UPTAKE BY CEMENTITIOUS MATERIALS

Experimental

The uptake of U(VI) by HCP and C-S-H phases has been investigated using batch sorption tests and luminescence spectroscopy. In the literature, a possible sorption mechanism for this actinide on cementitious materials has been proposed (e.g. Harfouche et al., 2006). However, further confirmation is needed.

Batch sorption tests were performed in glove boxes under N_2 atmosphere (pO_2, pCO_2 < 5 ppm). C-S-H phases were prepared in alkaline solutions (pH=12.5 or 13.3) following a procedure described elsewhere (Tits et al., 2006]. Aliquots of U-nat solutions with appropriate concentrations labeled with U-233, were added and the labeled suspensions were equilibrated on end-over-end shakers for 2 weeks. U(VI) concentrations in the suspensions and in the supernatant (after centrifugation at 90'000g(max)) were determined using liquid scintillation counting. The amount of radionuclide sorbed was obtained by subtracting the concentrations in the supernatant and in the suspension.

Luminescence experiments on wet pastes obtained from the batch sorption tests ((Macé *et al.* 2010) were carried out using a Nd:YAG pumped OPO laser (Spectra Physics). The luminescence emission spectra were collected at a temperature of 4K using a He cryostat. Spectra were recorded by a spectrometer consisting of a polychromator (300 lines/mm grating) and an intensified, gated photo diode array (Yobin Ivon).

Results

Fig. 1 shows the results of batch sorption tests on HCP and C-S-H phases with different compositions (Ca:Si ratios) in an artificial cement pore water (ACW, 0.11 M NaOH, 0.18 M KOH, pH=13.3) and in alkali-free solutions (10<pH<12.5). The aqueous Ca and Si concentrations are in equilibrium with the respective solid phases. This decrease in pH and variation in solution composition mimics the progressing degradation of the cement in a repository. The sorption isotherms were strongly dependent on the composition of the C-S-H phases. A significantly different uptake was observed for ACW systems and the alkali-free systems, both in terms of amount of U(VI) sorbed (much higher for non-alkali systems) and sorption behaviour with respect to the C:S ratio. These data suggest an increase of U(VI) sorption with progressing degradation of the cementitious material in a repository.

Luminescence emission spectra may give information on the symmetry of the oxygens in the first coordination sphere of the sorbed U(VI) and to a lesser extend on the e^-

donating properties of the equatorial ligands of the uranyl moiety.

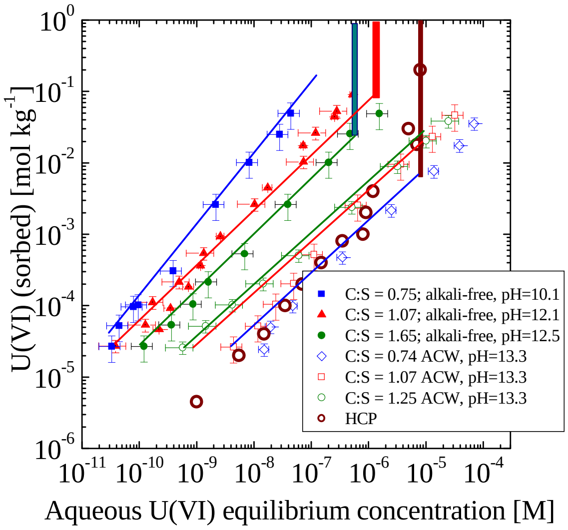


Fig 1: U(VI) sorption isotherms on HCP and C-S-H phases with different C:S ratios in alkali-free solutions and in ACW. Vertical lines represent the calculated U(VI) solubility limits. Solid lines represent the CSH3T-U model

In Fig. 2 the luminescence emission spectra of three U(VI)-silicate references and of U(VI) sorbed on a C-S-H phase and on HCP are compared. The position of the emission bands of the sorbed U(VI) species and of U(VI) in soddyite are very similar suggesting that the coordination symmetry of U(VI) in both environments is comparable. This is only possible when sorbed U(VI) is incorporated in the interlayer of the C-S-H structure. The lack of "structure" in the bands of the sorbed U(VI) species is probably caused by small variations in the site symmetry of different luminescence centers. Furthermore the luminescence spectra of U(VI) sorbed on the C-S-H sample and on HCP are almost identical proving that the U(VI) in HCP is sorbed on the C-S-H fraction.

