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REVIEW OF THE DOE REQUEST FOR MAGNESIUM OXIDE REQUIREMENT REDUCTION

September 2007



PECOS MANAGEMENT SERVICES, INC.

**ISO-2 Project
Carlsbad, NM**

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ACRONYMS

CCA	Compliance Certification Application
CO ₂	carbon dioxide
CPR	cellulosics, plastics, and rubbers
CRA	Compliance Recertification Application
DOE	Department of Energy
EPA	Environmental Protection Agency
LANL	Los Alamos National Laboratory
MgO	magnesium oxide
PECOS	PECOS Management Services, Inc.
PA	Performance Assessment
RTR	real-time radiography
SANDIA	Sandia National Laboratories
TRU	Transuranic
VE	visual examination
WIPP	Waste Isolation Pilot Plant
WTS	Washington TRU Solutions, LLC
WWIS	WIPP waste information system

Review of the DOE Request for Magnesium Oxide (MgO) Requirement Reduction

September 2007

I. PURPOSE AND SCOPE

The U.S. Department of Energy (DOE) has requested that the required quantity of magnesium oxide (MgO) placed in the Waste Isolation Pilot Plant (WIPP) repository be reduced from 1.67 times the maximum theoretical requirement to 1.2 times the theoretical requirement assuming all organic carbon is converted to carbon dioxide (CO₂). The purpose of this review and report is to summarize the technical and operational arguments presented, evaluate their basis and validity, and present an independent opinion as to the merits of the DOE request. The scope of the review includes the DOE request, the Environmental Protection Agency (EPA) request for additional information, DOE's response to the EPA request, additional documents referenced by the two parties, and additional information taken from the public domain.

II. BACKGROUND

WIPP, located near Carlsbad, New Mexico, is a repository for the disposal of legacy transuranic (TRU) radioactive waste produced by the Department of Defense weapons production activities and associated research. The disposal facilities for WIPP are located 2,150 feet below the surface in the Salado formation, a 250- million-year-old geologically stable salt deposit. TRU waste is characterized and containerized at several DOE facilities, shipped to WIPP, inspected, and transported underground for permanent emplacement.

A primary concern regarding the WIPP project is the assurance that radiation releases are limited to no more than the release limits or standards established by EPA,⁽¹⁾ information verified through the Performance Assessment (PA) for the WIPP. EPA has required that in addition to natural geologic and construction barriers, there be at least one engineered barrier designed to prevent inadvertent human accessibility to radiological waste for the 10,000-year period. An engineering barrier is defined by EPA as *“any material or structure that prevents or substantially delays movement of water or radionuclides toward the accessible environment. For example, a barrier may be a geologic structure, a canister, a waste form 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.”⁽²⁾ DOE proposed MgO as an engineered barrier, because laboratory evidence demonstrates that it can control pH and thus reduce solubility of actinides. EPA agreed that MgO meets the engineered barrier requirement provided there is sufficient quantity to satisfy the chemical requirements. EPA did not evaluate seals, shaft seals, or borehole plugs (i.e., structural attributes of the repository) as engineered barriers.

The analyses and models used to develop the PA have determined two credible scenarios for significant human exposure within the next 10,000 years: one entails drilling intrusions that bring to the surface waste cuttings, cavings, and spillings; the other involves actinide components of the waste that dissolve in the brine that may occupy the repository following its closure. For long-term, worst-case considerations, under the disturbed scenario, it is assumed that the repository will likely fill with brine, either from the Salado salt formation or from the underlying Castile formation in a human intrusion scenario, or from both formations. The extent to which the repository fills depends on several repository attributes such as permeability and Castile brine-reservoir pressure. The solubility of actinides under repository conditions depends on their chemical forms, oxidation states, the presence or absence of complexing agents, and the pH of the solution.

As described and referenced in the Compliance Certification Application (CCA)⁽³⁾ and Compliance Recertification Application (CRA)⁽⁴⁾ research has shown that microbial degradation of cellulose, plastics, and rubbers (CPR) in the waste will convert some of the organic carbon components into CO₂. The CO₂ will dissolve in brine and create an acidic condition, which will greatly increase the solubility of actinides.

EPA’s certification also established that placement of MgO among the TRU waste containers is an acceptable engineered barrier for reducing the amount of actinides that might reach the accessible environment. The MgO will sequester any CO₂ generated post-closure and will raise the pH of any brine inflow to the repository, thereby reducing actinide solubility.

