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Subparts B and C
Compliance Recertification Application 2014
for the
Waste Isolation Pilot Plant

Appendix MgO-2014
Magnesium Oxide as an Engineered Barrier

United States Department of Energy
Waste Isolation Pilot Plant

Carlsbad Field Office
Carlsbad, New Mexico

Compliance Recertification Application 2014
Appendix MgO-2014

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Acronyms and Abbreviations

%	percent
µm	micrometer
AMWTP	Advanced Mixed Waste Treatment Program
aq	aqueous
atm	atmosphere(s)
BRAGFLO	Brine and Gas Flow
C	Celsius
CCA	Compliance Certification Application
CFR	Code of Federal Regulations
CH-TRU	contact-handled transuranic
CPR	cellulosic, plastic, and rubber
CRA	Compliance Recertification Application
DOE	U.S. Department of Energy
ECO	Engineering Change Order
EPA	U.S. Environmental Protection Agency
ERDA	Energy Research and Development Administration
FMT	Fracture-Matrix Transport
g	gaseous or gram
GWB	Generic Weep Brine
HDPE	high-density polyethylene
K_d	matrix distribution coefficient
kg	kilogram
L	liter
lb	pound
M	molar
m^3	cubic meters
mL	milliliter
mm	millimeter
mol	mole
PA	performance assessment
PABC	Performance Assessment Baseline Calculations

PAVT	Performance Assessment Verification Test
ppm	parts per million
RH	relative humidity
RH-TRU	remote-handled transuranic
s	second(s) or solid
SPC	Salado Primary Constituents
TIC	total inorganic carbon
TRU	transuranic
WDS	Waste Data System
WIPP	Waste Isolation Pilot Plant
WTS	Washington TRU Solutions, LLC
XRD	X-ray diffraction

Elements and Chemical Compounds

Am	americium
An	actinide
Br	bromine
C	carbon
Ca	calcium
CaO	calcium oxide or lime
$CaSO_4$	anhydrite
CH_4	methane
Cl^-	chloride ion
Cl	chlorine
CO_2	carbon dioxide
CO_3^{2-}	carbonate ion
f_{co_2}	fugacity of CO_2
Fe	iron
H^+	hydrogen ion
H_2O	water
H_2S	hydrogen sulfide
Mg	magnesium

$Mg(OH)_2$	brucite
$Mg_2(OH)_3Cl \cdot 4H_2O$	phase 3
$Mg_3(OH)_5Cl \cdot 4H_2O$	phase 5
$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$	hydromagnesite (4323)
$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	hydromagnesite (5424)
$MgCO_3$	magnesite
$MgCO_3 \cdot 3H_2O$	nesquehonite
MgO	magnesium oxide
N_2	nitrogen
Na	sodium
$Na_2Ca(SO_4)_2$	glauberite
NaCl	sodium chloride or halite
Np	neptunium
O_2	oxygen
Pb	lead
pH	the negative, common logarithm of the activity of H^+
Pu	plutonium
SO_4	sulfate
Th	thorium
U	uranium

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MgO-1.0 Introduction

The U.S. Department of Energy (DOE) is emplacing magnesium oxide (MgO) in the Waste Isolation Pilot Plant (WIPP) repository to provide an engineered barrier that decreases the solubilities of the actinide (An) elements in transuranic (TRU) waste in any brine present in the postclosure repository (Compliance Certification Application (CCA), Appendix BACK and Appendix SOTERM (U.S. DOE 1996); the 2004 Compliance Recertification Application (CRA-2004) Appendix BARRIERS-2004, Appendix PA-2004, and Attachment SOTERM-2004 (U.S. DOE 2004); and the CRA-2009 Appendix MgO-2009 and Appendix SOTERM-2009 (U.S. DOE 2009)). Because it will decrease An solubilities, MgO helps meet the U.S. Environmental Protection Agency (EPA) requirement for multiple natural and engineered barriers, one of the assurance requirements for radioactive waste repositories in 40 CFR § 191.14(d) (U.S. EPA 1993).

In 40 CFR § 191.12 (U.S. EPA 1993), the EPA defined barriers as “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.”

The DOE proposed four engineered barriers in the WIPP CCA, submitted to the EPA in October 1996 (U.S. DOE 1996). The barriers proposed were MgO, panel closures, shaft seals, and borehole plugs. The EPA specified MgO as the only engineered barrier in the WIPP disposal system that meets the assurance requirement in its May 1998 certification rulemaking (U.S. EPA 1998a and U.S. EPA 1998b) because it considered panel closures, shaft seals, and borehole plugs to be part of the disposal-system design.

As used in the WIPP, MgO will decrease An solubilities by consuming essentially all of the carbon dioxide (CO_2) that would be produced should microbial activity consume all of the cellulosic, plastic, and rubber (CPR) materials in the TRU waste, waste containers, and waste-emplacement materials in the repository. Although MgO will consume essentially all the CO_2, minute quantities (relative to the quantity that would be produced by microbial consumption of all of the CPR materials) will persist in the aqueous (aq) and gaseous (g) phases. The residual quantities would be so small relative to the initial quantity that the term “essentially” is hereafter omitted in this appendix.

Consumption of CO_2 will decrease An solubilities by (1) buffering the fugacity of CO_2 (f_{CO_2}) at a value or within a range of values favorable from the standpoint of the speciation and solubilities of the An elements (the fugacity of a gaseous species, f_i, is similar to the partial pressure of that species, p_i); (2) controlling the pH at a value favorable from the standpoint of An solubilities; and (3) preventing the production of carbonate ion (CO_3^{2-}) in significant quantities. The effect of this residual CO_3^{2-} on the solubilities of An elements is described in Appendix SOTERM-2014, Section SOTERM-3.2.1 and Section SOTERM-3.3.1.3.

