SAND2007-3800P

Overview of Near-Field Geochemical Processes and Conditions Expected in the WIPP[1]

KHNP Training Program
Module 4: Repository Siting and Characterization

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Topics to Be Addressed

Overview of the Waste Isolation Pilot Plant (WIPP)

Characteristics of the Salado Formation That Will Affect Near-Field Geochemistry

Characteristics of TRU Waste That Will Affect Near-Field Geochemistry

Near-Field Geochemical Processes Expected in the WIPP

Near-Field Geochemical Conditions Expected in the WIPP

Topics to Be Addressed

Conclusions: Some Geochemical Considerations in Radioactive-Waste-Repository Site Selection

References

Topics to Be Addressed

Overview of the WIPP

Characteristics of the Salado

Characteristics of TRU Waste

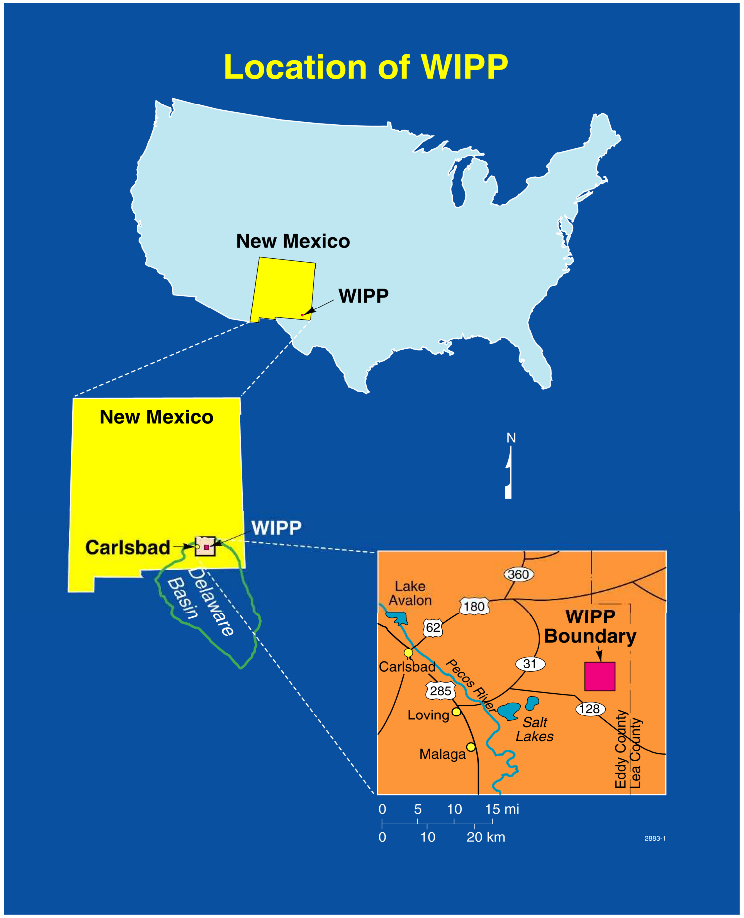
Near-Field Processes

Near-Field Conditions

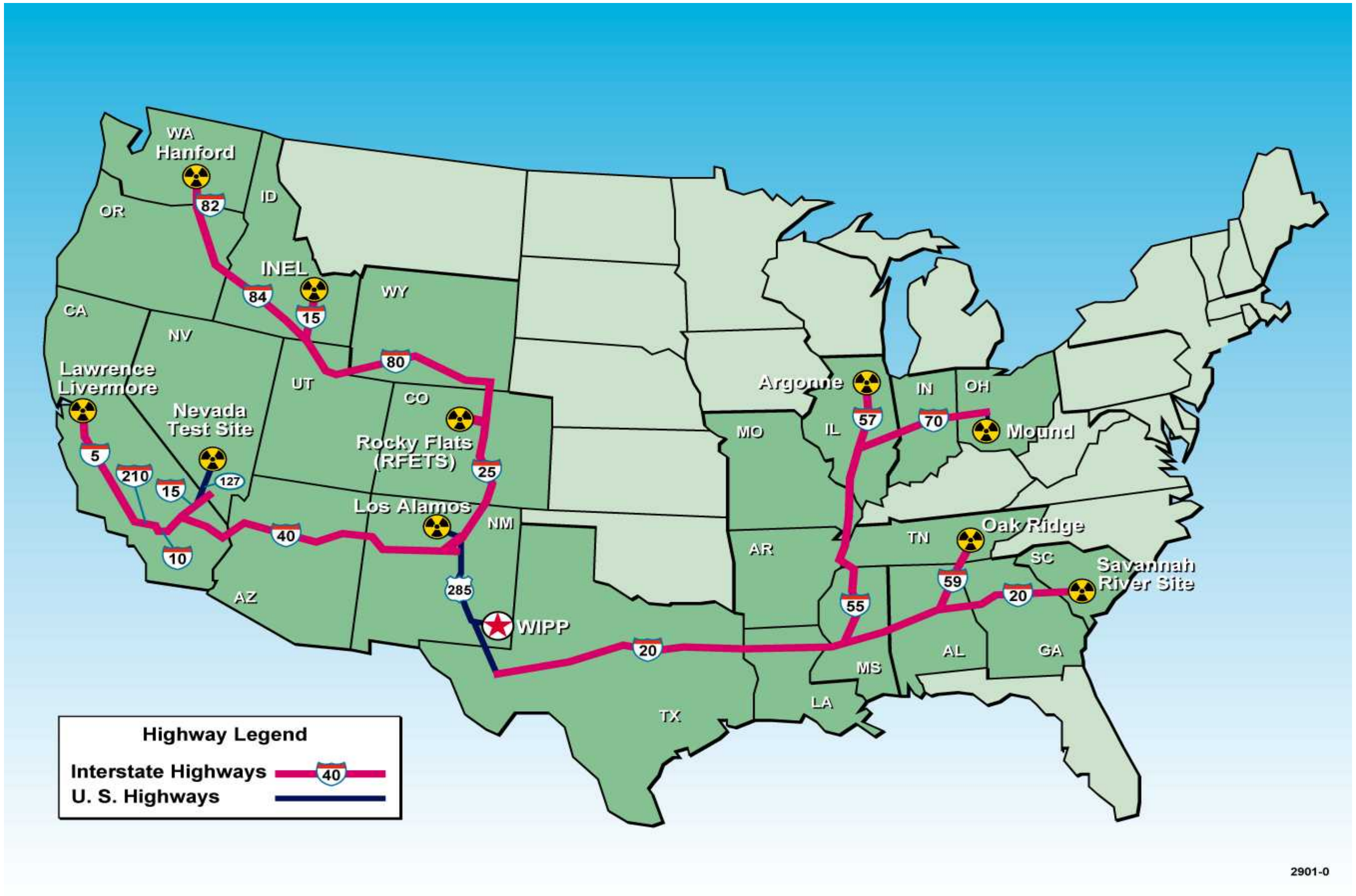
Conclusions

References

Location of the WIPP



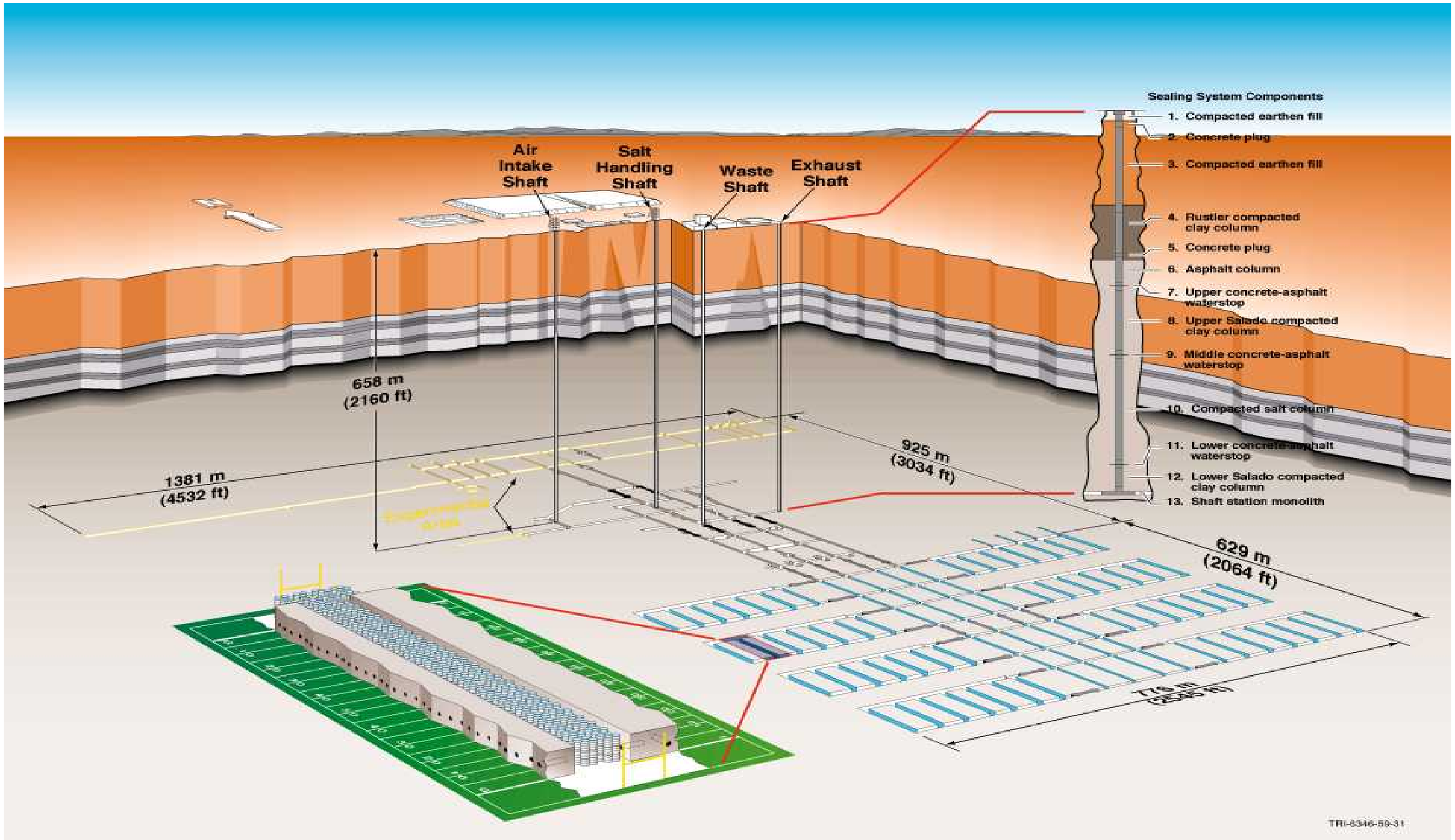
WIPP Transportation Routes



Transportation of CH TRU Waste

Aerial View of the WIPP

Cutaway View of the WIPP



TRI-6346-59-31

View along a WIPP Access Drift

Emplacement of CH TRU Waste

History of the WIPP, Emphasizing Geochemical Studies

1957: US National Academy of Sciences (NAS) Committee on Waste Management recommended deep geologic disposal, especially in salt formations, for high level waste (HLW) disposal

