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Use of Iron-Base Waste Packages in a Salt Repository[1]

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Topics to Be Addressed

Advantages of corrosion-allowance Fe-base waste packages

Behavior of Fe-base waste packages in the WIPP

Effects of anoxic corrosion of Fe-base waste packages in the WIPP

Use of Fe-base waste packages in a repository for thermally hot waste (THW)

References and backup slides

Advantages of Corrosion-Allowance Fe-Base Waste Packages

Corrosion-allowance, Fe-base materials are inexpensive relative to corrosion-resistant materials

Characterization of the behavior of corrosion-allowance materials is relatively straightforward

Corrosion-allowance, Fe-base materials can create strongly reducing near-field conditions

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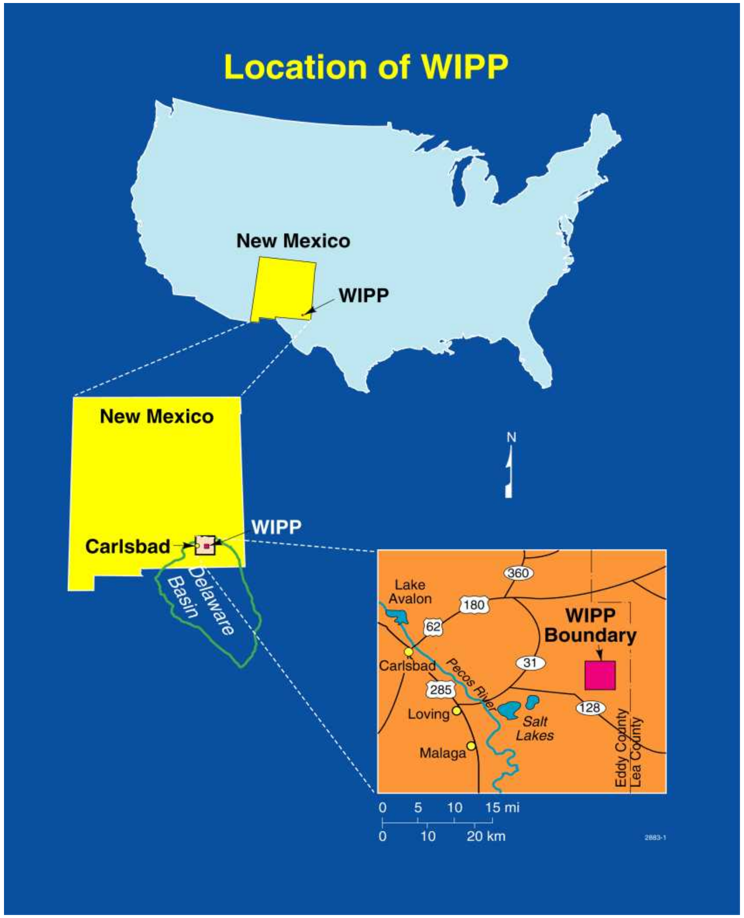
Behavior of Fe-Base Waste Packages in the WIPP

Overview of the Waste Isolation Pilot Plant (WIPP)

- A U.S. Department of Energy repository in southeast New Mexico for defense-related transuranic (TRU) waste
- Located in the Salado Fm., a Permian bedded-salt formation, at a subsurface depth of 655 m (2150 ft)
- Disposal of radioactive waste in salt formations recommended by the National Academy of Sciences (NRC, 1957)
- WIPP certified in May 1998
- WIPP opened in March 1999
- First WIPP recertification in April 2006
- Second recertification in November 2010

Location of the WIPP



Emplacement of Contact-Handled (CH) TRU Waste in the WIPP

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Cutaway View of CH TRU Waste

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Behavior of Fe-Base Waste Packages in the WIPP (cont.)

The DOE does not take credit for containment of TRU waste by the 208-L (55-gal) low-C-steel drums (or other low-C-steel waste containers) in the WIPP!

