



ENVIRONMENTAL EVALUATION GROUP

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Dear Mr. Marcinowski:

At our meeting on December 10, 1997 in Albuquerque, the EPA WIPP project staff asked us to provide a written description of each of the issues related to the EPA's draft rule on WIPP, that we presented that day. This letter is to provide you a summary of each of the issues that we presented, as well as summaries of the issues that we did not have the time to present that day. Where more details are needed, we have enclosed extended descriptions. As requested by your staff, we have made specific suggestions on how to resolve each of these issues. This letter is not a replacement for the material presented to the EPA, but supplements and amplifies it. Also, please note that our presentations at the 12/10/97 meeting, and this letter, constitute our initial reaction to the EPA's draft rule published on 10/30/97. As we continue to review the voluminous materials released with the draft rule, we will provide additional comments to you in the near future.

As we noted on December 10, the issues presented to the EPA were those for which we have additional analyses or arguments. The issues not discussed that day were those for which we have previously provided detailed comments to the EPA, but the EPA has disagreed with our position, as indicated in the Draft Rule. Those issues are also included here with our reasons for continuing to believe in our previously stated positions. We trust that this material will be of use to you in your continuing review of the DOE application.

SUMMARIES OF THE ISSUES PRESENTED ON 12/10/97

Solubility

In reviewing the basis for the selection of actinide solubilities in the CCA and PAVT calculations, the EEG finds that the FMT model is unique to WIPP and is not used elsewhere. Calculations

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using the FMT model result, for example, in a difference of 19 orders of magnitude between the projected solubility of thorium pentacarbonate in the Castile brine versus the Salado brine. This is hard to explain on the basis of differences in the brine compositions. Hence the code becomes suspect. It appears that the EPA verification was limited to an exercise in which EPA used the same computers, codes, and database (after correction of some errors in the database) as DOE, to determine the same numerical values. This is not the standard of verification that one normally applies to chemical modeling codes. Verification would require, at a minimum, an analysis and demonstration that the FMT code correctly solves the simultaneous equations, a thorough comparison with the results of calculations using a code that is used more widely in the modeling community, and a demonstration that the calculations are consistent with all relevant published data. For example, as a preliminary analysis, it would have been more informative if a widely used code such as EQ3 or PHREEQE had been used with the FMT database and then FMT had been used with a database from some other modeling group.

Plutonium will account for 82% of the WIPP radioactive inventory 100 years after closure. The CCA maintains that the plutonium will exist either as Pu(III) or Pu(IV). However, the plutonium data were not used for developing the FMT model to predict the solubility of Pu(IV). Rather, the CCA relied on data for uranium and thorium as analogs. But there are long recognized concerns about relying entirely on the oxidation state analogy to derive thermodynamic constants for modeling complex electrolyte systems. As stated in the NAS/NRC WIPP Committee report (Oct. 1996, p. 129):

Although the oxidation state model (the assumption that the chemistry of a given oxidation state is similar for all of the actinides) is an appropriate beginning to a difficult problem, deviations from the oxidation state analogy are well known in natural and experimental systems. Substantial experimental verification will be needed to establish the limits of this analogy.

In its technical support documentation, EPA discusses the shortcomings of the solubility uncertainty ranges advanced by DOE. There is no direct basis for the uncertainty ranges for actinides in oxidation states +4 and +6. Moreover, the uncertainty ranges for oxidation states +3 and +5 are derived primarily from non-actinide data. Nonetheless, EPA has accepted the ranges as adequate, commenting "It is not clear that including more data for the other actinide state would appreciably change this range" (EPA, III-B-17, p.35). The argument is weak. It also remains unclear that the range adequately brackets uncertainty for a population for which data have not been examined.

