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Overview of Long-Term, Near-Field WIPP Geochemistry*

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Topics to Be Addressed

Characteristics of the Salado Formation at the WIPP repository horizon

Characteristics of the TRU waste to be emplaced in the WIPP

Near-field geochemical processes and conditions expected in the WIPP

Predictions of radionuclide speciation and solubilities under expected near-field conditions

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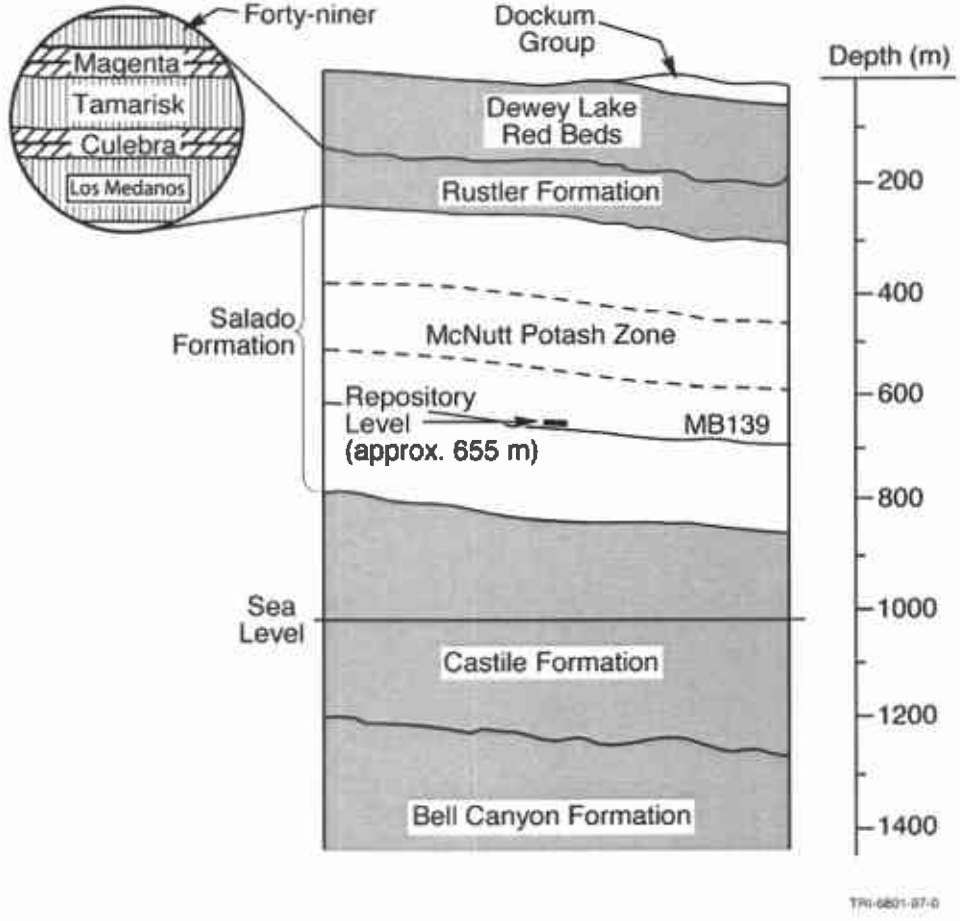
Stratigraphic Section



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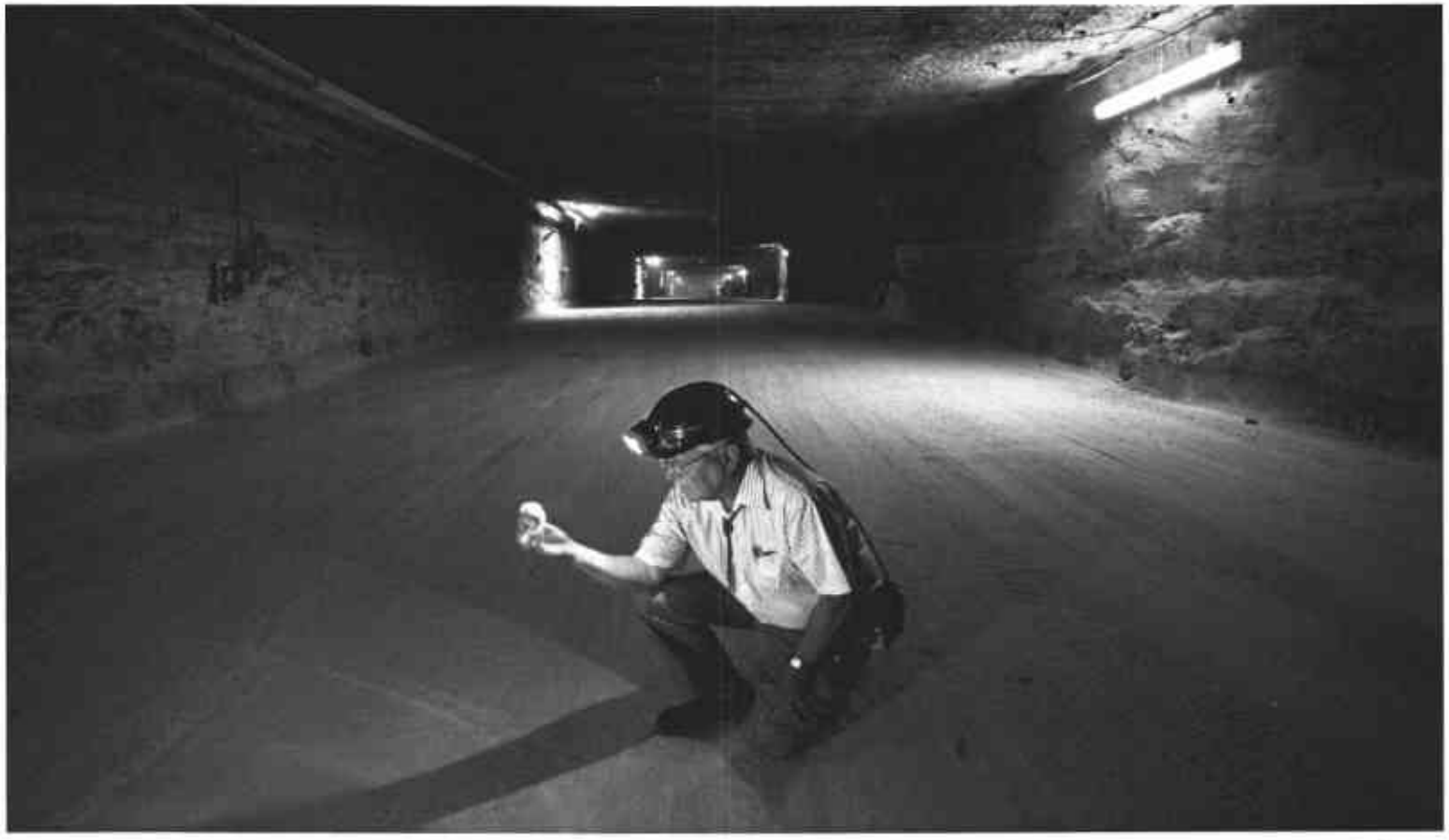
View Along a WIPP Access Drift



