IMPORTANT NOTICE: The current official version of this document is available via the Sandia National Laboratories WIPP Online Documents web site. A printed copy of this document may not be the version currently in effect.

Sandia National Laboratories
Waste Isolation Pilot Plant

Analysis of MgO Hydration and Carbonation Test Results, Analysis Plan AP-108, Rev. 1

BOE 1.4.2.5

Effective Date: 02/26/10

Author:	*Original signed by Haoran Deng* Haoran Deng, 6712	*2/24/10* Date
Technical Reviewer:	*Original signed by Greg Roselle* Greg Roselle, 6712	*2/24/2010* Date
QA Reviewer:	*Original signed by Janis Trone* Janis Trone, 6710	*2/25/2010* Date
Management Reviewer:	*Original signed by Christi Leigh* Christi D. Leigh, 6712	*2/24/2010* Date

© 2010 Sandia Corporation

CONTENTS

1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS 3

2 REVISION HISTORY 4

3 INTRODUCTION 4

4 OBJECTIVES 6

5 APPROACH 6

6 SOFTWARE DESCRIPTION 7

7 TASKS 7

8 SPECIAL CONSIDERATIONS 7

9 APPLICABLE PROCEDURES 7

10 REFERENCES 8

1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS

Table 1 defines the abbreviations, acronyms, and initialisms used in this analysis plan (AP).

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym or Initialism	Definition
AP	analysis plan
aq	aqueous
atm	atmosphere(s)
Brine A	A synthetic brine representative of intergranular Salado brines
brucite	$Mg(OH)_2$
C	carbon
CCA	(WIPP) Compliance Certification Application
CH_4	methane
CO_2	carbon dioxide
CO_3^{2-}	carbonate ion
CPR	cellulosics, plastics, and rubbers (in TRU waste)
CRA	(WIPP) Compliance Recertification Application
DOE	(U.S.) Department of Energy
EPA	(U.S.) Environmental Protection Agency
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
Fm.	Formation or formation, depending on usage
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
g	gaseous
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
H_2O	water (aq or g)
hydromagnesite	$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ or $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
magnesite	$MgCO_3$
Mg, Mg^{2+}	magnesium, magnesium ion

Table 1. Abbreviations, Acronyms, and Initialisms (cont.).

Abbreviation, Acronym or Initialism	Definition
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and ~5-10 wt % impuritities
NP	(SNL WIPP) Nuclear Waste Management Procedure
OH^-	hydroxide ion
PA	performance assessment
PAVT	(WIPP) Performance Assessment Verification Test
periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
pH	the negative, common logarithm of the activity of H^+
Rev.	revision
SNL	Sandia National Laboratories
TRU	transuranic waste
WIPP	(U.S. DOE) Waste Isolation Pilot Plant

2 REVISION HISTORY

The objectives and content of any revisions of this AP will be described in this section of subsequent versions. Changes to this AP, other than those defined as editorial changes by Sandia National Laboratories' (SNL's) Nuclear Waste Management Procedure (NP) 9-1 (see Section 9, Applicable Procedures), shall be reviewed and approved by the same organization(s) that carried out the original review and approval.

This is the first revision of this AP. In the current revision, we added an additional step in section 7 to evaluate the conceptual model by comparing it to the EQ3/6 prediction simulating the reaction path of MgO hydration and carbonation.

3 INTRODUCTION

The U.S. Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) is a deep geologic repository in southeast New Mexico for defense-related transuranic (TRU) waste. MgO is currently being emplaced in pre-packaged, polypropylene "supersacks" on top of the three-layer stacks of containers with transuranic (TRU) waste. The purpose of MgO is to serve as an engineered barrier in the WIPP disposal system by consuming the CO_2 that could be produced by possible microbial degradation of

cellulosics, plastics, and rubbers (CPR) in TRU waste after the repository is filled and sealed. Significant microbial gas generation in the WIPP is possible, but by no means certain. If significant microbial activity occurs, microbial degradation of the CPR in TRU waste could produce significant quantities of CH_4 and CO_2. To be an effective engineered barrier, MgO must consume essentially all of the microbial CO_2 and control the fugacity of CO_2 (f_{CO_2}) and the pH within ranges that result in low actinide solubilities.