1963–1967: Oak Ridge National Laboratory (ORNL) carried out Project Salt Vault in a salt mine near Lyons, KS

1970: Atomic Energy Commission (AEC) tentatively selected Lyons for a HLW repository; NAS endorsed its selection

1972: AEC abandoned Lyons site

History of the WIPP (cont.)

1972–1973: ORNL and the US Geological Survey (USGS) restarted the site-selection process in the Permian Basin

1973: AEC designated Los Medanos, NM, as its "prime study area" (included current WIPP site)

1975: AEC chose Sandia National Laboratories (SNL) as WIPP scientific advisor

1976: SNL and USGS identified "prime exploration zone" (current WIPP site)

History of the WIPP (cont.)

Mid 1970s–early 1980s: Geochemical, geohydrological, geomechanical characterization of Salado-Formation (Fm.) borehole samples

Mid-to-late 1970s: Lab studies of gas generation carried out to support establishment of WIPP Waste Acceptance Criteria

1979: WIPP Authorization Act passed by Congress

History of the WIPP (cont.)

1981–1988: Excavation of four shafts, design-validation and experimental rooms; completion of surface waste-handling facilities and first waste panel

1980s: In situ geochemical, geohydrological, geomechanical characterization of the Salado at and near repository horizon

1980s: Field and modeling studies of hydro-geochemistry of Culebra Member of Rustler Fm.

History of the WIPP (cont.)

1985: 40 CFR 191, generic regulations for HLW, spent fuels, and transuranic (TRU) repositories, issued by EPA

1987: Parts of 40 CFR 191 remanded by US First Circuit Court

1988–1995: Lab and modeling studies of gas generation carried out to support WIPP Performance Assessment[1]

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1. Lab study of microbial gas generation continued until 2003

History of the WIPP (cont.)

Early-to-late 1990s: Establishment of solubility models for +III, +IV, and +V actinide oxidation states based on lab studies and Pitzer activity-coefficient model

1992: WIPP Land Withdrawal Act passed by Congress (specified EPA as WIPP regulator; mandated revisions of 40 CFR 191 and issuance of certification criteria)

1993: 40 CFR 191 reissued by EPA

History of the WIPP (cont.)

Mid 1990s: Establishment of colloidal actinide source-term models for humic, intrinsic, microbial, and mineral-fragment colloids

1996: Magnesium oxide (MgO) added to WIPP disposal-system design

1996: 40 CFR 194 (WIPP-specific certification criteria) issued by EPA

1996: DOE submitted Compliance Certification Application to EPA

History of the WIPP (cont.)

1998: EPA certified that WIPP complies with its regulations for TRU waste

1999: First contact-handled TRU waste shipped to the WIPP on March 25-26, emplaced on March 27

2004: DOE submitted first Compliance Recertification Application (CRA-2004) to EPA

Mid 2000s to present: Lab and modeling studies to support DOE request for EPA approval to reduce excess MgO being emplaced in the repository

History of the WIPP (cont.)

2006: EPA recertified WIPP

2007: First remote-handled TRU waste received and emplaced at WIPP

First Waste Arrived March 26, 1999

Overview of the WIPP

Additional information

- **Mora (1999)**
- **NRC Committee on the WIPP (1996)**

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Overview of the WIPP

Characteristics of the Salado That Will Affect Near-Field Geochemistry

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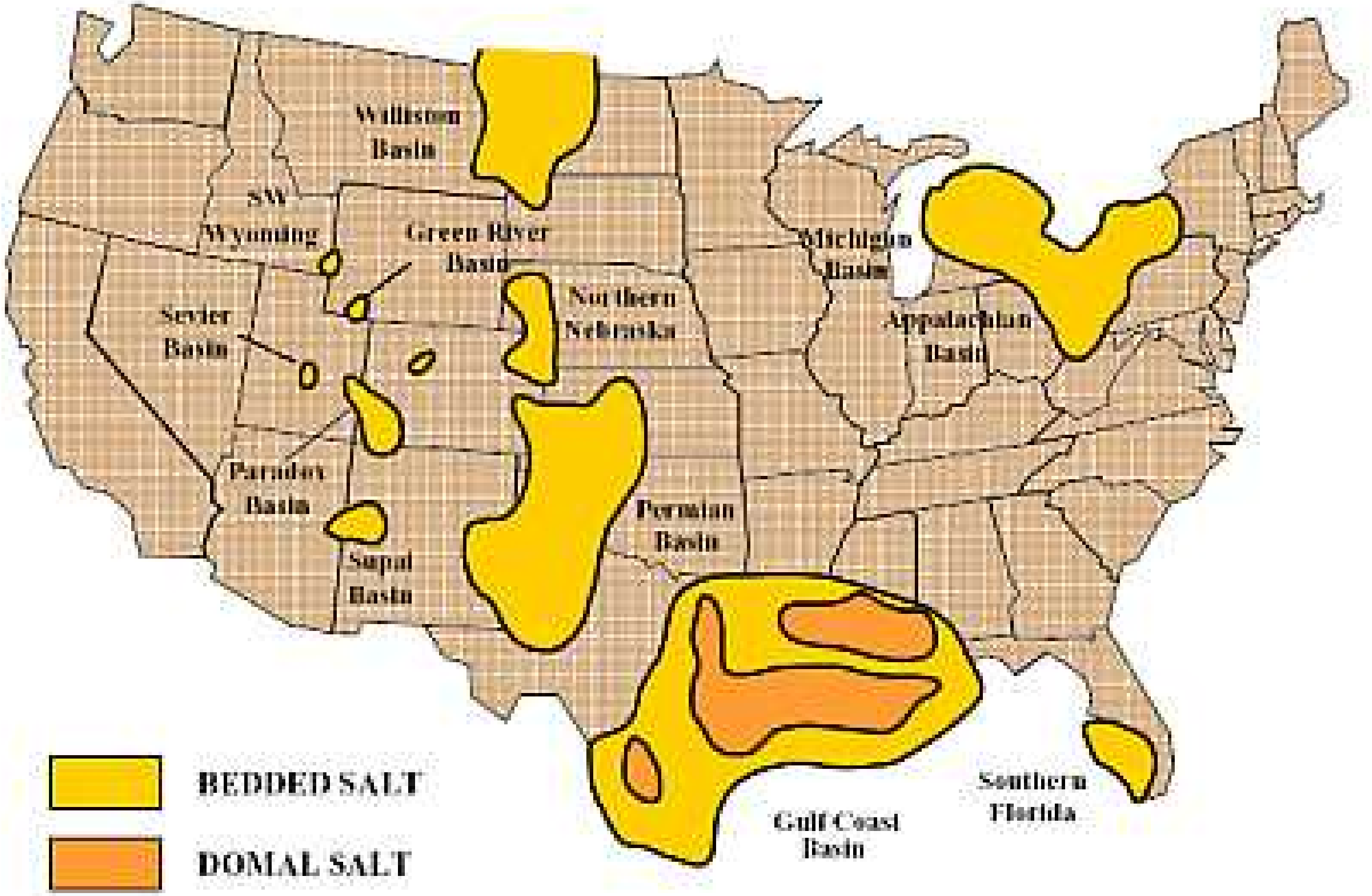
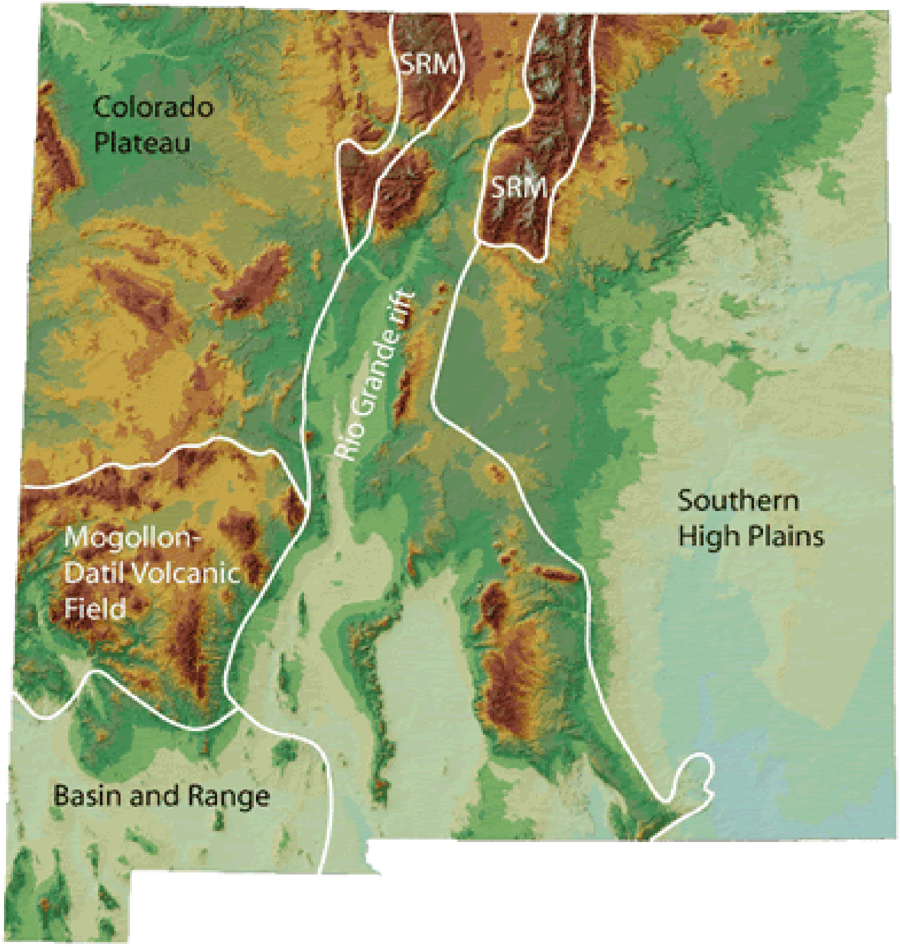
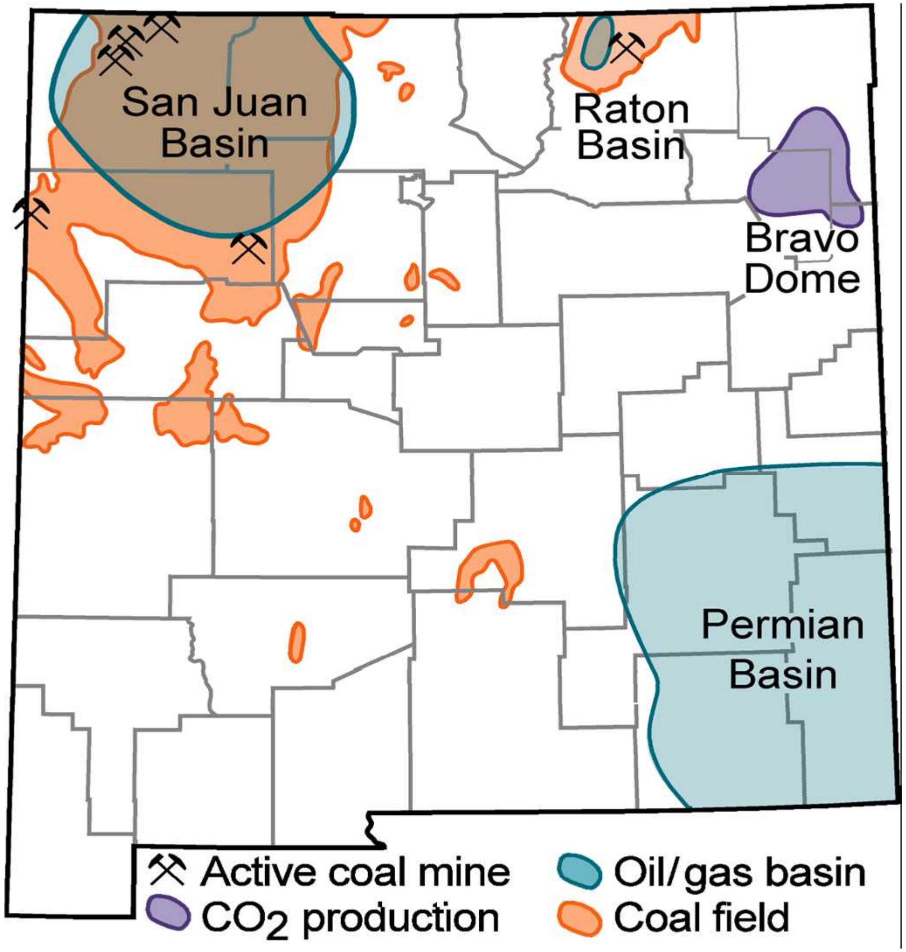
U.S. Salt Formations



