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Title: Chemistry of transuranium elements in salt-base repository

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Chemistry of transuranium elements in salt-base repository

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The mobility and potential release of actinides into the accessible environment continues to be the key performance assessment concern of nuclear repositories. Actinide, in particular plutonium speciation under the wide range of conditions that can exist in the subsurface is complex and depends strongly on the coupled effects of redox conditions, inorganic/organic complexation, and the extent/nature of aggregation. Understanding the key factors that define the potential for actinide migration is, in this context, an essential and critical part of making and sustaining a licensing case for a nuclear repository. Herein we report on recent progress in a concurrent modeling and experimental study to determine the speciation of plutonium, uranium and americium in high ionic strength Na-Cl-Mg brines. This is being done as part of the ongoing recertification effort in the Waste Isolation Pilot Plant (WIPP). The oxidation-state specific solubility of actinides were established in brine as function of pC_{H+}, brine composition and the presence and absence of organic chelating agents and carbonate [1,2]. An oxidation-state invariant analog approach using Nd^{3+} and Th^{4+} was used for An^{3+} and An^{4+} respectively. These results show that organic ligands and hydrolysis are key factors for An(III) solubility, hydrolysis at pC_{H+} above 8 is predominate for An(IV) and carbonates are the key factor for U(VI) solubility. The effect of high ionic strength and brine components measured in absence of carbonates leads to measurable increased in overall solubility over analogous low ionic strength groundwater. Less is known about the bioreduction of actinides by halo-tolerant microorganisms, but there is now evidence that bioreduction does occur and is analogous, in many ways, to what occurs with soil bacteria. Results of solubility studies that focus on Pitzer parameter corrections, new species (e.g. borate complexation), and the thermodynamic parameters for modeling are discussed.

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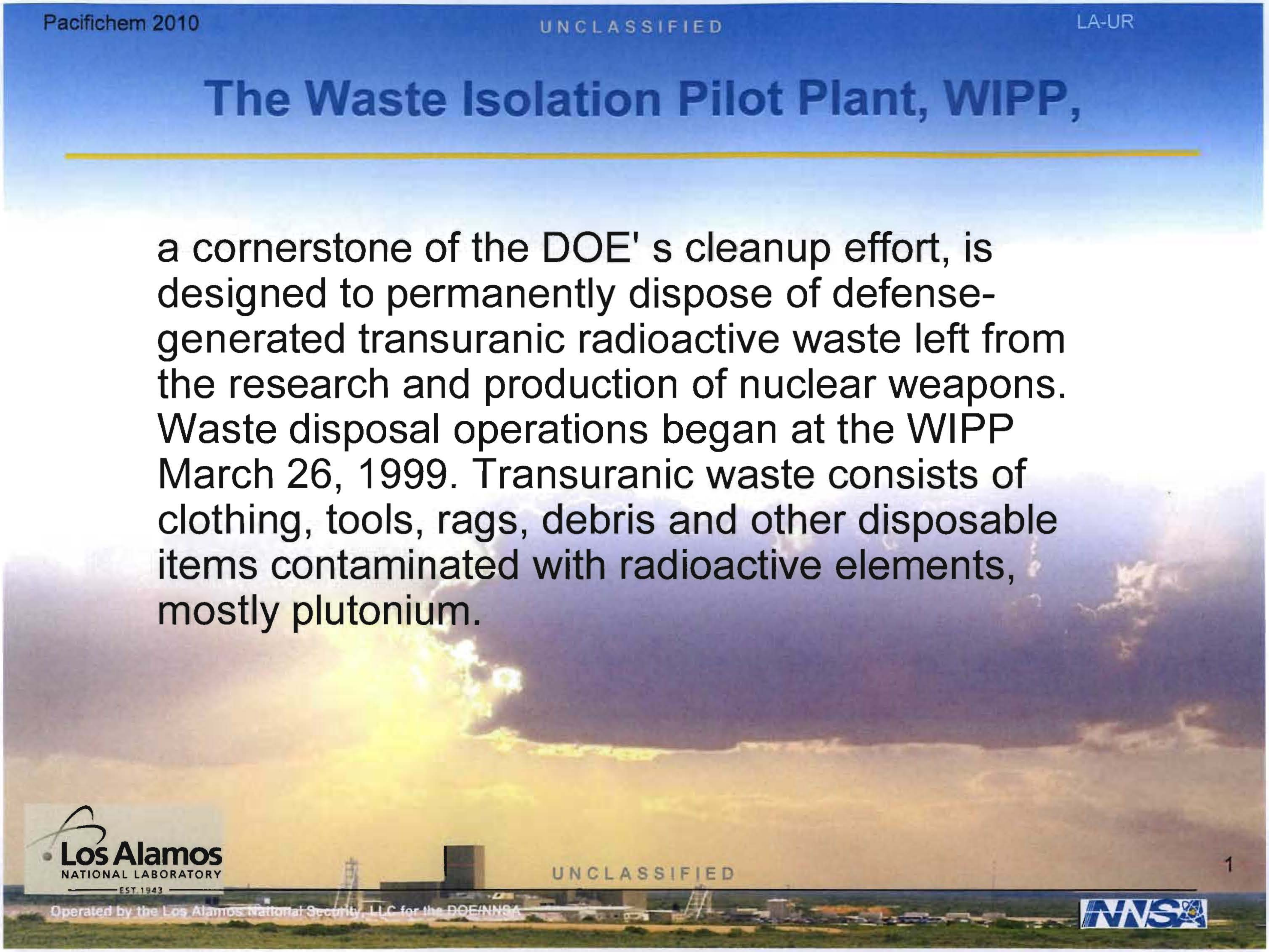
The Waste Isolation Pilot Plant, WIPP,



a cornerstone of the DOE' s cleanup effort, is designed to permanently dispose of defense-generated transuranic radioactive waste left from the research and production of nuclear weapons. Waste disposal operations began at the WIPP March 26, 1999. Transuranic waste consists of clothing, tools, rags, debris and other disposable items contaminated with radioactive elements, mostly plutonium.

WIPP Background

WIPP is a permanent disposal facility for transuranic (TRU) waste

- Located in southeast New Mexico
- Operated by U. S. Department of Energy (DOE)
- Regulated by U. S. Environmental Protection Agency (EPA) and New Mexico ED

Waste Generator Sites

Regulatory Chronology of WIPP

Environmental Protection Agency

1957 National Academy of Sciences concludes that the most promising disposal option for radioactive waste is in salt deposits

1979 Congress authorizes WIPP (Public Law 96-164)

1983 Mining of WIPP's first underground rooms is completed

1989 Nuclear Regulatory Commission certifies the TRUPACT-II shipping container

1992 WIPP Land Withdrawal Act designates EPA as WIPP's primary regulator

1993 EPA issues radiation standards for waste containment. Criteria for compliance follow in 1996

1998 EPA certifies WIPP (Grants a license to operate)

Regulatory Chronology of WIPP

WIPP's first waste shipment
March 26, 1999

1999 First shipment of waste arrives at WIPP from Los Alamos National Laboratory

New Mexico Environment Department issues a final hazardous waste permit for WIPP

2000 Nuclear Regulatory Commission certifies the RH-(remote handled) 72B cask for shipping remote-handled transuranic waste

