



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

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JAN 11 2001

OFFICE OF  
AIR AND RADIATION

Dr. Ines Triay  
Carlsbad Field Office  
Department of Energy  
P.O. Box 3090  
Carlsbad, NM 88221

Dear Dr. Triay:

Thank you for your letter dated July 21, 2000, in which you requested the Environmental Protection Agency's (EPA's) approval for the elimination of magnesium oxide (MgO) mini-sacks from the Waste Isolation Pilot Plant (WIPP). The elimination of the mini-sacks would result in a fifteen percent reduction in the total amount of MgO that must be placed in the WIPP, in accordance with the WIPP Compliance Certification Application and EPA's certification decision.

We have reviewed your request and agree that this change, which you have proposed to improve operational safety, will not significantly impact the WIPP's long-term performance (see the enclosed report). The quantity of MgO that the Department of Energy (DOE) is required to place in the WIPP is expected to prevent or delay substantially the movement of radionuclides to the accessible environment. Therefore, we approve your proposal.

We will place our report and your proposal in our public docket. We expect that DOE will track and report on this change in accordance with our guidance to DOE on recertification.

Sincerely,

Frank Marcinowski, Acting Director  
Radiation Protection Division

Enclosure

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## MgO Mini-sack Review

### 1.0 Introduction

This report summarizes EPA's review of DOE's proposal to eliminate magnesium oxide (MgO) mini-sacks from the Waste Isolation Pilot Plant (WIPP). This report responds to a formal request from Dr. Ines Triay of DOE dated July 21, 2000 (See Attachments 1 to 4). It includes information obtained during a DOE/EPA technical exchange meeting held in Washington, DC, on April 12-13, 2000 (See Attachment 5).

### 2.0 Overview of DOE Proposal

DOE requested that EPA approve the elimination of approximately 15% of the total quantity of MgO in the repository by removing backfill mini-sacks placed on and around waste drums and waste boxes (see Table 1). The backfill to be eliminated would be eighteen 25-lb bags (mini-sacks) of MgO around each waste stack and the mini-sacks from the floor around the waste containers. DOE states this proposal would "significantly enhance worker safety at the WIPP without adversely impacting repository performance" (see Attachment 2).

Table 1: DOE's Calculation of Excess of MgO

Case	Quantity	Value
Assume all organic carbon; cellulosics, papers, and rubbers, reacts to form CO <sub>2</sub>	Moles CO <sub>2</sub>	Maximum of 9.85 x 10 <sup>8</sup> moles of CO <sub>2</sub> generated
	Original planned MgO in repository	85,600 tons @ 40.3 gm/mole = 1.93 x 10 <sup>9</sup> moles
	Original CCA excess of MgO	1.95 times
	15% reduction	74,000 tons @ 40.3 gm/mole = 1.65 x 10 <sup>9</sup> moles
	New MgO excess	1.67 times

In the Compliance Certification Application (CCA) DOE proposed, and EPA subsequently approved, the emplacement of approximately 85,600 tons of MgO as an engineered barrier to achieve two purposes: remove carbon dioxide (CO<sub>2</sub>) gas created by microbial degradation of cellulosics, papers, and rubbers, and increase the pH in the repository to lower the solubility of dissolved actinides. As noted in DOE's letter of July 21, the amount of MgO presently planned for emplacement is almost twice that needed to sequester the CO<sub>2</sub> generated if all of the organic waste was converted to CO<sub>2</sub> (this constitutes a bounding assumption).

The primary benefits of this change would occur during the operational period by enhancing worker safety and decreasing cost. Decreasing the amount of MgO by 15% is not expected to significantly affect long-term repository performance, as discussed in Section 3.0 below.

### 3.0 Analysis

We reviewed relevant information in the CCA (especially Appendix BACK), EPA's Compliance Application Review Documents (CARDs) and Technical Support Documents (TSDs) for the certification rulemaking, the results of the CCA Performance Assessment (PA) and Performance Assessment Verification Test, and the DOE support documents submitted with the July 21<sup>st</sup> letter (Attachment 2).

Also, during a WIPP site visit in June following a technical meeting in Carlsbad, NM, EPA staff observed waste containers that had been placed in Panel 1 and noted that MgO mini-sacks were attached to containers and lay on the floor around the perimeter of the waste containers. Agency staff also evaluated the methods used to attach mini-sacks to waste containers. We found that DOE accurately represented the steps required to attach mini-sacks to the waste containers and the worker safety considerations involved in this activity (see Attachment 5).

DOE's conceptualization of MgO performance in the repository was very conservative. In CARD 44: Engineered Barriers, the Agency stated:

“... the reaction of MgO to brucite would consume water, an added benefit for which DOE did not take credit in the PA. Additionally, other mineral species that may form (dypingite ( $Mg_3(CO_3)_4(OH)_2 \cdot (5H_2O)$ ) and/or nesquehonite ( $MgCO_3 \cdot 3H_2O$ ) consume five and time times as much water, respectively. These factors constitute a conservative approach that accounts sufficiently for uncertainties in geochemical processes that may occur in the disposal system” (p. 44-9).

The elimination of mini-sacks does not impact the CCA or PAVT results because DOE proposes to reduce only excess MgO, which was not used in the performance calculations. Compliance with EPA's containment requirements is not altered because there would still be a large excess of MgO relative to any potential evolved carbon.

The ability of the MgO remaining in super-sacks to react with brine in the repository is important if the mini-sacks are eliminated. Attachment 4 concludes that molecular diffusion alone can effectively mix brine with MgO from degraded super-sacks in a repository that has experience salt creep closure. Super-sacks of MgO will break open as the height of the repository compresses from 3 meters to .8 to 1.4 meters, mixing the MgO with the degraded

waste and waste containers. If brine is introduced into the disposal rooms MgO will be readily available to react chemically. We reviewed DOE's calculations and agree these processes will function as expected and sufficient MgO will be available to react.

#### **4.0 Conclusion**

In conclusion, we determined that the analysis of the effectiveness of MgO backfill, as described in EPA's certification decision, would not be compromised by the elimination of the mini-sacks:

- MgO is still expected to remove CO<sub>2</sub> and to affect pH and actinide solubility
- the excess amount of MgO proposed for emplacement ensures that adequate MgO will still be available to provide expected chemical effects
- the plan for emplacing MgO remains feasible.

The elimination of the MgO mini-sacks is not significant to long-term repository performance. DOE's proposal to decrease the amount of MgO in the WIPP by 15% by eliminating the MgO mini-sacks is acceptable.

**Attachment 1**

**Letter, I. Triay to F. Marcinowski  
July 21, 2000**



**Department of Energy**

Carlsbad Area Office  
P. O. Box 3090  
Carlsbad, New Mexico 88221

July 21, 2000

Mini Sacks

Mr. Frank Marcinowski  
Office of Radiation and Indoor Air  
Environmental Protection Agency  
Center for Federal Regulation  
Ariel Rios Building  
1200 Pennsylvania Avenue, N. W.  
Washington, D. C 20460

Dear Mr. Marcinowski:

This purpose of this letter is to request approval from the Environmental Protection Agency for the elimination of the magnesium oxide (MgO) mini-sacks from the Waste Isolation Pilot Plant (WIPP) repository. We previously briefed your agency regarding this subject on April 13, 2000, in Washington, D. C.