Closure of WIPP disposal rooms will begin to crush the drums (and other waste containers) about 10-15 yrs after emplacement

If brine enters the repository, low-C-steel waste containers will corrode

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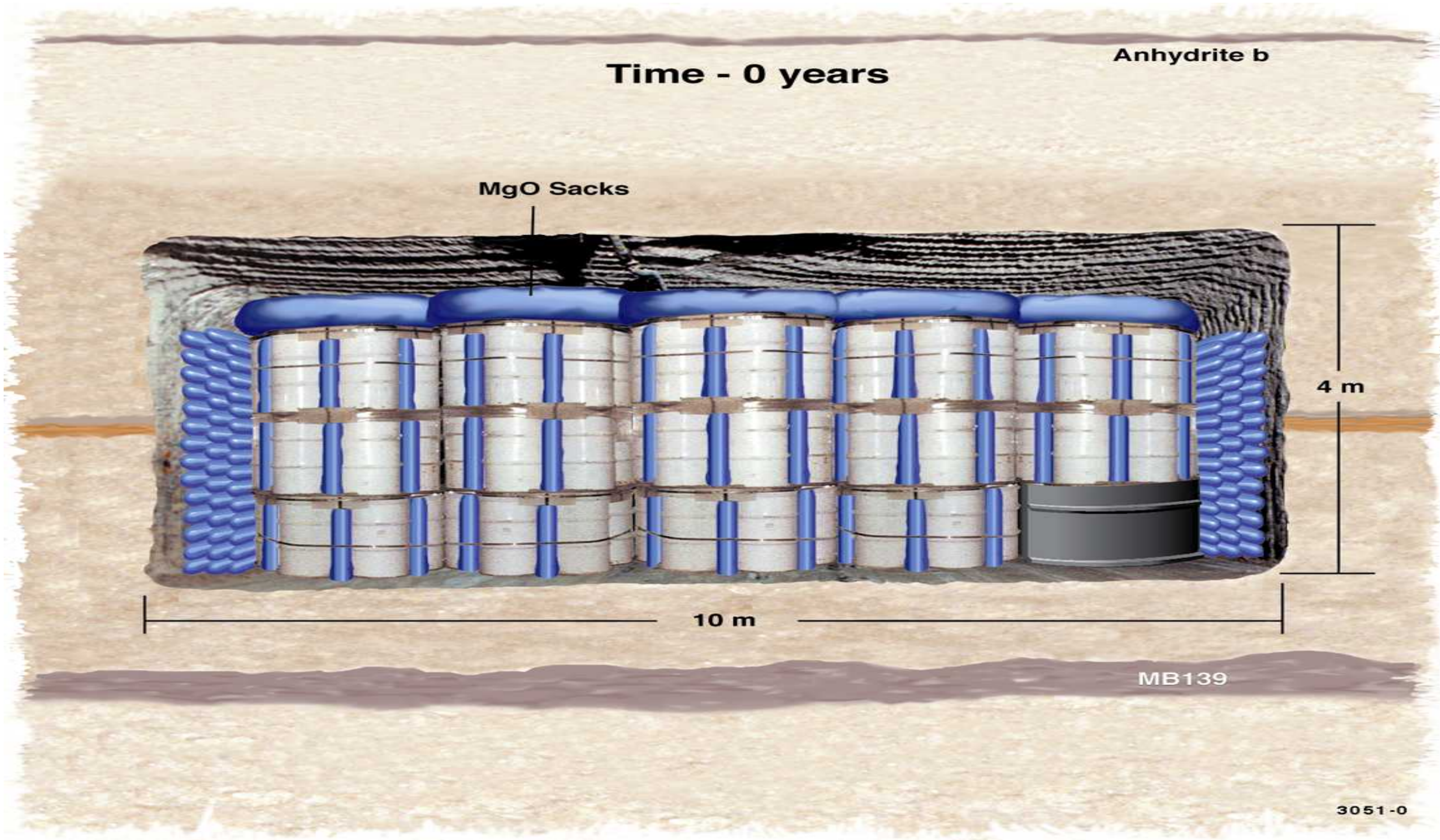
Behavior of Fe-Base Waste Packages in the WIPP (cont.)