Previous investigations showed that C-S-H phases are characterized by high recrystallisation rates. This information, together with the information from the wet chemistry and luminescence spectroscopy studies suggest that the uptake of U(VI) by C-S-H phases may be described by a solid solution model. The Compound Energy Formalism (CEF) was selected to develop an aqueous-solid solution thermodynamic model for U(VI) incorporation in C-S-H phases (CSH3T-U model, Gaona et al., 2010). Sub-lattices were filled in with species defined in accordance with spectroscopic observations, leading to an initial set of nine C-S-H-U(VI) end members. The optimization of the model was achieved by forward modelling runs using the GEMS-PSI code. The resulting optimized model was able to describe properly both the sorption isotherms in alkali-free systems and in ACW (Fig. 1).

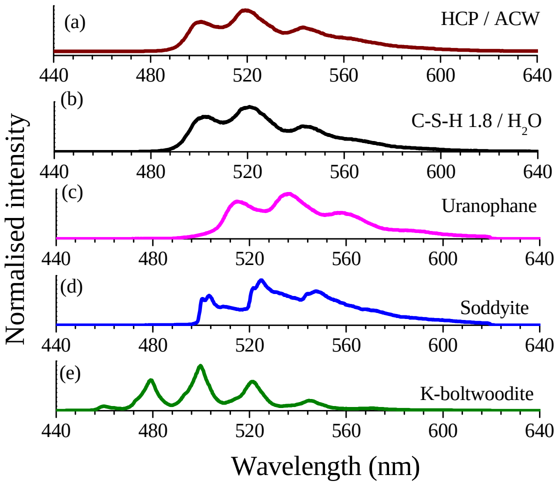


Fig. 2: U(VI) luminescence spectra from U(VI)-silicate references and from U(VI) sorbed on C-S-H and on HCP

Such a detailed system understanding allows the selection of sorption values for U(VI) for fresh and degraded cement in a SDB with a high degree of confidence Furthermore, the development of thermodynamic models allows the effect of varying chemical conditions such as changes in pH solution composition to be predicted.

REFERENCES

1. E. WIELAND, L.R. VAN LOON, PSI Report Nr. 03-06, Paul Scherrer Institute, Villigen, Switzerland and Nagra, Technical Report NTB 02-20, Nagra, Wettingen, Switzerland (2002).
2. M. HARFOUCHE, E. WIELAND, R. DAEHN, T. FUJITA, J. TITS, D. KUNZ, M. TSUKAMOTO, "EXAFS study of U(VI) uptake by calcium silicate hydrates," J. Colloid Interface Sci. **303**, 195 (2006).
3. J. TITS, E. WIELAND, C.J. MUELLER, C. LANDESMANN, M.H. BRADBURY, "A wet chemistry study of the strontium binding by calcium silicate hydrates", J. Colloid Interface Sci. **300**, 78 (2006).
4. X. GAONA, D. KULIK, N. MACE, E. WIELAND, Aqueous-solid solution thermodynamic model of U(VI) uptake in C-S-H phases. Geochim. Cosmochim. Acta, (2010) (in prep.)
5. N. MACE, J. TITS, M. MARQUES-FERNANDES, T. STUMPF, C. WALTHER, E. WIELAND, Speciation of the U(VI) uptake by cementitious materials using Time Resolved Laser Fluorescence Spectroscopy (TRLFS) at cryogenic conditions. Environm. Sci.& Techn. (2010) (in prep.)

Interactions of americium and uranium with cement alteration products under saline conditions

V. Metz, B. Kienzler, C. Bube and E. Bohnert

Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, E-mail: volker.metz@kit.edu

INTRODUCTION

Generally, the leach and alteration rate is considered to be the most significant criterion for assessing the quality of cemented radioactive waste products. Numerous studies on reactions of cemented waste products in aqueous solutions show that radionuclide species with a low charge density, e.g. $^{137}Cs^+$, are hardly retarded in the altered cement structure. In contrast, uranium and other actinides are significantly retarded during alteration of cemented waste products.