The DOE included MgO as an engineered barrier in the repository design proposed in the WIPP Compliance Certification Application (CCA) (U.S. DOE, 1996). The DOE asserted that MgO, along with panel closures, shaft seals, and borehole plugs, would satisfy the requirement for multiple natural and engineered barriers, one of the assurance requirements in the EPA's regulations (U.S. EPA, 1993), which also include containment requirements, and individual and groundwater protection requirements.

Wang (1996a, 1996b) used the reaction-path code EQ6, part of the EQ3/6 geochemical software package (Daveler and Wolery, 1992; Wolery, 1992a, 1992b; and Wolery and Daveler, 1992), to predict chemical conditions in the WIPP after filling and sealing. He concluded that equilibria among Brine A or ERDA-6 and brucite ($Mg(OH_2)$) and magnesite ($MgCO_3$) will buffer (control) brine composition, f_{CO_2}, and pH in the WIPP. Brine A is representative of intergranular (grain-boundary) brines from the Salado Formation at or near the stratigraphic horizon of the repository (Molecke, 1983); ERDA-6 typifies fluids in brine reservoirs in the underlying Castile Fm. (Popielak et al., 1983).

Brush et al. (2009) used the speciation and solubility code Fracture-Matrix Transport (FMT) (Babb and Novak, 1997) to show that the brucite and carbonate-bearing solids carbonation reaction will buffer f_{CO_2} in both GWB and ERDA-6. The carbonate-bearing solids includes calcite ($CaCO_3$), magnesite, hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) and nesquehonite ($MgCO_3{\cdot}3H_2O$). Brush et al. also predicted that the brucite dissolution reaction will buffer the pH at 8.98 in ERDA-6; and that the phase-5 will buffer the pH at 8.74 in GWB. They then used FMT to calculate actinide solubilities in WIPP brines. GWB (Snider, 2003), a synthetic Salado Formation brine more representative of the intergranular Salado Formation brines than Brine A, has been used for many WIPP laboratory and modeling studies since 2003.

In May 1998, the EPA certified that the WIPP complies with its regulations (U.S. EPA, 1998). However, the EPA recognized MgO as the *only* engineered barrier in the WIPP disposal system. Thus, MgO is an essential component of the certified design of the repository.

SNL carried out a laboratory study of the efficacy of MgO in Albuquerque, NM, during the late 1990s (see for example, SNL, 1997). Since 2000, SNL has carried out a laboratory study of MgO in Carlsbad, NM. The latter study has used mainly MgO from

Premier Chemicals in Gabbs, NV and Martin Marietta Magnesia Specialties LLC, the current supplier of MgO to the WIPP.

4 OBJECTIVES

The objective of the analysis described in this AP is to develop a kinetic model of the hydration and carbonation of Premier MgO under conditions expected in the WIPP after filling and sealing.

The laboratory studies of the efficacy of MgO at SNL in Albuquerque and Carlsbad have shown that MgO hydrates and carbonates slowly under expected WIPP conditions. Therefore, a kinetic model is necessary to demonstrate that MgO hydration and, especially, MgO carbonation will proceed to completion; and that MgO will be an effective engineered barrier. The kinetic model resulting from this analysis could be used to support the PA.

5 APPROACH

The analysis described in this AP will use results obtained from the laboratory studies of MgO at SNL in Carlsbad (Bryan and Snider, 2001a, 2001b; Snider, 2002; Snider and Xiong, 2002; Deng et al., 2006, 2007; Deng, 2007; Deng et al., 2009a, 2009b). These studies, underway since 2000, have used mainly Premier MgO or Martin Marietta MgO, the material currently being emplaced in the WIPP. Therefore, the kinetic model developed under this AP will be applicable to Premier MgO or Martin Marietta MgO.

The conceptual model of the hydration and carbonation of MgO will include solids such as periclase and brucite reacting with H_2O and CO_3^{2-} in WIPP brines. The conceptual model may also be extended to include H_2O vapor and CO_2 in the gaseous phase. Therefore, the model will emphasize experimentally observed reactions such as:

$$MgO + H_2O(aq \text{ or } g) \rightleftharpoons Mg(OH)_2; \tag{1}$$

$$5Mg(OH)_2 + 4CO_2(aq \text{ or } g) \rightleftharpoons Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O. \tag{2}$$

However, the model could also include intermediate hydration products such as the amorphous Mg-Cl-OH-H_2O phase observed in many of the experiments with Generic Weep Brine (GWB) at SNL in Carlsbad, or even to the crystalline solid $Mg_3(OH)_5Cl{\cdot}4H_2O$ observed in a few of the experiments with this brine.

