Title 40 CFR Part 191
Subparts B and C
Compliance Recertification Application 2019
for the
Waste Isolation Pilot Plant

Appendix MgO-2019
Magnesium Oxide as an Engineered Barrier

United States Department of Energy
Waste Isolation Pilot Plant

Carlsbad Field Office
Carlsbad, New Mexico
# Table of Contents

MgO-1.0 Introduction ............................................................................................................ MgO-1

MgO-2.0 Description of the Engineered Barrier System................................................... MgO-2
   MgO-2.1 Emplacement of MgO ................................................................................ MgO-2
   MgO-2.2 MgO Vendors ............................................................................................. MgO-3

MgO-3.0 Characteristics of MgO .................................................................................... MgO-4
   MgO-3.1 Changes since the CRA-2014 ................................................................. MgO-4

MgO-4.0 Effects of MgO on the WIPP Disposal System ................................................. MgO-5
   MgO-4.1 Effects of MgO on Colloidal An Concentrations ....................................... MgO-5
   MgO-4.2 Effects of MgO on Other Near-Field Processes and Far-Field
       Conditions and Processes .................................................................................. MgO-7
       MgO-4.2.1 Effects of MgO on Repository H₂O Content ..................................... MgO-7
       MgO-4.2.2 Effects of MgO on Gas Generation .................................................. MgO-7
   MgO-4.3 Effects of MgO on Room Closure ............................................................ MgO-8
   MgO-4.4 Effects of MgO on Far-Field An Transport .............................................. MgO-8

MgO-5.0 The MgO Excess Factor .................................................................................... MgO-8

MgO-6.0 References ........................................................................................................ MgO-8
# Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>percent</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous</td>
</tr>
<tr>
<td>atm</td>
<td>atmosphere(s)</td>
</tr>
<tr>
<td>CCA</td>
<td>Compliance Certification Application</td>
</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
</tr>
<tr>
<td>CH-TRU</td>
<td>contact-handled transuranic</td>
</tr>
<tr>
<td>CPR</td>
<td>cellulosic, plastic, and rubber</td>
</tr>
<tr>
<td>CRA</td>
<td>Compliance Recertification Application</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>ECO</td>
<td>Engineering Change Order</td>
</tr>
<tr>
<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>ERDA</td>
<td>Energy Research and Development Administration</td>
</tr>
<tr>
<td>g</td>
<td>gaseous or gram</td>
</tr>
<tr>
<td>GWB</td>
<td>Generic Weep Brine</td>
</tr>
<tr>
<td>HDPE</td>
<td>high-density polyethylene</td>
</tr>
<tr>
<td>K&lt;sub&gt;d&lt;/sub&gt;</td>
<td>matrix distribution coefficient</td>
</tr>
<tr>
<td>kD</td>
<td>kiloDalton</td>
</tr>
<tr>
<td>lb</td>
<td>pound</td>
</tr>
<tr>
<td>M</td>
<td>molar</td>
</tr>
<tr>
<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>cubic meters</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>PA</td>
<td>Performance Assessment</td>
</tr>
<tr>
<td>PABC</td>
<td>Performance Assessment Baseline Calculations</td>
</tr>
<tr>
<td>PAVT</td>
<td>Performance Assessment Verification Test</td>
</tr>
<tr>
<td>RH-TRU</td>
<td>remote-handled transuranic</td>
</tr>
<tr>
<td>s</td>
<td>second(s) or solid</td>
</tr>
<tr>
<td>SNL</td>
<td>Sandia National Laboratories</td>
</tr>
<tr>
<td>SPC</td>
<td>Salado Primary Constituents</td>
</tr>
<tr>
<td>TRU</td>
<td>transuranic</td>
</tr>
<tr>
<td>WIPP</td>
<td>Waste Isolation Pilot Plant</td>
</tr>
<tr>
<td>WTS</td>
<td>Washington TRU Solutions, LLC</td>
</tr>
</tbody>
</table>
Elements and Chemical Compounds