The quantity of MgO required for an effective barrier depends on numerous factors, including the quantity of CPR; the organic carbon content of the CPR; possible methanogenesis; the efficiency of organic carbon conversion to CO₂; and the effectiveness of MgO utilization. The quantity of CPR and associated carbon content is essentially determined during the characterization stage. Because it has not been shown conclusively that methanogenesis will occur, EPA requires the assumption that all available organic carbon be converted to CO₂. A remaining uncertainty involves the effectiveness of the MgO

based upon its distribution around the waste and the amount of CO₂ that may be sequestered by other substances in the repository.

Due to these uncertainties, DOE agreed, in the CCA, to emplace excess MgO to ensure the adequacy of the engineered barrier. Initially, DOE emplaced MgO in a supersack placed on top of each waste stack and in mini-sacks placed in the space between stacks and the room walls. This amount was determined to be equal to 1.95 times the amount required to sequester the theoretically maximum possible CO₂ production. The DOE subsequently provided an analysis to EPA that resulted in EPA's approval of the elimination of the mini-sacks which reduced the factor (alternately referred to as a load factor, excess factor, or safety factor) to 1.67 times the theoretical amount required to sequester the CO₂. Approval of this reduction was based on improving the safety of operations in the repository without compromising the engineered barrier.

In April 2006, DOE submitted a letter to EPA requesting approval to lower the MgO loading factor to 1.2 from the currently approved 1.67.⁽⁵⁾ This request was submitted in accordance with Title 40 CFR 194.4 along with the opinion that it is a non-significant change that does not require a rulemaking.

Along with the letter, DOE provided a supporting statement for the request consisting of a technical justification of the proposed change, safety considerations associated with transportation of MgO, and cost benefits. Emphasis was on both health-related and accident risks associated with transportation of MgO. Statistical data on emissions, accidents, and route populations were used to estimate safety risks associated with MgO transportation from Michigan to the WIPP site. These analyses showed that the proposed reduction in the loading factor would reduce the expected deaths from any health risk linked to truck emissions from one death every five years to one death every seven years. The DOE request also estimated a cost savings of \$15.2 million, including the costs of purchasing and transportation of the MgO but excluding emplacement cost.

DOE also argued that the impact of lowering of the MgO loading factor would be non-consequential with regard to long-term (10,000 years) WIPP performance after closure. This conclusion was reached after evaluating several contributing factors that indicated the 1.2 loading factor would ensure sufficient amounts of MgO to limit repository gas pressure and minimize actinide solubility. However, no data or discussion related to the uncertainties of CO₂ generation or the chemical and microbial impacts of MgO on the postulated waste/brine mix were provided by DOE.

The EPA responded in April 2006 to the DOE request by acknowledging the merits of the transportation safety analysis and the benefits of the cost reduction while expressing concern that the request did

not address uncertainties regarding the effectiveness of the MgO.⁽⁶⁾ In particular, EPA requested an analyses of the impact of super compacted waste and the uncertainties concerning the amounts of CPR disposed in the WIPP on the MgO loading factor. In November 2006, DOE provided a response to the EPA that presented further analysis and discussion of its justification for the change request to reduce the loading factor.⁽⁷⁾

III. SUMMARY OF FINDINGS

PECOS concentrated its review on the chemical and microbiological issues associated with the determination of the necessary amount of MgO to be included in the WIPP and associated long-term affects. A summary of this review follows.

IIIA. Performance Assessment

The DOE request stated that the proposed reduction in the quantity of MgO will not be a limiting factor in the PA for two reasons. First, the DOE is emplacing more than enough MgO to ensure the consumption of essentially all CO₂ that could be produced in the repository. Second, the reactivity of the MgO being emplaced in the WIPP is such that its carbonation rate exceeds the CO₂ production rate.⁽⁴⁾ Both of these conditions appear to continue to be met in excess at the proposed 1.2 loading factor. Therefore, there would be no impact on the PA as a result of changing the loading factor.

IIIB. MgO Quantity Control

DOE acknowledges that an excess over theoretical quantity of MgO is appropriate to accommodate uncertainties in determining the quantity of CPR and the effectiveness of MgO as an engineered barrier. DOE further asserts that the excess MgO required can be reduced, since these uncertainties have been minimized because:

- Recent changes to the WIPP waste information system (WWIS) have significantly enhanced the reliability of DOE's estimates of the emplaced masses of CPR and MgO.
- The timeliness of the WWIS information is such that the balance between CPR emplacement and MgO emplacement remains current. The WWIS now tracks the quantity of emplaced MgO and CPR on a near real time basis. This coupled with estimates of the additional CPR to be emplaced in the room allows the required additional MgO to be accurately determined on a room-by-room basis.
- An inspection and audit by EPA, cited in the DOE request, confirmed that the necessary

waste emplacement procedures are in place and WIPP personnel are properly trained.