From 1967 to 1978, about 126’000 drums of low- and intermediate-level waste, LLW / ILW (which contained $8 \cdot 10^{15}$ Bq), were disposed off in the salt mine “Asse II” near Remlingen, Germany [1,2]. In the salt mine at Morsleben, Germany, about 36’000 m^3 LLW / ILW (which contained $3 \cdot 10^{14}$ Bq) were disposed off between 1971 and 1991 [3]. Cemented waste products dominate the waste inventories of both repositories. Additionally, cement is brought into the near-field of the radioactive waste by self-shielding concrete containers and by construction materials. The risk associated with the disposal system depends on the radionuclide mobilization in case of groundwater intrusion into the repository. In the case of (saline) groundwater intrusion penetrating into a repository like Asse II or Morsleben, brines may interact with the waste products and other cementitious materials.

Numerous investigations have been performed to quantify the retention of radionuclides by cement or its alteration products. However, alteration, leaching and retention processes in cement / brine systems are quite different from those in systems with less concentrated aqueous solutions. There is a considerable lack of knowledge regarding the effectiveness of cement and its alteration products in concentrated salt solutions to retard actinides.

EXPERIMENTAL AND MODELING METHODS

In the present study, interactions of Am(III) and U(VI) with cement forms corroding in $MgCl_2$ brine are investigated using full scale leaching experiments, laboratory scale batch experiments and geochemical modeling. Since 1989, static experiments have been conducted with 336 kg uranium doped cement forms (951 g U(nat.) per sample), exposed to 135 liters $MgCl_2$ brine. Details on these long term experiments are given in Kienzler et al. [4]. In parallel, laboratory batch experiments are carried out to study equilibrium concentration of Am(III) and U(VI) using crushed cement products and the same type of leachant. Compositions of both altered solution and altered solid are analyzed to monitor the equilibration of the system. Using the EQ3/6 [5] and Geochemist’s Workbench [6] software packages, cement corrosion and the resulting solution composition are simulated.

RESULTS AND DISCUSSION

Experimental results agree well with the calculated composition of the altered solution as a function of the corrosion progress [7] and cement to solution mass ratio, respectively (Fig. 1). In the full scale experiments, pH_m (i.e. $-\log(m_{H+})$ of the bulk solution increased within few months to values ~8.5, mainly controlled by formation of Mg-oxychloride. Such a near neutral $MgCl_2$ dominated solution composition corresponds to a solution composition observed in lab experiments and simulations for $m(cement)/m(H_2O) < 0.2$ kg/(kg H_2O). After 10 years of exposure, dissolved Mg is consumed by Ca-Mg exchange reactions and consequently the pH_c increased to values ~11.5 in the full scale experiments [4]. The alkaline $CaCl_2$ dominated solution composition corresponds to that measured in lab experiments and calculated for $m(cement)/m(H_2O) < 0.6$ kg/(kg H_2O).

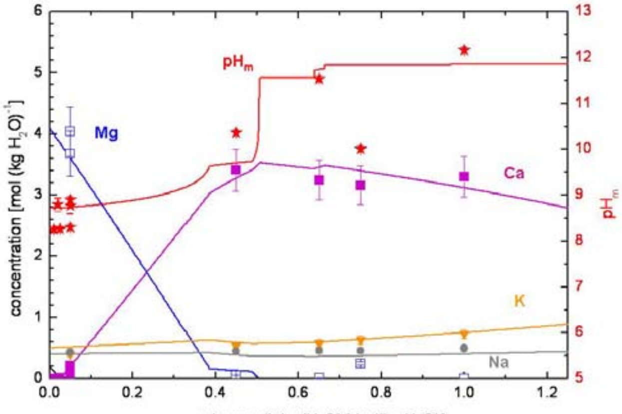


Fig. 1. Comparison of modeling results (lines) with concentrations measured in laboratory experiments (symbols).

The behavior of Am(III) and U(VI) is strongly affected by the change in solution compositions from near neutral $MgCl_2$-dominated to alkaline $CaCl_2$-dominated conditions. In the full scale experiments, dissolved uranium approached a concentration $\leq 5\times10^{-7}$ mol L^{-1} in the corroding brines after 17 to 18 years interaction time. The observations suggest that retention of the relatively high uranium inventory is controlled by solubility phenomena rather than by adsorption onto cement corrosion products. According to results of XRD, TRLFS and XANES/EXAFS analyses, uranophane ($Ca(UO_2)_2(SiO_3OH)_2{\bullet}5H_2O$) seems to be the dominant uranium bearing phase in the corroded cement [4].