2004 EPA approves DOE Characterization plans for RH TRU waste disposal at WIPP

2006 EPA recertifies the WIPP

RH Permit issued by New Mexico Environment Department

WIPP receives 5000th shipment

2007 WIPP receives first shipment of RH TRU Waste

Regulatory Chronology of WIPP

2009 DOE submits second Recertification to EPA

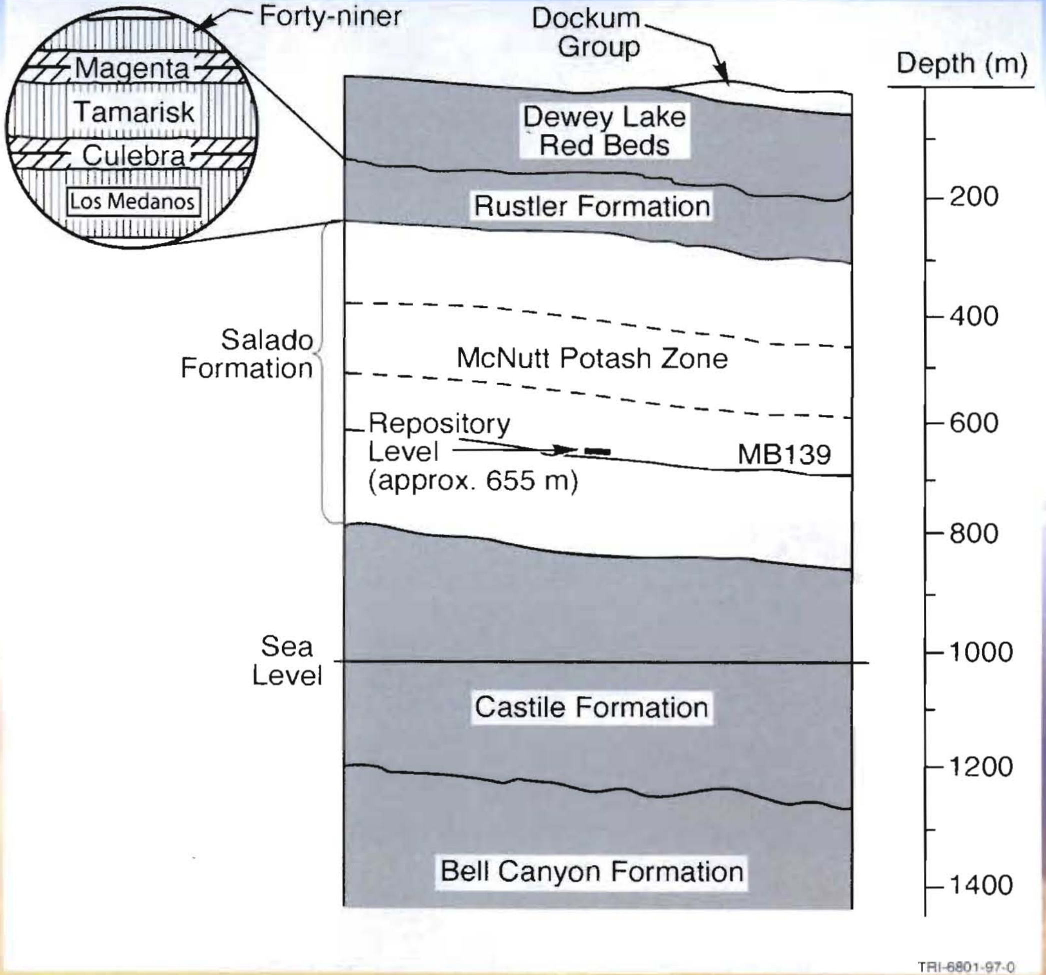
DOE submits Permit Renewal to NMED

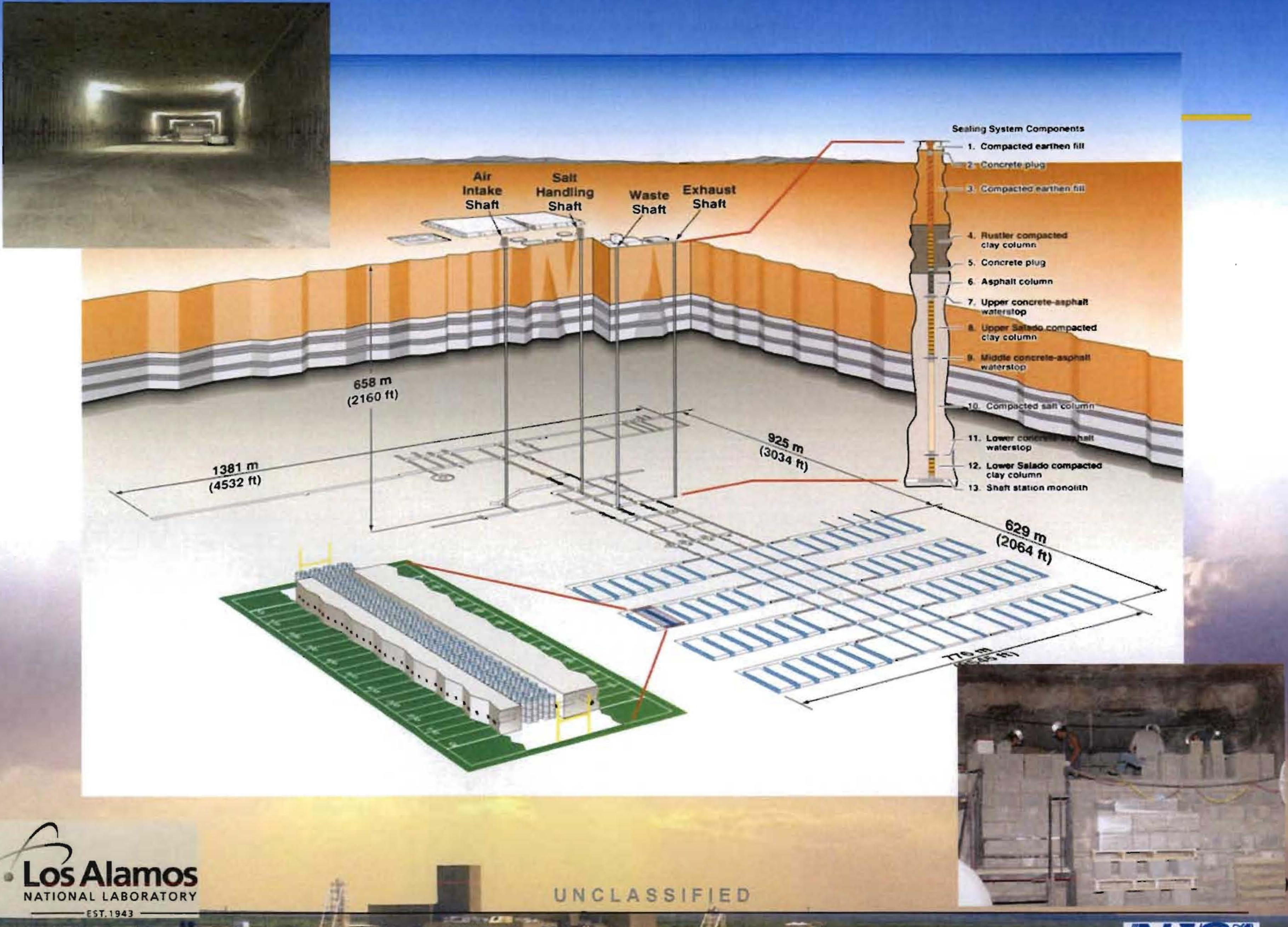
2010 DOE receives determination of completeness from EPA on recertification

Types of Waste

- Contact-handled (CH)
  - Large volume
    - ~169,200 m^3 capacity
  - No shielding required
  - Stacked on floor of waste rooms
- Remote-handled (RH)
  - Small volume
    - ~7,000 m^3 capacity
  - Contains short-lived gamma emitters
  - Shielding required
  - Emplaced in horizontal boreholes in waste room walls

Stratigraphic Section at the WIPP Site





Sealing System Components

1. Compacted earthen fill
2. Concrete plug
3. Compacted earthen fill
4. Rustler compacted clay column
5. Concrete plug
6. Asphalt column
7. Upper concrete-asphalt waterstop
8. Upper Salado compacted clay column
9. Middle concrete-asphalt waterstop
10. Compacted salt column
11. Lower concrete-asphalt waterstop
12. Lower Salado compacted clay column
13. Shaft station monolith