Am americium
An actinide
CaO calcium oxide or lime
CH₄ methane
Cl⁻ chloride ion
Cl chlorine
CO₂ carbon dioxide
CO₃²⁻ carbonate ion
Cs⁺ cesium ion
Cs cesium
$\textit{f}_\text{CO}_2$ fugacity of CO₂
Fe iron
H⁺ hydrogen ion
H₂ hydrogen gas
H₂O water
H₂S hydrogen sulfide
Mg magnesium
Mg(OH)₂ brucite
Mg₂Cl(OH)₃·4H₂O phase 3
Mg₃Cl(OH)₅·4H₂O phase 5
Mg₄(CO₃)₃(OH)₂·3H₂O hydromagnesite (4323)
Mg₅(CO₃)₄(OH)₂·4H₂O hydromagnesite (5424)
MgCO₃ magnesite
MgO magnesium oxide
NaCl sodium chloride or halite
O₂ oxygen
OH⁻ hydroxyl species
pH the negative, common logarithm of the activity of H⁺
Pu plutonium
Th thorium
U uranium
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 by consuming all the carbon dioxide (CO$_2$) that would be produced by microbial activity should all the cellulosic, plastic, and rubber (CPR) materials in the repository be consumed. Details are provided in following documents (Compliance Certification Application (CCA), Appendix BACK and Appendix SOTERM (U.S. DOE 1996); 2004 Compliance Recertification Application (CRA-2004) Appendix BARRIERS-2004, Appendix PA-2004, and Attachment SOTERM-2004 (U.S. DOE 2004); CRA-2009 Appendix MgO-2009 and Appendix SOTERM-2009 (U.S. DOE 2009); and CRA-2014 Appendix MgO-2014 and Appendix SOTERM-2014 (U.S. DOE 2014)). Because it will decrease An solubilities, MgO meets 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, 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. 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 CO$_2$ that would be produced should microbial activity consume all of the 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 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, as the partial pressure of CO$_2$(g) controlled by the assemblage of brucite-hydromagnesite(5424) in the
repository is so low (i.e., in the order of $\sim 10^{-6}$ atm). This assumption has been implemented in PA by (1) removing CO$_2$ from the gaseous phase in the Brine and Gas Flow 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 1996); (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, U.S. DOE 2014). These assumptions are not changed for CRA-2019.

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-2.1) and the vendors that provided or are providing MgO to the WIPP (Section MgO-2.2).

Washington TRU Solutions, LLC (WTS) (WTS 2009a) revised the specifications for the prepackaged MgO emplaced in the WIPP that continues to be used by the current Management & Operating Contractor, Nuclear Waste Partnership LLC.

**MgO-2.1 Emplacement of MgO**

Sections MgO-2.1.1 through MgO-2.1.4 of the Appendix MgO-2014 provided a history of the changes related to emplacement of MgO in the WIPP. One month prior to submittal of the CRA-2014, because of the occurrences of a fire on February 5, 2014, and a radiological release on February 14, 2014, in the WIPP underground, WIPP operations were shut down and emplacement operations discontinued. WIPP operations remained shut down until 2017. When WIPP resumed waste emplacement operations in 2017, emplacement of waste along with MgO was conducted according to the protocol that was in place when the shut-down began in February 2014. The DOE continues to emplace waste in several types of containers (Appendix DATA-2014, Attachment B) (U.S. DOE 2014), and is now emplacing MgO in 3000- and 4200-
lb supersacks. Waste Handling Operations is now using the Waste Data System 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. Engineering Change Order (ECO) 12137 (WTS 2009a) specified the addition of the reactivity test for periclase and lime (Appendix MgO-2014, Section 2.1.4) 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.

As of December 31, 2012, the DOE had emplaced 84,892.57 cubic meters (m³) of contact-handled transuranic (CH-TRU) waste in 17,108 stacks, and 309.68 m³ 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 MgO racks. These racks are used to stack multiple MgO supersacks in the footprint of one waste column. The overall MgO excess factor (see MgO-6.0) as of December 31, 2012, was 1.810 (Kouba 2013).

