
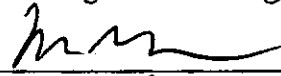
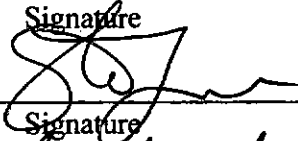
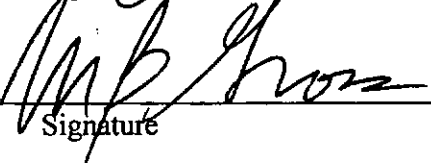




546377

**Sandia National Laboratories
Waste Isolation Pilot Plant**

**Uncertainties Affecting MgO Effectiveness and Calculation
of the MgO Effective Excess Factor,
Revision 1**

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WIPP:1.4.1.2:PA:QA-L:543261

Information Only

1.0 Executive Summary

The U. S. Environmental Protection Agency (EPA) currently requires the U. S. Department of Energy (DOE) to emplace 1.67 moles of magnesium oxide (MgO) in the Waste Isolation Pilot Plant (WIPP) for every mole of organic carbon in cellulose, plastic, and rubber (CPR) materials that is emplaced in the repository. The ratio of MgO to carbon is termed the MgO excess factor (EF).

The EPA has stated that they require this “relatively high excess amount” since “the extra MgO would overwhelm any perceived uncertainties that the chemical reactions would take place as expected” (Gitlin 2006). Consequently, when the DOE requested that the MgO excess factor be lowered from 1.67 to 1.2, the EPA requested that the DOE address “the uncertainties related to MgO effectiveness, the size of the uncertainties, and the potential impact of the uncertainties on long-term performance” (Gitlin 2006). To address this request, Sandia National Laboratories (SNL) has conducted an analysis of these uncertainties.

The analysis introduces the concept of the MgO “Effective Excess Factor” (EEF), a quantity that incorporates uncertainties into the current definition of the MgO excess factor. The uncertainties included in the EEF calculation are grouped into three categories:

- 1) uncertainties in the quantities of carbon dioxide (CO₂) produced by microbial consumption of the CPR;
- 2) uncertainties in the amount of MgO that is available to react with CO₂; and
- 3) uncertainties in the moles of CO₂ sequestered per mole of MgO that is available to consume CO₂.

These uncertainties are represented with random variables in the EEF calculation.

The EEF calculation includes several conservative assumptions, as well. For example, it is assumed that all organic carbon in the emplaced CPR materials will be consumed by microbes. Additionally, it is assumed that each mole of consumed organic carbon will yield 1 mole of CO₂ and that MgO is the only material that will sequester CO₂. The beneficial effects of the consumption of CO₂ by other substances in the waste materials are ignored. These conservative assumptions have the potential impact of significantly overestimating the amount of MgO that would be required to consume the CO₂. Because of the many and significant conservatisms included in this analysis, the mean EEF is the best indicator as to whether or not an EF of 1.2 will be sufficient to consume all CO₂.

Since the EEF considers the uncertainties affecting MgO effectiveness, it is necessary only for the EEF to be greater than 1.0 to ensure that chemical conditions are maintained as assumed in WIPP performance assessment (PA). Using standard techniques from statistical theory, the quantified uncertainties of the individual components were propagated to calculate the mean EEF. The mean EEF is calculated to be 1.03, greater than the minimum EEF (1.0) that guarantees the consumption of all CO₂ that could be generated by microbes. Thus, this analysis concludes that emplacing 1.2 moles of MgO for every mole of organic carbon in the emplaced CPR is more than sufficient to consume all CO₂ that could be generated by microbes and to maintain chemical conditions as assumed in WIPP PA. Furthermore, reducing the MgO excess factor to 1.2 would have no impact on the long-term performance of the repository.

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2.0 Introduction

Magnesium oxide (MgO) is the only certified engineered barrier for the Waste Isolation Pilot Plant (WIPP), and it is emplaced in the repository along with the waste as a chemical control agent to mitigate the potential effects of significant microbial consumption of organic carbon in the cellulose, plastic, and rubber (CPR) materials in the post-closure repository environment (Appendix Barriers, DOE 2004a). The MgO backfill is emplaced to consume microbially generated carbon dioxide (CO₂), resulting in two primary consequences. First, consumption of the CO₂ buffers “the fugacity of CO₂ (f_{CO_2}) and pH [of brine] within ranges favorable from the standpoint of the speciation and solubilities of the actinides” (Appendix Barriers, DOE 2004a). An additional effect of the CO₂ consumption by MgO is that repository pressures are lower than would be expected in the absence of MgO. Previous performance assessments (PAs) have shown that repository pressures have a significant role in determining spillings releases, direct brine releases, and other aspects of repository performance.

Since 1996, the U. S. Department of Energy (DOE) has quantified the amount of MgO being emplaced in the repository in terms of an MgO “excess factor.”¹ The DOE originally proposed placing one 4,000-lb MgO sack² (MgO super-sack) on top of each waste stack, as well as 25-lb MgO sacks (MgO mini-sacks) in between waste stacks and on the floor surrounding the waste, which resulted in an excess factor that was estimated to be 1.95 (DOE 1996). In June 2000, the DOE submitted a request to discontinue emplacement of MgO mini-sacks (DOE 2000), and in 2001, the U. S. Environmental Protection Agency (EPA) approved DOE’s request to remove the MgO mini-sacks and lower the MgO excess factor to 1.67 (Marcinowski 2001).

On April 10, 2006, the DOE submitted a planned change request (PCR) to the EPA requesting approval to “emplace 1.2 moles of magnesium oxide (MgO) for every mole of consumable carbon contained in the Waste Isolation Pilot Plant (WIPP)” (Moody 2006). This amount of MgO represents a reduction from the 1.67 moles of MgO per mole of organic carbon that the EPA currently requires. In response to the DOE’s request, the EPA indicated that “before EPA can evaluate DOE’s request to lower the excess MgO emplaced to nearly the ‘fully effective’ range (1.00), DOE needs to address the uncertainties related to MgO effectiveness, the size of the uncertainties, and the potential impact of the uncertainties on long-term performance” (Gitlin 2006).

To address the EPA’s request for additional information, Sandia National Laboratories (SNL) has conducted an analysis that reviews the uncertainties pertaining to the effectiveness of MgO and the calculation of the MgO excess factor. This report documents the uncertainty review and the results of that analysis. Section 3.0 reviews how the MgO excess factor is currently calculated and the assumptions and uncertainties related to this calculation. Additionally,

¹ DOE (1996, 2000), Marcinowski (2001), and other earlier documents related to MgO have discussed an MgO “safety factor” and “loading factor.” Because Moody (2006) contends that this factor is not a safety factor in the truest engineering sense and the previous analyses have been concerned with having enough of an “excess” of MgO to overwhelm uncertainties, this analysis uses the term MgO “excess factor,” and this term is intended to be synonymous with the term “safety factor.”

² DOE originally proposed emplacing 4,000-lb supersacks. However, the DOE currently emplaces 4,200-lb supersacks (WTS 2005).

Section 3.0 introduces the concept of the MgO "Effective Excess Factor" (EEF), a quantity that incorporates the uncertainties affecting MgO effectiveness into the excess factor calculation. The three primary groups of uncertainties included in the EEF calculation are uncertainties affecting the quantity of carbon dioxide (CO₂) generated by microbial degradation of organic carbon, uncertainties affecting the quantity of MgO that is available to react with CO₂, and uncertainties affecting the number of moles of CO₂ that are consumed by a single mole of available MgO. These categories are discussed in Sections 4.0, 5.0, and 6.0, respectively. The results of the EEF calculation are presented in Section 7.0, and conclusions from this analysis are discussed in Section 8.0.

3.0 Calculation of the MgO Excess Factor

Currently, the MgO excess factor (EF) is defined as the product of two ratios: the ratio of the moles of emplaced MgO to the maximum number of moles of CO₂ that could be generated from microbial consumption of all of the organic carbon in the emplaced CPR materials and the ratio of the moles of CO₂ consumed per mole of emplaced MgO. This definition is represented by the following equation:

$$3-1 \quad EF = \frac{M_{MgO}}{M_{CO_2}} \times \frac{1 \text{ mole of } CO_2 \text{ consumed}}{1 \text{ mole of MgO}}$$

The variable EF denotes the MgO excess factor, M_{MgO} represents the moles of emplaced MgO, and M_{CO_2} represents the maximum possible number of moles of CO₂ that could be generated by microbial consumption of all of the organic carbon in CPR materials. Presently, the EF is calculated for individual disposal rooms of the repository.

There are several inherent assumptions in the calculation of the excess factor.

- 1) It is conservatively assumed that all of the organic carbon in the emplaced CPR can and will be consumed by microbes.
- 2) It is conservatively assumed that this carbon will be consumed via denitrification and sulfate reduction, resulting in the maximum yield of 1 mole of CO₂ for every mole of consumed organic carbon.
- 3) It is assumed that every mole of emplaced MgO is available to react with CO₂.
- 4) It is assumed that every mole of MgO can consume 1 mole of CO₂ and that MgO is the only material that will sequester CO₂. The second ratio in Eq. 3-1 represents this assumption.

Under these assumptions, emplacing an MgO excess factor of 1 is sufficient to maintain the PA assumption that MgO consumes all³ CO₂ generated by microbial consumption of CPR materials.

³ "Although MgO will consume essentially all CO₂, minute quantities (relative to the quantity that would be produced by microbial consumption of all CPR materials) will persist in the aqueous and gaseous phases" (Appendix Barriers, DOE 2004a). Because this quantity will be so small relative to the initial quantity, the adverb "essentially" is omitted in this document.

However, there are several uncertainties associated with each of these assumptions, and they can be grouped into four categories:

- 1) uncertainties in the quantities of organic carbon that will be consumed;
- 2) uncertainties in the quantities of CO₂ produced by microbial consumption of the organic carbon in CPR materials;
- 3) uncertainties in the amount MgO that is available to consume CO₂; and
- 4) uncertainties in the moles of CO₂ sequestered by each mole of available MgO. This uncertainty also includes materials other than MgO that could potentially sequester CO₂.

The purpose of this analysis is to determine the impact of these uncertainties on the excess factor calculation. In order to do so, this analysis introduces the concept of the MgO “Effective Excess Factor.” This term incorporates uncertainties 2) – 4) listed above and is defined as follows:

$$3-2 \quad \text{EEF} = \frac{\text{available moles of MgO}}{\text{moles of CO}_2 \text{ produced}} \times \frac{\text{moles of CO}_2 \text{ consumed}}{1 \text{ mole of MgO}} = \frac{m \times M_{\text{MgO}}}{g \times M_C} \times r.$$

The term M_C denotes the total moles of organic carbon in the emplaced CPR mass that the DOE reports, and M_{MgO} is the total moles of MgO (defined previously in Eq. 3-1). The random variables g , m , and r represent the uncertainty in the quantities of CO₂ produced per mole of consumed organic carbon, the uncertainty in the amount of MgO available for CO₂ consumption, and the uncertainty in the moles of CO₂ sequestered per mole of emplaced MgO, respectively. (These variables are further defined and discussed in the Sections 4.0-6.0). Because these uncertainties are included in the EEF calculation, an EEF greater than 1.0 would indicate that sufficient MgO is being emplaced to ensure that chemical reactions will “take place as expected” and that PA assumptions related to the consumption of CO₂ are maintained.

It should be noted that the calculation of the MgO EEF still includes the conservative assumption that all of the organic carbon in the CPR materials can and will be consumed by microbes. In keeping with the EPA’s direction that “DOE needs to address the uncertainties related to MgO effectiveness, the size of the uncertainties, and the potential impact of the uncertainties on long-term performance” (Gitlin 2006), the uncertainties associated with this assumption are qualitatively discussed in Appendix A.