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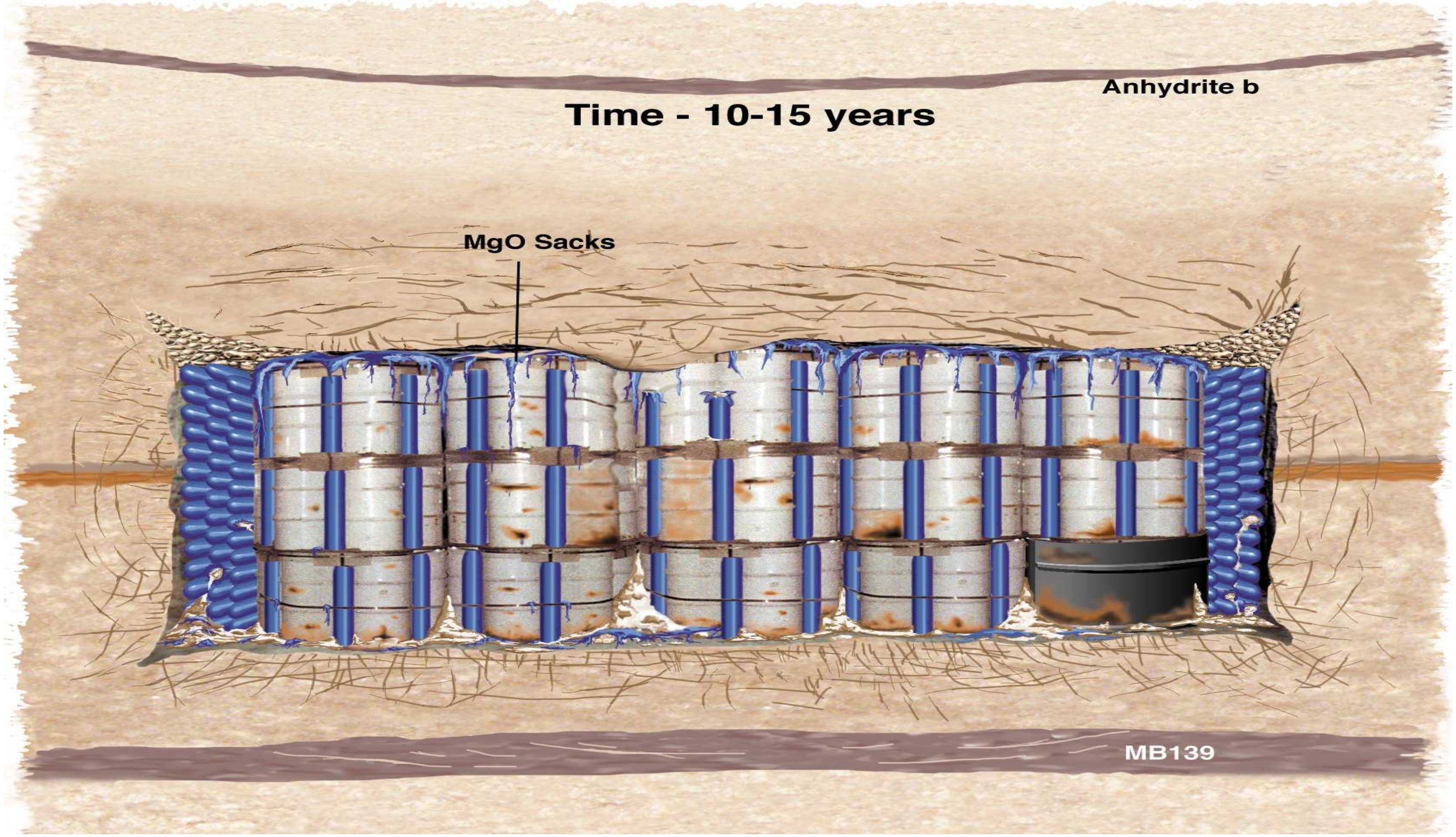