Between January 1, 2013, and January 8, 2018, the DOE had emplaced 6,994.03 m³ of CH-TRU waste in 1,234 stacks, and 46.88 m³ of remote-handled transuranic (RH-TRU) waste in 99 boreholes and 9 of shielded container assemblies in the repository. During the same time frame, the DOE had emplaced 708 of the 3,000-lb sacks and 121 of the 4,200-lb supersacks, but none of the 25-lb minisacks, 4,100-lb supersacks, or MgO racks. The overall MgO excess factor for the entire repository as of January 8, 2018, was 1.792 (Offner 2018).

Since the cause of the shut-down was fire-related, the DOE considered reducing the amount of cardboard in the repository by using metal stiffeners instead of cardboard stiffeners for the supersacks. However, metal stiffeners were found to interfere with the desire to have supersacks rupture under pressure, and therefore metal stiffeners were not used (Klein 2018). As of January 8, 2018, the packing material for MgO supersacks was still polypropylene with cardboard stiffeners (Klein 2018).

**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, and 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).

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 as of January 8, 2018.

**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). That information was repeated in CRA-2014, Appendix MgO, Section MgO-3.0 ([U.S. DOE 2014]). As of January 8, 2018, there is no new information beyond that already reported regarding the characteristics of the materials provided by these vendors.

**MgO-3.1 Changes since the CRA-2014**

From January 1 to December 31, 2013, the WIPP received 6 bulk shipments of MgO and conducted 60 reactivity tests. The average reactivity of these samples was 97.0 mol % ([Batchelder 2018a]).

From January 1 to December 31, 2014, the WIPP received 1 bulk shipment of MgO and conducted 10 reactivity tests. During the same year WIPP performed 3 extra reactivity tests on the bulk MgO pile at the bagging vendor. The average reactivity of these 13 samples was 95.3 mol % ([Batchelder 2018a]).

Therefore, the average reactivity of MgO was 96.2 mol % before the WIPP was shut down in February 2014 because of a fire and a radiological release that happened in that month (also see below). This average reactivity meets the EPA’s requirement of 96 mol %.

Because of the fire on February 5, 2014, and radiological release on February 14, 2014, no more bulk MgO shipments were requested. Also, the WIPP lost its bagging vendor in 2014, so all built and staged supersacks were moved to the WIPP surface facility ([Batchelder 2018a]).

From January 1 to December 31, 2016, the WIPP had roughly 577 tons (385 sacks) of MgO stored on the surface. Owing to the length of time the MgO was stored on the surface, a decision
was made to resample for reactivity. There were 18 reactivity tests done with an average reactivity of 95.9 mol % (Batchelder 2018a).

From January 1 to December 31, 2017, there were 21 reactivity tests done with an average reactivity of 96.1 mol % (Batchelder 2018a). This is also true for the cut-off date of January 8, 2018 (Batchelder 2018b).

Hence, the average reactivity of MgO was 96.0 mol % after the WIPP was re-opened and resumed operations. This average reactivity meets the EPA’s requirement of 96 mol %.

**MgO-4.0 Effects of MgO on the WIPP Disposal System**

This section reviews the effects of MgO on (1) mineral fragment colloid concentrations (Section MgO-4.1), (2) repository H2O content (Section MgO-4.2.1), (3) gas generation (Section MgO-4.2.2), (4) room closure (Section MgO-4.3); and (5) far-field An transport (Section MgO-4.4). The effects of MgO on brine composition, f CO2, and pH are discussed in Appendix GEOCHEM-2019.

**MgO-4.1 Effects of MgO on Colloidal An Concentrations**

CRA-2014, Appendix MgO-2014, Section 5.2; CRA-2009, Appendix MgO-2009, Section 5.2; and U.S. DOE 2004, Appendix BARRIERS, Section BARRIERS-2.3.3 (U.S. DOE 2004) described the effects of MgO on colloidal An concentrations. There has been no change to the conceptual colloid model since the CCA and the reader is referred to the CCA, Appendix SOTERM (U.S. DOE 1996), for information on the colloid conceptual model. However, a number of updated parameters in the colloid process model were implemented for the CRA-2014 (Appendix SOTERM-2014, Section 3.8), particularly since the EPA noted in its Technical Support Document related to CRA-2009, Appendix MgO, 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 Altmair et al. (Altmair et al. 2004) that discussed the formation of colloids of magnesium chloride hydroxide hydrate, Mg2Cl(OH)3•4H2O, which is called phase 3 in cement literature, in their experiments in 4.5 M MgCl2. The Altmair 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, investigation into the presence or absence of Mg-Cl-OH colloids under WIPP-relevant conditions was initiated, as the presence of such colloids could have an effect on the actinide source term.

