II-G-22: Conceptual Models Third Supplementary Peer Review Report, April 1997.

A Peer Review
Conducted By

Charles Wilson, Darrell Porter, John Gibbons,
Eric Oswald, Glen Sjoblom, Florie Caporuscio

for

U.S. Department of Energy
Carlsbad Area Office
Office of Regulatory Compliance

April 1997

EXECUTIVE SUMMARY

This report is a third supplement to a July 1996 report that presented the results of an independent technical peer review of the adequacy of 24 conceptual models representing features, events and processes involved in assessing the long-term performance of the Waste Isolation Pilot Plant (WIPP). The peer review was initially conducted from April through June 1996 at the U.S. Department of Energy's (DOE's) Sandia National Laboratories by a six-member interdisciplinary Review Panel having the requisite broad experience to address the range of issues associated with waste isolation over the 10,000-year regulatory time frame. The Panel selection process and the biographies of the Panel members are included in the July 1996 report.

In its January 1997 second supplementary report, the Panel stated that it continued to find two of the models not adequate to represent the future states of the repository. For the two models found not adequate, Spallings and Chemical Conditions, the Panel identified its remaining issues. In this third supplementary report the Panel considers the DOE's April 1997 responses to these remaining

In its January 1997 second supplementary report, the Panel stated that it continued to find two of the models not adequate to represent the future states of the repository. For the two models found not adequate, Spallings and Chemical Conditions, the Panel identified its remaining issues. In this third supplementary report the Panel considers the DOE's April 1997 responses to these remaining

issues. The Panel's evaluation of these responses is presented in Section 3 of this report. For the Spallings Model, the Panel concluded that the predicted volumes of spalled materials presented in the WIPP Compliance Certification Application (CCA) are reasonable based on additional consideration of processes that could lead to spalled releases. The Panel also concluded that the MgO backfill component of the Chemical Conditions Model will function as assumed in the CCA and that this model is adequate to represent the future states of the repository.

1.0 INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) Conceptual Models Peer Review Panel (Panel) issued its report in July 1996. The peer review was conducted in accordance with the regulatory requirements of 40 Code of Federal Regulations (CFR) 191 and the implementation of those requirements by 40 CFR 194. The U.S. Department of Energy (DOE) included the Conceptual Models Peer Review Report as part of its Compliance Certification Application (CCA) for WIPP that was submitted to the U.S. Environmental Protection Agency (EPA) in late October 1996.

A conceptual model is a statement of how important features, events, and processes such as fluid flow, chemical systems, or intrusion scenarios, are represented in the performance assessment. In the Conceptual Models Peer Review Report of July 1996, 24 conceptual models were evaluated using the evaluation criteria specified by the EPA, including those of NUREG 1297. The Panel's report identified 13 conceptual models as adequate for implementation in WIPP Performance Assessment and 11 as not adequate for implementation, based on information available to the Panel. The Panel's findings on each of the models judged inadequate were provided in the report. After that report was issued, DOE developed additional information, made changes to some of the conceptual models, and prepared responses to the findings in the Conceptual Models Peer Review Report of July 1996.

The DOE reconvened the Panel in October 1996 to review the changes to the conceptual models, the DOE responses to the findings in the July 1996 Panel report, and information available in the CCA. In December 1996 the Panel issued a report supplementing the July 1996 report, that assessed the changes to the models and the DOE responses. The Panel found that two of the models, Spallings and Chemical Conditions, continued to be not adequate for implementation, and identified the remaining issues with these models. DOE again reconvened the Panel in January 1997 to review additional information developed in response to the remaining issues of the Panel on these two models. The Panel issued a second supplementary report which continued to conclude that these two models were not adequate for implementation and reiterated the remaining issues.

The Panel subsequently communicated by teleconference from February through April to review action plans and monitor progress toward resolving the issues. In meetings held during the week of April 20, 1997, the Panel reviewed information detailing additional DOE work relative to Spallings and Chemical Conditions. This report documents the Panel's April 1997 findings and is a third supplement to the Panel's July 1996 report.

For the Spallings Model, DOE has not requested the Panel to reconsider its conclusion that the original model was not shown to be adequate to represent the future states of the repository, and has not asked the Panel to review a new model against the criteria of 40 CFR 194. For the present review, the Panel was instead requested to determine if the predicted volumes of spalled materials presented in the WIPP CCA are reasonable, based on additional consideration of processes that could lead to spalled releases. Additionally, for the Chemical Conditions Model, DOE has requested the Panel to determine whether the MgO backfill will function according to the conceptual model, as used in the CCA, with respect to reaction with generated CO_2 gas.

Section 2 of this report describes the process for this third supplementary review. Section 3 describes the additional information provided by DOE and the Panel's assessment of that information. Section 4 contains a summary of the Panel's assessments and conclusions.