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Characteristics of the Salado Fm.

Lithology

- Nearly pure halite (NaCl) with interspersed clay seams and "marker beds" containing anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), magnesite ($MgCO_3$), polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$), and clays

Mineralogy

- 90 to 95% halite
- 1 to 2% each anhydrite, gypsum, magnesite, polyhalite and clays

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Characteristics of the Salado (cont.)

In situ conditions at the repository horizon[1]

- P ≅ 150 atm (lithostatic); measured pore pressures close to lithostatic
- T = 28 °C

Permeabilities

- Nearly pure halite: $<10^{-20}$ m^2
- Marker beds: $<10^{-18}$ m^2

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1. Repository located at a subsurface depth of 655 m (2,150 ft)

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Characteristics of the Salado (cont.)

Water Content

- Contains both intergranular (grain-boundary) brine and intragranular brine (fluid inclusions)
  - Intergranular will flow into disposal rooms
  - Intragranular will not flow into disposal rooms
- Total water content from 1 to 2 wt %

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Compositions of Brines Used for Near-Field Studies (M)

	Brine A	G Seep	GWB	ERDA-6
B	0.02	0.144	0.157	0.063
Br	0.01	0.0171	0.027	0.011
Ca	0.02	0.00768	0.014	0.012
Cl	5.35	5.10	5.87	4.8
K	0.77	0.35	0.465	0.097
Mg	1.44	0.63	1.02	0.019
Na	1.83	4.11	3.53	4.87
pH	6.5	6.1	NA	6.17
SO_4	0.04	0.303	0.177	0.170

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Characteristics of the Salado Formation

Characteristics of the TRU waste to be emplaced in the WIPP

Near-field geochemical processes and conditions

Predictions of radionuclide solubilities

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Characteristics of Transuranic (TRU) Waste

U.S. definitions of TRU waste

- Waste with > 100 nCi of α-emitting TRU radioelements with half-lives > 20 years per g of waste

Volume of TRU waste to be emplaced in the WIPP

- 176,000 m^3
  - ➢ Equivalent to 844,000 208-L (55-gal) drums

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Characteristics of TRU Waste (cont.)

Types of TRU waste

- Contact-handled (CH) TRU waste
  - 169,000 m^3
  - Does not require shielding
- Remote-handled (RH) TRU waste
  - 7,080 m^3
  - Requires shielding for handling but not for disposal

Contents of TRU waste

- Clothing, paper, rags, tools, wood, solidified process sludges, etc., contaminated with TRU radioelements

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Cutaway View of CH TRU Waste

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Topics to Be Addressed

Characteristics of the Salado Formation

Characteristics of TRU waste

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Predictions of radionuclide solubilities