Again, in its Technical Support Document related to CRA-2014, Appendix MgO, the EPA stated that “Although formation of the Mg colloids observed by Altmair et al. (2004) remains unlikely because of differences in the brines and Mg chloride-hydroxide-hydrate solid phases between their experiments and WIPP brines, whether MgO reaction products in WIPP brines might form mineral fragment colloids capable of sorbing actinides remains unresolved. It would be
appropriate for DOE to address this issue by performing experiments with WIPP brines and MgO” (U.S. EPA 2017).

A series of experiments was 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 2014). For the WIPP Generic Weep Brine (GWB) from the Salado Formation in the presence of MgO, the thermodynamically favored Mg-Cl-OH phase is Mg₃Cl(OH)₅•4H₂O, called phase 5 in cement literature; no Mg-Cl-OH phase is thermodynamically favored in Energy Research and Development Administration (ERDA)-6 in the presence of MgO (Xiong and Lord 2008). The WIPP ERDA-6 brine is from the Castile Formation (Popielak et al. 1983). The experiments have progressed systematically since 2011 when they were initiated (Xiong et al. 2017). The aim of the experiments is to confirm the presence or absence of mineral fragment colloids related to MgO in high ionic strength solutions (brines).

Xiong et al. (2017) evaluated the possible formation of mineral fragment colloids using two approaches. The first approach was an analysis of long-term MgO hydration and carbonation experiments performed at Sandia National Laboratories (SNL) as a function of equivalent pore sizes. The MgO hydration products include Mg(OH)₂ (brucite) and Mg₃Cl(OH)₅•4H₂O (phase 5), and the carbonation product includes Mg₅(CO₃)₄(OH)₂•4H₂O (hydromagnesite). All these phases contain magnesium. Therefore, if mineral fragment colloids of these hydration and carbonation products were formed in the SNL experiments mentioned above, magnesium concentrations in the filtrate from the experiments would show a dependence on ultrafiltration. In other words, there would be a decrease in magnesium concentrations as a function of ultrafiltration with decreasing molecular weight (MW) cut-offs for the filtration. Therefore, Xiong et al. (2017) performed ultrafiltration on solution samples from the SNL hydration and carbonation experiments as a function of equivalent pore size. Xiong et al. (2017) filtered solutions using a series of MW cut-off filters at 100 kiloDalton (kD), 50 kD, 30 kD, and 10 kD. The results from these tests demonstrate that the magnesium concentrations remain constant with decreasing MW cut-offs, implying the absence of mineral fragment colloids.

In the work of Xiong et al. (2017), the second approach used spiked cesium ion (Cs⁺) to indicate the possible presence of mineral fragment colloids. Cs⁺ is easily absorbed by colloids. Therefore, Xiong et al. (2017) added Cs⁺ to a subset of SNL MgO hydration and carbonation experiments. Again, the solutions were filtered with a series of MW cut-off filters at 100 kD, 50 kD, 30 kD, and 10 kD. This time Xiong et al. (2017) measured the concentrations of Cs. The concentrations of Cs did not change as a function of MW cut-offs, indicating the absence of colloids from MgO hydration and carbonation products. Therefore, both approaches employed by Xiong et al. (2017) demonstrate the absence of mineral fragment colloids from MgO hydration and carbonation products.

Based on their experimental results, Xiong et al. (2017) state that mineral fragment colloids were not formed in the SNL MgO hydration and carbonation experiments.