The effects of MgO carbonation (consumption of CO_2) have been included in WIPP performance assessment (PA) calculations by assuming that there will be no CO_2 in the repository. This assumption has been implemented in PA by (1) removing CO_2 from the gaseous phase in the

Brine and Gas Flow (BRAGFLO) calculations, thereby somewhat reducing the predicted pressurization of the repository; and (2) using the values of f_{CO_2} and pH predicted for reactions among MgO, brine, and aqueous or gaseous CO_2 to calculate An solubilities. The assumption that there will be no CO_2 has been implemented in all compliance-related WIPP PA calculations. These include (1) the CCA PA calculations (Appendix SOTERM) (Novak, Moore, and Bynum 1996; U.S. DOE 1994); (2) the CCA Performance Assessment Verification Test (PAVT) (Novak 1997; U.S. EPA 1998c, U.S. EPA 1998d, and U.S. EPA 1998e); (3) the PA calculations for the CRA-2004 (Appendix PA and Attachment SOTERM) (Brush and Xiong 2003a, Brush and Xiong 2003b, Brush and Xiong 2003c, and Brush and Xiong 2003d; U.S. DOE 2004); (4) the CRA-2004 Performance Assessment Baseline Calculations (PABC) (Brush and Xiong 2005a and Brush and Xiong 2005b; Brush 2005; Leigh et al. 2005); (5) the PA calculations for the CRA-2009 (Appendix SOTERM-2009) (U.S. DOE 2009); (6) the CRA-2009 PABC calculations (Brush and Xiong 2009a and Brush and Xiong 2009b; Brush, Xiong, and Long 2009; U.S. DOE 2009); and (7) the CRA-2014 PA calculations (Appendix SOTERM-2014) (Brush, Domski, and Xiong 2012; Brush and Domski 2013a and Brush and Domski 2013b).

In this appendix, “MgO” refers to the bulk, granular material being emplaced in the WIPP to serve as the engineered barrier. MgO comprises periclase (pure, crystalline MgO–the main, reactive constituent of the WIPP engineered barrier) and various impurities described in Appendix MgO-2009, Section MgO-3.0 (U.S. DOE 2009). Pure, crystalline MgO is always referred to as periclase in this Appendix. The term periclase, and other mineral names used herein are, strictly speaking, restricted to naturally occurring forms of the materials that meet all the other requirements of the definition of a mineral (see, for example, Bates and Jackson 1984). However, mineral names are used in this report for convenience.

MgO-2.0 Description of the Engineered Barrier System

This section describes the emplacement of MgO in the WIPP disposal rooms (Section MgO-2.2) and the vendors that provided or are providing MgO to the WIPP (Section MgO-2.2).

Washington TRU Solutions, LLC (WTS) (WTS 2009b) provided the current specifications for the prepackaged MgO emplaced in the WIPP.

MgO-2.1 Emplacement of MgO

Sections 2.1.1 through 2.1.4 provide a history of the changes related to emplacement of MgO in the WIPP.

MgO-2.1.1 Supersacks

The DOE originally emplaced MgO in polypropylene supersacks atop each stack of waste containers. According to the original WTS specifications, each supersack contained 1905 ± 23 kilograms (kg) (4200 ± 50 pounds ([lb]) of MgO (WTS 2009b). (Section MgO-2.1.4 describes changes since the CRA-2009 in the placement of the supersacks on every other waste stack instead of every waste stack, and the weight of some of the supersacks.) Forklifts are used to place the supersacks on top of the waste stacks. Figure MgO-1 shows supersacks of MgO emplaced on top of the waste stacks.

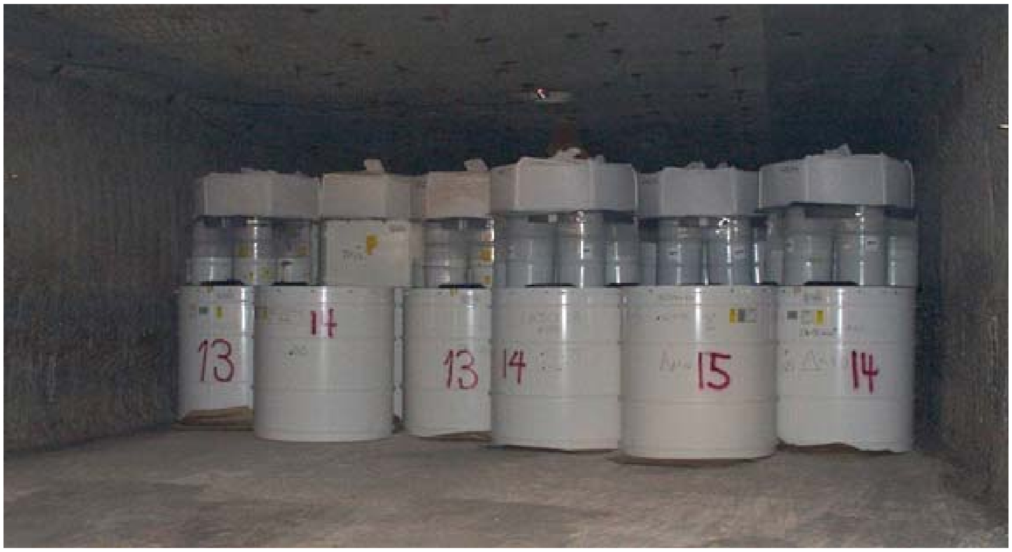

Figure MgO-1. Supersacks of MgO Emplaced on Top of the Waste Stacks

The use of supersacks facilitates handling and emplacement of the MgO, minimizes potential worker exposure to dust, and minimizes the exposure of periclase to atmospheric CO_2 and water (H_2O) during handling and emplacement, and prior to panel closure. WTS (WTS 2009b) provides the most current, detailed specifications for the supersacks. In particular, WTS (WTS 2009b) specifies that the supersacks “shall provide a barrier to atmospheric moisture and carbon dioxide (CO_2) … equivalent to or better than that provided by a standard commercial cement bag," and "must be able to retain [their] contents for a period of two years after emplacement without rupturing from [their] own weight." The specifications also require a certificate of compliance with all requirements of WTS (WTS 2009b) for every shipment of MgO (see Section MgO-3.1), and a certified chemical analysis for each new lot of MgO. The supersacks are subject to random receipt inspection at the WIPP to ensure compliance with the dimensions and labeling specified by WTS (WTS 2009b), and to identify any damage incurred during shipping.

