<div align="center">

Attachment A

Overview Summary of Planned Change Request Decision

</div>

I.   Introduction

DOE submitted a planned change request in April 2006 to decrease the amount of emplaced magnesium oxide (MgO) from 1.67 to 1.2 times the quantity of emplaced carbon in the disposed waste. EPA's position on the engineered barrier is that, as the quantity of magnesium oxide is decreased and approaches a one-to-one relationship with emplaced carbon, a better understanding of system uncertainties are needed. In April 2006, EPA requested that DOE analyze the importance of system uncertainties to gain an understanding of their impact on MgO performance. In November 2006, DOE responded with a detailed uncertainty analysis, but also introduced new issues related to MgO and their impact on the disposal system at the Waste Isolation Pilot Plant (WIPP) (see Attachment B for details). Since DOE's November 2006 response, EPA has been working to better understand and resolve these issues in order to assess the performance implications of the proposed change.

II.   EPA's Review

Because of potential uncertainties in predicting future characteristics at the WIPP and performance uncertainties of WIPP's only engineered barrier, MgO, EPA is concerned about any decrease in the amount of MgO emplaced with waste. MgO is emplaced to control disposal room chemical conditions, absorb carbon dioxide (CO_2) gas generated, and limit radioactive materials transport. Even though EPA has not made it a specific requirement, EPA has taken great comfort in the excess MgO, or safety factor. EPA believes that excess MgO overwhelms uncertainties associated with our understanding of the disposal system performance. Therefore, when DOE requested a change to the MgO emplacement, EPA wanted to ensure that this action would not be detrimental.

EPA's review determined that three areas and their uncertainties needed to be clearly understood: 1) How much carbon is in each disposal room, 2) How much carbon dioxide gas is generated, and 3) How will the MgO effectively control chemical conditions and limit radioactive material transport (see Section 1.0 of Attachment B for details). EPA also had an independent review of its contractor report to assure the adequacy of their work (see Attachments C and D for details). One final result of this review is that the approach and assumptions DOE used overestimates the amount of MgO needed.

IIA.   **How much carbon is in each room?**   EPA examined DOE's approach to estimating how much celluloses, plastics, and rubber materials (CPR) (the sources of

carbon at WIPP) are emplaced in the disposal system. EPA determined that DOE's approach appears adequate and that DOE reasonably estimates the amount of carbon in the waste emplaced at WIPP. The non-regulatory WIPP oversight group, PECOS Management Services, Inc. (PECOS), concluded that DOE's estimation approach is the weakest part of DOE's analysis but may be biased high for many waste streams and generally appears to overestimate the amount of carbon in the waste (see Attachment E Conclusions for details). EPA concluded that DOE reasonably estimates the amount of carbon in waste room when calculating the amount of MgO needed. (See Attachment B and E for more details)

IIB. **How much carbon dioxide gas is generated in a disposal room?** EPA concludes that DOE uses conservative estimates of the amount of CO_2 gas generated in a disposal room because it is assumed that all carbon is converted to CO_2 gas. Carbon dioxide is generated by microbial degradation of CPR waste materials placed in disposal rooms. To degrade CPR, microbes need a nurturing environment, sufficient food (CPR), access to this food source, and sufficient water to sustain the microbes' existence. Microbes operate along very particular pathways: first, they will consume along the denitrification pathway, and then the sulfate pathway, and finally the methanogenesis pathway (see Section 2.2 of Attachment B).

In addition, microbes may not be able to degrade some of the CPR, thus reducing the amount of carbon converted to CO_2 gas. Conditions have to be favorable for CO_2 to be generated, and conditions favorable for microbe survival may not occur in the disposal rooms. To be conservative, presently, EPA requires DOE to assume that ALL carbon in the waste in a room turns into CO_2. PECOS believes that this approach is "…overly conservative…" (See Attachment E page 8). The conservative requirement that all solid carbon is converted to gas compensates for errors that may be associated with estimates of CPR mass.

IIC. **Reactivity of the MgO** DOE provided information on the potential reactivity of the MgO at 96% from the current supplier. EPA found the information reasonable, and requires DOE to ensure that the MgO reactivity remains at 96% by regularly testing MgO samples.

IID. **Is this review conservative?** EPA believes that this approach is conservative. EPA notes a number of conservative assumptions during its review including: conservative estimates of available carbon from the degradation of CPR, and conservative estimates of the amount of CO_2 generated. It is likely that not all available carbon will react to generate CO_2 gas, and that CO_2 may react with other materials, but this effect is not included. In addition, methanogenesis is expected to take place but is not included (see Attachment B, page 5-3). PECOS also believes that DOE's approach is overly conservative (see Attachment E Sections IV and V for details).

III.   Independent Technical Review of SC&A Analysis (Attachments C and D)

EPA required its contactor, SC&A, to have a documented independent technical review of their report. SC&A's quality assurance manager selected Dr. Donald Langmuir to review SC&A's work. Dr. Langmuir agreed with SC&A's conclusions except two (see Attachment D, page 4 for details). He had concerns about segregation of MgO and molecular diffusion. Dr. Langmuir's comments were diligently considered and SC&A responded in Attachment D. The final report was modified as warranted (see Attachment B) to address and clarify these issues. SC&A and EPA believe that these issues have been abundantly dealt with during the history of the WIPP regulatory process, in particular during the Compliance Certification Application Conceptual Model Peer Reviews in 1996 and 1997. PECOS also concurs that these issues are not significant (see Attachment E, sections "The efficiency of mixing processes" and "The physical segregation of MgO from CO_2").

EPA also furthered addressed Dr. Donald Langmuir's main concern that MgO may make some form of a concrete-like material and not be able to react with CO_2 in a waste room (see Attachment E, Section 2.2; also see Attachment B, Section 3.2 and Attachment D). In summary, EPA reexamined work done during the past fifteen or more years on the ability of MgO to be available for reaction with CO_2. This includes the experimental work conducted for the conceptual model peer review at time of the WIPP certification. Based on the existing documentation that addresses this issue, EPA concludes that if CO_2 is generated by microbial activity, MgO will be available to react if DOE continues to use MgO of high purity and calculates the needed MgO on a room-by-room basis.

IV.   Stakeholder Comments:

From August 29, 2007 to October 11, 2007 EPA asked for comments from members of the public. PECOS Management Services, Inc (see Attachment E for details), provided a report with the conclusion that the safety factor reduction to 1.2 is appropriate and could even be reduced further. EPA received no other comments from individuals or groups on this topic.

V.   Conclusion:

EPA approves this planned change with conditions. First, DOE is to continue to calculate and effectively track both the carbon disposed and the required MgO needed on a room-by-room basis. In addition, DOE must, on a regular basis, verify that the reactivity of MgO is maintained at 96% as assumed in DOE's analyses.

Attachment B

Review of MgO-Related Uncertainties in the
Waste Isolation Pilot Plant.