4.0 Quantities of CO₂ Produced by Microbial Respiration

The amount of CO₂ that could be produced if all of the carbon in the emplaced CPR is consumed is the product of the moles of carbon in the emplaced CPR materials and the number of moles of CO₂ produced per mole of consumed carbon (i.e., the effective CO₂ yield). This calculation is expressed in the following equation:

$$4-1 \quad \text{moles of CO}_2 = y_{\text{yield}} \times \hat{M}_C.$$

The term \hat{M}_C represents the moles of carbon in CPR, and y_{yield} represents the effective CO₂ yield (in moles of CO₂ per mole of consumed carbon).

Two categories of uncertainties affect the quantities of CO₂ that can be produced via microbial respiration. First, there is uncertainty in the quantity of emplaced CPR. The DOE estimates the

quantity of CPR materials in each waste container that is shipped to the WIPP, and there is uncertainty associated with these estimates. To represent this uncertainty, \hat{M}_C is written as the product of two variables,

$$4-2 \quad \hat{M}_C = y_{CPR} \times M_C.$$

The term M_C represents the amount of carbon reported by the DOE, and y_{CPR} is a random variable that represents the uncertainty in the moles of carbon emplaced relative to the amount reported by DOE. Secondly, there is uncertainty in which microbial respiration pathway is utilized for consumption of CPR materials. Because different pathways result in different amounts of CO_2 produced per mole of consumed carbon, this uncertainty has the potential to impact the amount of CO_2 that could be produced. The variable y_{yield} represents this uncertainty. Hence, the denominator in Eq. 3-2 can be rewritten by substituting Eq. 4-2 into Eq. 4-1.

$$4-3 \quad \text{moles of } \text{CO}_2 \text{ produced} = y_{yield} \times y_{CPR} \times M_C,$$

where y_{CPR} and y_{yield} are random variables that represent the uncertainty in the moles of carbon emplaced relative to the amount reported by DOE and the uncertainty in the moles of CO_2 yielded per mole of consumed carbon when all of the CPR is consumed, respectively. These two variables are used to define g in Section 4.3.

4.1 CPR Estimates

Kirchner and Vugrin (2006) quantified the uncertainties in DOE's CPR estimates. In this analysis, an examination of the potential errors in the CPR mass estimates made using Real Time Radiography (RTR) showed that the effect of errors in these measurements is unlikely to cause the uncertainty in the total mass of CPR for a room to be of any practical significance. The analysis was based on differences between the Visual Examination (VE) and RTR estimates of mass paired by containers from various TRU waste sites. In this analysis the VE estimates were assumed to be the more accurate value and were treated as the true values. Monte Carlo methods were used to simulate potential errors in the RTR measurements and to construct a distribution representing the uncertainty in the total CPR quantity in a room. These results confirm that the relative uncertainty (defined as the standard deviation divided by the mean in Kirchner and Vugrin (2006)) on the total mass of CPR in a room would be less than 0.3%. Because no significant bias was observed in the RTR measurements, it is appropriate to assume that the total of the CPR estimates is the best estimate of the true value of the total mass of CPR.

In addition to quantifying the error in CPR measurements from RTR, Kirchner and Vugrin (2006) also bounded the relative uncertainty on the total mass of CPR from both RTR and VE in a room. For this assessment, the RTR and VE estimates are both assumed to be unbiased estimates of the true CPR mass, and Kirchner and Vugrin (2006) conclude that the relative uncertainty on the total mass of CPR from both RTR and VE in a room is bounded above by the 0.3%. This uncertainty is so small that its impact on calculating the MgO excess factor is negligible.

The number of containers in a disposal room has the potential to affect the relative uncertainty of the total mass of CPR in a room. Kirchner and Vugrin (2006) assume that each disposal room

contains 11,000 55-gallon drums, but actual disposal rooms may contain more or less than this number. Vugrin (2006) indicates that the number of supersacks per room in Panel 2 and in filled rooms in Panel 3 (rooms 4, 5, 6, 7) ranges between 363 and 540 supersacks⁴. To estimate the number of containers per room, one can assume that each supersack corresponds to one waste stack comprised of three 7-packs of 55-gallon drums. Thus, the number of containers in each room ranges between 7,623 and 11,340 containers ($363 \times 21 = 7,623$ and $540 \times 21 = 11,340$). Using the lower bound of 7,623 containers per room and the second equation from Section 4.4.2 of Kirchner and Vugrin (2006), the relative uncertainty on the total mass of CPR in a room is calculated to be 0.00246. Hence, the relative uncertainty on the total mass of CPR in a room is still less than 0.3% when the lower bound of containers per room is used.

Hailey (1994) conducted a comparison of individual RTR and VE estimates for a variety of waste characteristics, including CPR content. The analysis included CPR estimates for 32 drums from a single waste shipping site (Idaho National Laboratory). The analysis only compared estimates for individual drums and did not attempt to quantify the variability on the entire population of drums examined. Hailey (1994) noted that there were large differences between the RTR and VE CPR estimates for some containers, but Hailey (1994) did not discuss whether or not there was a bias in the estimation techniques.

Some of the individual containers included in the Kirchner and Vugrin (2006) analysis had large differences between the RTR and VE estimates of CPR, but Kirchner and Vugrin (2006) concluded that there was no bias in the estimates. Thus, due to "the large number of containers whose CPR masses are added to calculate the total CPR content in a room, random errors are expected, overall, to cancel out since overestimates of mass in some containers are compensated by underestimates of mass in other containers" (Kirchner and Vugrin 2006). This analysis will use the results from Kirchner and Vugrin (2006) rather than Hailey (1994) for the following reasons:

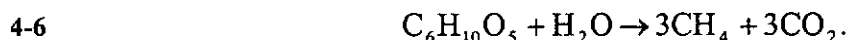
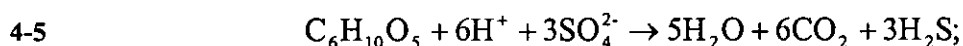
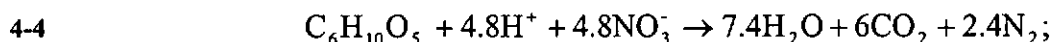
- 1) The number of drums included in the Kirchner and Vugrin (2006) analysis is more than 6 times the number of drums that Hailey (1994) compared.
- 2) Kirchner and Vugrin (2006) included drums from 3 waste shipping sites whereas Hailey (1994) analyzed drums from a single site.
- 3) The appropriate scale to examine uncertainties in CPR quantities is the room scale since the MgO EF is tracked on a per room basis. Hailey (1994) only considers estimates on a per drum basis.

Hence, the random variable y_{CPR} that represents the moles of carbon emplaced relative to the amount reported by DOE is assigned a mean value, μ_{CPR} , of 1.0, i.e. the mean CPR quantity in a room is equal to the sum of the CPR quantities in the individual containers that DOE reports. The standard deviation of y_{CPR} , σ_{CPR} , is conservatively set equal to 0.003, the upper bound on the relative uncertainty in the amount of CPR in a single room.

⁴ Because some rooms in Panel 1 were not completely filled, only the rooms in Panels 2 and 3 are used to determine the expected number of containers per room.

4.2 Microbial Respiration Pathways

Wang and Brush (1996) identify three potentially significant microbial respiration pathways in the repository: denitrification (Eq. 4-4), sulfate (SO_4^{2-}) reduction (Eq. 4-5), and methanogenesis (Eq. 4-6). These reaction pathways are described by the following equations:



These reactions are assumed to proceed sequentially as each electron acceptor (NO_3^- , SO_4^{2-}) is consumed. The yield is 1 mole of CO_2 per mole of organic carbon consumed from denitrification and sulfate reduction, and 0.5 moles of CO_2 per mole of organic carbon consumed from methanogenesis.

For the 2004 Compliance Recertification Application (CRA-2004), Snider (2003) estimated that if all of the CPR materials in the inventory were consumed sequentially by these pathways, (1) 4.72 mole % of the organic carbon in CPR materials will be consumed by denitrification, 0.82 mole % by SO_4^{2-} reduction, and 94.46 mole % by methanogenesis; and (2) if all of the organic carbon is consumed, the overall CO_2 yield will be 0.53 moles of CO_2 per mole of organic carbon consumed. The calculations by Snider (2003) only considered the emplaced waste as a possible source of sulfate. However, for the 2004 Compliance Recertification Application (CRA-2004) Performance Assessment Baseline Calculation (PABC), methanogenesis was not included because of the EPA's concern that there is enough sulfate available in the surrounding disturbed rock zone (DRZ) to maintain sulfate reduction indefinitely. The EPA directed that for the CRA-2004 PABC, only denitrification and sulfate reduction be considered as viable microbial respiration pathways for CO_2 generation (Cotsworth 2005). Consequently, when the updated inventory for the CRA-2004 PABC is considered, 4.48 mole % of the organic carbon in CPR materials will be consumed by denitrification and 95.52 mole % by sulfate reduction when all of the organic carbon is consumed (Nemer 2007). Sulfate reduction that uses only sulfate in the waste materials will consume 0.77 mole % of the organic carbon (Nemer 2007). Exclusion of methanogenesis resulted in a yield of 1 mole of CO_2 per mole of organic carbon consumed for the CRA-2004 PABC.

Clearly, uncertainty in microbial respiration pathways affects the uncertainty in the total amount of CO_2 that could be generated, and the following sections detail how this uncertainty is quantified for the EEF calculation. Section 4.2.1 discusses the uncertainties related to the effective CO_2 yield for sulfate reduction, and uncertainties related to methanogenesis are discussed in Section 4.2.2. Section 4.2.3 details the conservative approach that this analysis takes to model effective CO_2 yield for the EEF calculation.

4.2.1 Sulfate Reduction and Precipitation of CaCO₃-bearing Minerals

There are three possible sources of sulfate for microbial consumption of carbon via sulfate reduction (Kanney et al. 2004):

- 1) emplaced waste materials;
- 2) brine stored in the Salado formation and the Castile formation that underlies the Salado (Deal et al. 1995, Popielak et al. 1983); and
- 3) sulfate-bearing minerals such as anhydrite, gypsum and polyhalite in the Salado rock surrounding the disposal rooms (DOE 1983a,b).

These different sources are significant because a distinguishing characteristic between the brine sulfate source and the sulfate in the sulfate-bearing minerals is the quantity of calcium present along with the sulfate. This calcium has the potential to significantly affect the effective CO₂ yield.

It has been hypothesized that sulfate could be transported into the disposal rooms by diffusive transport from the surrounding minerals. If microbial sulfate reduction consumes the sulfate in the waste and in brines in contact with the waste via Eq. 4-5, a concentration gradient from the DRZ to the waste will be created. This gradient could allow for diffusive transport of sulfate from the DRZ to the waste areas. If sulfate diffuses from the DRZ through saturated voids to the waste, the dissolved sulfate concentrations in the DRZ would decrease. However, this decrease would result in dissolution of sulfate bearing minerals such as anhydrite, gypsum (CaSO₄·2H₂O), and polyhalite (K₂MgCa₂(SO₄)₄·2H₂O), present in both the marker beds and the nearly pure halite (NaCl) in the Salado.

The dissolution of sulfate bearing minerals would yield abundant calcium ions (Ca²⁺) if microbes consume naturally occurring sulfate to a significant extent after consuming all sulfate in the waste. The presence of large quantities of Ca²⁺ in the waste areas is significant because the released Ca²⁺ would consume CO₂ by precipitating calcite (CaCO₃), metastable polymorphs of calcite, hydrated CaCO₃, or minerals such as pirssonite (Na₂Ca(CO₃)₂·2H₂O). Consequently, the calcium could impact the CO₂ yield. Consumption of CO₂ by precipitation of CaCO₃-bearing minerals reduces the amount of MgO that must be emplaced for CO₂ sequestration, hence, impacting the EEF calculation.