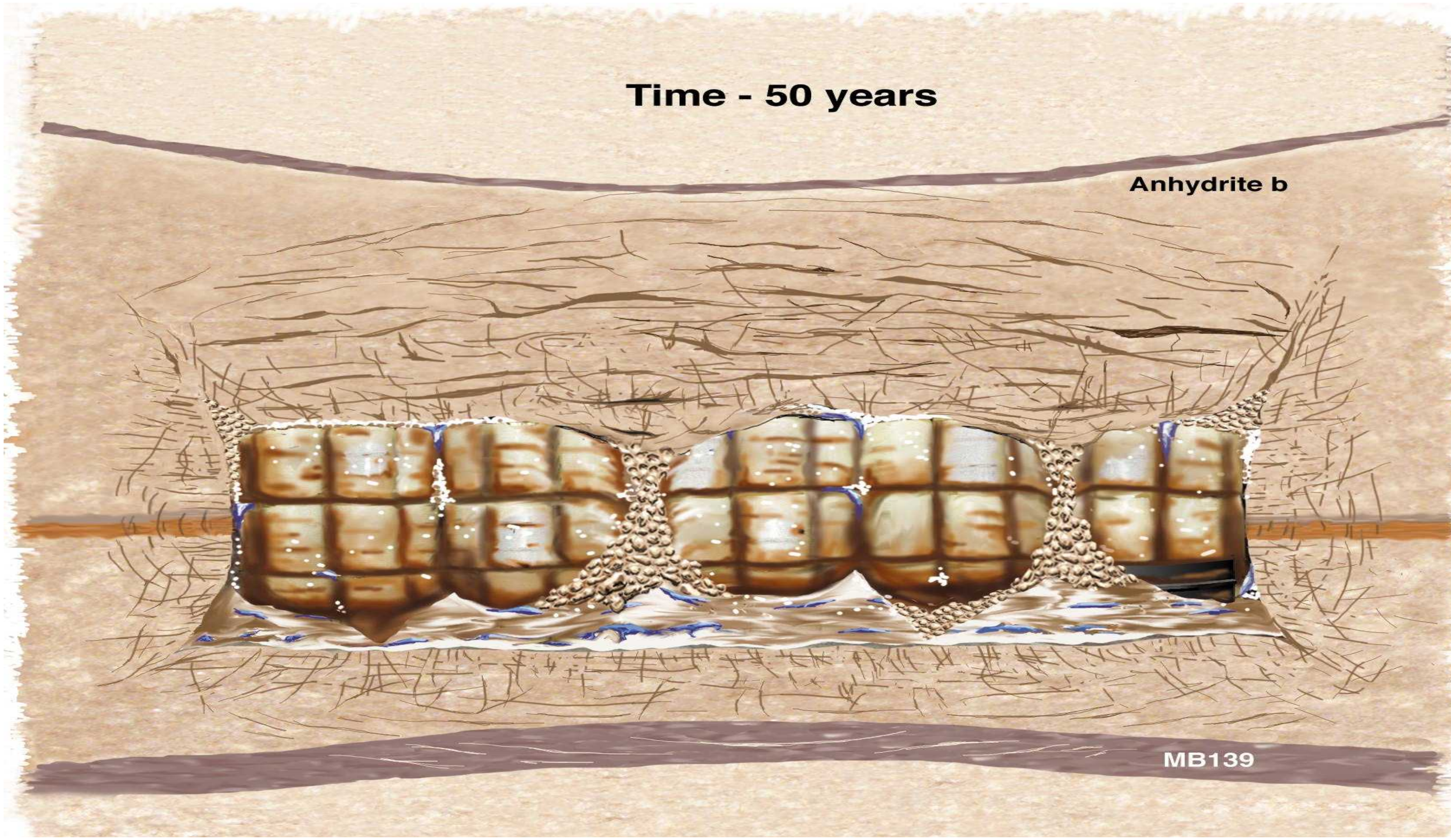
Behavior of Fe-Base Waste Packages in the WIPP (cont.)