2.0 SUPPLEMENTARY REVIEW PROCESS

This supplementary review was conducted at Sandia National Laboratories (SNL) in accordance with the DOE Quality Assurance requirements as modified in January 1997. The Panel was provided information relative to issues in its earlier reports during briefings and in written materials. The same review criteria were used to judge the acceptability of conceptual models as in the July 1996 report.

3.0 MODEL EVALUATIONS

Section 3.1 discusses the additional considerations of the Panel relative to the Spallings calculations and Section 3.2 discusses additional considerations relative to the use of MgO as part of the Chemical Conditions Model.

3.1. Spallings

3.1.1. Model Description

No changes were presented for the Spallings Model used in performance assessment.

3.1.2. Review of Criteria

The review of criteria for the Spallings Model remains unchanged.

3.1.3. Review of Responses to Panel Findings of January 1997

3.1.3.1. Summary of Findings

In its January 1997 report, the Panel found that additional information available on analogs, waste strength, other new model descriptions and calculations of tensile failure were either not adequately correlated with WIPP repository conditions or were not sufficiently complete or supported to provide the Panel with an adequate basis for determining that either the Spallings Model or the results obtained from that model were conservative.

3.1.3.2. Summary of DOE Responses to Findings

Surrogate Waste Materials

In response to the Panel's concern about the properties of the waste that would influence the spalling process, the DOE developed analogs for waste based on ranges of waste contents, corrosion and biodegradation that would perhaps be present following extended exposure to WIPP conditions. The surrogate samples contained varying amounts of corroded and uncorroded iron metal, including addition of goetite, crushed glass and soil, salt and concrete, and MgO in some cases. Physically degraded paper, plastic and peat were added to represent chemically degraded organics in the waste. These surrogate waste materials were mixed with brine, and consolidated to either 5 or 15 MPa to simulate repository conditions. Some of the samples were subsequently dried. Standard testing procedures were used, including Brazilian and hollow cylinder tensile tests, unconfined and triaxial compression tests, and permeability tests. Various parameters, including permeability, porosity, cohesion, tensile strength, compressive strength, Young's modulus, and Poisson's ratio were determined from the results of those tests. These parameters were then used in the various analytical calculations. DOE asserted that these parameters adequately represent the degraded waste expected in WIPP.

Analogs

The Panel was presented with documentation of analogs to the spalling process at WIPP, mostly rooted in petroleum production technology. Exceptions to the oil and gas analogs, such as seepage and earthquake-induced liquefaction and kimberlite pipe genesis, were quickly dismissed because of only tenuous similarity of phenomena. Drillhole blowouts, wellbore stability, sand production, hydrofrac proppant flowback, and cold production of low gravity viscous crude oil all were discussed in more detail and, although they were of qualitative value in understanding the spalling phenomenon, they were not found to be directly applicable as credible quantitative analogs. However, the dynamic cavitation of wellbores, specifically those through coal beds, was found to have notable attributes analogous to the spalling process at WIPP.

Dynamic cavitation has many similarities to the spalling process at WIPP, such as a pressure pulse phenomenon, gas-driven particulate removal, and a highly similar physical configuration. The ability to apply established computational codes, and the available database of results from this remarkably close analog help to corroborate testing and/or computational results. The DOE's draft Spallings Release Position Paper (SNL/CTAC, 1997) presents many of the pertinent similarities with instructive comments in Table 5-3, "Properties of a Characteristic Coalbed Methane Reservoir Used in Single Cycle Surge Modeling."

Computational Methods

In response to Panel findings that the existing model used to estimate spalling inadequately represented critical components of the spalling process, DOE initiated a new, mechanistically based computational approach. This approach is composed of three new computational methods which were used to develop additional information on the spalling process. These are called the cavity growth, the quasi-static, and the numerical computation methods. This approach represents the first time that borehole hydrodynamics and cavity growth have been linked.

The cavity growth method is presented as the primary method for estimating spall volumes. The method simulates the entire response period of the system to an intrusion event, not just the end point. Assuming initial gas pressures and waste strength, the method accounts for the progressive mechanical response of the waste to a transient solution of gas flow in the waste and includes the hydrodynamics of mud and waste ejection through the borehole. The cavity growth method predicts small spall volumes for assumed initial gas pressures below lithostatic (14.8 MPa) and a maximum spall volume of 0.25 m^3.

The quasi-static method is presented as the simplest of the three methods and, as such, is primarily used to examine sensitivities and verify complex calculations rather than estimate spall volumes. The method is applied to estimate gas volumes, gas pressure distributions and flow rates for comparison to those predicted by the cavity growth and numerical methods. Graphic comparisons of gas flows and pressures predicted by the cavity growth and quasi-static methods illustrate close agreement. The gas pressure distributions and flow-rates predicted by these two methods are higher than those predicted by the numerical solution for the important early time steps.