Elimination of the mini-sacks would reduce the total mass of MgO emplaced by about 15%, however a large excess of MgO was included in the quantity specified in the Compliance Certification Application (CCA). Based upon the conservative assumption that all organic carbon in the waste would be converted to carbon dioxide (CO<sub>2</sub>) by microbial degradation, the mass of MgO being emplaced was at least 1.95 times more than needed to sequester the entire resulting CO<sub>2</sub> inventory. In fact, it was appreciated at that time, and has been confirmed by experimental results, that methanogenesis, which only converts half of the organic carbon to CO<sub>2</sub>, will be the dominant biodegradation pathway in the WIPP and will account for 95% of overall carbon degradation. As a result, the quantity of MgO specified in the CCA is actually 3.7 times more than that required to sequester the entire possible inventory of CO<sub>2</sub>. Even with the elimination of the mini-sacks, there will still be a 3.2-fold excess of MgO in the repository.

As discussed in the enclosed paper, the elimination of the mini-sacks will have no impact on the expected performance of the MgO within the repository environment, as described in the compliance certification documentation that EPA used to certify WIPP in May 1998, but will enhance worker safety and afford substantial efficiencies in the WIPP operations.



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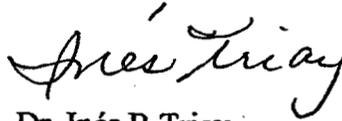
Mr. Frank Marcinowski

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July 21, 2000

If you have any questions, please contact George Basabilvazo at 505-234-7488 or Daryl Mercer at 505-234-7452.

Sincerely,



Dr. Inés R. Triay  
Manager

Enclosure

cc w/enclosure:

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RCRA PERMITS PROGRAM

**Attachment 2**

**DOE Proposal for  
Elimination of MgO Mini-sacks**

## **MgO Mini-Sack Elimination Submittal**

### **1 Executive Summary**

DOE recently conducted a review of operational procedures required for continued safe disposal of transuranic (TRU) waste at WIPP and determined that eliminating the mini-sacks that contain magnesium oxide (MgO) would significantly enhance worker safety at WIPP without adversely impacting repository performance.

Elimination of the mini-sacks would reduce the total mass of MgO emplaced by about 15%, however a large excess of MgO was included in the quantity specified in the Compliance Certification Application (CCA) (U.S. DOE, 1996a). Based upon the conservative assumption that all organic carbon in the waste would be converted to CO<sub>2</sub> by microbial degradation, the mass of MgO being emplaced was at least 1.95 times more than needed to sequester the entire resulting CO<sub>2</sub> inventory. In fact, it was appreciated at that time, and has been confirmed by recent experimental results (see Wang, 2000a: Attachment 1), that methanogenesis, which only converts half of the organic carbon to CO<sub>2</sub>, will be the dominant biodegradation pathway in the WIPP and will account for 95% of overall carbon degradation. As a result, the quantity of MgO specified in the CCA is actually 3.7 times more than that required to sequester the entire possible inventory of CO<sub>2</sub>. Even with the elimination of the mini-sacks, there will still be a 3.2-fold excess of MgO in the repository.

This document provides information regarding DOE's motivation for the proposed change and an impact assessment of the change. It is concluded that eliminating the mini-sacks of MgO improves worker safety without affecting either the functionality of MgO backfill as stated in the WIPP CCA, or other components of WIPP long-term performance that EPA certified in May 1998.

### **2 Introduction**

The WIPP is the DOE's operational repository in the United States designed for the disposal of defense-related transuranic (TRU) wastes. Certification of the repository by the EPA for operation was based both on the information provided in the CCA and independently developed by EPA regarding the selected backfill system which consists of magnesium oxide (MgO) emplaced in what would have otherwise been void space in the

1. Retain the function(s) of MgO as stated in the final EPA rule. This requirement ensures that performance of the repository remains unchanged from that predicted in PA calculations conducted in support of the CCA. Therefore, no additional PA calculations are required.
2. Retain an acceptable safety factor for performance of the backfill material. This requirement provides assurance that uncertainty in geochemical processes discussed in the CCA and considered probable in the repository is sufficiently accounted for in the backfill design and associated PA calculations.

Demonstration that these criteria are met ensures that the proposed elimination of mini-sacks does not constitute a change to activities pertaining to the disposal system that differs significantly from the CCA. Information presented in this document demonstrates that the proposed operational enhancement represents an insignificant change relative to the compliance baseline.

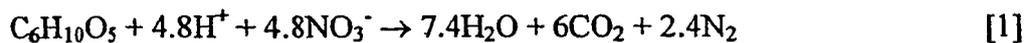
## 4 Impact of MgO on WIPP Performance

The function of MgO backfill in enhancing WIPP performance, and its effect on repository behavior is described in detail in the CCA. This section provides brief descriptions of performance-related functions for MgO at WIPP.

### 4.1 Function of the WIPP Backfill System

As stated in the CCA, the function of the MgO backfill is to control actinide solubilities by sequestering carbon dioxide generated by microbial degradation of organic materials in the waste. This controls the pH and CO<sub>2</sub> fugacity in the repository to a range where actinide solubilities in brine are minimized, and removes carbonate species which increase actinide solubilities. Actinide solubilities are an important consideration in the calculation of releases due to groundwater transport to the regulatory boundary, or releases which could occur due to an inadvertent human intrusion. In the absence of a chemical buffer, significant uncertainty would exist in the chemical conditions which influence actinide solubilities. The presence of MgO backfill supports the CCA assumption that chemical conditions in the repository will remain relatively constant with time, thereby simplifying PA calculations.

Microbial degradation of organic materials in the waste could have a significant impact on WIPP near-field chemistry. Biodegradation of cellulose, plastics, and rubbers, as described by Wang et al. (1997), follows a sequence of reaction pathways, according to the order of decreasing energy yield per carbon atom:



The generation of CO<sub>2</sub> in the above reactions can drive the pH of the repository into the acidic range. Furthermore, the dissolution of CO<sub>2</sub> in the brine will provide a strong complexing agent for actinide complexation. As a result, microbial gas generation in the repository can significantly increase actinide solubilities.

As a chemical control, MgO will react with water to form magnesium hydroxide (brucite), which will react with any available CO<sub>2</sub>, effectively removing carbonate from the system (Bynum et al., 1997):



MgO backfill will control the pH of the repository approximately in the range of 9 – 10 and the CO<sub>2</sub> fugacity at 10<sup>-7</sup> atm. Under such chemical conditions, actinide solubilities are minimized. The EPA concurred with DOE's conclusion that the emplacement of a large excess of MgO in the disposal areas would provide an additional factor of safety and thus account for uncertainties in the geochemical conditions that would affect CO<sub>2</sub> generation and MgO reactions (U.S. EPA, 1998a). Elimination of the mini-sacks has no impact on the actinide solubilities used in the CCA (or PAVT) because there is still sufficient MgO in the system to control the pH (CO<sub>2</sub> partial pressure) of the repository.

