SAND2010-5757P

Overview of WIPP Geochemical Modeling[1]

Presentation at
The ABC-SALT Workshop
September 15 and 16, 2010

L. H. Brush and Y.-L. Xiong
Carlsbad Programs Group
Sandia National Laboratories[2]
Carlsbad, NM 88220

1. This research is funded by WIPP programs administered by the U.S. Department of Energy (DOE).
2. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

NNSA National Nuclear Security Administration

Sandia National Laboratories

Topics to Be Addressed

Characteristics of the Salado Fm. and WIPP Waste

Conceptual Models of WIPP Chemistry

Codes Used to Implement Conceptual Models

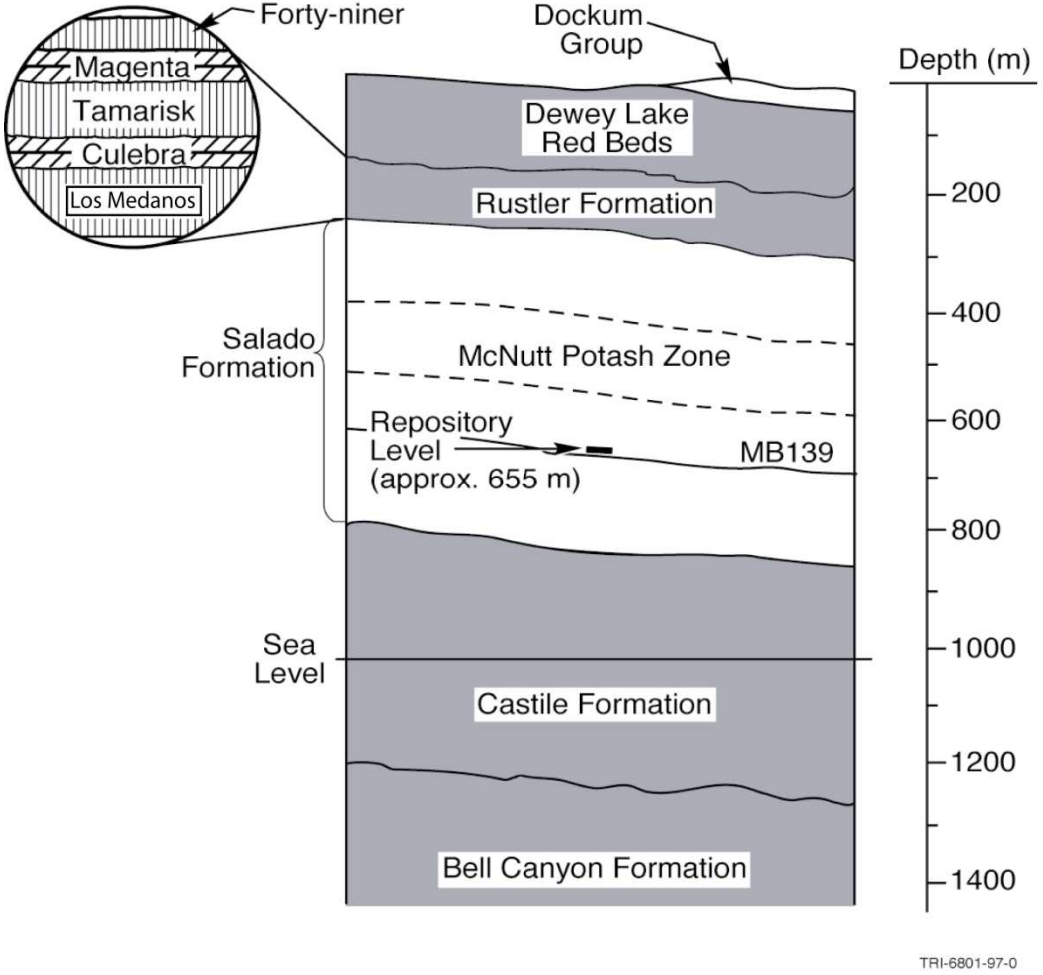
Predictions of Near-Field Chemical Conditions and Actinide Solubilities

