Preliminary Review of the Degradation of Cellulosic, Plastic, and Rubber Materials in the Waste Isolation Pilot Plant, and Possible Effects on Magnesium Oxide Safety Factor Calculations

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ACRONYM LIST

AMWTF	Advanced Mixed Waste Treatment Facility
ASTM	American Society for Testing and Materials
Atm	Atmospheres
$CaSO_4$	Anhydrite
CCA	Compliance Certification Application
CH	Contact handled
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CPR	Cellulosic, plastic, and rubber
CRA	Compliance Recertification Application
DOE	Department of Energy
EPA	Environmental Protection Agency
ERDA-6	Simulated Castile brine formulation
GWB	Generic Weep Brine simulated Salado brine formulation
Gy	Gray, SI unit for the energy absorbed from ionizing radiation, equal to one joule per kilogram
HCl	Hydrochloric acid
H_2S	Hydrogen sulfide
LET	Linear energy transfer
MgO	Magnesium oxide
Mrad	Megarads, unit of energy absorbed from ionizing radiation, 1 Mrad equals 10^4 Gy
NaCl	Halite
OECD	Organisation for Economic Co-operation and Development
PA	Performance Assessment
PABC	Performance Assessment Baseline Calculation
PAVT	Performance Assessment Verification Testing
PVC	Polyvinylchloride
RCRA	Resource Conservation and Recovery Act
RH	Remote handled
RSI	Institute for Regulatory Science
TRU	Transuranic
VOC	Volatile organic compound
WIPP	Waste Isolation Pilot Plant

EXECUTIVE SUMMARY

Cellulosic, plastic, and rubber (CPR) materials are placed in the Waste Isolation Pilot Plant (WIPP) repository as part of the waste inventory, as waste packaging materials, and as waste emplacement materials. These CPR materials could degrade during the 10,000-year regulatory period specified for WIPP, producing carbon dioxide (CO_2) and other gases, such as methane (CH_4) and hydrogen sulfide (H_2S). Because cellulosics and plastics contain 32% and 61%, respectively, of the estimated CPR carbon in the repository, degradation of these materials could provide significant amounts of CO_2. Because rubber contains only 7% of the estimated CPR carbon in the repository, its degradation would be expected to be a less-important source of CO_2. Carbon dioxide can reduce the pH of brines in the repository and can also form aqueous carbonate complexes with uranium and other actinides, thereby increasing the solubilities of these constituents. Consequently, anhydrous, granular, bulk magnesium oxide (MgO) is included by DOE as an engineered barrier in WIPP. The MgO backfill is designed to react with CO_2 and buffer both pH and CO_2 concentrations, so that actinide solubilities are constrained; removal of CO_2 by the MgO backfill is also expected to reduce gas pressures in the post-closure repository.

In DOE's Compliance Certification Application, DOE calculated that the MgO emplacement plan would create a 1.95 safety factor. EPA found this MgO excess to be reasonable to ensure adequate performance of the engineered barrier. In 2001, EPA approved DOE's request to remove the MgO mini-sacks and lower the excess to 1.67. DOE has requested a further reduction in the MgO safety factor to 1.2. EPA denied the request due to lack of adequate justification (EPA Docket A-98-49, Item II-B3-96).

The U.S. Department of Energy (DOE) used the Institute for Regulatory Science (RSI) to convene an expert panel to consider issues associated with the MgO backfill and microbial degradation of CPR in the WIPP repository (RSI 2006). This expert panel recommended that an expert elicitation panel be convened to determine the likely extent of degradation of CPR materials, and to determine if the amounts of MgO currently placed in the repository could be safely reduced. According to EPA regulation, expert judgment may be used to support compliance applications, but should not be substituted for existing data or for reasonable experiments that could be conducted to obtain the required data [40 CFR 194.26(a)]. An engineered barrier must be included in the WIPP repository [40 CFR 194.44], and the MgO backfill is the only engineered barrier incorporated in the repository design.

As a result of DOE's request to reduce the WIPP MgO safety factor, EPA developed this preliminary review to identify technical questions and uncertainties associated with a further reduction in the MgO safety factor. This assessment included a preliminary review of the available literature to establish whether relevant data appear to be available for resolving these questions, and if the questions might be addressed by reasonable additional experiments. The available data relevant to a number of MgO backfill-related issues were reviewed, including potential CO_2 generating degradation reactions that could occur within the repository, the extent to which these reactions could occur, and the reactivity of MgO in the repository environment. These issues were addressed by reviewing data generated by the WIPP program and surveying additional potentially relevant information. The possibility of conducting experiments to better define the reaction rates and possible extent of the degradation reactions was also considered.

A number of factors contribute to the high probability that cellulosics will be completely degraded in the WIPP repository. These factors include the abundance and variety of microorganisms that can degrade cellulosic materials, the general adaptability of microbes to their environment and available carbon sources, the abundant sulfate in the repository host rock, and the long regulatory time period. Although relatively few data appear to be available regarding the chemical effects of radiation on cellulose, it appears that low-level radiation may decrease polymer chain length and alter physical and chemical properties of cellulose. The overall effects of radiation on cellulose are likely to increase its microbial degradation potential. The available literature data appear to indicate that microbial and radiation-induced degradation of cellulosics may proceed virtually to completion if sufficient water is present in the WIPP repository.

Literature data are available regarding both microbial degradation and radiation-induced degradation of plastics, such as polyethylene and PVC, which are expected to comprise the majority of plastics in the WIPP repository. Microbial degradation of plastics generally is less extensive in the short term than microbial degradation of cellulosic materials, based on the data identified in the literature. Low-level radiolysis of plastics may alter their physical and chemical properties, making them either more or less susceptible to long-term microbial degradation. If a more extensive evaluation of the available scientific literature indicates that long-term microbial degradation of plastics is likely to be relatively minor, radiolytic degradation of plastics may become more important for performance assessment (PA) over the 10,000-year regulatory period. During irradiation of polyethylene and PVC, the amounts of gases produced, solid-phase changes, and hydrochloric acid production from PVC are likely to depend on radiation dose. The presence of oxygen in the repository before and shortly after closure can affect both radiolytic and microbial processes. A more extensive evaluation of the available microbial degradation data and the potential direct and indirect effects of radiolysis should be carried out before changes are made in the assumed extent of plastics degradation during the 10,000-year regulatory time period.

Available WIPP and literature data indicate that rubber materials expected to be present in the repository may be at least partially degraded by microbes. Radiation appears to affect both the physical and chemical properties of rubber, and in WIPP experiments, appeared to enhance microbial degradation. A more extensive evaluation of the available degradation data and the potential effects of radiolysis should be carried out before changes are made in the assumed extent of rubber degradation during the 10,000-year regulatory time period.

Experiments carried out as part of the WIPP program, experiments from outside the WIPP program, and natural occurrences of magnesium carbonate minerals indicate that brucite and hydromagnesite are likely to readily form in the WIPP repository and control brine pH and CO_2 concentrations. Magnesite formation could take place over a time scale of hundreds to thousands of years. As a consequence of the formation of brucite, hydromagnesite, and possibly magnesite, actinide and uranium solubilities in WIPP brines will be limited to concentrations lower than would be expected in the absence of MgO backfill (EPA 1998). Incomplete reaction of the MgO with brine and CO_2 is unlikely to occur unless the MgO is physically separated from the brine or CO_2. If such physical segregation should occur, the MgO safety factor would be decreased by an amount commensurate with the segregated MgO. The recent changes in MgO placement methods, with safety factors calculated for each disposal room, limit the potential effects of inhomogeneous distribution of CPR in the waste, and are likely to minimize the possible physical segregation of the MgO from brine and CO_2.

In the original certification review (EPA 1997), EPA accepted MgO as an assurance requirement, the only WIPP engineered barrier (40 CFR 194.44). This acceptance was predicated on the assumption that MgO was necessary to control chemical conditions in the disposal rooms. EPA (1997) also stated that excess MgO, i.e., the MgO safety factor, was a conservative measure necessary to overcome the uncertainty associated with predicting the expected future(s) of the WIPP disposal system. The engineered barrier is of critical importance because of a number of uncertainties associated with expected repository performance over the long regulatory time period. Assuming that all CPR carbon could be converted to CO_2 was a conservative assumption associated with the engineered barrier's performance. If this conservative assumption is no longer included in the determination of the MgO safety factor, the potential significance of other uncertainties would increase, such as those related to CPR inventory, CPR degradation rates and extents, and the possible physical segregation of small amounts of MgO. The MgO safety factor must account for these uncertainties in the absence of conservative assumptions regarding the extent of CPR degradation to form CO_2.

Uncertainties identified during the course of this investigation include the possibility of physical segregation of small quantities of MgO, CPR inventory uncertainty, potential radiolysis effects, the extent of CPR degradation over very long time periods, and the effects of early degradation processes on the long-term degradability of CPR in WIPP. In the absence of a conservative assumption that all CPR carbon could be converted to CO_2, these uncertainties should be considered in establishing the MgO safety factor by DOE.

EPA regulations require that expert judgment should not substitute for available experimental data or data that could be obtained from a reasonable set of experiments (40 CFR 194.26). The results of this review indicate that experimental data may be available and additional experiments might be conducted to reduce the uncertainties associated with the extent of CPR degradation in the WIPP repository and improve understanding of WIPP's performance. Consequently, use of expert judgment to assess the likely extents of CPR degradation in the WIPP repository would require adequate justification by DOE. A more extensive evaluation of the available literature should be conducted to determine whether data are sufficient for determining the extent of CPR degradation during the 10,000-year regulatory period, whether experiments might be designed to establish the likely extents of degradation of the various materials over this long time period, or if an expert elicitation can be justified. The goal of either the literature review or experimental studies would be to adequately quantify or capture system uncertainties, including both the uncertainties associated with the quantities of CPR in the repository and the chemical reaction uncertainties related to the CPR degradation reactions or reactions of the MgO backfill. Sufficient excess MgO (an adequate safety factor) needs to be emplaced in each disposal room to compensate for the range of uncertainties related to CPR degradation and the effective performance of the MgO engineered barrier, thereby ensuring WIPP’s expected safe performance in the future.

1.0 INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is an underground facility designed for permanent disposal of transuranic (TRU) defense-related waste, located at a remote site in southeastern New Mexico. The U.S. Department of Energy (DOE) operates the WIPP repository under U.S. Environmental Protection Agency (EPA) regulations. The WIPP was certified by EPA for contact-handled (CH) TRU waste disposal based on a review of DOE's Compliance Certification Application (CCA) and supporting information, including a revised performance assessment (PA) referred to as the Performance Assessment Verification Testing (PAVT). After the WIPP certification decision, DOE began accepting waste for disposal in March 1999. The Compliance Recertification Application (CRA) was submitted by DOE to EPA in March 2004 (DOE 2004b). After extensive review of the CRA and a revised PA called the Performance Assessment Baseline Calculation (PABC), EPA recertified WIPP for continued operation in March 2006 (EPA 2006a).

The WIPP is located approximately 2,000 feet below ground surface. Waste is placed in rooms mined within the Salado Formation, which is primarily composed of halite ($NaCl$) with interbedded anhydrite ($CaSO_4$). Cellulosic, plastic, and rubber (CPR) materials are placed in the repository as part of the waste inventory, are used as waste packaging materials, and are used for waste emplacement. These CPR materials could be microbially degraded during the 10,000-year regulatory period specified for WIPP, producing carbon dioxide (CO_2) and other gases, such as methane (CH_4) and hydrogen sulfide (H_2S). Carbon dioxide can reduce the pH of brines that may enter the repository and can also form aqueous carbonate complexes with uranium and other actinides, thereby increasing the solubilities of these constituents. Consequently, anhydrous, granular, bulk magnesium oxide (MgO) has been included as an engineered barrier in WIPP. The MgO backfill is predicted to react with CO_2, buffer pH and decrease CO_2 concentrations so that actinide solubilities are constrained; removal of CO_2 by the MgO backfill is also expected to reduce gas pressures in the post-closure repository.

DOE used the Institute for Regulatory Science (RSI) to convene an expert panel to consider issues associated with the MgO backfill and the microbial degradation of CPR in the WIPP repository (RSI 2006). This expert panel recommended that an expert elicitation panel be formed to determine the likely extent of degradation of CPR materials, and to determine if the amounts of MgO currently placed in the repository could be safely reduced. According to EPA regulation, expert judgment may be used to support compliance applications, but should not be substituted for existing data or for reasonable experiments that could be conducted to obtain the required data [40 CFR 194.26(a)].