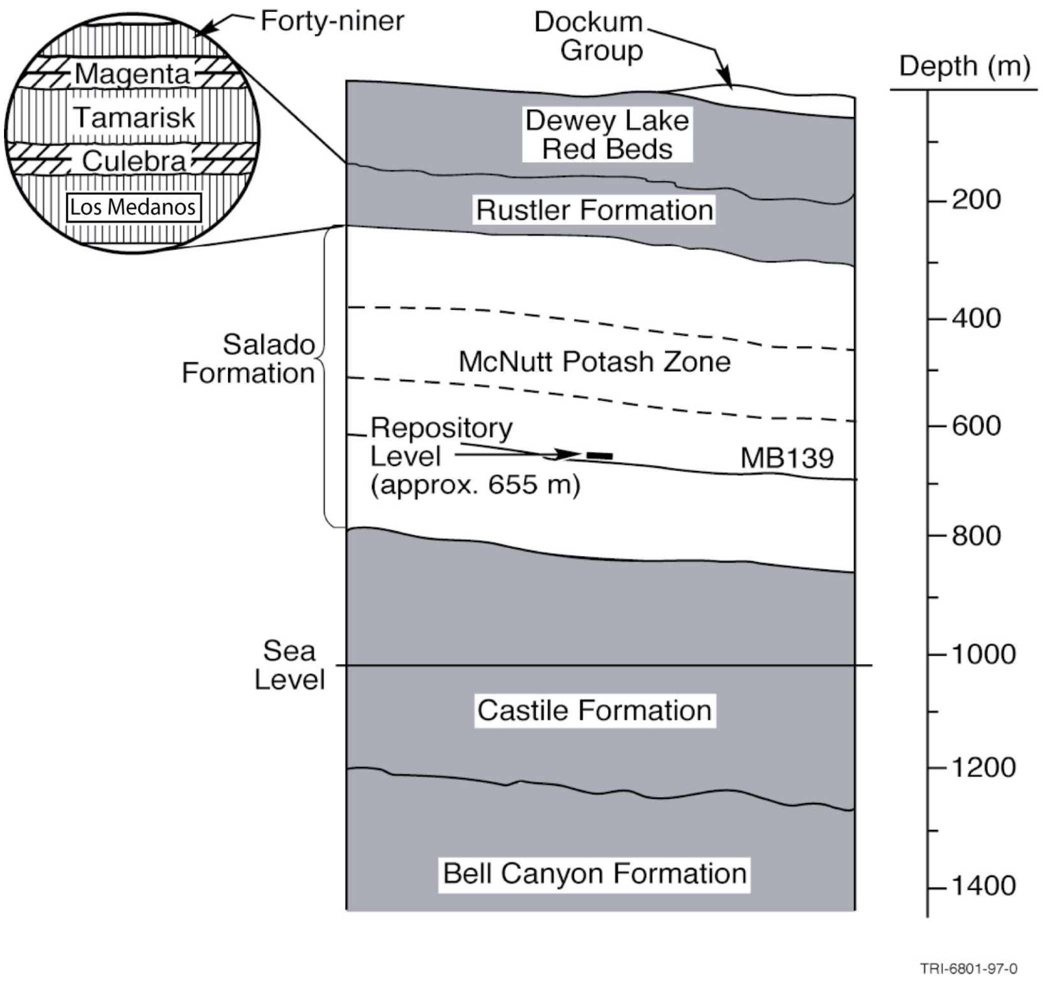
New Mexico – Topography with Geographic/Geologic Provinces



New Mexico – Energy Resources



Stratigraphic Section at the WIPP Site



Reconstruction of Pangea in Late Permian Time

Part of the Permian Basin in Late Permian Time

View North from McKittrick Canyon

The Guadalupe Mountains from the Southwest

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 ($K_2MgCa_2(SO_4)_4 \bullet 2H_2O$), and clays

Mineralogy

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

Characteristics of the Salado (cont.)

In situ conditions at the repository horizon[1]

- $P \cong 150$ 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)

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 %

Compositions of Brines Used for Near-Field Studies

	Brine A	G Seep	GWB	ERDA-6
B (mM)	20	144	155	63
Br (mM)	10	17.1	26	11
Ca (mM)	20	7.68	14	12
Cl (M)	5.35	5.10	5.51	4.8
K (mM)	770	350	458	97
Mg (M)	1.44	0.630	1.00	0.019
Na (M)	1.83	4.11	3.48	4.87
pH	6.5	6.1	NA	6.17
SO_4 (mM)	40	303	175	170

Characteristics of the Salado

Additional information

- Powers et al. (1976)
- Lowenstein (1983, 1988)
- Love et al. (1993)
- Hill (1996)

Topics to Be Addressed

Overview of the WIPP

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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

- 175,580 m^3
  - ➢ Equivalent to 844,000 208-L (55-gal) drums

TRU Waste in Context

Spent fuel

- Unreprocessed, irradiated reactor fuel

High level waste (HLW)

- Liquid or solid waste from reprocessing spent fuel

Transuranic (TRU) waste

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

Low-level waste (LLW)

- Not spent fuel, HLW, nor TRU
- Acceptable for disposal in shallow, land-disposal facilities

Characteristics of TRU Waste (cont.)

Types of TRU waste

- Contact-handled (CH) TRU waste
    - 168,500 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
- Important radioelements from the standpoint of long-term performance:
    - $\mathrm{Pu} \cong \mathrm{Am} >> \mathrm{U} > \mathrm{Th} >> \mathrm{Np}$

Cutaway View of CH TRU Waste

Characteristics of TRU Waste (cont.)