Behavior of Fe-Base Waste Packages in the WIPP (cont.)



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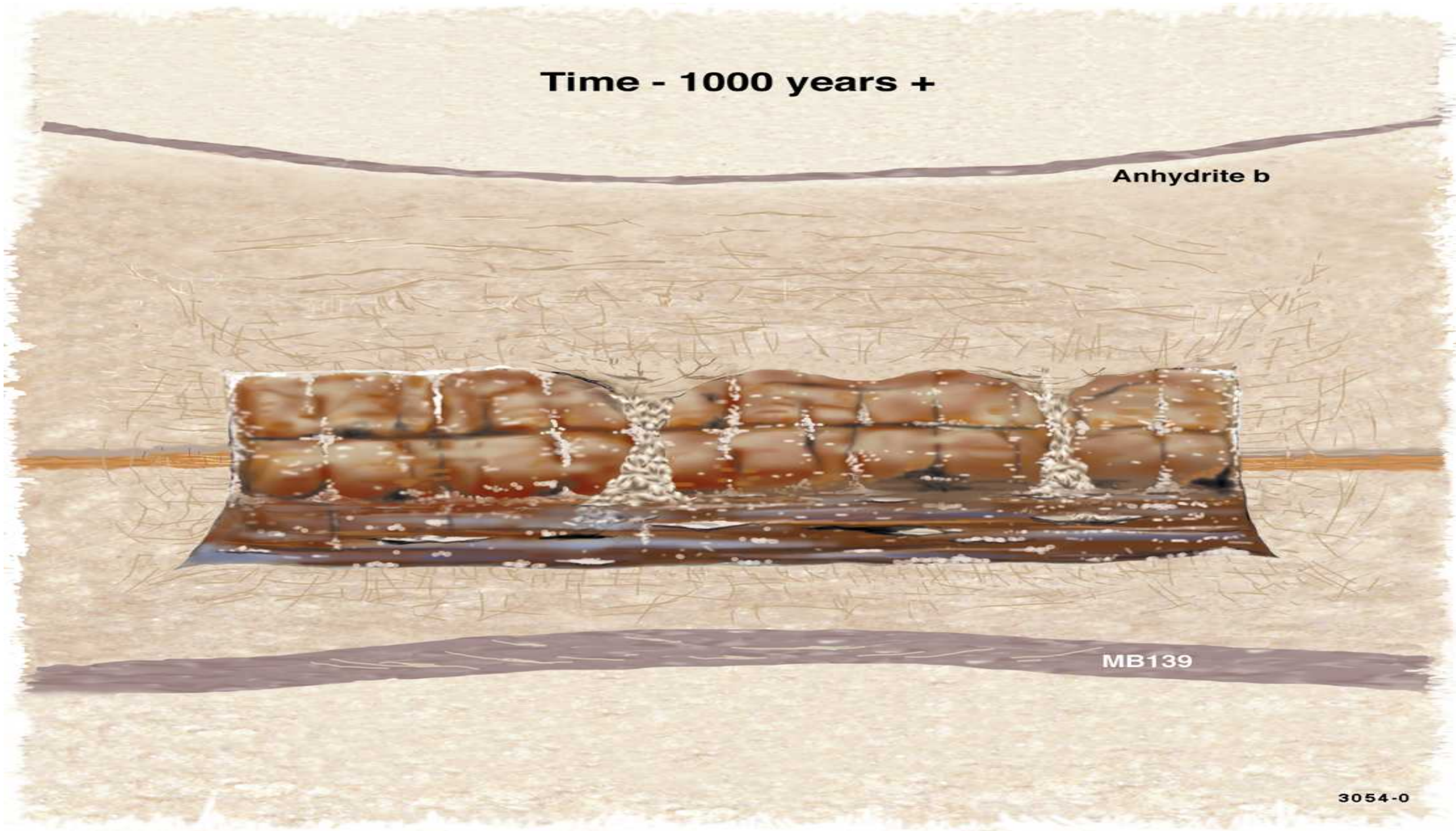
Behavior of Fe-Base Waste Packages in the WIPP (cont.)



Behavior of Fe-Base Waste Packages in the WIPP (cont.)

Previous or ongoing studies of anoxic corrosion of low-C-steels

- Haberman and Frydrych (1988)
- Westerman et al. (1988)
- Simpson and Schenk (1989)
- Grauer et al. (1991)
- Telander and Westerman (1993, 1997)
- Chivot (2004)
- Roselle (2009, 2010, 2011, this conference)

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Behavior of Fe-Base Waste Packages in the WIPP (cont.)

Oxic corrosion ≡ corrosion of low-C steels using aqueous or gaseous free molecular O_2

- $4Fe + 2H_2O + 3O_2 \rightleftharpoons 4FeO(OH)$

Anoxic corrosion ≡ corrosion of low-C steels without free molecular O_2

- $Fe + (x + 2)H_2O \rightleftharpoons Fe(OH)_2 \cdot xH_2O + H_2$
- $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$
- $Fe + H_2O + CO_2 \rightleftharpoons FeCO_3 + H_2$
- $Fe + H_2S \rightleftharpoons FeS + H_2$
- $Fe + 2H_2S \rightleftharpoons FeS_2 + 2H_2$

In the WIPP, anoxic corrosion >> oxic corrosion

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Behavior of Fe-Base Waste Packages in the WIPP (cont.)

So, where will the brine come from after the WIPP is filled and the panel closures are installed?

- Possible seepage into the repository from the disturbed rock zone (DRZ) around the repository
  - ➢ Total brine content of the Salado Fm. typically 1-2 wt %, but can be up to 3 wt %
- Possible seepage down the shafts from overlying formations
- Possible human intrusion (from inadvertent drilling) through the repository and into a brine reservoir in the the underlying Castile formation

Many WIPP scientists and engineers think that the quantities of brine predicted to enter the repository are overestimated

Behavior of Fe-Base Waste Packages in the WIPP (cont.)