IIIC. Uncertainties in Microbial Activity

In its November 2006 response to EPA, DOE presented further analysis and discussion of its justification for reducing the loading factor. The response provided an updated analysis of the uncertainties and the application of a mathematical model that predicted the effectiveness of the MgO. However, no new data with respect to the effects of MgO on the chemistry or microbiology of the TRU waste/brine mixture were included. This is the single biggest weakness in DOE’s efforts with respect to the MgO issue, as recognized in the 2004 CRA, which states, “No microbial experiments have been carried out with MgO since the use of this material was proposed in 1996 to consume CO₂ and control the fugacity of CO₂ (*f*CO₂) and pH in the WIPP.”⁽⁴⁾

In addition, the DOE stated that the following conservative assumptions were made for the uncertainty analysis:

- Microbes remain active through the lifetime of the repository.
- Microbes will consume all of the organic carbon in the CPR materials that are emplaced in the repository.
- Other materials in the waste, such as lime and the corrosion products of iron-based materials, do not react with CO₂.

The first assumption is arguably realistic given the presence of microbial life in comparably harsh environments. The second has not been supported by any directly applicable research that we found. The third contradicts what has been observed in applicable research as reported by Sandia,⁽⁸⁾ though Sandia did acknowledge caveats concerning differences with actual WIPP conditions. There is no scientific justification provided for these assumptions, which have a major impact on the entire MgO issue. Rather, the justification provided by DOE is: first, they are necessary to support the EPA required assumption of one mole of CO₂ for each mole of organic carbon; and second, reactions of CO₂ with other substances have process uncertainties that cannot be quantified at this time. The cumulative effect of these conservative assumptions is to significantly overestimate the amount of MgO needed.

IIID. Uncertainties in MgO Effectiveness

As noted above, the uncertainty in the required amount of MgO is directly related to the amount of CPR in the TRU waste emplaced in each room and panel of the WIPP. It is also broadly attributable to the

completeness of conversion of the CPR to CO₂, the completeness of the CO₂ and MgO reaction, and the physical distribution of the MgO (i.e., the place of need for MgO is accessible to the place of supply of MgO). DOE identified 15 contributing uncertainties in its response to EPA's concerns. The uncertainty analysis prepared by Sandia ⁽⁸⁾ categorized these uncertainties into three groups: 1) uncertainties related to the quantity of CO₂ produced; 2) uncertainties in the amount of MgO available to react with CO₂; and 3) uncertainties in the moles of CO₂ sequestered per mole of MgO available to consume CO₂.

In conducting this analysis, DOE began by defining an effective excess factor (EEF) that starts with an emplaced MgO quantity based on the loading factor of 1.2 and modifying it in accordance with the value of the other identified uncertainties. Depending on the nature of the uncertainty of identified contributing factors, the EEF may be less than or greater than 1.2. However, after accounting for all identified uncertainties, an EEF of at least 1.0 is required to ensure an effective engineered barrier.

Sandia assigned a mean and standard deviation to uncertainties modeled as random variables and included the remaining uncertainties by assigning assumed values. Using this technique, they determined an EEF mean value of 1.03 with a standard deviation of 0.07⁽⁸⁾.

PECOS' evaluation of the uncertainties is organized below by the three categories identified by DOE.

1. Uncertainties related to the quantity of CO₂ produced

The quantity of CPR in the emplaced waste: There are several factors that affect this uncertainty. They include the accuracy of the formula used to determine the amount of MgO required for each room and the accuracy of the estimates of the mass of each component of the CPR emplaced in each room. Our review of the formula is presented under "Other Observations" below.