Contents of TRU waste that are especially important for near-field geochemistry

- Metallic Fe in steel waste containers, and metallic Fe and Al in the waste
  - Subject to anoxic corrosion if brine contacts these materials
- Cellulosic, plastic, and rubber (CPR) materials in the waste, plastic drum liners, and cellulosic and plastic waste-emplacement materials
  - Potential microbial substrates under inundated <u>or</u> humid conditions
- NO_3^- and SO_4^{2-} in process sludges
  - Potential microbial electron acceptors (oxidants)
- CaO in portland cements used to dewater process sludges
  - Could affect brine pH

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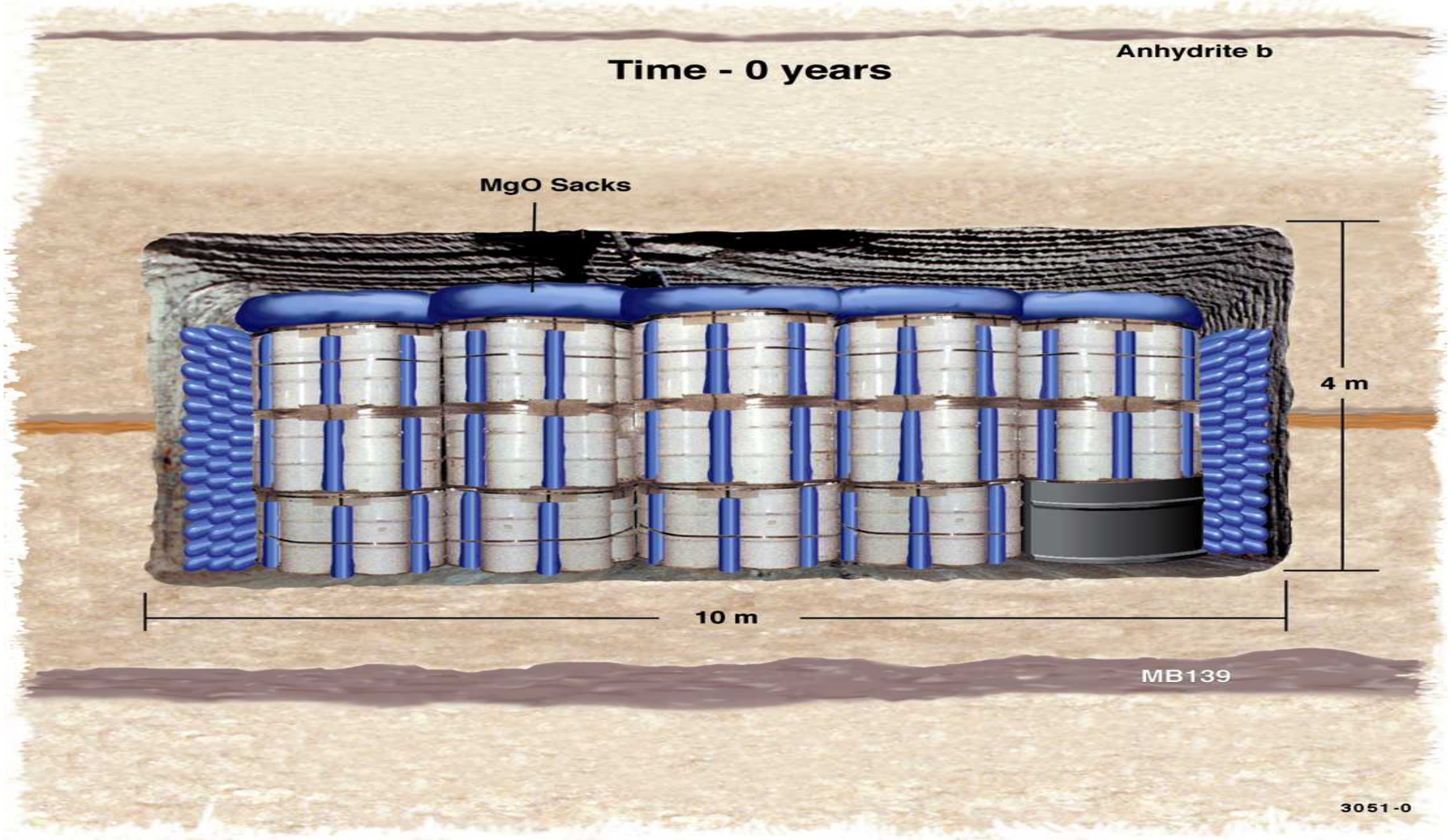
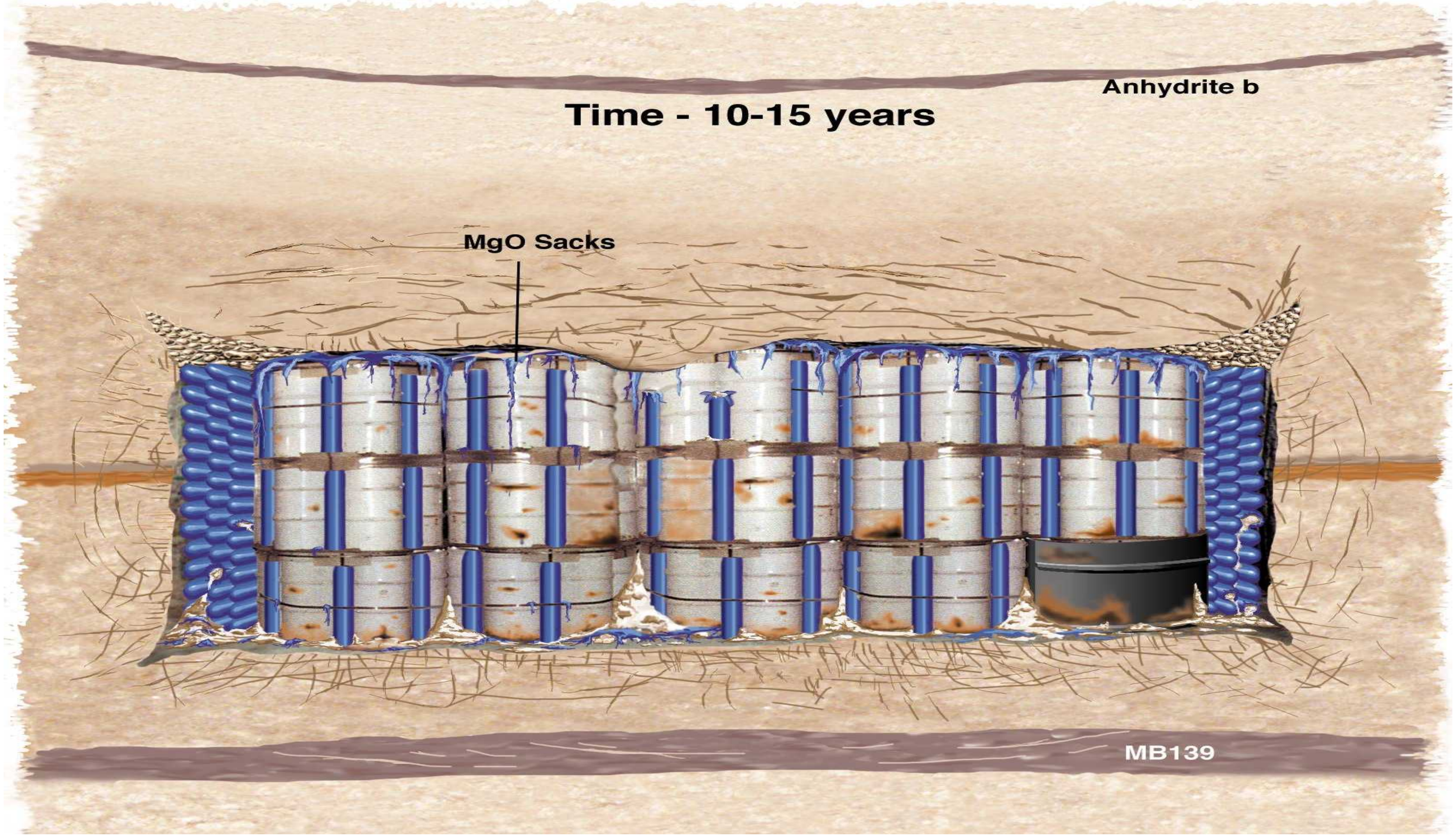
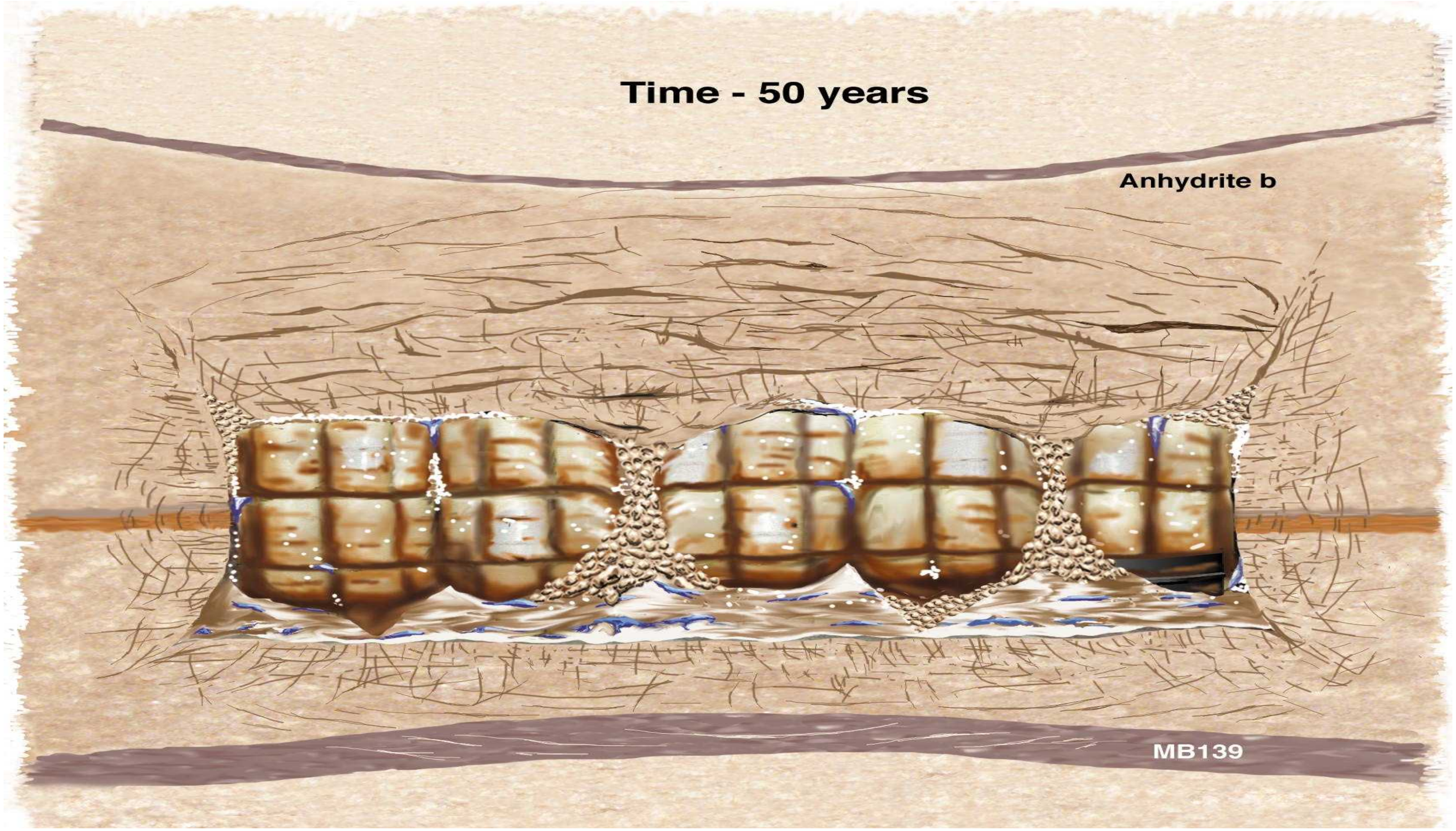
Evolution of the Near Field