Additional Model Development

References

Sandia National Laboratories

Stratigraphic Section at the WIPP Site



Sandia National Laboratories

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 ($CaSO_4 \cdot 2H_2O$), magnesite ($MgCO_3$), polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$), and clays

Mineralogy

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

Sandia National Laboratories

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

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 %

---

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

Sandia National Laboratories

Characteristic of WIPP Waste

Sandia National Laboratories

Topics to Be Addressed

Characteristics of the Salado Fm. and WIPP Waste

Conceptual Models of WIPP Chemistry

Codes Used to Implement Conceptual Models

Predictions of Near-Field Chemical Conditions and Actinide Solubilities

Additional Model Development

References

Sandia National Laboratories

Conceptual Models of WIPP Chemistry

Near-field conceptual models (Salado Formation)

- Gas generation
- Chemical conditions
- Dissolved actinide source term
- Colloidal actinide source term
- Actinide transport in the Salado

Far-field conceptual models (Culebra Member of the Rustler Formation)

- Dissolved actinide transport
- Colloidal actinide transport

A total of 24-EPA-certified conceptual models used for PA

Sandia National Laboratories

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
- Homogeneous chemical conditions assumed

Standard brines

- Generic Weep Brine (GWB) simulates intergranular Salado brines (Krumhansl et al., 1991; Snider, 2003)
- U.S. Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) simulates Castile brines (Popielak et al., 1983)
- Use of these two brines is “adequate” for laboratory and modeling studies
  - Use of mixtures not required (end-member brines will bracket effects of mixing)

Sandia National Laboratories

WIPP Near-Field Conceptual Models (cont.)

Solids included in modeling

- Halite and anhydrite
  - The two most important Salado minerals
- Brucite ($Mg(OH)_2$), phase 3 ($Mg_2(OH)_3Cl{\cdot}4H_2O$) and/or phase 5 ($Mg_3(OH)_5Cl{\cdot}4H_2O$), and the "5424" polymorph of hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$)
  - 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

Sandia National Laboratories

WIPP Near-Field Conceptual Models (cont.)

Solids excluded from modeling

- Gypsum, magnesite, polyhalite, and clays
  - Gypsum, magnesite, polyhalite, and clays are less important Salado minerals
  - Magnesite, the thermodynamically stable MgO carbonation product, excluded by the EPA from compliance-related calculations
  - The EPA has specified that hydromagnesite (5424) be used instead of magnesite because it is unclear whether magnesite will replace hydromagnesite during the 10,000-yr WIPP regulatory period

WIPP Near-Field Conceptual Models (cont.)

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

- $5Mg(OH)_2 + 4CO_2(aq \text{ or } gas) \rightleftharpoons Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
  - 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

Possible long-term f_{CO_2} buffer reaction

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

Reaction that will increase pH to basic values

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

Sandia National Laboratories

Topics to Be Addressed

Characteristics of the Salado Fm. and WIPP Waste

Conceptual Models of WIPP Chemistry

Codes Used to Implement Conceptual Models

Predictions of Near-Field Chemical Conditions and Actinide Solubilities

Additional Model Development

References

Sandia National Laboratories

Codes Used to Implement Conceptual Models

Implementation in process modeling

- Speciation-and-solubility component of Fracture-Matrix Transport (FMT) used to predict near-field chemical conditions and actinide solubilities
- Essentially no reaction-path functionality
- Speciation-and-solubility component of the FMT software package QA'ed for use by the WIPP by Babb and Nowak (1995, 1997 and addenda) and Wang (1998)

Codes Used to Implement Conceptual Models (cont.)

Implementation in process modeling

- EQ3/6 used to predict near-field chemical conditions after instantaneous reactions with solids
  - Compositions of GWB and ERDA-6 after equilibration
  - f_{CO_2}, pH, etc.
- Have used several versions of the EQ3/6 software package since the 1980s (e.g., Wolery, 1992; Wolery and Jarek, 2003)
- EQ3/6 will soon be used to predict Th(IV), Np(V), and Am(III) solubilities
  - Includes a reaction-path component (EQ6)
  - Widely recognized and accepted
  - Easier to use
- Have completed qualification of EQ3/6 for actinide-solubility calculations according to SNL/WIPP quality assurance (QA) procedures
- The EPA must still approve our qualification of EQ3/6

Sandia National Laboratories

Codes Used to Implement Conceptual Models (cont.)