Unlike U, measured Am concentrations are orders of magnitude below solubilities of Am(III) solids. Sorption equilibria in Am/brine/cement systems at pH_m ~8.5, ~10 and ~12 were approached within less than one year. Linear isotherms were derived from these three experimental series showing stronger sorption of Am(III) under $pH_m \geq 10$ compared to sorption at weakly alkaline conditions.

Future work will focus (i) on compiling a consistent dataset for calculating stabilities of relevant U(VI) phases in the altered cement / brine systems and (ii) determining sorption equilibria in Pu/brine/cement systems between pH_m ~8.5 and ~12.

Acknowledgements

This study has been partly funded by the German Federal Office for Radiation Protection (BfS). The authors would like to thank M. Schlieker, B. Brendebach, N. Finck, J. Lützenkirchen, M. Plaschke, T. Rabung and D. Schild for their contributions in the experimental part. We are grateful to V. Neck† and M. Altmaier for fruitful discussions regarding the thermodynamic calculations.

REFERENCES

1. G. KAPPEI, “100 years salt-mine Asse II”. Int’l Conference on Radioactive Waste Disposal in Geological Formations. Braunschweig, Germany: Bundesamt für Strahlenschutz and Gesellschaft für Anlagen- und Reaktorsicherheit (2007).
2. H. BOSSY, "The Closure of the Asse Research Mine," Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management Second Review Meeting, May 17th 2006, Federal Ministry of Education and Research, Bonn, Germany (2007).
3. BUNDESAMT FÜR STRAHLENSCHUTZ, “Endlager Morsleben - das Endlager für radioaktive Abfälle vor der Stilllegung”. Bundesamt für Strahlenschutz, Salzgitter, Germany (2001).
4. B. KIENZLER et al., “Chemical status of U(VI) in cemented waste forms under saline conditions.” *Radiochim. Acta,* **98,** 1–10 (2010).
5. T. J. WOLERY, "EQ3/6, A software package for geochemical modeling of aqueous systems:Package overview and installation guide (Version 7.0)," UCRL-MA-110662 PT 1 (1992).
6. C. M. BETHKE, S. YEAKEL, The Geochemist's Workbench. Release 8.0 - reference manual”, University of Illinois, Urbana-Champaign (2009).
7. B. KIENZLER et al., “Geochemically based safety assessment”. *J. Nucl. Sci. Techn.* **44**, 470-476 (2007).

Overview of WIPP Geochemical Modeling[1]

L.H. Brush and Y.-L. Xiong

Sandia National Laboratories,[2] 4100 National Parks Hwy. Carlsbad, NM 88220, lhbrush@sandia.gov

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 CO_2 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.

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 ($CaSO_4$), brucite ($Mg(OH)_2$), and the "5424" polymorph of hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) 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 ($MgCO_3$) 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 GWB[8] and 8.98 in ERDA-6[8].

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

---

[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.

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 analogy[9] 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 GWB[8]; and 6.98×10^{-8} M, 8.75×10^{-7} M, and 1.51×10^{-6} M in ERDA-6[8].

REFERENCES

1. J.L. Krumhansl, K.M. Kimball, and C.L. Stein, *Intergranular Fluid Compositions from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico,* SAND90-0584, Sandia National Laboratories, Albuquerque, NM (1991).
2. A.C. Snider, "Verification of the Definition of Generic Weep Brine and the Development of a Recipe for This Brine," unpublished report, Sandia National Laboratories, Carlsbad, NM. ERMS 527505 (2003).
3. R.S. Popielak, R.L. Beauheim, S.R. Black, W.E. Coons, C.T. Ellingson and R.L. Olsen. *Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant Project, Southeastern New Mexico,* TME 3153, U.S. Department of Energy WIPP Project Office, Carlsbad, NM (1983).
4. S.C. Babb, S.C. and C.F. Novak. "User's Manual for FMT Version 2.3: A Computer Code Employing the Pitzer Activity Coefficient Formalism for Calculating Thermodynamic Equilibrium in Geochemical Systems to High Electrolyte Concentrations;" unpublished report, Sandia National Laboratories, Albuquerque, NM: ERMS 243037 (1997 and addenda).
5. Y. Wang, "WIPP PA Validation Document for FMT (Version 2.4), Document Version 2.4," unpublished report, Sandia National Laboratories, Carlsbad, NM, ERMS 251587 (1998).
6. T.J. Wolery, *EQ3/6, a Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0)*, UCRL-MA-110662 PT I. Lawrence Livermore National Laboratory, Livermore, CA (1992).
7. T.J. Wolery and R.L. Jarek, "Software User's Manual: EQ3/6, Version 8.0," Software Document No. 10813 UM-8.0-00, unpublished report, Sandia National Laboratories, Albuquerque, NM (2003).
8. L.H. Brush, Y.-L. Xiong, and J.J. Long. "Results of the Calculations of Actinide Solubilities for the CRA-2009 PABC," unpublished report, Sandia National Laboratories, Carlsbad, NM, ERMS 552201 (2009).
9. G.R. Choppin, "Utility of Oxidation State Analogs in the Study of Plutonium Behavior," *Radiochimica Acta*, Vol. 85, pp. 89–95 (1999).
10. U.S. EPA, "Technical Support Document for Section 194.24: Evaluation of the Compliance Recertification – Actinide Source Term and Culebra Dolomite Distribution Coefficient Values," EPA Air Docket A 98-49, Item II B1-3, U.S. Environmental Protection Agency Office of Air and Radiation, Washington, DC (2006).