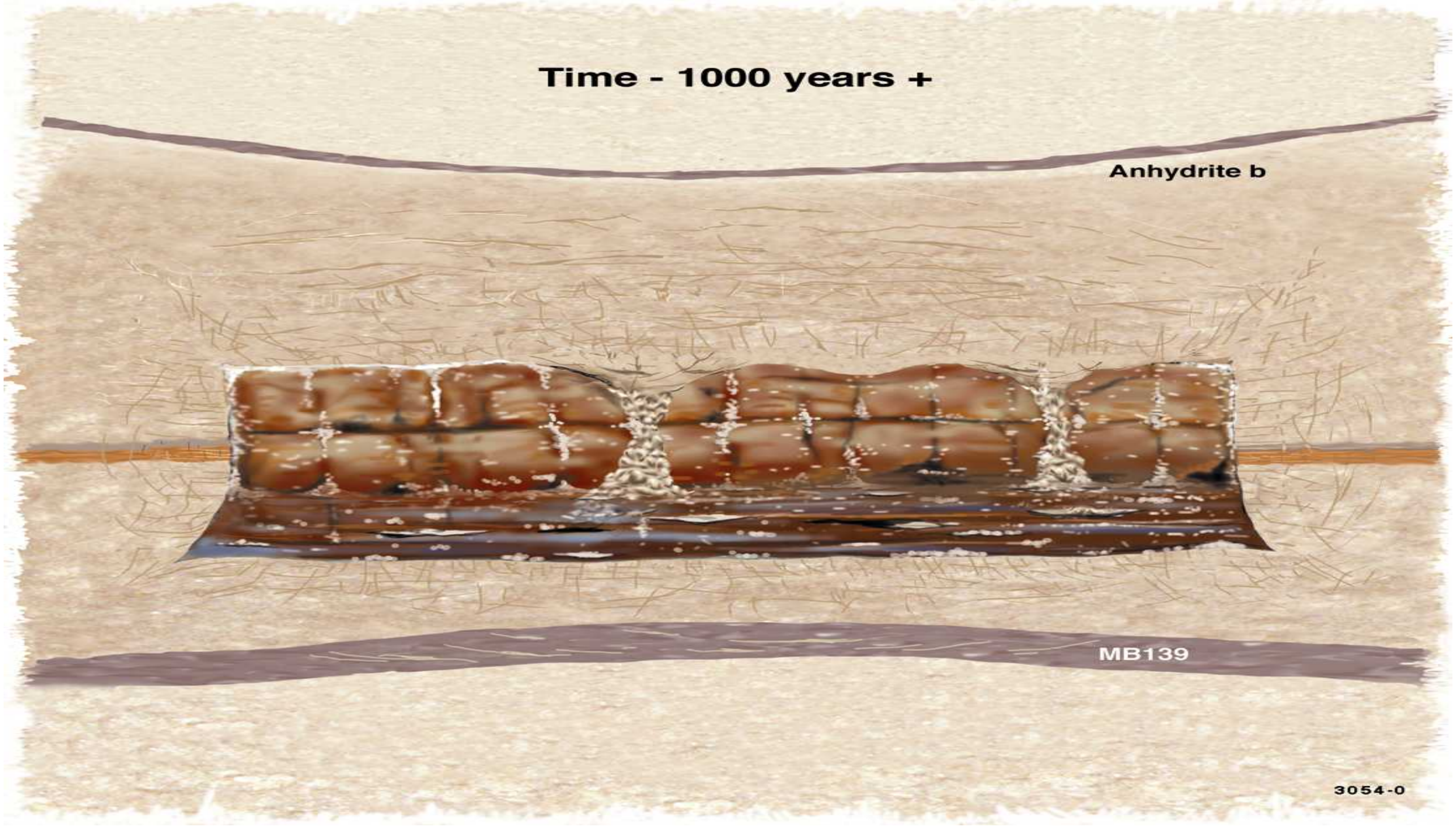
Evolution of the Near-Field (cont.)



Evolution of the Near-Field (cont.)



Evolution of the Near Field (cont.)



Gas Generation

Corrosion of Fe- and Al-base metals

- Will produce H_2; could consume H_2O initially and release it later

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

- Could produce CH_4, CO_2, H_2S, N_2; effect on H_2O budget is unclear

Alpha radiolysis of H_2O in brine, and of CPR materials

- Will produce H_2, O_2, other gases; and consume H_2O

Relative importance of these processes:

- Corrosion $\cong$ microbial activity >> radiolysis

Gas Generation (cont.)

Effects of gas generation on other conditions and processes in the WIPP

- Will affect brine inflow and outflow
- Will affect conditions that control the actinide source term
  - Eh
  - f_{CO_2}
  - pH
- Will impede 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
- Will drive spallings releases

Anoxic Corrosion

Anoxic corrosion of steels, other Fe-base metals, and Al-base metals expected in the WIPP under inundated, but not humid, conditions

- **Could produce significant quantities of H_2**
- **Could consume significant quantities of H_2O if $Fe(OH)_2 \cdot xH_2O$ forms**
- **Would release H_2O if $Fe(OH)_2 \cdot xH_2O$ carbonates to form $FeCO_3$, or sulfidizes to form FeS**
  - **Significant quantities of CO_2 and H_2S cold be produced by microbial consumption of CPR materials**
- **Anoxic corrosion could create strongly reducing conditions**

Anoxic Corrosion (cont.)

Oxic corrosion is corrosion of metals using aqueous or gaseous, free molecular O_2

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

Anoxic corrosion is corrosion of metals without free molecular O_2

- $Fe + H_2O \rightleftharpoons Fe(OH)_2 + H_2$

Anoxic Corrosion (cont.)

Extensive laboratory studies carried out by the WIPP Project

- Mid-to-late 1970s
- Late 1980s to mid 1990s

Anoxic corrosion incorporated in WIPP PA

- Based on results of short- and long-term laboratory experiments by Telander and Westerman (1993, 1997) at Pacific Northwest National Laboratory (PNNL)

Controversial issue!

Anoxic-Corrosion Reactions

Experimentally observed anoxic-corrosion reactions[1]

- $Fe + (x + 2)H_2O \rightleftharpoons Fe(OH)_2 \cdot xH_2O + H_2$
- $Fe + H_2O + CO_2 \rightleftharpoons FeCO_3 + H_2$
- $Fe + H_2S \rightleftharpoons FeS + H_2$
- Observed under inundated, but not humid, conditions[1]

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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1. Telander and Westerman (1993, 1997)

Microbial Activity

Microbial consumption of CPR materials possible in the WIPP under humid or inundated conditions

- Could produce significant quantities of CH_4, CO_2, H_2S, and N_2
- Could create reducing conditions
- Effect on H_2O budget unclear

Extensive laboratory studies carried out by the WIPP Project

- Mid-to-late 1970s
- Late 1980s to early 2000s

Microbial Activity

Microbial gas generation incorporated in WIPP PA

- Initially based on results of long-term laboratory experiments by Francis and Gillow (1994) and Francis et al. (1997) at Brookhaven National Laboratory (BNL)
- Currently based on longer-term results from BNL

Very controversial issue!