#### **4.2 Backfill System Safety Factor**

As noted by the EPA, the large excess of MgO present in the repository sufficiently addresses uncertainties in geochemical processes in the WIPP disposal areas. The safety factor of 1.95 calculated by EPA (U.S. EPA, 1997) assumed that all carbon present in organic materials disposed at WIPP could be converted to CO<sub>2</sub>. Thus, if all the organic carbon in the repository is converted to CO<sub>2</sub> there will be 9.85x10<sup>8</sup> moles of CO<sub>2</sub>. The CCA calls for 85,600 tons of MgO, or 1.95x10<sup>9</sup> moles to be emplaced, or a 1.95-fold excess. However, the average stoichiometry model for microbial gas generation implemented in the CCA assumed that microbial degradation followed the reaction pathways described in Section 4.1. It was noted in the CCA (U.S. DOE 1996b and 1996c) that, because of limited availability of sulfates and nitrates in the inventory, methanogenesis (Equation 3) will constitute the dominant reaction pathway (about 95%) for any microbial degradation at WIPP. This point was acknowledged by the EPA (U.S. EPA, 1998b) and is discussed in Wang (2000a: Attachment 1). In the case of methanogenesis only half of the organic carbon will be converted to CO<sub>2</sub>, thus leading to a maximum possible quantity of CO<sub>2</sub> of 5.17x10<sup>8</sup> moles and an excess MgO by a factor of 3.7.

Elimination of the mini-sacks would reduce the mass of MgO in the repository by about 15%, thus maintaining a safety factor of about 3.2. This value significantly exceeds the safety factor currently accepted by EPA. These calculations are summarized in Table 1.

**Table 1: Calculation of excess quantity of MgO**

Case	Quantity	Value	Source
All organic carbon to CO <sub>2</sub>	Moles CO <sub>2</sub>	9.85x10 <sup>8</sup> moles	EPA CARD 44.A.6 (U.S EPA, 1997)
	MgO in repository	85,600 tons @40.3 gm/mole = 1.93x10 <sup>9</sup> moles	CCA Section 3.3.3 (U.S. DOE, 1996g)
	Excess of MgO	1.95	
Methanogenesis dominant	Moles CO <sub>2</sub>	5.17x10 <sup>8</sup> moles	Wang (2000a)
	MgO in repository	85,600 tons @ 40.3 gm/mole = 1.93x10 <sup>9</sup> moles	CCA Section 3.3.3 (U.S. DOE, 1996g)
	Excess of MgO	3.73	
Methanogenesis dominant – mini-sacks removed	MgO in repository	74,000 tons @40.3 gm/mole = 1.67x10 <sup>9</sup> moles	CCA Section 3.3.3 (U.S. DOE, 1996g)
	Excess of MgO	3.23	

**4.3 Effect on total amount of gas to be generated in WIPP**

Microbial gas generation contributes significantly to predicted WIPP repository pressures (U.S. DOE, 1996d). In the CCA calculations, an average-stoichiometry gas generation model was used (U.S. DOE, 1996e; Wang and Brush, 1996). The model first estimates the fraction of each biodegradation path (Reactions 1 to 3, Section 4.1) and then calculates the total moles of gas generated by microbial reactions. In the model, any CO<sub>2</sub> generated by microbial degradation in the repository is assumed to be removed by MgO reaction thus reducing the total amount of gas that can be accumulated. Based on the TRU waste inventory estimates, microbial degradation will be dominated by methanogenesis (Wang and Brush, 1996; Wang, 2000a). The effect of methanogenesis on repository pressure has been fully included in the average-stoichiometry gas generation model for the CCA calculations. Elimination of mini-sacks does not affect the average-stoichiometry gas generation used in the CCA BRAGFLO computer code.

**4.4 Possible effect on other components of WIPP performance**

MgO backfill will occupy a part of the void space in the repository. Filling this space will have an effect on the closure rate of the repository. DOE has demonstrated that this effect will have minimal impact on the performance calculations (U.S. DOE, 1996f). Therefore, MgO backfill was not included in waste compaction and room-closure calculations for the CCA.

MgO backfill may affect other aspects of the WIPP repository that were not included in the CCA calculation. For instance, MgO will consume water by hydration and will cement wastes by forming Sorel cement. As noted by the EPA, "the reaction of MgO to brucite would consume water, an added benefit for which DOE did not take credit in the PA. Additionally, the other mineral species that may form ... consume ... water. These

*I A technical meeting DOE/ISNE stated that it would not fit Sorel cement but a flaky material with little strength.*

factors constitute a conservative approach that accounts sufficiently for uncertainties in geochemical processes ..." (U.S. EPA, 1997).

## 5 Description of the WIPP Backfill System

The current backfill emplacement system in use at the WIPP site (WID, 1996) relies upon several design considerations, including handling and storage equipment, storage facilities, environmental control, spill prevention, industrial safety, industrial hygiene interference with waste handling operations, radiological exposure, systemic impacts, hazard assessment, and costs. Several options for emplacement of MgO in the disposal areas were considered (WID, 1996). The selected method uses polyethylene sacks filled with backfill that are placed on the top of the stacks, in the voids spaces between drums, hung from the Standard Waste Boxes, and placed on the floor along the ribs. This method has the following advantages:

- Even distribution of material throughout waste stacks
- Handled with existing equipment – minimal changes to any existing processes
- Material protected from the environment, yet readily available when needed
- Low material costs
- Low storage costs
- Backfill material completely contained

The compliance baseline of 85,600 tons of MgO is described in the CCA, Chapter 3 (U.S. DOE, 1996g) and Appendix BACK. The weight distribution of MgO presented in the CCA is described in Table 2. Note that EPA carried out an independent calculation which concluded that the total loading would be 86,920 tons, a 2% difference due to slightly different assumptions on the mini-sack loading.

**Table 2. Calculation of MgO mass emplaced in the repository (CCA, Section 3.3.3: U.S. DOE, 1996g)**

Container Type	Quantity per Panel	Total Quantity
Super Sacks	3700 linear feet x 4000 pounds per linear foot = 7400 tons per panel	74,000 tons
Mini-sacks between drums or waste packages	10,836, 6-packs of MgO mini-sacks at 150 pounds per 6-pack $\cong$ 800 tons per panel	8,000 tons
Mini-sacks along ribs	100 pounds per linear foot = 360 tons per panel	3,600 tons
<b>TOTAL</b>	<b>8,560 tons per panel</b>	<b>85,600 tons</b>

## **6 Proposed Change and Impact to Operations and Performance**

### **6.1 Proposed Change and Impact to Operations**

In this submittal, DOE proposes elimination of the mini-sacks between the waste drums and stacked along the ribs. This constitutes removal of approximately 15% of the total mass of MgO from the repository, but retains 74,000 tons, or an equivalent of  $1.65 \times 10^9$  moles of MgO in the waste disposal areas.

Removal of the mini-sacks from the backfill system results in elimination of industrial safety and radiological exposure risks associated with placement of the mini-sacks. As described in Section 3, worker safety issues, including industrial hazards and reduction of radiological exposure, constitute the motivation for this change.

### **6.2 Impact of Change on Repository Performance**

EPA requirements and expectations for MgO as the engineered barrier for WIPP are clearly stated in the final ruling. EPA (U.S. EPA, 1998c) concurred that the backfill system included:

“a large amount of MgO in and around waste drums in order to provide an additional factor of safety and thus account for uncertainties in the geochemical conditions that would affect CO<sub>2</sub> and MgO reactions.”

Therefore, the proposed change must ensure that MgO will continue to function in a manner that is equivalent to that described in the CCA, and must also maintain an adequate safety factor to account for system uncertainties.