In the solubility calculations, the CCA inappropriately discounts the role of organic ligands on plutonium solubility. The CCA provides information on the amounts and complexing properties of EDTA and then argues that other organic ligands, such as citrate, will be unimportant despite

the fact that citrate is the most abundant water-soluble organic constituent. Citrate forms extremely strong complexes with actinides in the +4 oxidation state [e.g. Th(IV)], but very weak complexes with other cations. Moreover, the DOE and EPA have each assumed that the actinides and the brine would be evenly distributed and well mixed throughout the repository. The problem with this assumption is that the plutonium and citrate are located in the same drums. These waste forms result from chemical separations of Pu and do not fit the classic description by DOE of TRU waste as contaminated tools, rags, gloves, booties, etc. The solubility of the plutonium for these waste forms must also be calculated as a very stable plutonium citrate complex where other cations in the brine diffusing into the drum cannot compete effectively with the complexed actinides (IV).

Perhaps the most important questionable assumption made in projecting the solubility values used in the CCA and the PAVT is the presence of hydromagnesite as the dominant stable mineral species resulting from the MgO backfill. DOE's experimental efforts with MgO predominantly produced nesquehonite, a magnesium carbonate mineral, with the later appearance of an unidentified phase. Hydromagnesite was not formed in the experiments reported by the DOE (Van Bynum's 4/23/97 report); a hydromagnesite-like unnamed mineral is reported. The chemical structure of this mineral is in fact more like nesquehonite. The DOE and the EPA believe that "hydromagnesite will be the metastable hydrated magnesium carbonate phase and nesquehonite will be an intermediate phase." (EPA Technical Support Document III-B-17, p.2). There is no experimental data for the length of time that nesquehonite is expected to exist. The distinction between the projected hydromagnesite-dominated or nesquehonite-dominated chemical environment in the repository is important because the actinide solubilities in the presence of nesquehonite are 3 to 4 orders of magnitude higher than in the presence of hydromagnesite.

The EEG therefore recommends that the EPA reexamine these issues and provide additional justification for the CCA and the PAVT solubility values. If convincing justification is not available, then the "no backfill", or "nesquehonite" solubilities should be used in a new performance assessment calculation.

The EEG has investigated the effect of actinide solubilities on the mean CCDF plots, using the EPA's PAVT releases, and making no other changes. The investigation (Enclosure 1) included the "CCA" solubilities, "no backfill" solubilities, and "nesquehonite" solubilities. The overall mean CCDF curve for "nesquehonite" solubility moved one order of magnitude closer to the compliance limit at 10^{-3} probability compared to the CCA solubilities (Enclosure 1, Fig.1).

Three Dimensional Processes and Boundary Conditions

This issue was presented to the EPA staff on December 10, 1997 as "2D/3D Modeling in BRAGFLO". The EEG first brought this issue to the EPA's attention as an attachment titled "Brine Inflow From Salado: 2-D versus 3-D Geometry in BRAGFLO" to the 3/14/97 Neill to

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Marcinowski letter. The DOE submitted a response as an attachment to the 6/27/1997 letter from G.E. Dials to L. Weinstock. The Draft Rule includes this issue as Issue F in CARD #23. The EEG position is summarized by the EPA as Comment #553 on page 115 of CARD #23, and the EPA response is provided on page 116. EEG's detailed response to the DOE and the EPA positions is provided as Enclosure 2 to this letter. A summary of the issue, the EEG's response, and the EEG recommendation to resolve the issue, follow.

The results of FEP S-1 screening analysis suggest that the two dimensional BRAGFLO model used in the CCA calculations may be misrepresenting repository performance at pressures above the anhydrite fracture pressure. There is the potential of substantially greater brine saturation in the repository at higher pressures than calculated for the CCA. The discrepancy between the 2D and 3D versions of BRAGFLO may have resulted in an underestimate of radionuclide releases to the surface.

To resolve this issue, the EEG recommends that several 3D BRAGFLO simulations of the repository should be performed using the parameter values of vectors used in the CCA performance assessment. The 3D BRAGFLO simulations should be used to provide repository conditions for the normal suite of direct brine release calculations. The calculations should also be assessed in terms of impact on spillings calculations. Spallings simulations are probably not required to assess the impact. The following criteria may be used to select the CCA vectors for running the 3D simulations to bound the magnitude of the problem:

- Since the discrepancy occurs above the fracture initiation pressure, the simulations should be limited to parameter vectors that result in pressures above 12.7 MPa at some time during the 10,000 year time frame.
- Direct brine release calculations should be sensitive to increased brine saturations above the waste residual brine saturation. Vectors that had either large brine saturations or a mobile brine component (saturations above the residual saturation) are more likely to be sensitive to increased brine inflow. Figure 5.1.5 of the preliminary sensitivity analysis report (Helton, 1996) indicates one vector with a 10,000 year pressure above 14 MPa and a brine saturation above 0.4. This is a likely candidate.
- The potential for brine consumption by corrosion should be assessed. Vectors with both slow and fast corrosion rates that also meet the above two criteria should be run.
- If the first simulations indicate a large change in saturation, then assess whether the 3D BRAGFLO simulations indicate a much larger number of significant direct brine releases than those calculated in the CCA. Simulations using brine saturations on the order of 0.1 and 0.3 should be performed.

Review of the EPA Spallings Investigation

The EPA funded a separate investigation of the spallings phenomena that focused on potential limits on spall material reaching the surface because of insufficient lofting capacity of gases vented from the repository (TSD III-B-10 and TSD III-B-11). The EPA investigation determined that venting of the repository would not be energetic enough to bring spall material to the surface. The conclusion is valid for evaluating the CCA spallings model but cannot be extended to the most recent DOE spallings model. The investigation's focus is on relatively long term transport capability consistent with the CCA spallings model. It should be on the immediate transport of material from the formation of an explosive spall cavity, as in the most recent DOE model.

The EPA modeling is superceded by the new spallings model presented in January 1997 (Hansen et al., 1997) to the DOE's Conceptual Model Peer Review Panel. The Panel rejected the CCA model and accepted this new model. This new model predicts that almost all spall would come from the face of the drilling cavity and that the spall process would occur in the first few seconds of repository depressurization.

The permeability reduction used in the EPA model is inappropriate to address removal of the initial spall material. The spallings model of *Hansen et al.* predicts that spalling will stop after a few seconds and that depressurization is negligible beyond roughly 1.5 meters at this time. During this initial depressurization, the source of flow is from the region close to the borehole. It is this local depressurization that would cause spalling to progress away from the drilling bit.

The temporal and spatial discretization of the EPA investigation is far too coarse to investigate the potential for evacuation up the borehole of spall material created in the first few hundred seconds. For example, in the case of a two foot penetration with 0.25 m³ spall cavity, the first element of the EPA analysis is 0.39 m thick. In the *Hansen et al.* model, the first element is 0.01 m thick. In the EPA investigation the first time step is 86 seconds compared to 0.001 seconds in the *Hansen et al.* model. These differences in both temporal and spatial discretization are an indication that the EPA modeling cannot predict gas velocities from local depressurization reliably. Hence, the EPA model cannot be used to judge the conservatism of the spall model described by *Hansen et al.*, nor the extension of the *Hansen et al.* model to potential spall from air drilling.

Hansen et al. also considered the issue of maximum particle size that could be transported up the borehole. Their results indicate that particles as large as 10,000 microns may be transported to the surface after the mud column has been expelled from the borehole, about 250 seconds after intrusion, and that transport of such large particles could occur for much more than 200 seconds. Two-hundred and fifty seconds is still very early in the EPA investigation (3 time steps). The discretization of the EPA model is too coarse to accurately calculate the flow rates this early in

the 11-day period. In conclusion, the calculations of *Hansen et al.* indicate that transport of spall material up the borehole will not limit the release of spall material to the surface.

The EEG therefore recommends to the EPA to **not** use the results of simplified modeling contained in the draft rule attachments TSD III-B-10 and III-B-11 to confirm the validity of the CCA spallings model, or to limit the potential releases from air drilling.