Requirements for Microbial Activity

Halophilic or halotolerant microbes present when repository filled and sealed

Halophilic or halotolerant microbes survive for a significant fraction of the 10,000-year regulatory period

Sufficient H_2O present in brine in the repository and available to microbes

Sufficient electron acceptors present and available

Sufficient nutrients present and available

Possible Sources of Microbes

WIPP Site and vicinity

- Abundant halophiles present
- Salt lakes in Nash Draw
  - ➢ Transport to the excavated areas via wind, the Air Intake Shaft, and the mine ventilation system
- Soils near the WIPP Site
  - ➢ Same transport mechanisms
- Salado Fm. (Permian microbes)?
  - ➢ Viable Permian microbes reported by Vreeland et al. (2000). See also Parkes (2000)
  - ➢ Permian microbes still controversial (e.g., Hazen and Roedder, 2001; Vreeland et al., 2001)
  - ➢ Permian microbes (if present) not an issue for PA

Possible Sources of Microbes (cont.)

TRU waste

- Probably nonhalophilic, but could include halotolerant strains
- Nonhalophilic and nonhalotolerant strains could produce gas under humid conditions prior to container rupture and contact of waste by brine
- Could produce gas thereafter if halophilic or halotolerant strains are present, or if halotolerant strains develop

Can We Rule Out Microbial Activity in the WIPP?

Expected conditions

- Pressure
  - $P_{\text{in situ}} \cong 150$ atm (lithostatic)
  - Measured pore pressures close to lithostatic
  - Excavation decreases P to ~1 atm
  - Gas generation will repressurize the WIPP to ~150 atm
  - P clearly not a problem for microbes
- Temperature
  - $T_{\text{in situ}} = 28$ ºC
  - RH TRU waste will increase T by a few ºC
  - T also not a problem for microbes

Can We Rule Out Microbial Activity (cont.)?

Expected conditions (cont.)

- Water content
  - Viable microbes currently present in the WIPP despite absence of brine and low RH
  - $MgO-Mg(OH)_2$ hydration reaction could buffer f_{H2O} at ~10^{-6} atm
  - MgO hydration could prevent microbial activity prior to first human intrusion
  - f_{H2O} in WIPP brines will be ~$10^{-0.135}$ to $10^{-0.126}$ atm (RH = 73.2 to 75.8%) after complete hydration of MgO
  - H_2O content would be high enough for microbial activity after first human intrusion, unless MgO hydration and other processes redesiccate the repository

Can We Rule Out Microbial Activity (cont.)?

Expected conditions (cont.)

- Salinity
  - Ionic strength = 6.80 to 7.66 m after equilibration with MgO
  - Salinity not a problem
- pH
  - In situ pH of WIPP brines = ~6.1 to 6.5
  - Equilibration with the MgO engineered barrier will increase pH to about ~9
  - pH not a problem

Can We Rule Out Microbial Activity (cont.)?

Expected conditions (cont.)

- Radiation
  - ➢ α doses from CH TRU waste, and α and γ doses from RH TRU waste << than those from HLW and spent fuel
  - ➢ Direct damage to cellular material and Indirect damage by oxidizing species from brine radiolysis could inhibit - but will not prevent - microbial activity
  - ➢ Radiation from TRU waste not a problem

Can We Rule Out Microbial Activity (cont.)?

Expected conditions (cont.)

- **Possible toxicity of MgO**
  - **Numerous papers in the literature on inhibitory and/or biocidal effects of MgO**
  - **MgO could inhibit microbial activity in the WIPP, but would probably not prevent it**

Can We Rule Out Microbial Activity (cont.)?

Sterilization

- Autoclaving
  - Main technique used by microbiologists
  - 121ºC, 18 psi, 20 to 30 min in steam autoclave
  - Feasible (but expensive) to autoclave TRU waste containers prior to emplacement
  - Recontamination likely during or after emplacement
  - Sterilization of rooms and drifts unfeasible
- Chemical sterilization
  - Biocides such as formalin and Na azide very effective for small samples (up to a few grams), but unfeasible for TRU waste

Can We Rule Out Microbial Activity (cont.)?

Sterilization (cont.)

- Filtration
  - Used by microbiologists (thermolabile liquids), backpackers, and (some) travelers in less-developed countries
  - 0.25 μ bacteriological filter
  - Unfeasible for solids
- Radiation
  - γ, UV, etc.
  - Feasible (but expensive) to irradiate TRU waste containers prior to emplacement
  - Recontamination likely during or after emplacement
  - Sterilization of rooms and drifts unfeasible

Probability of Significant Microbial Activity

Significant microbial activity possible, but by no means certain

- Probability implemented in the 1996 CCA PA, 1997 PAVT, and CRA-2004 PA (certified by the EPA in 1998)

Microbial activity certain, but may not be significant because of use of a sampled "effectiveness factor" (and lower gas-production rates) in PA

- Probability of microbial gas generation specified by the EPA for the CRA-2004 PABC

Microbial Activity (cont.)

Sequential use of electron acceptors (oxidants) by microbes

- Communities of microbes use the best electron acceptor that is available (i.e., the electron acceptor that yields the most energy per mole of organic C consumed)
- After depletion of the best available electron acceptor, other microbes begin to consume the next best
- Sequential use of electron acceptors observed in many natural and anthropogenically influenced environments
  - Soils
  - Sediments (lacustrine, riverine, estuarine, and oceanic)
  - Landfills

Microbial Activity (cont.)

Sequential use of electron acceptors (oxidants) by microbes

- O_2 (referred to as aerobic respiration)
- NO_3^- (denitrification)
- Mn(IV) oxides and hydroxides (Mn(IV) reduction)
- Fe(III) oxides and hydroxides (Fe(III) reduction)
- SO_4^{2-} (SO_4^{2-} reduction)
- CO_2 (methanogenesis)

Aerobic respiration, denitrification, Mn(IV) reduction, Fe(III) reduction, SO_4^{2-} reduction, and methanogenesis are referred to as microbial respiratory pathways

Microbial Activity (cont.)

Potentially significant and insignificant microbial respiratory pathways in the WIPP[1]

- Aerobic respiration
  - Little O_2 expected relative to the quantity of CPR materials
- Denitrification
  - NO_3^- present in process sludges
- Mn(IV) reduction
  - Little or no Mn(IV) expected
- Fe(III) reduction
  - Little or no Fe(III) expected

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1. Potentially significant respiratory pathways in green font; insignificant respiratory pathways in red font

Microbial Activity (cont.)

Potentially significant and insignificant microbial respiratory pathways in the WIPP[1]

- SO_4^{2-} reduction
  - SO_4^{2-} present in process sludges, Salado and Castile brines, and Salado minerals
- Methanogenesis
  - CO_2 could be produced by denitrification and SO_4^{2-} reduction
  - Methanogenesis could occur after NO_3^- and SO_4^{2-} are consumed

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1. Potentially significant respiratory pathways in green font; insignificant respiratory pathways in red font

Microbial Activity (cont.)

Reactions for potentially significant microbial respiratory pathways

- Denitrification
  - $C_6H_{10}O_5 + 4.8H^+ + 4.8NO_3^- \rightarrow 7.4H_2O + 6CO_2 + 2.4N_2$
  - CO_2 yield = 1 mol per mol of organic C consumed
- SO_4^{2-} reduction
  - $C_6H_{10}O_5 + 6H^+ + 3SO_4^{2-} \rightarrow 5H_2O + 6CO_2 + 3H_2S$
  - CO_2 yield = 1 mol per mol of organic C consumed
- Methanogenesis
  - $C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2$
  - CO_2 yield = 0.5 mol per mol of C consumed

Magnesium Oxide (MgO)

MgO added to the WIPP disposal system by the DOE in 1996 to satisfy the EPA's requirement for "multiple natural and engineered barriers"

- **Other engineered barriers proposed by the DOE (borehole plugs, panel seals, shaft seals)**

MgO recognized by the EPA as the only engineered barrier as part of its 1998 certification of the WIPP

Extensive laboratory studies carried out by the WIPP Project

- **Mid 1990s to present**

MgO (cont.)

In WIPP-speak, “MgO” refers to the bulk, granular material being emplaced in the repository to serve as the engineered barrier

MgO comprises mostly periclase (pure, crystalline MgO – the main constituent of the engineered barrier) and a small amount of lime (pure, crystalline CaO)

Periclase and lime will consume CO_2 and H_2O and form various carbonated and/or hydrated solids

Regulatory Role of the MgO Engineered Barrier

One of the EPA's assurance requirements specifies that the WIPP disposal system must include "multiple natural and engineered barriers"

Regulatory Role of the MgO Engineered Barrier (cont.)

The EPA's definition of an engineered barrier:

“any material or structure that prevents or substantially delays movement of water or radionuclides toward the accessible environment. For example, a barrier may be a geologic structure, a canister, a waste form …, or a material placed over and around waste provided that the material or structure substantially delays movement of water or radionuclides”

Geochemical Role of MgO

Functions as the WIPP engineered barrier by consuming essentially all CO_2 that could be produced by microbial activity, thereby decreasing actinide solubilities

- Will prevent acidification of brine that would result if microbes consumed significant quantities of cellulosic, plastic, and rubber materials during the 10,000-year regulatory period
- Will limit the extent of complexation of actinide elements by CO_3^{2-}
- Will buffer pH at ~9

Consumption of significant quantities of H_2O by MgO (and other materials) could also affect long-term performance

Geochemical Role of MgO (cont.)

Hydrated phases

- Brucite: $Mg(OH)_2$
- Mg-Cl-OH-H_2O-bearing phase: $Mg_3(OH)_5Cl \bullet 4H_2O$ (crystalline Sorel cement)
- Mg-Cl-OH-H_2O phase (amorphous Sorel cement)
- Portlandite: $Ca(OH)_2$

Carbonated phases

- Magnesite: $MgCO_3$
- Hydromagnesite: $Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$ or $Mg_4(CO_3)_3(OH)_2 \bullet 3H_2O$
- Nesquehonite: $MgCO_3 \bullet 3H_2O$
- Calcite: $CaCO_3$

Geochemical Role of MgO (cont.)