The foundation for establishing the amount of MgO needed in the WIPP is the weight of the CPR being emplaced. Therefore, the initial question is, "What is the accuracy of the methods used to determine the weight of CPR?" This should be an easy question to answer, since there should be a quality control procedure established for waste characterization that includes the process used to establish the weight of CPR in each container and the accuracy of that determination. Unfortunately, the uncertainty of the estimates of the mass of CPR is unknown, at least from the standpoint of the documents reviewed for this report. The 1996 edition of the *Transuranic Waste Characterization Sampling and Analysis Manual* ⁽⁹⁾ indicated that the weight of CPR was to be estimated from reference tables prepared by each generator if radiography was used for waste characterization. If visual examination (VE) was used, it was recommended (preferred) that the individual items of waste be weighed—estimates were only used for bags of wastes that did not need to be opened. The manual also presented an evaluation of the

weights estimated using radiography versus VE indicating that radiography consistently estimated greater weights for CPR (3 percent higher for plastic, 17 percent higher for rubber, and 64 percent higher for cellulose). There was no discussion in the manual regarding the overall accuracy of the process. As discussed below, a second investigation of VE and RTR determinations of CPR quantities using a much larger sample from a variety of waste streams showed close agreement between VE and RTR.

The latest revision of the WIPP Waste Acceptance Criteria (Rev 6)⁽¹⁰⁾ simply requires that the generating sites “estimate” the CPR weights without guidance as to how to perform the estimate or the acceptable accuracy of those estimates with the exception of one waste stream, debris, (S5000). For that waste stream, the WAC states that the entire waste stream will be reported as plastic with the weight calculated as the volume of the waste container multiplied by 620 kg/m³ up to the weight of the container. The Quality Assurance Project Plans for various sites (Idaho National Laboratory, Savannah River Site) indicate that the weights of CPR in each container are estimated by identifying the CPR objects in the container (either by VE or RTR) and using historically derived waste-weight estimating tables to estimate the weight for each object. The actual weighing of the items in a drum is only done if the waste cannot be described clearly enough to use the waste-weight estimating tables and if the acceptable knowledge is insufficient to establish the weight of the items in question. No discussion was found in any document that we reviewed regarding the uncertainty (accuracy) of either the waste-weight tables or, in the case of debris waste, the uniform conversion factor.

There are two concerns about the use of waste-weight tables. First each operator may have a consistent bias in estimating the volume of the CPR materials which would carry over into the weight estimate. Second, the waste-weight tables may be biased. For example, the weight of wood depends on the type of wood (pine, fir, oak, etc.) and the construction of the wood which may include a substantial amount of glue (plywood, particle board) so a simple table that sets one weight value for wood regardless of the wood type is inherently biased. Similarly, the use of a uniform conversion factor such as is applied to the S5000 waste stream very probably overestimates the overall organic carbon weight since most debris wastes will include some metals, woods, and rubbers, all of which would result in a lower estimate of organic carbon weight than an assumption based upon all plastics. Thus, if any of these biases exist, which it appears they do, then all estimates of CPR weight prepared by using the tables will be biased—high or low.

The DOE argument presented in the uncertainty analysis regarding the ability to measure (estimate) the amount of CPR in each TRU waste container seems to center on the question as to whether real-time radiography (RTR) is as accurate as VE for the estimate of CPR when summed over a large number of containers, such as a room-full⁽¹¹⁾. The uncertainty in quantity was determined by comparing VE

results with RTR results. It was assumed that the VE results were the more accurate value and they were treated as the “true value”⁽¹¹⁾, which is logical if the current VE practice still includes actually weighing the waste items. The RTR results were found to agree with differences distributed randomly above and below the VE value. This exercise yielded an estimate of plus or minus 0.3 percent error boundary defined as dividing the standard deviation by the mean. Sandia did not detect a plus or minus bias, thus confirming the randomness of the differences between VE and RTR and supporting the equivalency of VE and RTR when summed over large sample sizes.

The yield of CO₂ per mole of emplaced organic carbon: DOE indicated that this was one of the more dominant uncertainties. However, EPA required that the CO₂ yield be taken as one mole of CO₂ per mole of organic carbon. While DOE takes exception to this requirement in its uncertainty analysis, indicating that a more realistic assumption is between 0.53 and 0.72 moles of CO₂ per mole of emplaced organic carbon, the one mole requirement was still used in the uncertainty analysis. This EPA specification seems overly conservative as further discussed below.

The role of methanogenesis: The production of methane is also identified as a dominant uncertainty by DOE. Methanogenesis could reduce the amount of organic carbon converted to CO₂ by almost 50 percent.⁽⁸⁾ However, EPA raised questions regarding the assumptions of sulfate availability made by DOE. As a result, it is assumed in the Sandia uncertainty studies that methanogenesis is not a significant factor and there would be 100 percent conversion of organic carbon to CO₂. Nevertheless, the uncertainty analysis does include a discussion of circumstances in which this may not be a valid assumption as well as the associated impacts on the ratio of moles of CO₂ to moles of organic carbon.