The supersacks contain dry, granular MgO, of which less than 0.5% can exceed 9.5 millimeters (mm) (3/8 inch) in diameter (WTS 2009b). Emplacement of granular MgO instead of powder reduces the likelihood of dust formation and release in the event of premature supersack rupture, and ensures that the permeability of the material is high enough to promote complete reaction with aqueous or gaseous CO_2.

Creep closure of WIPP disposal rooms will rupture the supersacks and disperse the MgO among and within the ruptured waste containers. This will, in turn, expose the MgO to the room's atmosphere, to any CO_2 produced by the microbial consumption of CPR materials, and to H_2O vapor and any brine present.

MgO-2.1.2 Minisacks

From the first receipt of TRU waste at the WIPP in March 1999 until January 2001, the DOE emplaced MgO in both supersacks and 11-kg (25-lb) minisacks. During this period, the minisacks were emplaced among the waste containers and between the waste containers and the ribs (sides) of the disposal rooms. The MgO supersacks and minisacks constituted about 85% and 15%, respectively, of the total quantity of MgO emplaced in the repository.

In 2000, the DOE requested EPA approval to eliminate the minisacks (Triay 2000; U.S. DOE 2000); the EPA approved this request in 2001 (Marcinowski 2001; U.S. EPA 2001). Appendix MgO-2009, Section MgO-2.1.2 provides details on the DOE's request and the EPA's approval of this request.

MgO-2.1.3 Use of Racks to Emplace Additional MgO

In March 2004, the EPA approved the emplacement in the WIPP of compressed (supercompacted) waste from the Advanced Mixed Waste Treatment Project (AMWTP) at the Idaho National Engineering and Environmental Laboratory (Marcinowski 2004; Trinity Engineering Associates 2004; U.S. EPA 2004). However, the EPA required that the DOE maintain an MgO excess factor (Section MgO-6.0) of 1.67 on a room-by-room basis. Some of the AMWTP waste contains concentrations of CPR materials that are high relative to the average concentration of CPR materials in TRU waste, thereby necessitating the emplacement of additional MgO in the repository. To account for this, the DOE has emplaced additional MgO supersacks on racks among the waste containers. Each rack contains five supersacks identical to those placed on top of the waste containers, and spans the same vertical distance normally occupied by the waste stack and the supersack emplaced atop the waste stack. Thus, emplacing additional MgO in the repository uses space normally occupied by contact-handled transuranic (CH-TRU) waste. Figure MgO-2 shows a rack used to emplace additional MgO in the WIPP.

In February 2008, the EPA approved the DOE's request for a reduction of the MgO excess factor from 1.67 to 1.2 (see Appendix MgO-2009, Section MgO-6.2.4.6) (U.S. DOE 2009).