#### **6.2.1 Safety Factor**

The safety factor criteria has been discussed in Section 4.2. There it was noted that, given that methanogenesis would dominate microbial degradation, the quantity of MgO prescribed in the CCA was 3.7 times that required to sequester the CO<sub>2</sub>. After removal of the mini-sacks the safety factor is still 3.2. The assumptions in the CCA regarding actinide solubilities, which rely on the chemical buffering capabilities of MgO, do not change since there is still a significant excess of MgO. The excess ensures that the assumption of relatively constant chemical conditions in the waste remains valid.

With respect to microbial gas generation, the effect of MgO on this process was incorporated into the CCA calculations. As long as an excess of MgO is present in the repository, there is no correlation between the proposed mass of MgO and the gas generation rate, or the total volume of gas which could be generated.

#### **6.2.2 MgO/Brine Accessibility**

There is no impact on MgO/brine accessibility due to the elimination of the mini-sacks. The material for the MgO super-sacks has been designed and tested to ensure that they will burst, thus exposing the backfill material to any brine which flows into the disposal

areas. Mixing of the backfill material and any brine present in the disposal areas can be readily established, i.e., molecular diffusion alone will be sufficient to make MgO accessible to the brine (Wang, 2000b: Attachment 2). A 15% reduction in the mass of MgO in the repository does not change the process for mixing of the backfill material and brine that was described in the compliance certification documentation.

### 6.2.3 Summary of Impact Assessment

The elimination of MgO mini-sacks retains a large safety factor for the WIPP engineered barrier. This mini-sack elimination will also not affect the compliance baseline assumptions relating to relatively constant chemical conditions in the repository, accessibility of brine to the MgO backfill, or actinide solubilities. Therefore, the function of MgO as a chemical control for pH and CO<sub>2</sub> fugacity is retained. The result of the impact assessment is summarized in Table 3.

**Table 3. Summary of impact assessment for elimination of MgO mini-sacks.**

Components of WIPP Operations and Performance	Effect of elimination of MgO mini-sacks	Justification
Operational constraints	No impact (improves disposal operations)	Eliminates industrial safety risks and radiological exposure associated with mini-sack emplacement.
Actinide source term	No impact on the actinide solubility ranges as calculated as used in the CCA or PAVT calculations	A large safety factor is maintained. Accessibility of MgO backfill is not affected.
Total amount of gas generated	No impact on average-stoichiometric gas generation model in BRAGFLO	The dominance of methanogenesis in microbial gas generation was acknowledged in the CCA. A sufficient amount of MgO is still retained for sequestering all CO <sub>2</sub> that could possibly to be generated. As long as an excess of MgO is present in the repository, there is no correlation between the proposed mass of MgO and the gas generation rate, or the total volume of gas which could be generated.
Waste compaction and room closure	No impact on creep closure calculation (SANTOS and BRAGFLO codes)	MgO was not included in the room-closure model for CCA calculations.
Others (e.g., water budget, waste mechanical property)	No impact	Water consumption and waste cementation were not included in the CCA calculations.

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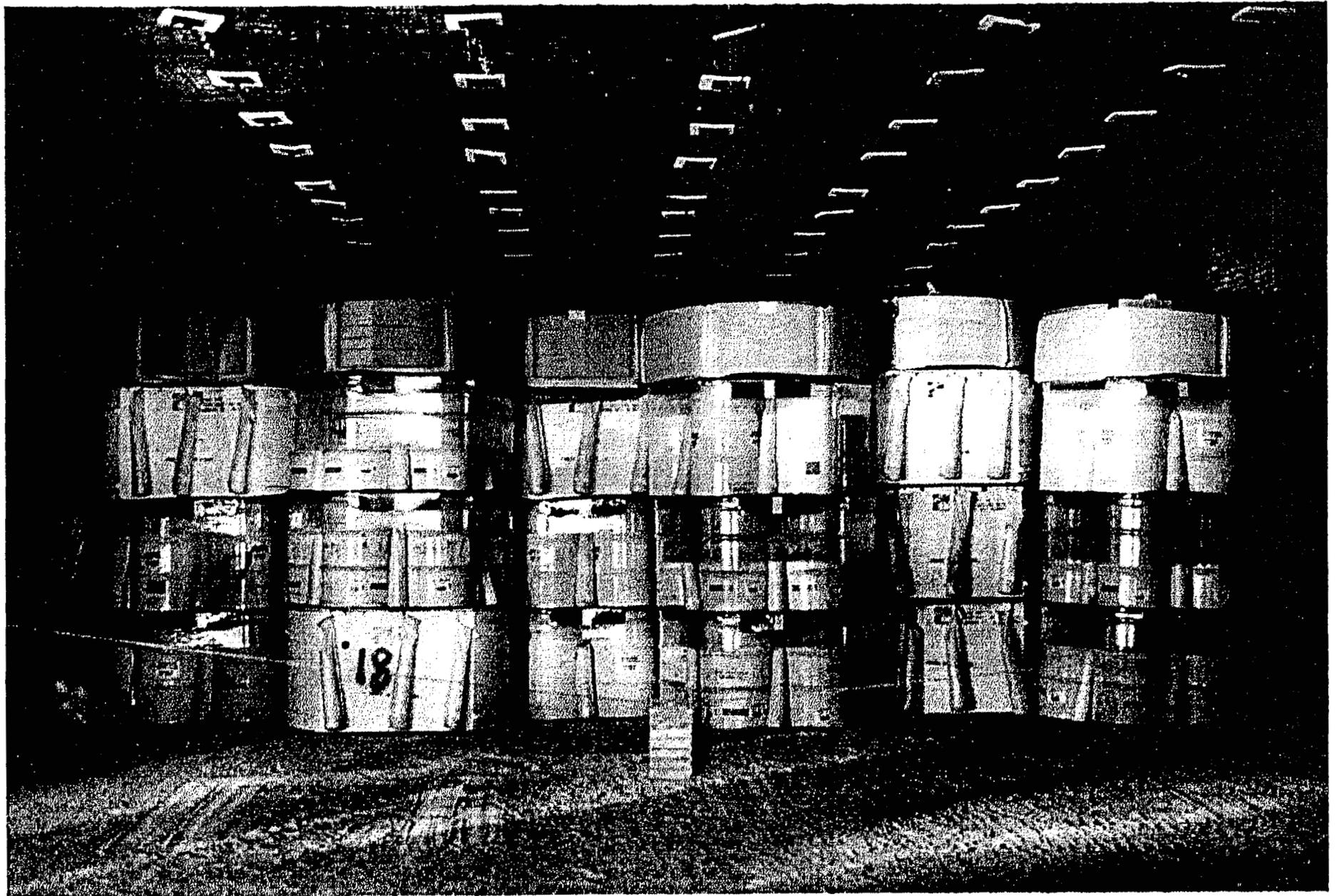


Figure 1: Current Backfill System Arrangement

**Attachment 3**

**DOE Report:  
Methanogenesis and Carbon Dioxide Generation at the  
Waste Isolation Pilot Plant (WIPP)**



**date:** January 5, 2000

**to:** Bryan A. Howard (Org. 6821)

**from:** Yifeng Wang (Org. 6821)

**subject:** Methanogenesis and Carbon Dioxide Generation at the Waste Isolation Pilot Plant (WIPP)

## INTRODUCTION

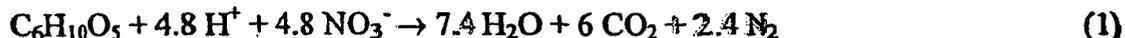
Microbial gas generation will have a significant impact on the near field chemistry of the Waste Isolation Pilot Plant (US DOE, 1996, appendix SOTERM). To mitigate the effect of microbially-generated carbon dioxide on actinide solubility, the Department of Energy (DOE) decided to emplace 77,640 metric tons (equivalent to  $2 \times 10^9$  moles) of MgO as a backfill into the WIPP (Bynum et al., 1998). This total amount of MgO was estimated based on the following assumptions (Peterson, 1996):

- (1) Organic materials (cellulosics, plastics, and rubber) will be completely degraded over 10,000 years,
- (2) one mole carbon (C) in organic materials will be converted to one mole of carbon dioxide (CO<sub>2</sub>),
- and
- (4) there will be sufficient space for the emplacement of MgO.