The numerical method is presented as a tool for evaluating complexities not clearly represented by the other methods. The numerical method couples fluid pressure to the stress response in the waste following a drilling intrusion. Numerical calculations implemented through various computer codes were used to investigate solids mass transport, sensitivity of waste panel geometry and effects of waste heterogeneity, in addition to predictions of gas pressures and flow rates.

Numerical calculations were applied to predict gas pressures and flow rates for comparison to semi-analytic results. The numerical calculations consistently predict lower pressure gradients and lower gas flow rates than the other methods. The gradients and rates predicted by the numerical method are significantly lower than those of the other methods at early time steps. Investigations of layered and random configurations of heterogeneous waste using numerical calculations resulted in a reduction in key parameters that determine spall volume. Solids mass transport was investigated and determined to be limited prior to mud ejection. Tensile strength was determined to govern the system response, thereby minimizing the overall effects of waste panel geometry and flow properties.

3.1.3.3. Panel Review of Responses

Liquefaction, Plastic Deformation, and Cavity Stability

In the seminal paper by Vaziri and Byrne (1990), the detailed discussion providing the groundwork for the consideration of the mechanical stability of deep wells cites liquefaction as the strain mechanism responsible for cavity formation. Subsequent work has developed a more complete picture of stress-strain relationships around an unstable wellbore. Stabilization of a cavity in a wellbore that is in transient instability depends, in part, on the formation of a "stress arch" around the cavity whose extent and geometry depend on the shear strength of the geologic materials. Shear strain controls the formation of the stabilizing zone, which is in a compressive state around the cavity and is characterized by plastic deformation.

In rocks having sufficient tensile strength and cohesion, the primary strain mode leading to cavity formation may be tensile failure due to differences in pore pressures around the cavity. Models used to predict cavity formation by air pressure pulsing in coal gas recovery wells have been developed and tested against bench models and field observations. In this useful analog of cavity formation caused by the release of gas due to an intrusion by drilling into the WIPP repository, a tensile failure of the cleated coal creates the cavity, and a broad plastic zone (tens of meters wide) forms around the cavity. Even after many repeated pressure pulses the cavity in the coal eventually stabilizes and cannot be made larger. This ultimate stabilization is due to the formation of the broad zone of plastic yield and the resultant concentric compressive stress zone (arch) around the cavity following repeated perturbations.

The WIPP surrogate waste exhibits cohesion and tensile strength as well as a significant tendency to ductile (plastic) deformation under experimental conditions. This has led the DOE to characterize the cavitation process as the result of a tensile failure zone surrounding the cavity at some short distance at any moment during the single short and rapid period of failure. The details of disaggregation and fragmentation of the spalled material moved into the cavity by tensile failure around the periphery of the cavity are not considered. Liquefaction may play a role in spall fragmentation, but all stress states leading to failure at the periphery of the cavity and beyond are characterized by non-zero states of effective stress. No liquefaction is predicted at or beyond the cavity margin.

The representation of cavity formation presented by the DOE is reasonable within the range of tensile strengths and cohesions proposed on the basis of surrogate waste experiments, the proposed stress environment, and the proposed strain processes. Although strain leading to cavity formation takes place over a very short period of time, the absolute magnitudes of continuous strain are relatively small. The rapid strain rates at the time of failure tend to enhance brittle behavior, but the small strain magnitudes and the large ductilities exhibited by the surrogate waste imply that the formation of a plastic zone and a stabilizing compressive shear arch is reasonable.

Distribution of stress and subfailure strain domains in the waste may be spatially complex and subtle. The principle driving mechanism for stress in the waste is pore pressure contrast distributed around the point of repository penetration as relatively symmetrical hemispherical gradients. Formation of the plastic zone and other complexities are secondary features which are kinematic responses to cavity development and relaxation of the waste due to degassing. Small magnitude tensile stress regions outside the compressive plastic zone and stress regions of incomplete symmetry are predicted by some published models and by closed-form numerical calculations presented by the DOE. These stress regions are limited by the small predicted dimensions of the cavity formed in the waste relative to the entire volume of waste in the room and by the inefficient transfer of small elastic strains by very porous and relatively weak media during second order kinematic adjustments. No loss of strength outside of the tensile zone in the immediate vicinity of the intruded borehole is reasonably expected.

Strength and other properties of the waste are thought to be modified by several aspects of the repository environment. Some of these aspects of waste character are speculative and are not demonstrable so that no representation of their effects is included in the spall volume calculations. Waste heterogeneity and layering, the cementing effect of MgO, and other proposed strengthening effects of degradation are examples of possible but undemonstrated factors in waste physical behavior. Halite cementation of completely dry waste is apparently demonstrated by the increased strength of surrogate waste specimens prepared with added salt, wetted with brine, compacted, dried and tested. Some specimens were tested wet and some were tested after drying. Dried specimens of similar composition were about twice as strong under tensile testing as similar saturated specimens, using two types of tensile tests. Degradation of waste reduces mean grain size and implies the presence of brine to facilitate the degradation processes. Degraded and dry waste may be considerably stronger than undegraded or wet waste.