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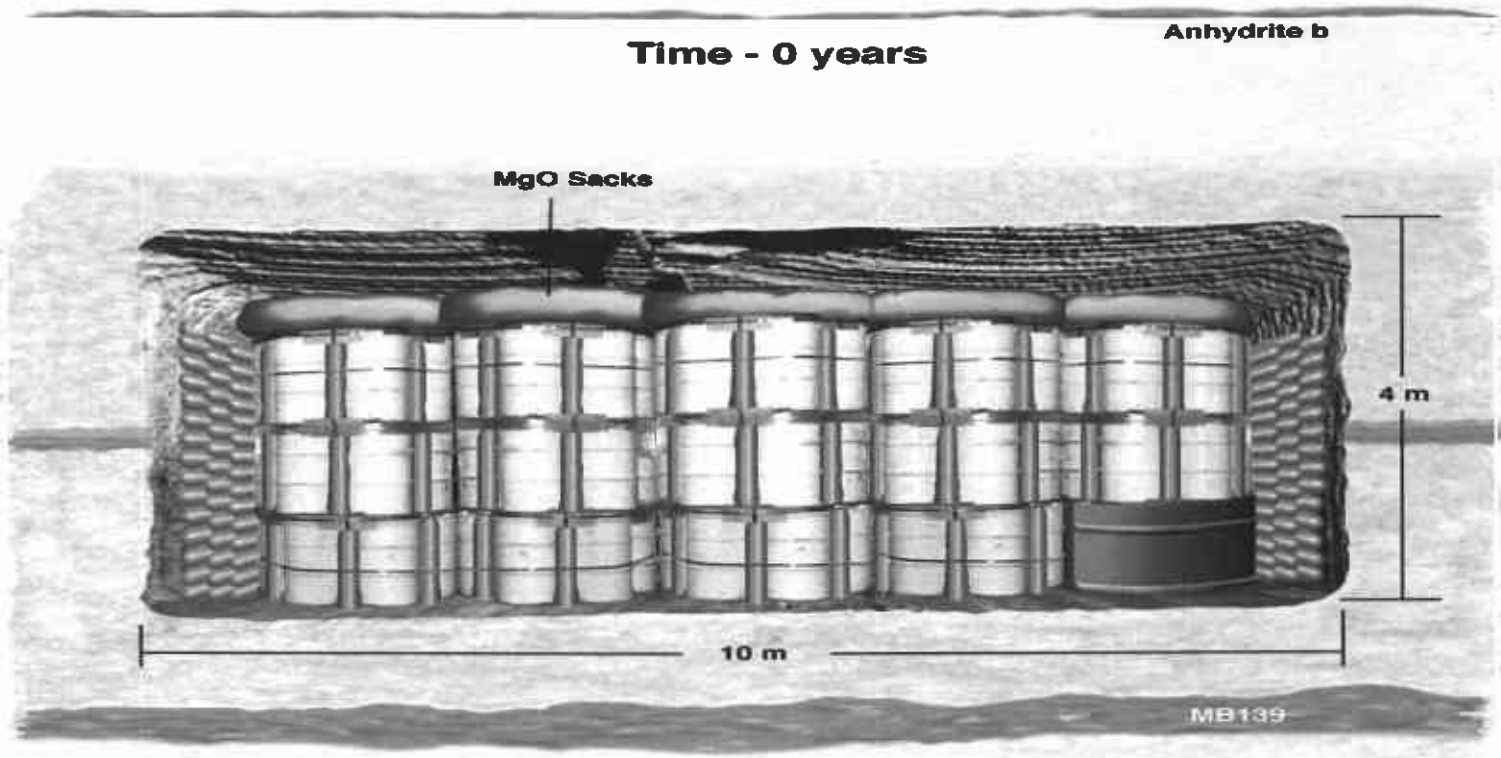
Emplacement of CH TRU Waste



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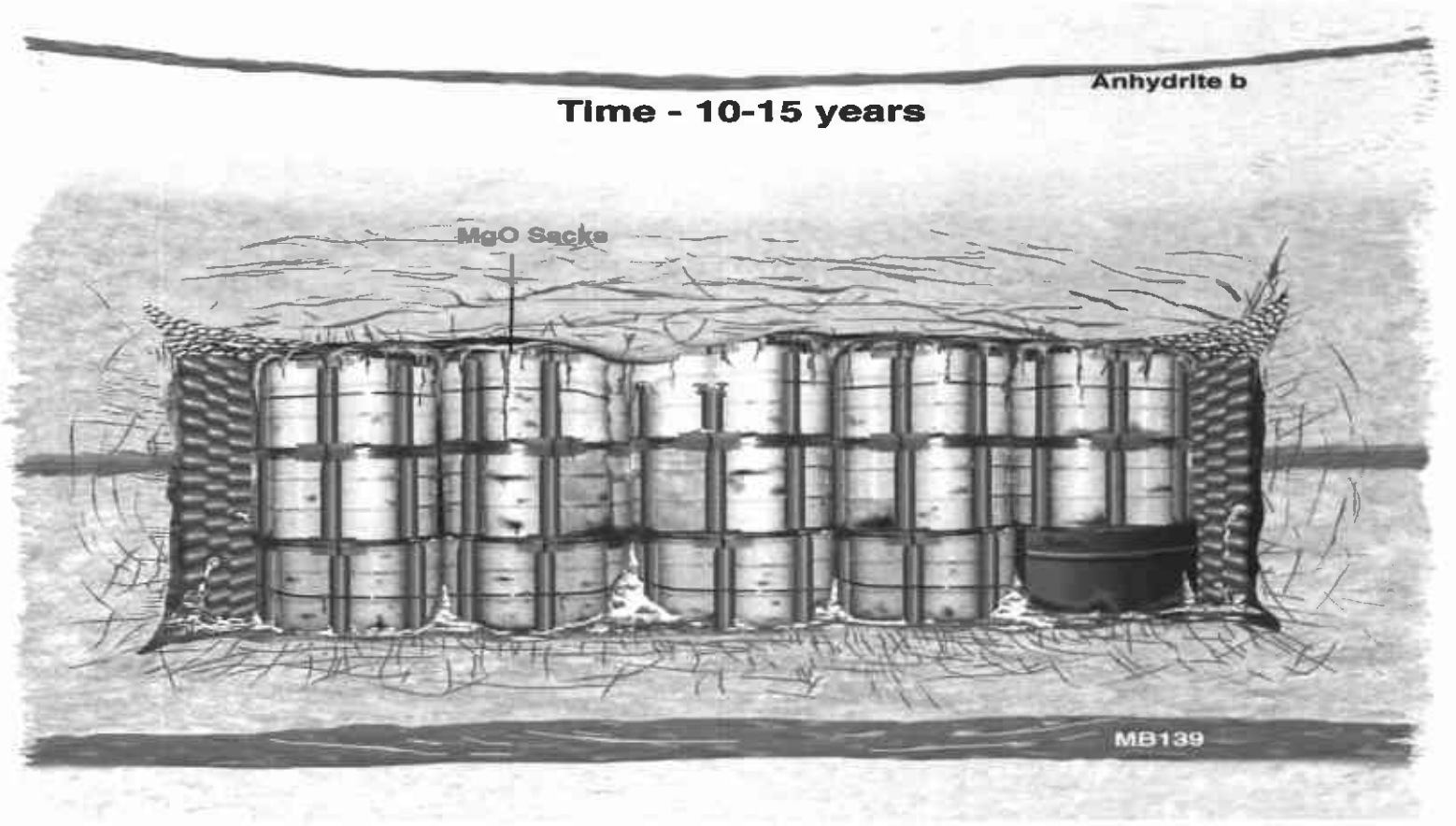
Future States of CH TRU Waste



