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MEMO

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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

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 CO₂ consumed) can be decreased from 1.67 to 1.2, where the CO₂ consumed equals the maximum amount of CO₂ 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 CO₂ produced by microbial degradation of CPR
- Uncertainty related to the amount of MgO available to react with CO₂
- Uncertainty in the moles of CO₂ consumed per mole of available MgO, and in the moles of CO₂ 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:

$$EEF = \frac{(m x M_{MgO})}{(g x M_{CO_2})} r \quad (1)$$

where M_{MgO} is the total moles of emplaced MgO and M_{CO_2} the maximum number of moles of CO₂ 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 CO₂ produced per mole of consumed CPR, m the uncertainty in the moles of MgO available for CO₂ consumption, and r the uncertainty in the moles of CO₂ 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.

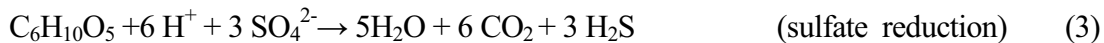
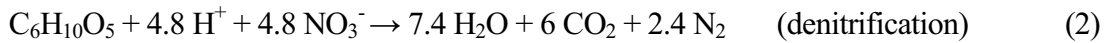
2.0 Uncertainty in the Quantity of CPR

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 CO₂ 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 CO₂. 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 C₆H₁₀O₅) these reactions are (Draft Report, p. 2-5 & 2-6):



Denitrification and sulfate reduction reactions yield 1 mole of CO₂ for every mole of carbon in CPR. The first methanogenesis reaction produces 0.5 moles of CO₂ per mole of carbon in CPR, whereas the second methanogenesis reaction actually consumes CO₂.

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 CO₂-produced ratio of 1:1. The occurrence of any methanogenesis, which may be unlikely, would reduce the amount of CO₂ produced. Thus, assuming as does the DOE and the Draft Report, that 1 mole of CO₂ 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 CO₂ on average per mole of C in the CPR..

2.2 Uncertainty in the Amount of MgO Available to React with CO₂

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 CO₂ 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 CO₂ from the breakdown of CPR. These include: (1) MgO physical segregation from the brine and CO₂; (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 CO₂; (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 CO₂. Among these (1) through (6) could reduce, and (7) could increase the percent of MgO available to react with the CO₂ 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 CO₂ 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 CO₂ that could be precipitated as hydromagnesite because of high Mg concentrations in the GWB (Salado) brine, suggests that possibly 2.2% of the CO₂ from CPR breakdown could be so precipitated. This, of course, is conservative, and leaves more unreacted MgO available to consume the remaining CO₂ 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 H₂O and CO₂ 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 CO₂ Consumed per Mole of Available MgO, and in Moles of CO₂ Consumed by Reaction with Other Materials

It is generally assumed that most of the CO₂ 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 CO₂ produced to MgO consumed is 4 to 5, or 0.8. If the product is magnesite the CO₂ 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 CO₂ 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 CO₂ (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 CO₂ in siderite (FeCO₃) (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 Ca²⁺ to repository brines which can be expected to react with dissolving CO₂,

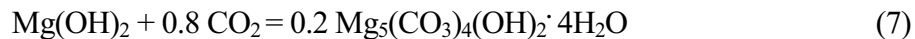
precipitating calcite, and possibly pirssonite $[\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}]$ (Draft Report, p. 4-7). Other possible sinks for the CO_2 from CPR are unreacted lime in Portland cements that have been used to solidify waste sludges, and incorporation of the carbon of 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

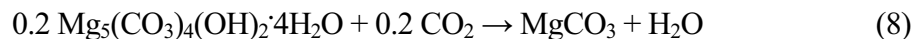
There is a general consensus that in brine or humid environments MgO rapidly hydrates to form $\text{Mg}(\text{OH})_2$ (cf. Snider and Xiong, 2002).



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, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, which subsequently alters to hydromagnesite) will be hydromagnesite, which forms according to the reaction:



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:



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 $[\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}]$ 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°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.

Carbonation

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 CO₂ pressure, and decrease with increasing Mg²⁺ concentration. Because of the slow rate of conversion at the low temperatures and CO₂ 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 CO₂ from CPR breakdown. The first of these is the ability of periclase to react to completion (with CO₂). DOE assumes that all of the periclase will react with and consume all of the CO₂. The second issue is the segregation of MgO from CO₂. DOE assumes no physical segregation of the MgO, and thus that all of the MgO remains available for reaction with CO₂.

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 where 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 CO₂ in the repository has been consumed...” Note they do not say that the experimental results obtained to date prove 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”.

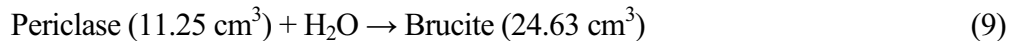
Further, SC&A (2006, p. vi.) comments that “Uncertainties identified during the course of this investigation include the possibility of physical segregation of small quantities of MgO....” “The goal of either...literature review or experimental studies would be to adequately quantify or capture system 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/ft³ (WTS, 2005). This is equivalent to a density of 1.39 g/cm³. The density of pure, solid MgO is 3.58 g/cm³ (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 [Mg₅(CO₃)₄(OH)₂·4H₂O] or magnesite (MgCO₃). 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 cm³) is from Mincryst info. card No. 2070 (http://database.iem.ac.ru/mincrist/s_carta2.php?2070+MAIN).

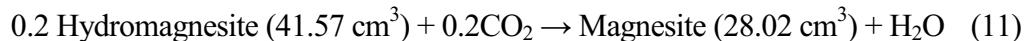


(219% solids volume increase)



(169% solids volume increase from brucite,

370% solids volume increase from periclase)



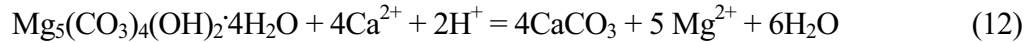
(67% solids volume decrease from hydromagnesite,

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 CO₂ Pressure

The DOE and the Draft Report express confidence that the pH and CO₂ 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 CO₂ 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:



for which

$$K_{eq} = \frac{[\text{Ca}^{2+}]^4 [\text{H}^+]^2}{[\text{Mg}^{2+}]^5} \quad (13)$$

Equation (13) shows that at calcite/hydromagnesite equilibrium, the pH is a complex function of the Ca²⁺ to Mg²⁺ ratio in the brine. The likelihood that this reaction will control pH and CO₂ 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 CO₂ 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 CO₂ equilibrium values.

Assuming equilibrium of the brine with brucite and hydromagnesite PHREEQC computed that pH and Pco₂ 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 Pco₂ 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 Pco₂ 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 CO₂ 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 will 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 CO₂; 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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