The requirement imposed by EPA that all organic carbon in the waste be assumed to be converted to CO₂ by microbial action requires several concurrent assumptions, including the assumption that the brine/waste/MgO solution is always mixed, so the nutrients required for ongoing microbial activity are replenished and waste products that might poison the activity are removed. Complete mixing would also support an assumption of 100% utilization of the MgO for CO₂ sequestration, as discussed further below.

In summary, the combination of the conservative assumptions discussed above supports the hypothesis that if DOE can demonstrate that its methods for determining the weight of CPR consistently overestimate that mass, then it is reasonable to assume that no more than one mole of MgO per mole of organic carbon in the CPR will be sufficient for CO₂ sequestration.

2. Uncertainties in the amount of MgO available to react with CO₂

The fraction of reactive constituents in commercial grade MgO: Commercial grade products always contain impurities or non-functioning components that reduce the product's effectiveness. The Washington TRU Solutions (WTS) specifications for MgO require a minimum of 95 weight percent MgO plus Calcium Oxide with MgO being at least 90 weight percent. The original supplier, National Magnesia Chemicals, was replaced by Premier Chemicals. Premier Chemicals notified WTS that they were running out of ore suitable for meeting this specification at the completion of Panel 2, Room 2. (Panels are filled back to front beginning at Room 7). Since then, MgO has been supplied by Martin Marietta Magnesia Specialties, LLC. The uncertainty analysis assumes that MgO with current Martin Marietta specifications will be available throughout the operating life of the repository. Sandia has studied MgO from the various suppliers to verify its effectiveness meets their assumptions.⁽¹²⁾ Further, the WTS quality assurance program constantly audits the supplier's determination of the chemical composition of the MgO, so there is very low risk that there will be less reactive constituents available than necessary. Therefore, this uncertainty has no impact on the 1.67 versus 1.2 loading factor issue.

The carbonation of MgO prior to emplacement: MgO is bagged in material used for preserving Portland cement and is effectively sealed from humidity exposure for long periods of time, especially if stored in a dry environment, as is the case at the WIPP. Inasmuch as the WIPP appears to consume MgO regularly without a large inventory, the Sandia treatment of this factor—namely that there will be minimal carbonation—is deemed appropriate and does not impact the 1.67 versus 1.2 loading factor issue.

The extent of reaction of MgO and/or CaO: Numerous experiments have been conducted to determine the effectiveness of the commercial-grade MgO emplaced in the repository. To date, all results have indicated that all MgO and CaO will react to consume CO₂. In order to test for any tendency for MgO to lithify, Sandia prepared “cemented-cake” samples by heating a layer of Premier MgO in a beaker containing synthetic brine at temperatures up to 90°C for up to 6 months.⁽¹²⁾ Some indication of lithification was observed, but the results of ongoing tests continue to support the conclusion that all MgO and CaO would remain active. Therefore, this uncertainty has no significant impact on the 1.67 versus 1.2 loading factor issue.

The loss of MgO to brine outflow from the repository: Sandia⁽¹³⁾ evaluated the loss of MgO through outflow from the repository by relating it to total brine loss, MgO solubility, and the timing of brine loss corresponding to five human intrusion scenarios. Using a Monte Carlo approach to determine probability distributions for calculations, possible MgO losses from each panel were determined. Losses were converted to the fractions of MgO emplaced in each panel. The results were summed and used to develop a complementary cumulative distribution function relating maximum losses to probability of

occurrence. The result was a median of 0.8 percent loss of MgO from the repository with a standard deviation of 1.9 percent. Thus, uncertainties related to brine loss do not present a significant impact on the 1.67 versus 1.2 loading factor issue.

The likelihood of MgO supersack rupture: The mechanism of supersack rupture has three possibilities: bursting by roof pressure, rupture by falling roof pieces, or microbial activity. Given that 100 percent of plastics are assumed to be consumed through the respiratory process of microbes, the Sandia analysis assumes any MgO sacks not ruptured by physical processes will be ruptured in the microbial process. However, given the possibility of a super compacted waste container pier supporting the roof at various locations, rupture of some supersacks may be delayed or may be dependent upon microbial rupture or falling roof pieces. In addition, it appears that microbial attack on plastics may be delayed until after the cellulose is consumed, which may cause a major delay in the breaching of some supersacks. For super compacted piers to remain structurally sound, their contents must remain isolated from the brine and associated microbial activity, which would temporarily decrease the MgO requirement. Thus, it seems highly unlikely that supersack rupture failure will be significant, particularly considering the hundreds of years that will pass prior to human intrusion. Therefore, this uncertainty has no significant impact on the 1.67 versus 1.2 loading factor issue.