[EPA contractor report]

Attachment C

Letter Report of the SC&A Draft Report "Review of MgO-Related
Uncertainties in the Waste Isolation Pilot Plant

[Independent Review of Attachment B]

HSC hydrochem systems corporation

P.O. Box 23257	1545 Legend Lake Circle	Tel & Fax (970) 262-0655 (Silverthorne)
Silverthorne, CO 80498	Silverthorne, CO 80498	Tel & Fax (720) 570-3474 (Denver)
(U.S. Mail)	(Shipping)	cell (720) 318-7688
		<d.langmuir@comcast.net>

MEMO

To: Dr. Steven L. Ostrow, Work Assignment QA Manager, S. Cohen & Associates, Vienna VA, 22182

From: Dr. Donald Langmuir, QA Technical Specialist, Hydrochem Systems Corp., Silverthorne CO, 80210

Date: November 4, 2007

Subj: Letter report review of the SC&A Draft Report "Review of MgO-Related Uncertainties in the Waste Isolation Pilot Plant". Contract No. EP-D-05-002, Work Assignment No. 3-07

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1.0   Introduction

This is my letter review of the Draft Report. As charged, in this review I will address the following questions:

   a. Does the work product contain a sound and thorough discussion of the problem under investigation, the methodology employed, and the significance of the results?

   b. Have uncertainties been appropriately considered in the review?

   c. Does the review/analysis support the final recommendations/conclusions?

   d. Does the review contain proper documentation of any codes, spreadsheets, problems, data sources, inputs and outputs?

The principal focus of the subject SC&A draft report is to determine if, as the DOE has requested, the excess (safety) factor (EF) for MgO (total moles emplaced MgO/total moles CO_2 consumed) can be decreased from 1.67 to 1.2, where the CO_2 consumed equals the maximum amount of CO_2 that can be produced by breakdown of the estimated amount of carbon disposed of in the Waste Isolation Pilot Plant (WIPP). This decrease in EF if agreed to, should not unacceptably compromise the safe performance of the repository.   In support of their request to reduce the EF from 1.67 to 1.2, the DOE has addressed the following four sources of uncertainty in their calculations of EF (Vugrin et al., 2006) which are either quoted or paraphrased here:

   • Uncertainty in the quantity of CPR (total organic matter, which occurs in cellulose, paper and rubber)

- Uncertainty associated with the quantities of CO_2 produced by microbial degradation of CPR

- Uncertainty related to the amount of MgO available to react with CO_2

- Uncertainty in the moles of CO_2 consumed per mole of available MgO, and in the moles of CO_2 that could be consumed by reaction with other materials

These uncertainties were addressed by DOE (Vugrin et al, 2006; 2007) using the Effective Excess Factor (EEF) which is given by:

$$EEF = \frac{(mxM_{MgO})}{(gxM_{CO2})} r \tag{1}$$

where M_{MgO} is the total moles of emplaced MgO and M_{co2} the maximum number of moles of CO_2 that could be generated by microbial breakdown of all carbon in the CPR. Among the other terms, g is the uncertainty in the moles of CO_2 produced per mole of consumed CPR, m the uncertainty in the moles of MgO available for CO_2 consumption, and r the uncertainty in the moles of CO_2 consumed per mole of emplaced MgO.

The Draft Report evaluates DOE's quantification of the uncertainties through Eq. (1). A fundamental approach taken to the uncertainties in this equation by the DOE and largely agreed to by the Draft Report has been to incorporate, in general, highly conservative assumptions in the calculations.
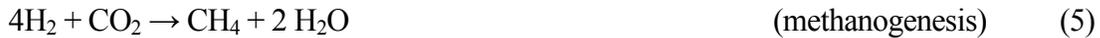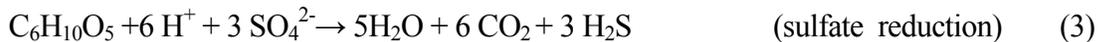
2.0 Uncertainty in the Quantity of CPR

The author of the Draft Report has reevaluated the inventory of total moles of CPR carbon proposed for emplacement in the repository. This reevaluation included a review of the probable chemical composition of the CPR, and calculation of reasonable upper and lower range estimates of the total moles of CPR carbon, which are 1.32×10^9 moles and 1.18×10^9 moles, respectively (p. 2-4). These upper and lower range estimates are 9% greater and 3% lower respectively than estimates of the moles of CPR calculated using the assumptions of Wang and Brush (1996). The assumptions and calculations of the author of the Draft Report appear reasonable.

2.1 Uncertainty in the Quantity of CO_2 Produced by Microbial Degradation of CPR

The DOE (Kirchner and Vugrin, 2006) and the Draft Report conservatively assume that all of the CPR will be microbially degraded to CO_2. This is in spite of expert opinion that the rubber (7% of the C in CPR) and plastics (61% of the C in CPR)(Draft MgO Review, 2007) may experience little or no breakdown during the 10,000 year WIPP regulatory period (Draft Report, 2007, p. 6-1; and SCA, 2006a, Expert Panel Report p. 3-1).

The microbial degradation reactions of CPR may include denitrification, sulfate reduction, and methanogenesis. If for simplicity CPR is assumed to be in its most reactive form, which is cellulose (assumed formula $C_6H_{10}O_5$) these reactions are (Draft Report, p. 2-5 & 2-6):

$$C_6H_{10}O_5 + 4.8\ H^+ + 4.8\ NO_3^- \rightarrow 7.4\ H_2O + 6\ CO_2 + 2.4\ N_2 \qquad \text{(denitrification)} \qquad (2)$$

$$C_6H_{10}O_5 + 6\ H^+ + 3\ SO_4^{2-} \rightarrow 5H_2O + 6\ CO_2 + 3\ H_2S \qquad \text{(sulfate reduction)} \qquad (3)$$

$$C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3\ CO_2 \qquad \text{(methanogenesis)} \qquad (4)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O \qquad \text{(methanogenesis)} \qquad (5)$$

Denitrification and sulfate reduction reactions yield 1 mole of CO_2 for every mole of carbon in CPR. The first methanogenesis reaction produces 0.5 moles of CO_2 per mole of carbon in CPR, whereas the second methanogenesis reaction actually consumes CO_2.

There is little nitrate in the repository, however sulfate occurs in the waste and brines and in minerals in the Salado Formation including anhydrite, gypsum and polyhalite. Vugrin et al. (2006) and EPA (2006) have concluded that there is sufficient sulfate present and available from these sources to degrade all of the carbon in CPR via sulfate reduction. This would suggest a CPR-C to CO_2-produced ratio of 1:1. The occurrence of any methanogenesis, which may be unlikely, would reduce the amount of CO_2 produced. Thus, assuming as does the DOE and the Draft Report, that 1 mole of CO_2 is produced by the microbial breakdown of 1 mole of carbon in CPR is conservative, not just because most of the CPR is relatively unreactive, but because its microbial degradation may produce less than 1 mole of CO_2 on average per mole of C in the CPR..