The DOE suggests that in cases in which high gas pressures occur in the waste, brine consumption during degradation depletes moisture in the waste so that the waste encountered in the top of the repository is likely to be dry. This justifies the assumption in the DOE model that the tests exhibiting the weakest (lowest tensile strengths) surrogate material strengths are highly improbable representations of waste strength at high repository gas pressures. The combined low probabilities of high gas pressure and the presence of saturated, degraded waste during a first intrusion late in the repository history seem to support this premise.

Method Validation

The Panel raised the issue of experimental validation of the new calculational methods, particularly those used to calculate flow and pressure drop through the porous media under highly transient conditions, because these calculations are very critical to the determination of waste stress conditions. The Panel was provided with verification and validation information that generally supports the use of the series of calculational methods, although the Panel did not review all of the available material in detail. DOE stated that the flow equations use Darcy's law, which is applicable except for extremely transient conditions and higher Reynold's numbers in the waste, when gas phase inertial effects could become important. The Panel noted that these calculational methods are used in many applications in situations involving flows in geologic settings and believes they are useful and appropriate for the calculations presented to the Panel, although the literature available apparently did not contain experimental validation under highly transient conditions. The Panel did note that if the calculational flow methods were later proffered for use as part of a new Spallings Conceptual Model, it would be prudent to ensure that the flow calculational methods were fully verified and validated against experimental data for the specific range of conditions of use.

Review of Analogs

The Panel agrees with the conclusion of the DOE analog presentations that the gas pressure gradient and waste cohesion, not the magnitude of the reservoir pressure, controls failure and that the WIPP gas pressure gradients are likely to be less steep than those gradients found effective in coalbed methane production practice. This less steep WIPP gradient is further supported because the WIPP borehole size is approximately a quarter of the cross section area of that used in coalbed treatments, and there will always be a further net borehole area reduction in the WIPP case due to the presence of the downhole drill string.

In the coalbed analog, the volume of solids released increases when the well is pulsed. While pulsing is not a requirement for the cavitation, this fact is important in that the mechanism is a repetitive event and WIPP is only a single cycle, or pulse. Cohesion is also observed to be a factor in the spalling process. Based on the work of Palmer and Vaziri (1994), the DOE's Spallings Release Position Paper (SNL/CTAC, 1997) suggests that because the WIPP waste cohesion is expected to be more than 25% higher than that of the coal tested, cavitation is unlikely. The Palmer and Vaziri modeling, which simulates failure initiation and progressive cavity evacuation by explicitly coupling flow, deformation, and failure, clearly represents events that can be expected of the WIPP waste panel at a time of intrusion.

The Panel concludes that coal methane gas stimulation by cavitation is a highly plausible analog for depicting the spalling process. Its advantages over other analogs considered by DOE are its physical similarities, as well as its relationships to situations and configurations that can be further studied, tested, and defended by well established computer codes, theory, and available corroborative data. However, this analog does not necessarily cover all aspects of the spalling and release process, such as gas erosional effects, liquefactions, and borehole transport mechanisms. The cavity growth calculations presented to the Panel by DOE are based on the same physical and theoretical principles as the Palmer and Vaziri coal gas cavity completion model.

Adequacy of Surrogate Waste Strength

The Panel considered the adequacy of the values of waste tensile strength used in the tensile failure calculations. The Panel concluded that there is some uncertainty in the degree to which the values measured on waste surrogates truly represent the actual waste following extended exposure in WIPP, but that generally, the selected values are reasonable for the intended purposes. The Panel considered the magnitude of spall volume that could result if the actual waste tensile strength were as low as one half of the lower value chosen by DOE for dry waste. In this case, the calculated spall volume at 14.8 MPa initial pressure was roughly estimated by the Panel to increase from 0.25 m^3 to 0.9 m^3. DOE strongly believed that it was not correct to assume such low waste strength values because it introduced unreasonable conservatism into the calculations, and indicated that additional failure criteria would need to be considered if waste strength were significantly lower than the selected values. The Panel agreed with this belief. The Panel notes that the higher spall volume, though perhaps overly conservative, is still lower than most of the values used in the CCA, which ranged from 0.5 m^3 to 4.0 m^3.

Occurrence of Maximum Pressure Gradient

The DOE calculations presented indicated that the maximum pressure gradients, and therefore tensile stresses within the waste adjacent to an intrusion borehole, occurred within two seconds of the drill penetration into the top of a waste panel, prior to expelling the drilling mud. The Panel questioned whether the gradients and stresses in the few seconds after the drilling mud expulsion might actually be higher. The DOE presented information which showed that this second transient was not expected to be quite as rapid as the first transient, would be at much lower pressure, and would therefore not cause additional spalling volume. The Panel accepted this explanation.