The purpose of this report is to identify specific technical questions that must be answered and uncertainties that must be addressed before EPA can consider changing the amounts of MgO backfill that must be placed in the repository to maintain the effectiveness of the engineered barrier. Therefore, a preliminary review of the available data relevant to a number of issues related to the MgO backfill was carried out. This review included chemistry-related issues such as the potential CO_2-generating microbial degradation reactions that could occur within the repository, the extent to which these reactions could occur, and the reactivity of MgO in the repository environment. These issues were addressed by consulting the available scientific literature, including data generated by the WIPP program and a survey of other relevant information. The possibility of conducting experiments to better define the reaction rates and possible extent of the microbial degradation reactions was also considered. Regulatory requirements related to engineered barriers in the WIPP and ways in which uncertainties must be addressed were evaluated as well, and are summarized in this report.

2.0 GAS GENERATION AND BACKFILL REACTIONS IN THE REPOSITORY

The conceptual models and approach used to include the effects of gas generation and reaction of MgO in the WIPP PA were recently evaluated as part of EPA's review of the CRA (EPA 2006b and 2006c). Potential gas-generation reactions were also considered during EPA's review of Advanced Mixed Waste Treatment Facility (AMWTF) supercompacted waste disposal at WIPP (TEA 2004). Because detailed discussions were included in these review documents, these topics are only summarized below. Gas generation due to radiolytic degradation of CPR could take place in the repository. However, DOE determined that gas generation from radiation-induced degradation of CPR would be much less important than gas generation from microbial processes and corrosion (Molecke 1979, DOE 2004b Appendix PA Attachment SCR). Therefore, only gas generation from microbial degradation of CPR and corrosion were considered for PA.

2.1 GAS GENERATION REACTIONS AND REACTION PRODUCTS

For the purposes of PA, the significant sources of gas generation in WIPP are assumed to be degradation of CPR and anoxic steel corrosion (DOE 2004b, Appendix PA). The reactions potentially involved in these processes are described below.

2.1.1 Microbial Degradation of Cellulosic, Plastic, and Rubber Materials

DOE assumed that CPR present in the repository could be approximated by the chemical formula for cellulose monomer ($C_6H_{10}O_5$).[1] DOE's conceptual model for CPR degradation includes the assumption that the major pathways for microbial degradation of CPR are the following reactions (DOE 2004b Appendix PA Attachment SOTERM):

$$C_6H_{10}O_5 + 4.8\ H^+ + 4.8\ NO_3^- \rightarrow 7.4\ H_2O + 6\ CO_2 + 2.4\ N_2 \qquad (1)$$
$$C_6H_{10}O_5 + 6\ H^+ + 3\ SO_4^{2-} \rightarrow 5\ H_2O + 6\ CO_2 + 3\ H_2S \qquad (2)$$
$$C_6H_{10}O_5 + H_2O \rightarrow 3\ CH_4 + 3\ CO_2 \qquad (3)$$

These reactions are referred to as denitrification (reaction 1), sulfate reduction (reaction 2), and methanogenesis (reaction 3). In addition to reaction (3), methanogenesis could proceed according to the following:

$$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O \qquad (4)$$

However, DOE did not include reaction (4) in their assessment of potential gas generation reactions in the WIPP repository because experimental rate data were unavailable (Wang and Brush 1996).

The reactions are assumed to proceed sequentially according to the energy yield of the reactions (Wang and Brush 1996). If limited amounts of nitrate and sulfate are present in the system, the

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[1] The formula for cellulose polymer is $(C_6H_{10}O_5)_n$.

dominant degradation reactions would proceed from reactions (1) to (3) as first nitrate and then sulfate are consumed. The particular reactions involved in microbial degradation of CPR are important because reactions (1) and (2) produce one mole of CO_2 for every mole of CPR carbon that is consumed. However, methanogenesis (reaction 3) produces only 0.5 moles of CO_2 for every mole of CPR carbon consumed. Consequently, a much smaller total amount of CO_2 could be generated in the repository if a significant proportion of CPR degradation takes place via reaction (3) instead of reactions (1) or (2).

2.1.2 Anoxic Steel Corrosion

The corrosion of iron and iron-based alloys is expected to remove residual oxygen in WIPP shortly after closure. As a result, iron and iron-based alloys are predicted to principally undergo anoxic corrosion according to the reactions (DOE 2004b, Appendix PA, Attachment SOTERM):

$$Fe + (x + 2)\ H_2O \rightarrow Fe(OH)_2 \bullet xH_2O + H_2 \qquad (5)$$
$$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2 \qquad (6)$$
$$Fe + H_2O + CO_2 \rightarrow FeCO_3 + H_2 \qquad (7)$$
$$Fe + H_2S \rightarrow FeS + H_2 \qquad (8)$$

These reactions are expected to consume water as well as CO_2 and H_2S produced by microbial degradation reactions. DOE calculations did not consider the potential consumption of CO_2 by reaction (7) to determine the required amounts of MgO backfill (Wang and Brush 1996; DOE 2004b). Based on the experimental data available from WIPP testing, reaction (7) does occur in the presence of a CO_2 atmosphere, and this reaction appeared to passivate the steel surface at CO_2 pressures above approximately 7.8 atm (Telander and Westerman 1997). However, it is unclear whether significant amounts of CO_2 will be consumed by reaction (7) at the low CO_2 pressures expected in the presence of MgO backfill and in the presence of H_2S pressures that may result from sulfate reduction (reaction 2). DOE has prepared a test plan describing experiments to determine whether reaction of iron and lead in the repository will consume significant amounts of CO_2 (Wall and Enos 2006). Based on the schedule outlined in the test plan, complete results from these experiments will not be available for several years.

2.2 MAGNESIUM OXIDE HYDRATION AND CARBONATION REACTIONS

MgO in the WIPP backfill is expected to react in humid conditions and under inundated conditions with Castile brine (ERDA-6) to form brucite:

$$MgO(s) + H_2O \rightleftharpoons Mg(OH)_2(s) \qquad (9)$$

However, under inundated conditions with Salado brine (GWB), MgO may also hydrate to form $Mg_2Cl(OH)_3 \bullet 4H_2O(s)$:

$$2\ MgO(s) + Cl^- + H^+ + 5\ H_2O \rightleftharpoons Mg_2Cl(OH)_3 \bullet 4H_2O(s) \qquad (10)$$

Brucite is expected to buffer brine pH in the repository via the dissolution reaction:

$$Mg(OH)_2(s) + 2\ H^+ \rightleftharpoons Mg^{2+} + 2\ H_2O \qquad (11)$$

At equilibrium in the WIPP repository, brucite will react with CO_2 to form the carbonate phase magnesite:

$$Mg(OH)_2(s) + CO_2(g) \rightleftharpoons MgCO_3(s) + H_2O \qquad (12)$$

However, because of kinetic constraints, metastable phases are more likely to form initially, either hydromagnesite:[2]

$$5\ Mg(OH)_2(s) + 4\ CO_2(g) \rightleftharpoons Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O(s) \qquad (13)$$

or nesquehonite:

$$Mg(OH)_2(s) + CO_2(g) + 2\ H_2O \rightleftharpoons MgCO_3 \bullet 3H_2O(s) \qquad (14)$$

The identity of the magnesium-carbonate phase most likely to form in the repository is important, because hydromagnesite and nesquehonite will control the CO_2 fugacity at higher levels than magnesite, resulting in higher predicted actinide solubilities. Because hydromagnesite and nesquehonite are not thermodynamically stable under repository conditions, they would be expected to eventually dehydrate to form magnesite:

$$Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O(s) + CO_2(g) \rightleftharpoons 5\ MgCO_3(s) + 5\ H_2O \qquad (15)$$

$$MgCO_3 \bullet 3H_2O(s) \rightleftharpoons MgCO_3(s) + 3\ H_2O \qquad (16)$$

The rate of hydromagnesite or nesquehonite conversion to magnesite is uncertain, so for the PAVT, the CRA PA, and the PABC, it was assumed that hydromagnesite would form in the repository and control CO_2 concentrations in the brines.

2.3 MAGNESIUM OXIDE SAFETY FACTOR CALCULATIONS

The MgO safety factor has been defined as the moles of MgO available to react with CO_2 in the repository divided by the maximum number of moles of CO_2 that could be generated. For the CCA, DOE calculated that the mass of MgO required to react with the maximum estimated amount of CO_2 was 43,700 tons (EPA 1997). DOE calculated a safety factor of 1.95 which was based on DOE's plan to place 85,600 tons of MgO in the repository (EPA 1997). MgO was originally placed in the repository in supersacks on top of each waste stack, as well as in minisacks that were placed around each waste stack. Use of the MgO minisacks was eliminated to improve operational safety; discontinuing use of the minisacks decreased the planned amounts of MgO to 74,000 tons (EPA 2001). This decrease resulted in a safety factor of 1.67, based on the assumption that 9.85×10^8 moles of CO_2 could be generated and 1.65×10^9 moles of MgO would be present (EPA 2001).

In 2002, DOE submitted to EPA an assessment of the effects on PA of including supercompacted waste from the AMWTF in the repository (DOE 2002). One issue identified by EPA during

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[2] Two formulas for hydromagnesite have been reported in the literature; however, only the hydromagnesite composition observed in WIPP experiments is considered in this report.

their review of AMWTF waste disposal at WIPP was the higher CPR density in supercompacted AMWTF waste compared to average WIPP CH waste (TEA 2004). Because of the higher CPR density and the possibility that supercompacted waste could be localized within the repository, some assumptions regarding MgO availability were no longer applicable. For their evaluation of AMWTF waste disposal at WIPP and for the CRA, DOE assumed that only the limited amounts of nitrate and sulfate in WIPP wastes would be available for reaction. Therefore, DOE determined that the majority of CPR degradation would proceed through methanogenesis (reaction 3) after reactions (1) and (2) had consumed the limited quantities of nitrate and sulfate in the wastes. Because methanogenesis produces less CO_2 per mole of CPR carbon consumed than denitrification or sulfate reduction, the MgO safety factor calculated by DOE was higher than if they had assumed that all CPR carbon could be converted to CO_2.

EPA reviewed DOE's assumptions for the AMWTF and CRA calculations and observed that DOE had not considered the large quantities of sulfate present in the anhydrite minerals in the Salado Formation, and had not accounted for the potential concentration of CPR in disposal rooms containing large proportions of AMWTF waste (TEA 2004, EPA 2006c). Therefore, EPA directed DOE to continue calculating the required quantities of MgO backfill and the MgO safety factor by assuming all CPR carbon could be converted to CO_2 (EPA 2004a, EPA 2004b). To address concerns regarding non-homogeneous AMWTF waste emplacement, DOE has improved tracking of MgO emplacement and can now ensure that the 1.67 MgO safety factor is being maintained in each room of the repository. Using DOE's current MgO emplacement plan, the safety factor is calculated for each room as it is filled, and additional MgO is added to rooms with higher masses of CPR to ensure the appropriate safety factor is maintained (DOE 2004a).

3.0 EXPERT PANEL REPORT

DOE used RSI to convene an expert panel to evaluate issues associated with DOE's use of MgO as an engineered barrier at WIPP (RSI 2006). The panel has addressed questions related to MgO and its performance in the repository, and also discussed a number of regulatory requirements. The expert panel report contains a project summary, prepared by DOE, which describes the use of MgO backfill and PA issues associated with its use. Because this project summary presents information that was previously reviewed for the CRA (EPA 2006b and 2006c), the project summary is not considered in this report.

RSI (2006) cited recommendations made by a National Academy of Science (NAS) review committee related to WIPP backfill performance in the repository (NAS 2001). One recommendation relevant to MgO backfill and gas generation was (NAS 2001):

> *The committee recommends that the net benefit of MgO used as backfill be reevaluated. The option to discontinue emplacement of MgO should be considered.*

Removing the MgO backfill from the repository design will likely affect predictions of gas generation and actinide solubilities. Additional information would be necessary before EPA could consider elimination of, or significant modifications to, the MgO backfill. EPA regulations require assurance requirements (40 CFR 191.14), including an engineered barrier, to compensate for uncertainties in the prediction of future repository performance and provide increased confidence in the disposal system. The MgO backfill is the only engineered barrier in the WIPP repository, and an engineered barrier is required by regulation (see Section 3.2.1 below).

The NAS committee made an additional recommendation relevant to CPR degradation (NAS 2001):

> *The committee recommends pre-closure monitoring of gas generation rates, as well as of the volume of hydrogen, carbon dioxide, and methane produced. Such monitoring could enhance confidence in the performance of the repository, especially if no gas generation is observed. Observation should continue at least until the repository shafts are sealed and longer if possible. The results of the gas generation monitoring program should be used to improve the performance assessment for recertification purposes.*

DOE has not provided EPA with repository air sample data that would allow for a re-evaluation of gas generation rates. However, laboratory information from testing with actual and simulated CPR waste is available, and EPA considered this information in their recent review of the CRA (EPA 2006b, EPA 2006c).