The first two assumptions are overly conservative. This memorandum intends to demonstrate that the conservatism associated with the second assumption conflicts with current data showing that methanogenesis will be a dominant biodegradation pathway in the WIPP repository. Therefore, at most one half of organic carbon can possibly be converted to CO<sub>2</sub>.

## METHANOGENESIS IN WIPP

Cellulosics, plastics, and rubbers have been identified as major organic materials to be emplaced in the WIPP repository (DOE/CAO, 1996) and could be degraded by microbes in 10,000 years (Brush, 1995). Depending on the availability of electron acceptors (e.g., NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>), microorganisms will degrade organic materials by the following reaction pathways (Brush, 1995):



The reaction pathways of aerobic respiration, Mn(IV) and Fe(III) dissimilatory reduction are ignored here, because the quantities of O<sub>2</sub>, Mn(IV) and Fe(III) initially present in the

repository will be negligible relative to the other electron acceptors. The above reactions generally proceed sequentially from Reaction (1) to (3) according to a decreasing order of energy yields of the reactions (e.g., Berner, 1980; Criddle et al., 1991; Chapelle, 1993; Wang and Cappellen, 1996; Hunter et al., 1998). It is important to notice that methanogenesis produces only half mole of carbon dioxide from one mole of organic carbon.

Aside from theoretical consideration of the energetic perspective, the biodegradation sequence summarized above is widely observed in the nature (e.g., Berner, 1980; Criddle et al., 1991; Chapelle, 1993). The occurrence of methanogenesis following denitrification and sulfate reduction is commonly observed in marine sediments, especially in coastal sediments, which receive a high input of organic matters (e.g., Schlesinger, 1997, p.284). Methanogenesis can be a dominant biodegradation process in many terrestrial geochemical systems such as freshwater wetlands and lakes, where the supply of sulfate is usually limited (e.g., Schlesinger, 1997, p.237). Methanogenesis is observed to occur in either pristine or contaminated groundwater systems (e.g., Chapelle, 1993). Methane generation in landfills is a typical example (Baedecker and Back, 1979). In all these systems, the occurrence of methanogenesis follows, with no exception, the biodegradation sequence summarized by Reaction (1) to (3). Therefore, it follows that methanogenesis is likely to occur in the WIPP repository after all nitrate and sulfate are consumed. It is worth noting that Nirex has included methanogenesis in the performance assessment for low-level waste disposal (Nirex, 1997).

In the previous gas generation experiments, which were used to derive gas generation parameters for the WIPP Compliance Certification Application (CCA) (Wang and Brush, 1996), cellulose samples were incubated for 1228 days with microorganisms collected from WIPP-relevant environments (Francis et al., 1997). At the time of the CCA calculations no methane production was detected in any of those samples. There are two possible explanations for the absence of methane production. The first possibility is that microbial degradation in the samples had not reached the methanogenesis stage, due to a relatively short incubation time and also because of high nitrate or sulfate concentration in the brine. If this is the case, methane would be produced after the samples are incubated for a long enough time and all nitrate and sulfate in the samples are consumed. The second possibility is the lack of active methanogenic microbes in the samples. If this were the case, no methane would be produced even if the samples were incubated for a very long time. To test these possibilities, A. J. Francis and J. Gillow at Brookhaven National Laboratory (BNL) have conducted more headspace gas measurements on samples that have been preserved from the previous WIPP gas generation program (See WIPP Test Plan TP99-01). The objective of these measurements was to check if methane had been produced in those samples after extended incubation (~ 7.5 years). Methane was analyzed in selected brine-inundated samples and the results are summarized in Table 1 (Francis and Gillow, 2000).

Methane was produced in most anaerobic samples except those with excess nitrate. Nitrous oxide was detected in the headspace of samples containing excess nitrate. The lack of methane production in samples amended with nitrate-compounds indicates the inhibitory effect of nitrate on methanogenic bacterial activity. In fact, most of the methane detected was in samples that were not amended with any nitrate-containing compounds ( $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ ) at all (unamended and unamended/inoculated samples). This supports the hypothesis of biogenic origin of methane in these samples. Of the initially aerobic samples, only two treatments contained methane (unamended and unamended/inoculated (without bentonite)). In all of the other initially aerobic treatments, the combination of oxygen, nitrate-compounds,

and other alternate electron acceptors ( $\text{Fe}^{3+}$  provided by bentonite) may have an inhibitory effect on methanogenesis.

**Table 3.** Methane analysis of inundated cellulose samples. All samples have been corrected for the gas produced in control treatments (without cellulose). nd = not detected.

Sample	1228 Days (nmol g <sup>-1</sup> cellulose)	2718 Days (nmol g <sup>-1</sup> cellulose)
<b>Anaerobic</b>		
Unamended	nd	3.92 ± 0.27
Unamended/Inoculated	nd	4.03 ± 1.38
Amended/Inoculated	nd	0.85 ± 0.7
Amended/Inoc. + Exc. Nitrate	nd	nd
<b>Anaerobic + Bentonite</b>		
Unamended	nd	3.84 ± 0.40
Unamended/Inoculated	nd	3.52 ± 0.20
Amended/Inoculated	nd	1.12 ± 0.03
Amended/Inoc. + Exc. Nitrate*	nd	nd
<b>Initially Aerobic</b>		
Unamended	nd	1.25 ± 0.29
Unamended/Inoculated	nd	1.10 ± 0.13

Although the quantities of methane detected are small, the new measurements have demonstrated that the absence of methane production in the previous measurements was due to the inhibitory effect of nitrate or sulfate and the insufficient incubation time period. Based on the experimental data and the observations on natural systems, it can be concluded that methanogenesis will take place in the WIPP repository after microorganisms consume all

nitrate and sulfate. In the next section, based on waste inventory estimates, it is further demonstrated that methanogenesis can eventually become a dominant reaction pathway in the WIPP repository.