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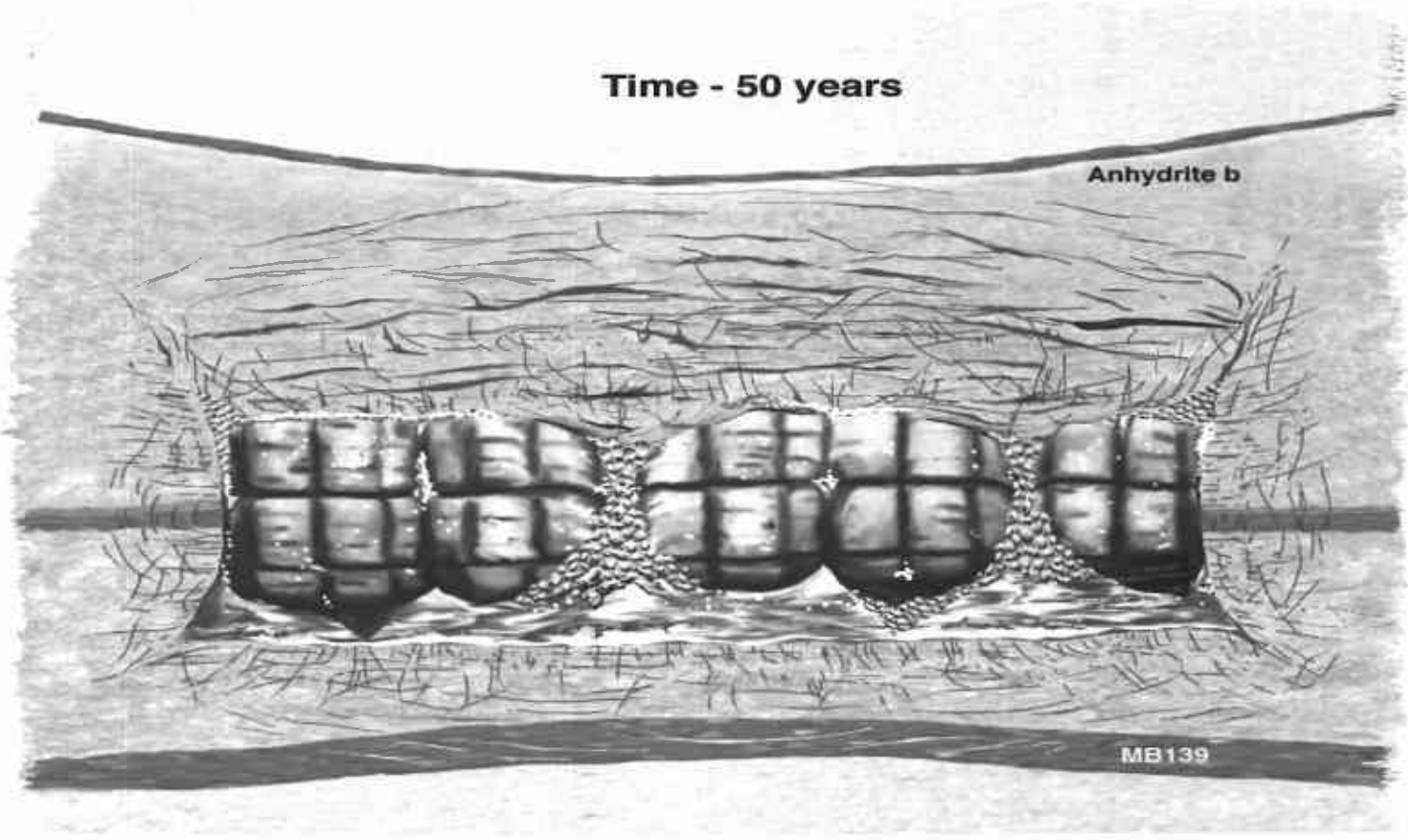
Future States of CH TRU Waste