3.1 EXPERT PANEL FINDINGS AND RECOMMENDATIONS

The expert panel issued a series of findings and recommendations as a result of their review of information provided by DOE related to MgO reactivity and CPR degradation in the WIPP environment (RSI 2006). The expert panel's findings are summarized below, with some limited discussion of the findings.

Finding 1. The expert panel found that assuming cellulosic materials could be consumed by microbes in the WIPP repository is consistent with scientific and engineering principles, standards, and practices. The expert panel did not attempt to quantify the rate or extent of cellulosics biodegradation.

Finding 2. The expert panel found that assuming plastic materials will be completely metabolized by microbes under WIPP conditions is inconsistent with scientific and engineering principles, standards, and practices. The panel found that plastics may be partially consumed by microbes. However, if microbial degradation of plastics does occur, then its rate and extent of reaction would likely be significantly lower than the rates and extent of degradation of cellulosics. The panel also noted that EPA had defined a number of plastics as non-biodegradable (see Section 3.2.3 below). However, the expert panel did not address whether this definition would be valid for WIPP conditions and the 10,000-year repository performance period. The expert panel concluded that only a small fraction of plastics would be expected to biodegrade under WIPP conditions. The expert panel did not attempt to quantify the rate or extent of plastics biodegradation.

Finding 3. The expert panel found that assuming commercial rubber materials will be completely metabolized by microbes under WIPP conditions is inconsistent with scientific and engineering principles, standards, and practices. The expert panel also stated that the extent of biodegradation of rubber materials, if it occurs, is likely to be significantly lower than the extent of degradation of plastics, and very much less than the extent of degradation for cellulosics. The expert panel did not attempt to quantify the rate or extent of rubber biodegradation.

Finding 4. The expert panel observed that the proportion of MgO in a disposal room available for reaction will be a complex function of a number of processes, including creep closure, gas generation, and brine inflow. Because of these processes, the panel stated that the environment within a disposal room is likely to be heterogeneous and pockets of unreacted MgO are likely to persist. However, the expert panel stated that most MgO would be available for reaction.

Finding 5. If only cellulosic materials are biodegraded in the absence of MgO backfill, the expert panel found that radionuclide releases to the accessible environment will be below the EPA regulatory limits. However, the expert panel qualified this finding, stating that the evidence they had received was insufficient to definitely support this conclusion.

Finding 6. Assuming that all CPR materials are biodegraded in the absence of MgO backfill, the expert panel found that radionuclide releases to the accessible environment will be below the EPA regulatory limits. However, the expert panel qualified this finding, stating that the evidence they had received was insufficient to definitely support this conclusion.

Finding 7. The expert panel concluded that the application of Acceptable Knowledge is reasonable and consistent with scientific and engineering principles, standards, and practices. The expert panel also suggested the use of process knowledge as an alternative approach. However, the definition of Acceptable Knowledge provided by EPA in 40 CFR 194.2 is as follows:

> *Acceptable knowledge means any information about the process used to generate waste, material inputs to the process, and the time period during which the waste was generated, as well as data resulting from the analysis of waste, conducted prior to or separate from the waste certification process authorized by EPA's Certification Decision, to show compliance with Condition 3 of the certification decision (appendix A of this part).*

Therefore, Acceptable Knowledge as defined by EPA already includes process knowledge, and the expert panel appears to have misunderstood its definition. The expert panel also recommends using inference from measurements, which they defined as follows (RSI 2006):

> *… based on knowledge of past measurements made on similar wastes from the same facility, supported by knowledge of process changes that have been made since then. This approach can include the application of scaling factors, and the conduct of surrogate measurements (such as waste package density - kg per unit volume) that may be indicative of the relative amounts of CPR present.*

Finding 8. Based on the findings regarding the likely extent of CPR biodegradation, MgO reactivity, and the likelihood of meeting EPA release standards without MgO backfill, the expert panel concluded that the current 1.67 MgO safety factor is unnecessary.

Finding 9. The expert panel observed that current actinide solubility calculations include a number of conservative assumptions. They recommended the formation of an expert elicitation panel to assess the fractions of cellulosics, plastics, and rubber in the repository that would be likely to degrade in the repository environment. The expert elicitation panel would also address the fraction of MgO likely to react in the repository environment, and the possible consequences of a partial or complete shortfall in the MgO buffering capacity. The expert panel identified the objective of this effort to be an assessment of "release scenarios, using more realistic values for the required input factors, and considering their associated uncertainties."

The expert panel recommended formation of an expert elicitation panel, as described above in Finding 9. The expert panel also recommended that DOE consider performing a single-room "realistic" analysis of the processes related to the performance of the MgO backfill, including gas generation, chemical reactions, biodegradation, and mechanical creep.

3.2 REGULATORY ISSUES

The expert panel report addressed the WIPP regulatory requirement for engineered barriers and recommended the use of an expert elicitation panel to address some of their findings. Therefore, information regarding the regulations specifying the required engineered barrier and the circumstances under which expert judgment can be used in WIPP compliance applications are summarized below. The expert panel report also stated that a Resource Conservation and Recovery Act (RCRA) regulation defined some plastic materials as non-biodegradable; based on this definition, the expert panel suggested that plastic and rubber materials might not biodegrade significantly in the WIPP environment. Therefore, in this report, the RCRA definition of some plastics as non-biodegradable was evaluated to determine its applicability to WIPP.

3.2.1 Engineered Barrier Regulatory Requirements

The use of at least one engineered barrier at WIPP is required by 40 CFR 194.44 to "prevent or substantially delay the movement of water or radionuclides toward the accessible environment." For the CCA, DOE identified and EPA approved MgO backfill in the disposal rooms as the only WIPP engineered barrier (DOE 1996). MgO backfill was designed to maintain alkaline pH and mitigate the effects of CO_2 generation in the disposal rooms, thereby controlling actinide solubilities in intruding brines (EPA 1997). The inclusion of MgO backfill as an engineered barrier remained unchanged for the CRA, although the required safety factor and backfill emplacement strategy have changed since the CCA (see Section 2.3 above).

3.2.2 Expert Elicitation Panel Requirements

Requirements related to the elicitation of expert judgment for use in compliance applications are provided in 40 CFR 194.26. With regard to the circumstances under which expert judgment can be used for compliance applications, the regulation states [40 CFR 194.26(a)]:

> *Expert judgment, by an individual expert or panel of experts, may be used to support any compliance application, provided that expert judgment does not substitute for information that could reasonably be obtained through data collection or experimentation.*

3.2.3 Resource Conservation and Recovery Act Designation of Plastics as Non-Biodegradable

RSI (2006) cited EPA's RCRA regulations at 40 CFR 264.314 and 40 CFR 265.314 to support the contention that "the fraction of plastics that is expected to be biodegraded under conditions existing within the WIPP is small" (Finding 2). For example, 40 CFR 264.314 lists a number of high molecular weight polymers, such as polyethylene, polypropylene, and ground synthetic rubber, as non-biodegradable sorbents to sequester free liquids prior to disposal in surface hazardous landfills. EPA has listed in its *Federal Register* notice "Final Rule Regarding Liquids in Hazardous Waste Landfills" (57 FR 54452) on November 18, 1992, of certain high-density polymers as non-biodegradable sorbents in RCRA landfills. The *Federal Register* notice did not, however, provide any background information supporting the contention that such high molecular weight polymers were non-biodegradable. The Agency merely stated that such materials "have proved to be highly resistant to biodegradation." In an earlier *Federal Register* notice of June 1987, when EPA first proposed the use of high molecular weight polymers as non-biodegradable sorbents, the notice stated the following (52 FR 23695):

> *… the Agency now believes that a different criterion should be used to determine if an organic polymer is biodegradable. The Agency proposes to determine this alternative criterion by using tests which involve incubating the absorbent materials with prepared stock cultures of various microorganisms under ideal conditions for their growth. This incubation demonstrates the fungal resistance of polymers and is used by the American Society for the Testing of Materials laboratory test ASTM Method G21-70….*

The relevance of the fact that certain plastics and rubbers are defined as non-biodegradable for use as sorbents in RCRA surface landfills to the assumption that such materials are non-biodegradable in the context of the WIPP environment is questionable based on the following considerations:

- Under 40 CFR 264.117, post-closure monitoring is limited to 30 years unless extended by the EPA Regional Administrator, while at the WIPP, regulatory compliance must be demonstrated through PA for 10,000 years.

- Under 40 CFR 264.314, EPA offers three tests to demonstrate that materials not specifically listed as non-biodegradable sorbents in §264.314(e)(1)(i) and (ii) can be used as non-biodegradable sorbents. Two of the tests are American Society for Testing and Materials (ASTM) procedures and one is an Organisation for Economic Co-operation and Development (OECD) procedure. In 1995, EPA decided to add the OECD test to §264.314(e)(2) as described in its *Federal Register* notice (60 FR 35703). In the *Federal Register* notice, EPA noted that:

  > *… the OECD test 301B is a test for biodegradability in an aerobic environment, as are the two ASTM tests that were promulgated in the November 18, 1992 rule. The Agency also recognizes that the actual environment in which the sorbents will be used, i.e., in a container in a landfill, will be anaerobic. The Agency does not know, however, of any published widely accepted tests for the biodegradability of materials in anaerobic conditions that would be practical for purposes of this rule. The Agency believes, however, that OECD 301B is an acceptable surrogate for determining if a sorbent will biodegrade in containerized liquids in a hazardous waste landfill.*

  The environment in the WIPP will become anaerobic shortly after closure and will remain so throughout the regulatory period. Therefore, the assumption that high molecular weight polymers will not biodegrade may not be valid at WIPP.

- While materials may be judged functionally as non-biodegradable sorbents in RCRA surface landfills, they can achieve that functionality even if limited biodegradation actually occurs. In the WIPP, on the other hand, at least one mole of MgO backfill must be provided for each mole of CO_2 generated from CPR decomposition. This places a greater burden on defining quantitatively the extent to which biodegradation occurs at the WIPP.

The RCRA definition of some plastic sorbents as non-biodegradable is based mainly on observations over relatively short time frames and testing in aerobic environments. These conditions do not appear relevant to the long-term WIPP environment or regulatory period of performance. Therefore, the RCRA definition of some plastic sorbents as non-biodegradable appears to have essentially no relevance to the determination of whether plastic and rubber materials are likely to be substantially biodegraded in the WIPP repository.

3.2.4 Uncertainties in Cellulosics, Plastics, and Rubber Inventory

For each waste component identified as influencing containment of waste [40 CFR 194.24(b)(1) and (b)(2)] and included in PA, DOE is required to specify the upper or lower limiting value in the total WIPP inventory and the associated uncertainty for this limiting value [40 CFR 194.24(c)]. Cellulosics, plastics, and rubber are waste components quantified for PA because of the potential for microbial gas production from these materials [40 CFR 194.24(b), DOE 2004b Appendix TRUWASTE]. The uncertainties associated with the CPR inventory were not directly addressed by DOE in the CRA. These uncertainties appear to be unimportant, because CO_2 production is not expected to affect PA since MgO backfill will react with the CO_2. The current MgO safety factor of 1.67 would be expected to account for any uncertainties in the CPR inventory. However, if smaller quantities of MgO are to be placed in the repository, reducing the safety factor, a more explicit consideration of the uncertainties associated with the CPR inventory may be necessary.

4.0 AVAILABLE INFORMATION RELATED TO CELLULOSICS, PLASTICS, AND RUBBER DEGRADATION AND BACKFILL REACTIONS

Because of uncertainties associated with the possible extent of CPR degradation, DOE assumed for the Performance Assessment Baseline Calculations (PABC) that complete degradation of all CPR was possible during the 10,000-year WIPP regulatory period for 25% of the PA realizations, but only cellulosics degradation was possible for the other 75% of the realizations;[3] DOE assumed that all CPR carbon could form CO_2 for the purpose of calculating the MgO safety factor. The excess MgO present in the repository and the conservatism of assuming that all CPR could degrade to form CO_2 adequately addressed any uncertainties associated with chemical processes in the WIPP repository or with the CPR inventory and allows MgO to perform its function as an assurance requirement. To determine whether the amount of MgO emplaced in the backfill can be safely reduced, additional information is required. The required technical information about chemical processes in the WIPP includes:

- The mechanism(s) by which CPR is likely to degrade in the WIPP, and the likely rates and extents of these degradation processes in the WIPP for 10,000 years
- The proportion of MgO in a disposal room that will be available for reaction
- The possible effects on actinide solubilities and gas generation if the amount of MgO available for reaction is less than the amount required to react with the CO_2 that is generated

In addition, an understanding of the uncertainties associated with this technical information would be required. A preliminary review of WIPP information and literature data was performed to evaluate whether this information is likely to be available.