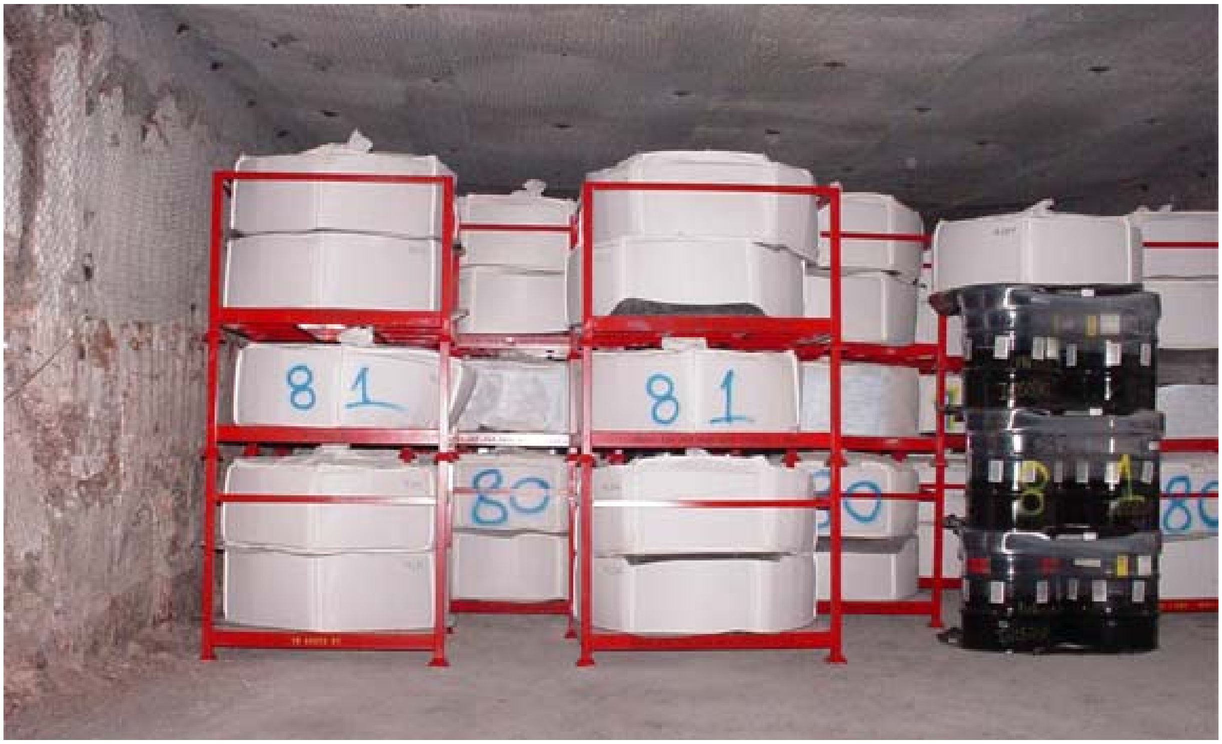

Figure MgO-2. Racks Used to Emplace Additional MgO

MgO-2.1.4 Changes since the CRA-2009

In February 2012, the DOE submitted a planned change notice with an alternative placement scheme for MgO supersacks (Franco 2012). This scheme consists of emplacing the MgO supersacks on every other row of waste stacks, and adjusting this frequency if necessary to accommodate high-CPR waste streams. The DOE proposed this new process because the data it had obtained by tracking the amounts of CPR materials and MgO emplaced in the repository for the last four years demonstrated that the MgO excess factor had exceeded the value of 1.2 approved by the EPA in February 2008 (see Appendix MgO-2009, Section MgO-6.2.4.6) (U.S. DOE 2009). The DOE stated that its new emplacement scheme would: (1) continue to calculate the excess factor at the end of each shift when waste-emplacement data are uploaded to the WIPP Waste Data System (WDS), (2) continue to allow designated personnel to direct that additional MgO be emplaced during the next shift if necessary, and (3) result in a more efficient distribution of MgO based on the CPR contents of the emplaced waste containers. The DOE's change notice included an analysis based on Kanney and Vugrin (Kanney and Vugrin 2006) that showed that molecular diffusion of microbially produced CO_2 through brine following a human intrusion into the repository would be sufficient to transport CO_2 from the waste to the MgO supersacks placed on every other row of waste stacks.

In July 2012, the EPA concurred with the DOE's change notice to emplace MgO supersacks on every other row of waste stacks and adjust this frequency if necessary for high-CPR waste streams (Peake 2012).

The DOE continues to emplace waste in several types of containers (Appendix DATA-2014, Attachment B), and is now emplacing MgO in 3000- and 4200-lb supersacks. WTS specified the addition of 1361 ± 23 kg (3000 ± 50 lb) supersacks in Engineering Change Order (ECO) 12137 (WTS 2009a). WTS added the 3000-lb supersacks after calculations using past MgO emplacement data and an MgO excess factor of 1.2 instead of 1.67 established that using both 3000- and 4200-lb supersacks would be more economical than using only 4200-lb supersacks. Furthermore, the WDS calculations showed that using both sizes would decrease the number of racks required (see Appendix MgO-2014, Section 2.1.3). Waste Handling Operations is now using the WDS to calculate which sizes of supersacks to emplace on every other row of waste stacks in order to maintain an MgO excess factor of 1.2 and to minimize the use of racks. ECO 12137 (WTS 2009a) also specified the addition of the reactivity test for periclase and lime (Appendix MgO-2014, Section 2.3.1) that was required by the EPA when it approved the DOE's request for a reduction of the MgO excess factor from 1.67 to 1.2 (Appendix MgO-2009, Section MgO-6.2.4.6) (U.S. DOE 2009). ECO 12137 necessitated the replacement of the previous specifications for prepackaged MgO emplaced in the WIPP (WTS 2005) with the current specifications (WTS 2009b). The first 3000-lb supersack was emplaced on August 25, 2009, in Panel 5 of Room 6. The DOE informed the EPA of this change during the EPA's annual inspection of the WIPP site on June 28, 2010 (U.S. EPA 2010a).

As of December 31, 2012, the DOE had emplaced 84,892.57 cubic meters (m^3) of CH-TRU waste in 17,108 stacks, and 309.68 m^3 of remote-handled transuranic (RH-TRU) waste in 620 boreholes in the repository. As of the same date, the DOE had emplaced 12,550 25-lb minisacks, 3,807 3,000-lb sacks, 71 4,100-lb supersacks, and 13,776 4,200-lb supersacks, and 142 racks. The overall MgO excess factor (see MgO-6.0) as of December 31, 2012, was 1.810 (Kouba 2013).

MgO-2.2 MgO Vendors

National Magnesia Chemicals in Moss Landing, CA, was the first vendor to provide MgO for the WIPP. National Magnesia supplied MgO from the opening of the WIPP in March 1999 through mid-April 2000; during this period, waste was emplaced only in Panel 1, Room 7. This vendor was sometimes referred to as National Refractory Materials (e.g., Papenguth 1999). Note that in every seven-room WIPP panel, waste is first emplaced in Room 7, at the back of the panel, and is last emplaced in Room 1, at the front of the panel.

After National Magnesia stopped producing MgO, WTS considered Martin Marietta Magnesia Specialties LLC, currently headquartered in Baltimore, MD, and Premier Chemicals of Gabbs, NV, as potential vendors. At the request of the DOE Carlsbad Area Office, Papenguth (Papenguth 1999) carried out a technical evaluation of MgO from both Martin Marietta and Premier to support the selection of a new vendor. The criteria used for this evaluation included density, particle size, purity, and reactivity, quantified using a test developed by Krumhansl (Krumhansl et al. 1997). Based on cost and the results of the technical evaluation, WTS selected Premier Chemicals. Appendix MgO-2009, Section MgO-3.2 (U.S. DOE 2009) provides the results of the characterization of Premier MgO. This vendor supplied MgO from mid-April 2000 (Panel 1, Room 7) through January 2005 (Panel 2, Room 2).

Premier Chemicals informed WTS in 2004 that it would soon be unable to provide MgO that met the requirement for the minimum concentration of MgO specified by WTS (WTS 2003): "The sum of MgO plus calcium oxide (CaO) shall be a minimum of 95%, with MgO being no less than 90%."

Martin Marietta Magnesia Specialties, LLC, was selected and has supplied MgO to the WIPP since January 2005 (Panel 2, Room 2). The company was selected based on cost and a technical evaluation of suitability (Wall 2005). Appendix MgO-2009, Section MgO-3.3.2 (U.S. DOE 2009) contained the results of the evaluation and a detailed characterization of Martin Marietta MgO.

Martin Marietta is still providing MgO to the WIPP.

MgO-3.0 Characteristics of MgO

The CRA-2009, Appendix MgO-2009, Section MgO-3.0 (U.S. DOE 2009) described the characteristics of the MgO provided to the WIPP by National Magnesia Chemicals (Section MgO-3.1), Premier Chemicals (Section MgO-3.2), and Martin Marietta Magnesia Specialties, LLC (the current vendor). There is no new information since the CRA-2009 regarding the characteristics of these vendors and materials provided.