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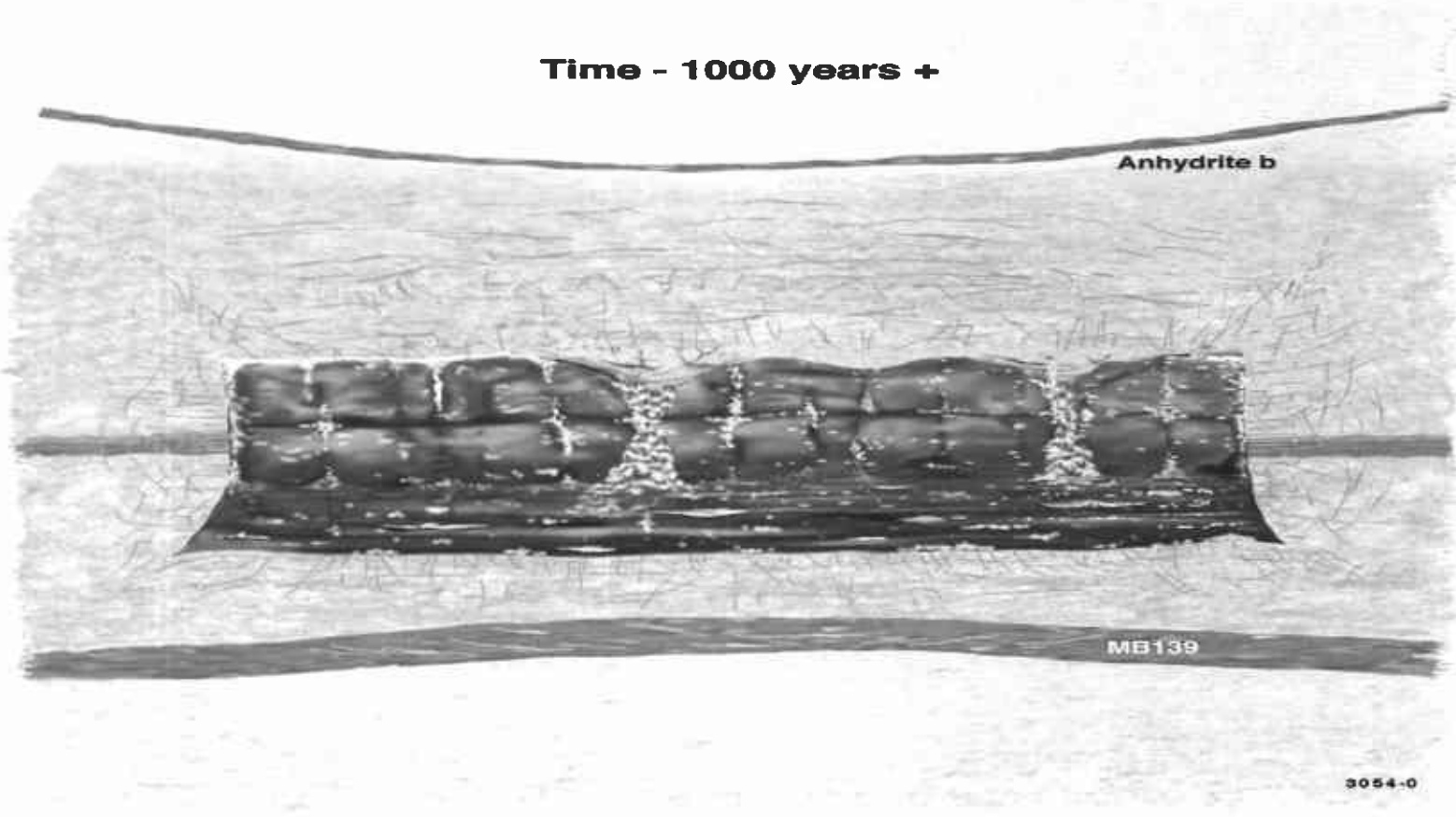
Future States of CH TRU Waste



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Gas Generation

Corrosion of Fe- and Al-base metals

- Will produce H_2, consume H_2O

Possible microbial consumption of cellulosic, plastic, and rubber (CPR) materials

- Could produce CH_4, CO_2, H_2S, N_2
- Significant microbial activity is "possible, [but] by no means certain" in the WIPP
- However, the EPA now specifies a probability of 1 for microbial activity in WIPP PA

Alpha radiolysis of H_2O in brine, and of CPR materials

Corrosion ≅ microbial activity >> radiolysis

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Gas Generation (cont.)

Effects of gas generation on long-term performance of the repository

- Brine inflow and outflow
- Chemical conditions that affect the actinide source term
  - Eh
  - f_{CO_2}
  - pH
- Room closure
  - Porosity and permeability of materials in the repository, DRZ, and marker beds
  - Resistance of waste to erosion and spalling in the event of human intrusion
- Gas drives spallings releases

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Anoxic Corrosion

Relative importance of different types of corrosion:

- Anoxic corrosion >> oxic corrosion

Experimentally observed anoxic corrosion reactions

- $Fe + (x + 2)H_2O \rightleftharpoons Fe(OH)_2 \cdot xH_2O + H_2$
- $Fe + H_2O + CO_2 \rightleftharpoons FeCO_3 + H_2$
- $Fe + H_2S \rightleftharpoons FeS + H_2$

Other possible anoxic corrosion reactions

- $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$
- $Fe + 2H_2S \rightleftharpoons FeS_2 + 2H_2$

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Microbial Activity

Implementation in the CCA PA, the PAVT, and the CRA-2004 PA

- Microbial consumption of all cellulosic materials possible:
  - Probability = 0.25 (included in ~25% of the PA vectors)
- Microbial consumption of all CPR materials possible:
  - Probability = 0.25 (included in ~25% of the vectors)
- No microbial activity:
  - Probability = 0.50 (included in the other~50% of the vectors)

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Microbial Activity

Implementation in the CRA-2004 PABC

- For the PABC, the EPA stipulated that microbial activity can occur in ALL vectors
- However, the EPA allowed the use of lower microbial gas-generation rates based on long-term results from the laboratory study of microbial gas generation at BNL
- Furthermore, the EPA established a scaling factor, which can vary from 0 to 1, used to multiply the sampled value of the microbial gas generation rate
- Microbial consumption of all cellulosic materials possible:
  - Probability – 0.75 (included in ~ 75% of the PA vectors)
- Microbial consumption of all CPR materials possible:
  - Probability ~ 0.25 (included in the other ~25% of the vectors)

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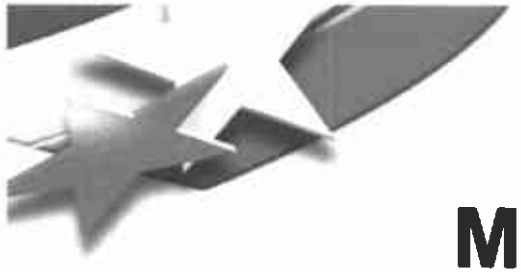

Microbial Activity (cont.)