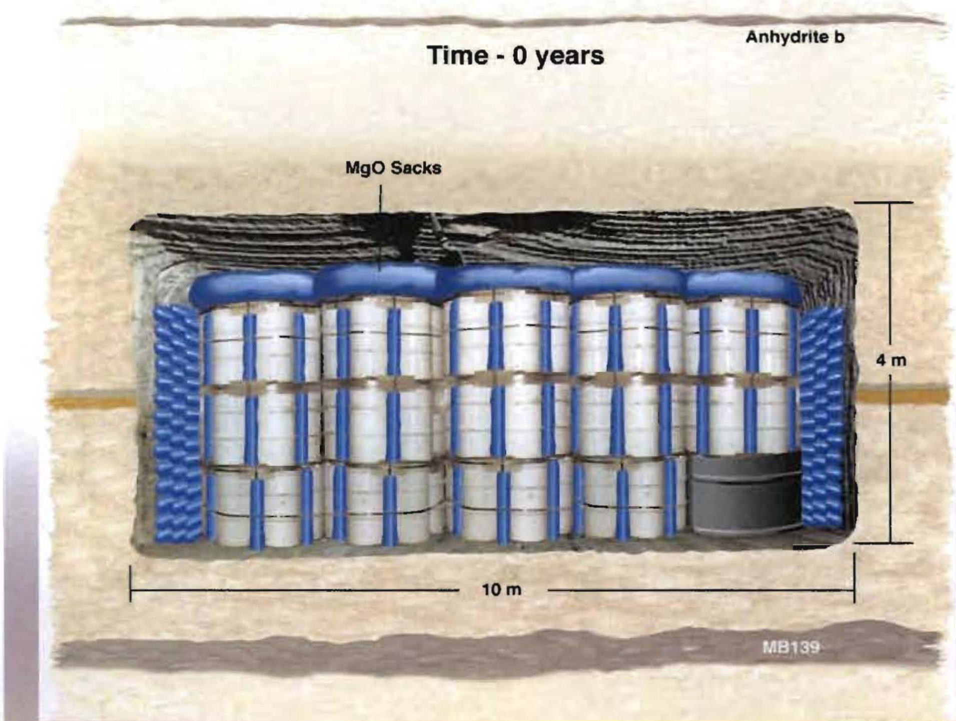
Inventory (Panels 1-4 and Projected)

Amount (in kilograms) of Key Waste Package Components and Actinides Present in the WIPP

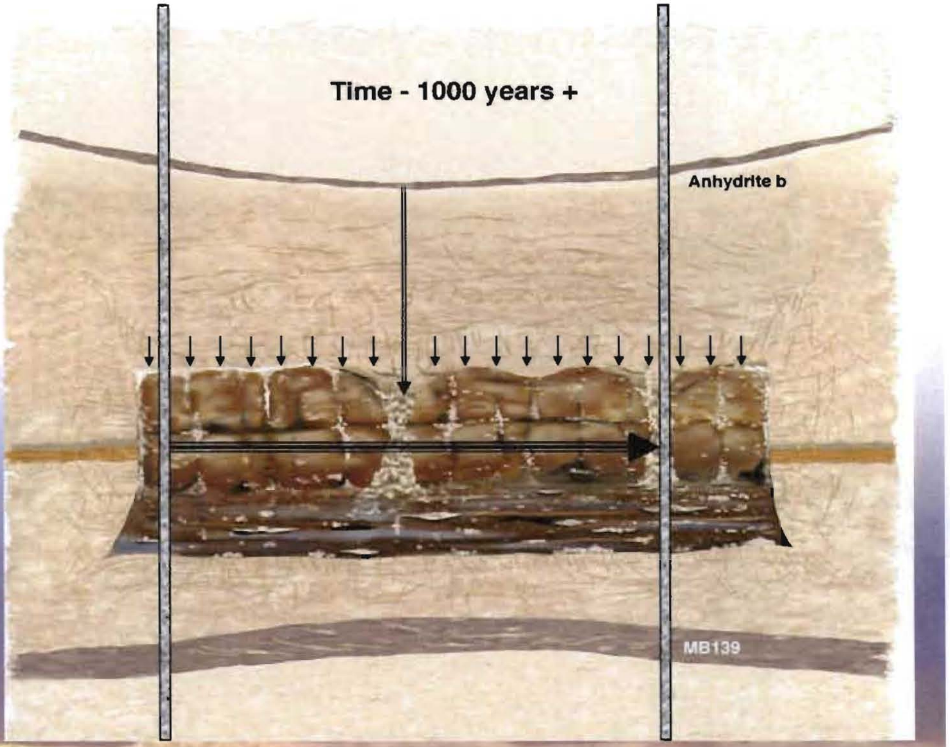
Isotope/Material	Panel 1	Panel 2	Panel 3	Panel 4	WIPP (total projected)
Radionuclide (in kg)					
Am-241	34.63	9.21	7.65	3.58	136.5
Pu	2571.00	1405.00	441.10	341.60	9,727
Pu-239	2416.00	1306.00	404.80	311.10	9,210
U	22160.00	6844.00	1504.00	1723.00	642,000
U-238	22090.00	6802.00	1487.00	1704.00	638,000
Np-237	0.58	1.26	0.98	3.37	10
Emplaced/Waste Materials (in kg)					
Iron based alloys	3,327,871	4,922,035	4,559,000	4,380,000	51,416,000
Aluminum based alloys	5,459	17,730	9,859	9,437	259,000
Other alloys	46,793	121,526	89,370	26,130	5,795,000
MgO – Eng. Barrier	4,482,000	6,667,000	6,437,000	6,445,000	>75,000,000
Cellulosics	706,141	477,213	548,280	833,066	10,175,000
Plastic	522,688	876,399	890,640	1,065,040	10,188,000