Quantifying the amount of CO₂ that could be consumed by precipitation of CaCO₃-bearing minerals is a difficult task as there are many uncertainties that could affect this process and the overall effective yield from sulfate reduction. These uncertainties include:

- 1) The presence of materials that inhibit calcite precipitation and their impact on CO₂ consumption.
- 2) The fraction of the DRZ that is available to provide sulfate to the waste areas. The extent of the DRZ that is available to provide sulfate to the waste areas via diffusion would determine the amount of sulfate and calcium that could also be transported to the waste areas. Kanney et al. (2004) previously considered this uncertainty.
- 3) The quantity of sulfate that could enter the waste areas from Castile brines. Castile brines do not contain significant quantities of calcium (Popielak et al. 1983), so if these brines were the primary source of sulfate microbes in the absence of DRZ sulfate, there would be little consumption of CO₂ by precipitation of CaCO₃-bearing minerals.

- 4) The quantity of sulfate that could enter the waste areas from Salado brines. The Mg^{2+} concentration in Salado brines is more than 50 times higher than the Mg^{2+} concentration in Castile brines (Popielak et al. 1983). This difference is significant since even though Salado brines can provide a source of sulfate reduction, the Mg^{2+} from the brines can carbonate and sequester CO_2 , reducing the effective CO_2 yield.

The analysis herein does not attempt to quantify the impact that these uncertainties have on the effective yield for sulfate reduction. Rather, it acknowledges that there are many uncertainties that could affect the yield. Section 4.2.3 discusses how uncertainties related to the effective CO_2 yield for sulfate reduction are handled for the EEF calculation.

4.2.2 Methanogenesis

As mentioned in Section 4.2, denitrification and sulfate reduction are preferential microbial respiration pathways when compared to methanogenesis. However, if neither nitrates nor sulfates are available, microbial respiration can only proceed via methanogenesis. The fraction of organic carbon in the repository that is consumed via methanogenesis is relevant to EEF calculations because methanogenesis results in 0.5 moles of CO_2 per mole of consumed carbon, as opposed to 1.0 moles per mole of consumed carbon from denitrification and sulfate reduction (without including the effects of calcite precipitation).

- Kanney et al. (2004) conducted an analysis that attempted to bound the quantities of sulfate that could enter the disposal rooms by diffusive and advective transport mechanisms. Despite the conservative nature of that analysis, the results indicated that the quantities of sulfate entering the repository due to advective transport of sulfate in the event of a human intrusion or diffusive transport of sulfate in the undisturbed scenario do not preclude methanogenesis.

However, the EPA stated that the analysis by Kanney et al. (2004) did not “adequately address all sources of natural sulfate that could be available to the repository” (EPA 2004a). EPA questioned the rate of DRZ healing and fracturing discussed in the Kanney et al. (2004) analysis and postulated that a significant quantity of sulfate could be introduced into disposal rooms in the event of room collapse (EPA 2004a). The EPA concluded that the Kanney et al. (2004) analysis did not adequately bound the quantity of sulfate that could enter the repository (EPA 2004a) and directed that WIPP PA conservatively assume that only denitrification and sulfate reduction be considered as viable microbial respiration pathways for CO_2 generation for the CRA-2004 PABC (Cotsworth 2005).

The analysis herein does not attempt to derive a conservative bound on the total amount of sulfate that could enter the repository. Rather, it acknowledges that there is some uncertainty in the quantity of sulfate that could enter the repository and, hence, uncertainty in the fraction of the organic carbon in the emplaced CPR materials that could be consumed via methanogenesis. This uncertainty has not been quantified to date. The following section discusses how uncertainties related to methanogenesis are handled for the EEF calculation.

4.2.3 CO₂ Yield

As discussed in Section 4.2, the current PA technical baseline (established by the CRA-2004 PABC) includes only denitrification and sulfate reduction as microbial respiration pathways for the consumption of organic carbon. Methanogenesis was not included in the CRA-2004 PABC. The current baseline also does not include consumption of CO₂ by magnesium in Salado brines or by precipitation of CaCO₃-bearing minerals. Consequently, the effective CO₂ yield corresponding to the baseline assumptions is 1 mole of CO₂ per mole of consumed organic carbon. This value represents the maximum yield that could occur.

Because of the complexity involved with quantifying the uncertainty in the effective CO₂ yield, this analysis will model the yield in a conservative manner consistent with the CRA-2004 PABC. That is, it will be assumed that:

- 1) Denitrification and sulfate reduction are the only microbial respiration pathways for the consumption of organic carbon.
- 2) Methanogenesis does not occur.
- 3) No CO₂ is consumed by precipitation of CaCO₃-bearing minerals.
- 4) No CO₂ is consumed by magnesium in Salado brines.

Consequently, this analysis will assume that the effective CO₂ yield is 1 mole of CO₂ per mole of consumed organic carbon. This value represents the maximum effective yield that could occur, so modeling the yield in this manner is conservative. The variable y_{yield} represents the effective CO₂ yield in this analysis, and it will be assigned a constant value of 1 mole of CO₂ per mole of consumed organic carbon. If it was possible to quantify this uncertainty and the uncertainty was included in calculation of the EEF, it would have the impact of increasing the mean EEF and increasing the standard deviation.

4.3 Random Variables Affecting CO₂ Production

As in Eq. 4-3, the quantity (in moles) of CO₂ produced by microbial respiration is the product of the variables y_{yield} and y_{CPR} and the moles of carbon in the emplaced CPR materials, M_C . Since this product represents the denominator in the EEF calculation ($g \times M_C$ in Eq. 3-2), these two terms can be equated to define the random variable g :

$$4-7 \quad g = y_{yield} \times y_{CPR}$$

This calculation makes the following assumptions:

- 1) All of the organic carbon in the emplaced CPR materials is consumed.
- 2) Denitrification and sulfate reduction are the only microbial respiration pathways for the consumption of organic carbon.
- 3) None of the organic carbon in the CPR materials is consumed via methanogenesis
- 4) No CO₂ is consumed by precipitation of CaCO₃-bearing minerals.
- 5) No CO₂ is consumed by magnesium in Salado brines.

5.0 Quantities of MgO Available for Reaction

The numerator in the EEF calculation represents the amount of MgO that is available to sequester CO₂. This quantity is represented in the EEF calculation as the product of the number of moles of emplaced MgO (M_{MgO}) and a random variable, m , that represents the fraction of the emplaced moles that are available for reaction (Eq. 5-1).

$$5-1 \quad \text{available moles of MgO} = m \times M_{MgO}$$

Several uncertainties have the potential to impact the random variable m , and these uncertainties are grouped into two categories: issues related to MgO characteristics and performance and issues related to the repository characteristics and performance. The individual uncertainties associated with these categories and their impacts on the random variable m are detailed in Sections 5.1 and 5.2.

5.1 MgO Characteristics and Performance

Three issues that are related to characteristics of MgO and its performance and could potentially affect the amount of MgO available for reaction have been identified. They are:

- 1) the concentration of reactive constituents in MgO;
- 2) the possibility of carbonation of periclase prior to emplacement; and
- 3) the extent of the reaction of MgO with CO₂.

5.1.1 Reactive Constituents in MgO

Brush and Roselle (2006) reviewed a set of previously conducted experiments that were conducted to assess the concentration of reactive constituents in the MgO that is emplaced in the repository. Brush and Roselle (2006) present results for MgO from two of the three vendors that have supplied WIPP with MgO. Because a reduction in the EF would only affect quantities of MgO from the current supplier and not previous suppliers, this analysis restricts discussion to the MgO received from the current supplier.

The current provider of MgO for the WIPP is Martin Marietta Magnesia Specialties LLC. The main reactive constituent of MgO is periclase, pure crystalline MgO, and lime (CaO), another reactive constituent, is also expected to be found in the emplaced MgO. Table 1 shows the results from a "loss on ignition" (LOI) experiment to assess the concentration of reactive constituents in two MgO materials from Martin Marietta, MagChem 10 WTS-20 and MagChem 10 WTS-60. ("MagChem 10" is omitted hereafter.) WTS-60 is the material that is currently being emplaced in the repository.

Brush and Roselle (2006) state that

LOI at 750 °C yields higher brucite and portlandite contents (and, by assumption, higher initial periclase and lime contents) than LOI at 500 °C ... LOI at 750 °C was unsuccessful for WTS-20 and WTS-60 due to decrepitation of these samples at this temperature. Wall (2005) was unable to develop a procedure for LOI at

750 °C that prevented decrepitation of these samples. However, the fact that LOI for WTS-60 at 500 °C yielded a higher brucite and portlandite content than LOI with WTS-30 at this temperature strongly suggested that the sample of WTS-60 tested by Wall (2005) had a periclase and lime content greater than or equal to that of WTS-30, and that the brucite and portlandite content of WTS-60 from LOI at 750 °C would equal or exceed 96 mol %, or 97 wt % (see [Table 1]). Therefore, it seemed reasonable to conclude that WTS-60, the MgO that is currently being emplaced in the WIPP, contains 96 mol % (97 wt %) periclase and lime.

Brush and Roselle (2006) describe another MgO study by Deng et al. (2006a) that has quantified the concentration of reactive constituents in WTS-60. Brush and Roselle (2006) write the following:

Deng et al. (2006b) conducted chemical, and LOI and thermal gravimetric (TGA) analyses of WTS-60. They analyzed for Mg, Ca, Al, Fe, and Si by gravimetric determination of SiO₂, which involved: (1) dissolution in nitric acid, (2) analysis of the liquid by ICP-AES, and (3) weighing the remaining solids (Deng et al, 2006b, Appendix B, Subsection B.1). They performed LOI and TGA by determining the weight percent of H₂O released by hydrated MgO from 150-800 °C and assuming that nonreactive components do not hydrate to a significant extent and that any unbound water will be lost at temperatures below 150 °C (Deng et al., 2006b, Appendix B, Subsection B.2).

Deng et al. (2006b) conclude that the mean mole fraction of periclase plus lime in WTS-60 is 96% and the standard deviation of that mole fraction is 2%.

Thus, the concentration of reactive constituents in WTS-60 was calculated using two different methods, and both analyses concluded that the mean mole fraction of periclase and lime in WTS-60 was 96 %. These corroborating analyses provide confidence that the concentration of reactive constituents has accurately been calculated. Thus, the random variable y_{RC} will be used to represent the uncertainty in the concentration of reactive constituents in the emplaced MgO, and y_{RC} will be assigned a mean of 0.96 ($\mu_{RC}=0.96$) and standard deviation of 0.02 ($\sigma_{RC}=0.02$).

Table 1 Effects of Temperature Used for LOI Analysis of MgO Hydration Products on the Brucite + Portlandite Contents of the Samples (Excerpted from Wall (2005), Table 1)

	Temperature Used for LOI			
	500 °C		750 °C	
Material	Mole % ¹	Wt % ¹	Mole % ¹	Wt % ¹
WTS-30	87 ± 5	91 ± 4	96 ± 5	97 ± 3
WTS-60	90 ± 3	93 ± 2	ND	ND

¹Uncertainties reported represent two standard deviations.