MgO-3.1 Changes since the CRA-2009

A new test to determine the concentration of the reactive constituents of the MgO (periclase and lime, or CaO) was developed by Sandia National Laboratories to satisfy one of the EPA's requirements that it specified when it approved the DOE's request for a reduction of the MgO excess factor from 1.67 to 1.2 (see Appendix MgO-2009, Section MgO-6.2.4.6) (U.S. DOE 2009). WTS specified the use of this test, entitled "Reactivity (mole % Periclase + Lime) Acceptance Test," in ECO 12137 (WTS 2009a), and it was incorporated in the current specifications for prepackaged MgO emplaced in the WIPP (WTS 2009b). An independent outside laboratory carries out the reactivity test to ensure that the MgO fulfills the EPA's requirement that the MgO contain a minimum of 96 mole (mol) % of reactive constituents. Since the implementation of the reactivity test in April 2009 through December 31, 2012, Waste Handling Operations purchased 37 shipments containing 250 tons of MgO. A total of 370 samples from these shipments were analyzed; the average reactivity of these samples was 97.4 mol % (Chavez 2013). These results are archived in the WIPP WDS.

MgO-4.0 Hydration and Carbonation of MgO

This section provides the results of the DOE studies of the hydration and carbonation of MgO (Section MgO-4.1 and Section MgO-4.2, respectively).

MgO-4.1 Hydration of MgO

The CRA-2009, Appendix MgO-2009, Section MgO-4.1 (U.S. DOE 2009) described the hydration of MgO provided by Premier Chemicals (the previous MgO vendor) and Martin Marietta Magnesia Specialties, LLC (the current vendor). There is no new information since the CRA-2009 regarding the hydration of Premier or Martin Marietta MgO (see Appendix MgO-2009 for discussions of the hydration of these products). However, some of the previous text is retained herein to provide background information for new results on the relative stabilities of two of the MgO hydration products expected in the WIPP.

Based on previous experiments (Appendix MgO-2009, Sections 4.1.1 and 4.1.2), the most important hydration reaction expected in the WIPP is

$$MgO(s) + H_2O(aq\ or\ g) \rightleftharpoons Mg(OH)_2(s). \qquad (MgO.1)$$

Reaction (MgO.1) was the only hydration reaction observed in the humid experiments. Reaction (MgO.1) was also the only hydration reaction observed in the inundated runs with ERDA-6 brine (Snider 2003b). ERDA-6 brine is a synthetic brine representative of fluids in brine reservoirs in the Castile Formation (Popielak et al. 1983). In inundated experiments with Generic Weep Brine (GWB), however, hydration produced both brucite and a crystalline Mg-OH-Cl-H_2O phase (Snider 2003a). GWB is the average composition of intergranular fluids collected from the Salado Formation at the original stratigraphic horizon of the repository (Krumhansl, Kimball, and Stein 1991; Snider 2003b). X-ray diffraction (XRD) analysis identified this phase as $Mg_3(OH)_5Cl\cdot 4H_2O$, referred to herein as “phase 5” because its OH/Cl ratio (the molar ratio of OH to Cl) is five (Snider et al. 2003a). On the other hand, the thermodynamic speciation and solubility code Fracture-Matrix Transport (FMT) (Babb and Novak 1997 and addenda; Wang 1998), which was used at the time to predict near-field chemical conditions and An solubilities in the WIPP, predicted that both brucite and a similar Mg-OH-Cl-H_2O phase, $Mg_2(OH)_3Cl\cdot 4H_2O$ (phase 3), would be present in GWB and Salado Primary Constituents (SPC) brine after these brines equilibrate with the solids in WIPP disposal rooms (Section MgO-5.1). SPC brine (Novak 1997) is similar to Brine A, another synthetic fluid that was used to represent intergranular Salado brines (see Section MgO-5.1.1.2 and Molecke 1983). The FMT thermodynamic database contained phase 3, but not phase 5, at the time. If phase 5 had been in the database, FMT would have predicted that phase 5 would be present in GWB instead of phase 3 (Section MgO-5.1). The hydration reaction that produces phase 5 is:

$$3Mg(OH)_2 + 3H_2O + H^+ + Cl^- \rightleftharpoons Mg_3(OH)_5Cl\cdot 4H_2O \qquad (MgO.2)$$

It should be noted that Freyer (Freyer 2012) concluded that phase 3 is stable with respect to phase 5 under the conditions expected in a German domal salt repository (see Section MgO-4.1.1).

MgO-4.1.1 Results since the CRA-2009

Deng et al. (Deng et al. 2009) conducted long-term hydration experiments with Martin Marietta MgO primarily to obtain information on the solid phases produced by the hydration of Martin Marietta MagChem 10 WTS MgO. This MagChem 10 WTS MgO is apparently identical to the Martin Marietta MagChem WTS-60 MgO, used by Deng, Xiong and Nemer (Deng, Xiong and Nemer 2007, Section 5) in their accelerated hydration experiments (see Appendix MgO-2009, Section MgO-4.1.2) (U.S. DOE 2009), because the particle-size distributions reported by Deng, Xiong, and Nemer (Deng, Xiong, and Nemer 2007, Section 5) and Deng et al. (Deng et al. 2009) are identical. Deng et al. (Deng et al. 2009) used MgO with three particle sizes (as-received, < 75 μm, and 1.0-2.0 mm), three brines (GWB, “simplified GWB” (1 M $MgCl_2$ + 3.6 M NaCl), and ERDA-6), and two MgO/brine ratios (0.0403 and 0.273 grams per milliliter (g/mL)). They hydrated the MgO in 30 mL high-density polyethylene (HDPE) centrifuge tubes or 125 mL HDPE serum bottles at 28 °C for periods of up to about 16 months. Deng et al. (Deng et al. 2009) used a fractional factorial matrix similar to that used by Deng, Xiong and Nemer (Deng, Xiong and Nemer 2007, Section 5) in their accelerated hydration experiments (see above). Deng et al. (Deng et al. 2009) performed XRD and scanning electron microscopy analyses that confirmed that brucite and phase 5 (but not phase 3) form in GWB and simplified GWB, but that only brucite forms in ERDA-6 brine.