WIPP Disposal Room

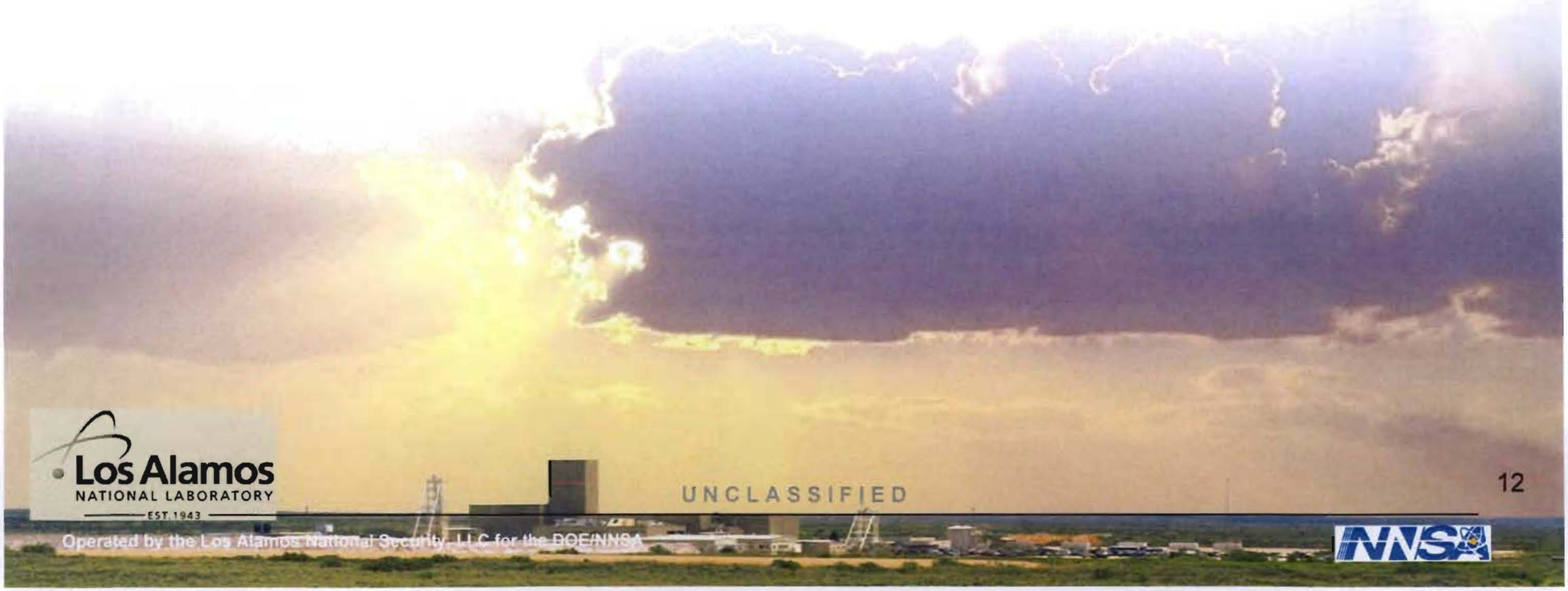
At Time of Closure …



and 1000+ Years Later

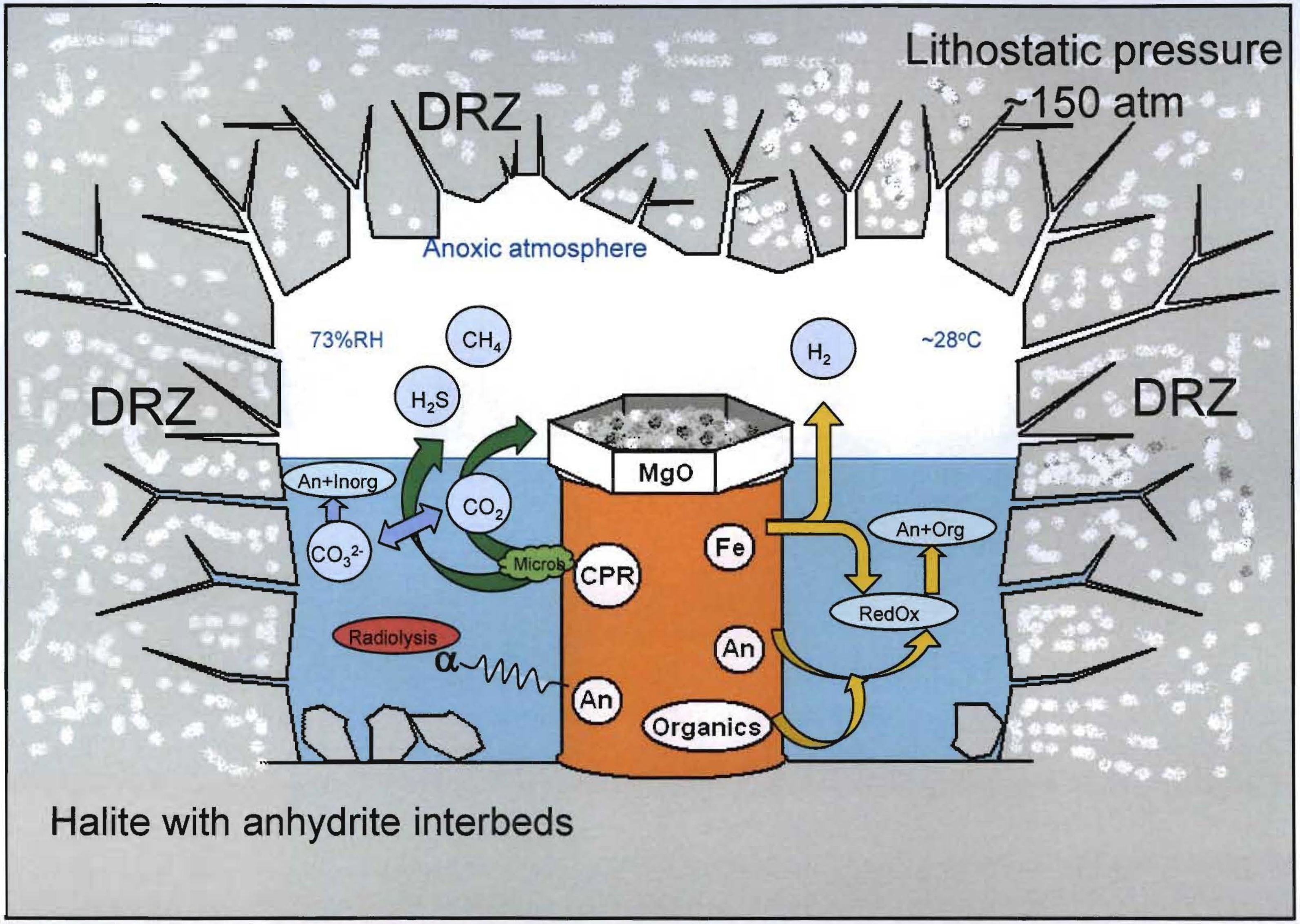


Actinide Chemistry in Brine



WIPP Actinide Chemistry

- Actinides are the key, essentially only, contributors to dose-to-man release calculations
- Conservative assumptions that define actinide release are in place – this is the basis of the license case and the 2004 and 2009 re-certifications of WIPP
- DOE/CBFO supports ongoing research projects to further establish WIPP-relevant chemistry and actinide chemistry
- Confirm the conservatism of current assumptions
- Improve the robustness of the model and add more realism
- Address regulator/stakeholder issues as they arise
- Maintain consistency of WIPP chemistry models in relation to latest actinide research, particularly in high ionic strength brine solutions.


Lithostatic pressure
~150 atm
DRZ
Anoxic atmosphere
73%RH
CH_4
H_2
~28°C
DRZ
H_2S
DRZ
MgO
An+Inorg
CO_2
CO_3^{2-}
Microbes
CPR
Fe
An+Org
RedOx
Radiolysis
α
An
An
Organics
Halite with anhydrite interbeds

Gas Generation

Various gasses will be generated by corrosion of steel (H_2) and microbial activity (CO_2, N_2, H_2S, CH_4).

Microbes will generate gasses using CPR materials via denitrification, sulfate reduction and methanogenesis.

Pressure will be reduced by reaction of CO_2 and H_2S with engineered barrier (MgO) and waste components.

EPA assumption: organic ligands are NOT biodegradable.

Engineered Barrier

MgO is used as the engineered barrier

Sequesters CO_2 and buffers pH~9.0

Hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ controls CO_2 fugacity

Excess factor of MgO is equal to 1.2 in respect to all carbon atoms placed in WIPP

pH~9.0 reduces actinide solubilities

Redox Processes

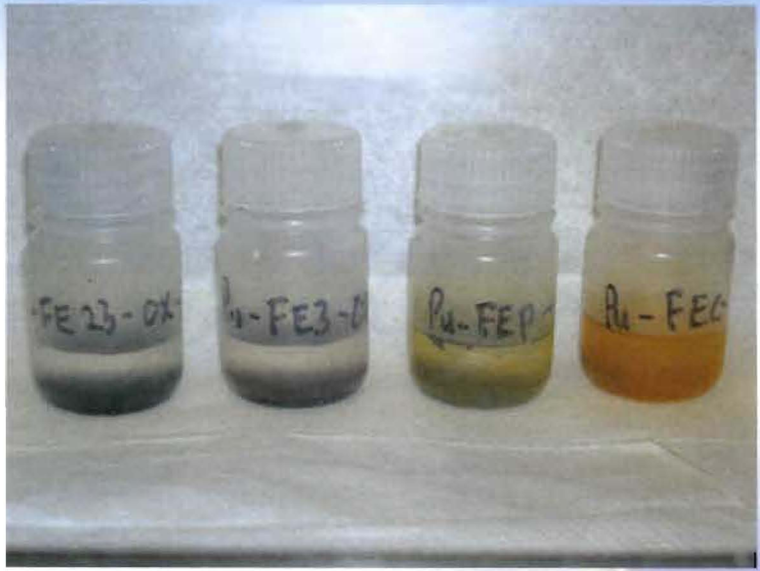
Steel corrosion will quickly remove O_2 and WIPP conditions will be strongly reducing (H_2, Fe^0, Fe^{2+}).

