PERMANENT GEOLOGIC ISOLATION OF ACTINIDES IN A SALT REPOSITORY: UPDATE OF THE WIPP SAFETY CASE

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BACKGROUND AND OVERALL PROGRESS/STATUS

The Waste Isolation Pilot Plant (WIPP) transuranic repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. Although the project is currently dealing with operational issues that led to a shutdown of operations, the long-term safety case for the permanent disposal of transuranic (TRU) waste remains intact and was largely unaffected. The WIPP is now pursuing its third recertification (submitted in March 2014) and there remain ongoing discussions about possible expanded missions and additional nuclear repository concepts in a Salt geology within the United States. Research to strengthen the scientific basis of the safety case for actinide containment in high ionic-strength brine systems continues and is ongoing.

An understanding of the actinide and brine chemistry in the WIPP is needed to address the low-probability scenario that brine inundation and release could occur due to human intrusions and is driven by regulatory requirements for the repository license case. The overall ranking of actinides, from the perspective of potential contribution to release from the WIPP, is: Pu ~ Am > U >> Th and Np and remains unchallenged from past recertification. An updated inventory of the predicted TRU content and key waste constituents is given in the Table below. The oxidation state distribution of key multivalent actinides, which is based on expert opinion and the predicted redox environment, also remains unchanged: U – 50% U(IV) and 50% U(VI); Pu – 50% Pu(III) and 50% Pu(IV); with Am/Cm as the III oxidation state and thorium as the IV oxidation state. These actinide/analog oxidation states are the focus of the site-specific redox and solubility studies being performed.

In this recertification cycle, thorium solubility studies in brine were completed; substantial progress was made on the characterization of indigenous microorganisms and the investigation of key actinide-microbial interactions; and the performance assessment (PA) approach to define the contribution of colloidal species to the actinide source term was re-examined and updated. These data [2-6] continue to extend our understanding of high ionic-strength actinide chemistry and strengthen and improve the scientific basis for the safety case for a nuclear repository in salt.

Table 1. Projected Actinide Inventory and Key Waste Constituents in the WIPP [1]

Actinide	Activity in Ci	Mass in Kg
Th	7.04	1.35×10^4
U	528	2.26×10^5
Np	23.2	32.5
Pu	2.02×10^6	1.20×10^4
Am	7.05×10^5	203
Cm	9.97×10^3	0.122
Waste Material		Total Mass (Kg)
Iron-Based metals/alloys		4.91×10^7
CPR (Cellulosic/Plastic/Rubber)		1.54×10^7
MgO (Engineered Barrier)		5.14×10^7
Organic Ligands (Citrate)		7.78×10^3
Organic Ligands (EDTA)		3.76×10^2

Importance of Actinides and Oxidation State Distribution in the WIPP

Overall Release: Pu ~ Am >> U > Th >> Np, Cm and fission products

Oxidation State: III > IV >> VI > V

Oxidation State Distribution of Key Actinides in WIPP Performance Assessment

Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

WIPP SAFETY CASE: SALT REPOSITORY CONCEPT

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.

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.

Safety Case for a Nuclear Repository

Key Concepts for the Geologic Disposal of Nuclear Waste

- Geologic isolation
- Favorable thermodynamics
  - Reducing conditions
  - Reactive redox control
- Cost is an issue
- Favorable local politics

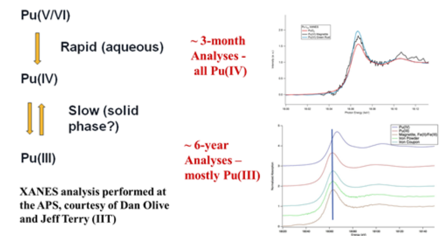
WIPP TRU Waste Repository

Microbial activity can influence both the near-field and far-field in repository performance

REDOX CHEMISTY AND EFFECTS

There is no change in the overall position on redox and oxidation-state distribution in the WIPP. New data is centered on the observation that reduced iron reduced Pu(V/VI) to Pu(III) in long-term multiyear experiments with Pu-242 (i.e., very low radiolysis impacts). The E_h brine measurements, when performed with excess reduced iron in solution, qualitatively correlated with the Fe^{2+} content in the brine systems. This reduced iron is very reactive in brine across a wide pH range and is very effective in reducing multivalent actinides to their lowest possible oxidation state: U(IV), Pu(III) and Np(IV). These experimental results support the overall WIPP PA assumptions and establish them to be conservative with respect to overall solution concentration of mobile actinide species. The one important and key area that is not fully resolved is the long-term stability of the Pu(III) phases being observed and in particular the effects of radiolysis, the more repository-relevant condition, will have on the distribution of plutonium between Pu(III) and Pu(IV). It was already demonstrated that reduced iron is very effective in reducing Pu(V/VI) in radiolysis-affected systems [7]. This lower oxidation-state equilibration remains the focus of our ongoing research.