In the WIPP repository, both microbial degradation and radiation-induced degradation of CPR may occur. DOE compared gas generation rates from microbial processes, corrosion, and radiation-induced degradation, and determined that gas generation from radiation-induced degradation of CPR will be relatively unimportant (Molecke 1979, DOE 2004b Appendix PA Attachment SCR). Radionuclides in WIPP waste will emit alpha, beta, and gamma radiation (Leigh and Trone 2005). This radiation may cause the evolution of gases from polymers, and may also affect the chemistry of the solid phase, which could alter subsequent microbial degradation. Therefore, both microbial- and radiation-induced degradation of CPR were included in this review.

The factors expected to be important for determining the mechanisms, rates, and extent of CPR degradation are summarized below. WIPP-specific experiments related to microbial degradation rates of CPR have been carried out and were recently evaluated for the CRA (EPA 2006c); the

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[3] For the CCA PA, the PAVT, and CRA PA microbial gas generation calculations, DOE assumed that there was a 50% probability of no significant microbial degradation of CPR, a 25% probability that only cellulosics could be microbially degraded, and a 25% probability that cellulosics, plastics, and rubber could be microbially degraded. For the PABC, DOE assumed a 75% probability that only cellulosics could be microbially degraded and a 25% probability that all cellulosics, plastics, and rubber could be microbially degraded (EPA 2006b).

results of these experiments are also summarized. A preliminary review of the scientific literature was also performed to establish whether relevant data may be available for assessing the likely extent of CPR biodegradation and radiation-induced degradation in the WIPP environment.

4.1 FACTORS THAT INFLUENCE RATES AND EXTENT OF CPR DEGRADATION

The rates and extent of CPR degradation during the 10,000-year WIPP regulatory period are likely to be influenced by the following:

- Composition of the CPR materials
- Microbial population
- Chemical and physical environment, including the quantity and salinity of the repository brines, redox conditions, pH, and temperature
- Radiation dose to the CPR materials and associated brines
- Interactions of different processes

4.1.1 Material Composition

The composition of CPR materials in the repository will significantly affect degradation rates and the possible extent of degradation. Cellulosics, plastics, and rubber are primarily polymeric materials composed of linked carbon units. These linked carbon units form the “backbone” of the material structure.

“Cellulosics” in WIPP waste are defined as materials such as paper, cloth, and wood, all of which contain mostly cellulose, hemicellulose, and lignin. Wood is composed of 40% to 50% cellulose, 25% to 35% hemicellulose, and 18% to 35% lignin, with minor amounts of extraneous materials (Pettersen 1984). Cellulose is a partially crystalline polysaccharide composed of unbranched chains of glucose [$(C_6H_{10}O_5)_n$]. Hemicellulose has a lower molecular weight and is less crystalline than cellulose. Hemicellulose is typically closely associated with cellulose and forms a structural component of the plant (Pettersen 1984). Lignin is a phenolic substance made up of variously bonded hydroxy- and methoxy-substituted phenylpropane units. Lignin is a macromolecule and forms a framework for the cellulose in plants. The combination of cellulose, hemicellulose, and lignin in plant materials is sometimes referred to as lignocellulose. Paper is produced from wood by removing varying quantities of lignin in the pulping process. Cotton bolls, used to create both cloth and paper, are almost pure cellulose (Lynd et al. 2002). Cellulose may be processed further to create cellophane and rayon. The proportions of cellulose and lignin in WIPP waste “cellulosics” may be important, because cellulose is usually more rapidly biodegraded than lignin (Benner et al. 1984).

Plastics are synthetic polymers, the majority of which are based on carbon monomer units. However, the polymer backbone in some plastics may include oxygen, nitrogen, sulfur, or chlorine. The nature and arrangement of chemical groups attached to the polymer backbone, also referred to as substituents, affect the physical properties of the plastic. Examples of substituents include chlorine in polyvinylchloride (PVC) or benzene in polystyrene. Plastics may be composed of both amorphous and crystalline materials; the amorphous material provides elasticity, whereas the crystalline material provides strength to the plastic. Polymers with covalent crosslinks between the polymer strands are called thermoset plastics because they cannot be reformed upon heating. Thermoplastics, on the other hand, have weaker associations between the polymer strands. Thermoplastics are brittle and glassy below a glass transition temperature (T_g), melt above a higher temperature (T_m), and are a plastic or deformable mixture of amorphous and crystalline material between T_g and T_m. Polyethylene and PVC are examples of thermoplastics. Plasticizers, often phthalates such as bis(2-ethylhexyl) phthalate, are sometimes added to thermoplastics to reduce the glass transition temperature and make the material more elastic at lower temperatures.

Rubbers or elastomers are polymers with high molecular weights that usually have been lightly crosslinked to eliminate flow. They exhibit the unique property of long-range reversible extensibility, frequently to extensions of over 600% under relatively small applied stress. Rubber may be either natural or synthetic. Natural rubber is a polymer made up of isoprene monomer units, and is derived from some plants. Polyisoprene (Figure 4-1), styrene butadiene rubber, and butyl rubber are some examples of synthetic rubbers that are widely used. Neoprene and Hypalon® are reported to be significant components of the rubber found in WIPP waste (DOE 2004b, Appendix DATA, Attachment F). Neoprene is a synthetic rubber based on polychloroprene [$(C_4H_5Cl)_n$] (Figure 4-2); Hypalon® is a chlorosulfonated polyethylene synthetic rubber trademarked by Dupont.

Elastomers generally have a large amount of unsaturation (C=C bonds) in the polymer backbone. Crosslinking, also referred to as curing, is an irreversible process during which an elastomer undergoes a change in its chemical structure. Crosslinking causes the elastomer to become less plastic and more resistant to swelling by organic liquids, while its elastic properties are improved. Uncured (not crosslinked) elastomer molecules exist in a shape analogous to spaghetti. Through crosslinking, the molecules are tied together by a few permanent chemical bonds to give the material a three-dimensional network with a stable shape, which improves the properties of the rubber. There are different methods of crosslinking rubber, but the most common method uses sulfur as the crosslinking agent. The crosslinks formed by this system are mainly polysulfide ($-C-S_x-C-$), disulfide (-C-S-S-C-), or monosulfide (-C-S-C-). Depending on the nature of the crosslink, the rubber can have different properties. Vulcanization of natural rubber is an example of a curing process that makes rubber quite stable against microbial attack.

4.1.2 Microbial Population

A variety of microorganisms, including bacteria and fungi, may degrade polymeric materials (Albertsson 1992, Lynd et al. 2002). The growth of microorganisms depends on pH, temperature, availability of mineral nutrients, and oxygen concentrations. Humidity or water saturation is also important, because water is required for the growth of microorganisms. Bacteria are either aerobic or anaerobic and generally exhibit optimum growth in the pH range from 5 to 7. Actinobacteria are a type of bacteria that are most commonly found in soil and can thrive in low-nutrient environments. They can survive in both aerobic and anaerobic conditions, although most are aerobic. The most important role of the Actinobacteria is decomposition of organic nutrients, such as cellulose, and they are one of the few bacteria able to consume lignocellulose. Generally, Actinobacteria grow aerobically in the pH range of 5 to 7 over a wide range of temperatures.

Fungi (molds) commonly require oxygen and a pH range of 4.5 to 5 to proliferate. Fungi grow at temperatures ranging up to 45 °C, although optimum growth rates generally occur at temperatures between 30 °C and 37 °C. Because most fungi require oxygen, they may only be available at WIPP for CPR degradation before closure and for a relatively short time after repository closure. There is some evidence that anaerobic fungi may degrade lignocellulosic materials (Lynd et al. 2002, Ximenes et al. 2005), although there is no evidence that these fungi will be present in the WIPP repository. Thus, this review is focused primarily on the ability of anaerobic bacteria and anaerobic Actinobacteria to degrade polymers.

Biodegradation processes can affect polymers in a number of ways (Albertsson 1992). Microbial processes that can affect polymers include mechanical damage caused by growing cells, direct enzymatic effects leading to breakdown of the polymer structure, and secondary biochemical effects caused by excretion of substances other than enzymes that may directly affect the polymer or change environmental conditions, such as pH or redox conditions. Although microorganisms such as bacteria generally are very specific with respect to the substrate utilized for growth, many are capable of adapting to other substrates over time. Microorganisms produce enzymes that catalyze reactions by combining with a specific substrate or combination of substrates. The conformation of these enzymes determines their catalytic reactivity towards polymers. Conformational changes in these enzymes may be induced by the changes in pH, temperature, and other chemical additives. Over time, if the chemical structures of the polymers in WIPP change due to radiolytic or microbial degradation, microorganisms present in the repository would be likely to adapt by initiating the production of new enzymes capable of attacking the evolving substrates. Therefore, during the long time period relevant to WIPP, it appears likely that various enzymes may be produced by microorganisms as they adapt to the evolving chemical composition of the CPR materials. This adaptation would increase the likelihood of significant microbial degradation of CPR over the 10,000-year regulatory time period.

DNA analysis was performed on bacteria present in the WIPP cellulose degradation experiments; these bacteria were obtained from various sources representative of those at WIPP (Gillow and Francis 2003). Identified bacteria included *Halobacterium, Haloarcula*, *Halobacter*, *Natranobacterium*, *Halococcus*, *Natranomonas* and *Clostridium* (Gillow and Francis 2003). This analysis demonstrated that a diverse microbial population is likely to be present in the repository. Some of these microbes apparently are capable of at least partially consuming CPR materials (see Sections 4.2.1, 4.3.1, and 4.4.1). However, identification of bacteria in the cultures was believed to have been limited by the size of the databases used, because these databases are relatively less populated with environmentally relevant halophilic or halotolerant bacteria (Gillow and Francis 2003).

4.1.3 Repository Chemical and Physical Environment

The repository chemical and physical environment will influence CPR degradation reactions. The temperature of the repository is expected to remain within a few degrees of the ambient temperature of 28ºC (DOE 2004b, Appendix PA, Attachment SOTERM). This temperature is within the optimal growth range of many microorganisms, and repository temperature is not expected to significantly inhibit microbial activity.

Because microbial degradation of polymers requires the presence of water, the relative humidity or brine saturation in the waste will affect CPR degradation. For the PABC, brine saturation in the repository was modeled to increase rapidly during the first 100 years following closure, but brine inflow is expected to slow as pressures equalize (Leigh et al. 2005a). Anoxic corrosion is expected to consume water, and gas-generation reactions may drive brine from the waste-filled areas of the repository; both of these processes may limit brine saturation of the waste (Leigh et al. 2005a). MgO will consume water by initially reacting to form brucite, $Mg_2Cl(OH)_3 \bullet 4H_2O(s)$, or hydromagnesite (see Section 2.2, above). If these phases react to form magnesite in the long-term repository, on the other hand, this water would be released. The possible consumption of water by MgO has not been included in PA (DOE 2004b Appendix BARRIERS). Brine saturation is used in modeling CPR degradation rates in PA because of the different rates developed for inundated and humid conditions (DOE 2004b Appendix PA). The presence of brine may also contribute to radiolytic degradation of CPR (see Section 4.1.4 below). Uncertainties in the brine inflow calculations can therefore increase uncertainties in CPR degradation rates.

Microbes likely to be present in the repository appear to be capable of degrading cellulosics and rubbers in the presence of brine (see Sections 4.2.1 and 4.4.1 below), so the salinity of the repository brine is not expected to limit the potential microbial degradation of CPR. The MgO backfill is expected to buffer brine pH at a relatively basic pH of 9. This pH would not be expected to significantly inhibit microbial activity, because viable halophilic and halotolerant microbes are frequently observed in alkaline lakes and alkaline lakes near WIPP and may serve as sources of bacteria in the repository (DOE 2004b, Appendix BARRIERS).

The existence of aerobic or anaerobic conditions in the repository is potentially important, because the presence of oxygen affects the activity of the different microbes that can degrade CPR and may also affect radiolytic degradation of polymers (see Section 4.1.4). At the time of closure, a relatively small amount of oxygen is expected to remain in the repository atmosphere. It is likely that metal corrosion and aerobic microbial degradation of CPR will consume this residual oxygen shortly after closure. Consequently, it is expected that for most of the 10,000-year regulatory time period, reducing or anaerobic conditions will prevail in the repository. For both the CCA and the CRA, DOE estimated that the repository would have a reducing environment after 100 years (DOE 1996, Appendix SOTERM; DOE 2004b, Appendix PA, Attachment SOTERM).

4.1.4 Radiolysis Effects

Radiolysis of cellulosic, plastic, and rubber materials has been determined by DOE to be a relatively unimportant source of gas generation in the WIPP repository compared to microbial degradation or anoxic corrosion (DOE 2004b, Appendix PA, Attachment SCR). The effects of radiolysis of gas production were not included in the CCA and CRA determinations of gas generation rates because of the expected minor contribution to total gas. However, low-level radiolysis may indirectly affect microbial gas generation by altering the structure of polymers, making them either more or less resistant to microbial degradation. For example, both abiotic and microbial processes have been shown to contribute to the degradation of polyethylene (Albertsson 1992). It is uncertain whether the radioactivity in the waste is high enough for this to be an important process.