2.2 Uncertainty in the Amount of MgO Available to React with CO_2

A number of studies have examined the composition and reactivity of commercial MgO used or considered for emplacement in the repository. The MgO currently being emplaced and projected for future emplacement, which is manufactured by Martin Marietta, is described as MagChem® 10 WTS-60 MgO. Repeated chemical analyses listed in the Draft Report (p. 3-1) indicate that this product contains 98.5 wt% MgO with an uncertainty of ±2.5 wt% or less. DOE has established a performance specification that 96±2 (1σ) mole% reactive MgO plus CaO be present in 10 WTS-60 MgO. The Draft Report reasonably concludes that 10 WTS-60 MgO will probably continue to meet this specification. Conservatively, the DOE ignores the expected consumption of CO_2 by the lime in WTS-60 MgO.

Several scenarios have been considered that could potentially reduce (or increase) the percent of commercial MgO that would be available to react with CO_2 from the breakdown of CPR. These include: (1) MgO physical segregation from the brine and CO_2; (2) loss of MgO to brines that might leave a waste panel because of a drilling intrusion; (3) incomplete mixing of the waste, brine and CO_2; (4) partial carbonation of the MgO before emplacement; (5) the likelihood that a significant number of MgO supersacks will not rupture; (6) that the supersacks contain less MgO than assumed; and (7) reaction of dissolved Mg in the Salado brine with the CO_2. Among these (1) through (6) could reduce, and (7) could increase the percent of MgO available to react with the CO_2 from CPR.

The Draft Report (see also Vugrin et al., 2007) concludes:

(1) Physical segregation of the MgO is unlikely to be significant;

(2) MgO loss to brine outflow will be less than 1%;

(3) Mixing in the disposal rooms by molecular diffusion alone will assure that all of the MgO and the CO_2 have a chance to react during the 10,000 yr regulatory period;

(4) Partial carbonation of the MgO prior to emplacement is likely to consume less than 0.1% of the MgO;

(5) The MgO supersacks will rupture because of lithostatic load (cf. DOE, 2004) and microbial degradation; and

(6) Uncertainty in the amount of MgO in each supersack (4,200±50 lbs, WTS, 2005) is probably random and insignificant.

(7) Calculation of the amount of CO_2 that could be precipitated as hydromagnesite because of high Mg concentrations in the GWB (Salado) brine, suggests that possibly 2.2% of the CO_2 from CPR breakdown could be so precipitated. This, of course, is conservative, and leaves more unreacted MgO available to consume the remaining CO_2 from CPR.

I agree with the conclusions expressed by DOE and the Draft Report with regard to items (2) and (4) through (7), and consider them properly documented and supported. However, physical segregation of the MgO (Item (1)) may occur (see below), and the calculation of mixing in disposal rooms assuming molecular diffusion (Item (3)) (cf. Kanney and Vugrin, 2006) presumes that such diffusion of H_2O and CO_2 will readily occur through supersack MgO and through its reaction products in the disposal rooms during the 10,000 y regulatory period. This assumes that the initial porosity of 10 WTS-60 MgO (commercial MgO) will remain open to diffusive transport at all times after emplacement. Further discussion of Item 3 is presented later in this review.

2.3   Uncertainty in Moles of CO_2 Consumed per Mole of Available MgO, and in Moles of CO_2 Consumed by Reaction with Other Materials

It is generally assumed that most of the CO_2 from microbial breakdown of CPR will be captured by reaction with MgO (actually with Mg $(OH)_2$) forming either hydromagnesite or magnesite. If this is the case and the reaction product is hydromagnesite, the ratio of CO_2 produced to MgO consumed is 4 to 5, or 0.8. If the product is magnesite the CO_2 to MgO ratio is 1. As discussed below, there are reasons to doubt that all of the MgO in supersacks will be available to react with all of the CO_2 from CPR assuming all of the CPR is biodegraded.

The Draft Report notes that other reactions and processes in the repository may consume some of the CO_2 (cf. Brush and Roselle, 2006; Vugrin et al., 2006). Reducing conditions and dissolved ferrous iron can be expected because of the presence of iron metal in waste containers and in TRU wastes and their corrosion products. This should lead to precipitation of a substantial amount of the CO_2 in siderite ($FeCO_3$) (Brush and Roselle, 2006). Lead materials may also result in minor amounts of lead carbonate precipitate. Also, dissolution of calcium minerals, anhydrite, gypsum and polyhalite in the salt formations will contribute dissolved Ca^{2+} to repository brines which can be expected to react with dissolving CO_2,

precipitating calcite, and possibly pirssonite [$Na_2Ca(CO_3)_2 \cdot 2H_2O$](Draft Report, p. 4-7). Other possible sinks for the CO_2 from CPR are unreacted lime in Portland cements that have been used to solidify waste sludges, and incorporation of the carbon of CO_2 in biomass (Draft Report, p. 4-12). Because the significance of all of these potentially CO_2-consuming secondary processes and reactions has been assessed theoretically but not experimentally, the DOE has decided conservatively to ignore them. This conservative approach is reasonably also adopted by the Draft Report.

3.0　Assumed Reactions of MgO with Water and CO_2 in the Repository

There is a general consensus that in brine or humid environments MgO rapidly hydrates to form $Mg(OH)_2$ (cf. Snider and Xiong, 2002). .

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad\qquad (6)$$

It is now generally agreed also (Snider and Xiong, 2002; DOE, 2004) that under repository conditions the first Mg carbonate to precipitate by reaction of the brucite with CO_2 from CPR breakdown (other than unstable nesquehonite, $MgCO_3 \cdot 3H_2O$, which subsequently alters to hydromagnesite) will be hydromagnesite, which forms according to the reaction:

$$Mg(OH)_2 + 0.8\ CO_2 = 0.2\ Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \qquad\qquad (7)$$
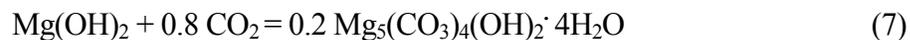
and that later during the 10,000 yr regulatory period, an unknown fraction of the hydromagnesite will react with additional CO_2 and convert to thermodynamically more stable magnesite (DOE, 2004; Brush and Roselle, 2006) by the reaction:

$$0.2\ Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O + 0.2\ CO_2 \rightarrow MgCO_3 + H_2O \qquad\qquad (8)$$
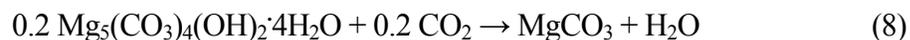
3.1　Experimental and Geologic Analog Evidence Related to the Hydration and Carbonation of MgO

MgO Hydration

Sandia National Laboratories has performed a number of small-scale laboratory experiments to study the hydration and carbonation of MgO (Zhang et al., 2001; Bryan and Snider, 2001; Xiong and Snider, 2003; EPA, 2006). In some of these, termed humid-condition experiments, pellets of MgO or commercial powdered MgO were suspended over salt solutions that defined different relative humidities ranging from 35 to 95%, and temperatures from 25 to 90°C. In other experiments MgO was immersed in DI water and in different salt solutions from 25 to 90°C.