5.1.2 Carbonation of Periclase Prior to Emplacement in the WIPP

During the original WIPP certification, EPA asked for “evidence that CO₂ would not diffuse through or otherwise penetrate the bags during the operational phase and reduce the post-closure capability of the MgO” (DOE 1997). DOE provided an analysis demonstrating less than 0.1% of the MgO would be lost from CO₂ penetrating the bag over 30 years. Later, the EPA asked the same question during the recertification as comment C-23-12 (EPA 2004b). DOE responded to this question in their 6th response submittal (DOE 2004b) by referencing the Compliance Certification Application (CCA) response and providing information on the MgO supersack specification. The specification requires the supersack to be “equivalent to or better than...a standard commercial cement bag” to ensure that the supersack will effectively prevent atmospheric CO₂ and H₂O from reacting with the periclase and lime prior to creep closure of the repository and concomitant rupture of the supersacks. This analysis will conservatively assume that, due to carbonation of periclase prior to emplacement, 0.1% of the emplaced MgO will be unavailable to sequester CO₂ after closure of the repository.

5.1.3 Expected Extent of Reaction of Periclase and/or Brucite with CO₂

Brush and Roselle (2006) reviewed a set of experiments that were conducted to “determine whether lithification [i.e. “caking”] of MgO will occur in the WIPP and, if so, whether it would affect the rate of hydration of MgO.” Brush and Roselle (2006) state that it can be said that all results to date - either from studies carried out for the WIPP Project or those for other applications - imply that the periclase present in MgO will continue to react until all CO₂ is consumed.” Brush and Roselle (2006) further note, however, that “proving that a process will not occur in 10,000 years is very difficult.”

This analysis will assume that all of the periclase will be available to react and will continue to react until all of the CO₂ is consumed. However, because the uncertainty in this assumption cannot be fully quantified, it will not be included in calculation of the EEF. If it was possible to quantify this uncertainty and the uncertainty was included in calculation of the EEF, it would have the potential impact of decreasing the mean EEF and increasing the standard deviation. The magnitudes of these changes are expected to be small.

5.2 Repository Characteristics and Performance

Five issues that are related to characteristics of the repository and its performance and could potentially affect the amount of MgO available for reaction have been identified. They are:

- 1) the likelihood that the MgO supersacks will rupture making MgO available to sequester CO₂;
- 2) the loss of dissolved MgO out of waste areas due to brine outflow;
- 3) the mass of MgO in individual supersacks;
- 4) the probability that CO₂ will be able to be transported to MgO for sequestration via brine mixing processes; and
- 5) physical segregation of MgO from CO₂.

5.2.1 Likelihood of Supersack Rupture

There are two primary mechanisms that are expected to cause supersack rupture. In DOE's March 8, 2005 letter to Bonnie Gitlin of the EPA (DOE 2005), DOE stated that microbial biodegradation would provide the failure mechanism for the MgO supersacks. This is a reasonable argument because additional quantities of MgO will only be needed in those situations where plastic and rubber materials are expected to degrade by microbial action. It is consistent with this analysis to conclude that microbial action will provide the failure mechanism for supersack rupture because this analysis assumes that all of the organic carbon in the emplaced CPR materials (including the MgO supersack bags) will be consumed

Hansen (2005) also addressed the issue of supersack rupture. Hansen (2005) stated that

"approximate bearing stress over the area of the [supersack] at the point of rupture is about six pounds per square inch (6 psi). The vertical stress that the creeping salt will apply to the waste stack will approach the lithostatic pressure of approximately 2000 psi, a stress that is hundreds of times greater than the maximal loading specifications for super sack rupture. This calculation is an example of an ideal loading condition. The actual features of the underground would most likely cut, puncture or tear the fabric before salt creep imparts significant compressive load to the bags."

Thus, this analysis assumes that all MgO supersacks will rupture due to either microbial degradation or lithostatic loading, making the MgO available for consumption of CO₂.

5.2.2 Loss of MgO to Brine Outflow

MgO that has dissolved in brine may possibly leave the waste areas before reacting with CO₂ when brine flows out of the repository (Clayton and Nemer 2006). This process is termed the "loss of MgO to brine outflow" in this analysis.

Clayton and Nemer (2006) conducted a Monte Carlo analysis to calculate the probability distribution for the fraction of MgO that could be lost due to brine outflow during the 10,000 year regulatory time period. This analysis incorporated brine outflow results from the CRA-2004 PABC analysis (Nemer and Stein 2005) with a Monte Carlo simulation of 1,000 possible drilling futures. Under the assumption that DOE uses an MgO EF of 1.2 for MgO emplacement, on average, 0.007 of the emplaced MgO would be lost due to brine outflow (Nemer 2007). The standard deviation for the distribution of the fraction of MgO lost due to brine outflow is 0.017 (Nemer 2007). Both the mean and standard deviation are dimensionless quantities.

The random variable y_{L2B} is used to represent the uncertainty in the fraction of MgO lost due to brine outflow, and y_{L2B} is assigned a mean of 0.007 ($\mu_{L2B} = 0.007$) and standard deviation of 0.017 ($\sigma_{L2B} = 0.017$). Both μ_{L2B} and σ_{L2B} are dimensionless quantities.

5.2.3 Mixing Processes

As part of DOE's MgO mini-sack removal analysis, Wang (2000) analyzed diffusion processes in the repository. Wang (2000) concluded that diffusion processes alone are sufficient to mix CO₂ with WIPP brines over length scales corresponding to final room height, during time scales corresponding to maximum average brine flows.

The analysis of Wang (2000) was updated by Kanney and Vugrin (2006) for conditions that reflect the CRA-2004 PA Baseline Calculation (PABC) technical baseline. The conclusions of Wang (2000) did not change for the new technical baseline.

Furthermore, to address the EPA's concern that emplacement of supercompacted waste could affect MgO effectiveness (Gitlin 2006), Kanney and Vugrin (2006) applied the analysis of Wang (2000) in a modified form to the results of the Advanced Mixed Waste Treatment Project (AMWTP) analysis performed by Hansen et al. (2004). The conclusions drawn in Wang (2000) were not impacted by supercompacted waste and heterogeneous waste emplacement.

It should be noted that the analysis of Kanney and Vugrin (2006) does not include gaseous diffusion of CO₂ throughout a room. Because the rate of gaseous diffusion of CO₂ is orders of magnitude faster than aqueous diffusion, gaseous diffusion of CO₂ is very rapid and will maintain uniform conditions in the areas in a room above the brine when a diffusion pathway exists. Thus, the analysis of Wang (2000) and Kanney and Vugrin (2006) can be considered conservative because gaseous diffusion is not considered.

Additionally, under most flow conditions, mixing rates due to advection and dispersion should dominate over molecular diffusion, and since Kanney and Vugrin (2006) do not include these mixing mechanisms in their analysis, these results indicate that one should have a high level of confidence that sufficient mixing will occur throughout the regulatory period. Thus, this analysis will assume that the mixing processes expected in the repository will be sufficient to maintain a well-mixed brine.

5.2.4 Physical Segregation of MgO

Physical segregation of a quantity of MgO from brine or CO₂ due to roof collapse could potentially impact the quantity of MgO available to sequester CO₂; however, the probability of this segregation and the potential impact is negligible. It is probable that any roof failure will occur by lowering of a roof beam onto the waste/MgO stack so that the failed material will not intrude into the stack. Secondly, any failed roof which might occur in smaller blocks will be fractured and will maintain a fairly high permeability to brine and gas for a significant amount of time. Finally, any small scale spalling of the roof into the interstices of the stacks will also probably maintain a high permeability either because grains will not re-cement easily, or if they do, they will form a coherent mass with brine, MgO, and gas outside of them.

Furthermore, the current method that DOE uses to emplace the MgO and calculation of the MgO excess factor on a room basis likely minimizes the possible physical segregation of MgO from brine and CO₂. Operational controls guarantee one MgO supersack is emplaced on each stack of

waste. If this quantity is not sufficient to meet the required MgO EF for a room, additional MgO is emplaced. These EPA audited operations are detailed in WIPP technical procedures (WTS 2006).

Thus, no MgO is expected to be unavailable due to physical segregation, and this analysis will assume such. The uncertainty with this assumption cannot presently be quantified, so the uncertainty will not be included in EEF calculations. If it was possible to quantify this uncertainty and the uncertainty was included in calculation of the EEF, it would have the potential impact of decreasing the mean EEF and increasing the standard deviation. The magnitudes of these changes are expected to be small.

5.2.5 Mass of MgO in a Supersack

The uncertainty in the mass of MgO per supersack is controlled by the procurement specification on MgO. The specification requires that each supersack must weigh 4,200 pounds, plus or minus 50 pounds (WTS 2005). The uncertainty of MgO in an individual supersack contributes to the uncertainty in the mass of MgO in a room.

Mood et al. (1974) give the following results that are used to calculate the uncertainty in the mass of MgO in a single room:

Let $X_{total} = \sum_{i=1}^n X_i$, where X_i are elements of the same population having mean μ and standard deviation σ and that their measurement is free from bias. Then

5-2
$$X_{total} = n\mu$$

and

5-3
$$\sigma_{total} = \sigma(X_{total}) = \sigma\sqrt{n}.$$

Thus the relative variability, or coefficient of variation (CV), for the total is

5-4
$$CV = \frac{\sigma_{total}}{X_{total}} = \frac{\sigma}{\mu\sqrt{n}}.$$

The masses of MgO in a supersack are expected to be independent and free from bias, so the above result from Mood et al. (1974) can be used to calculate the uncertainty in the total mass in the entire room.

Vugrin (2006) indicates that the number of supersacks per room in Panel 2 and closed rooms in Panel 3 (rooms 4, 5, 6, 7) ranges between 363 and 540 supersacks⁵. The number of supersacks per room for an EF of 1.2 is estimated to range between 260 and 388 ($363 \times 1.2 / 1.67 = 260$ and

⁵ Because some rooms in Panel 1 were not completely filled, only the rooms in Panels 2 and 3 are used to determine the expected number of supersacks per room.

540×1.2/1.67=388). By conservatively using the low end of the range of supersacks per room, the relative variability in mass of MgO in a room is calculated to be 0.00037 (Eq. 5-5). A standard deviation of 25 pounds is used since it is assumed that the possible 50 pound deviation from 4,200 pounds in the procurement specification represents two standard deviations.

$$5-5 \quad \frac{\sigma_{Total}}{X_{Total}} = \frac{25}{4200\sqrt{260}} = 0.00037.$$

Because the moles of emplaced MgO are multiplied by the random variable m in the numerator of the EEf calculation (Eq. 3-2), it is necessary to know uncertainty in the amount of MgO present in the repository relative to the amount that DOE tracks. Since the DOE takes credit for 4,200 lbs of MgO for each supersack that is emplaced, regardless of the variability of masses in the individual supersacks, the expected mass of MgO in a room, X_{Total} , is equal to the mass of MgO for which the DOE takes credit. Thus, the ratio of these two quantities is 1. The relative uncertainty, as calculated in Eq. 5-5, is 0.00037. This analysis will use the random variable y_{SS} to represent the uncertainty in the amount of MgO present in the repository relative to the amount that DOE tracks, and this random variable will have a mean value of 1 ($\mu_{SS}=1$) and standard deviation 0.00037 ($\sigma_{SS}=0.00037$).