Potentially significant microbial respiratory pathways

- Denitrification
  - $C_6H_{10}O_5 + 4.8H^+ + 4.8NO_3^- \rightarrow 7.4H_2O + 6CO_2 + 2.4N_2$
- SO_4^{2-} reduction
  - $C_6H_{10}O_5 + 6H^+ + 3SO_4^{2-} \rightarrow 5H_2O + 6CO_2 + 3H_2S$
- Fermentation and methanogenesis
  - $C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2$

Implementation in PA

- Sequential use of electron acceptors
- However, the EPA has disallowed the use of methanogenesis
- Given the current inventory, denitrification will consume 4% and SO_4^{2-} reduction will consume 96% of the CPR materials in the repository <u>if</u> all CPR materials are consumed

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Role of MgO

Functions as an engineered barrier by consuming CO_2 from possible microbial activity, thereby decreasing actinide solubilities

- **Will react with CO_2 and H_2O in brine and water vapor to form hydrous and, eventually, anhydrous Mg carbonates**
- **Will consume essentially all CO_2 and remove CO_3^{2-} from brine**
- **Will buffer pH at ~9**

Consumption of significant quantities of H_2O could also affect long-term performance

The DOE is emplacing sufficient MgO to consume all CO_2 that could be produced by microbial consumption of all cellulosic, plastic, and rubber (CPR) materials

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Role of MgO (cont.)

DOE asserted in the 1996 Compliance Certification Application (CCA) that borehole plugs, MgO, panel closures, and shaft seals would help satisfy the EPA's assurance requirement for multiple natural and engineered barriers

- **Barriers defined as "any material or structure that prevents or substantially delays movement of water or radionuclides toward the accessible environment." Barriers can be "... a geologic structure, a canister, a waste form, or a material placed over and around waste provided that material or structure substantially delays movement of water or radionuclides"**

MgO recognized as the only engineered barrier in the WIPP disposal system in the EPA's 1998 certification of the WIPP

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Role of MgO (cont.)

Hydration of periclase to form brucite:

- $MgO + H_2O = Mg(OH)_2$

Carbonation of brucite to form hydromagnesite or magnesite

- $5Mg(OH)_2 + 4CO_2 \rightleftharpoons Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
  - Reaction assumed to control f_{CO_2} for the actinide-solubility calculations
- $Mg(OH)_2 + CO_2 \rightleftharpoons MgCO_3 + H_2O$
  - Likely long-term carbonation reaction

Reaction that will buffer pH:

- $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

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Emplacement of MgO

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Compositions of Brines Before And After Reaction with MgO (M)

	GWB (before)	GWB (after)	ERDA-6 (before)	ERDA-6 (after)
B	0.157	0.166	0.063	0.062
Br	0.027	0.28	0.011	0.011
Ca	0.014	0.009	0.012	0.011
Cl	5.87	5.38	4.8	5.3
K	0.465	0.490	0.097	0.096
Mg	1.02	0.578	0.019	0.11
Na	3.53	4.35	4.87	5.33
pH	NA	8.69	6.17	8.94
SO_4	0.177	0.228	0.17	0.17

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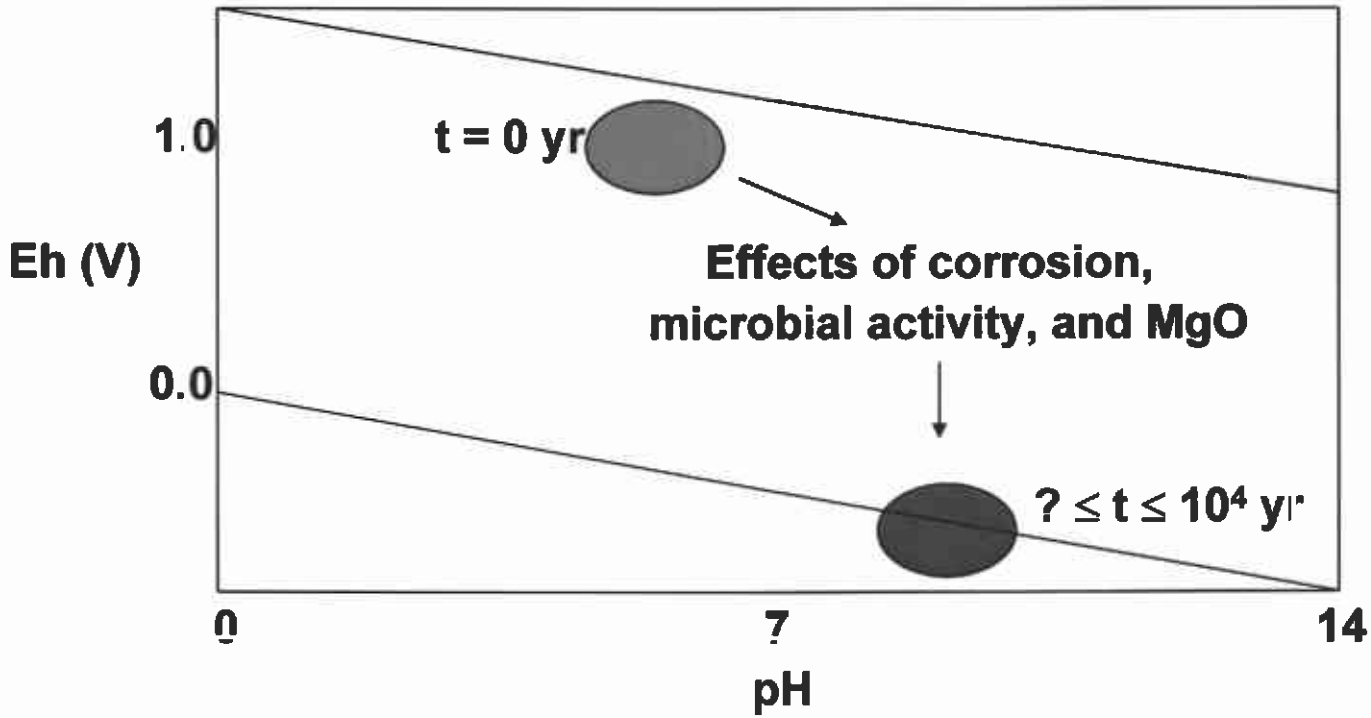
Effects of Gas Generation & Reaction with MgO on Eh and pH