The interaction of radiation with polymers may produce ionization and excitation in the polymer molecules, causing reactions that lead to chemical changes (O'Donnell 1991). Scission and crosslinking of the polymer molecules, formation of gaseous molecules, and modification of the chemical structure of the polymer cause changes in the polymer's material properties and could lead to changes in biodegradation potential. Polymer degradation reactions can be influenced by the presence of oxygen, the temperature during and after irradiation, the molecular structure of the polymer, degree of polymer crystallinity, the chemical environment, and whether irradiation takes place in the presence of a gas or liquid phase (O'Donnell 1991).

Polymeric materials in the repository can be directly or indirectly affected by radiation. Direct irradiation effects occur when alpha particles, beta particles, and gamma rays from radioactive decay interact directly with the polymeric materials. Indirect irradiation effects occur when the radiation interacts with water present in the repository, producing hydrated electrons (e_{aq}^-), hydroxyl radicals ($^\bullet OH$), and hydrogen atoms ($H^\bullet$). Alpha radiolysis of brines in the repository may also produce reactive chloride species, such as hypochlorite (ClO^-), which is a strong oxidant.

Hydrated electrons and hydrogen free radicals are reducing species. The reactivity of the hydrated electron with a polymer is enhanced by electron-withdrawing substituents adjacent to double bonds or attached to aromatic rings, where bond breakage occurs very rapidly through a dissociative electron capture process:

$$e_{aq}^- + RX \rightarrow (RX)^- \rightarrow R\bullet + X^- \qquad (17)$$

where RX represents the affected polymer.

The hydroxyl radical ($^\bullet OH$) is a powerful oxidant that readily extracts H from C-H bonds. It is expected that $^\bullet OH$ radicals will be produced in WIPP through a Fenton-type reaction (Equation 18). The presence of ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2, from radiolysis of water) can easily initiate this reaction according to the following:

$$Fe^{2+} + H_2O_2 \rightarrow {}^\bullet OH + Fe^{3+} + OH^- \qquad (18)$$

The production of $^{\bullet}OH$ radicals will enhance oxidation processes of polymers in WIPP; $^{\bullet}OH$ reacts very rapidly with organic materials, producing free radicals that initiate polymer fragmentation processes.

In addition, Fe^{2+} can also react with oxidation products in the polymers, such as organic peroxides (ROOH), producing alkoxyl radicals ($RO^{\bullet}$), which are relatively strong oxidative species (Spinks and Woods 1990).

$$Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{\bullet} + OH^{-} \qquad (19)$$

Therefore, the presence of iron in the repository may lead to enhanced radiolytic degradation of CPR.

Chemical changes produced in polymers by ionizing radiation include the following (O'Donnell 1991):

- Scission of the polymer molecules leading to a decrease in molecular weight
- Crosslinking of the polymer molecules leading to an increase in molecular weight
- Changes in the molecular composition and structure of the polymer molecules, including unsaturation (C=C bonds) in PVC
- Evolution of gas molecules, such as H_2, carbon monoxide (CO), CO_2, and methane

Identification and measurement of volatile products during polymer irradiation provides valuable information about the mechanism of the radiation-induced chemical reactions.

The potential effects of radiation on the CPR materials in the WIPP repository could be estimated using the probable dose rates and cumulative doses to the waste from radionuclides in the inventory. Radiation is likely to have more effects on polymer materials in the presence of oxygen. A quantitative estimate of the length of time oxygen may persist in the repository atmosphere would be useful for predicting radiolytic degradation effects on CPR in the repository. Low concentrations of oxidants may also be available from brine radiolysis or from oxygen dissolved in the polymers (Woods and Pikaev 1994), which could affect polymer degradation.

The potential for sterilization of the waste through radiation derived from radionuclides in the inventory is not expected to have a significant effect on microbial degradation of CPR, because radiation levels are expected to be low in CH waste. The possibility of using gamma irradiation to sterilize waste was considered by DOE, but sterilization was not considered practical, because the adjacent rock in the repository could not be sterilized by irradiation (Brush 1995). Waste heterogeneity in terms of radionuclide inventory and CPR inventory would also tend to limit sterilization of the waste. For example, AMWTF wastes have relatively high CPR densities and relatively low radionuclide densities (TEA 2004). Consequently, it appears that these wastes with a high potential for microbial CO_2 production are unlikely to be sterilized by radiation. On the other hand, RH wastes have relatively high radiation levels. Even if the RH waste radiation levels are sufficient to sterilize the RH wastes, the quantities of CPR in RH waste represent only a small fraction of the total CPR inventory.

4.1.5 Degradation Process Interactions

Several degradation processes have been identified for polymeric materials that are unlikely to have significant direct effects on gas generation rates in the long-term WIPP repository. These processes include photolytic degradation, degradation of CPR by aerobic bacteria, and fungal degradation of CPR. The direct effects of these processes are likely to be limited by the physical and chemical conditions in the WIPP repository. For example, aerobic degradation of CPR is expected to be limited by the long-term anaerobic conditions in the repository. However, there is some evidence in the scientific literature that these processes could cause relatively minor surface effects on the polymers affecting long-term, anaerobic degradation rates.

A number of studies in the scientific literature have focused on the synergistic effects of photolysis or radiolysis with microbial degradation. Radiolytic and photolytic degradation of polymers occur through similar mechanisms (Schnabel 1992). Any potential photolysis of polymers in the WIPP would be limited to the relatively short time periods associated with its manufacture, storage, and use. After polymers are placed in waste containers, or after closure in the case of polymers used for waste emplacement, photolytic degradation of polymers will cease. Given the relatively small amounts of photolysis likely to take place in the waste or waste emplacement materials, it is reasonable to expect that radiolysis effects will be of greater potential importance than photolysis to the long-term degradation of CPR in the repository.

Aerobic or fungal degradation of CPR may occur during storage of waste prior to its emplacement and during the period before and shortly after repository closure. During this time period when oxygen is present, both microbial degradation and radiolysis could affect the polymer material properties. These changes in polymer properties, in turn, could affect the longer-term anaerobic biodegradability of the polymers. Consequently, the possible long-term effects of the interactions of radiolysis and aerobic microbial degradation on long-term CPR degradation should be considered.

4.2 CELLULOSICS DEGRADATION

Cellulosic material in the WIPP inventory was defined in the CRA (DOE 2004b, Appendix DATA, Attachment F) as including the following:

> *… those materials generally derived from high polymer plant carbohydrates. Examples are paper, cardboard, kimwipes, wood, cellophane, cloth, etc.*

Recent estimates of the density and total mass of cellulosics in the WIPP inventory are listed in Table 4-1. Assuming that the formula for cellulosics in the repository can be approximated by $C_6H_{10}O_5$, the chemical formula for cellulose monomer, cellulosic materials contribute approximately 32% of CPR carbon in the repository. Therefore, the extent of biodegradation of cellulosics could be significant for calculating the required amounts of MgO backfill, because cellulosics contain a significant fraction of the carbon in the repository that could be converted to CO_2.

Cellulose undergoes enzymatic and acidic degradation. To utilize cellulose, microorganisms produce hydrolyzing enzymes called cellulases (Lynd et al. 2002). Cellulase enzymes needed to metabolize cellulose are produced by aerobic saprophytes, anaerobic rumen bacteria, and anaerobic thermophilic spore formers. Enzyme systems produced by bacteria often are also capable of metabolizing hemicellulose. Lignin is more recalcitrant and is usually not as easily degraded by bacteria (Lynd et al. 2002). However, lignin can be utilized by some microbes (Benner et al. 1984).

Experimental data related to microbial degradation of cellulosics have been obtained by the WIPP program using an inoculum that simulated various sources of microorganisms that could enter the repository (Gillow and Francis 2003). Relevant data are also available from the scientific literature on microbial and radiation-induced degradation of cellulose. A brief summary of these data is provided below.

4.2.1 Waste Isolation Pilot Plant Data

Experiments with cellulosic materials (filter paper, paper towels, and laboratory wipes) were carried out under humid conditions and under inundated conditions with a natural brine sample (G-Seep brine) from the repository. A mixed inoculum was prepared from a variety of samples selected to simulate various sources of microorganisms that could enter the WIPP, and this inoculum was used in most of the experiments. Some samples were amended with nutrients, using a pH 7 stock solution that contained ammonium nitrate, potassium phosphate, and yeast extract. Bentonite was used in some experiments, because bentonite was a potential backfill material at the time the experiments began. Experiments were not carried out with MgO, because MgO backfill was included in the repository design at a later time.

Analyses carried out for the experiments included total gas production, CO_2 production, and methane production. Results from the inundated experiments with cellulose indicated that total gas production, as well as carbon dioxide production, occurred in nearly all experiments (Gillow and Francis 2003). Gas production was observed in initially aerobic, unamended with nutrients, uninoculated samples, which indicated that the microbial population naturally present in G-Seep brine could metabolize organic carbon. The only experiments in which gas production and carbon dioxide production were not observed were those that were initially anaerobic, unamended with nutrients, uninoculated, and without bentonite (Gillow and Francis 2003). Some methane production was observed in the inundated experiments with cellulosics, although the rate of carbon dioxide generation was higher than the rate of methane production. Experiments conducted under humid conditions indicated that microorganisms in the inoculum biodegraded cellulose. The presence of bentonite enhanced gas production under humid conditions, and methane was detected only when bentonite was present (Gillow and Francis 2003).

The WIPP experiments with cellulosic materials indicate that bacteria likely to be present in the repository are capable of degrading cellulose and producing CO_2 under inundated and humid conditions. After initially rapid rates of CO_2 production, slower rates were observed in the experiments. These experiments, while applicable to WIPP repository conditions, have some limitations. These experiments did not contain excess sulfate, which is likely to be available from anhydrite in the Salado Formation. In addition, bentonite was used instead of MgO to simulate the effects of backfill on the biodegradation reactions. The possible effects of low levels of radiation expected in the repository on the structure and ultimate degradation of cellulosics also were not addressed by the WIPP experiments.

4.2.2 Relevant Literature Data

Extensive research has been performed on cellulolytic microorganisms, focusing on their ability to produce cellulases that catalyze the hydrolysis of cellulose (Klyosov 1990, Lednicka et al. 2000, Amano and Kanda 2002, Zhang and Lynd 2005). Biodegradation of cellulose occurs in both aerobic and anaerobic conditions with the eubacterial orders *Actinomycetales* and *Clostridiales*, respectively, and also amongst a broad range of fungi (Amano and Kanda 2002, Burrell et al. 2004). A few examples of cellulolytic aerobic bacteria that have been studied are *A. cellulolyticus, B. pumilis, S. reticuli*, and *C. hutchinsonii* (Amano and Kanda 2002, An et al. 2005). Cellulolytic anaerobic bacteria include, but are not limited to, *D. thermophilum, B. fibrisolvens,* and *E. cellulosolvens* (Petitdemange et al. 1984, Desvaux et al. 2000, Amano and Kanda 2002, Barnes and Keller 2004, O'Sullivan et al. 2005, Syutsubo et al. 2005). The mechanisms of cellulose degradation are different for aerobes and anaerobes, with aerobes typically excreting large quantities of cellulases extracellularly and anaerobes requiring attachment to the cellulosics due to much smaller amounts of secreted enzymes (Amano and Kanda 2002). It has been reported that customized bacterial communities containing multiple strains can successfully degrade cellulose in many environments, including a wide range of pH and temperature conditions (Johnson et al. 1985, Lamed et al. 1985, Kato et al. 2004, Kato et al. 2005, Niu et al. 2005, Patel et al. 2005, Patel et al. 2006).

The three main types of enzymes that act on cellulose are endo-type cellulase, exo-type cellulase, and β-glucosidase. The endocellulases attack the cellulose chain at random, creating cellobiose and glucose. On the other hand, the exocellulases digest polymers at the non-reducing end to produce cellobiose and cellotriose (Klyosov 1990, Amano and Kanda 2002). The methods of enzymatic degradation are quite complex and often each organism produces a number of enzymes that work in synergy. Experimentally observed end products of aerobic degradation are typically acetic acid and CO_2 that form from glucose, while the end products of anaerobic degradation are ethanol, acetic acid, formic acid, lactic acid, H_2, and CO_2 (Klyosov 1990, Amano and Kanda 2002). Short-chain organic compounds, such as acetic acid, are in turn likely to be degraded further to form CO_2. Sulfur has a profound impact on cellulose degradation and methanogenesis, with a complete lack of sulfur inhibiting both processes and large quantities of sulfur limiting methanogenesis (Khan and Trottier 1978). Kim et al. (1997) investigated the degradation of cellulose and lignocellulose materials under sulfate-reducing and methanogenic conditions. In the presence of excess sulfate ion and sulfate-reducing bacteria, this study demonstrated that sulfate-reducing bacteria outcompeted the methanogens, and the rates and percentages of organic carbon biodegradation were higher than under methanogenic conditions.