Pressure Bleedoff through the Disturbed Rock Zone

The Panel questioned whether the high gas pressures would bleed off through the disturbed rock zone and Marker Bed 138 before the drill penetrated the top of a waste panel. DOE indicated that, based on the permeability and storativity of these regions, there would not be sufficient time during drilling for such bleedoff to significantly affect waste panel pressures at the time of penetration or to stop drilling operations as a result of interruption of drilling mud flow. The Panel accepted this explanation.

Entrainment of Contaminated Brine Flow During Spallings Events and Release of Radionuclides From Beyond the Tensile Failure Zone

In its earlier reports, the Panel raised the issue of entrainment of contaminated brine in rapid gas flow during a spalling event (p. 98 of the July 1996 report and p. 32 of the December 1996 report). The Panel concluded in the December report that use of the inadequate Spallings Model could not be the basis for an adequate resolution of this issue. The Panel has revisited this issue, which questions whether, in addition to spall of solid waste material due to tensile failure and cavity formation, there would be additional releases of waste particulates and dissolved actinides in liquid brine entrained in rapid gas flow through the waste. This has not been included in spallings calculations. DOE reviewed the calculations methodology in the Direct Brine Release Model and reminded the Panel that full two-phase flow of gas and brine are included for all intrusions, thereby resolving this issue. The Panel also raised the issue of whether solid waste in localized areas of low waste strength would be preferentially released, even from beyond the zone of tensile failure. DOE indicated that these materials would have to penetrate through the other materials and this was highly unlikely. DOE also provided information showing that if channels were to form, this would greatly decrease the pressure gradients and retard the growth of the tensile failure zone. The Panel accepted this as reasonable resolution of these issues.

Effect of Repository Gas Composition

The Panel raised the issue of the effect that the actual repository gas composition would have on the spallings process, since the calculations of spallings volume were performed using gas viscosity and density for hydrogen. Actual gas composition would be approximately one half methane, which is eight times as dense and 10 percent more viscous than hydrogen. DOE presented calculations addressing the effect of methane, which compared pressures and flows of methane and hydrogen separately. DOE indicated that the most significant effect would be to slightly slow the velocity of flow due to the higher viscosity and density. DOE concluded this would have about a 10 to 20 percent effect on the bottom hole pressure and no significant effect on the waste cavity growth.

The Panel has considered the implications of the use of viscosity and density of a mixture of hydrogen and methane, coupled with the issue of the appropriateness of Darcy flow for the highly transient conditions. It was noted that waste exit velocities are clearly well below the transonic range where further considerations would become highly important. DOE indicated that under somewhat less but still highly transient conditions, where inertial effects may be more important, a rigorous treatment would involve a more complete solution to the Navier-Stokes equation. However, as a first estimate, DOE felt that the increased pressure gradients would probably be commensurate with the steeper stress gradients calculated by the quasi-static method, as opposed to the cavity growth method, as shown in the Spallings Release Position Paper (SNL/CTAC, 1997, pp. 3-32, 33). For this reason, spallings volumes might be more in line with the values of the quasi-static method in Table 3-3 on p. 3-29 of the Spallings Release Position Paper, which represents an approximately threefold increase to a maximum of about 0.7 m^3. These higher values would still be lower than most of the values in the CCA, which ranged from 0.5 m^3 to 4 m^3. Again, the Panel believes that if a new conceptual model were proffered, the combined effects would need to be addressed more rigorously.

Waste Permeability Effects

It was noted by the Panel that the waste permeability values used in the modeling were the same as those used in performance assessment (1.7×10^{-13} m^2), rather than the lower value of about 4×10^{-15} m^2 experimentally determined for the surrogate waste. While the importance of maintaining consistency with performance assessment is understandable, in view of the analog information relating lower permeabilities with higher pressure gradients and therefore larger cavity volumes, the Panel requested the DOE to further discuss the consequences of assuming a higher waste permeability in the analyses than may actually exist in the degraded state. In responding, the DOE referred to sensitivity studies on waste permeability that had been performed with the quasi-static method in which the waste permeability was reduced to 1×10^{-15} m^2. The results indicated that although the pressure gradients did increase at these lower permeabilities, the volumetric flow rate of gas issuing from the waste was insufficient to eject the mud from the borehole, and therefore no spall event could occur. The Panel noted that this conclusion was similar to that reached from modeling studies presented by DOE in January 1997, where it was determined that partial depressurization of the waste panels would not be expected during borehole penetration of the overlying disturbed rock zone because its assigned permeability of 1×10^{-15} m^2 was too low to allow sufficient gas flow to occur. On this basis, the Panel concurred that the higher permeability values used in performance assessment were reasonable for this application.