### AMOUNT OF CARBON DIOXIDE TO BE GENERATED IN WIPP

#### Inventories of organic materials and electron acceptors ( $NO_3^-$ and $SO_4^{2-}$ ):

Based on the Transuranic Baseline Inventory Report (DOE/CAO, 1996), the total equivalent cellulose to be emplaced in the WIPP is estimated to be  $2.656 \times 10^7$  kg, equivalent to  $9.84 \times 10^8$  moles of C (Peterson, 1996). The total amounts of nitrate and sulfate in the waste are estimated to be  $1.6 \times 10^6$  kg and  $6.3 \times 10^5$  kg, respectively, and equivalently  $2.6 \times 10^7$  moles of  $NO_3^-$  and  $6.6 \times 10^6$  moles of  $SO_4^{2-}$  (DOE, 1996, p. B6-1; Wang and Brush, 1996, p.14). A certain amount of sulfate can be brought into the repository by brine inflow; however, this amount of sulfate is estimated to be less than  $4 \times 10^6$  moles (Wang and Brush, 1996). Therefore, the total amount of sulfate to be present in the repository is estimated to be  $1 \times 10^7$  moles.

#### Fraction of methanogenesis:

As mentioned above, the biodegradation of organic materials in the WIPP will proceed sequentially from Reaction (1) to (3). The fractions of individual degradation pathways can be calculated as follows:

Molar fraction of organic carbon degraded via denitrification

$$= 1.25 \times \text{moles of nitrate} / \text{moles of organic carbon}$$

$$= 1.25 \times 2.6 \times 10^7 / 9.84 \times 10^8 = 3.3\%$$

Molar fraction of organic carbon degraded via sulfate reduction

$$= 2 \times \text{moles of sulfate} / \text{moles of organic carbon}$$

$$= 2 \times 1 \times 10^7 / 9.84 \times 10^8 = 2\%$$

Molar fraction of organic carbon degraded via methanogenesis

$$= 1 - \text{molar fractions of both denitrification and sulfate reduction}$$

$$= 1 - 3.3\% - 2\% = \sim 95\%.$$

Therefore, based on the currently inventory estimates, methanogenesis will account for 95% of overall organic carbon degradation.

#### Total possible quantity of $CO_2$ to be generated:

Using the fractions of biodegradation pathways calculated above, it can be estimated that one mole of organic C will be converted to  $(1 - 95\%) + 95\% \times 0.5 = 0.525$  mole of  $CO_2$ . Accordingly, the total possible quantity of  $CO_2$  to be generated in the repository is estimated to be  $0.525 \times 9.84 \times 10^8 = 5.17 \times 10^8$  moles, which is about 47.5% less than that estimated for the CCA (Peterson, 1996).

Given the fact that metal corrosion in the repository will generate a significant quantity of  $H_2$ , another methanogenesis pathway may also exist, in which methanogenic microbes use both  $CO_2$  and  $H_2$  as substrates to produce methane:  $CO_2 + 4H_2 = CH_4 + H_2O$  (Brush, 1995,

p.E-16). As a result, the conversion ratio of organic carbon to CO<sub>2</sub> can be even smaller. Because of lack of experimental data, the second methanogenesis pathway is ignored here.

## CONCLUSION

Methanogenesis will be a dominant biodegradation pathway in the WIPP repository and account for 95% of overall organic carbon degradation. Based on the current waste inventory, it is estimated that one mole of organic C will be converted to 0.525 mole of CO<sub>2</sub>. Accordingly, the total quantity of CO<sub>2</sub> potentially to be generated in the repository is calculated to be  $5.17 \times 10^8$  moles, which is about 47.5% less than that estimated for the CCA (Peterson, 1996).

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**Attachment 4**

**DOE Report:  
Effectiveness of Mixing Processes in the Waste Isolation  
Pilot Plant Repository**



Sandia National Laboratories

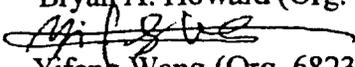
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4100 National Parks Highway  
Carlsbad, NM 88220

Phone: (505) 234-0030  
Fax: (505) 234-0061  
Internet: ywang@sandia.gov

date: June 21, 2000

to: Bryan A. Howard (Org. 6822)

  
from: Yifeng Wang (Org. 6823)

subject: Effectiveness of Mixing Processes in the Waste Isolation Pilot Plant Repository

MgO backfill is being used in the Waste Isolation Pilot Plant (WIPP) as a chemical control agent to mitigate the effect of microbial CO<sub>2</sub> generation on actinide mobility in a post-closure repository environment. MgO is emplaced as super-sacks on the top of waste container stacks and as mini-sacks between and around waste containers. To enhance worker safety, the Department of Energy (DOE) proposes to eliminate the emplacement of MgO mini-sacks. This memorandum supports the DOE's assessment that the elimination of MgO mini-sacks will not impact MgO/brine accessibility in the WIPP and therefore the functionality of MgO as a chemical control will remain effective as stated in the Compliance Certification Application (CCA). Using a bounding calculation, the memo demonstrates that molecular diffusion alone will be sufficient to mix brines with MgO backfill in the repository without the presence of MgO mini-sacks.

In the following bounding calculation, only molecular diffusion is considered. The diffusion of a chemical species in a porous medium can be described by Fick's equation (e.g., Richardson and McSween, 1989, p.132):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left( D_{eff} \frac{\partial C}{\partial X} \right) \quad (1)$$

where  $C$  is the concentration of the diffusing chemical species;  $t$  is the time;  $X$  is the distance; and  $D_{eff}$  is the effective diffusivity of the chemical species in a given porous medium.  $D_{eff}$  is related to the porosity ( $\phi$ ) of the medium by (e.g., Oelkers, 1996):

$$D_{eff} = \phi^2 D \quad (2)$$

where  $D$  is the diffusivity of the species in pure solution. The  $D$  values for most aqueous species at room temperatures fall into a narrow range, and  $10^{-5}$  cm<sup>2</sup>/sec is a good approximation (e.g., Richardson and McSween, 1989, p.138). From the CCA calculations (Bean et al., 1996, p.7-29; WIPP PA Department, 1993, equation B-8), the porosity in the WIPP waste panels after room closure is calculated to be 0.4 to 0.7. From Equation (2), the effective diffusivity  $D_{eff}$  in the waste is estimated to be  $2 \sim 5 \times 10^{-6}$  cm<sup>2</sup>/sec ( $= 6 \sim 16 \times 10^{-3}$  m<sup>2</sup>/year).

Given a time scale of  $T$ , the typical diffusion penetration distance ( $L$ ) can be determined by scaling Equation (1):

$$L = \sqrt{D_{eff}T} . \quad (3)$$

Using Equation (3), the diffusion penetration distance in the WIPP can be calculated as a function of diffusion time, as shown in Figure 1.