Where does the H_2 go?

- According to probabilistic performance-assessment (PA) calculations carried out by the WIPP Project, anoxic corrosion of low-C steels could produce enough H_2 to increase the pressure in the repository to lithostatic (~150 atm)
- Any additional H_2 production initiates fracturing, or reopens preexisting fractures, in the marker beds
- When this happens, PA predicts that H_2 migrates up and out into the marker beds just above the repository

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Behavior of Fe-Base Waste Packages in the WIPP (cont.)

How far does anoxic corrosion go in the WIPP?

- According to WIPP PA calculations, anoxic corrosion of low-C steels is brine-limited
- Because anoxic corrosion of low-C steels occurs under brine-inundated conditions but not under humid conditions, anoxic corrosion of low-C steels is self-limiting
- Nevertheless, anoxic corrosion pressurizes the repository to lithostatic pressure and fractures the marker beds in some of the PA calculations

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Effects of Anoxic Corrosion of Fe-Base Waste Packages in the WIPP

What are the effects of anoxic corrosion on near-field chemical conditions?

- **Strongly reducing**
  - **At or even below the lower stability limit of H_2O on an Eh-pH diagram**
- **f_{O_2} is so low that H_2O is unstable in the WIPP**
  - **H_2O is reduced to H_2 by low-C steels**

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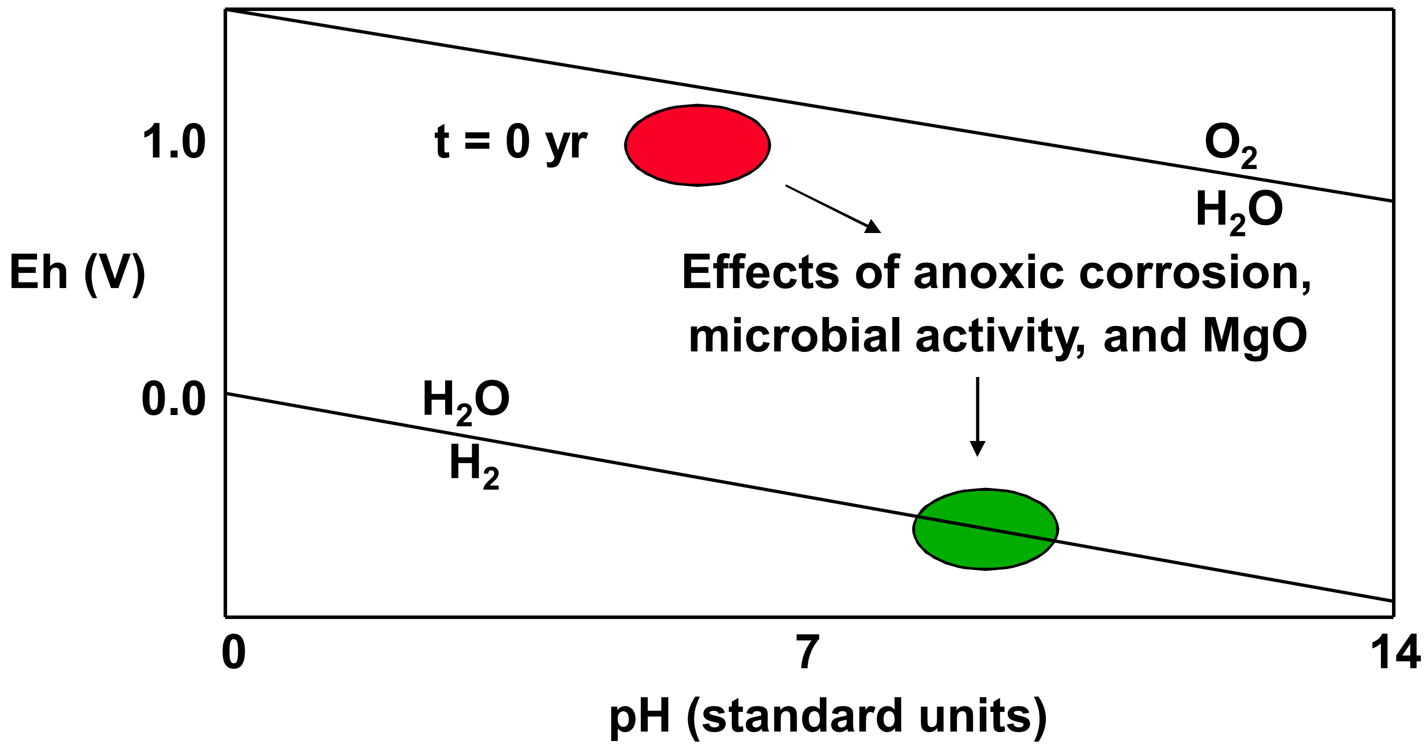
Effects of Anoxic Corrosion of Fe-Base Waste Packages (cont.)