Because the results of numerous laboratory studies of MgO hydration showed that phase 5 forms in GWB instead of phase 3 (Wang and Bryan 2000; Wang, Bryan, and Wall 2001; Snider and Xiong 2002a and Snider and Xiong 2002b; Snider, Xiong, and Wall 2004; Deng et al. 2009), Xiong et al. (Xiong et al. 2009 and Xiong et al. 2010) determined the solubility of phase 5 and added its solubility product to the DATA0.FM1 database that was qualified for An-solubility calculations along with the EQ3/6 geochemical software package (Wolery 2008; Wolery et al. 2010; Xiong 2011a and Xiong 2011b). Therefore, EQ3/6 now predicts that the hydration of MgO in GWB will produce brucite and phase 5 instead of brucite and phase 3, and that hydration of MgO in ERDA-6 brine will produce only brucite. Therefore, both experimental and modeling studies now agree that phase 5 is stable with respect to phase 3 under conditions expected in WIPP disposal rooms.

Freyer (Freyer 2012), however, concluded that phase 3 is stable with respect to phase 5 under the conditions expected in a German domal salt repository. It is possible that phase 5 is stable under expected WIPP conditions but that phase 3 is stable in German domal salt repositories because the conditions expected in the WIPP differ from those in German repositories (e.g., different brine compositions, elevated temperatures in German repositories but not in the WIPP, etc.). Brush, Xiong, and Long (Brush, Xiong, and Long 2009) demonstrated that whether phase 3 or phase 5 is stable in GWB has very little effect on the predicted composition of this brine, including An solubilities. (Neither phase 3 nor phase 5 ever forms in ERDA-6 brine, so which of these phases is stable is irrelevant in the case of PA calculations using An solubilities predicted for this brine.)

MgO-4.2 Carbonation of MgO

The CRA-2009, Appendix MgO-2009, Section 4.2 (U.S. DOE 2009) discussed the carbonation of MgO, the formation of hydromagnesite and (perhaps) magnesite in the WIPP, and the possible passivation of MgO.

MgO-4.2.1 Results since the CRA-2009

Since the CRA-2009, Xiong determined the solubility constant of hydromagnesite (5424) ($Mg_5(CO_3)_4(OH)_2$ $4H_2O$) in NaCl solutions up to 4.4 M (Xiong 2011c).

MgO-5.0 Effects of MgO on the WIPP Disposal System

This section reviews the effects of MgO on (1) brine composition, f_{CO_2}, pH, and An solubilities, including changes since the CRA-2009 (Section MgO-5.1); (2) colloidal An concentrations (Section MgO-5.2); (3) other near-field processes and conditions, including repository H_2O content, gas generation, and room closure (Section MgO-5.3); and (4) far-field An transport (Section MgO-5.4).

MgO-5.1 Effects of MgO on Brine Composition, f_{CO_2}, pH, and An Solubilities

The DOE is emplacing MgO in the WIPP to decrease the solubilities of the An elements in TRU waste by consuming all the CO_2 that would be produced by microbial activity should all the CPR materials in the repository be consumed. Consumption of CO_2 will decrease An solubilities by (1) buffering f_{CO_2} at a low value or within a low range of values, (2) maintaining a mildly basic pH, and (3) preventing the production of significant carbonate ion (CO_3^{2-}) quantities.

The effects of MgO carbonation have been included in WIPP PA by removing CO_2 from the gaseous phase in BRAGFLO calculations, and using the values of f_{CO_2} and pH predicted for reactions among MgO, brine, and aqueous or gaseous CO_2 to calculate An solubilities.

Table MgO-1 provides the initial compositions of GWB and ERDA-6 brine and their compositions predicted by EQ3/6 for the An-solubility calculations for the CRA-2014 PA (Brush and Domski 2013b) after equilibration with (1) the MgO hydration and carbonation products brucite ($Mg(OH)_2$) and hydromagnesite (5424), respectively; (2) halite (NaCl) and anhydrite ($CaSO_4$), two of the most abundant minerals in the Salado; and (3) the An-bearing solids $Am(OH)_3$; hydrous, amorphous ThO_2; and $KNpO_2CO_3$. In addition to these solids, which are specified in the input files, EQ3/6 predicted that (1) the solids phase 5 and whewellite (Ca oxalate hydrate, or $CaC_2O_4{\cdot}H_2O$) would precipitate from GWB; and (2) glauberite ($Na_2Ca(SO_4)_2$) and whewellite would precipitate from ERDA-6 brine if these brines equilibrate with brucite, hydromagnesite (5424), halite, and anhydrite. Note that the prediction that phase 5 would precipitate from GWB but not ERDA-6 brine is consistent with previous laboratory and modeling studies of the hydration of MgO carried out for the WIPP (see Sections MgO-4.1 and MgO-4.1.1). Note also that because oxalate (and other organic ligands) was included in these brines for the CRA-2014 PA calculations, Brush and Domski (Brush and Domski 2013b) predicted that whewellite would precipitate.

EQ3/6 predicts that equilibration of these brines with the solids listed above will (1) establish a total inorganic carbon (TIC) concentration of 3.79×10^{-4} M in GWB, and decrease the TIC concentration from 1.6×10^{-2} M to 4.55×10^{-4} M in ERDA-6 brine; (2) buffer f_{CO_2} at 3.14×10^{-6} atmospheres (atm) in both brines; and (3) establish a pH of 8.82 in GWB and increase the pH from 6.17 to 8.99 in ERDA-6 brine.

Equilibration of GWB and ERDA-6 brine with these solids will also change the concentrations of the major and other minor elements in these brines. In particular, the concentration of Mg in GWB will decrease from 1.02 to 0.330 M, but will increase from 0.019 to 0.136 M in ERDA-6 brine (Table MgO-1).