Results of some of these experiments have been inconsistent and others ambiguous in part because of a lack of quantitative identification of the brucite (EPA, 2006). However, generally, they show that the MgO hydrates readily above 35% relative humidity and in solution to form brucite. Hydration rates increase with temperature and relative humidity and decrease with increasing ionic strength. In GWB brine a magnesium-chloride-hydroxide

hydrate salt [$Mg_2Cl(OH)_3 \cdot 4H_2O$] was formed initially, although it converted to brucite with time.

Some of the comments and findings of the Sandia researchers regarding their laboratory hydration results are noteworthy. In her inundation experiments at $90^{\circ}C$, Snider (2003) observed that hydration ceased once 85% of the commercial MgO had been hydrated. The unreacted 15% of material which was apparently not MgO, was not identified.

In the discussion of agitation in their experiments, Snider and Xiong (2002) observed: "Sample agitation was performed to eliminate the formation of lithified hydration products, minimizing the likelihood that cake formation would inhibit hydration by limiting brine access to unhydrated MgO". And "however, hydration products may still inhibit hydration by coating individual particles, or by plugging the internal pores in the MgO grains". Nevertheless, Snider (2002) did observe that in experiments with GWB brine, hydration rates were similar in agitated and unagitated experiments, even when some cementation of the unagitated solids occurred. Regardless, it is important to remember that agitation will not occur in the repository.

<div align="center">Carbonation</div>

Laboratory experiments involving carbonation have been performed for inundated conditions only, using DI water, 4 m NaCl, GWB brine and ERDA-6 brine. Carbon dioxide pressures used have ranged from near atmospheric ($10^{-3.5}$ bars) to 5% CO_2. At atmospheric pressures, Snider and Xiong, (2002) detected hydromagnesite and calcite after 327 days of reaction. Carbonation rates decreased with increasing ionic strength. Nesquehonite was only formed in experiments with 5% CO_2, and it tended to convert to hydromagnesite with time (Snider and Xiong, 2002).

Deng et al. (2006, p. 29) has described presently ongoing DOE studies of carbonation of brucite "to gain a more mechanistic understanding of Mg carbonation". The authors are performing additional laboratory inundation experiments using WIPP brines. As with the experiments described above, their experimental conditions are not realistically related to conditions in the repository which will involve MgO supersacks, and considerably higher MgO solid to brine ratios than have been used in any of the laboratory experiments.

Natural analog studies are consistent with thermodynamic calculations, and show that magnesite is the likely long-term carbonation product of periclase and brucite, and that hydromagnesite is unstable relative to magnesite (Draft Report, p. 4-1; Brush and Roselle, 2006). However, such studies also show that hydromagnesite can persist unaltered for thousands of years (Vance et al., 1992).

Magnesite is found in the Salado Formation. However its occurrence in the Salado, which is about 200,000 million years old, provides no information on the rate of conversion of hydromagnesite to magnesite during the 10,000 y regulatory period.

A number of researchers have studied the kinetics of conversion of hydromagnesite to magnesite in laboratory experiments as a function of ionic strength and temperature in different salt solutions (Sayles and Fyfe, 1973; Zhang et al., 2000). The conversion rate has

generally been found to increase with temperature, ionic strength and CO_2 pressure, and decrease with increasing Mg^{2+} concentration. Because of the slow rate of conversion at the low temperatures and CO_2 pressures expected in the repository, rates have been extrapolated to assumed repository conditions. The assumption of different kinetic models for the extrapolation has led to ambiguous conclusions regarding the conversion rate to be expected at lower repository temperatures.

Because the rate of conversion of hydromagnesite to magnesite is not well defined, the Draft Report (p. 4-7) assumes conservatively and reasonably, that the r parameter in Eq. 1 ranges from 0.8 (hydromagnesite only) to 1.0 (magnesite only), with a uniform distribution across this range.

3.2 Applicability of DOE's Experimental Results for MgO Hydration and Carbonation to the WIPP Repository

Vugrin et al. (2007, Table 3) have listed twelve issues that affect "the fraction of MgO available for Sequestration". All but two of these issues have no impact or have a conservative impact on the calculated EEF in Eq. 1. The remaining two issues, if incorrectly judged by the DOE, could have a major negative impact on the ability of the MgO backfill to sequester CO_2 from CPR breakdown. The first of these is the ability of periclase to react to completion (with CO_2). DOE assumes that all of the periclase will react with and consume all of the CO_2 . The second issue is the segregation of MgO from CO_2. DOE assumes no physical segregation of the MgO, and thus that all of the MgO remains available for reaction with CO_2.

It seems highly dubious that the results of DOE's small-scale laboratory experiments can be extrapolated to conditions in the WIPP repository to support these two assumptions. An obvious difference between the experiments and repository conditions is the solution to MgO ratio in the inundated experiments, where brine volumes vastly exceed the volume of MgO, versus in the repository were brines may only occupy (if they can access them) pore spaces in the MgO or its hydration product $Mg(OH)_2$.

The DOE has not performed any hydration or carbonation experiments under conditions or at a scale that attempts to reproduce the conditions under which hydration and carbonation reactions will occur in the WIPP repository.

Regarding the applicability of the laboratory hydration and carbonation results to the repository, Brush and Roselle (2006, p. 8) state "…all results to date imply that the periclase and lime present in MgO will be available to react – and will continue to react –until all CO_2 in the repository has been consumed…" Note they do not say that the experimental results obtained to date <u>prove</u> that the periclase will be available to react.

Others have also questioned the confidence with which DOE has extrapolated the results of its laboratory experiments to repository conditions. An expert panel quoted by SC&A (2006) states as its 4th finding, that the environment within a disposal room is likely to be heterogeneous and pockets of unreacted MgO are likely to persist. In its 9th finding the same expert panel recommends the formation of an expert elicitation panel to "….address the

fraction of MgO likely to react in the repository environment, and the possible consequences of a partial or complete shortfall in the MgO buffering capacity".
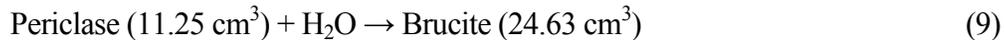
Further, SC&A (2006, p. vi.) comments that "Uncertainties identified during the course of this investigation include the possibility of physical segregation of small quantities of MgO…." "The goal of either…literature review or experimental studies would be to adequately quantify or capture system uncertainties, including….chemical reaction uncertainties related to….reactions with MgO backfill".