Concluding Statements

Upon reviewing the DOE's written materials, oral presentations, and responses to specific issues raised by the Panel, the Panel concluded that no significant issues remained regarding the reasonableness of the spallings volumes used by DOE in its CCA for the WIPP. Although the additional waste strength, analog information, and calculational results that were presented to the Panel could be further refined, the Panel determined that this information was sufficiently accurate and complete to support a conclusion that the spallings volumes used in the CCA are reasonable, and in fact appear to overestimate the actual waste volumes that would be expected to be released by the spallings process.

3.2. Chemical Conditions

3.2.1 Model Description

No changes to this model were presented.

3.2.2 Review of Criteria

The review of criteria for the Chemical Conditions Model remains unchanged.

3.2.3 Review of Responses to Panel Findings of January 1997

3.2.3.1. Summary of Findings

With regard to the Chemical Conditions Model, the Panel concluded that the ongoing test program had not sufficiently progressed to provide a definitive verification that the MgO will perform as planned under repository conditions. The Panel was particularly concerned about whether the results of early tests indicated that reaction rims would inhibit the ability of the MgO to react completely and rapidly with CO_2 to buffer the chemical system and limit actinide solubility.

3.2.3.2. Summary of DOE Responses to Findings

The DOE provided a draft report(1) to the Panel, "Chemical Conditions Model:

Results of the MgO Backfill Efficacy Investigation," dated April 23, 1997, along with oral briefings on this report. This report summarizes the currently available data and analyses developed from SNL Test Plan TP-97-01.

Based on current information, DOE indicates that of the various phases formed from the contact of brine with MgO pellets, the initial phase, brucite, will crystallize to nesquehonite and hydromagnesite during short to intermediate times and, over long periods, will dehydrate to magnesite. DOE states that the brine pH and CO_2 fugacity are controlled at levels throughout the process which effectively lead to low actinide solubilities.

Earlier short-term experiments at high CO_2 contact rates indicated the formation of reaction rims. Current results for longer periods with high CO_2 contact rates indicate the growth of brucite films, followed by increasing density of nesquehonite needles projecting from the pellets. Shortly thereafter, hydromagnesite forms among the nesquehonite needles, as well as farther from the pellets. DOE concludes that while there is considerable retardation of CO_2 access to the pellets, accessibility for transfer is maintained. DOE further indicates that the predominant chemical diffusing species are $MgOH^+$ diffusing from the pellets and HCO_3^- diffusing toward the pellets. This gives rise to the precipitation of hydrous magnesium carbonates outside the pellets. DOE further indicates that, in contrast to the experiments, where relatively high CO_2 fluxes occur, the brine at WIPP will become saturated with magnesium compounds before significant introduction of CO_2 species occurs. The reactions will occur at nucleation sites still farther from the pellets, further improving the contact between the reacting species and reducing the formation of reaction rims. This supports the conceptual model assumption that the CO_2 will rapidly and completely react with the MgO. The DOE also reiterated that four times the amount of MgO needed to react with the total quantity of CO_2 generated will be emplaced in the repository.

DOE reviewed the effect of MgO control of pH and CO_2fugacity in actinide solubility, with hydromagnesite being the predominant intermediate carbonate phase. DOE concluded that most solubilities would be lower with hydromagnesite than if the transition to magnesite occurred, as had been assumed earlier. DOE also concluded that the results of the test program and analyses demonstrate that MgO will function in the WIPP according to the Chemical Conditions Model in the CCA.

3.2.3.3. Panel Review of Responses

Reaction Rim Isolation Potential

The fundamental issue that concerned the Panel was whether there would be an inability of the CO_2 to react with the interior of MgO pellets, especially as a function of carbonate reaction rim thickening. The present DOE report has efficiently dealt with this issue. A combination of experimental results, petrographic analyses (both optical and scanning electron microscopy [SEM]), modeling predictions, analog comparisons, and phase equilibria information have satisfied the Panel that reaction rims will not hinder the ability of CO_2 to react with various forms of hydrated MgO pellets. The most compelling evidence that was presented hinged on two factors: 1) the experimental results indicating that hydrous magnesium carbonate phases could nucleate away from the pellet surface and in the saturated brine, and 2) SEM photographs showing partially dissolved cores remaining within reaction rims.