The model will include kinetics of these and, perhaps, other chemical reactions; and mass transport of reactants and products via fractures or (perhaps) other pathways

through the solid hydrated phase(s) and carbonated phase(s) resulting from these reactions. A mathematical description of those processes will be generated and solved in terms of model parameters. These parameters will be quantified by least-squares fits to results from the hydration and carbonation experiments at SNL in Carlsbad.

6 SOFTWARE DESCRIPTION

Microsoft Excel will be used for least-squares fits of model parameters to the results of the hydration and carbonation experiments. EQ3/6 version 8.0 (Wolery, 2003) or the most current version will be used to predict the hydration and carbonation reaction path.

7 TASKS

The tasks required to develop a kinetic model of MgO hydration and carbonation under expected WIPP conditions are: (1) generate a conceptual kinetic model of the hydration and carbonation of MgO in WIPP brines such as ERDA-6 and GWB (and, perhaps, other aqueous solutions) containing dissolved CO_2 reaction products, and possibly significant contaminants; (2) generate a mathematical description of the conceptual model and solve it for model parameters that can be evaluated by fitting to experimental data; (3) quantify all of the model parameters resulting from the second task by least-squares fitting to experimental data; (4) evaluate the conceptual model by comparing it to EQ3/6 prediction simulating the reaction path of MgO hydration and carbonation in a closed system containing WIPP brines and CO_2; (5) evaluate the model by comparing fitted values of parameters to the values of similar parameters reported in the peer-reviewed literature or in other reports, if possible; (5) write up the model in summary reports.

PI conducting the MgO hydration and carbonation research will summarize the kinetic models in summary reports by the end of physical year 2010.

8 SPECIAL CONSIDERATIONS

There are no special considerations applicable to this AP.

9 APPLICABLE PROCEDURES

The following NPs are applicable to the work described in this AP. This list does not identify the current version of these NPs; the current versions of these and other procedures are provided on the SNL WIPP web site (www.nwmp.sandia.gov/onlinedocuments).

- NP 2-1, “Qualification and Training;”
- NP 6-1, “Document Review Process;”

- NP 9-1, “Analyses;”
- NP 9-2, “Parameters;”
- NP 17-1, “Records;”
- NP 19-1, “Software Requirements.”

10 REFERENCES

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

Brush, L.H., Xiong, Y., and Long, J.J. 2009. “Results of the Calculations of Actinide Solubilities for The WIPP CRA-2009 PABC.” Carlsbad, NM. Sandia National Laboratories. ERMS# 552201.

Bryan, C.R., and A.C. Snider. 2001a. “MgO Hydration and Carbonation at SNL/Carlsbad,” “Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.4, Repository Investigations, Milestone RI010, January 31, 2001.” Carlsbad, NM: Sandia National Laboratories. ERMS 516749. 66-83.

Bryan, C.R., and A.C. Snider. 2001b. “MgO Experimental Work Conducted at SNL/CB: Continuing Investigations with Premier Chemicals MgO,” “Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.4, Repository Investigations, Milestone RI020, July 31, 2001.” Carlsbad, NM: Sandia National Laboratories. ERMS 518970. 5-1 to 5-15.

Deng, H., Y. Xiong, B.M. Nemer, and S. Johnsen, 2009a. “Experimental Work Conducted on MgO Long-term Hydration.” Carlsbad, NM. Sandia National Laboratories. ERMS# 551421.

Deng, H., Y. Xiong, B.M. Nemer, and S. Johnsen, 2009b. “Experimental Work Conducted on MgO Characterization and Hydration.” Scientific Basis for Nuclear Waste Management XXXII, edited by R.B. Rebak, N.C. Hyatt, D.A. Pickett (Mater. Res. Soc. Symp. Proc. Volume 1124, Warrendale, PA, 2009), 1124-Q05-05. ERMS# 550767.