The amount of MgO in each room: As discussed above, it can be reasonably assumed that DOE's procedures for determining the mass of CPR in each TRU waste container and emplaced waste unit can be shown to consistently overestimate the actual mass. Therefore, the ongoing procedure of tracking waste mass and composition and adjusting MgO quantity accordingly acceptably minimizes the possibility that an insufficient quantity of MgO will be emplaced in each room and panel.

The efficiency of mixing processes: Sandia ⁽¹⁴⁾ has studied the efficiency of mixing of the inflowing brine with the contents of the repository by comparing diffusion times for transport across repository spatial distances to the hydraulic residence time of brine based upon the repository attributes such as volume and porosity. The scenarios included panels filled with different mixes of standard waste, super compacted waste, and pipe over packs. In all cases, the mixing by diffusion was predominant and the required mixing times were much less than residence times. Thus, Sandia concluded that the mixing efficiency will be very high and will not be a limiting factor in MgO utilization. We agree with this conclusion, particularly since mixing by advection and dispersion in the brine, as well as diffusion in the vapor space were ignored, which added an element of conservatism. Therefore, this uncertainty has no impact on the 1.67 versus 1.2 loading factor issue.

The physical segregation of MgO from CO₂: Any CO₂ in the vapor space will have access to any unsubmerged MgO. Segregation of solid MgO from brine may result from it resting on top of drums or other containers. This phenomenon would be temporary pending drum degradation from anoxic and anoxic corrosion. Thus, any impact of segregation would be expected to be temporary and not of long-term consequence given the 10,000-year period. Therefore, this uncertainty has no significant impact on the 1.67 versus 1.2 loading factor issue.

In summary, the analysis of the above uncertainties indicates that because of the assumption of complete mixing, a loading factor is not necessary as long as the error in the estimates of mass of CPR can be shown to have a positive bias.

3. Uncertainties in the moles of CO₂ sequestered per mole of MgO available to consume CO₂

The conversion of hydromagnesite to magnesite: It is anticipated that the thermodynamically stable form is magnesite, which will sequester one mole of CO₂ per mole of MgO. Hydromagnesite sequesters only 0.8 mole of CO₂ per mole of MgO and will form at a faster rate. Over time, the hydromagnesite will convert to magnesite and in so doing react with additional CO₂. Sandia⁽⁸⁾ handled this uncertainty in the sequestering of moles of CO₂ per mole of MgO as a random variable distributed uniformly between the extremes of 0.8 and 1.0. PECOS has found no other basis on which to evaluate the kinetics of hydromagnesite conversion to magnesite.

The consumption of CO₂ by materials other than MgO: Any consumption of CO₂ by materials other than MgO decreases the demand for MgO, thus increasing the EEF. DOE acknowledges that the wastes as deposited in the WIPP will contain many possible types of materials that may consume CO₂ including iron-based materials and their corrosion products, lead-based materials and their corrosion products, and lime and portlandite products contained in waste sludge. Natural sources of CO₂ sequestering sources in the WIPP include dissolved calcium species that could be produced from the reduction of Ca⁺⁺ bearing minerals as well as the Mg⁺⁺ ions present in either the Salado formation or the brine from the Castillo formation. The uncertainty analysis prepared by Sandia does not take credit for any consumption by materials other than MgO.⁽⁸⁾ There will be a very large quantity of iron from the steel drums as well as other metals, especially aluminum, and metal oxides in the waste that likely will form carbonates. Therefore, taking no credit for CO₂ sequestering by this mechanism seems very conservative. In fact, Sandia has estimated that the materials in the wastes alone (iron, lead, aluminum, etc.) could sequester close to 30 percent of the CO₂.⁽⁸⁾ Sandia also recognizes the potential that naturally occurring minerals will also sequester CO₂ but does not provide an estimate for the amount of CO₂ that might be sequestered by these minerals.