Most studies of the effects of radiation on cellulosic materials have considered physical effects rather than chemical changes induced in the materials. In general, the predominant reaction of cellulosic polymers upon radiation is main-chain scission. The scission is a direct consequence of interactions of gamma photons and electrons with the polymers leading to the breakage in the polymer backbone (Farhataziz and Rodgers 1987, Tabata et al. 1991). The irradiation of cellulose predominantly causes degradation by splitting of the glycosidic bond (Farhataziz and Rodgers 1987). The mechanisms of the cleavage of the glycosidic bond do not involve oxygen. In fact, it has been found in biological systems that the presence of oxygen limits the radical-induced scission of glycosidic bonds (von Sonntag 1987). The chemical yield of main-chain scission of cellulose irradiated with low linear energy transfer (LET) radiation (low-energy beta and gamma radiation) at room temperature and in the absence of oxygen is 3.3–6.8 (number of broken main-chain bonds per 100 eV) (Schnabel 1978). The degradation happens randomly, in both the crystalline and amorphous regions of cellulose, and the ultimate product is a powdery material (Charlesby 1955, Saeman et al. 1952). Both the degree of crystallinity and the average size of the crystallites of cellulose decrease with increasing gamma radiation (Kasprzyk et al. 2004). The changing crystallinity influences the elasticity, absorptive capacity, and other physical properties of cellulose (Bhuiyan et al. 2001).

There is some evidence that radiolysis of cellulose may decrease its ability to be microbially degraded. For example, there is some evidence of the occurrence of branching in irradiated cellulose, as shown by light scattering and viscosity studies on irradiated dextran (Price et al. 1954). The formation of reducing groups, such as reducing sugars (e.g., glucose) in the case of cellulose, with increasing dose indicates depolymerization of the fundamental glucose chain. At a dose of $\sim 2.9 \times 10^6$ Gy (290 Mrad),[4] where the cellulose becomes completely soluble and where the production of fermentation acids starts to decrease, it can be estimated that the minimum chain length is approximately six $C_6H_{10}O_5$ units. In the case of wood at this relatively high dose, although cellulose is completely vulnerable to attack by the bacteria, it must be assumed that it is no longer in a form that can readily be fermented. A reduction in particle size to the order of cellular dimensions (up to 6 microns), where a larger fraction of the cellulose should be exposed to bacterial fermentation, did not significantly increase the bacterial attack on the unirradiated wood. This suggests that the relative indigestibility of the cellulose in the untreated wood is not due to an encrusting layer of lignin (Lawton et al. 1951). For starch, the formation of reducing groups seems to be unaffected by the moisture content of the specimen, even though degradation is less in the samples with the higher moisture content (Ehrenberg et al. 1957). Although there is some evidence that radiation-induced effects could limit cellulose biodegradation, the overall effects of radiation on cellulose appear to enhance its microbial degradation.

4.2.3 Conclusions Regarding Cellulose Degradation

A number of factors contribute to the high likelihood that cellulosics will be completely degraded in the WIPP repository. These factors include the variety of microorganisms that can degrade cellulosic materials, the general adaptability of microbes to their environment and

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[4] This dose is smaller than the "low-dose" irradiation used to evaluate the effects of radiation on microbial degradation of plastics and rubber by Gillow and Francis (2003), as described in Sections 4.3.1 and 4.4.1 of the present report.

available carbon sources, the abundant sulfate in the repository, and the long regulatory time period.

Although relatively little data appear to be available regarding the chemical effects of radiation on cellulose, it appears low-level radiation may decrease polymer chain length and alter physical and chemical properties of cellulose. It is expected that radiation-induced degradation of cellulose in the WIPP will occur through direct and indirect interaction with ionizing radiation from radionuclides in the waste. The direct interactions, which are interactions of the ionizing radiation with the solid cellulose, initiate scissions on the backbone of the molecules leading to degradation; however, a very small yield of branching also can occur. The presence of oxygen in the repository environment is not required for these scission reactions. Indirect interactions will occur through the radiolysis of water. As mentioned above in Section 4.1.4, the radiolysis of water produces hydroxyl radicals ($^{\bullet}OH$). Hydroxyl radicals can cause hydrolytic cleavage of glycoside linkages in cellulose, which would be expected to facilitate microbial degradation.

Although some radiation-induced effects could act to limit cellulose biodegradation, on balance, the overall effects of radiation on cellulose appear to increase the likelihood of microbial degradation of cellulose through cleavage of the polymer backbone and decreased molecular weight. The available literature appears to indicate that microbial and radiation-induced degradation of cellulosics may proceed virtually to completion over 10,000 years if water is present in the WIPP repository.

4.3 PLASTICS DEGRADATION

Plastics in the WIPP inventory were defined in the CRA (DOE 2004b, Appendix DATA, Attachment F) as including the following:

> *... generally manmade materials, often derived from petroleum feedstock. Examples are polyethylene, polyvinylchloride, Lucite®, Teflon®, etc.*

Recent estimates of the density and total mass of plastics in the WIPP inventory are listed in Table 4-1. Assuming that the plastics are composed of 80% polyethylene and 20% PVC (Wang and Brush 1996), plastics would contribute approximately 61% of the CPR carbon in the repository that could be converted to CO_2 by biodegradation. Therefore, the extent of plastics biodegradation could have an important effect on required amounts of MgO, because a large fraction of the carbon in the repository is contained in plastics.

For the enzymatic degradation of synthetic plastic polymers, it may be assumed that polymers containing hydrolysable groups in the polymer backbone would be especially prone to microbial attack, because many microorganisms are capable of producing hydrolases (enzymes catalyzing hydrolysis). In general, aliphatic polyesters, polyurethane, polyethers, and polyimides are more easily degraded by commonly occurring microorganisms. Generally, higher molecular weight polymers and branched polymers are more resistant to microbial degradation. Polyethylene and PVC are considered to be relatively resistant to microbial degradation. However, some bacterial strains have been identified that can degrade polyethylene, including *Rhodococcus rubber* and *B. borstelensis* (Hadad et al. 2005).

The ability of microorganisms to adapt to a new source of nutrients is highly noteworthy in any evaluation of the microbial degradation of plastic materials. Evidence of adaptation of bacteria for the degradation of plastics has been shown in several cases. For example, it was found that *Pseudomonas aeruginoa* started proliferation 56 days after the bacteria were brought into contact with polyamide-6 polymer (Gumargalieva and Zaikov 1998). Inoculation of previously untreated polyamide with these bacteria resulted in immediate growth on the new substrate. Because of the 10,000 year repository performance period, the adaptability of microbes increases the uncertainty associated with estimating the likely reaction mechanisms and potential extent of plastic degradation.

4.3.1 Waste Isolation Pilot Plant Data

Both unirradiated and electron-beam irradiated plastics (polyethylene and PVC) were tested to determine the rate and extent of gas generation caused by microbial degradation (Gillow and Francis 2003). The irradiated plastics received an absorbed dose of either 5×10^6 Gy to 7×10^6 Gy (500 to 700 Mrad, low dose) or 4×10^7 Gy to 6×10^7 Gy (4,000 to 6,000 Mrad, high dose). Each sample bottle contained a piece of polymer and a mixture of G-Seep Brine, WIPP muck-pile salt slurry, and surficial lake brine/sediment slurry and mixed inoculum. Some samples were amended with nutrients, using a pH 7 stock solution that contained ammonium nitrate, potassium phosphate, and yeast extract. Control samples without polymer and with and without nutrients were also prepared.

Total gas production in most samples with polyethylene, including both irradiated and unirradiated samples, was only slightly higher than in control samples, which Gillow and Francis (2003) attributed to the use of polyethylene as a substrate for more effective utilization of dissolved organic carbon and trace nutrients in the inoculum, rather than to degradation of the polyethylene. Irradiated PVC generally had an inhibitory effect on total gas production. Based on the results of the experiments, Gillow and Francis (2003) concluded that there was little overall evidence for biodegradation of polyethylene or PVC in the experiments after 7 to 8 years of testing. There was no evidence of methanogenesis caused by biodegradation of the polyethylene or PVC (Gillow and Francis 2003).

The possible effects of radiolysis on PVC and polyethylene have been evaluated for the WIPP program. Molecke (1979) summarized gas generation experiments that included an evaluation of radiolysis of PVC and polyethylene. The reported results indicated that gas generation occurred as the result of radiolysis, but the overall rates of gas generation were determined to be relatively unimportant compared to microbial degradation and corrosion processes. Reed and Molecke (1993) and Reed et al. (1997) reported results from alpha radiation experiments with PVC and polyethylene. Reed and Molecke (1993) reported that PVC and polyethylene evolved hydrogen, CO_2, and low-molecular weight volatile organic compounds (VOCs) as a result of absorbed surface-layer doses from alpha radiation of 1.1×10^5 to 1.2×10^5 Gy (11–12 Mrads) during 8-week experiments. Irradiation of PVC also resulted in the production of hydrochloric acid (HCl). Different yields and VOC products were observed, depending on whether irradiation was carried out in air or in a nitrogen atmosphere.

The experiments described by Reed et al. (1997) were carried out to determine gas generation rates and processes in drums that were sealed for transport. Therefore, the atmosphere used in the experiments initially contained oxygen, to simulate the drum atmosphere immediately after it was sealed for transport. Oxygen in the experiments was consumed by reaction with the polyethylene or PVC solids, as well as by production of CO_2. Compared to irradiation of PVC, polyethylene had a higher yield of hydrogen and CO_2, with higher oxygen depletion. PVC irradiation resulted in a higher net production of VOCs, and the plasticizer present in different PVC samples appeared to affect the radiolysis yields.

4.3.2 Relevant Literature Data

A preliminary survey of the literature indicated that data potentially relevant to the effects of radiation and biodegradation on plastics are available from outside the WIPP program. The focus of this literature survey was on PVC and polyethylene degradation, because these plastics are expected to make up the majority of the plastics in WIPP waste and the WIPP waste emplacement materials.

Although polyethylene has historically been classified as a non-biodegradable plastic, recent studies have shown that oxidation of the polymer surface makes polyethylene more amenable to microbial degradation by increasing its hydrophilicity, allowing synergy between the abiotic and biotic stages (Albertsson and Hakkarainen 2004, Bonhomme et al. 2003). Surface oxidation of polyethylene and smaller polymer chains may occur in WIPP because of radiolysis; oxidizing the polyethylene surface may allow the attachment of microorganisms to the surface (Albertsson 1998). The formation of a biofilm on the surface of polyethylene is integral to its biodegradation (Gilan et al. 2004). Studies have shown that while longer-chain-length polyethylene is seemingly resistant to degradation, shorter-chain-length samples can be slowly degraded into CO_2 (Potts 1978, Zheng et al. 2005). *Brevibaccillus borstelensis* and *Rhodococcus ruber* have been shown to degrade the CH_2 backbone and use polyethylene as its sole carbon source due to the hydrophobic nature of the cell membranes (Hadad et al. 2005, Sivan et al. 2006). When combined with carbonyl formation on the surface, *Pseudomonas aeroginosa, Aspergillus fumigatus,* and other microorganisms have shown an ability to degrade polyethylene (Albertsson 1978, Bonhomme et al. 2003, Agamuthu and Faizura 2005).

Despite being one of the most commercially important plastics, the biodegradation of PVC has only recently been studied under limited conditions. It has been reported in a few studies that PVC is largely considered a non-degradable plastic, especially under landfill conditions (Schnabel 1992, Mersiowsky et al. 2001). Recently, however, a study has shown the biodegradation of PVC by white rot fungi under aerobic conditions. PVC of lower chain length was exposed to the fungi under optimal growing conditions and significant decay of the plastic was observed (Kirbas et al. 1999). No literature data were identified related to PVC biodegradation under anaerobic conditions.