Pu(V/VI) Reduction by Lower-Valent Fe in Brine



XANES analysis performed at the APS, courtesy of Dan Olive and Jeff Terry (IIT)

WIPP PA COLLOID PARAMETERS AND EFFECTS OF ORGANIC CHELATING AGENTS

Colloidal Contributions and Effects of Organic Chelating Agents on the Solubility of thorium in WIPP brine

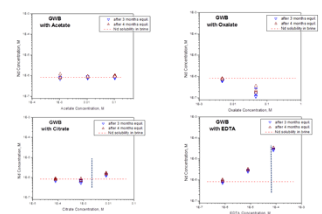
Further studies have been completed to establish the effects of organics and understand the colloidal nature of the thorium species observed in site-specific simulated brine systems. We have previously reported [5] that long times (greater than two years) are needed for thorium concentrations to approach model-predicted equilibration values and these data qualitatively agree with results reported elsewhere [8]. The underlying reason for this long-term equilibration in WIPP brine is not yet fully understood. Further studies explore the relationships between ionic strength and the lesser brine constituents on the colloids formed. In addition, the effects of organic chelating agents on this process as well as the overall solubility of thorium were investigated. The organic complexants do not, in the end, lead to a significant increase in the thorium solubility although metastable complexes can be formed and persist.

Colloidal fraction of the actinides in the WIPP

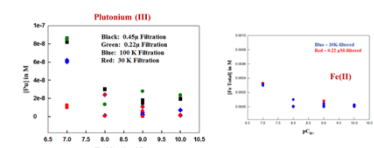
The mineral, intrinsic and microbial contributions to the WIPP mobile colloidal actinide source term model [6] continue to be re-examined under conditions specific to the WIPP safety case. Colloidal species can potentially contribute to the WIPP actinide source term and are currently accounted for in WIPP PA. Data for all key actinides as well as further and more detailed interpretation of the biocolloidal contribution will be updated.

In all, there is continued progress towards establishing more realism in the WIPP PA models and these strengthen the safety case for nuclear waste disposal in a salt repository.

Effect of Organics on An(III) Solubility in GWB; Neodymium (III) was used as the analog



Plutonium (III) Association with Iron Colloids



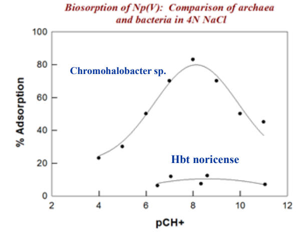
Long-term Pu studies with iron show colloidal enhancement well above the >10 nm operational definition of intrinsic plutonium colloids and correlates with the [Fe] present in solution. states

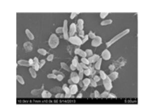
MICROBIAL CHARACTERIZATION IN THE WIPP

Microbial Characterization and Interactions with Actinides

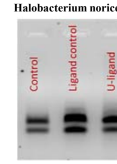
Significant progress has already been reported in the microbial characterization of WIPP-indigenous (salt and nearby brines) microorganisms [2, 3]. See Poster PSUS-2 for more detailed information. Current work extends this to sequence the genomic and metagenomic DNA of select isolates and samples to determine the presence of genes that encode the enzymes necessary for specific metabolic pathways. Growth and stress responses of microorganisms to specific actinide species are being explored to establish and further understand the mechanisms that lead to actinide toxicity. Additionally, the biosorption of specific isolates towards Np(V), Th(IV) and Nd/Am(III) were extended to a broader pH range and work is ongoing to look at structure-specific features of this sorptive process [4,6].

Biosorption of Np(V): Comparison of archaea and bacteria in 4N NaCl





Halobacterium noricense



RNA from U(VI) exposed and unexposed Hbt noricense

References and Acknowledgement

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