5.3 Random Variables Affecting MgO Availability

Based upon the preceding discussion in Sections 5.1 and 5.2, the moles of MgO available for sequestration of CO₂ can be calculated as follows:

$$5-6 \quad \text{moles of available MgO} = y_{SS} \times y_{RC} \times 0.999 \times M_{MgO} - y_{L2B} \times M_{MgO}$$

$$5-7 \quad = (y_{SS} \times y_{RC} \times 0.999 - y_{L2B}) \times M_{MgO}$$

where the random variable y_{SS} represents the uncertainty in the amount of MgO present in the repository relative to the amount that DOE tracks, y_{RC} is a random variable representing the uncertainty in the concentration of reactive constituents in MgO, and y_{L2B} is a random variable representing the fraction of MgO lost to brine outflow. Since Eq. 5-7 represents the numerator in the EEf, equating the right-hand side of Eq. 5-7 with the right-hand side of Eq. 5-1 yields the following definition of the random variable m :

$$5-8 \quad m = y_{SS} \times y_{RC} \times 0.999 - y_{L2B}.$$

This calculation makes the following five assumptions:

- 1) All of the periclase in the MgO will be available to react and will continue to react until all of the CO₂ is consumed.
- 2) 0.1% of the periclase in the MgO will carbonate prior to emplacement, leaving only 99.9% of the emplaced MgO available for sequestration of CO₂ after closure of the repository. (Hence, the multiplicative 0.999 factor in Eq. 5-8). The 0.1% represents a conservative upper bound on the fraction that could carbonate prior to the closure of WIPP..
- 3) All MgO supersacks will rupture, making MgO available for consumption of CO₂.
- 4) The mixing processes expected in the repository will be sufficient to maintain a well-mixed brine.
- 5) No MgO is rendered unavailable for CO₂ consumption due to physical segregation.

6.0 Consumption of CO₂ by MgO and Other Repository Features

The variable r in Eq. 3-2 represents the uncertainty in the moles of CO₂ that an individual mole of MgO will consume. Four issues affecting this uncertainty have been identified:

- 1) consumption of CO₂ by hydromagnesite and magnesite;
- 2) consumption of CO₂ by materials other than MgO;
- 3) dissolution of CO₂ in WIPP brines; and
- 4) incorporation of CO₂ in biomass.

These uncertainties are discussed in the following sections.

6.1 Hydromagnesite and Magnesite

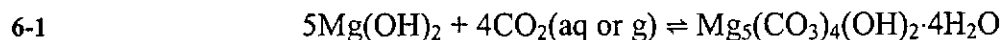
Since the CCA, DOE's position has been that MgO will carbonate rapidly in the presence of CO₂ (gaseous or aqueous) to form hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O(s)), and the hydromagnesite will subsequently convert to magnesite over hundreds to thousands of years (Appendix Barriers of DOE 2004a). EPA has made confirmatory statements in their CCA and CRA technical support documents (TSDs). On pg. 30 of Subsection 5.1 of EPA's CRA TSD for 194.24 (EPA 2006), EPA states:

"Based on a review of the literature (US EPA 1998c)[see EPA (1998) in References Section 9.0], the Agency developed the following conceptualization of the sequence and time scales of reactions between infiltrating brine and MgO backfill in the WIPP repository:

1. *Rapid reaction of MgO with brine to produce brucite (hours to days);*
2. *Rapid carbonation of brucite to produce nesquehonite and possibly hydromagnesite (hours to days);*
3. *Rapid conversion of nesquehonite to hydromagnesite (days to weeks);*
4. *Slow conversion of hydromagnesite to magnesite (hundreds to thousands of years).*

The available rate data indicate that some portion, perhaps all, of the hydromagnesite will be converted to magnesite over the 10,000-year period for repository performance. The exact time required for complete conversion has not been established for all chemical conditions. However, the available laboratory and field data clearly indicate that magnesite formation takes from few hundred to, perhaps, a few thousand years. Thus, the early repository conditions can be best represented by the equilibrium between brucite and hydromagnesite. These conditions will eventually evolve to equilibrium between brucite and magnesite."

The number of moles of CO₂ sequestered per mole of MgO depends on magnesite formation. When brucite reacts and consumes CO₂ (Eq. 6-1), hydromagnesite is formed, and four moles of CO₂ are consumed for every five moles of magnesium. The subsequent conversion of hydromagnesite to magnesite (Eq. 6-2) returns magnesium which can consume an additional mole of CO₂.



Consequently, the formation of magnesite has the potential to affect the moles of CO₂ sequestered per mole of MgO and, consequently, the EEf calculation.

As noted above, there is some uncertainty in the length of time required for hydromagnesite to convert to magnesite. Thus, this analysis includes an approach that does not require the rate of magnesite formation to model the uncertainty in the moles of CO₂ sequestered per mole of MgO. Two bounding scenarios are considered for modeling purposes:

Scenario 1: No hydromagnesite converts to magnesite. In this scenario, each mole of MgO can consume 0.8 moles of CO₂, and this value represents the lower bound for the moles of CO₂ sequestered per mole of MgO.

Scenario 2: All hydromagnesite converts to magnesite. In this scenario, each mole of MgO can consume 1 mole of CO₂, and this value represents the upper bound for the moles of CO₂ sequestered per mole of MgO.

For the EEf calculation, the moles of CO₂ sequestered per mole of MgO are modeled as a random variable with a uniform distribution on [0.8,1]. Representing the quantity in this manner incorporates the lower and upper bounds associated with Scenarios 1 and 2 and maximizes the uncertainty since the distribution is not weighted towards any particular value on [0.8,1].

6.2 Consumption of CO₂ by materials other than MgO

Brush and Roselle (2006) identify four types of materials that could consume CO₂ (in addition to the MgO engineered barrier):

- 1) Fe-base metals in steel waste containers and in the TRU waste being emplaced in the repository, and the corrosion products of these metals;
- 2) Pb-base metals in the waste, and their corrosion products;
- 3) lime and portlandite in portland cements associated mainly with process sludges in the waste; and
- 4) dissolved Ca species that would be produced in significant quantities in Ca- and SO₄²⁻-bearing minerals such as anhydrite, gypsum, and polyhalite.

Brush and Roselle (2006) state that "It is likely that these processes will consume significant amounts of CO₂ in addition to that consumed by MgO." Consumption of CO₂ by these materials is important because of the impact that they could have on the EEf calculation and chemical conditions in the repository.

The possible consumption of CO₂ by dissolved Ca species has already been discussed in Section 4.2.1. Brush and Roselle (2006) note that inclusion of the effects of CO₂ consumption by the other materials "would be difficult because of the uncertainties associated with these processes." However, these materials could consume 29.0%, 1.25%, and 0.163% of the CO₂ that would be produced by complete microbial consumption of all CPR materials (Nemer 2007). Because of these uncertainties, this analysis will use the conservative assumption that CO₂ will not be consumed by Fe-base metals or their corrosion products, Pb-base metals or their corrosion products, or lime and portlandite in portland cements. However, if it were possible to quantify

the expected quantities of CO₂ that would be consumed by these materials and the associated uncertainty in calculation of the EEF, it would increase the mean EEF and possibly the EEF uncertainty. The magnitude of these increases is not known.

6.3 Dissolution of CO₂ in WIPP Brines

Brush and Roselle (2006) state that “Dissolution of CO₂ in WIPP brines cannot consume significant quantities of CO₂ relative to the quantity that would be produced by microbial consumption of all CPR materials in the repository. This is because the solubility of CO₂ in brines is too low, and the volumes of brines that could flow through the repository are too low to dissolve significant amounts of CO₂.” In fact, Brush and Roselle (2006) conclude that 1,000,000 m³ of ERDA-6⁶ would contain less than a tenth of a percent of the total quantity of CO₂ that would be produced by microbial consumption of all CPR materials in the repository. For the sake of comparison, it is worth noting that the total volume of the empty waste panels in the WIPP is less than 500,000 m³.

Because the quantities of CO₂ dissolved in WIPP brines will be so small relative to the quantity that would be produced by microbial consumption of all CPR materials in the repository, this factor will have little or no impact on EEF calculations. Hence, this analysis will assume that no CO₂ is consumed by dissolution in brine.

6.4 Incorporation of CO₂ in Biomass

If significant microbial activity occurred in the WIPP during the 10,000 year regulatory time period, it is possible that organic carbon in CPR materials would be incorporated into biomass (cellular material) rather than “being oxidized to CO₂” (Brush and Roselle 2006). This process is relevant to the EEF calculation because incorporation of significant quantities of carbon into biomass could potentially affect the quantity of MgO that would be required to sequester microbially generated CO₂. However, Brush and Roselle (2006) state that “it would be difficult to predict defensibly how much C would be sequestered in biomass... Because of potential difficulties in calculating and defending the mass and ultimate fate of biomass in the WIPP, we cannot quantify this uncertainty.”

Because the uncertainty in the quantity of organic carbon that might be sequestered in biomass cannot presently be quantified, this analysis will conservatively assume that no organic carbon in CPR materials will be incorporated into biomass. If it was possible to quantify this uncertainty and the uncertainty was included in calculation of the EEF, it would have the impact of increasing the mean EEF and increasing the standard deviation. The magnitudes of these changes are not known.

⁶ ERDA-6 is a synthetic brine representative of fluids in brine reservoirs in the Castile Formation (Popielak et al., 1983)

6.5 Quantifying r

Due to the difficulty quantifying the amount of CO₂ consumed by materials other than MgO, this analysis will conservatively assume that MgO is the only material in the waste areas that consumes CO₂. Specifically, the following assumptions are made to quantify the variable r :

- 1) CO₂ will not be consumed by Fe-base metals or their corrosion products, Pb-base metals or their corrosion products, or lime and portlandite in portland cements.
- 2) No CO₂ is consumed by dissolution in brine.
- 3) No organic carbon in CPR materials will be incorporated into biomass.

Thus, MgO is considered to be the only material that can consume CO₂ for this analysis. As discussed in Section 6.1, this analysis assumes that the moles of CO₂ sequestered per mole of MgO is a random variable with a uniform distribution on [0.8,1]. Thus, r is assigned a mean value equal to 0.9 ($\mu_r = 0.9$) and a standard deviation equal to 0.0577 ($\sigma_r = 0.0577$).

7.0 Calculation of the MgO Effective Excess Factor

As indicated in Section 3.0, there are three primary sources of uncertainty included in the Effective Excess Factor calculation:

- 1) uncertainties in the quantities of CO₂ produced by microbial consumption of the CPR;
- 2) uncertainties in the amount MgO that is available to consume CO₂; and
- 3) uncertainties in the moles of CO₂ sequestered by each mole of available MgO.

Eq. 7-1 incorporates all of the quantified uncertainties that are included in the EEF calculation.

$$7-1 \quad EEF = \frac{m \times M_{MgO}}{g \times M_C} \times r = \frac{(y_{SS} \times y_{RC} \times 0.999 - y_{L2B}) \times M_{MgO}}{(y_{yield} \times y_{CPR}) \times M_C} \times r$$

The term M_C is the total moles of organic carbon in the emplaced CPR mass reported by the DOE, and M_{MgO} is the total moles of emplaced MgO. The variables g and m are random variables defined in Eqs. 4-7 and 5-8 and represent the uncertainty in the quantities of CO₂ produced and the uncertainty in the amount of MgO available for CO₂ consumption, respectively. The r term represents the moles of CO₂ consumed by each mole of emplaced MgO and is also a random variable.

Table 2, Table 3, and Table 4 list all of the issues discussed in Sections 4.0, 5.0, and 6.0 that could potentially affect calculation of the EEF. These tables indicate in which sections the issues were discussed, how the issues are included in the EEF calculation, and means and standard deviations if the issues were quantified or how the issue could potentially impact the EEF calculation if the issue was not completely quantified.

Table 2 Issues Affecting CO₂ Production

Issue	Section	Inclusion in EEF as Random Variable (RV) or Assumption?	Mean (μ) and Std. Dev. (σ) if RV / Expected Impact if not RV
CPR Estimates	4.1	RV: y_{CPR}	$\mu_{CPR} = 1.00$, $\sigma_{CPR} = 3 \times 10^{-3}$
Effective CO ₂ yield	4.2 and subsections of 4.2	Assume CO ₂ is produced at the maximum yield, i.e., y_{yield} is a constant and $y_{yield} = 1$	Conservative assumption decreases the mean EEF.
Methanogenesis	4.2.2	Assume that methanogenesis does not occur.	Inclusion of methanogenesis would increase mean EEF and increase uncertainty.