Deng, H., Y. Xiong and B.M. Nemer 2007. “Experimental Work Conducted on MgO Characterization and Hydration”. Carlsbad, NM. Sandia National Laboratories. ERMS# 546570

Deng, H 2007. "MgO Hydration Rate" Carlsbad, NM. Sandia National Laboratories ERMS# 545757.

Deng, H., S. Johnsen, Y. Xiong, G.T. Roselle, and B.M. Nemer. 2006. "Analysis of Martin Marietta MagChem 10 WTS-60 MgO". Carlsbad, NM. Sandia National Laboratories ERMS# 544712 (2006).

Daveler, S.A., and T.J. Wolery. 1992. *EQPT, A Data File Preprocessor for the EQ3/6 Software Package: User's Guide and Related Documentation (Version 7.0).* UCRL MA 110662 PT II. Livermore, CA: Lawrence Livermore National Laboratory.

Molecke, M.A. 1983. *A Comparison of Brines Relevant to Nuclear Waste Experimentation.* SAND83-0516. 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. ERMS 242085.

Snider, A.C. 2002. "MgO Studies: Experimental Work Conducted at SNL/Carlsbad. Efficacy of Premier Chemicals MgO as an Engineered Barrier," "Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.3, Compliance Monitoring; WBS 1.3.5.4, Repository Investigations, Milestone RI110, January 31, 2002." Carlsbad, NM: Sandia National Laboratories. ERMS 520467. 3.1-1 to 3.1-18.

Snider, A.C. 2003. "Verification of the Definition of Generic Weep Brine and the Development of a Recipe for This Brine." Unpublished report, April 8, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527505.

Snider, A.C., and Y.-L. Xiong. 2002. "Carbonation of Magnesium Oxide," "Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.3, Compliance Monitoring; WBS 1.3.5.4, Repository Investigations, Milestone RI130, July 31, 2002." Carlsbad, NM: Sandia National Laboratories. ERMS 523189. 4.1-1 to 4.1-28.

SNL. 1997. "Chemical Conditions Model: Results of the MgO Backfill Efficacy Investigation." Unpublished report, April 23, 1997. Albuquerque, NM: Sandia National Laboratories. ERMS 419794.

U.S. DOE. 1996. *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Vol. 1-21*. Carlsbad, NM: U.S. Department of Energy Carlsbad Area Office.

U.S. EPA. 1993. "40 CFR Part 191 Environmental Radiation Protection Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes; Final Rule. *Federal Register*, Vol. 58, 66398-66416. Washington, DC: U.S. EPA Office of Radiation and Indoor Air.

U.S. EPA. 1998. "40 CFR 194, Criteria for the Certification and Recertification of the Waste Isolation Pilot Plant's Compliance With the Disposal Regulations. Certification Decision: Final Rule," *Federal Register*. Vol. 63, 27354-27406. Washington, DC: U.S. EPA Office of Radiation and Indoor Air.

Wang, Y. 1996a. "Define Chemical Conditions for FMT Actinide Solubility Calculations." Unpublished memorandum to M.D. Siegel, March 18, 1996. Albuquerque, NM: Sandia National Laboratories.

Wang, Y. 1996b. "Estimate of Repository pH and f_{CO2} Distribution for the Long-Term WIPP Performance Assessment (PA)." Unpublished memorandum to M.S. Tierney and C.T. Stockman, March 29, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 237415.

Wolery, T.J. 1992a. *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.J. 1992b. *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0).* UCRL-MA-110662 PT III. Livermore, CA: Lawrence Livermore National Laboratory.

Wolery, T.J., and S.A. Daveler. 1992. *EQ6, A Computer Program for Reaction-Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0).* UCRL-MA-110662 PT IV. Livermore, CA: Lawrence Livermore National Laboratory.

Wolery, T.J., 2003, *EQ3/6 - Software for Geochemical Modeling (Version 8.0)*, UCRL-CODE-2003-009, Lawrence Livermore National Laboratory, Livermore, California.

NOTICE: This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness or any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof or any of their contractors.

This document was authored by Sandia Corporation under Contract No. DE-AC04-94AL85000 with the United States Department of Energy's National Nuclear Security Administration. Parties are allowed to download copies at no cost for internal use within your organization only provided that any copies made are true and accurate. Copies must include a statement acknowledging Sandia Corporation's authorship of the subject matter.