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Expected Near-Field Conditions

Strongly reducing Eh

- H_2O reduced to H_2 by corrosion of Fe- and Al-base metals

$f_{CO_2} = 10^{-5.50}$ atm

pH ≅ 9

a_{H_2O} ≅ 0.73 to 0.75 in brines (RH ≅ 73 to 75% in gaseous phase)

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Important Constituents of Transuranic (TRU) Waste

Radioelements per equivalent 208-L (55-gal) drum of waste[1]:

- Th: 36.5 g; U: 759 g; Np: 0.0202 g; Pu: 11.6 g; Am: 0.177 g

Relative Importance of radioelements based on their potential effects on WIPP PA:

- Pu ≅ Am >> U > Th >> Np
  - Np not transported by PA, but included in the WIPP lab studies and speciation-and-solubility modeling

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1. Based on inventory used for the solubility calculations for the CRA-2004 PABC

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Important Constituents of TRU Waste

Organics

- Acetate, citrate, EDTA, lactate, oxalate
  - Used for actinide separation and decontamination
- Humics
  - Possible microbial degradation of cellulosic materials
  - Soils in TRU waste

Reductants

- Metals
  - Steel drums and boxes
  - Fe- and Al-base materials in the waste
- Cellulosic, plastic, and rubber materials
  - Possible microbial substrates
- H_2S in Castile brines

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Oxidation-State Speciation

Under the strongly reducing, mildly basic conditions expected in the WIPP:

- Th: Th(IV)
- U: U(IV) or U(VI)
- Np: Np(IV) or Np(V)
- Pu: Pu(III) or Pu(IV)
- Am: Am(III)

Implementation in PA

- Th(IV), U(IV), Np(IV), Pu(III), and Am(III)
  - Probability = 0.5 (this combination of oxidations states included in ~50% of the PA vectors)
- Th(IV), U(VI), Np(V), Pu(IV), and Am(III)
  - Probability = 0.5 (included in the other ~50% of the vectors)

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Development of Solubility Models

Developed thermodynamic speciation-solubility models for An(III), An(IV), and An(V) based on Pitzer activity-coefficient model

- Developed for the PA calculations for the WIPP Compliance Certification Application (CCA), submitted to EPA in October 1996
- Modified for the EPA's 1997 PA Verification Test (PAVT), part of the EPA's review of the CCA
- Updated for the CRA-2004

Used estimates for An(VI)

- Used an estimate of 1×10^{-5} m for both Salado and Castile brines for the CCA PA, PAVT, and CRA-2004 PA
- Used an EPA-specified value of 1×10^{-3} M for the CRA-2004 PABC

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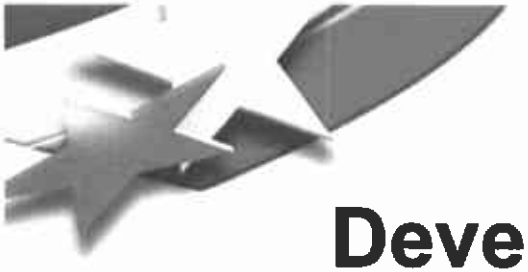

Development of Models (cont.)

Used oxidation-state analogy

- An(III) model
  - Based on WIPP-specific lab studies and literature data for Nd(III), Am(III), and Cm(III)
  - Used to predict solubilities of Pu(III) and Am(III)
- An(IV) model
  - Based on WIPP-specific lab studies and literature data for Th(IV)
  - Used to predict solubilities of Th(IV), U(IV), Np(IV), and Pu(IV)
- An(V) model
  - Based on literature data and WIPP-specific lab studies for Np(V)
  - Used to predict solubility of Np(V)

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Development of Models (cont.)