Actinides will be present at lower oxidation states: Pu^{III}, Pu^{IV}, Am^{III}, Np^{IV}, Np^{V}, U^{VI} and U^{IV}.

The lower oxidation states have also lower solubilities.

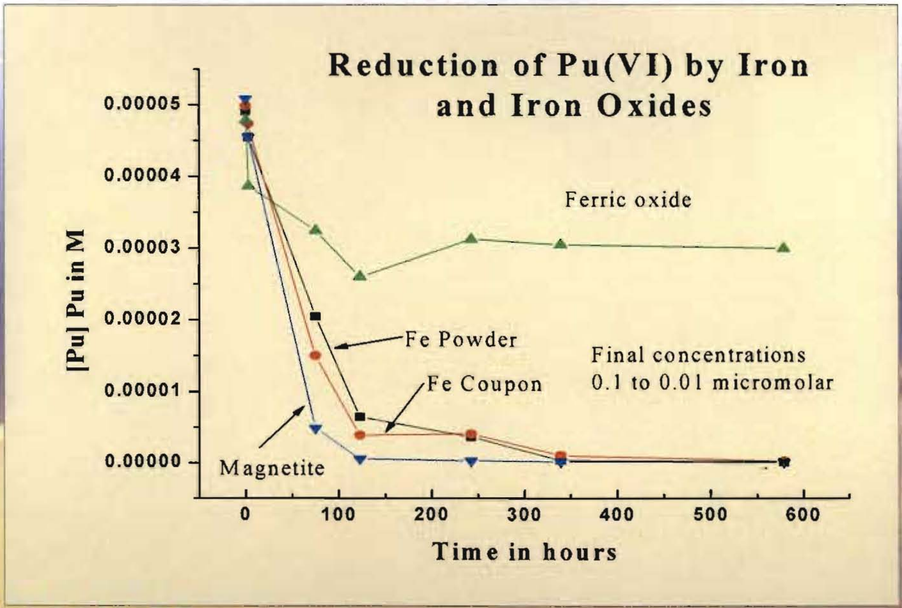
Metal reducing bacteria and other metals (Al, Pb) will enhance redox processes.

LANL/ACRSP Study of Pu Reduction by Iron$^{(0,II)}$

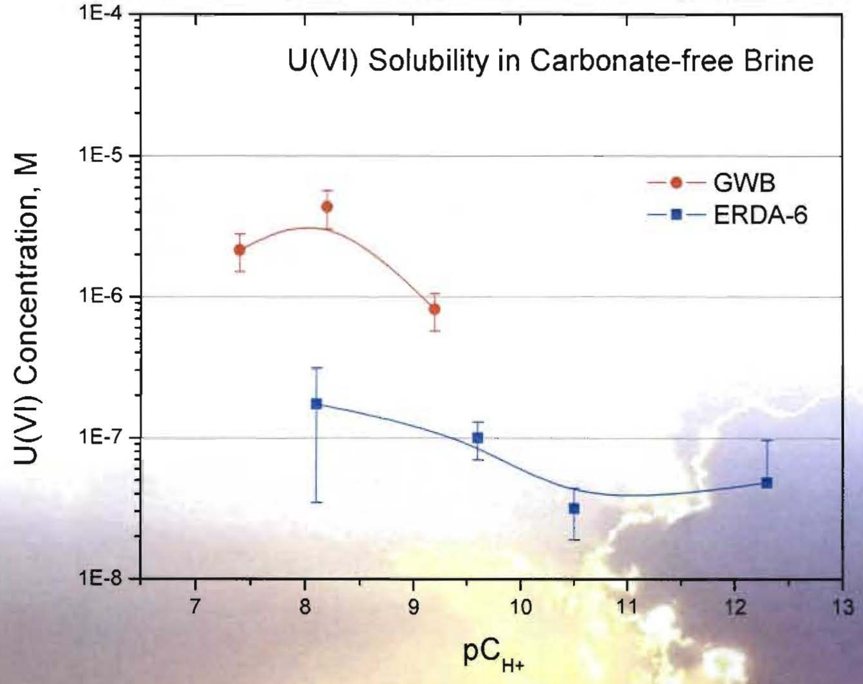


- Very different appearances in iron reaction products were noted depending on pH, brine and initial iron phase
- Plutonium was associated with the Fe phases
- Green rust was often noted at the higher pH
- XANES established the green rust to be an Fe2/3 phase with a bromide center
- This green rust phase was linked to Pu as Pu(IV)

Pu(VI) reduction was fastest when there was available Fe(II) ; no reactivity noted with Fe(III) phases (as expected)



U(VI) Solubility in Carbonate-Free Brine



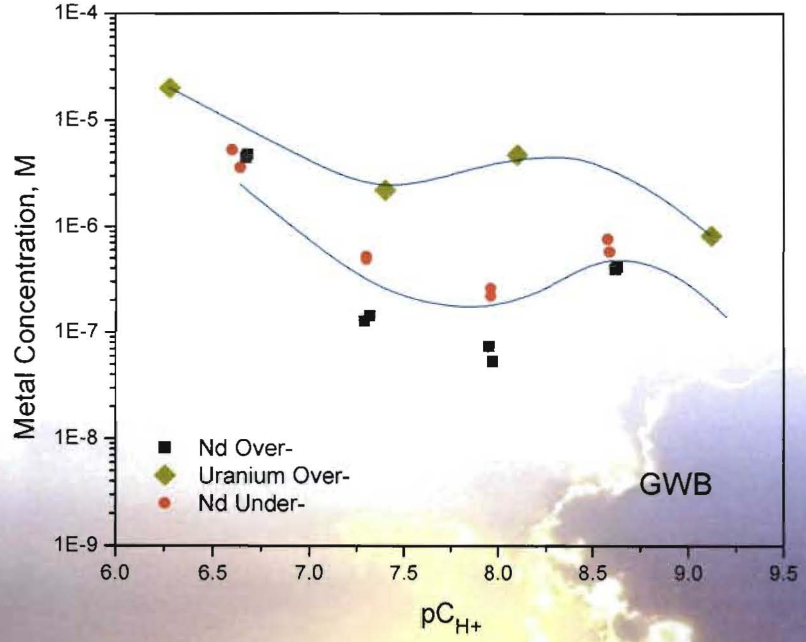
The solubilities of uranium measured in carbonate-free ERDA-6 and GWB were different over the investigated pC_{H+} range.