Table MgO-1. Compositions of GWB and ERDA-6 Brine Predicted by EQ3/6 for the An-Solubility Calculations for the CRA-2014 PA (Brush and Domski 2013b) (M, Unless Otherwise Noted) before and after Equilibration with Brucite, Hydromagnesite, Halite, Anhydrite, Other Solids and Organics

Dissolved Element or Property	GWB before Reaction with Solids[a]	GWB after Reaction with Solids[b]	ERDA-6 Brine before Reaction with Solids[c]	ERDA-6 Brine after Reaction with Solids[d]
B(III)	0.158	0.186	0.063	0.0623
Na(I)	3.53	4.77	4.87	5.30
Mg(II)	1.02	0.330	0.019	0.136
K(I)	0.467	0.550	0.097	0.0960
Ca(II)	0.014	0.0111	0.012	0.0116
S(VI)	0.177	0.216	0.170	0.182
Cl(−I)	5.86	5.36	4.8	5.24
Br(−I)	0.0266	0.0313	0.011	0.0109
f_{CO_2} (atm)	-	3.14×10^{-6}	-	3.14×10^{-6}
Ionic strength	-	6.44	-	5.99
pH[e] (std. units)	-	8.82	6.17	8.99
pcH	-	9.54	-	9.69
RH (%)[f]	-	73.5	-	74.7
TIC	-	3.79×10^{-4}	16	4.55×10^{-4}

[a] From Krumhansl et al. (1991) and Snider (2003b).

[b] From Brush and Domski (2013b, Table 5, 1 × Minimum).

[c] From Popielak et al. (1983).

[d] From Brush and Domski (2013b, Table 6, 1 × Minimum).

[e] The Pitzer scale is an unofficial pH scale consistent with pH values calculated using single-ion activity coefficients based on the Pitzer activity-coefficient model for brines and evaporite minerals of Harvie (Harvie et al. 1984), extended to include Nd(III), Am(III), and Cm(III); Th(IV); and Np(V). T. J. Wolery of Lawrence Livermore National Laboratory proposed the term "Pitzer scale" unofficially.

[f] Relative humidity.

MgO-5.2 Effects of MgO on Colloidal An Concentrations

The CRA-2009, Appendix MgO-2009, Section 5.2, and U.S. DOE 2004, Appendix BARRIERS, Section BARRIERS-2.3.3 (U.S. DOE 2009) described the effects of MgO on colloidal An concentrations. There has been no change to the conceptual colloid model since the CRA-2009; however, a number of parameters have been updated for the CRA-2014 (Appendix SOTERM-2014, Section 3.8). Refer to the CCA, Appendix SOTERM (U.S. DOE 1996), for information on the colloid conceptual model.

MgO-5.2.1 Changes since the CRA-2009

In its Technical Support Document related to CRA-2009, Appendix MgO, the EPA (U.S. EPA 2010b) stated that "although the mineral-fragment colloids reported in the recent literature are not expected to be stable in WIPP brines, examination of the data used to develop the colloidal actinide source term model has shown that possible formation of mineral fragment colloids by

MgO and its hydration and carbonation products under WIPP-relevant conditions has not been evaluated" (U.S. EPA 2010). This statement is partially in response to a study by Altmaier (Altmaier et al. 2004) that discussed the formation of colloids of magnesium chloride hydroxide hydrate, $Mg_2Cl(OH)_3{\bullet}4H_2O$, which is termed as phase 3 in cement literature, in their experiments in 4.5 M $MgCl_2$. The Altmaier (Altmaier et al. 2004) study raised the possibility that Mg-Cl-OH colloids could form in brines in the presence of MgO and that these colloids could sorb radionuclides and transport them. Therefore, the investigation into the presence or absence of Mg-Cl-OH colloids under the WIPP relevant conditions was necessary, as the presence of such colloids could have an effect on the actinide source term.

Since the CRA-2009, a series of experiments has been developed to investigate the potential formation of Mg-Cl-OH colloids under WIPP-relevant conditions and, if formed, the capacity of such colloids to sorb Th(IV) as mineral-fragment colloids in the WIPP source term (Xiong and Kim 2011). For GWB in the presence of MgO, the thermodynamically favored Mg-Cl-OH phase is $Mg_3Cl(OH)_5{\bullet}4H_2O$, termed as phase 5 in cement literature; no Mg-Cl-OH phase is thermodynamically favored in ERDA-6 in the presence of MgO (Xiong and Lord 2008). These experiments are in progress and results will be reported as they are available. As part of this effort, the study of Altmaier (Altmaier et al. 2004) was critically evaluated. Based on the results of this analysis it can be concluded that the formation of Mg-Cl-OH mineral fragment colloids in the Altmaier (Altmaier et al. 2004) study was an artifact of the experimental setup. The colloids formed due to the drastic pH shift when two disequilibrium solutions (concentrated $MgCl_2$ brine containing dissolved Th-nitrate and NaOH solution) were mixed. This "rapid precipitation" process that lead to the formation of colloids would not be expected to form within an actual system. These conclusions were substantiated in personal communication with Dr. Marcus Altmaier (Sassani 2013).

MgO-5.3 Effects of MgO on Other Near-Field Processes and Conditions

Section MgO-5.3.1, Section MgO-5.3.2, and Section MgO-5.3.3 are based on the text in the CRA-2004, Appendix BARRIERS, Section BARRIERS-2.3.4.1, Section BARRIERS-2.3.4.2, and Section BARRIERS-2.3.4.3.

MgO-5.3.1 Effects of MgO on Repository H_2O Content

The hydration of periclase could consume significant quantities of H_2O in the WIPP (Reaction [MgO.1]). The carbonation of brucite to form hydromagnesite (5424) or, less likely, hydromagnesite (4323), will not release this H_2O unless hydromagnesite (5424) or (4323) goes on to form magnesite. Furthermore, even if large quantities of magnesite form during the 10,000-year regulatory period, there will still be large quantities of periclase available for hydration because the DOE is emplacing more MgO than necessary to consume all the CO_2 that would be produced by microbial activity should all the CPR materials in TRU waste and waste containers be consumed.