Results of experimental runs were conveyed in carbon uptake curves that plot mole percent conversions versus time. An unusual S-shape to the curves (schematically shown in Figure 4-1 of the draft Chemical Conditions Report [SNL, 1997]) indicated that a substantial amount of magnesium was going into solution in the brine. During the experiments, which were accelerated due to high CO_2 concentrations, the magnesium saturated brines would combine with CO_2 to form hydrous magnesium carbonates at the most convenient nucleation sites. These sites included pellet surfaces, interstices between pellets, and free grains in the brine (the so-called milky appearance). In Figure 5-1 of the Chemical Conditions Report, precipitation fronts were indicated for carbonate minerals in both the experimental situation and for WIPP conditions. These two diagrams indicated that for WIPP conditions in particular, magnesium would dissolve from the pellets and go into solution. Therefore, the CO_2 would not be required to react with the pellet outer surface to form hydrous magnesium carbonates. This was compelling evidence that any coating that forms on the pellets is a secondary influence of carbonate nucleation.

It was also shown by the carbon uptake curves that the materials deposited on the pellets (nesquehonite and hydromagnesite) form a porous mantling (previously thought to be reaction rims) that allows magnesium to continue dissolving out of the pellets and go into solution in the brine at a somewhat reduced rate. This factor was strongly substantiated by SEM photomicrographs (Figure 4-5 of the Chemical Conditions Report) which show various states of pellet dissolution within concentric shells of mixed nesquehonite and hydromagnesite.

Metastable Hydrous Phases

In both the written presentation (Chemical Conditions Report [SNL, 1997]) and the oral presentation (on April 25, 1997), mention was made that the predominant hydrous magnesium carbonate phases formed in the experiments were nesquehonite and hydromagnesite. That is not surprising since Christ and Hostetler (1970) state " no carbonate mineral has proven more difficult to investigate experimentally than magnesite." These hydrous phases were produced easily in the experiments because of the elevated CO_2 concentrations used. The five order of magnitude higher CO_2 concentration in the experiments relative to predicted WIPP values was used to facilitate carbonate growth in a restricted time frame. Both phases were reported to be metastable, and would dehydrate (mature) with time to magnesite. The predicted time frame for dehydration reactions ranges from approximately 100 to 1000 years, depending on exact chemical conditions in the repository. This hypothesis was well supported by the following information: 1)natural analogs, 2) phase equilibria, and 3) Arrhenius plots.

The most pertinent natural analog study is that of Usdowski (1994), which observed that hydromagnesite would undergo a phase transformation to magnesite in a natural setting in Australia. The chemical conditions of that setting (ionic concentrations relative to ionic proportion and magnesium to calcium ratios) would encompass those of the Salado and Castile brines within the WIPP, as seen in Figure 5-2 of the Chemical Conditions Report. Phase equilibria determinations by Langmuir (1965) and especially Lippman (1973), as represented by Figure 4-3, have indicated that the metastable phases nesquehonite and hydromagnesite would transform to magnesite with sufficient time. The reaction pathway is easily seen in Figure 5-5, which predicts that the two hydrous phases of interest would dehydrate (mature) with time to produce magnesite. The way in which the accelerated experiments provided by DOE could be scaled to the conditions found at WIPP are by Arrhenius plots. This is a well documented and commonly used technique in experimental petrology to scale experimental results to field conditions that are not conducive to laboratory parameters and time frames. The Arrhenius plot presented to the Panel (Figure 5-4) indicates that magnesite would form in place of the hydrous magnesium carbonate in several hundred years. This supporting information is taken by the Panel as satisfactory evidence that the laboratory phases produced by DOE will in fact transform to magnesite well within the time constraints needed for the Chemical Conditions Model.

Water Sequestration

In the process of forming magnesian minerals in the repository, free water will be sequestered by the first step in the reaction series, the formation of brucite. Some of that water is later returned to the repository by the progressively less hydrous minerals generated in the transformations from brucite through hydromagnesite to magnesite. Since there will be excess MgO in the repository above that necessary to convert all the generated CO_2, most of this sequestered water will remain in brucite, permanently unavailable to react with the waste. The water that is returned will not change the volume of water assumed in performance assessment to be available to react with the waste. However, the reaction with that part of the water will be delayed while it is held by the metastable hydrous magnesium carbonate mineral phases. The process of carbonate hydroxide generation and the eventual dehydration of the anhydrous mineral phases which returns some free water to the system is expected to end after about 2000 years. This is during the period of most rapid brine inflow into the repository, and the return of that water to the waste is not expected to significantly change waste degradation rates at that time or later. The net overall effect of MgO hydration to brucite is to make the repository nominally drier.

Competition of Anions and Cations

The Panel asked whether other anions or cations that would be present in the waste or repository environment would inhibit the desired reaction between magnesium cation species and carbonate anion species. DOE indicated that anion species such as nitrate, sulphates, and chlorides do not significantly precipitate magnesium due to their solubility, and therefore would not prevent magnesium from being available to react with carbonate anions. Similarly, DOE indicated that other cations, such as calcium and iron would, if anything, also precipitate additional carbonate anions, and the resulting compounds are chemically compatible with magnesium carbonate species. Thus, other anions and cations would not interfere with the reactions between magnesium and carbonate species.