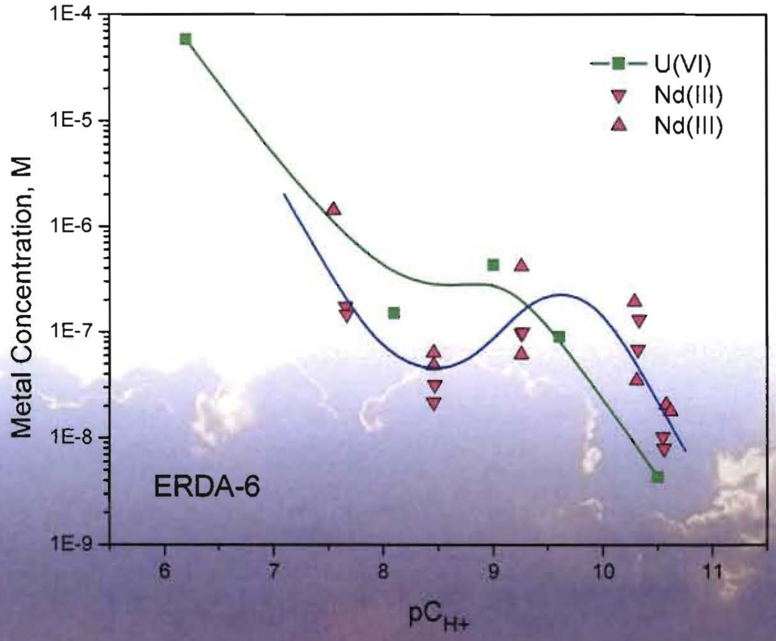
For carbonate-free GWB brine and $7 \leq pC_{H+} \leq 9.2$, the slight increase in the middle of this pC_{H+} range may reflect the effect of borate complexation, as it was found in our neodymium solubility experiments.

For carbonate-free ERDA-6 brine the solubility of uranium (VI) was smaller and ranged from 3×10^{-8} to 2×10^{-7} M and probably was caused by different solids controlling U(VI) solubility.

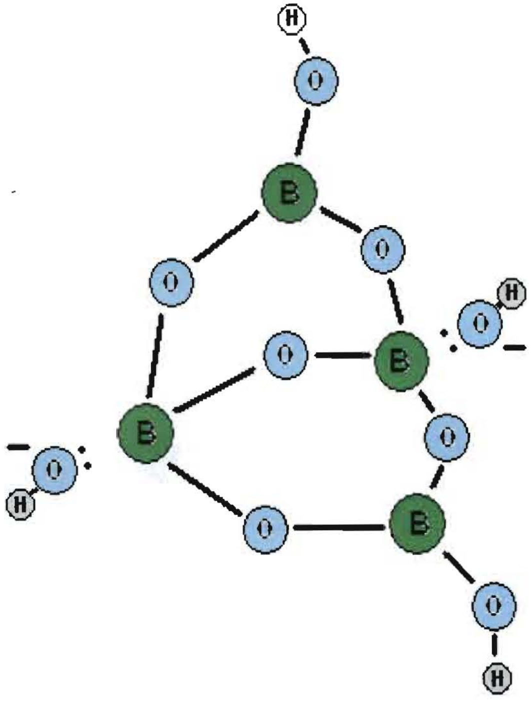
No evidence for amphotericity was observed.

Comparison of U^{VI} and Nd^{III} solubilities, effect of tetraborate complexation



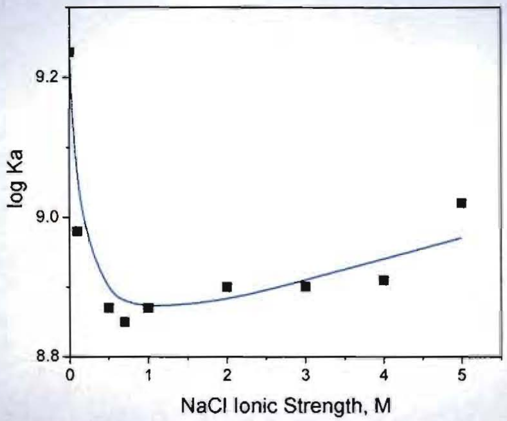


Dissociation constant of boric acid as a function of ionic strength at 25 °C

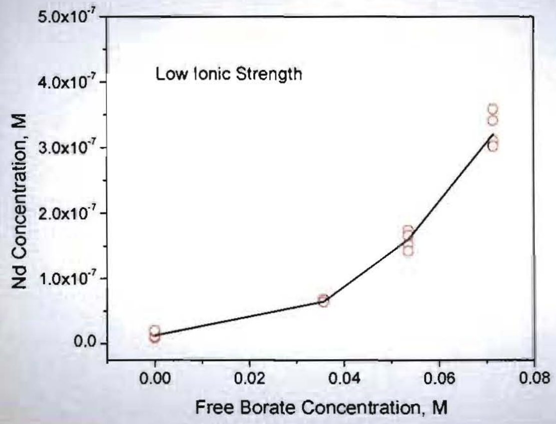


$B_4O_5(OH)_4^{2-}$

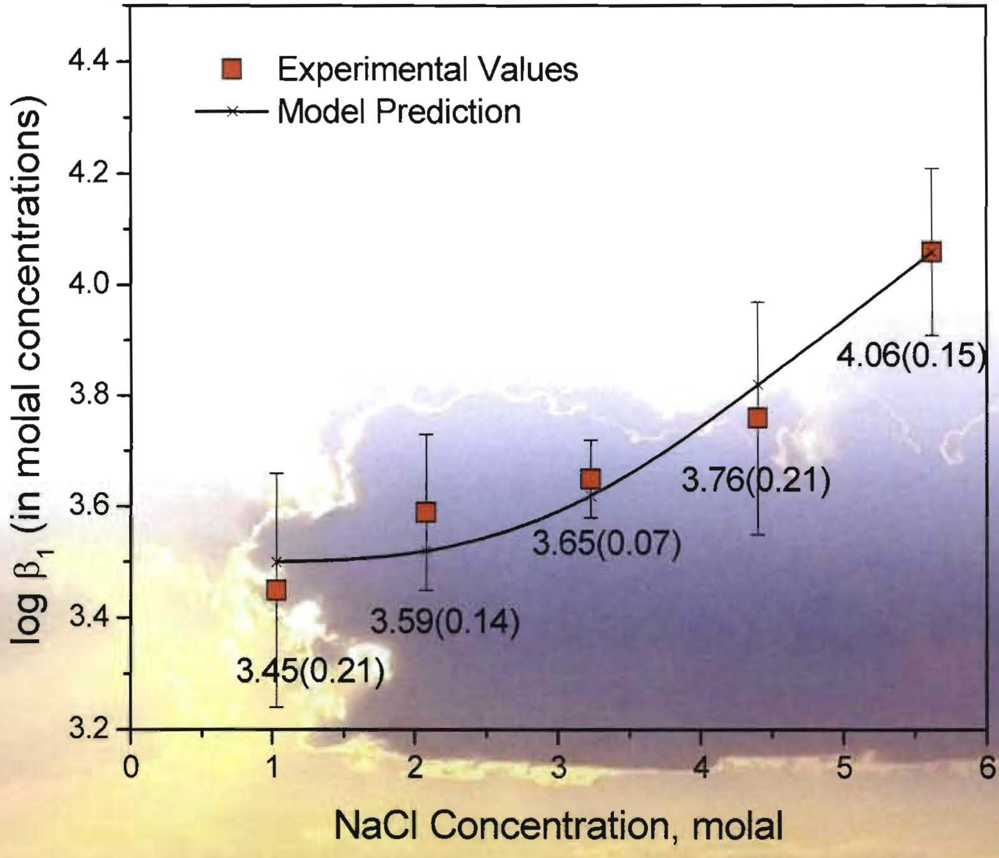
pK$_a$ of Tetraboric acid



Tetraborate effect on Nd^{III} solubility



Experimentally determined neodymium with tetraborate stability constants



Pitzer parameters determined:

Binary Pitzer Parameters

Species *i*	Species *j*	β^0_{ij}	β^1_{ij}	$\beta^{2}_{ij}{}^{*}$	C^{ϕ}_{ij}	Reference
Nd^{3+}	Cl^-	0.612	5.4	0	-0.0184	Felmy 1990
Na^+	$B_3O_3(OH)_4^-$	-0.056	-0.91	0	0	Felmy 1986^A
$NdHB_4O_7^{2+}$	Cl^-	-0.0352	1.74	0	-0.0131	Present work