Implementation in performance assessment (PA) codes

- **BRAGFLO**
  - Calculates H_2 production and H_2O consumptions from anoxic corrosion of steels and other Fe-base metals
  - Calculate gas production from microbial consumption of cellulosic, plastic, and rubber materials
  - Calculates volumes of brine released directly to the surface
- **PANEL**
  - Calculate the dissolved, colloidal, and total source term
- **NUTS**
  - Calculates transport of actinides within the Salado Fm. and from the Salado to the Culebra Member of the Rustler Fm.

Sandia National Laboratories

Codes Used to Implement Conceptual Models (cont.)

Implementation in PA codes (cont.)

- CCDFGF
  - Calculates cuttings and cavings, direct-brine, and spallings releases to the surface
  - Calculates brine releases to and from the Culebra
- MODFLOW
  - Calculates flow of brine in the Culebra
- SECOTP2D
  - Calculates transport of actinides in the Culebra

Topics to Be Addressed

Characteristics of the Salado Fm. and WIPP Waste

Conceptual Models of WIPP Chemistry

Codes Used to Implement Conceptual Models

Predictions of Near-Field Chemical Conditions and Actinide Solubilities

Additional Model Development

References

Sandia National Laboratories

Predictions of Near-Field Conditions

$f_{CO_2} \cong 3 \times 10^{-6}$ 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 (Brush et al., 2009)

Sandia National Laboratories

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. Composition before reactions with solids and organic ligands
B. Composition predicted by FMT after reactions with solids & organics (Brush et al. (2009)

Sandia National Laboratories

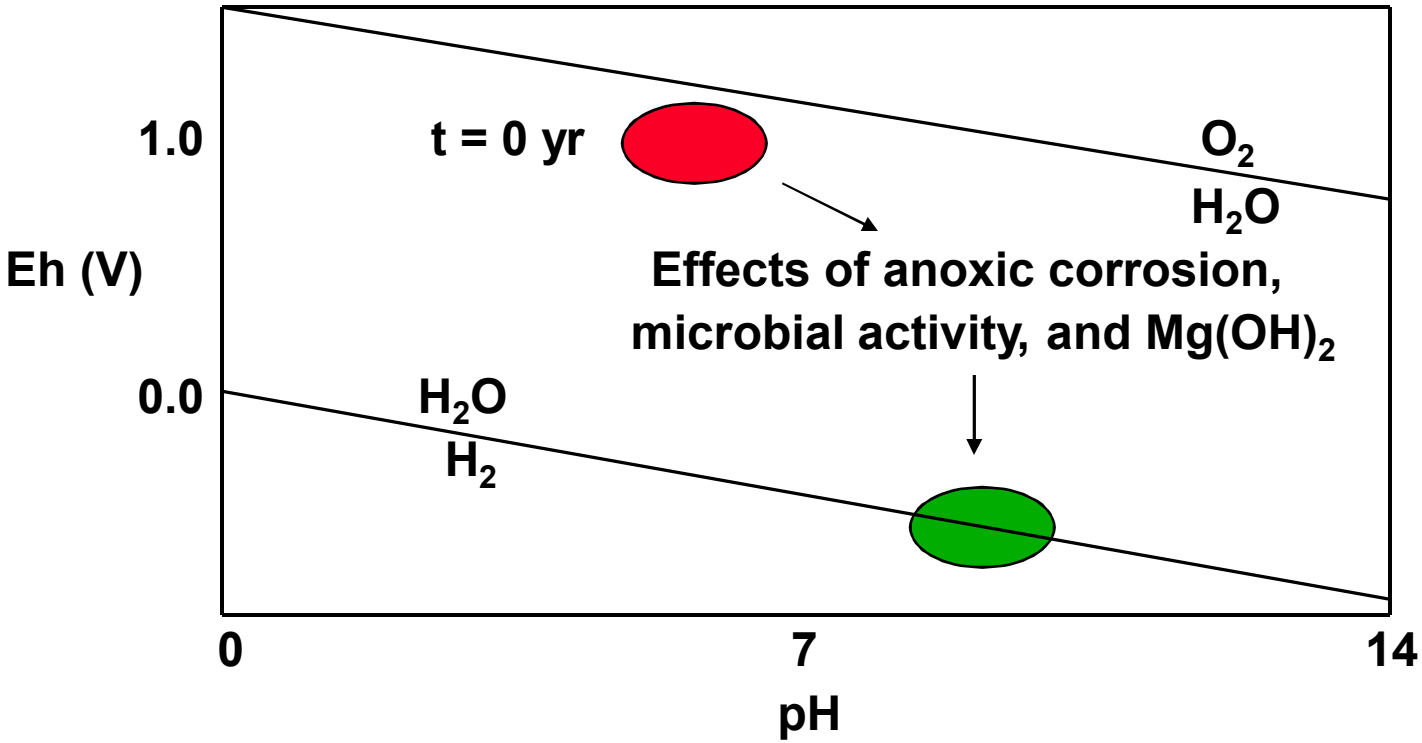
Effects of CO_2-Bearing Solids on Log f_{CO_2} (atm) and pH[A]