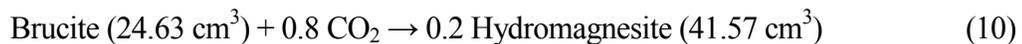## 4.0   Volume Changes that Accompany MgO Hydration and Carbonation

Nothing has been said by the DOE regarding the massive increase in the volume of Mg salts that will result from the hydration and carbonation of MgO. This volume increase will undoubtedly affect the performance and reactivity of the MgO backfill.

The density of the commercial MgO is 87 ± 5 lb/ft^3 (WTS, 2005). This is equivalent to a density of 1.39 g/cm^3. The density of pure, solid MgO is 3.58 g/cm^3 (Weast, 1976), which indicates that the porosity of the commercial MgO is 61%. This porosity may be completely filled and clogged by the hydration and carbonation products of MgO alteration .

Shown below are changes in the molar volume of periclase (MgO) when it is hydrated to form brucite [$Mg(OH)_2$], and when the brucite is later carbonated to form hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] or magnesite ($MgCO_3$). To permit direct comparison, the changes in molar volume of the solids and the cumulative volume increases starting with MgO are shown in terms of one mole of Mg in each solid. Molar volumes of periclase, brucite and magnesite are from Weast (1976). The molar volume of hydromagnesite (207.84 cm^3) is from Mincryst info. card No. 2070 (http://database.iem.ac.ru/mincryst/s_carta2.php?2070+MAIN).

$$\text{Periclase (11.25 cm}^3\text{)} + H_2O \rightarrow \text{Brucite (24.63 cm}^3\text{)} \tag{9}$$

(219% solids volume increase)

$$\text{Brucite (24.63 cm}^3\text{)} + 0.8\ CO_2 \rightarrow 0.2\ \text{Hydromagnesite (41.57 cm}^3\text{)} \tag{10}$$

(169% solids volume increase from brucite,

370% solids volume increase from periclase)

$$0.2\ \text{Hydromagnesite (41.57 cm}^3\text{)} + 0.2 CO_2 \rightarrow \text{Magnesite (28.02 cm}^3\text{)} + H_2O \tag{11}$$

(67% solids volume decrease from hydromagnesite,

249% volume increase from periclase)

If in fact the MgO emplaced in the repository becomes coated or armored with $Mg(OH)_2$, and that $Mg(OH)_2$ clogs its porosity because of the 219% volume increase, then some MgO and some $Mg(OH)_2$ may be unavailable for further reaction.

5.0   Calcite/Hydromagnesite Versus Bruce/Hydromagnesite Controls on pH and CO_2 Pressure

The DOE and the Draft Report express confidence that the pH and CO_2 pressure in the repository will be buffered by the reaction between brucite and hydromagnesite or brucite and magnesite. However, if the $Mg(OH)_2$ produced by hydration of periclase reacts with CO_2 and becomes coated or armored with a Mg carbonate, which initially is likely to be hydromagnesite (a net 370% volume increase from MgO to hydromagnesite), then some of the brucite may not contact the brine and so not buffer repository pH as assumed. In this case repository pH is likely to be buffered by the hydromagnesite/calcite reaction which is:

$$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O + 4Ca^{2+} + 2H^+ = 4CaCO_3 + 5\ Mg^{2+} + 6H_2O \qquad (12)$$
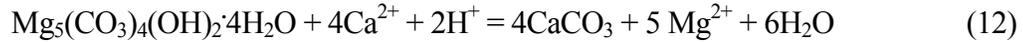
for which
$$K_{eq} = \frac{[Ca^{2+}]^4[H^+]^2}{[Mg^{2+}]^5} \qquad (13)$$

Equation (13) shows that at calcite/hydromagnesite equilibrium, the pH is a complex function of the Ca^{2+} to Mg^{2+} ratio in the brine. The likelihood that this reaction will control pH and CO_2 pressures in the repository, is suggested by the results of Snider and Xiong (2003) who ran MgO carbonation experiments in DI water, 4 M NaCl, GWB brine and ERDA-6 brine, bubbling humidified air through the solutions to maintain atmospheric CO_2 pressures. After 327 days in all four sets of experiments they detected hydromagnesite and calcite by XRD analysis.

5.1   Geochemical Modeling of Brine Geochemistry

A number of computer runs were performed using PHREEQC and the Pitzer approach (Parkhurst and Appelo, 1999) to address possible mineral reactions in the Castile and Salado Brines, in part with the purpose of comparing computed results to DOE's results from such calculations performed using the Pitzer EQ3/6 data base (Wolery, 1992: Draft Report, p. 4-8). In the PHREEQC runs, based on the reported mineralogy of the Salado Formation, it was assumed that Brine A was equilibrated with an excess of halite, gypsum, calcite, polyhalite and hydromagnesite, with or without brucite. The DOE did not include polyhalite in their geochemical modeling calculations. However, given the composition of this salt (it contains no carbonate), its inclusion in the PHREEQC modeling should not have significantly affected computed pH and CO_2 equilibrium values.

Assuming equilibrium of the brine with brucite and hydromagnesite PHREEQC computed that pH and Pco_2 values were buffered at about pH 8.2 and $10^{-5.44}$ bars. This roughly agrees with results of the same calculation performed with the FMT model (DOE, 2004) that indicates buffered pH and Pco_2 values of 8.69 and $10^{-5..50}$ bars, respectively for the brucite/hydromagnesite reaction. In contrast, if we assume that brucite is armored and not in contact with the brine, the PHREEQC calculations indicate that the calcite/hydromagnesite reaction buffers the pH and Pco_2 at more troublesome values of pH 7.2 and $10^{-3..30}$ bars. Similar results are obtained from PHREEQC modeling of ERDA-6 (Castile) brine.

6.0   Effective Excess Factor Calculations

The Draft Report (p. 5-1) modifies and reevaluates the effective excess factor (EEF) equation (Eq. 1), to incorporate the uncertainty associated with a revised chemical composition of the

CPR. The result is an EEF value of 1.0±0.0775 (1σ), in which the uncertainty differs negligibly from the value of ±0.0719 computed by Vurgin et al. (2006, 2007). This EEF value indicates that sufficient MgO will be present to react with all the CO_2 that might be derived from the breakdown of CPR. Assuming this assessment is correct, the DOE's proposed reduction of the EF from 1.67 to 1.2 would not significantly affect WIPP groundwater chemistry.

The Draft Report reiterates the conservative assumptions inherent in this computed value of the EEF and its uncertainty. These include that: no calcite with precipitate resulting from sulfate mineral dissolution; methanogenesis will not occur (CPR degradation will be via microbial nitrate and sulfate reduction), and every mole of C in CPR will be degraded and form CO_2; and no other carbonate minerals including those of Fe, Pb and Ca will form. As noted previously, these are all highly conservative assumptions. However, the EEF calculation retains the non-conservative and inadequately supported assumption that all of the emplaced MgO will be carbonated.