^{A} Used as an analog to the interaction of Na^+ with $HB_4O_7^-$

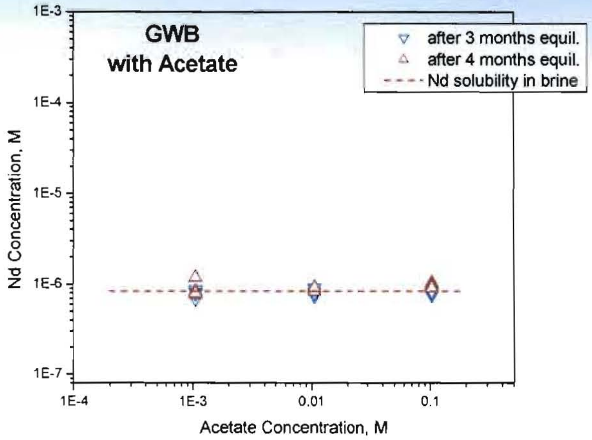
Species or Formation Reaction	μ°/RT for Species or log β_1 for Formation Reaction
$NdHB_4O_7^{2+}$	–1365.508
$Nd^{3+} + HB_4O_7^{1-} \leftrightarrows NdHB_4O_7^{2+}$	4.99

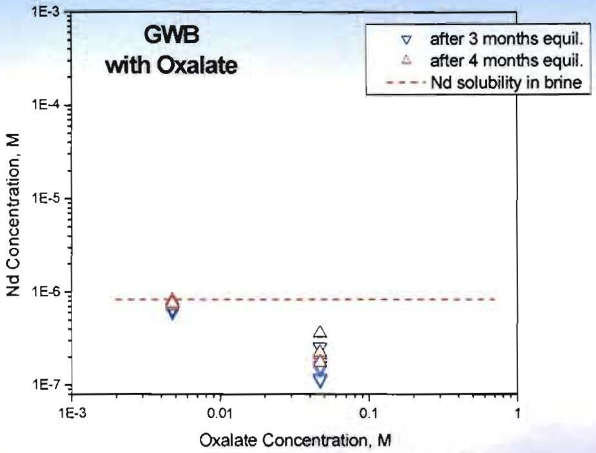
Concentrations of Organic Ligands Expected in the WIPP

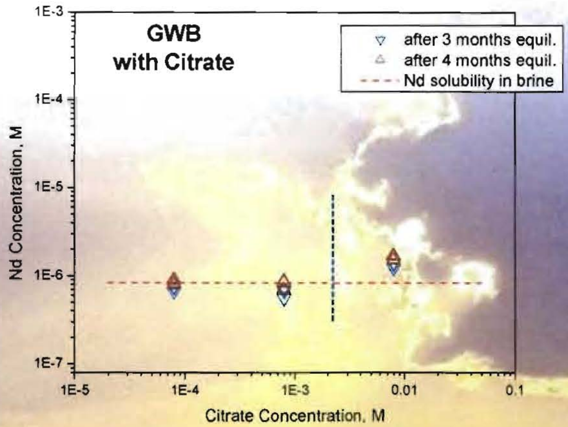
Organic Ligand	Concentration, M	
	PABC 2004	Inventory 2008
Acetate	1.06×10^{-2}	1.94×10^{-2}
Citrate	8.06×10^{-4}	2.38×10^{-3}
EDTA	8.14×10^{-6}	6.47×10^{-5}
Oxalate	4.55×10^{-2}	1.73×10^{-2}

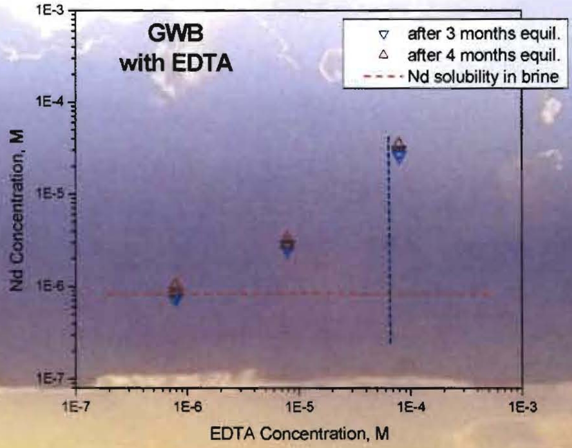
Brine volume used for CRA 2009 calculations was equal to 17,400m^3. Assumptions: all organics are totally dissolved in the brine and are not degraded.

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

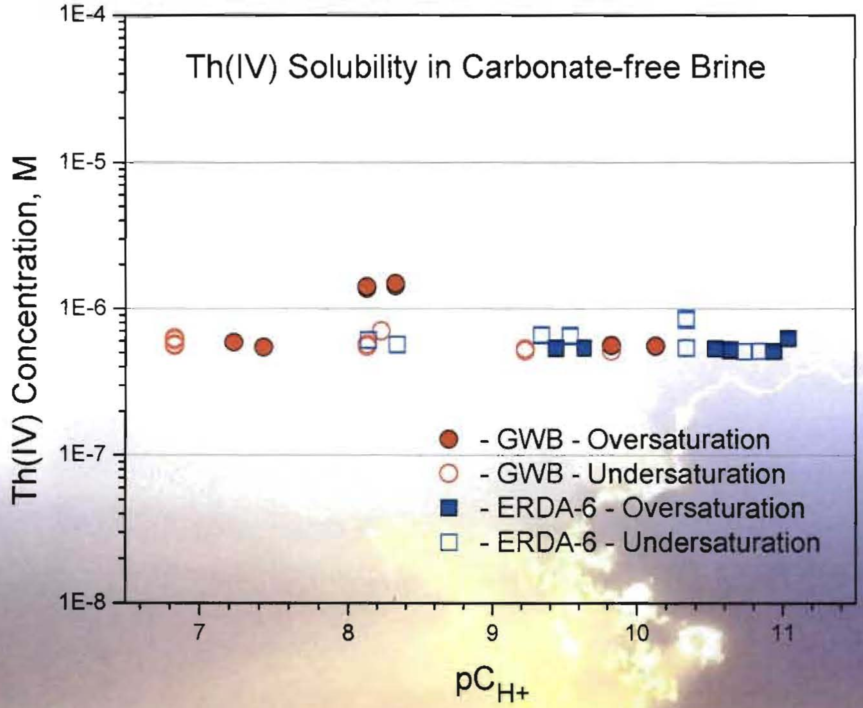








Th(IV) Solubility in Carbonate-Free Brine



The thorium solubility measured from under- and over-saturation were similar in both brines over the entire pC_{H+} range. 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.

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 [Altmaier 2004] where thorium hydroxy-oxide $ThO(OH)_2$ was solubility-controlling phase.