	Calcite	Magnesite	Hydromag.	Nesquehonite
Log f_{CO_2}, GWB	-5.42	-6.92	-5.50	-3.85
Log f_{CO_2}, ERDA-6	-6.09	-6.91	-5.50	-3.86
pH, GWB	8.69	8.69	8.69	8.69
pH, ERDA-6	8.96	8.98	8.98	8.98

A. FMT calculations with organic ligands for the CRA-2009 PABC (Brush et al., 2009, Tables 10 and 11)

Sandia National Laboratories

Predictions of Near-Field Chemical Conditions (cont.)



Sandia National Laboratories

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 Fracture-Matrix Transport (FMT) to calculate solubilities of Th(IV), Np(V), and Am(III)

- **In addition, EQ3/6 will soon be used to calculate solubilities**

Sandia National Laboratories

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 (U.S. EPA, 2006, pp. 55-58)

Sandia National Laboratories

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 (Brush et al., 2009, Tables 10 and 11)

B. EPA estimate (U.S. EPA, 2006, pp. 55-58)

Sandia National Laboratories

Topics to Be Addressed

Characteristics of the Salado Fm. and WIPP Waste

Conceptual Models of WIPP Chemistry

Codes Used to Implement Conceptual Models

Predictions of Near-Field Chemical Conditions and Actinide Solubilities

Additional Model Development

References

Sandia National Laboratories

Possible Additional Th(IV) Model Development

Modify to predict less dissolved Th present as ($Th(OH)_4(aq)$) and more eigencolloids present as ($Th(OH)_4(coll)$) in nearly neutral and basic brines (Altmaier et al., 2004)

Parameterize additional ternary (1yz) complexes (i.e., $Th(OH)_y(CO_3)_z^{4-y-2z}$ species)

- **The WIPP model currently includes:**
  - **$Th(OH)_4(aq)$, $Th(OH)_3(CO_3)^-$, and $Th(CO_3)_5^{6-}$**
- **Altmaier et al. (2005, Figure 5) concluded that the "most important species" are:**
  - **$Th(OH)_4(aq)$, $Th(OH)_2(CO_3)_2^{2-}$, $Th(OH)(CO_3)_4^{5-}$, $Th(CO_3)_5^{6-}$**
- **Altmaier et al. (2005, Figure 5) identified "further … complexes":**
  - **$Th(OH)_2(CO_3)(aq)$, $Th(OH)_3(CO_3)^-$, and $Th(OH)_4(CO_3)^{2-}$**

Sandia National Laboratories

Possible Additional Th(IV) Model Development (cont.)

Current model still adequate for compliance-related calculations

- Model overpredicts total mobile (dissolved + colloidal) Th(IV) concentrations
- Important $Th(OH)_y(CO_3)_z^{4-y-2z}$ species of Altmaier et al. (2005) not included in WIPP model are only important at TIC concentrations higher than those expected in the WIPP

Sandia National Laboratories

Possible Additional Th(IV) Model Development (cont.)