7.0   Concluding Concerns and a Suggestion

In this review I have argued that the DOE's extrapolation of available laboratory experimental results related to MgO hydration and carbonation, to confidently predict the course of these reactions in the WIPP repository, seems questionable. Others have also disputed the certainty of DOE's predictions which are based only on laboratory experiments and theoretical calculations, pointing out the need for field validation at the WIPP site. The expert panel reported on by SC&A (2006, p. 3-3) in fact recommends that "DOE consider performing a single-room "realistic" analysis of the processes related to the performance of the MgO backfill, including gas generation, chemical reactions, biodegradation, and mechanical creep".

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Attachment D

Response to Comments By Langmuir

[Contractor Response to Attachment C Issues]

RESPONSE TO COMMENTS BY LANGMUIR (2007)

December 1, 2007

Comments

The comments made by Langmuir (2007) regarding a draft report on the MgO Excess Factor Planned Change Request by DOE (SCA 2007) can be summarized as follows:

Comment #1 – It is not certain that all MgO will react to completion with CO_2; DOE assumes that all periclase present in the MgO will react, which may not be adequately supported.

Comment #2 – Physical segregation of MgO from CO_2 may prevent complete reaction; DOE assumes this will not occur.

Comment #3 – It is questionable whether the results of DOE's small-scale laboratory experiments can be extrapolated to conditions in the WIPP repository to support the assumption that all MgO in the repository will be available to react:

- Because of differences in the solution to MgO ratios between the inundated experiments and repository conditions;

- DOE has not performed hydration or carbonation experiments under conditions or at a scale that attempts to reproduce the conditions under which hydration and carbonation reactions will occur in the WIPP repository.

- The environment within a disposal room is likely to be heterogeneous and pockets of unreacted MgO are likely to persist;

- There will be a massive increase in the volume of magnesium solids that will result from the hydration and carbonation of MgO, which will affect the performance and reactivity of the MgO backfill. If the MgO emplaced in the repository becomes coated or armored with $Mg(OH)_2$, and that $Mg(OH)_2$ clogs its porosity because of the large volume increase, then some MgO and some $Mg(OH)_2$ may be unavailable for further reaction.

Response

The performance of the MgO backfill is important to the WIPP performance assessment under both humid and inundated conditions. Under humid conditions, the amount of brine present in the repository is insufficient for release of radionuclides by direct brine release. In the absence of direct brine release, the repository chemical conditions and resulting actinide solubilities are not important for repository performance. Consequently, the only important function of the MgO backfill under humid conditions is to control gas pressures by reaction with most of the CO_2. This issue was specifically addressed by the Conceptual Models Peer Review Panel; the Panel determined that DOE had sufficiently resolved the issue of MgO reactivity for the purposes of the Gas Generation conceptual model by demonstrating that sufficient access of brine and CO_2 to the MgO would occur to substantially remove CO_2 as a pressure source (Wilson et al. 1996b, Section 3.21.3.3).

The questions raised by Langmuir (2007) regarding the effectiveness of the MgO barrier to control chemical conditions are only relevant to inundated conditions, when sufficient brine is available for a direct brine release. Under inundated conditions, the MgO must react to control pH and CO_2 partial pressures and constrain actinide solubilities; these inundated conditions may occur after an initial period of humid conditions. The responses to these comments are organized according to the factors that could affect the availability of the MgO backfill for complete reaction.

Physical Segregation. Langmuir (2007) noted that the issue of physical segregation of MgO was raised by an expert panel, who stated that "local pockets of un-reacted MgO are likely to be present for long periods of time" (RSI 2006, Finding 4, page 63). However, RSI (2006) did not provide the basis for this finding or an explanation of the mechanism by which such pockets of MgO might be isolated from brine and gas in the repository. Physical segregation of MgO as a potential source of uncertainty in the MgO Excess (Safety) Factor was discussed by SCA (2006, page 6-1). SCA (2006) stated that this uncertainty was small because of the methods currently used to emplace MgO in the repository, but that this small remaining uncertainty should be incorporated into the MgO Excess Factor. Vugrin et al. (2007, page 18) addressed the possible physical segregation of MgO by roof collapse, and found that physical segregation was unlikely to occur by intrusion of the roof block into the waste because the roof was likely to lower onto the waste stacks and MgO. In addition, Vugrin et al. (2007) explained that failures of smaller portions of the roof (small blocks or spallings) were unlikely to physically segregate MgO because of the small scale of the blocks and spallings and the likelihood of fractures and high permeability in these smaller failed portions of the roof.

The assumption of significant physical segregation of part of the waste-gas-brine-MgO system is inconsistent with the assumption of chemical homogeneity that was accepted by the Conceptual Models Peer Review Panel (Wilson et al. 1996a). The Conceptual Models Peer Review Panel found that the assumption of chemical homogeneity "should be wholly valid over the time frame involved" (Wilson et al. 1996a, page 3-154). No contradictory evidence has been presented since the Conceptual Models Peer Review, and DOE has adequately explained why physical segregation is unlikely to occur after repository closure (Vugrin et al. 2007). Consequently, the possibility of physical segregation of MgO does not require reconsideration and it does not appear to be a significant source of uncertainty. To improve the explanation of the basis for assuming that physical segregation of MgO would have an insignificant effect on the amount of MgO available for reaction, the SCA (2007) report was revised to include a discussion of the Conceptual Models Peer Review Panel's acceptance of the assumption of chemical homogeneity (Section 3.4, page 3-9).

Formation of Reaction Rims on MgO Pellets. The possibility that individual MgO pellets could become coated by reaction products and thereby be rendered unavailable for reaction was considered an important source of uncertainty by the Conceptual Models Peer Review Panel (e.g., Wilson et al. 1996b, Section 3.22.3.3). In response to requests for additional information from the Panel, SNL (1997) provided experimental evidence demonstrating that hydromagnesite would nucleate away from the surface of the periclase grains under inundated repository conditions and that isolating reaction rims would not

form. The evidence reviewed by the Panel included experimental results, optical microscopy, scanning electron microscopy, modeling predictions, analogue comparisons, and phase equilibria information. Based on a review of this information, the Conceptual Models Peer Review Panel agreed that the formation of reaction rims on hydrated MgO pellets would not significantly affect the function of the MgO engineered barrier (Wilson et al. 1997b, Section 3.2.3.3); the Panel found the most compelling evidence to be "1) the experimental results indicating that hydrous magnesium carbonate phases could nucleate away from the pellet surface and in the saturated brine, and 2) SEM photographs showing partially dissolved cores remaining within reaction rims."