ASCEM: Advanced Simulation Capability for Environmental Management

Bruce A. Robinson
Paul R. Dixon

Los Alamos National Laboratory, Mail Stop D446, Los Alamos, NM, 87545 robinson@lanl.gov

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.

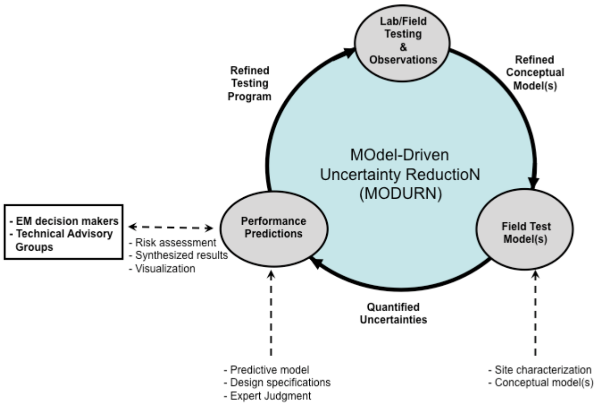


Figure 1. Schematic of the Model-Driven Uncertainty Reduction paradigm.

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.

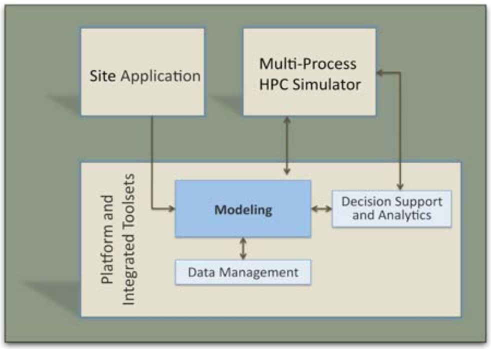


Figure 2. *The 3 technical thrust areas of ASCEM: Multi-Process HPC Simulator, Platform and Integrated Toolset, and Site Applications.*

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

M. Altmaier[1], C. Bube[1], V. Brendler[2], C.M. Marquardt[1], H. C. Moog[3], V. Neck[1], A. Richter[2], T. Scharge[3], W. Voigt[4], S. Wilhelm[5], G. Wollmann[4]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, PO 3640, 76021 Karlsruhe, Germany
[2]FZ Dresden-Rossendorf e.V., Institute of Radiochemistry, PO 510119, 01314 Dresden, Germany
[3]Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Theodor-Heuss-Str. 4, 38122 Braunschweig, Germany
[4]TU Bergakademie Freiberg, Institute of Inorganic Chemistry, Leipziger Str. 29, 09596 Freiberg, Germany
[5]AF-Colenco Ltd, Groundwater Protection and Waste Disposal, Täfernstr. 26, 5405 Baden-Dättwil, Switzerland

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, SO_4^{2-} for temperatures up to 393 K
- The above system with CO_2/CO_3^{2-} 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.