In summary, the issue mentioned in the Technical Support Document (U.S. EPA 2017) has been fully addressed in the work of Xiong et al. (2017).
MgO-4.2 Effects of MgO on Other Near-Field Processes and Far-Field Conditions and Processes

Section MgO-4.2.1, Section MgO-4.2.2, and Section MgO-4.3 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-4.2.1 Effects of MgO on Repository H₂O Content

The hydration of periclase could consume significant quantities of H₂O in the WIPP (Reaction MgO.1).

\[
\text{MgO(s) + H}_2\text{O (aq or g)} \rightleftharpoons \text{Mg(OH)}_2(s)
\]  (MgO.1)

The brucite will react with essentially all of the CO₂ that could be produced by complete microbial consumption of the CPR materials in the waste, and will create hydromagnesite (Reaction MgO.2).

\[
5\text{Mg(OH)}_2(s) + 4\text{CO}_2(g) \rightleftharpoons \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2(s) \cdot 4\text{H}_2\text{O}
\]  (MgO.2)

The carbonation of brucite to form hydromagnesite (5424) or, less likely, hydromagnesite (4323), will not release this H₂O unless hydromagnesite (5424) or (4323) goes on to form magnesite.

\[
\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}(s) \rightleftharpoons 4\text{MgCO}_3(s) + \text{Mg(OH)}_2(s) + 4\text{H}_2\text{O}(l)
\]  (MgO.3)

These three reactions are reflected in water balance calculations in performance assessments for WIPP. Since hydromagnesite is not thermodynamically stable under repository conditions, it is expected to dehydrate to form magnesite, as indicated in Reaction (MgO.3). The timing for the hydromagnesite to dehydrate to form magnesite is uncertain and is therefore represented by a distribution of reaction times in Pa.

There is no additional work regarding the effect of MgO on repository water content since the CRA-2014.

MgO-4.2.2 Effects of MgO on Gas Generation

The two gas-producing processes included in WIPP PA are anoxic corrosion of steels and other Fe-based alloys, which will produce H₂, and microbial consumption of CPR materials, which will produce mainly CO₂, hydrogen sulfide (H₂S), and potentially methane (CH₄). The major effect of MgO is to remove CO₂. The presence of MgO has an effect on steel corrosion because the brines that come in contact with steel in the repository are assumed to be in equilibrium with hydration/carbonation products of MgO as well as the minerals in the host rock, as a solubility controlling-assemblage. Thus, the brine composition is altered from that in equilibrium with the host rock alone. In turn, the brine composition affects corrosion. However, the effect of CO₂(g) on the steel corrosion rates is expected to be negligible. This is because, as mentioned in Section MgO-1.0, the partial pressure of CO₂(g) controlled by the assemblage of brucite-
hydromagnesite(5424) in the repository is so low (i.e., in the order of $\sim 10^{-6}$ atm). This process is described in more detail in Appendix GEOCHEM-2019.

With regard to 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 in Brine A, 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.

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 ($\sim 1.0$ M) and can tolerate pH up to 9.5.

**MgO-4.3 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. No new information was introduced in CRA-2014, and no new information is being introduced for CRA-2019.

**MgO-4.4 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 ($K_{d}$s) for dissolved thorium (Th), uranium (U), plutonium (Pu), and americium (Am) in the Culebra Member of the Rustler Formation. Since the CRA-2009, there have been changes in these $K_{d}$s; however, there have been no changes in the effects of MgO on these $K_{d}$s. No new information was introduced in CRA-2014, and no new information about the effect of MgO on these $K_{d}$s is being introduced for CRA-2019.

**MgO-5.0 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. No new information was introduced in CRA-2014, and no new information is being introduced for CRA-2019.

**MgO-6.0 References**

(*Indicates a reference that has not been previously submitted.)

Batchelder, T. 2018a. E-mail message to Yongliang Xiong (Subject: [EXTERNAL] FW: Reactivity Test for MgO, January 31, 2018. Carlsbad, NM: Nuclear Waste Partnership LLC. ERMS 569318.*

Batchelder, T. 2018b. E-mail message to Yongliang Xiong (Subject: [EXTERNAL] FW: Reactivity Test for MgO, February 28, 2018. Carlsbad, NM: Nuclear Waste Partnership LLC. ERMS 569511.*


Kouba, S., 2013. E-mail message to Laurence H. Brush (Subject: RE: MgO Emplacement Factor as of December 31, 2012; Attachment: CBFO_Emplacement_Statistics-12-31-2012.txt), October 8, 2013. Carlsbad, NM: Nuclear Waste Partnership LLC.


