

Overview of WIPP Geochemical Modeling¹

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Overview of the WIPP Project

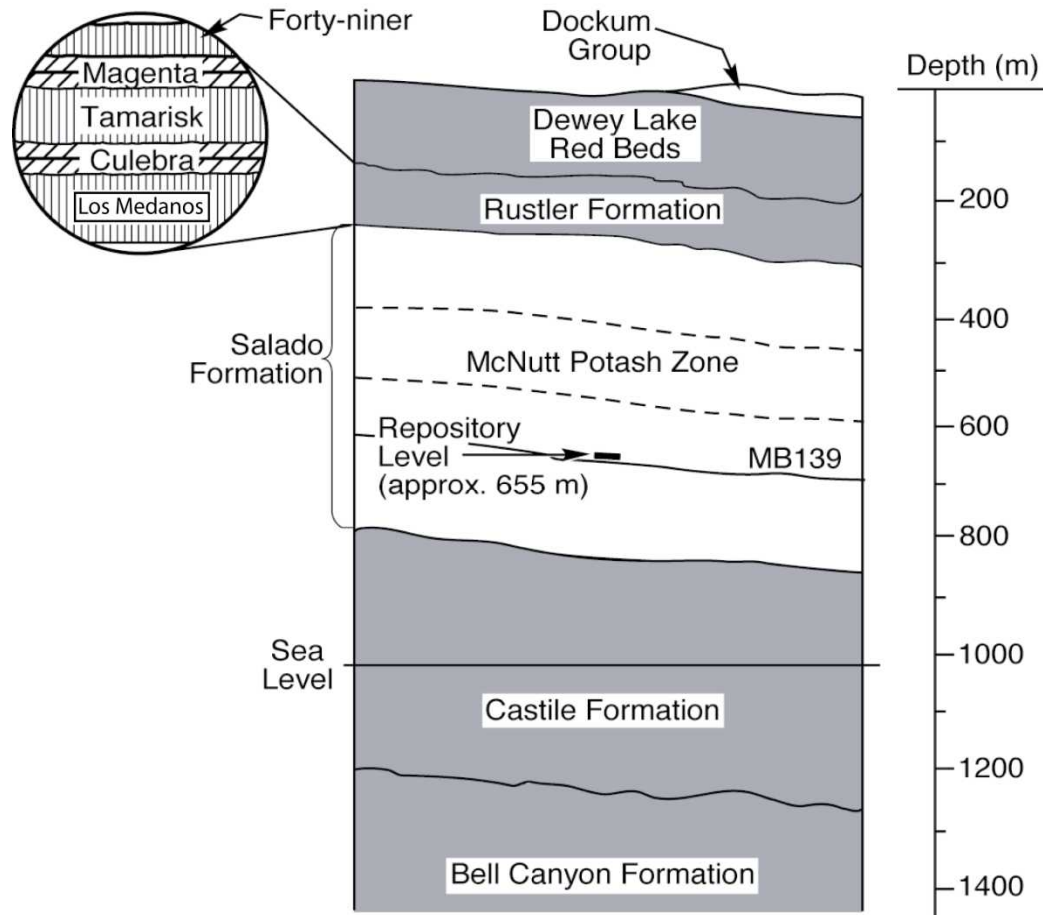
Waste Isolation Pilot Plant (WIPP)

- A U.S. Department of Energy repository in southeast New Mexico for defense-related transuranic waste
- Certified in May 1998
- Opened in March 1999
- First recertification in April 2006

Description

- Located in the Salado Fm., a Permian bedded-salt formation, at a subsurface depth of 655 m (2150 ft)

Stratigraphic Section at the WIPP Site



TRI-6801-97-0



Characteristics of the Salado Fm.

Lithology

- Consists mostly of nearly pure halite (NaCl)
- Also includes clay seams and “marker beds” with anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), magnesite (MgCO_3), polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), and clays

Mineralogy

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



Characteristics of the Salado (cont.)