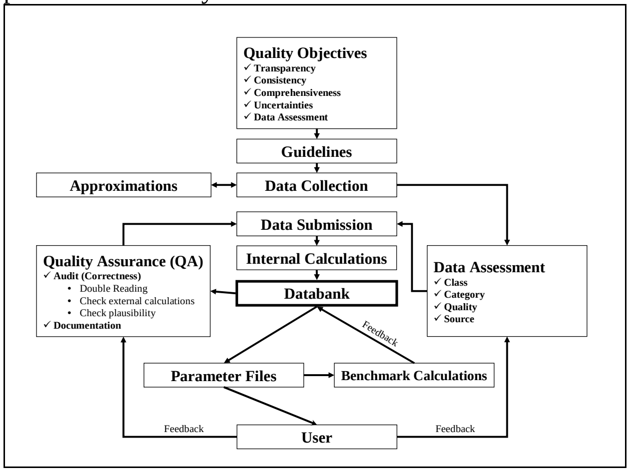


Fig. 1. Elements of Quality Assurance and their mutual relationships in THEREDA

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 technologic 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.

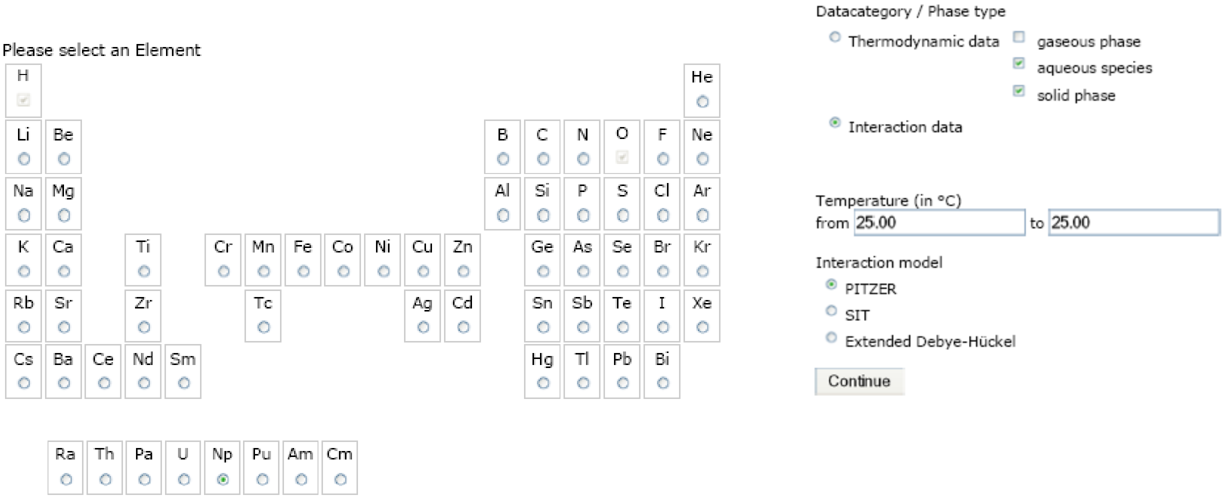
FUTURE DIRECTIONS

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 $MgCl_2$ and $CaCl_2$ 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.

REFERENCES

1. F. J. Mompean and H. Wanner, *Radiochim. Acta*, **91**, 617 (2003).
2. Hummel et al., "Nagra/PSI Chemical Thermodynamic Data Base 01/01", Nagra Technical Report NTB 02-16, Universal Publishers, Parkland, Florida (2002).
3. Wagman et al., "The NBS tables of chemical and thermodynamic properties", *J. Phys. Chem. Ref. Data (11, Supplement No. 2,)*, 392p. (1982).
4. Cox et al., *CODATA Key Values for Thermodynamics*, Final report of the CODATA task group on key values for thermodynamics, Hemisphere Publishing Corporation, ISBN 0-89116-758-7, (1989).
5. Altmaier et al., Report FZK-INE 002/04; Neck et al., Pure Appl. Chem. **81(9)**, 1555 (2009);Altmaier et al., Abstract for Migration '09, Book of Abstract p. 38 (2009).
6. Harvie, C.E. and Weare, J.H., Geochim. Cosmochim. Acta **44**, 981 (1980)
7. Harvie et al., Geochim. Cosmochim. Acta **48**, 723 (1984)

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



● Np

Datacategory / Phase type
○ Thermodynamic data ☐ gaseous phase
☑ aqueous species
☑ solid phase
● Interaction data

Temperature (in °C)
from 25.00 to 25.00

Interaction model
● PITZER
○ SIT
○ Extended Debye-Hückel

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

Actinide Sorption Database

Vinzenz Brendler, Anke Richter

FZ Dresden-Rossendorf, P.O.Box 510191, D-01314 Dresden, Germany, V.Brendler@fzd.de

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 RES^{3}T – 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 RES^{3}T 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.