Conclusion

Based on the information presented to the Panel in the written material and in oral discussion, the Panel concludes that the results available provide an adequate basis to determine that the MgO backfill will function according to the Chemical Conditions Conceptual Model, as used in the CCA, with respect to reaction with generated CO_2 gas.

4.0 SUMMARY

This third supplementary report documents the Panel's evaluation of additional information regarding the two conceptual models that were not previously determined to be adequate, the Spallings Model and the Chemical Conditions Model.

The additional information on the spallings process included strength data for surrogate waste materials, analog information, and results from computational methods developed since the Panel's January 1997 report. The new information was not presented to the Panel as a new conceptual model, but rather to support DOE's belief that the spallings volumes used in the CCA were reasonable. In reviewing this additional information, the Panel was requested by DOE to determine if the predicted volumes of spalled materials presented in the WIPP

CCA are reasonable, based on additional consideration of processes that could lead to spalled releases.

The written materials and oral presentations on the spallings process prepared by the DOE, and the DOE's responses to specific issues raised by the Panel, were based on a detailed evaluation of the conditions, events, and processes at the WIPP that could lead to a spallings release, and on mathematical representations describing the sequence of physical events that could occur. Although further refinement in understanding and predictive capability for spallings events would be desirable as part of a new conceptual model, the Panel has determined that the additional information presented by the DOE is sufficiently complete at this time to support a conclusion that the spallings volumes used in the CCA are reasonable, and may actually overestimate the actual waste volumes that would be expected to be released by the spallings process at the WIPP.

The significance of possible entrainment of brine by expanding gases upon intrusion of a waste panel by a borehole was raised as an issue by the Panel in its July and December 1996 reports. DOE's initial response to this issue was not accepted by the Panel because it was based on computations using the inadequate Spallings Model. In further discussion of this issue during the April 1997 meetings, it was determined that the BRAGFLO-DBR model used to calculate direct brine releases computes two-phase flow effects in both the repository and the intrusion borehole, and accounts for the driving effects of gas expansion. This issue is therefore considered by the Panel to be satisfactorily resolved.

The additional information for the Chemical Conditions Model included further data from the MgO test program regarding hydration of MgO and transition toward magnesite, reaction rates with carbonate species, control of pH, and effect on actinide solubility. The Panel's only remaining concern for this model related to the lack of a demonstrated ability of the MgO backfill to function according to the assumptions in the conceptual model as used in the CCA with respect to reaction with the generated CO_2gas. The results of the information and analysis are sufficiently complete at this time for the Panel to conclude that the MgO backfill will function as assumed in the CCA and that this model is adequate to represent the future states of the repository.

With the exception of the Spallings Model presented in the CCA, which the Panel continues to find inadequate, all remaining conceptual models have been determined to be adequate and all significant issues regarding their adequacy have been resolved.

5.0 REFERENCES

Christ, C.L., and P.B. Hostetler. 1970. "Studies in the System MgO-SiO_2-CO_2-H_2O (II): The Activity-Product Constant of Magnesite." *American Journal of Science.* Vol. 268, no. 4, 439-453.

Langmuir, D. 1965. "Stability of Carbonates in the System MgO-CO_2-H_2O." *Journal of Geology.* Vol. 73, no. 5, 730-754.

Lippman, F. 1973. *Sedimentary Carbonate Minerals.* New York, NY: Springer-Verlag. 228 p.

Palmer, I.D., and H.H. Vaziri. 1994. "Modeling of Openhole Cavity Completions in Coalbed Methane Wells." Paper SPE 28580 presented at the 1994 Annual Technical Conference and Exhibition, New Orleans, LA, September 25-28.

SNL/CTAC. 1997. "Spallings Release Position Paper: Description and Evaluation of a Mechanistically Based Conceptual Model for Spall." Draft. Sandia National Laboratories and Carlsbad Area Office Technical Assistance Contractor, Albuquerque, NM. April 17.

SNL. 1997. "Chemical Conditions Model: Results of the MgO Backfill Efficacy Investigation." Draft. Sandia National Laboratories, Albuquerque, NM. April 23.

Usdowski, E. 1994. "Synthesis of Dolomite and Geochemical Implications." *Dolomites: A Volume in Honour of Dolomieu.* Eds. B. Purser, M. Tucker, and D. Zenger. Special Publication No. 21 of the International Association of Sedimentologists. Oxford; Boston: Blackwell Scientific Publications. 345-360.

Vaziri, H.H. and P.M. Byrne. 1990. "Analysis of Stress, Flow and Stability

Around Deep Wells." *Geotechnique* vol. 40, No. 1, 63-77.

ACRONYMS

CCA	Compliance Certification Application
CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
SEM	Scanning Electron Microscopy
SNL	Sandia National Laboratories
WIPP	Waste Isolation Pilot Plant