Table 3 Issues Affecting the Fraction of MgO Available for CO₂ Sequestration

Issue	Section	Inclusion in EEF as Random Variable (RV) or Assumption?	Mean (μ) and Std. Dev. (σ) if RV// Expected Impact if not RV
Concentration of reactive constituents in MgO	5.1.1	RV: y_{RC}	$\mu_{RC} = 0.96, \sigma_{RC} = 0.02$
Carbonation of MgO prior to emplacement	5.1.2	Assume that 0.1% of MgO carbonates prior to emplacement.	Conservative assumption decreases the mean EEF.
Ability of periclase to react to completion	5.1.3	Assume that all periclase will react until all CO ₂ is consumed.	Inclusion of this uncertainty in the EEF could decrease the mean and increase the uncertainty for the EEF. The expected magnitude of these changes is small.
Loss of MgO to brine	5.2.2	RV: y_{L2B}	$\mu_{L2B} = 0.007, \sigma_{L2B} = 0.017$
Rupturing of supersacks	5.2.1	Assume that all MgO supersacks rupture.	Certainty of this process results in no impact on EEF.
Amount of MgO in each room relative to the amount tracked by DOE	5.2.5	RV: y_{SS}	$\mu_{SS} = 1.00, \sigma_{SS} = 3.7 \times 10^{-4}$
Mixing processes	5.2.3	Assume that a well-mixed brine will be maintained.	Certainty of this process results in no impact on EEF.
Physical segregation of MgO from CO ₂	5.2.4	No MgO is rendered unavailable for CO ₂ consumption due to physical segregation.	Inclusion of this uncertainty in the EEF could decrease the mean and increase the uncertainty for the EEF. The expected magnitude of these changes is small.

Table 4 Issues Affecting the Moles of CO₂ Consumed by a Single Mole of Available MgO

Issue	Section	Inclusion in EEF as Random Variable (RV) or Assumption?	Mean (μ) and Std. Dev. (σ) if RV / Expected Impact if not RV
Hydromagnesite and magnesite formation	6.1 and 6.5	RV: r	$\mu_r = 0.9, \sigma_r = 0.0577$
Consumption of CO ₂ by materials other than MgO	6.2	Assume Fe-base metals or their corrosion products, Pb-base metals or their corrosion products, or lime and portlandite in portland cements do not consume CO ₂	Inclusion of CO ₂ consumption by these materials could increase the mean EEF and increase uncertainty.
Dissolution of CO ₂ in WIPP brines	6.3	Assume CO ₂ is not consumed by dissolution in brine.	Exclusion of this process results in no impact on EEF because of the extremely small quantities of CO ₂ that could be consumed by this mechanism.
Incorporation of CO ₂ in biomass	6.4	Assume no organic C is sequestered in biomass.	Inclusion of sequestration of organic C in biomass would increase the mean EEF and increase uncertainty.

7.1 Calculated EEF Means and Uncertainties

Using Eq. 7-1, the means, standard deviations, and relative uncertainties were calculated for the random variables EEF, g , m , and r (Table 5). The key result from this analysis is that the mean EEF is 1.03, greater than the minimum EEF (1.0) that guarantees the consumption of all CO₂ that could be generated by microbes. Thus, on average, emplacing 1.2 moles of MgO for every mole of emplaced organic carbon will be sufficient to consume all CO₂ that could be generated by microbes. The calculations for the results in this section and the associated statistical methods used in these calculations are detailed in Appendix B.

Table 5 Means and Uncertainties for the Random Variables *EEF*, *g*, *m*, and *r*

Variable	Mean: μ	Standard Deviation: σ	Relative Uncertainty: σ/μ
EEF	1.03	0.0719	0.0700
<i>g</i>	1.00	0.003	0.003
<i>m</i>	0.952	0.0262	0.0276
<i>r</i>	0.900	0.0577	0.0642

8.0 Summary and Conclusions

The EPA currently requires the DOE to emplace 1.67 moles of MgO for every mole of organic carbon in emplaced CPR. The EPA has stated that they require this “relatively high excess amount” since “the extra MgO would overwhelm any perceived uncertainties that the chemical reactions would take place as expected” (Gitlin 2006). Thus, when the DOE requested that the MgO excess factor be lowered from 1.67 to 1.2, the EPA required that the DOE address “the uncertainties related to MgO effectiveness, the size of the uncertainties, and the potential impact of the uncertainties on long-term performance” (Gitlin 2006). To address this request, SNL has conducted an analysis of these uncertainties.

This analysis introduces the concept of the MgO “Effective Excess Factor,” a quantity that incorporates uncertainties into the current definition of the MgO excess factor. The uncertainties included in the EEF calculation are grouped into three categories:

- 1) uncertainties in the quantities of carbon dioxide (CO₂) produced by microbial consumption of the CPR;
- 2) uncertainties in the amount MgO that is available to react with CO₂; and
- 3) uncertainties in the moles of CO₂ sequestered per mole of MgO that is available to consume CO₂.

These uncertainties are represented with random variables in the EEF calculation.

The EEF calculation includes several conservative assumptions, as well. These assumptions include:

- 1) It is conservatively assumed that all organic carbon in emplaced CPR materials will be consumed by microbes. While this analysis has not attempted to quantify the fraction of CPR that might be consumed or the probabilities associated with these percentages, inclusion of this conservative assumption has the potential to significantly overestimate the amount of CO₂ produced and, consequently, underestimate the mean EEF.
- 2) It is conservatively assumed that each mole of consumed organic carbon will yield 1 mole of CO₂. This yield represents the maximum amount of CO₂ that could be produced and does not include any uncertainties that could result in a lower yield. For example, it is conservatively assumed that methanogenesis will not occur. Since methanogenesis yields half the amount of CO₂ than the denitrification and sulfate reduction reactions.

- 3) It is conservatively assumed that MgO is the only material that will sequester CO₂. The beneficial effects of the consumption of CO₂ by iron-base metals, lead-base metals, lime, and other substances in the waste materials are ignored.

Because of the many and significant conservatisms included in this analysis, the mean EEF is the best indicator as to whether or not an EF of 1.2 will be sufficient to consume all CO₂.

Since the EEF considers the uncertainties affecting MgO effectiveness, it is necessary only for the EEF to be greater than 1.0 to ensure that chemical conditions are maintained as assumed in WIPP PA. Using standard techniques from statistical theory, the quantified uncertainties of the individual components were propagated to calculate the mean and uncertainty for the EEF. The mean EEF is calculated to be 1.03, greater than the minimum EEF (1.0) that guarantees the consumption of all CO₂ that could be generated by microbes. This analysis concludes that emplacing 1.2 moles of MgO for every mole of organic carbon in the emplaced CPR is more than sufficient to consume all CO₂ that could be generated by microbes and to maintain chemical conditions as assumed in WIPP PA. Furthermore, reducing the MgO excess factor to 1.2 would have no impact on the long-term performance of the repository.

9.0 References

- Brush, L.H. 1995. Systems Prioritization Method - Iteration 2 Baseline Position Paper: Gas Generation in the Waste Isolation Pilot Plant. Sandia National Laboratories. Albuquerque, NM. ERMS 228740.
- Brush, L.H. 2004. Implications of New (Post-CCA) Information for the Probability of Significant Microbial Activity in the WIPP. Sandia National Laboratories. Carlsbad, NM. ERMS 536205.
- Brush, L. H., and G. T. Roselle. 2006. Geochemical Information for Calculation of the MgO Excess Factor. Memo to Eric D. Vugrin, November 17, 2006. Sandia National Laboratories. Carlsbad, NM. ERMS 544840.
- Clayton, D. J. and M. B. Nemer. 2006. Normalized Moles of Castile Sulfate Entering the Repository and Fraction of MgO Lost Due to Brine Flow Out of the Repository. Memo to Eric D. Vugrin, October 9th, 2006. Sandia National Laboratories. Carlsbad, NM. ERMS 544385.
- Cotsworth, E. 2004. Untitled letter with enclosure to R.P. Detweiler with first set of CRA comments, May 20, 2004. Washington, DC: U.S. Environmental Protection Agency Office of Air and Radiation. ERMS 535554.
- Cotsworth, E. 2005. EPA Letter on Conducting the Performance Assessment Baseline Change (PABC) Verification Test. U.S. EPA, Office of Radiation and Indoor Air. Washington, D.C. ERMS 538858.
- Deal, D. E., R. J. Abitz, D. S. Belski, J. B. Case, M. E. Crawley, C. A. Givens, P. P. J. Lipponer, J. Myers, D. W. Powers, and M. A. Valdiva. 1995. Brine Sampling and Evaluation Program

1992-1993 Report and Summary of BSEP Data Since 1982. Contractor Report DOE-WIPP 94-011, U.S. Department of Energy WIPP Project Office. Carlsbad, NM.

Deng, H., S. Johnsen, G. Roselle, and M. Nemer. 2006a. Preliminary Analysis of Martin Marietta MagChem 10 WTS-60 MgO. Sandia National Laboratories. Carlsbad, NM. ERMS 544712.

Deng, H., M.B. Nemer, and Y. Xiong. 2006b. Experimental Study of MgO Reaction Pathways and Kinetics, Rev. 0. TP 06-03, Rev. 0, June 6, 2006. Sandia National Laboratories. Carlsbad, NM. ERMS 543633.

DOE. 1983a. Results of Site Validation Experiments, Waste Isolation Pilot Plant (WIPP) Project, Southeastern New Mexico. Vol. I. Executive Summary, Text, and Supporting Documents 1 through 4. TME-3177, Vol. I, U.S. Department of Energy Waste Isolation Pilot Plant, Albuquerque, NM.

DOE. 1983b. Results of Site Validation Experiments, Waste Isolation Pilot Plant (WIPP) Project, Southeastern New Mexico. Vol. II. Supporting Documents 5 through 14. TME-3177, Vol. II, U.S. Department of Energy Waste Isolation Pilot Plant, Albuquerque, NM.

DOE. 1996. Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot. DOE/CAO-1996-2184, U.S. Department of Energy Waste Isolation Pilot Plant, Carlsbad Area Office, Carlsbad, NM.

DOE. 1997. DOE Response to Comments to EPA December 19, 1996 letter, EPA docket A-93-02 Item II-I-10, EPA Comment Enclosure 2, Page 3, 194.23(a)(3)(i) February 1997.

DOE. 2000. Proposal for Elimination of MgO Mini-sacks. U. S. Department of Energy Carlsbad Field Office, Carlsbad, NM. ERMS 543262.

DOE. 2004a. Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant, Vol. 1-8. DOE/WIPP 2004-3231. U.S. Department of Energy Carlsbad Field Office. Carlsbad, NM.

DOE. 2004b. DOE's 6th Response Submittal to Comments from EPA's 2nd Request for Additional Information December 2004.

DOE. 2005. Letter from Ines Tray, Acting Manager of the Carlsbad Field Office to Bonnie Gitlin, Acting Director of EPA Radiation Protection Division, Plans for Emplacement of Additional MgO, March 8, 2005.

EPA. 1998. Technical Support Document For Section 194.24; EPA's Evaluation of DOE's Actinide Source Term. EPA Docket A-93-02, Item V-B-17, May, 1998. Washington, DC: U. S. Environmental Protection Agency, Office of Radiation and Indoor Air, Center for the Waste Isolation Pilot Plant.