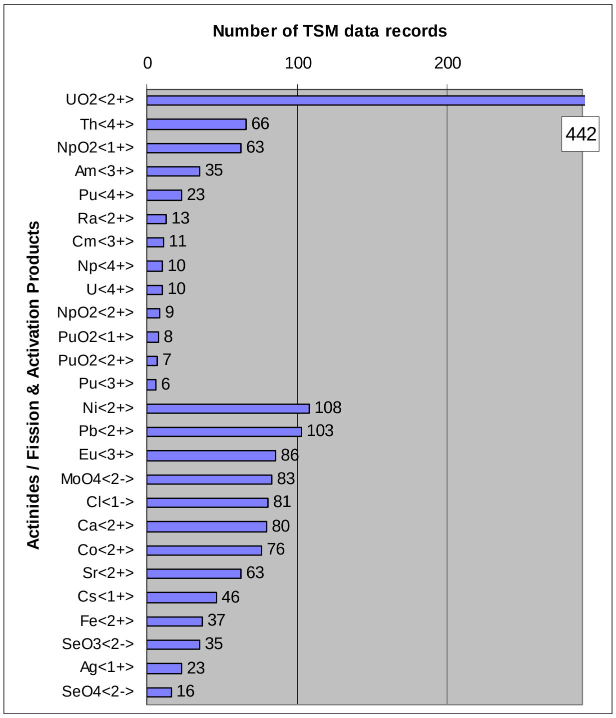


Fig. 1. Amount of surface complexation constants for actinides and relevant fission/activation products in RES³T.

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.

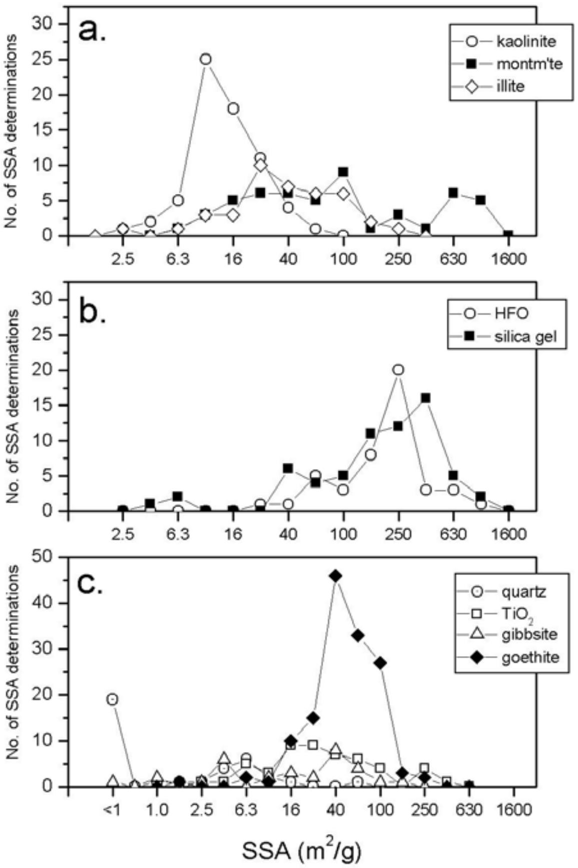


Fig. 2. Plot of experimental mineral surface areas, each point indicates the number of SSA measurements in each size range. a) Clay minerals – kaolinite, montmorillonite and illite. b) Amorphous coating minerals – ferrihydrite (HFO) and silica gel. c) Various crystalline oxides – quartz (SiO_2), gibbsite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

REFERENCES (if needed)

1. W. STUMM, *Chemistry of the solid-water interface*, p. 448, Wiley, New York (1992).
2. R.G. WILHELM, P. BEAM, “Understanding variation in partition coefficient, Kd, values.” EPA Report 402-R-99-004A, Washington (1999).
3. V. BRENDLER et al., “RES³T - Rossendorf expert system for surface and sorption thermodynamics.” *J. Contam. Hydrol.*, **61**, 281 (2003).
4. T.E. PAYNE, V. BRENDLER, M.J. COMARMOND, C. NEBELUNG, “Assessment of Surface Area Normalisation for Interpreting Distribution Coefficients (Kd) for Uranium Sorption”. *J. Environ. Radioactivity (online available), 2010.*

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

Bernhard Kienzler

Karlsruhe Institute of Technology (KIT), Campus North, Institut für Nukleare Entsorgung (INE):
Hermann von Helmholtz Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
bernhard.kienzler@kit.edu

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.