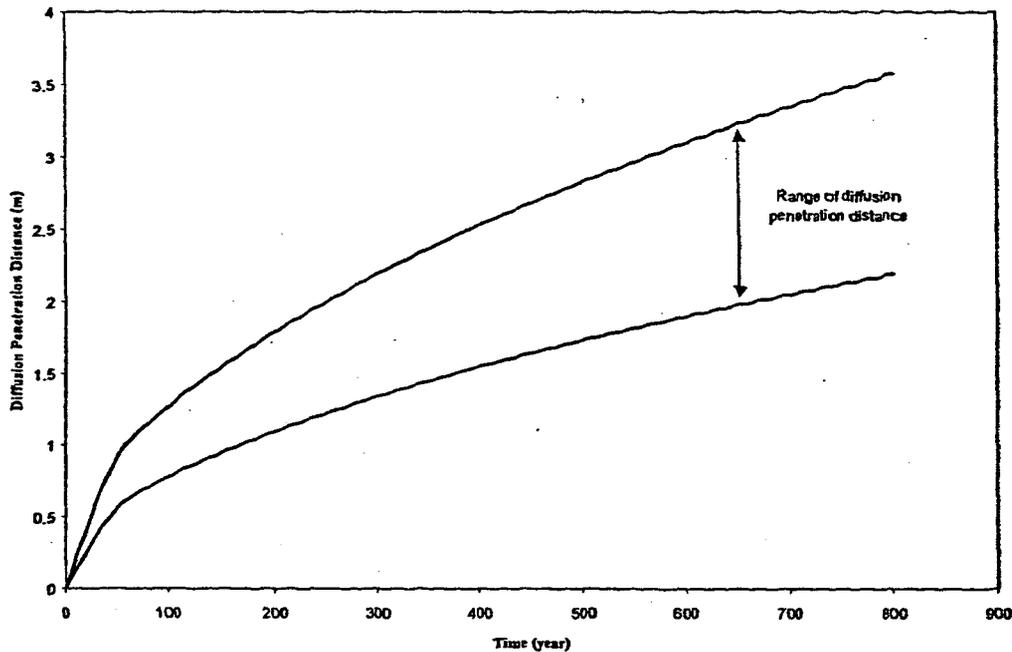


Figure 1. Diffusion penetration distance in the WIPP as a function of diffusion time

The average time for a brine pocket to remain in a waste panel after it enters the repository is characterized by a so-called mean residence time ( $T_{residence}$ ), which can be calculated by:

$$T_{residence} = \frac{V_{\phi}}{F} \quad (4)$$

where  $V_{\phi}$  is the pore volume in a waste panel; and  $F$  is the rate of brine flow up to the Culobra formation through a borehole. From the CCA calculations, the pore volume in a waste panel after room closure ranges from 2,500 to 7,000  $m^3$  (Helton et al., 1998, p.8-50), and the maximum flow rate is 5.5  $m^3/year$  (Helton et al., 1998, p.8-69). Using these values,  $T_{residence}$  is estimated to be  $> 450$  years. Over this time scale, according to Equation (3) and Figure 1, molecular diffusion alone can mix brine composition effectively at least over a distance of 1.6 m.

The height of waste stacks in the repository after room closure ( $h$ ) can be calculated by:

$$h = \frac{h_0(1 - \phi_0)}{1 - \phi} \quad (5)$$

where  $h_0$  and  $\phi_0$  are the initial height of waste stacks and the initial porosity of wastes, which are assumed to be 4 m and 0.88, respectively, in the CCA. For  $\phi = 0.4 - 0.7$ ,  $h$  is estimated to be 0.8 to 1.4 m, which is less than the calculated diffusion penetration distance. Since MgO super-sacks are directly placed on the top of waste stacks in the current waste emplacement configuration, it can be concluded that molecular diffusion alone can effectively mix brines with super-sack MgO (in a vertical direction) without the presence MgO mini-sacks. In other words, the elimination of MgO mini-sacks will not affect MgO accessibility by brine in the WIPP.

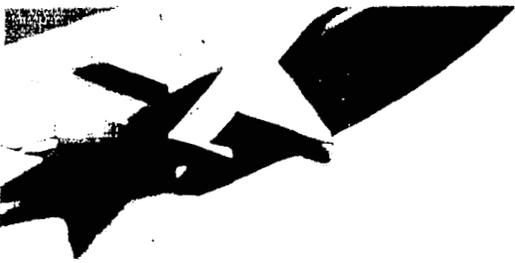
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**Attachment 5**

**Handouts from EPA/DOE Meeting  
April 12-13, 2000**



# MgO Background

Bryan Howard

April 13, 2000



# Summary

- Very compelling reasons exist for mini-sack elimination
- A very compelling technical justification is currently being compiled by the CAO



# MgO Background

## **Engineered Barriers are Required**

- LWA Section 8g) Engineered and Natural Barriers(s) Required
- 40 CFR § 191.14(d) Assurance Requirement - Engineered and Natural Barriers Required



# MgO Background

## EPA Guidance

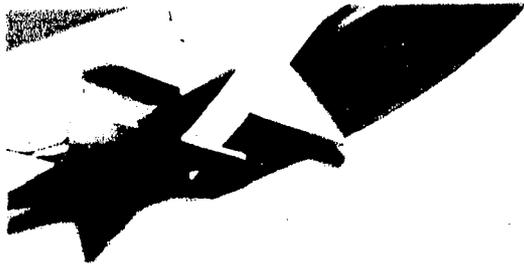
- CFR § 194.44 Engineered Benefit/Detriment Analysis used to justify Selection and Rejection of Engineered Barriers - Required Peer Review
- “The DOE performed an Engineered alternatives Cost/Benefit Study (see Appendix EBS) to examine the benefits and detriments associated with an array of engineered barrier alternatives. This study, in combination with past sensitivity and other analysis, was used to make a decision about an additional engineered barrier, a chemical backfill that will improve performance of the WIPP. The DOE has chosen an MgO backfill to buffer the chemical composition of brine that may enter the repository over the 10,000-year regulatory period. The principal beneficial performance characteristic resulting from this backfill is a reduction in actinide solubility in brine.” (CCA Section 3.3)



# MgO Background

## Decision Making

- DOE looked at various ways to emplace a backfill. Used EPA's definition of a barrier as a basis for the decision making process.
  - “For example, a barrier may be a geologic structure, a canister, a waste form with physical and chemical characteristics that significantly decrease the mobility of radionuclides, *or a material placed over and around waste*, provided that the material or structure substantially delays movement of water or radionuclides.”



# MgO Background

## **Decision Making**

- DOE considered a number of backfill emplacement strategies
- The compliance baseline configuration of MgO emplaced in the disposal regions includes the use of mini-sacks



B2

# MgO EMPLACEMENT CONSIDERATIONS

D. H. Haar

WESTINGHOUSE - WASTE  
ISOLATION DIVISION

April 13, 2000

## Objective

- Place 85,600 tons of MgO into the repository. This equates to 8560 tons per panel, or 1223 tons per room.

How much material is this?

Enough to fill an entire panel, in and of itself.

## Emplacement System Design Considerations

- **Handling and Storage Equipment** – the system needs to maximize the use of existing equipment. This will minimize the new equipment costs associated with procurement, maintenance, and operational training of personnel.
- **Storage Facilities** – adequate space will be needed both on the surface and in the underground to keep this material readily available yet out of the way.
- **Environmental Control** – the material must be packaged to prevent premature exposure to the environment, yet available when needed.

## Emplacement System Design Considerations (Continued)

- **Spill Prevention** – The material should be packaged to minimize any cleanup required in case of a handling or storage accident.
- **Spill Recovery** – equipment and processes should be available to minimize impact to personnel or operations from a spill of the material.
- **Industrial Safety** – The handling, storage, and emplacement processes must be structured to minimize industrial hazards, such as reduced visibility, or the lifting of heavy or awkward packages.
- **Industrial Hygiene** - The material should be packaged to minimize contact with personnel.