DOE has continued investigating the reaction of MgO backfill materials with brine and CO_2 (Bryan and Snider 2001a; Bryan and Snider 2001b; Snider 2001; Zhang et al. 2001; Snider 2002; Snider and Xiong 2002; Snider 2003; Xiong and Snider 2003). Hydration experiments have been conducted under inundated and humid conditions, and carbonation experiments have been conducted under inundated conditions. Several WIPP Test Plans (Bynum 1997, Snider et al. 2004, Deng et al. 2006) have described potential humid MgO/brucite carbonation experiments, but no results have been reported from these experiments; consequently it appears that these carbonation experiments under humid conditions have not been performed. In the humid hydration experiments and in the inundated hydration and carbonation experiments performed since the Conceptual Models Peer Review, there has been no evidence of reaction rim formation on the MgO pellets that would hinder complete reaction.

The SCA (2007) report was modified to include a more detailed explanation of the experimental results that indicate impermeable reaction rims are not expected to form on individual MgO pellet surfaces. Information was also added to indicate that this issue was thoroughly reviewed by the Conceptual Models Peer Review Panel, who found that this issue had been adequately addressed (Section 3.2, pages 3-4 to 3-6).

Reaction Rind Formation on Masses of MgO. The Conceptual Models Peer Review Panel expressed concern that the formation of reaction products on the outside of the MgO backfill packages could seal off a significant amount of the MgO and prevent complete reaction (Wilson et al. 1996a, page 3-155). This concern was attributed to the formation of lower density and lower permeability material upon initial contact with brine on the outside of the packages (Wilson et al. 1996b, Section 3.21.3.3). The final Conceptual Models Peer Review consideration of MgO reactivity (Wilson et al. 1997b) did not explicitly discuss the effects of the volume changes that could occur during the hydration and carbonation of MgO. However, these issues were raised in the Panel's previous reports (Wilson et al. 1996a, Wilson et al. 1996b, Wilson et al. 1997a). Consequently, the Panel's conclusion that the MgO barrier would function as designed appears to have included consideration of this issue. The basis of this conclusion was the evidence provided by SNL (1997) that (1) the magnesium carbonate reaction products would not form in place, but would nucleate elsewhere in the repository; and (2) the magnesium carbonate reaction products that formed would remain permeable to brine.

During a review of the MgO backfill performance, EPA accepted DOE's assertion that the formation of reaction products on the surfaces of the backfill material would not have a significant effect on the ability of the MgO to maintain predicted repository chemical conditions (EPA 1997, pages 44-6 through 44-11). EPA stated that, based on a review of

information in Bynum et al. (1996), "The formation of reaction products on the surfaces of the backfill material do(es) not have a significant, detrimental impact on the ability of the MgO to maintain the predicted chemical conditions." EPA also noted DOE's intention to emplace sufficient MgO backfill in the repository to ensure CO_2 consumption would exceed the rate of CO_2 production.

The possible effects of volume changes and the formation of impermeable masses during the hydration and carbonation of the MgO backfill were addressed during EPA's review of the CCA (EPA 1997, EPA 1998). This issue was raised in Comment 6.W.5 (EPA 1998, page 6-67). EPA stated in their response that the effects of increased reaction product volume as well as the consumption of water were likely to be beneficial to backfill performance. Although EPA stated in their response that the formation of dense, cementitious layers of backfill could limit access of brine to the waste, the evidence reviewed above shows that such cementitious layers are not expected to form. Comments 5.E.2, 5.E.5, 5.E.9, 5.E.10, 5.E.15, 5.E.16, 5.E.18, 5.E.23, and 5.E.24 raised questions regarding the effects of MgO backfill on waste permeability (EPA 1998, pages 5-25 through 5-30). EPA (1998, page 5-31 through 5-33) calculated the change in porosity in a waste disposal room caused by the precipitation of hydromagnesite; the results demonstrated that the overall reduction in porosity caused by hydromagnesite precipitation was likely be only 1.4% of the initial porosity. EPA (1998) related the permeability to the porosity and concluded that the MgO backfill and its reaction products were unlikely to significantly affect permeability in the waste region of the repository.

The possible "lithification" of MgO during hydration under inundated conditions was investigated in a series of experiments with 5 to 15 mm-thick layers of MgO backfill material (Snider 2002). Although there was significant scatter in the results, there was no evidence that an impermeable mass of hydration products formed.

Volume changes will occur as the periclase in the MgO pellets is hydrated and carbonated, as noted by Langmuir (2007). However, these volume changes would be unlikely to significantly limit access of brine and gas to unreacted periclase in the MgO because the carbonation reaction products are expected to nucleate throughout the repository, not just on the MgO (SNL 1997, Wilson et al. 1997b). The dissolution of MgO and the ability of magnesium carbonates to nucleate away from the surface of the MgO pellets were demonstrated by SNL (1997) to the satisfaction of the Conceptual Models Peer Review Panel and EPA, as described above. In addition, evidence has been presented that the reaction products will remain permeable to brine (Bynum et al. 1996, SNL 1997). This evidence was considered and accepted by both the Conceptual Models Peer Review Panel (Wilson et al. 1997b) and the EPA (EPA 1997, 1998). Other factors that may limit the formation of a dense, impermeable mass of MgO carbonation products would be fracturing of the reaction products during room closure or fracturing as a result of the volume changes that would occur as reaction proceeds. No new evidence is available indicating that MgO hydration and carbonation products will form impermeable masses that interfere with the functioning of the MgO engineered barrier. Although DOE originally planned to include a large excess of MgO in the repository, neither the Conceptual Models Peer Review Panel nor the EPA state that this large excess was a critical factor in their determination that the MgO barrier would perform as expected.

Consequently, in the absence of new data, there does not appear to be a basis for revising the assumption that essentially all MgO will be available for reaction. The resolution of this issue was clarified in SCA (2007) by including a discussion of the experimental results reported by Bynum et al. (1996) and SNL (1997) and the consideration of this issue by the Conceptual Models Peer Review Panel and EPA (Section 3.2, pages 3-4 to 3-6). The effects of hydromagnesite precipitation on porosity and permeability were addressed by inserting a discussion of the EPA (1998) calculations in the SCA (2007) report (Section 3.4, page 3-9).

Applicability of MgO Experiments to the WIPP Environment. Experiments have been conducted at Sandia National Laboratories to determine the likely reactions of the MgO backfill in the WIPP repository environment. Some of these experiments were conducted under conditions designed to accelerate reaction rates over those expected in the repository to ensure the experiments could be completed within a reasonable amount of time. Some hydration and carbonation experiments have been conducted at higher temperatures and CO_2 partial pressures than those predicted for the repository environment, with agitation of the samples, and with higher solution to solids ratios than anticipated in the repository. Conducting the hydration and carbonation experiments at conditions different from those expected in the WIPP repository could affect the applicability of the results to repository conditions.