In situ conditions at the repository horizon


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

Water content

- Contains both intergranular (grain-boundary) brine and intragranular brine (fluid inclusions)
 - Intergranular will flow into disposal rooms after formation of the disturbed rock zone increases Salado permeability
 - Intragranular will not flow into disposal rooms
- Total brine content typically 1-2 wt %, but can be up to 3 wt %

Characteristic of WIPP Waste





WIPP Near-Field Conceptual Models

Instantaneous, reversible equilibria among brines and solids will control chemical conditions

- Equilibration is fast with respect to 10,000-year regulatory period
- MgO added to consume microbial CO₂, decrease actinide solubilities, and create homogeneous conditions
 - MgO is the only engineered barrier certified by the EPA

Standard brines

- Generic Weep Brine (GWB) simulates intergranular Salado brines
- U.S. Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) simulates Castile brines



WIPP Near-Field Conceptual Models (cont.)

Solids included in modeling

- Halite and anhydrite
 - The two most important Salado minerals
- Brucite ($\text{Mg}(\text{OH})_2$), phase 3 ($\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$) and/or phase 5 ($\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$), and the “5424” polymorph of hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O}$)
 - MgO hydration and carbonation products predicted by modeling and observed in lab experiments with GWB
- Brucite and hydromagnesite
 - Predicted by modeling and observed in lab experiments with ERDA-6



Brine Compositions Before and After Equilibration (M)

	GWB^A	GWB^B	ERDA-6^A	ERDA-6^B
B	0.158	0.176	0.063	0.0624
Na	3.53	4.31	4.87	5.28
Mg	1.02	0.584	0.019	0.136
K	0.467	0.521	0.097	0.0961
Ca	0.014	0.0098	0.012	0.0112
SO₄	0.177	0.210	0.170	0.176
Cl	5.86	5.40	4.8	5.23
Br	0.0266	0.0297	0.011	0.0109
TIC (mM)	-	0.350	16	0.448

A. Before reactions with solids and organic ligands

B. Predicted for the CRA-2009 PABC by FMT after reactions with solids & organics



WIPP Near-Field Conceptual Models (cont.)

Reaction that will buffer f_{CO_2} , at least initially

- $5\text{Mg}(\text{OH})_2 + 4\text{CO}_2(\text{aq or gas}) \rightleftharpoons \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
 - Hydromagnesite (5424) is metastable with respect to magnesite, but could persist for hundreds to thousands of years
 - The EPA has specified that the brucite-hydromagnesite carbonation reaction be used to calculate f_{CO_2} for actinide-solubility calculations

Possible long-term f_{CO_2} buffer reaction

- $\text{Mg}(\text{OH})_2 + \text{CO}_2(\text{aq or gas}) \rightleftharpoons \text{MgCO}_3 + \text{H}_2\text{O}(\text{aq or gas})$
 - Magnesite is stable with respect to hydromagnesite (5424), and is present in the Salado

Reaction that will increase pH to basic values

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



Predictions of Near-Field Conditions

$f_{\text{CO}_2} \cong 3 \times 10^{-6}$ possibly decreasing to 1×10^{-7} atm^A

- TIC $\cong 3 \times 10^{-4}$ M (GWB) or 4×10^{-4} M (ERDA-6), possibly decreasing to 1×10^{-5} M (GWB) or 2×10^{-5} M (ERDA-6)

Very low f_{O_2} (at or even below the lower stability limit of H_2O on an Eh-pH diagram)