Any improvements would have to be proposed to and funded by the DOE after the second WIPP recertification

According to the EPA's regulatory requirements (U.S. EPA, 1996, 40 CFR 194.27), major changes in conceptual models would have to be reviewed according to the procedures of Altman et al. (1988), then approved by the EPA

Sandia National Laboratories

Additional Am(III) Model Development

Currently extending Am(III) model to include complexation of Am(III) by B(III)(aq) species

- Laboratory experiments under way at Los Alamos National Lab – Carlsbad Operations
  - Complexation of Nd(III) (a good analog of Am(III)) by $H_2B_4O_7(OH)^-$
- Sandia will fit Pitzer parameters to data

Sandia National Laboratories

Topics to Be Addressed

Characteristics of the Salado Fm. and WIPP Waste

Conceptual Models of WIPP Chemistry

Codes Used to Implement Conceptual Models

Predictions of Near-Field Chemical Conditions and Actinide Solubilities

Additional Model Development

References

Sandia National Laboratories

References

Altmaier, M., V. Neck, and T. Fanghänel. 2004. "Solubility and Colloid Formation of Th(IV) in Concentrated NaCl and MgCl2 Solution," *Radiochimica Acta*. Vol. 92, 537-543

Altmaier, M., V. Neck, R. Müller, and T. Fanghänel. 2005. "Solubility of ThO2·xH2O*(*am*)* in Carbonate Solution and the Formation of Ternary Th(IV) Hydroxide-Carbonate Complexes," *Radiochimica Acta*. Vol. 93, 83-92

Altman, W.D., J.P. Donnelly, and J.E. Kennedy. 1988. *Peer Review for High-Level Nuclear Waste Repositories – Generic Technical Position*. NUREG-1297. Washington, DC: U.S. Nuclear Regulatory Commission

Sandia National Laboratories

References (cont.)

Babb, S.C., and C.F. Novak. 1995. "WIPP PA User's Manual for FMT, Version 2.0." Albuquerque, NM: Sandia National Laboratories. ERMS 228119

Babb, S.C., and C.F. Novak. 1997 and Addenda. "User's Manual for FMT Version 2.3: A Computer Code Employing the Pitzer Activity Coefficient Formalism for Calculating Thermodynamic Equilibrium in Geochemical Systems to High Electrolyte Concentrations." Albuquerque, NM: Sandia National Laboratories. ERMS 243037

Brush, L.H., Y.-L. Xiong, and J.J. Long. 2009. "Results of the Calculations of Actinide Solubilities for the CRA-2009 PABC." Analysis Report, October 7, 2009. Carlsbad, NM: Sandia National Laboratories. ERMS 552201

Sandia National Laboratories

References (cont.)

Krumhansl, J.L., K.M. Kimball, and C.L. Stein. 1991. *Intergranular Fluid Compositions from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico*. SAND90-0584. Albuquerque, NM: Sandia National Laboratories

Popielak, R.S., R.L. Beauheim, S.R. Black, W.E. Coons, C.T. Ellingson and R.L. Olsen. 1983. *Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant Project, Southeastern New Mexico*. TME 3153. Carlsbad, NM: U.S. Department of Energy WIPP Project Office

Snider, A.C. 2003. "Verification of the Definition of Generic Weep Brine and the Development of a Recipe for This Brine." Analysis report, April 8, 2003

Sandia National Laboratories

References (cont.)

U.S. EPA. 2006. "Technical Support Document for Section 194.24: Evaluation of the Compliance Recertification - Actinide Source Term and Culebra Dolomite Distribution Coefficient Values." EPA Air Docket A 98-49, Item II B1-3. Washington, DC: U.S. Environmental Protection Agency Office of Air and Radiation

Wolery, T.J. 1992. EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0). UCRL-MA-110662 PT I. Livermore, CA: Lawrence Livermore National Laboratory

Wolery, T.W., and R.L. Jarek. 2003. "Software User's Manual: EQ3/6, Version 8.0." Software Document No. 10813-UM-8.0-00. Albuquerque, NM: Sandia National Laboratories

Sandia National Laboratories