The Dissolution of CO₂ in WIPP brines: Sandia⁽¹²⁾ has calculated, based upon the solubility of CO₂ and the volume of the repository, that less than 0.04 percent of the total CO₂ could be lost by flow through the repository of releases equal to the total volume of the repository. This small loss has no significant impact on the 1.67 versus 1.2 loading factor issue.

The incorporation of CO₂ in biomass: The uncertainty analysis does not assume any organic carbon is sequestered in microbial biomass. With regard to biomass sequestering organic carbon, the taking of no credit for this event is very likely correct inasmuch as, again referring to non-WIPP scenarios in a waste treatment situation, live microbes invariably consume the dead ones when left with no other choice and any impact would be minimal. Therefore, this uncertainty has no significant impact on the 1.67 versus 1.2 loading factor issue

In summary, the conservative assumptions presented in the above set of uncertainty analyses indicate that the amount of MgO required in the WIPP is overestimated.

III.E. Other Observations

PECOS has identified the following information that may also impact the quantity of MgO required in the WIPP:

1. A study at Brookhaven National Laboratory⁽¹⁵⁾ with material similar to WIPP CPR but without the addition of MgO to the test brine found that microbial gas generation rates were initially quite high but decreased fairly rapidly over time and may have stopped all together by the end of the study. This suggests that much of the simulated WIPP waste may not be acceptable as substrate that supports microbial attack. It is also noted that after 7 years, the microbes had not consumed all of the cellulosics or any of the plastics and rubber. These results raise doubts as to whether the hypothesis of complete conversion of all carbon in the CPR to CO₂ is valid (2004 CRA, Appendix Barriers).⁽⁴⁾ This argues for a modification of the EPA assumption of the conversion of all organic carbon. However, since no data exist for the periods associated with possible microbial action in the WIPP (1000+ years), a worst-case assumption is justifiable but probably conservative.
2. The presence of sufficient essential nutrients to support life even at the microbe level has not been established. In the treatment of some industrial wastewaters, for instance, phosphorous and nitrogen must be added to sustain microbial activity.⁽¹⁶⁾ An insufficiency of nutrients would stop or at least slow down the microbial activity since they would necessarily have to be recycled

through microbe cannibalism. An assumption of unlimited nutrient supplies in the WIPP is difficult to justify since there is not expected to be any significant brine movement in the repository once equilibrium is reached by the brine inflow from the Castile formation. Hence, it is doubtful that the total amount of organic carbon will be converted to CO₂. Further, if it is assumed there is sufficient and continuing brine inflow to provide the nutrients for 100 percent organic carbon conversion to CO₂, then it must also be recognized that there will be additional amounts of cations available to react with the CO₂ as discussed in more detail in point 5. below.

3. The uncertainties examined above address the loading factor and subsequent EEF. The loading factor relates to the quantity of MgO to be emplaced by the equation:

$$M_{\text{MgO}} = \text{LF}(M_{\text{C}} + M_{\text{R}} + 1.7M_{\text{P}}) 6\text{MW}_{\text{MgO}}/\text{MW}_{\text{Cell}}$$

where

- M = mass
- LF = loading factor
- MW = molecular weight, and
- C, R, and P = cellulosics, rubber, and plastic.

The implied MR multiplier of 1 is based upon a rubber mixture of 50 percent neoprene and 50 percent hypalon, and the 1.7 multiplier for plastic is based upon 80 percent polyethylene and 20 percent polyvinyl chloride.⁽¹⁷⁾ In practice, rubber and plastic objects include fillers and additives to impart specific characteristics. These added materials may range from 5 to 50 percent of the product with 10 to 20 percent being typical. The significance is that the filler may be either carbon black or an inorganic such as silica or calcium sulfate, the extender will likely be a hydrocarbon, and the dispersant an inorganic such as lead oxide. Hydrocarbons are likely biodegradable but inorganics are not. Additionally, Rook⁽¹⁸⁾ determined that carbon black is not biodegradable though the study involved conditions different from those of WIPP.

4. Compounding substances will have either a positive or a negative impact depending upon whether they contain organic carbon and are biodegradable or not. Neither carbon black nor inorganic materials meet these criteria. The overall impact of not excluding the non-biodegradable materials results in a bias and an over-estimate of the amount of organic carbon available. The size of that over-estimate depends on the amount (percentage) of rubber and plastic. From a review of the CRA (Appendix Data) and the Transuranic Waste Baseline Inventory Report,⁽¹⁹⁾ it appears that rubber plus plastic averages about 50 percent of the CPR. Consequently, the impact of overestimating the organic carbon in CPR leads to the formula likely overestimating the required amount of MgO by 5 to 10 percent.