Used pre-existing Harvie-Møller-Weare database for nonradioactive elements in brines

Obtained Pitzer parameters experimentally by measuring solubilities and stability constants for actinides and oxidation-state analogs

- **Interactions between actinides and important elements in brines**
- **Interactions between actinides and organics**
- **Interactions between Mg and organics**

Used NONLIN to fit Pitzer parameters to experimental data

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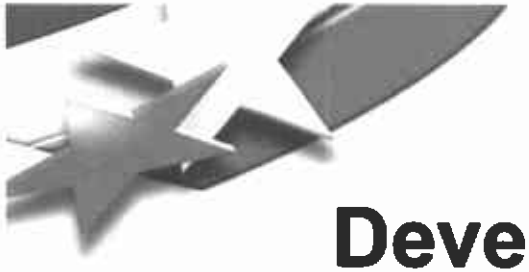

Development of Models (cont.)

Used EQ3/6 and Fracture-Matrix Transport (FMT) to predict brine composition, especially f_{CO_2} and pH

Used FMT to predict speciation and solubilities of An(III), An(IV), and An(V) in brines

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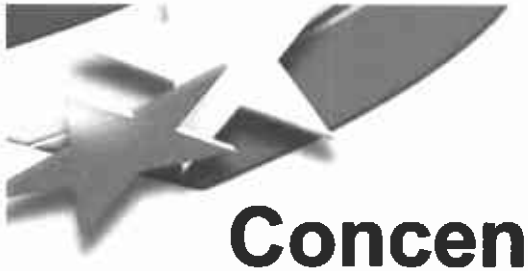

Concentrations of Organic Ligands[1]

Organic Ligand	Concentration (M)
Acetate	1.06×10^{-2}
Citrate	8.06×10^{-4}
EDTA	8.14×10^{-6}
Oxalate[2]	4.55×10^{-2}

1. Calculated assuming all organic ligands in the inventory used for the CRA-2004 PABC dissolve in 10,011 m^3 of brine, "a reasonable minimum volume of brine in the repository required for a brine release."
2. Calculation included precipitation of Ca oxalate.

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Equilibrium Assemblage(s) for or from FMT for the CRA-2004 PABC

CO_2 buffer

- Brucite-hydromagnesite carbonation reaction

pH buffer

- Brucite dissolution-precipitation reaction

Solubility-controlling solids

- An(III): $Am(OH)_3$
- An(IV): amorphous, hydrous ThO_2
- An(V): $KNpO_2CO_3$

Other solids in the equilibrium assemblage

- Halite (NaCl), anhydrite ($CaSO_4$), ± glauberite ($Na_2Ca(SO_4)_2$), ± $Mg_2Cl(OH)_3 \cdot 4H_2O$

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Conditions Predicted by FMT for the CRA-2004 PABC

	GWB	ERDA-6
Log f_{CO_2}	-5.50	-5.50
pH	8.69	8.94
l (m)	7.66	6.80
a_{H_2O}	0.732	0.748
RH	73.2%	74.8%
ρ (g/cm^3)	1.23	1.22

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Actinide Solubilities Predicted for the CRA-2004 PABC (M)

	GWB	ERDA-6
An(III)[A]	3.87×10^{-7}	2.88×10^{-7}
An(IV)[B]	5.64×10^{-8}	6.79×10^{-8}
An(V)[C]	3.55×10^{-7}	8.24×10^{-7}
An(VI)[D]	1.00×10^{-3}	1.00×10^{-3}

A. Model developed using experimental data for Nd(III), Am(III), and Cm(III); and applied to Pu(III) and Am(III).

B. Model developed using data for Th(IV) and applied to Th(IV), U(IV), Np(IV), and Pu(IV).

C. Model developed using data for Np(V) and applied to Np(V).

D. Value specified by the EPA and applied to U(VI).

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An(III) Speciation Predicted for the CRA-2004 PABC (M)[1]

	GWB	ERDA-6
$An(OH)_2^+$	2.07×10^{-7}	9.99×10^{-8}
$AnEDTA^-$	1.75×10^{-7}	1.86×10^{-7}
$AnOH^{+2}$	2.46×10^{-9}	7.04×10^{-10}
$AnAc^{+2}$	1.12×10^{-9}	2.01×10^{-10}
$An(OH)_3(aq)$	5.99×10^{-10}	6.82×10^{-10}
AnCit(aq)	4.45×10^{-10}	2.18×10^{-10}

1. Model developed using experimental data for Nd(III), Am(III), and Cm(III); and applied to Pu(III) and Am(III).

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An(IV) Speciation Predicted for the CRA-2004 PABC (M)[1]

	GWB	ERDA-6
$An(OH)_4(aq)$	4.53×10^{-8}	4.76×10^{-8}
$An(OH)_3CO_3^-$	1.11×10^{-8}	2.03×10^{-8}
$An(CO)_3^{-5}$	3.97×10^{-16}	1.72×10^{-17}
$An(SO_4)_3^{-2}$	1.59×10^{-17}	8.17×10^{-19}
AnEDTA(aq)	7.54×10^{-18}	4.11×10^{-18}
$An(SO_4)_2(aq)$	2.98×10^{-19}	1.55×10^{-20}

1. Model developed using data for Th(IV) and applied to Th(IV), U(IV), Np(IV), and Pu(IV).

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An(V) Speciation Predicted for the CRA-2004 PABC (M)[1]

	GWB	ERDA-6
AnO_2^+	1.27×10^{-7}	1.74×10^{-7}
$AnO_2CO_3^-$	1.04×10^{-7}	4.08×10^{-7}
$AnO_2Ac(aq)$	7.34×10^{-8}	1.60×10^{-7}
AnO_2Ox^-	4.39×10^{-8}	6.19×10^{-8}
$AnO_2OH(aq)$	4.34×10^{-9}	1.04×10^{-8}
$AnO_2(CO_3)_2^{-3}$	1.16×10^{-9}	8.66×10^{-9}

1. Model developed using data for Np(V) and applied to Np(V).

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