Ionizing radiation-induced effects on PVC have been studied extensively. A number of studies have been carried out to evaluate radiation degradation of PVC as a function of dose rate in the presence of air (Clough and Gillen 1981, Wilski 1984). It has been noted that PVC properties begin to change at radiation levels of approximately 2×10^5 Gy (20 Mrad, Kircher and Browman 1964), and significant damage is observed at an absorbed dose of approximately 1×10^6 Gy (100 Mrad); these doses are less than the “low-dose” treatment used by Gillow and Francis

(2003) in their investigations for WIPP (see Section 4.3.1, above). The dehydrochlorination of PVC (production of HCl) has been reported as a function of temperature and radiation dose (Clegg and Collyer 1991, Kircher and Browman 1964, Salovey 1973, Woods and Pikaev 1994, Zahran et al. 1985). It has been observed that dehydrochlorination is a major reaction in the presence of nitrogen (under anaerobic conditions), and more dechlorination was observed during radiation under anaerobic conditions than under aerobic conditions (Miller 1959). When PVC is irradiated at very high doses (20 MGy), a material is formed that appears to have a structure that is mainly composed of carbon and in some cases is crystalline in nature (Adem et al. 1992, Cota et al. 1994). Although these very high doses are unlikely to be observed in the WIPP waste, the overall effect of radiation is expected to be some level of PVC dechlorination, which may enhance its ability to be biodegraded.

Among the various polymers, radiolysis of polyethylene is probably the most widely studied (Mark 1996). When irradiation is carried out on polyethylene at room temperature, no obvious changes in polymer behavior are seen until very high doses are reached, on the order of 10 MGy (Ahmad and Charlesby 1976, Charlesby and Callaghan 1958, Farhataziz and Rodgers 1987). In the presence of oxygen, polyethylene generates a number of products on radiation-induced oxidation, including carbonyl compounds, peroxides, possibly alcohols, and carbonyl compounds; the carbonyl compounds include both aldehydes and ketones (Dole 1973). The oxidation process may involve oxygen already present (i.e., dissolved) in polyethylene, or oxygen that diffuses into the polyethylene during or after irradiation. Oxidation may occur during irradiation or in post-irradiation processes (Woods and Pikaev 1994). Post-irradiation oxidation of polyethylene occurs via macroradicals trapped in the crystalline regions of the polymer; radicals in the amorphous regions react rapidly with the oxygen that diffuses relatively easily into these sections of polyethylene. Radicals in the crystalline regions slowly diffuse to the surface of the crystallites, where they react with oxygen (Dunn et al. 1979, Seguchi et al. 1981). Gaseous products formed by irradiation of polyethylene include a relatively high yield of hydrogen gas, and smaller amounts of methane and CO_2 (Chappas and Silverman 1980, Mandelkern 1973, Spinks and Woods 1990). In the absence of oxygen, polyethylene undergoes cross-linking reactions upon irradiation. Usually, radiation-induced cross-linking reactions of polyethylene are associated with high yields of hydrogen gas production (Lyons 1965, Lyons 1983).

4.3.3 Conclusions on Plastics Degradation

Literature data are available regarding both microbial degradation and radiation-induced degradation of plastics such as polyethylene and PVC. Microbial degradation of plastics generally is less extensive in the short term than microbial degradation of cellulosic materials, based on the data identified in the literature. Radiolytic processes may degrade plastics directly, and also may indirectly contribute to the long-term biodegradability of plastics by altering their chemical and physical properties. The likelihood of significant radiolytic effects on plastics degradation would depend on the dose. The dose to WIPP waste can be calculated from the DOE's inventory projections (Leigh and Trone 2005). The presence of oxygen in the repository before closure and for a period of time after closure could affect both radiolytic and microbial processes. This preliminary evaluation of the data indicates that plastic degradation may occur over 10,000 years in the WIPP repository.

4.4 RUBBER DEGRADATION

Rubber materials in the WIPP inventory were defined in the CRA (DOE 2004b, Appendix DATA, Attachment F) as including the following:

> *… natural or manmade elastic latex materials. Examples are Hypalon®, neoprene, surgeons' gloves, leaded-rubber gloves (rubber part only), etc.*

Recent estimates of the density and total mass of rubber in the WIPP inventory are listed in Table 4-1. Assuming that rubber materials in the repository are composed of 50% neoprene and 50% Hypalon® (Wang and Brush 1996), rubber would contribute approximately 7% of the carbon in the CPR that could be converted to CO_2 by biodegradation. Consequently, the extent of biodegradation of rubber in the WIPP environment is likely to be less important than cellulosics and plastics for determining the required amounts of MgO backfill.

Studies of microbial degradation of natural and synthetic rubber are impeded by the slow growth of microbes that use rubber as a sole carbon source (Rose and Steinbüchel 2005). In addition, additives in rubber may promote or inhibit biodegradation. However, bacteria and fungi have been identified that can biodegrade synthetic and natural rubber (Rose and Steinbüchel 2005).

4.4.1 Waste Isolation Pilot Plant Data

Both unirradiated and electron-beam irradiated rubber materials were tested to determine the rate and extent of gas generation caused by microbial degradation. The rubber materials used in the experiments were neoprene, leaded Hypalon®, and unleaded Hypalon®. The irradiated neoprene received an absorbed dose of either 5×10^6 Gy to 7×10^6 Gy (500 to 700 Mrad, low dose) or 4×10^7 Gy to 6×10^7 Gy (4,000 to 6,000 Mrad, high dose). Only unirradiated and low-dose irradiated Hypalon® samples were tested, because high-dose irradiation of the leaded sample caused extensive melting (Gillow and Francis 2003). Each sample bottle contained a piece of polymer and a mixture of G-Seep Brine, WIPP muck-pile salt slurry, surficial lake brine/sediment slurry, and mixed inoculum. Some samples were amended with nutrients, using a pH 7 stock solution that contained ammonium nitrate, potassium phosphate, and yeast extract. Control samples without polymer and with and without nutrients were also prepared (Gillow and Francis 2003).

Total gas and carbon dioxide production data indicated long-term degradation of unirradiated and irradiated neoprene, unleaded Hypalon®, and leaded Hypalon® in both initially aerobic and anaerobic experiments (Gillow and Francis 2003). Irradiation of neoprene and Hypalon® appeared to enhance CO_2 production. There was no evidence of methanogenesis caused by biodegradation of the rubber materials after 7 to 8 years of testing (Gillow and Francis 2003).

Reed and Molecke (1993) reported that neoprene and Hypalon® evolved hydrogen, CO_2, and low-molecular weight VOCs as a result of absorbed surface-layer doses from alpha radiation of 1.1×10^5 to 1.2×10^5 Gy (11–12 Mrads) during 8-week experiments. For neoprene, hydrogen and CO_2 yields were higher in air than in a nitrogen atmosphere; however, for Hypalon®, the CO_2 yield was slightly higher in nitrogen than in air.

4.4.2 Relevant Literature Data

Microbial degradation of natural rubber has been studied for many years. Bacteria and fungi are capable of degrading rubber. Rubber-degrading bacteria are usually divided into two groups according to their growth type and other characteristics (Rose and Steinbüchel 2005). Representatives of the first group belong to the Actinomycetes that form clear zones on latex plates and metabolize polyisoprene by secretion of one or more enzymes. Most of the representatives of this group show weak growth on natural rubber and synthetic rubber. The second group does not grow on latex plates and requires direct contact with a polymer. However, they have shown relatively strong growth on polyisoprene. These bacteria belong to the *Corynebacterium-Noccardia-Mycobacterium* group (Rose and Steinbüchel 2005). Although the degradation mechanisms for both groups have not been completely characterized, it has been reported that both natural and synthetic rubber are degraded by all strains via an oxidative cleavage of the polyisoprene molecule at the double bond position (Bode et al. 2001, Enoki et al. 2003). In addition, most degradation products contain aldehyde and keto groups that result from endo-type cleavage of the rubber, in which the polymer chains are cleaved somewhere within the chain (Bode et al. 2001, Rose et al. 2005).

Extensive studies have been performed related to various strains of rubber-degrading bacteria, including *Streptomyces coelicolor, Thermomonospora curvata*, *Streptomyces* sp. strain K30, and *Gordonia polyisprenivorans* strain VH2 (Rook 1955, Tsuchii et al. 1985, Tsuchii and Takeda 1990, Heisey and Papadatos 1995, Jendrossek et al. 1997, Gallert 2000, Bode et al. 2001, Rose and Steinbüchel 2005, Rose et al. 2005). While a majority of these bacteria are present in aerobic conditions and would be active within WIPP only until oxygen is consumed in the repository following closure, some anaerobic microbes have been reported that could continue rubber biodegradation after this initial period (Bode et al. 2001). Expected yields of CO_2 based on weight loss throughout the biodegradation process have been reported; however, CO_2 yield has not been determined by direct measurement (Bode et al. 2001).

Literature data indicate that the mechanism of rubber decomposition by ionizing radiation strongly depends on whether oxygen is present. Therefore, radiation-induced degradation of rubber in the WIPP is likely to proceed via different mechanisms during the initial oxic period and during the later anoxic period. The effects of radiation on various rubbers have been studied for many years (Bohm and Tveekrem 1982, Hagiwara and Kagiya 1983). However, much of the data focus on the physical properties of the rubber and not on chemical changes. The deteriorating effects of radiation are similar and complementary to those of aging and depend on absorbed dose. The effects also depend on dose rate if significant other agents capable of degrading rubber, such as oxygen, are present in the system (Harper 1992). All vulcanized rubbers deteriorate under prolonged exposure to radiation, mostly by hardening; however, butyl rubber and polysulfide rubber soften, eventually resulting in a tarry residue (Blow and Hepburn 1982). The rubbers most resistant to irradiation are natural, styrene butadiene, and polyacrylate elastomers, and the least resistant are silicone-, fluorosilicone-, and fluorocarbon-rubbers (Blow and Hepburn 1982, Kircher and Bowman 1964). The majority of rubbers are degraded either by radiation oxidation or by removal of some volatile products (Scott 1990, Zaharescu et al. 1996).

It has been reported that when oxygen is present, gamma-radiation-induced oxidation of ethylene propylene diene (EPDM) and ethylene propylene rubber (EPR) will occur, with high radiochemical yield occurring at the double bond of the diene (Rivaton et al. 2005). Although these particular rubber materials may not be present in the repository, degradation mechanisms and products are likely to be similar for WIPP rubber materials. The oxidation products are hydroperoxides, ketones, carboxylic acids, alcohols, peracids, and peroxides. In the absence of oxygen, after the closure of WIPP, one would expect that radiation will induce the formation of hydrogen gas and crosslinking in the rubber (Zaharescu et al. 2001, Sen et al. 2003, Rivaton et al. 2004).

4.4.3 Conclusions Regarding Rubber Degradation

Available WIPP and literature data indicate that rubber materials likely to be present in the WIPP repository will be partially degraded by microbes. Radiation appears to affect both the physical and chemical properties of rubber, and in WIPP experiments appeared to enhance microbial degradation. The presence of oxygen in the repository before closure and immediately after closure could affect the physical and chemical properties of the rubber. This preliminary evaluation of the data indicates that rubber degradation may occur over 10,000 years in the WIPP repository.

4.5 MAGNESIUM OXIDE HYDRATION AND CARBONATION REACTIONS

DOE carried out laboratory experiments to evaluate the hydration and carbonation of MgO in the WIPP repository (Bryan and Snider 2001a; Bryan and Snider 2001b; Snider 2001; Zhang et al. 2001; Snider 2002; Snider and Xiong 2002; Snider 2003; Xiong and Snider 2003). These experiments were previously reviewed in detail (EPA 2006c). The experiments indicated that MgO in the WIPP backfill is expected to react in humid conditions and under inundated conditions with ERDA-6 brine to form brucite, which will buffer brine pH at values likely to limit actinide and uranium solubilities.

Under inundated conditions with GWB brine, MgO was found to form $Mg_2Cl(OH)_3 \bullet 4H_2O(s)$. In the experiments, formation of brucite and $Mg_2Cl(OH)_3 \bullet 4H_2O(s)$ from the MgO occurred relatively rapidly. Long-term experiments with GWB indicated that $Mg_2Cl(OH)_3 \bullet 4H_2O(s)$ may be replaced by brucite. Either $Mg_2Cl(OH)_3 \bullet 4H_2O(s)$ or brucite are expected to buffer pH at values consistent with lower actinide and uranium solubilities.

Inundated experiments at atmospheric CO_2 concentrations showed that brucite reacted to form the metastable magnesium-carbonate phase hydromagnesite. Hydromagnesite formation was observed in the experiments after less than 1 year of reaction, although complete conversion of brucite to hydromagnesite was not observed. No evidence of magnesite formation was observed. Nesquehonite formation was observed in some experiments carried out at relatively high CO_2 partial pressures, but the nesquehonite converted to hydromagnesite within days to weeks. DOE compared the rates of CO_2 consumption in experiments carried out at room temperature and atmospheric CO_2 partial pressure to the predicted rate of CO_2 production by microbial degradation of CPR. Based on this analysis, it appeared that CO_2 consumption rates are likely to exceed CO_2 production rates by several orders of magnitude. Therefore, it was concluded that the MgO backfill should effectively limit CO_2 partial pressures in the repository (Xiong and Snider 2003).