Th Solubility in GWB with Complexing Agents

All organics were present simultaneously, pC_H~9.3

Th	Acetate	Oxalate	Citrate	EDTA
7.34×10^{-7}M	2.42×10^{-3}M	3.02×10^{-2}M	3.62×10^{-3}M	9.25×10^{-5}M
Initial organic ligand concentr.	2.33×10^{-3} M	2.76×10^{-2} M	3.85×10^{-3} M	9.27×10^{-5} M
Concentrations expected in WIPP	1.94×10^{-2} M	1.73×10^{-2} M	2.38×10^{-3} M	6.47×10^{-5} M

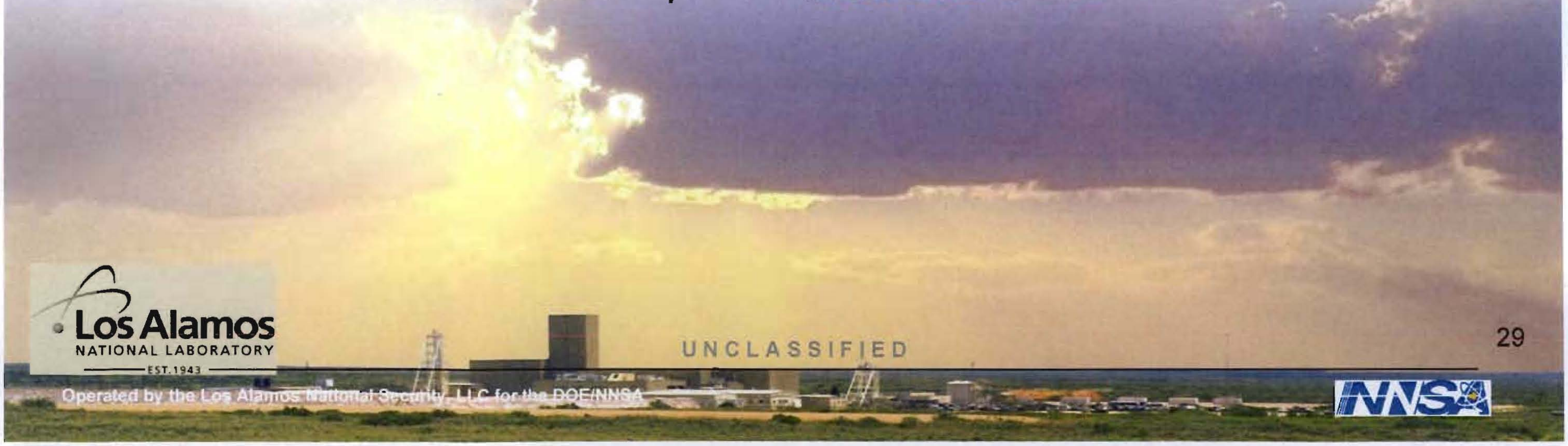
Measurements have been done after 7 days.

An(III) and An(IV) Solubilities in WIPP brine Calculated (FMT) in Molar units:

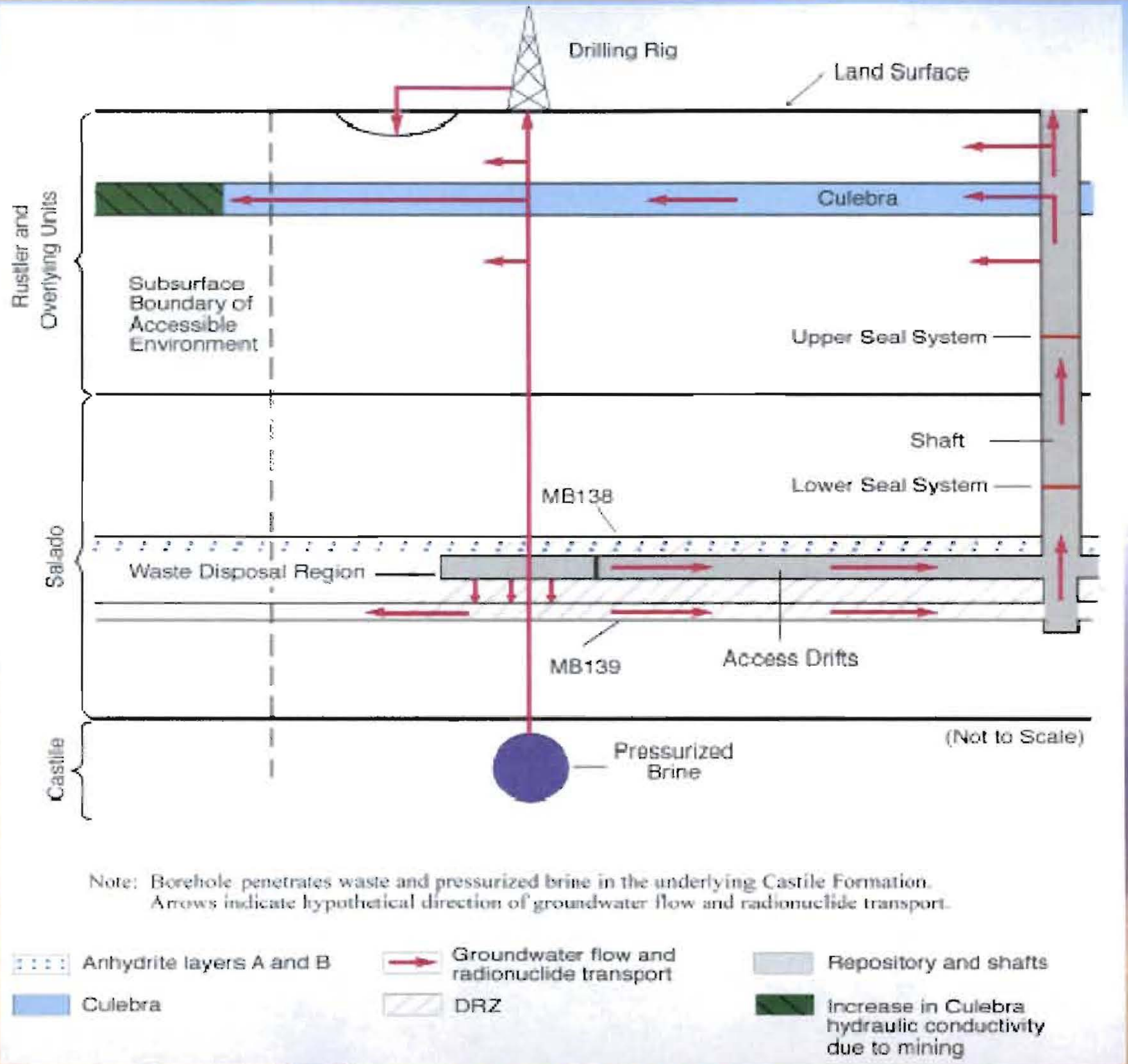
	Brine	PAVT	CRA microbial	PABC-04	PABC-09
An(III)	Salado	1.2×10^{-7}	3.1×10^{-7}	3.9×10^{-7}	1.7×10^{-6}
An(III)	Castile	1.3×10^{-8}	1.7×10^{-7}	2.9×10^{-7}	1.5×10^{-6}
An(IV)	Salado	1.3×10^{-8}	1.2×10^{-8}	5.6×10^{-8}	5.6×10^{-8}
An(IV)	Castile	4.1×10^{-9}	2.5×10^{-8}	6.8×10^{-8}	6.8×10^{-8}

WIPP Regulatory Requirements

- Regulatory requirements were primary determinant for the development of the PA structure
  - The WIPP must be designed to provide *reasonable expectation* that *cumulative releases* of radionuclides to the accessible environment for *10,000 years* after disposal from all *significant processes and events* shall be less than specified *releases limits*



Disturbed Repository Performance



Note: Borehole penetrates waste and pressurized brine in the underlying Castile Formation.
Arrows indicate hypothetical direction of groundwater flow and radionuclide transport.

Conclusions

WIPP is a successful effort in clean up of radioactive waste generated under the US defense program.

In10 years of WIPP work about 130 000 containers have been permanently disposed in salt-bed.

4 of 12 panels were filled with TRU waste and closed.

Safety is primary important for WIPP. No fatality or serious accident was noted during mining, transport and waste disposal.

Actinide Chemistry Repository Science Program supports WIPP in recertification process and evaluation of the ongoing understanding of actinide chemistry.

WIPP is world leader in the transuranic waste disposal.

Acknowledgments

The view of waste in a WIPP Disposal Room. On September 27, 2010 the amount of 137,177 (409 RH) containers are disposed in the underground.

This work was conducted
under the Actinide Chemistry Repository Science Program
and sponsored by Department of Energy Carlsbad Field Office.