List of Attendees: ABC-Salt Workshop

Carlos Abeyta	Los Alamos National Laboratory icabeyta@lanl.gov
Marcus Altmaier	Karlsruhe Institute of Technology marcus.altmaier@kit.edu
David Ams	Los Alamos National Laboratory dams@lanl.gov
Marian Borkowski	Los Alamos National Laboratory marian@lanl.gov
Guido Bracke	Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH Guido.Bracke@grs.de
Vinzenz Brendler	FZ Dresden-Rossendorf Institute of Radiochemistry V.Brendler@fzd.de
Larry Brush	Sandia National Laboratories lhbrush@sandia.gov
Christopher Chancellor	Los Alamos National Laboratory chancellor@lanl.gov
Dan Clayton	Sandia National Laboratories djclayt@sandia.gov
Jim Conca	New Mexico State University jconca@cemrc.org
Ned Elkins	Los Alamos National Laboratory elkins@lanl.gov
David Fellhauer	JRC-ITU Karlsruhe, European Commission David.Fellhauer@ec.europa.eu
Daniela Freyer	University Freiberg, Germany Daniela.Freyer@chemie.tu-freiberg.de
Xavier Gaona	Paul Scherer Institute Email: Javier.Gaona@psi.ch
Greg Roselle	Sandia National Laboratories gtrosel@sandia.gov
Frank Hansen	Sandia National Laboratories fhanse@sandia.gov
Tim Hayes	Los Alamos National Laboratory tahayes@lanl.gov
Horst-Jürgen Herbert	Gesellschaft für Anlagen-und Reaktorsicherheit (GRS) mbH, Horst-Juergen.Herbert@grs.de

Je-Hun Jang	Sandia National Laboratories djang@sandia.gov
Bernhard Kienzler	Karlsruhe Institute of Technology bernhard.kienzler@kit.edu
Dugwhan Kim	Korean Radioactive Waste Management Corporation
Christi Leigh	Sandia National Laboratories cdleigh@sandia.gov
Jean-Francois Lucchini	Los Alamos National Laboratory lucchini@lanl.gov
Christian Marquardt	Karlsruhe Institute of Technology christian.marquardt@kit.edu
Volker Metz	Karlsruhe Institute of Technology volker.metz@kit.edu
Henry Moll	FZ Dresden-Rossendorf Institute of Radiochemistry H.Moll@fzd.de
Helge Moog	Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH helge.moog@grs.de
Roger Nelson	Department of Energy, Carlsbad Field Office rnelson@wipp.ws
Seungjun Oh	Korean Radioactive Waste Management Corporation
Eunsang Park	Korean Radioactive Waste Management Corporation
Russ Patterson	Department of Energy, Carlsbad Field Office Russ.Patterson@wipp.ws
Don Reed	Los Alamos National Laboratory dreed@lanl.gov
Norbert Rempe	Washington TRU Solutions Norbert.Rempe@wipp.ws
Michael Richmann	Los Alamos National Laboratory Richmann@lanl.gov
Alex Roberts	Los Alamos National Laboratory aroberts@lanl.gov
Bruce Robinson	Los Alamos National Laboratory robinson@lanl.gov
Julie Swanson	Los Alamos National Laboratory jsswanson@lanl.gov

Jeff Terry	Illinois Institute of Technology jterry@iit.edu
Punam Thakur	New Mexico State University pthakur@cemrc.org
Bill Thompson	Subcontractor to WRES Bill_Thompson@golder.com
Jan Tits	Paul Scherrer Institute jan.t@psi.ch
Clemens Walther	Karlsruhe Institute of Technology clemens.walther@kit.edu
Yong-Liang Xiong	Sandia National Laboratories yxiong@sandia.gov
Namjin Yun	Korean Radioactive Waste Management Corporation