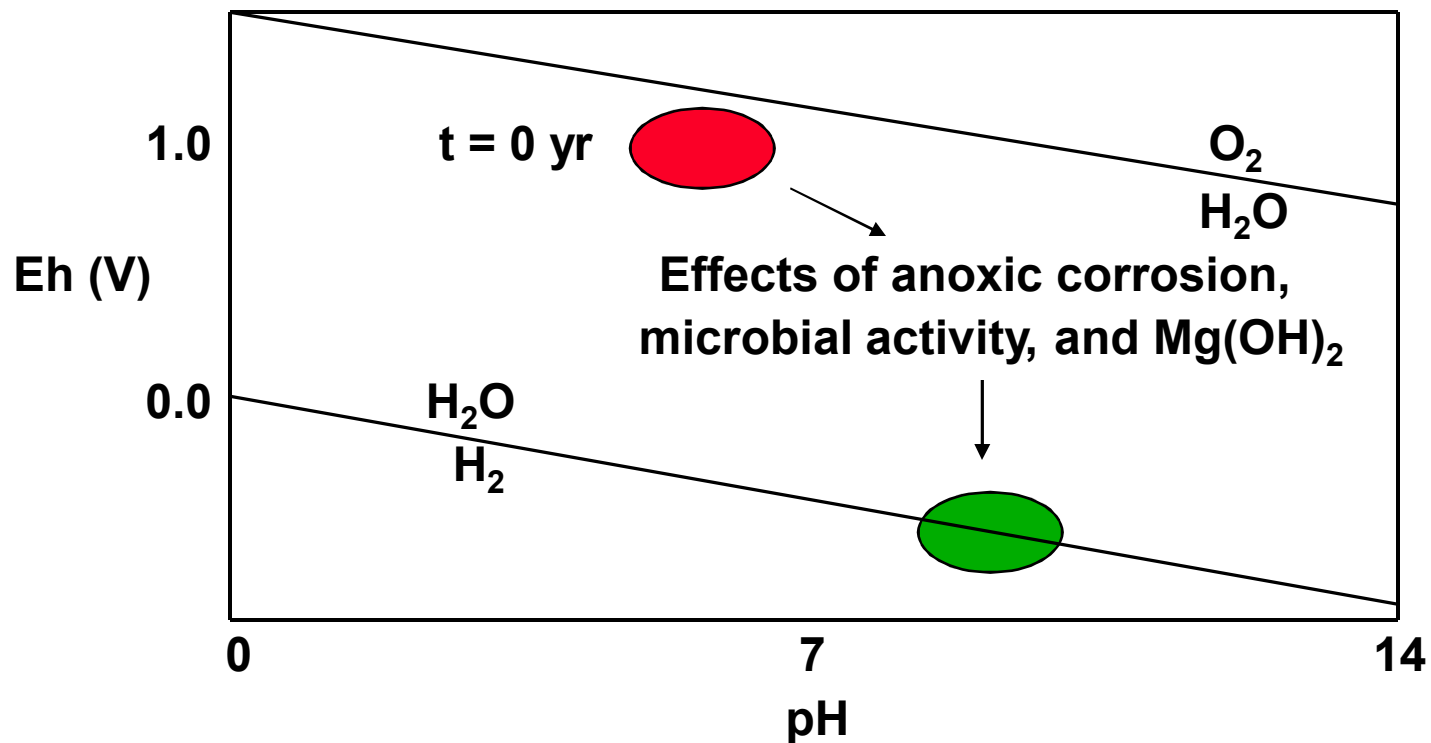
- H_2O unstable in the WIPP (reduced to H_2 by steels and other metals)

pH $\cong 9^A$

Relative humidity (RH) $\cong 73$ to $75\%^A$

A. FMT calculations for the CRA-2009 PABC

Predictions of Near-Field Chemical Conditions (cont.)





Predictions of “Baseline” Actinide Solubilities

Thermodynamic models based on Pitzer activity-coefficient model for Th(IV), Np(V), and Am(III)

Inclusion of acetate, citrate, EDTA, and oxalate

Use of the speciation-solubility component of Fracture-Matrix Transport (FMT) to calculate solubilities of Th(IV), Np(V), and Am(III)

- EQ3/6 will soon replace FMT

Inclusion of uncertainties in predictions of solubilities established by comparisons of measured and predicted solubilities



Predictions of “Baseline” Actinide Solubilities (cont.)

Strongly reducing conditions will cause actinides to speciate as:

- Th(IV), U(IV), Np(IV), Pu(III), and Am(III) (probability of 0.5 in PA) or
- Th(IV), U(VI), Np(V), Pu(IV), and Am(III) (probability of 0.5 in PA)

Use of oxidation-state analogy to:

- Apply solubilities calculated for Th(IV) to U(IV), Np(IV), and Pu(IV)
- Apply solubilities calculated for Am(III) to Pu(III)

Use of a solubility estimate for U(VI)

- Did not develop a U(VI) model
- Current estimate of 1×10^{-3} M specified by the EPA



Predictions of “Baseline” Actinide Solubilities (M) (cont.)

	GWB	ERDA-6
Th(IV) ^A	5.63×10^{-8}	6.98×10^{-8}
Np(V) ^A	3.90×10^{-7}	8.75×10^{-7}
Am(III) ^A	1.66×10^{-6}	1.51×10^{-6}
U(VI) ^B	1.00×10^{-3}	1.00×10^{-3}

A. FMT calculations for the CRA-2009 PABC with organic ligands

B. EPA estimate