5. An assumption that the brine inflow has the chemical characteristics of the Castile formation does not recognize the fact that as the brine comes in contact with the salts of the Salado formation it will exchange chemicals from those salts. In other words, since the mixing efficiency is high and the repository surfaces will fracture and break up in response to creep stress, the chemical composition of the Castile brine will, over time, become similar to the pore brine in the Salado formation. The net result will be that the magnesium concentration (19 millimoles [mM]) in the Castile brine that flows into the WIPP will approach the 1.0 M magnesium concentration found in the Salado brine. Consequently, this increase in the naturally available magnesium will reduce the amount of MgO required.

6. The assessment of methanogenesis is accepted as presented with a couple of notes from other situations. First, in anaerobic waste treatment processes pH is maintained near neutral because production of methane is an objective and at pH 9 or above no methane is produced. Second, sea floor research has shown that in a bottom silt containing sulfate, the methane is oxidized to CO₂. Thus, even if methane is produced in the repository early on it may convert to CO₂ given enough sulfate in the brine from the Castile formation that is introduced by human intrusion.

IV. CONCLUSIONS

Of all of the uncertainties considered in determining the amount of MgO needed in the WIPP, the two that are the easiest to accurately determine are the weight of CPR in each room and panel and the chemical composition of the MgO. It appears that DOE has established a satisfactory procedure for both. However, no data have been presented as to the accuracy of the methods (physical measurements or estimating tables) used to make those determinations for the weight of CPR. In fact, DOE essentially considers all CPR estimates as ‘true values’ and assumes there are no positive or negative biases in the estimates. However, our review indicates that it is very likely that the weight of CPR is continuously overestimated.

The complete conversion of the organic carbon in the CPR to CO₂ is possible, but not proven for the conditions expected in the WIPP over the future hundreds to thousands of years. Therefore, the conservatism of this assumption alone is sufficient to mitigate any need for a load factor greater than one.

The assumption of taking no credit for sequestering of CO₂ by metals or other cation sources in the waste or by the minerals present in the salt or brine is very conservative even though it is difficult to quantify. We note that even if sequestering is limited by iron pacification, that pacification will likely be by

iron carbonate, which in, of itself, acknowledges some CO₂ sequestering, and thus reduces the amount of MgO needed for complete sequestration.

Sufficient sulfate to assure complete carbon conversion to CO₂ will be accompanied by cations that will be available to sequester CO₂ on the basis of one mole of CO₂ sequestered per two moles generated. This will reduce the amount of MgO needed for complete sequestration.

The treatment of CPR as consisting only of the named chemical substances ignores the fact that the mass of some of the components includes fillers, extenders and other additives. To the extent that these materials are not biodegradable, the current practice overestimates the mass of CPR and the associated quantity of MgO required.

PECOS believes the quantitative evaluation by Sandia showing a mean EEF of 1.03 with a standard deviation of .07 represents a worst-case scenario.

Given the consistent approach of assigning conservative values to each contributing attribute or conservatively not including attributes that are not amenable to quantifiable evaluation with current knowledge, PECOS believes it is appropriate to reduce the load factor to the proposed value of 1.2.

V. RECOMMENDATIONS

PECOS further believes that there is a significant potential for further lowering the required quantity of MgO emplaced based upon the use of a more likely case scenario rather than the worst-case scenario. We recommend that DOE continue to research and gather information toward the goal of establishing a defensible proposal for further lowering the MgO emplacement requirements. In a stochastic approach, the most probable requirement could represent a more likely scenario. Once the amount of MgO needed was more realistically determined, then the safety or load factor could then be based upon a multiplier of a statistically sound value such as the standard deviation. PECOS believes that such an approach would likely result in further lowering (or eliminating) the amount of MgO required which would lower the current operational health and safety risk as well as providing additional cost savings without jeopardizing long-term protection.

PECOS also believes that there is a consistent positive bias in the estimates of the weight of CPR being emplaced in the WIPP based upon the description of the procedures used for those estimates. As a result, DOE is continuously emplacing more MgO than required irrespective of the required load or safety

factor. Given DOE's interest in reducing transportation risks and lowering costs, efforts should be made to improve the accuracy of the determinations of the weight of CPR and thereby reduce the required amounts of MgO.

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