MgO experiments conducted at higher temperature and CO_2 partial pressures (e.g., SNL 1997) have been supplemented by experiments conducted at temperature and CO_2 partial pressure conditions more consistent with expected repository conditions (e.g., Snider 2003, Xiong and Snider 2003). Higher CO_2 partial pressures (5% CO_2) have resulted in the initial formation of nesquehonite [$MgCO_3 \bullet 3H_2O(s)$] in some experiments; however, this nesquehonite was observed to disappear, being replaced by hydromagnesite (Snider and Xiong 2002). If nesquehonite formed and persisted in the repository, predicted CO_2 partial pressures and actinide solubilities would be higher than if hydromagnesite or magnesite formed. However, experiments conducted at lower CO_2 partial pressures ($10^{-3.5}$ atm) produced hydromagnesite (Snider and Xiong 2002), demonstrating that nesquehonite is unlikely to form or persist under repository conditions.

The results of experiments designed to determine the effects of sample agitation on the potential formation of reaction rims or impermeable masses were reported by Snider (2002); these "cemented cake" experiments were discussed above. The experiments showed that sample agitation did not have a consistent effect on reaction rates. In addition, because the available evidence shows that impermeable reaction rinds will not form on MgO pellets, sample agitation is likely to have relatively minor effects on the results of the inundated hydration and carbonation experiments.

Many of the MgO backfill hydration and carbonation experiments have included relatively high solution to solid ratios. The larger amounts of solution were used to facilitate solution sampling. However, Bynum et al. (1996) and SNL (1997) reported a series of experiments designed to more closely simulate the lower solution to solids ratios expected in the repository. In these experiments, MgO pellets were placed in a porous bag that was partially suspended in brine through which CO_2 was bubbled. At the end of the experiments, the porous bag was removed from the brine, placed in a dye solution,

removed from the dye, cemented in epoxy, then sectioned and examined to determine the ability of the dye to permeate the reaction products. The experimental results indicated that MgO was likely to continue to react and maintain the required repository chemical conditions. There is relatively little evidence that the solution to solids ratios of the experiments had a significant effect on the nature of the solid reaction products. Bryan and Snider (2001b) reported the results of experiments with varying ratios of GWB brine to solids. In the experiments with GWB brine, a magnesium-chloride-hydroxide-hydrate material was observed to form. The proportions of this phase were found to increase with higher solution to solids ratios in the experiments. Consequently, at the lower solution to solids ratio in the repository, little of this phase is expected to form, and its formation is not expected to have a significant effect on the function of the MgO engineered barrier.

There are a number of inherent difficulties in performing large-scale MgO hydration and carbonation experiments that would more closely reproduce expected repository conditions, especially given the relatively slow reaction rates and long time frame involved. These difficulties led to the review of the Chemical Conditions model by the Conceptual Models Peer Review Panel. Based on a consideration of the experimental data and the conclusions of the Panel, the available data appear to be reasonably representative of repository conditions and additional large-scale experiments do not appear to be required for an understanding of MgO hydration and carbonation reactions in the repository environment. The information incorporated in response to the comments regarding the potential formation of reaction rims on individual periclase granules and of reaction rinds on masses of MgO more fully describe the available experiments and address this issue (Section 3.2, pages 3-4 to 3-6).

Reaction Sequence. During additional review of SCA (2007), it appears that the report may not clearly state that the expected reaction sequence in the repository and in the carbonation experiments is for the initial hydration of periclase in the MgO to brucite and in GWB, magnesium-hydroxide-chloride hydrate, followed by carbonation of these magnesium hydroxide phases. Changes were made on pages 4-1, 4-3, 4-5, and 4-12 of SCA (2007) to make the discussion of this reaction sequence more consistent throughout the report.

Summary and Conclusions–The issues raised by Langmuir (2007) in the review of SCA (2007) include issues that were considered by the Conceptual Models Peer Review Panel (Wilson et al., 1996a, 1996b, 1997a, 1997b) and by EPA (1997, 1998) during the review of the CCA and CCA PAVT. These issues relate to the assumption of chemical homogeneity and the possible formation of hydration and carbonation reaction products that could limit access of brine and CO_2 to the interior of the MgO pellets or to the interior of the masses of MgO emplaced in the repository. No new data have been developed since the time of the Conceptual Models Peer Review or the CCA PAVT to contradict the assumptions that were accepted by the Conceptual Models Peer Review Panel or EPA at that time. The available documentation clearly states that the formation of reaction rims on the MgO pellets was not expected to occur and the assumption of chemical homogeneity was reviewed and accepted. It is also clear that the formation of cementitious layers by the hydrated and carbonated MgO was considered by the EPA and Conceptual Models Peer Review Panel and that they determined that formation of

cementitious layers would not prevent the engineered barrier from controlling chemical conditions (EPA 1998).

The documentation of the Peer Review Panel's and EPA's evaluation of the ability of the MgO barrier to perform as expected to control chemical conditions does not provide much information regarding the importance of the large excess of MgO that was originally proposed to be placed in the repository. At the time of the CCA, it was estimated that complete biodegradation of all CPR in the repository would result in the carbonation of only 26% of the MgO backfill because of the large amounts of MgO to be emplaced and the assumption that methanogenesis will be a significant process in CPR degradation (SNL 1997). However, recent evaluation of the available sulfate in the Salado formation resulted in the bounding assumption that all CPR carbon could be transformed into CO_2. This assumption, combined with the proposed reduction in the MgO Excess Factor from 1.67 to 1.2, makes the assumption that all MgO will be available for reaction with CO_2 more critical. For example, if reaction of only 26% of the MgO was required to maintain chemical conditions in the repository, the segregation of less than 74% of the MgO by reaction product formation would not affect chemical conditions. However, given the theoretical possibility that all CPR degradation could take place by denitrification and sulfate reduction that would transformed the CPR carbon into CO_2, combined with the proposed smaller proportion of the moles of MgO to moles of CPR carbon to be placed in the repository, even a small amount of MgO segregation, if it occurred, could affect chemical conditions.

Because of the difficulties associated with developing experiments that would simulate the behavior of the MgO in the repository environment over 10,000 years, it would be extremely difficult to design useful, large-scale experiments that would determine whether a significant fraction of MgO could be sequestered by the volume changes associated with MgO hydration and carbonation. In cases where experiments cannot be performed, a peer review must be carried out of the necessary assumptions. The Conceptual Models Peer Review Panel previously reviewed and approved the Chemical Conditions conceptual model (Wilson et al. 1997b). Consequently, because it appears that no new information has been developed that would contradict their conclusions, chemical homogeneity in the WIPP repository and the essentially complete reaction of the MgO engineered barrier can continue to be assumed. On this basis, it appears that sufficient technical information is available for EPA to determine the appropriate Excess Factor for MgO in the WIPP repository.

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Attachment E

Review of the DOE Request for Magnesium Oxide Requirement
Reduction

[PECOS Management Services, Inc. stakeholder comments]