- EPA. 2004a. Review of Effects of Supercompacted Waste and Heterogeneous Waste Emplacement on WIPP Repository Performance. Washington D.C.
- EPA. 2004b. Letter from Elizabeth Cotsworth, EPA Director of Radiation and Indoor Air to Paul Detwiler, CBFO Acting Manager requesting additional information for a completeness determination, ERMS 536771.
- EPA. 2006. Technical Support Document For Section 194.24; Evaluation of the Compliance Recertification Actinide Source Term and Culebra Dolomite Distribution Coefficient Values. EPA Docket A-98-49, Item II-B1-3, March, 2006. Washington, DC: U. S. Environmental Protection Agency, Office of Radiation and Indoor Air, Center for the Waste Isolation Pilot Plant.
- Gillow, J. B., and A. J. Francis. 2003. Microbial Gas Generation Under Expected Waste Isolation Pilot Plant Conditions: Draft Final Report, Rev. 0, October 6, 2003. Brookhaven National Laboratory. Upton, NY. ERMS 532877.
- Gitlin, B. C. 2006. Letter to D. C. Moody Concerning the DOE's Request to Reduce the MgO Excess Factor from 1.67 to 1.2, dated April 28, 2006.
- Hailey, S. M. 1994. A Comparison of Real-Time Radiography Results and Visual Characterization Results with Emphasis on WIPP WAC and TRAMPAC Compliance Issues. Idaho National Laboratory. Idaho Falls, ID.
- Hansen, C. W., L. H. Brush, M. B. Gross, F. D. Hansen, B.-Y. Park, J. S. Stein, and T. W. Thompson. 2004. Effects of Supercompacted Waste and Heterogeneous Waste Emplacement on Repository Performance, Revision 2. Sandia National Laboratories. Carlsbad, NM. ERMS 533551.
- Hansen, F. D. 2005. Magnesium Super Sack Rupture under WIPP Conditions. Memo to D. Kessel, dated May 11, 2005. Sandia National Laboratories. Carlsbad, NM. ERMS 539724.
- Kanney, J. F., A. C. Snider, T. W. Thompson, and L. H. Brush. 2004. Effect of Naturally Occurring Sulfate on the MgO safety Factor in the Presence of Supercompacted Waste and Heterogenous Waste Emplacement. Sandia National Laboratories. Carlsbad, NM. ERMS 534150.
- Kanney, J. F. and E. D. Vugrin. 2006. Updated Analysis of Characteristic Time and Length Scales for Mixing Processes in the WIPP Repository to Reflect the CRA-2004 PABC Technical Baseline and the Impact of Supercompacted Mixed Waste and Heterogeneous Waste Emplacement. Sandia National Laboratories. Carlsbad, NM. ERMS 544248.
- Kirchner, T. B. and E. D. Vugrin. 2006. Uncertainty in Cellulose, Plastic, and Rubber Measurements for the Waste Isolation Pilot Plant Inventory. Sandia National Laboratories, Carlsbad, NM. ERMS 543848.

- Marcinowski, F. 2001. Environmental Protection Agency's (EPA's) Approval for the Elimination of Magnesium Oxide (MgO) Mini-sacks from WIPP. Sandia National Laboratories, Carlsbad, NM. ERMS 519362.
- Mood, A. M., F. A. Graybill and D. C. Boes. 1974. Introduction to the Theory of Statistics. McGraw-Hill, New York, NY.
- Moody, D. C. 2006. Letter to E. A. Cotsworth Requesting a Reduction in the MgO Excess Factor from 1.67 to 1.2, dated April 10, 2006. ERMS 543262.
- Nemer, M. B. 2007. Effects of Not Including Emplacement Materials in CPR Inventory on Recent PA Results. Carlsbad, NM: Sandia National Laboratories. ERMS 545689.
- Nemer, M. B. and J. S. Stein 2005. Analysis Package for BRAGFLO, 2004 Compliance Recertification Application Performance Assessment Baseline Calculation. Sandia National Laboratories, Carlsbad, NM. ERMS 540527.
- Popielak, R. S., R. L. Beauheim, S. R. Black, W. E. Coons, C. T. Ellingson, and R. L. Olsen. 1983. Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant (WIPP) Project, Southeastern New Mexico. TME-3153, U.S. Department of Energy Waste Isolation Pilot Plant, Albuquerque, NM.
- Snider, A. C. 2003. Calculation of MgO Safety Factors for the WIPP Compliance Recertification Application and for Evaluating Assumptions of Homogeneity in WIPP PA. Analysis report, September 11, 2003. Sandia National Laboratories. Carlsbad, NM. ERMS 531508.
- Vugrin, E. D. 2006. Total Number of MgO Supersacks per Room in Panels 1, 2, and 3 as of August 17, 2006. Carlsbad, NM. Sandia National Laboratories. ERMS 544234.
- Wall, N.A. 2005. Preliminary Results for the Evaluation of Potential New MgO. Sandia National Laboratories. Carlsbad, NM. ERMS 538514.
- Wang, Y. and L.H. Brush. 1996. Estimates of Gas-Generation Parameters for the Long-Term WIPP Performance Assessment. Memorandum to M.S. Tierney, January 26, 1996. Sandia National Laboratories. Albuquerque, NM. ERMS 231943.
- Wang, Y. 2000. Effectiveness of Mixing Processes in the Waste Isolation Pilot Plant Repository. Technical Memorandum. Sandia National Laboratories, Carlsbad, NM. ERMS 519362.
- Washington TRU Solutions (WTS). 2005. Specifications for Repackaged Backfill, Waste Isolation Pilot Plant Procedure D-0101, Revision 7, May 2005.
- WTS. 2006. CH Waste Processing, Technical Procedure WP05-WH1011, Revision 23, January 2006.

10.0 Appendix A

The calculation of the EEF includes the conservative assumption that all of the organic carbon in the emplaced CPR materials will be consumed by microbes. This assumption affects the quantity of CO₂ that can be produced by microbial respiration and, hence, impacts the EEF calculation.

Even though this analysis conservatively assumes that all of the organic carbon will be consumed, it should be noted that, in fact, there are several uncertainties associated with this assumption. In keeping with the EPA's direction that "DOE needs to address the uncertainties related to MgO effectiveness, the size of the uncertainties, and the potential impact of the uncertainties on long-term performance" (Gitlin 2006), the uncertainties associated with this assumption are qualitatively discussed in this appendix.

Several factors affect the quantity of organic carbon in CPR materials that could be consumed by microbes. Brush (1995) described seven issues:

- 1) Whether microbes will be present in the repository when it is filled and sealed;
- 2) Whether the emplaced waste and other contents of the repository will be sterilized;
- 3) Whether microbes will survive for a significant fraction of the 10,000 year regulatory time frame;
- 4) Whether sufficient water will be present for significant microbial respiration to take place;
- 5) Whether sufficient quantities of biodegradable substrates will be present for significant microbial respiration to take place;
- 6) Whether sufficient electron acceptors will be present and available for significant microbial respiration to take place; and
- 7) Whether enough nutrients, especially nitrogen (N) and phosphorous (P), will be present and available for significant microbial respiration to take place.

These issues, identified in Brush (1995) and updated in Brush (2004), are summarized herein.

10.1 *Presence of Microbes in the Repository*

Brush (1995) concluded "halophilic microorganisms capable of carrying out [potentially significant] respiratory pathways ... probably exist throughout the WIPP underground workings." DOE (2004a, Appendix Barriers) further notes that the results of the long-term Brookhaven National Laboratory (BNL) study of microbial gas generation (Gillow and Francis 2003) "have confirmed that viable halophilic fermenters and methanogens capable of metabolizing cellulosic materials under expected near-field conditions are present in the WIPP underground workings." Thus, Brush (2004) concluded that halophilic microbes are expected to be present and that this issue was not a significant source of uncertainty.

10.2 Sterilization of the Waste and Other Repository Contents

Brush (1995) states that sterilization of the waste to preclude microbial activity is infeasible. However, Brush (2004) states that MgO and compounds derived from MgO have been observed to possess inhibitory or even biocidal properties. Generally, biocides are required to be in contact with microbes to ensure that the biocide is effective. The large volume of waste in rooms in the repository would make it difficult to ensure contact between the MgO and microbes, so it is unlikely that the presence of MgO would preclude all microbial activity (Appendix Barriers, DOE 2004a). However, it is possible that the MgO could reduce the rate of microbial gas generation in the WIPP (Appendix Barriers, DOE 2004a), and a reduction in microbial gas generation rates could potentially limit the amount of organic carbon in CPR materials that could be consumed.

Inhibition of microbial activity by MgO has not been quantified in repository-specific laboratory experiments simulating expected WIPP conditions. Because of the uncertainties associated with the possible inhibition or reduction of microbial activity, this issue is conservatively excluded from the uncertainty analysis.

10.3 Survivability of Microbes

As discussed in Section 10.1, there is a high probability that microbes will be present when the repository is closed. However, after the shafts and surrounding boreholes are sealed, the contents of the repository will be isolated from the surface environment until a potential human intrusion. Thus, the survivability of microbes for a significant period of time during the 10,000 year regulatory time period is a large and important source of uncertainty.

As discussed in Brush (2004), the rates of microbial activity and microbial gas production in the long-term BNL study of microbial gas generation by Gillow and Francis (2003) were "relatively high initially, but soon decreased significantly, and have quite possibly decreased to zero" (Brush 2004). Brush (2004) further states that because the gas production has ceased or nearly ceased after less than 0.1% of the 10,000 year regulatory time period, the results of Gillow and Francis (2003) decrease the certainty that microbes will survive long enough to affect repository performance.

Brush (2004) also notes that the presence of MgO may decrease the survivability of microbes through two separate mechanisms. First, as described in Section 10.2, the MgO may possess biocidal or inhibitory properties that affect microbes. Secondly, hydration of MgO will maintain dry conditions for a potentially significant period of time, thereby decreasing the probability of survival of viable microbes.

10.4 Presence of Sufficient Quantities of Water

Hydration of MgO will maintain dry conditions in the repository for a potentially significant period of time, thus limiting the quantities of water available to microbes for a potentially significant period of time (Brush 2004). This length of time has not been precisely quantified, but "this period could be long enough - and the activity of water during this period could be low

enough - to decrease the probability of survival of microbes” (Brush 2004). Hence, the amount of organic carbon in CPR materials that is consumed by microbial activity could be affected by MgO hydration and a lack of available water.

10.5 Presence of Sufficient Quantities of Biodegradable Substrates

As discussed in Section 10.3, the rates of microbial activity and gas production in the BNL study of microbial gas generation were initially relatively high before decreasing significantly, and quite possibly ceasing altogether (Gillow and Francis 2003). Brush (2004) reported that less than 5% of cellulosic materials were consumed before gas production ceased or nearly ceased, and there was very limited gas production from the irradiated plastic and rubber materials. Though these results are from a study that was carried out for less than 0.1% of the 10,000 year regulatory time period, they add to the uncertainty that all of the CPR materials will be consumed. DOE plans to further investigate this issue in the future.

10.6 Presence of Sufficient Electron Acceptors

Cotsworth (2004) stated,

“In addition, sulfate present in brine and in minerals in the Salado Formation surrounding the repository are likely to be available for reaction, so sufficient electron acceptors may be expected to be present.”

If sulfate from the brine and minerals in the Salado Formation was readily available to microbes in the repository, this source alone would be a sufficient source of electron acceptors. Kanney et al. (2004) conducted an analysis that conservatively bounds the quantities of sulfate that could enter the repository via diffusion and advection, but amongst other issues, the EPA commented that roof collapse could bring sulfate-bearing minerals⁷ into direct contact with brines in the repository (EPA 2004a). Thus, there is considerable uncertainty in the amount of sulfate that would be present in the repository.