## Emplacement System Design Considerations (Continued)

- **Interference with Waste Handling Operations** – The handling of the material must be coordinated to minimize conflicts with existing operations, such as using the currently available hoisting times.
- **Radiological Exposure** – The handling operations must be structured to minimize the time personnel are required to be in close proximity to radiological sources, such as the waste drums.
- **Systemic Impacts** – The material must be evaluated to ensure there are no significant impacts to existing systems, such as the CAMs.

## Emplacement System Design Considerations (Continued)

- **Hazard Assessment** – The handling operations must be reviewed to ensure no additional hazards are introduced which would alter the emergency planning hazards assessment or the facility Safety Analysis Report.
- **Costs** – Various procurement and material configuration options must be evaluated to minimize costs.

## Delivery Systems Considered

- Unpackaged dry bulk material, delivered by conveyance or blown around the waste stack
- Unpackaged wet slurry or grout, pumped or injected around the waste stack
- Wet or dry material poured, compacted, or molded into the floor of a disposal room
- Wet or dry material adhered to or embedded in the walls of a disposal room
- Prepackaged material incorporated into the waste stack (waste containers filled with MgO)
- Prepackaged material integrated into the waste stack (super-sacks and mini-sacks)

Selected system - Prepackaged material integrated into the waste stack

Advantages

- Handled with existing equipment
- Material protected from premature exposure to environment
- Material readily available when needed
- Packaging limits potential spillage and cleanup
- Packaging limits contact of backfill with personnel
- Packaging limits impacts to other systems (e.g., CAMs)
- Minimal changes to existing processes
- Low material costs

Selected system - Prepackaged material integrated into the waste stack

Disadvantages

**Industrial Safety Issues**

- Ergonomic considerations with the manual handling of eighteen 25-lb bags for each waste stack
- Safety issues with ladder usage on an uneven surface

**Occupational Radiological Exposure of personnel**

- Placement of mini-sacks requires personnel be in close proximity to the waste containers.
- Assuming 17 full shipments a week, 4 minutes per 7-pack of waste drums, and 20mrem/hr dose rate, this amounts to 7 man-rem per year

**Interference with Waste Handling Operations**

- The time required to emplace mini-sacks is equivalent to the time required to emplace a super-sack

## Conclusion

If the mini-sack portion of the backfill system is eliminated, the disadvantages associated with this system are significantly reduced. Ergonomic considerations are completely removed, the majority of radiological exposure is eliminated, and the time required to install the backfill is reduced essentially by half.

As the mini-sacks account for no more than 15% of the MgO to be emplaced in the repository, and a significant excess of MgO is designed into the emplacement process, elimination of the mini-sacks will not adversely affect backfill performance.

#C

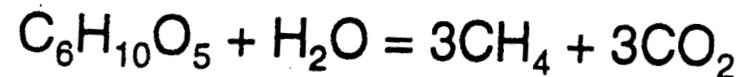
# Effects of Change to WIPP MgO Backfill System

M.K. Knowles

SNL Team Lead for WIPP  
Technical Support Program

# Technical Basis: Initial Selection

- Primary Driver for Using MgO Backfill - Chemical Control
  - Microbial degradation of organic materials will generate CO<sub>2</sub>, acidifying repository brine.



- *High solubility:* Without MgO, CO<sub>2</sub> fugacity can be up to 60 atm and pH can be down to 4.5. Under these conditions, actinide solubilities are very high.
- *Large uncertainty:* Without MgO, actinide solubilities in WIPP brines can span over a very wide range.

# Baseline MgO Backfill System

Table 1. Estimated weight and moles of MgO emplaced in waste disposal region.

MgO Location	Total Weight Calculated by EPA (tons)	Total Moles MgO ( $\times 10^9$ )
Super Sacks	74,000	1.65
Mini-Sacks along Ribs	3,920	0.10
Mini-Sacks between Containers	9,000	0.20
Total	86,920	1.95

\* Taken from EPA CARD No. 44, Attachment A

0.30  
1.65

# MgO in the Repository

- If *all* CPR in the repository is converted to CO<sub>2</sub>, then have  $9.85 \times 10^8$  moles CO<sub>2</sub>
- CCA calls for 86,920 tons of MgO, or  $1.95 \times 10^9$  moles
- Excess MgO by factor of about 1.95

# MgO in the Repository

- Gas generation studies show that 95% of degradation of CPR will be by methanogenesis forming equal molar amounts of CO<sub>2</sub> and CH<sub>4</sub>
  - Maximum possible CO<sub>2</sub> is 4.93x10<sup>8</sup> moles
- Excess MgO by factor of 3.9

# Impacts of MgO on the WIPP Disposal System

In the CCA, Appendix BACK, the following impacts were identified:

- Gas Generation: CO<sub>2</sub> sequestration
- Actinide Source Term: Solubility influenced by brine pH
- Creep Closure: Bounded by PORSURF calculations

# Technical Basis: Initial Selection

## Gas Generation: Reaction Pathways

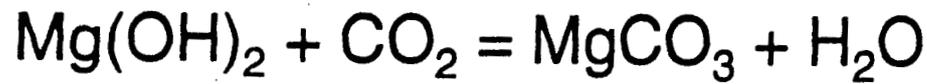
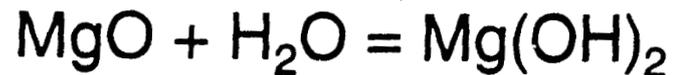
- $C_6H_{10}O_5 + 4.8H^+ + 4.8NO_3^- \rightarrow 7.4H_2O + 6CO_2 + 2.4N_2$
- $C_6H_{10}O_5 + 6H^+ + 3SO_4^{2-} \rightarrow 5H_2O + 6CO_2 + 3H_2S$
- $C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2$

*methanogenesis?*



# Impact Assessment: Gas Generation

- Remove CO<sub>2</sub> by forming MgO carbonate mineral.



CO<sub>2</sub> fugacity will be buffered at 10<sup>-6</sup> bar and pH is controlled within 9 - 10.

**This process is included in the BRAGFLO stoichiometric gas generation model used in the CCA PA calculations.**

# Impact Assessment: Actinide Source Term

CO<sub>2</sub> fugacity will be buffered at 10<sup>-6</sup> atm and pH is controlled within 9 - 10.

- Under these conditions, actinide solubilities are low. The uncertainties associated with these solubilities are significantly narrowed.

**Unchanged from the CCA baseline.**

# Impact Assessment of Change to WIPP Disposal System

Evaluation of CCA conceptual models and parameters shows that the modification will result in no changes to the system.

- **Gas Generation: No change**
- **Creep Closure: No change**
- **Actinide Source Term: No change**

# Impact Assessment: Waste Heterogeneity

- Assume molecular diffusion alone; a mixing length is defined as  $L = \sqrt{D_{\text{mixing}} t_r}$

- $D_{\text{mixing}} = \text{mixing coefficient} \approx 1.6 \times 10^{-6} \text{cm}^2/\text{s}^{(1)}$

$$t_r = V_{\text{total}} / V_f ; V_f \approx 6 \text{m}^3/\text{yr}^{(2)}$$

$$V_{\text{total}} \approx 4 \times 10^4 \text{m}^3$$

then  $L > 2\text{m}$ .

- Molecular diffusion alone can homogenize 20 drums of waste

(1) A systems analysis of the disposal area and Salado Formation at the WIPP. July 31, 1998

(2) Analysis Package for the Salado Flow calculations. 1996,

WPO#40814