MgO-5.3.1.1 Changes since the CRA-2009

During its completeness review of the CRA-2009, the EPA identified implementation of a more comprehensive H_2O budget for WIPP disposal rooms as a possible improvement in the WIPP PA

(U.S. EPA 2010). Previous PAs (e.g., the 1997 PAVT, and the CRA-2004 PABC) included the effects of H_2O consumption and hydrogen (H_2) production by anoxic corrosion of steels and other iron-base (Fe-base) alloys in steel waste containers and in steels and other alloys in the waste. These PAs also included production of various gases by microbial consumption of CPR materials; and implicitly included hydrogen sulfide (H_2S) and CO_2 consumption by sulfidation of steels and other Fe-base alloys and carbonation of MgO, respectively. However, it was assumed that microbial consumption of CPR materials, sulfidation of steels and other Fe-base alloys, and MgO carbonation neither consumed nor produced H_2O (Camphouse 2013).

The CRA-2014 PA included: (1) hydration of periclase (MgO) to form brucite, which consumes H_2O; (2) carbonation of brucite to form hydromagnesite, which neither consumes nor produces H_2O; and (3) the reaction of hydromagnesite to form magnesite ($MgCO_3$) and brucite, which releases H_2O (Camphouse 2013). The reaction of hydromagnesite to magnesite was included because hydromagnesite is thermodynamically unstable with respect to magnesite and thus might proceed to a significant extent during the 10,000-year WIPP regulatory period. Another possible hydromagnesite-magnesite reaction, which consumes CO_2 and releases H_2O but does not produce brucite (Appendix MgO-2009, Equation MgO.9 (U.S. DOE 2009)), was not included in the CRA-2014 PA. Appendix PA-2014 provides additional details regarding the inclusion of MgO hydration and carbonation in the near-field H_2O budget and the results of this change.

MgO-5.3.2 Effects of MgO on Gas Generation

The two gas-producing processes included in WIPP PA are anoxic corrosion of steels and other Fe-base alloys, which will produce H_2, and microbial consumption of CPR materials, which will produce mainly CO_2, hydrogen sulfide (H_2S), and methane (CH_4).

MgO-5.3.2.1 Gas Generation from Anoxic Corrosion

Appendix MgO-2009, Section 5.3.2.1 (U.S. DOE 2009) provided a description of the effects of MgO on gas generation from anoxic corrosion of steels and other Fe-base alloys. Since the CRA-2009, a new series of steel and lead corrosion experiments has been conducted (Roselle 2009, Roselle 2010, Roselle 2011a, Roselle 2011b, and Roselle 2013). The object of these experiments has been to determine steel and lead corrosion rates under more WIPP-relevant conditions. In these experiments, steel and lead coupons were immersed in brines under WIPP-relevant conditions using a continuous gas flow-through system. The experimental apparatus maintained the following conditions: pO_2 less than 5 parts per million (ppm); temperature of 26 °C; relative humidity at 78% ± 10%; and a range of CO_2 concentrations (0, 350, 1500 and 3500 ppm, balance N_2). Four high-ionic-strength brines were used: GWB, ERDA-6 brine, GWB with organic ligands (EDTA, acetate, citrate, and oxalate), and ERDA-6 brine with the same ligands. The composition of the experimental brines used was that calculated by Brush (Brush 2005) for brines equilibrated with MgO, halite and anhydrite. Therefore, the anoxic corrosion experiments of Roselle (Roselle 2009, Roselle 2010, Roselle 2011a, and Roselle 2011b) incorporated the effects of MgO on brine chemistry.

MgO-5.3.2.2 Microbial Gas Generation

Experiments by Leonard (Leonard et al 1999) on the potential toxicity of MgO to WIPP-relevant microorganisms suggested that MgO inhibited growth at concentrations above 0.5 grams per liter (g/L), but only in the absence of a pH buffer. The effects of MgO on microbial gas generation in this study were inconclusive. Appendix MgO-2009, Section MgO-5.3.2.2 (U.S. DOE 2009) reviewed studies of the potential toxicity of MgO to non-WIPP microorganisms.

No additional studies of the effects of MgO on microbial gas generation by WIPP-relevant microorganisms under expected WIPP conditions have been carried out since Leonard (Leonard et al 1999). However, WIPP-specific data obtained by Swanson (Swanson et al 2012) demonstrate that many WIPP-relevant microbes, especially haloarchaea, grow well at high $MgCl_2$ concentrations (~1.0 M) and can tolerate pH up to 9.5.

MgO-5.3.3 Effects of MgO on Room Closure

Appendix MgO-2009, Section 5.3.3 (U.S. DOE 2009) described the effects of MgO on room closure. There is no new information since the CRA-2009 on the effects of MgO on this process.

MgO-5.4 Effects of MgO on Far-Field An Transport

The CRA-2009, Appendix MgO-2009, Section 5.4 (U.S. DOE 2009) discussed the effects of MgO on far-field An transport. In particular, this discussion focused on the effects of MgO on the matrix distribution coefficients (K_ds) for dissolved thorium (Th), uranium (U), Pu, and americium (Am) in the Culebra member of the Rustler Formation. Since the CRA-2009, there have been changes in these K_ds; however, there have been no changes in the effects of MgO on these K_ds.

MgO-6.0 The MgO Excess Factor

The CRA-2009, Appendix MgO-2009, Section MgO-6.0 (U.S. DOE 2009) provided a detailed description of the MgO excess factor and its use in the WIPP. The MgO excess factor is defined as the ratio of the total amount of MgO to be emplaced in the WIPP divided by the total amount required to consume all of the CO_2 produced by microbial activity should all of the CPR materials in the repository be consumed. There have been no changes in the MgO excess factor since the CRA-2009.

MgO-7.0 References

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