During their review of the CCA, EPA considered the reactivity of the MgO backfill and its ability to control pH and CO_2 concentrations in brine. For this assessment, EPA (1998) reviewed information about magnesium carbonate mineral formation that included experimental data from outside the WIPP program. Davies and Bubela (1973) and Davies et al. (1977) carried out experiments in magnesium carbonate solutions and observed the relatively rapid conversion of nesquehonite to hydromagnesite through intermediate phases [e.g., protohydromagnesite, $(MgCO_3)_4 \bullet Mg(OH)_2 \bullet 4H_2O$]. EPA (1998) noted that higher-temperature rate data for the formation of magnesite (Usdowski 1994, Sayles and Fife 1973) were used by DOE to estimate that the time required for magnesite formation would be a few hundred years, based on extrapolation of an Arrhenius plot. Therefore, experimental data from outside the WIPP program indicates that hydromagnesite will form relatively rapidly in the WIPP repository, with much slower formation of magnesite.

EPA (1998) also reviewed information about natural occurrences of magnesium carbonate minerals. Field observations of carbonate mineral occurrences in recent sediments have been used to infer periods of a few hundred to a few thousand years for magnesite formation (Graf et al. 1961, Irion and Müller 1968), which is consistent with the experimental data evaluated by EPA (1998). Natural occurrences of hydromagnesite and magnesite are typically found in saline environments and are more common than nesquehonite (Irion and Muller 1968, Renaut and Long 1989, Stamatakis 1995). An example of the natural occurrence of magnesium carbonates is provided by Stamatakis (1995), who described a Quaternary age deposit of hydromagnesite, magnesite, dolomite [$CaMg(CO_3)_2$], and huntite [$Mg_3Ca(CO_3)_4$] in northern Greece.

In summary, experiments carried out as part of the WIPP program, experiments from outside the WIPP program, and natural occurrences of magnesium carbonate minerals indicate that brucite and hydromagnesite are likely to readily form in the WIPP repository and control brine pH and CO_2 concentrations. Magnesite formation could take place over a time scale of hundreds to thousands of years. As a consequence of the formation of brucite, hydromagnesite, and possibly magnesite, actinide, and uranium solubilities in WIPP brines will be limited to concentrations lower than would be expected in the absence of MgO backfill (EPA 1998).

Table 4-1. Inventory Estimates of Cellulosic, Plastic, and Rubber Materials[1]

Waste Material	CH Waste and Packaging Density (kg/m^3)	RH Waste and Packaging Density (kg/m^3)	Waste Emplacement Materials (kg)	Total Mass[2] (kg)	Carbon (moles)[3]
Cellulosics	60	9.3	2.07 × 10^5	1.04 × 10^7	3.84 × 10^8 (32%)
Plastics	60	11.1	1.48 × 10^6	1.17 × 10^7	7.40 × 10^8 (61%)
Rubber	13	6.7	0	2.24 × 10^6	8.28 × 10^7 (7%)

[1] - Waste densities, packaging densities, and amounts of waste emplacement materials obtained from Leigh et al. (2005b).

[2] - Mass estimated based on the CH volume limit of 168,485 m^3 and the RH volume limit of 7,079 m^3.

[3] - Plastics were assumed to be 80% polyethylene and 20% polyvinylchloride; rubber was assumed to be 50% Hypalon® and 50% neoprene. Formulas, molecular weights and assumptions regarding proportions of materials that make up the plastic and rubber inventories were taken from Wang and Brush (1996).

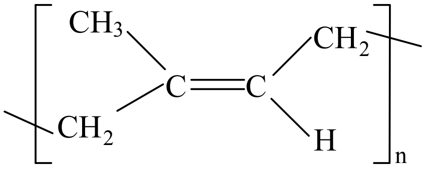

Figure 4-1. Structure of Polyisoprene

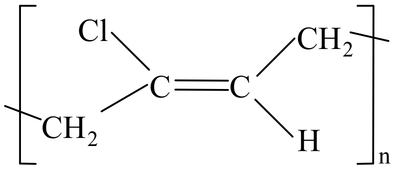

Figure 4-2. Structure of Neoprene [poly(2-chloro-trans-2-butene)]

5.0 EFFECTS OF CHANGES IN BIODEGRADATION AND OTHER REACTIONS ON SAFETY FACTOR CALCULATIONS

The MgO safety factor is currently calculated assuming that all CPR carbon could be converted to CO_2. Assuming incomplete reaction for CPR would increase the safety factor for a fixed amount of MgO. The assumption that either cellulosics or plastic materials can be only partially degraded to form CO_2 or would not degrade at all could have significant effects on the safety factor, because these waste materials represent a combined 93% of the current estimates of CPR carbon in the inventory (Table 4-1). The assumption that rubber materials will not completely degrade would have less effect on the safety factor calculations, because rubber constitutes only an estimated 7% of carbon in the CPR inventory.

Some conservative assumptions related to CO_2 consumption were included in calculating the MgO safety factor. It was assumed that CO_2 would not react with H_2 to form methane, and that significant amounts of CO_2 would not be removed from the gas phase by reaction to form $FeCO_3(s)$. If, in fact, significant amounts of CO_2 were consumed by these reactions, the safety factor would be higher than the calculated value for the same amount of emplaced MgO. However, because little information is available regarding the rates and likely extents of these reactions, the effects of these assumptions on the conservatism of the MgO safety factor cannot be determined at this time. DOE apparently plans an experimental investigation of CO_2 consumption in the WIPP repository by the corrosion of lead and iron alloys and formation of carbonate phases (Wall and Enos 2006). These experiments may provide data regarding the potential importance of the formation of iron and lead carbonate phases to safety factor calculations. Review of the available information related to MgO reactivity indicates that MgO is likely to react in the repository to control CO_2 concentrations in the brine. However, it is possible that a small fraction of the MgO could become unavailable for reaction because of physical segregation. This relatively small source of uncertainty has been adequately accounted for by using an MgO safety factor greater than one.

In the original certification review (EPA 1997), EPA accepted MgO as the only engineered barrier (40 CFR 194.44). This acceptance was predicated on the assumption that MgO was necessary to control chemical conditions in disposal rooms. EPA (1997) also stated that excess MgO, i.e., the MgO safety factor, was a conservative measure, an assurance requirement, necessary to overcome the uncertainty associated with predicting the expected future(s) of the WIPP disposal system. The engineered barrier is of critical importance because of a number of uncertainties associated with repository performance over the long regulatory time period. Assuming that all CPR carbon could be converted to CO_2 was a conservative assumption associated with the engineered barrier's performance. If this conservative assumption is no longer included in the determination of the MgO safety factor, the potential significance of other uncertainties would increase, such as those related to CPR inventory, CPR degradation rates and extents, and the possible physical segregation of small amounts of MgO. The MgO safety factor must account for these uncertainties in the absence of conservative assumptions regarding the extent of CPR degradation to form CO_2. Because of the importance of the MgO backfill, an understanding of the potential effects of a shortfall would be necessary before the technical feasibility of significantly reducing the MgO safety factor could be assessed.

6.0 SUMMARY AND CONCLUSIONS

A review of biodegradation data from the WIPP program and a preliminary review of literature data related to biodegradation and radiolysis indicate that CPR is likely to at least partially degrade and produce CO_2 in the WIPP environment during the 10,000-year period of repository performance. During this review, a number of potential technical issues were identified related to whether the amount of MgO placed in the repository can be reduced without affecting repository safety. These issues and the possible uncertainties associated with them include:

Availability of MgO. The available experimental data and data from natural systems indicate that MgO hydration will be relatively rapid upon contact with brine, and hydromagnesite formation should also occur quickly. Formation of magnesite, if it occurs, is likely to occur later in the repository history because of the slow rate of this reaction at low temperatures. Therefore, the MgO backfill is likely to perform as designed and control brine pH and CO_2 concentrations in the repository. Incomplete reaction of the MgO with brine and CO_2 is unlikely to occur unless the MgO is physically segregated from the brine or CO_2; if such physical segregation should occur, the effective MgO safety factor would be decreased by a commensurate amount. The recent changes in MgO placement methods, with a constant safety factor calculated for each disposal room, limit the potential effects of inhomogeneous distribution of CPR in the waste, and are likely to minimize the uncertainties associated with possible physical segregation of the MgO from brine and CO_2. However, the small remaining uncertainty related to physical segregation should be addressed by the MgO safety factor.

CPR Inventory Uncertainties. Up to the present time, uncertainties in the CPR inventory have been addressed by emplacing excess MgO in the repository. If the MgO safety factor is to be significantly reduced in the future, the uncertainties in the CPR inventory must be quantified. This uncertainty should be incorporated into the MgO safety factor to ensure that an adequate amount of MgO is emplaced.

Importance of Radiolysis. A preliminary evaluation of the literature established that potentially relevant data related to radiolytic degradation of polymers are available. In addition to direct radiolysis effects, this review indicated that iron may have a significant effect on polymer radiolysis because of Fenton-type reactions. A more thorough literature review and data analysis would be necessary to evaluate the potential significance of radiolytic degradation of CPR in the WIPP repository. This evaluation should include calculations of the likely radiation dose to CPR in the repository and an assessment of the chemical effects of this radiation on the waste and its eventual biodegradation. This information would indicate whether adequate data already exist or if additional experiments could reasonably be performed to establish the effects of radiolysis on CPR degradation.

A significant gap in the data appears to exist regarding the possible interactions of radiolytic and microbial processes specific to WIPP. The low levels of radiation expected in the waste may affect the chemistry of the polymeric materials that make up the CPR. Such radiation-induced changes in the polymers may alter their microbial degradation potential over the 10,000-year regulatory period. WIPP-specific experiments may be warranted to address this data gap; these experiments could investigate whether low-level radiolysis of CPR would be likely to promote or inhibit the microbial degradation of CPR. Because the effects of radiolysis on long-term microbial degradation have not been well-defined for WIPP, there is associated uncertainty in estimates of the likely extent of CPR degradation in the WIPP repository.

Extent of CPR Degradation and Effects of Early Degradation Processes. The results of the preliminary review described in this report indicate that cellulosics may be completely degraded in the repository environment over the 10,000-year regulatory period. The preliminary review of information regarding the possible extent of plastics and rubber degradation in the repository is less conclusive; therefore, additional literature review and experimental investigations may be necessary to determine the likely extent of radiolytic and microbial degradation of plastics and rubber during the 10,000-year regulatory period. Processes likely to affect waste during use, storage, transport, and the early disposal period include degradation by aerobic bacteria and fungi, and radiolysis in the presence of oxygen. Estimation of the length of time oxygen will persist in the repository and the radiation doses to waste could be used to determine the likely effects of these processes. Although these processes may not significantly affect short-term rates and extents of degradation of CPR, their effects could influence mechanisms, rates, and extents of CPR degradation over the long WIPP regulatory time period. The available literature should be reviewed to determine whether these early degradation processes and long-term radiolysis under anaerobic conditions are likely to make CPR more susceptible to microbial degradation in the longer-term anaerobic WIPP environment.

Any assessment of the extents of degradation of CPR should include an estimation of associated uncertainties, which should be incorporated in the MgO safety factor. These estimated uncertainties should reflect all possible physical and chemical processes that might occur over 10,000 years including:

- The adaptability of microbes to different substrates and environments
- Potential physical segregation of small quantities of MgO from brine
- CPR inventory uncertainties
- Effects of short-term aerobic radiolysis and biodegradation reactions on long-term microbial degradation of CPR
- Effects of long-term anaerobic radiolytic processes on CPR biodegradation
- Uncertainties associated with the predicted availability of brine in the repository

EPA regulations require that expert judgment should not be substituted for available experimental data or data that could be obtained from a reasonable set of experiments (40 CFR 194.26). The results of this review have indicated that literature describing experimental data is available that might be used to reduce the uncertainties associated with the extent of CPR degradation in the WIPP repository and improve understanding of WIPP’s future performance. Consequently, use of expert judgment to assess the likely extents of CPR degradation in the WIPP repository may not be justified at this time and would require adequate justification by DOE. If the use of expert judgment is justified, this judgment should include not only the likely extents of CPR degradation, but also the associated uncertainties, taking into account the factors listed above.

A more extensive evaluation of the available WIPP and non-WIPP literature should be carried out to determine whether the data are sufficient for estimating the likely extent of CPR degradation during the 10,000-year regulatory period, or whether experiments might be designed to determine the probable extents of degradation of the various materials over this long regulatory time period. The goal of the literature review and experimental studies would be to adequately quantify or capture system uncertainties, including both the uncertainties associated with the quantities of CPR in the repository and the chemical uncertainties related to the CPR degradation reactions and reactions of the MgO backfill. Sufficient excess MgO (an adequate safety factor) needs to be emplaced in each disposal room to compensate for the range of uncertainties related to CPR degradation and the effective performance of the MgO engineered barrier, thereby ensuring WIPP's expected safe performance in the future.

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