Reaction that will buffer f_{CO_2} initially

- $5Mg(OH)_2 + 4CO_2$(aq or gas) $\rightleftharpoons$ $Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$
  - 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 carbonations reaction be used to calculate f_{CO_2} for actinide solubility calculations

Long-term f_{CO_2} buffer reaction

- $Mg(OH)_2 + CO_2$(aq or gas) $\rightleftharpoons$ $MgCO_3 + H_2O$(aq or gas)
  - Magnesite is stable with respect to hydromagnesite (5424), and is present in the Salado

Reaction that will buffer pH

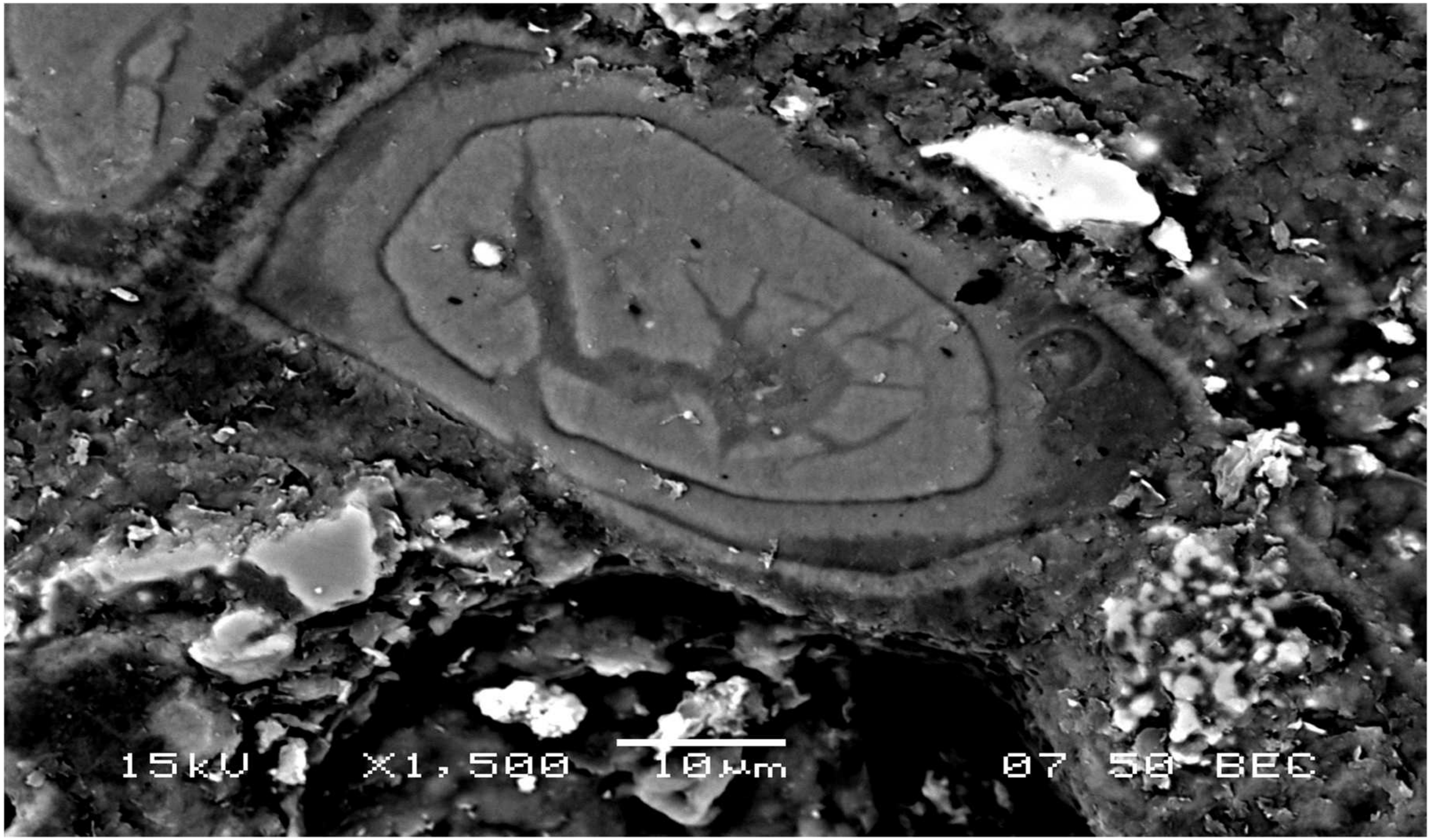
- $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

Laboratory Studies of MgO

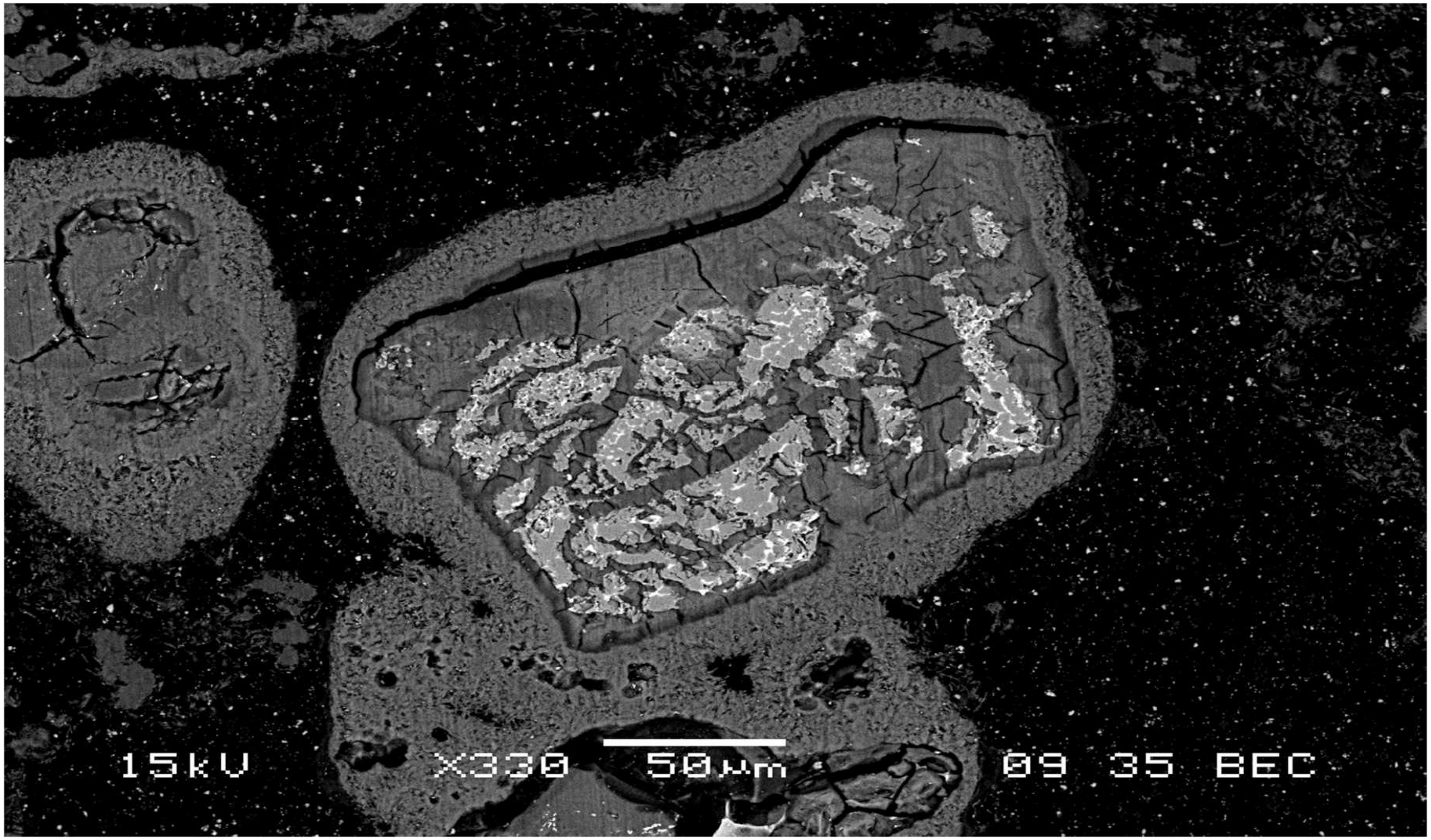
Studies of MgO under way or completed at Sandia

- Characterization of MgO being emplaced in the repository
- MgO hydration
  - Humid
  - Inundated
- MgO carbonation
  - Humid
  - Inundated
- Lithification and its possible effects on hydration
  - Inundated only
- Possible formation of Mg-bearing colloids