However, even if the amount of sulfate was limited, microbial consumption of CPR materials is expected to proceed via methanogenesis. Hence, the possibility of the presence of sufficient electron acceptors cannot be ruled out presently.

10.7 Presence of Sufficient Nutrients

Brush (2004) states that microbes require a variety of nutrients, including C, O, N, H, P, S, K, Na, Ca, Mg, Cl, Fe, Mn, Zn, Mo, Cu, and Co. Many of these nutrients are found in WIPP brines and waste materials. However, Brush (2004) indicates that “it is unclear whether nutrients would actually be available to microbes. For example, precipitation of PO_4^{3-} by highly insoluble phases such as apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$) could effectively sequester this nutrient, especially if

⁷ It should be noted that the sulfate-bearing minerals found in the disturbed rock zone also contain significant quantities of calcium. The presence of calcium is significant because the calcium has the potential to react with CO_2 and precipitate CaCO_3 -bearing minerals, thus sequestering CO_2 . This process is discussed in Section 4.2.1.

apatite contains appreciable concentrations of inhibitory, toxic, or radiotoxic heavy metals such as the actinides in TRU [transuranic] waste.” Hence, it is uncertain whether microbes will have sufficient nutrients for significant microbial activity.

10.8 *Impact of the Uncertainties on the MgO Excess Factor*

None of the uncertainties discussed in Sections 10.1-10.7 are included in this analysis because calculation of the MgO excess factor and the MgO EEF includes the conservative assumption that all of the organic carbon in CPR materials can and will be consumed by microbial activity. If these uncertainties could be quantified and were included in the EEF calculations, they would have the effect of reducing the expected amount of CO₂ that could be produced and of increasing the uncertainty. Consequently, the expected impact of including these uncertainties is an increase in the mean EEF and an increase in the EEF’s standard deviation. The magnitude of these increases is not presently known.

11.0 Appendix B

As indicated in Eq. 7-1, the EEF is a random variable since it is a function of random variables. The following sections detail how to calculate the mean and uncertainty (standard deviation) for the random variables g , m , r , and EEF.

11.1 Background

Before calculating the mean and uncertainties associated with the EEF, it is necessary to state the theorems required for these calculations. Theorem 1 can be used to calculate the mean of a random variable that is the function of two independent random variables, X and Y (Mood et al. 1974):

Theorem 1: Let X and Y be independent random variables with means μ_X and μ_Y , respectively. If $Z=X \pm Y$, $W = X \times Y$, and $V=cX$ where c is a constant, then their respective means are $\mu_Z = \mu_X \pm \mu_Y$, $\mu_W = \mu_X \times \mu_Y$, and $\mu_V = c\mu_X$.

Mood et al. (1974) state that there are no simple formulas for calculating the mean of the quotient of two random variables. The following theorem from Mood et al. (1974) is useful for approximating the mean:

Theorem 2: Let X and Y be random variables with respective means μ_X and μ_Y . If $Z=X/Y$, then

$$11-1 \quad \mu_Z \approx \frac{\mu_X}{\mu_Y} - \frac{1}{\mu_Y^2} \text{cov}[X, Y] + \frac{\mu_X}{\mu_Y^3} \text{var}[Y.]$$

The following two theorems from Taylor (1982) are used to calculate the uncertainties for g and m :

Theorem 3: Suppose X and Y are measured with uncertainties σ_X and σ_Y , and the measured values are used to compute $Z=X \pm Y$. If the uncertainties in X and Y are known to be independent and random, then the uncertainty in Z , σ_Z , is

$$11-2 \quad \sigma_Z = \sqrt{(\sigma_X)^2 + (\sigma_Y)^2}.$$

In any case,

$$11-3 \quad \sigma_Z \leq \sigma_X + \sigma_Y.$$

Theorem 4: Suppose X and Y are measured with uncertainties σ_X and σ_Y , and the measured values are used to compute $Z = X \times Y$ and $W = X/Y$. If the uncertainties in X and Y are known to be independent and random, then the fractional uncertainties in Z and W , $\frac{\sigma_Z}{|Z|}$ and $\frac{\sigma_W}{|W|}$, are

$$11-4 \quad \frac{\sigma_Z}{|Z|} = \frac{\sigma_W}{|W|} = \sqrt{\left(\frac{\sigma_X}{|X|}\right)^2 + \left(\frac{\sigma_Y}{|Y|}\right)^2}.$$

In any case,

$$11-5 \quad \frac{\sigma_Z}{|Z|} \leq \frac{\sigma_X}{|X|} + \frac{\sigma_Y}{|Y|}$$

and

$$11-6 \quad \frac{\sigma_W}{|W|} \leq \frac{\sigma_X}{|X|} + \frac{\sigma_Y}{|Y|}.$$

11.2 Random Variables g , m , and r

Recall from Eq. 4-7 that the random variable g in the EEF calculation is defined as follows:

$$11-7 \quad g = y_{\text{yield}} \times y_{CPR}$$

The variable y_{yield} is a constant equal to 1, so g can be equated with y_{CPR} . Since y_{CPR} has a mean value of 1 and a standard deviation of 0.003 (Table 2), g has the same mean and standard deviation (i.e., $\mu_g = 1$ and $\sigma_g = 0.003$). The fractional uncertainty in g , $\frac{\sigma_g}{|g|}$, is 0.003.

The random variable m was first defined in Eq. 5-8 and is repeated below:

$$11-8 \quad m = y_{SS} \times y_{RC} \times 0.999 - y_{L2B}.$$

Before calculating the mean and standard deviation of m , the independence of the random variables y_{SS} , y_{RC} , and y_{L2B} must be assessed. The mass of an MgO supersack is independent of the percentage of reactive constituents of the materials in that supersack, so the random variables y_{SS} and y_{RC} are considered independent. The amount of MgO lost to brine outflow depends on the volumes of brine that leave the waste areas and the quantities of MgO dissolved in that brine. With the amounts of MgO that are expected to be emplaced in the repository, the quantities of MgO dissolved in brine will be independent of the mass of the supersacks and the percentage of reactive constituents in the emplaced MgO. The same is true for the amount of brine outflow. Hence, this analysis considers that the variables y_{SS} , y_{RC} , and y_{L2B} are independent, and Theorems 1-4 can be used to calculate the mean and standard deviation of the random variable m .

Application of Theorem 1 to Eq. 11-8 results in a mean m value of 0.952 ($\mu_m = 0.952$) (Eq. 11-9)⁸.

$$11-9 \quad \begin{aligned} \mu_m &= \mu_{SS} \times \mu_{RC} \times 0.999 - \mu_{L2B} \\ &= 1 \times 0.96 \times 0.999 - 0.007 = 0.952 \end{aligned}$$

⁸ Numerical values reported in Sections 11.2 and 11.3 have been calculated in a spreadsheet and were then rounded for this document.

Eq. 11-10 indicates how to calculate the relative uncertainty in m using Theorem 3.

$$11-10 \quad \frac{\sigma_m}{|\mu_m|} = \frac{\sqrt{(0.999 \times \sigma_{SS \times RC})^2 + (\sigma_{L2B})^2}}{|\mu_m|}$$

The term $\sigma_{SS \times RC}$ in Eq. 11-10 represents the uncertainty in the random variable ($y_{SS} \times y_{RC}$) and is calculated to be 0.02 (Eq. 11-11).

$$11-11 \quad \begin{aligned} \sigma_{SS \times RC} &= |\mu_{SS \times RC}| \times \frac{\sigma_{SS \times RC}}{|\mu_{SS \times RC}|} \\ &= |\mu_{SS \times RC}| \times \sqrt{\left(\frac{\sigma_{SS}}{|\mu_{SS}|}\right)^2 + \left(\frac{\sigma_{RC}}{|\mu_{RC}|}\right)^2} \\ &= 0.96 \times \sqrt{\left(\frac{3.7 \times 10^{-4}}{1.00}\right)^2 + \left(\frac{0.02}{0.96}\right)^2} \\ &= 0.02 \end{aligned}$$

Consequently, the relative uncertainty in m is 0.0276 (Eq. 11-12) and the standard deviation is 0.0262 (Eq. 11-13).

$$11-12 \quad \frac{\sigma_m}{|\mu_m|} = \frac{\sqrt{(0.999 \times 0.02)^2 + (0.017)^2}}{0.952} = 0.0276$$

$$11-13 \quad \sigma_m = \frac{\sigma_m}{|\mu_m|} \times |\mu_m| = 0.0276 \times 0.952 = 0.262.$$

As shown in Table 4, r is assigned a mean value equal to 0.9 ($\mu_r = 0.9$) and a standard deviation of 0.0577 ($\sigma_r = 0.0577$).

11.3 *EEF Calculation*

It should be noted that in the following calculations, the random variables g , m , and r are considered to be independent. The estimation techniques that are used to calculate quantities of CPR that are emplaced in the repository, the supersack masses, the quantities of MgO lost to brine outflow, the reactive constituents in MgO, and the quantity of CO₂ consumed by a single mole of MgO are all independent from one another. Consequently, g , m , and r are independent.

If it is assumed that 1.2 moles of MgO are emplaced for every mole of organic carbon in the emplaced CPR, i.e. $M_{MgO} = (1.2)M_C$ in Eq. 7-1, then

$$11-14 \quad EEF = \frac{1.2 \times m \times r}{g}$$

The mean of the product of m and r , $\mu_{m \times r}$, is equal to 0.857 and is calculated with Theorem 1 by taking the product of their respective means. The standard deviation of the product of m and r , $\sigma_{m \times r}$, is determined by Theorem 4 and equal to 0.0598. This calculation is shown in Eq. 11-15.

$$\begin{aligned}
 \sigma_{m \times r} &= \mu_{m \times r} \times \frac{\sigma_{m \times r}}{\mu_{m \times r}} \\
 11-15 \quad &= \mu_{m \times r} \times \sqrt{\left(\frac{\sigma_m}{\mu_m}\right)^2 + \left(\frac{\sigma_r}{\mu_r}\right)^2} \\
 &= 0.857 \sqrt{(0.0276)^2 + (0.0642)^2} = 0.0598
 \end{aligned}$$

The mean EEF, μ_{EEF} , is equal to 1.03 and calculated using Theorem 2 with the following equation:

$$\begin{aligned}
 \mu_{EEF} &= 1.2 \left(\frac{\mu_{m \times r}}{\mu_g} + \frac{\mu_{m \times r}}{\mu_g^3} \sigma_g^2 \right) \\
 11-16 \quad &= 1.2 (0.857 + 0.857 \times 0.003^2) \\
 &= 1.03.
 \end{aligned}$$

(Since g , m , and r are independent, the covariance term in Eq. 11-1 is 0.) The standard deviation for EEF is 0.0719 (Eq. 11-17) and is calculated with Theorem 4. The relative uncertainty for EEF is 0.0700.

$$\begin{aligned}
 \sigma_{EEF} &= \mu_{EEF} \frac{\sigma_{EEF}}{\mu_{EEF}} \\
 11-17 \quad &= \mu_{EEF} \sqrt{\frac{\sigma_{m \times r}^2}{(\mu_{m \times r})^2} + \frac{\sigma_g^2}{(\mu_g)^2}} \\
 &= 1.03 \sqrt{\frac{(0.0598)^2}{(0.857)^2} + \frac{(0.003)^2}{(1)^2}} = 0.0719
 \end{aligned}$$

11.4 References

Mood, A. M., F. A. Graybill and D. C. Boes. 1974. Introduction to the Theory of Statistics. McGraw-Hill, New York, NY.

Taylor, J. R. 1982. An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements. University Science Books, Mill Valley, CA.