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Effects of Anoxic Corrosion of Fe-Base Waste Packages (cont.)

What are the effects of these conditions on radioelement mobilities?

- **Radioelements that can speciate in more than one oxidation state, but are less mobile when they occur in their lower or lowest oxidation states would be reduced and thus immobilized under the strongly reducing conditions produced**
  - **U, Np, Pu, and Am in the TRU waste in the WIPP**
  - **Se, Tc, U, Np, Pu, and Am in spent fuel or high-level waste in a bedded or domal salt repository**

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Use of Fe-Base Waste Packages in a Salt Repository for THW

Will there be as much brine as we conservatively predict for the WIPP?

- **Other bedded-salt formations probably have brine contents similar to those of the Salado Fm. (typically 1-2 wt %, but can be up to 3 wt %)**
- **Domal salt formations, however, have brine contents much lower than those of the Salado (average = 0.003 wt %, but anomalous zones in salt domes can have up to 0.03 wt %, according to Knauth and Kumar, 1981)**

Use of Fe-Base Waste Packages in a Salt Repository for THW (cont.)

Will brine migrate up the thermal gradient to the waste packages?

- Jenks and Claiborne (1981)
- Hadley (1981)
- Knauth and Kumar, (1981)
- Olander (1982, 1984)
- Müller (1985)
- Nowak and McTigue (1987)
- Hwang et al. (1990)

Use of Fe-Base Waste Packages in a Salt Repository for THW (cont.)

Some conclusions

- All-liquid (brine-filled) fluid inclusions move up the thermal gradient
- Gas-liquid fluid inclusions move down the thermal gradient
  - ➢ Possible near-field radioelement transport mechanism
- Fluid inclusions can cross grain boundaries
- Brine migration more likely to be significant in bedded salt than in domal salt

Use of Fe-Base Waste Packages in a Salt Repository for THW (cont.)

Some possible solutions if brine migrates up the thermal gradient or if other brine-transport mechanisms are significant

- **Aging THW long enough to prevent the development of thermal gradients sufficient to drive brine migration**
- **Emplacement of backfill material(s) to prevent brine from contacting the waste packages**
- **Use of waste packages thick enough to prevent breaching during the thermal period**
- **Use of a corrosion-resistant alloy such as C-22 or Ti Grade 12**

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Use of Fe-Base Waste Packages in a Salt Repository for THW (cont.)

Site-specific studies would be required to determine if brine migration, anoxic corrosion, and H_2 pressurization are issues for salt formations under consideration for disposal of THW and, if so, which approach(es) would best resolve them

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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
SO_4	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

Solids Included in Reactions That Will Control Chemical Conditions

Type of Solid	GWB	ERDA-6
Salado minerals	Halite[A] Anhydrite[B]	Halite[A] Anhydrite[B]
MgO alteration products	Brucite[C] Hydromagnesite[D] Phase 3[E] or phase 5[F]	Brucite[C] Hydromagnesite[D] -
Phases predicted to precipitate	- Whewellite[H]	Glauberite[G] Whewellite[H]

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Solids Included in Reactions That Will Control Conditions (cont.)

Type of Solid	GWB	ERDA-6
Actinide-bearing solids	ThO_2(am) $KNpO_2CO_3$ $Am(OH)_3$	ThO_2(am) $KNpO_2CO_3$ $Am(OH)_3$

[A]Halite = NaCl

[B]Anhydrite = $CaSO_4$

[C]Brucite = $Mg(OH)_2$

[D]Hydromagnesite = $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$

[E]Phase 3 = $Mg_2(OH)_3Cl \cdot 4H_2O$

[F]Phase 5 = $Mg_3(OH)_5Cl \cdot 4H_2O$

[G]Glauberite = $Na_2Ca(SO_4)_2$

[H]Whewellite = $CaC_2O_4 \cdot H_2O$

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