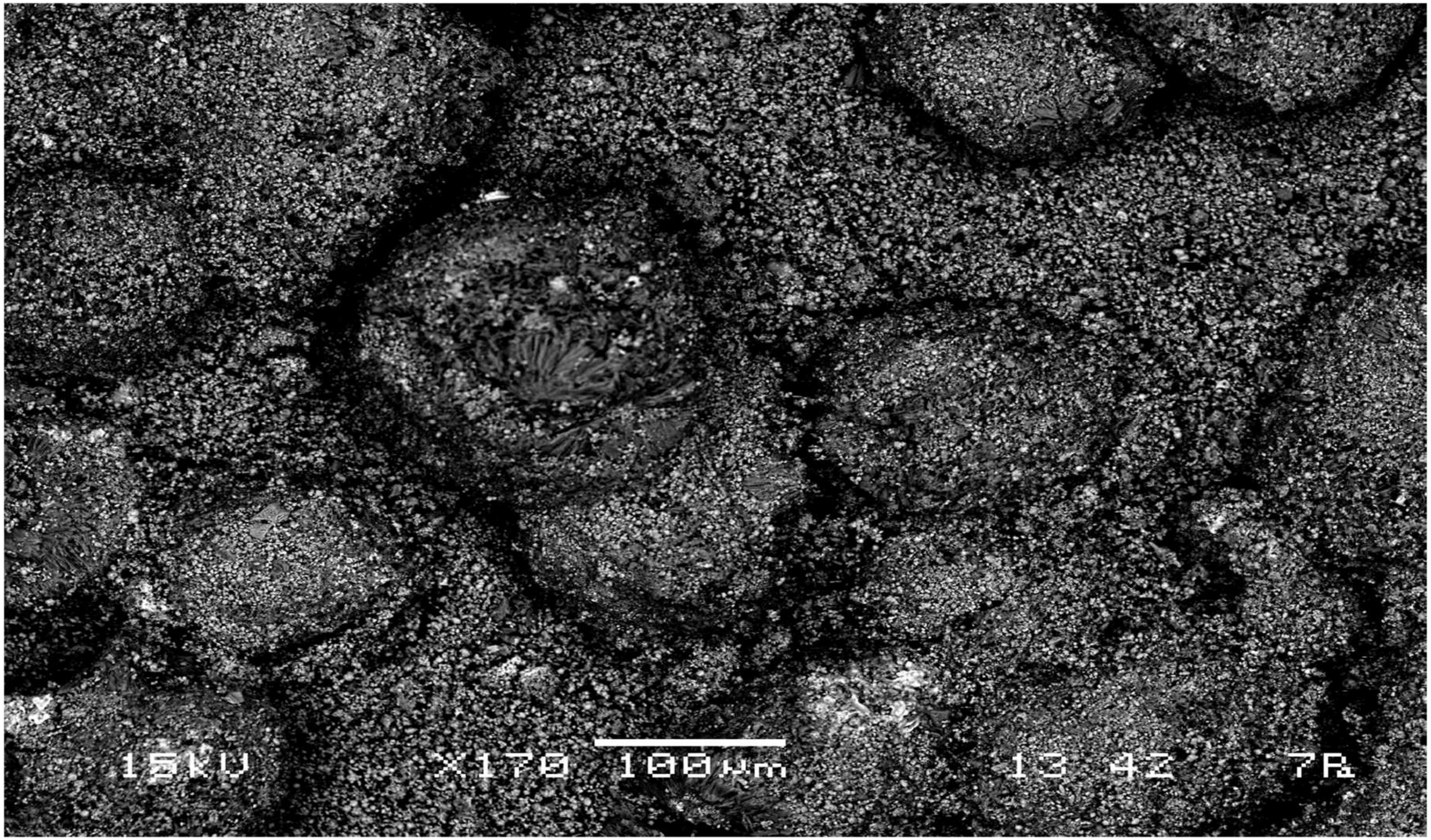
Hydration in ERDA-6: Periclase → Brucite



Hydration in GWB: Periclase → Mg-Cl-OH-H_2O → Brucite



Carbonation in ERDA-6: Brucite → Hydromagnesite(5424)



Chemical Conditions Conceptual Model

Repository assumed to be homogeneous

Equilibrium assumed to be instantaneous and reversible for some chemical reactions

- Brine-rock reactions
- MgO hydration and carbonation reactions
- Sulfidization of steels

Other reactions proceed at experimentally measured rates

- Anoxic corrosion of steels
- Microbial consumption of CPR materials

MgO will buffer (control) f_{CO_2} and pH

Expected Near-Field Processes

Additional information

- Francis and Gillow (1994)
- Francis et al. (1997)
- Hazen and Roedder (2001)
- Parkes (2000)
- Powers et al. (2001)
- Rothschild and Mancinelli (2001)
- Telander and Westerman (1993, 1997)
- Vreeland et al. (2000)

Topics to Be Addressed

Overview of the WIPP

Characteristics of the Salado

Characteristics of TRU Waste

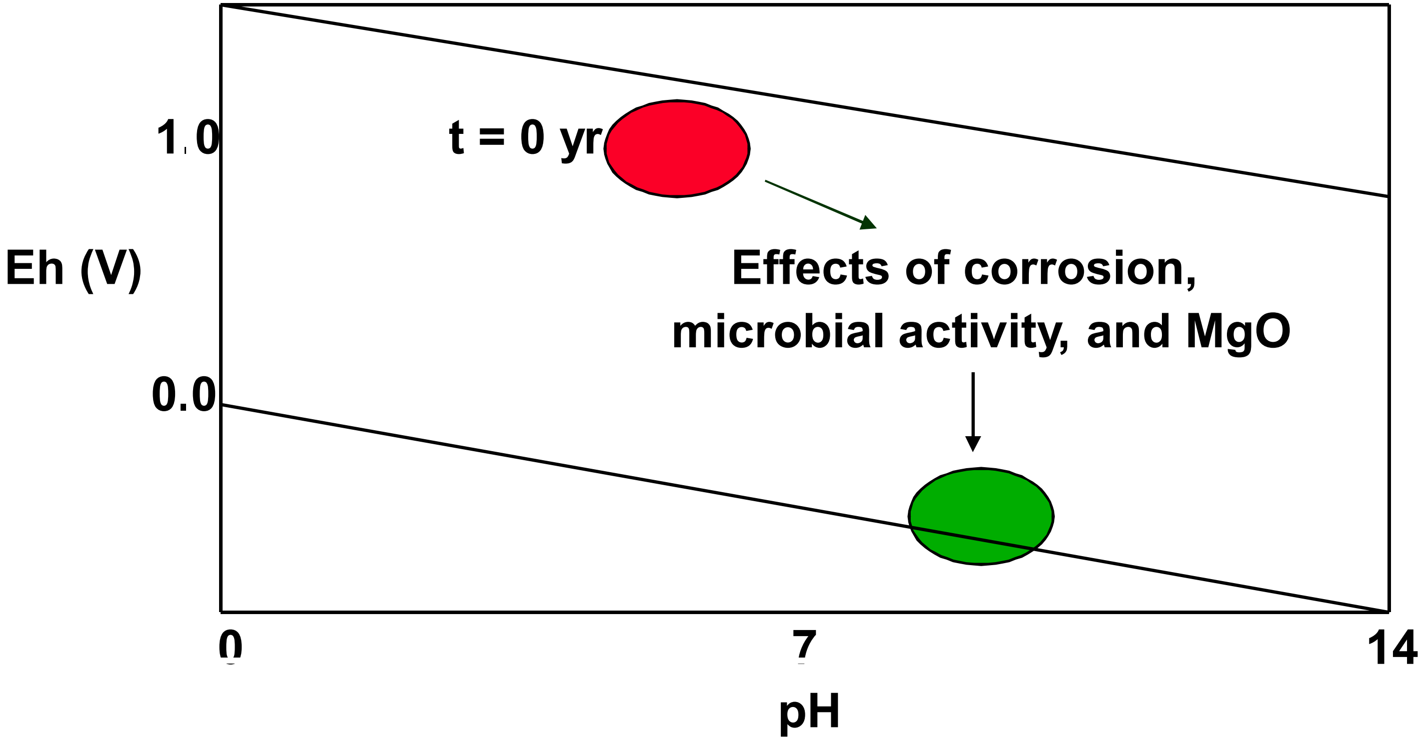
Near-Field Processes

Near-Field Geochemical Conditions Expected in the WIPP

Conclusions

References

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



t = 0 yr

Effects of corrosion, microbial activity, and MgO

Expected Near-Field Conditions

Strongly reducing Eh

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

$f_{CO_2} = 10^{-5.48}$ (short-term) to $10^{-6.15}$ atm (long-term)

pH $\cong$ 9

Relative humidity $\cong$ 73 to 75% in gaseous phase ($a_{H_2O} \cong$ 0.73 to 0.75 in brines)

Effects of Near-Field Conditions

Strongly reducing conditions important for redox speciation of actinide elements

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

Effects of CO_2-Bearing Solids on Log f_{CO_2} (atm) and pH[A, B]

	Calcite	Mag.	Hydromag. (5.4.2.4)	Hydromag. (4.3.2.3)	Nesq.
Log f_{CO_2}, GWB	-5.48	-6.92	-5.50	-5.39	-3.84
Log f_{CO_2}, ERDA-6	-6.15	-6.91	-5.50	-5.39	-3.86
pH, GWB	8.69	8.69	8.69	8.69	8.69
pH, ERDA-6	8.99	9.02	9.02	9.02	9.00

A. Results from the FMT calculations for the CRA-2004 PA

B. Results include organic ligands

Actinide Solubilities Predicted for the CRA-2004 PABC^{A} (M)

	GWB	ERDA-6
An(III)	3.87×10^{-7}	2.88×10^{-7}
An(IV)	5.64×10^{-8}	6.79×10^{-8}
An(V)	3.55×10^{-7}	8.24×10^{-7}
An(VI)	$1.00 \times 10^{-3,\ B}$	$1.00 \times 10^{-3,\ B}$

A. Calculations included 1.06×10^{-2} M acetate, 8.06×10^{-4} M citrate, 8.14×10^{-6} M EDTA, and 4.55×10^{-2} M oxalate.

B. Concentration specified by EPA

Topics to Be Addressed

Overview of the WIPP

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Near-Field Conditions

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References

Geochemical Considerations in Repository Site Selection

Geochemical considerations are one of several important criteria for radioactive-waste-repository site selection

- Stability
  - Geologic
  - Climatic
  - Hydrologic
- Low population density and low potential for future population growth
- Low probability of exploration for and development of natural resources
- Transport properties of host rock and over- and underlying formations
- Geochemical characteristics

Geochemical Considerations in Repository Site Selection

No site satisfies all of the criteria

- There is no perfect site!

Geochemical characteristics

- Redox
  - Reducing conditions strongly preferred
- Groundwater composition
  - Low-ionic-strength (low-I) groundwaters are easier to model than high-I groundwaters
- Sorptive ability and capacity of host-rock minerals

Topics to Be Addressed

Overview of the WIPP

Characteristics of the Salado

Characteristics of TRU Waste

Near-Field Processes

Near-Field Conditions

Conclusions

References

Sandia National Laboratories

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