Stuck Pipe/Gas Erosion Scenarios

“Stuck pipe” is a scenario that occurs when, due to very low permeability of the waste and extremely high pressures in the repository, the amount of failed waste (spall) is more than the carrying capacity of the drilling mud. The spall then presses against the drill string sufficiently hard to slow down the rotation of the drill bit, preventing normal drilling. To free the jammed bit, the drillers pull the drill string up and start drilling again. If the pressures remain high, the driller may have to bring the bit up several times, thus allowing significant quantities of waste to be brought to the surface. “Gas erosion” refers to the scenario in which the failed waste is slowly eroded by the drilling mud when the repository pressure is just above hydrostatic and the waste permeability is low. Under these conditions, waste may be released into the drilling mud at a rate undetectable by the driller. Gas erosion would continue until the repository pressure is in equilibrium with the drilling fluid, and may bring significant quantities of waste to the surface in the process. Both these scenarios were considered by the DOE in an earlier exercise in the WIPP performance assessment (Systems Prioritization Method, 1995), but were not considered in the CCA because the permeability of the waste was assumed to be higher than the threshold for these processes to occur.

The CCA (Chapter 6, p. 6-100) states that permeability of the waste compacted under a lithostatic load was found to be in the range of 10^{-12} to 10^{-16} m², but assigns a constant value of 1.7×10^{-13} m², which is much greater than the assumed threshold of 10^{-16} m² for the “stuck pipe” scenario.

This issue was first raised in my February 7, 1997 letter to you, and has been numbered 540 in the draft rule (CARD 23). The response to Comment 540 states that the phenomena of stuck pipe will not occur because the permeability of the waste in the CCA (DOE, 1996-Chapter 6) was greater than the threshold permeability for stuck pipe stated in the CCA (DOE, 1996-Appendix CUTTINGS_S). The EPA quotes additional studies of permeability made by the DOE, in which the waste permeability was found to be 100 times less than the CCA value (Hansen et al., 1997), but still greater than the threshold permeability. Thus, the EPA does not believe that stuck pipe and gas erosion are processes to be considered in the CCA spallings model.

The EEG continues to believe that the “stuck pipe” is a plausible scenario because the threshold of 1×10^{-16} m² for stuck pipe and gas erosion may be faulty. This value resulted from the CCA Spallings model (as part of CUTTINGS_S), which was found to be conceptually flawed.

Berglund (1994) states that, for model simplicity, a value of $1 \times 10^{-16} \text{ m}^2$ will be used for a cutoff for blowout. The new spillings model, GASOUT (Hansen et al., 1997), shows that blowout will cease when permeability is between 10^{-14} and 10^{-15} m^2 . Berglund (1994) has shown that when blowout stops, the stuck pipe and gas erosion mechanisms of spall take over because the failed waste will be introduced into the borehole cavity and will not be blown out. Thus, the permeability threshold for the stuck pipe and the gas erosion scenarios appears to be 10^{-14} to 10^{-15} , rather than 10^{-16} . In any case, because of the stuck pipe and the gas erosion scenarios coming into play when the blowout ceases, release to the surface will occur even when the conditions for blowout of the mud column cease. We therefore recommend that it should be assumed that all of the calculated spall material will reach the surface.

Furthermore, the permeability of the waste in the WIPP repository is quite likely to be lower than that anticipated by the DOE. None of the waste surrogates for permeability testing included MgO as a backfill material. It is suspected that MgO precipitation will decrease the permeability by providing material for interstitial cementation, which has been postulated by the DOE's Particle Size Expert Elicitation Panel to be a major contributor to increased waste strength and lower permeability. Since the permeability of the waste is such a key parameter in assessing compliance with the standards, additional permeability measurements on surrogate waste that includes magnesium chloride cement should be carried out. Until this is done, the calculations may sample on the 10^{-12} to 10^{-16} range.

To get a perspective on the potential magnitude of impact of these scenarios on compliance, the EEG conducted calculations to investigate the amount of spillings release through either the stuck pipe or the gas erosion process that would violate the EPA standard. Enclosure 3 shows that if between 8 m^3 and 64 m^3 of spalled material is assumed to reach the surface, the standard is violated at 10^{-1} probability. The EEG is in the process of computing the releases from the stuck pipe and the gas erosion scenarios, and will transmit the results to the EPA as soon as possible.

Brine Release in Air Drilling

The EEG has investigated the effect of air drilling on direct brine release, and the results are shown in Enclosure 4. The results show that brine releases to the surface could be between 1000 and 2000 m^3 , compared to a maximum of 180 m^3 from the EPA's PAVT computations. The CCDF from the EEG's runs show that the overall mean for all types of releases (including brine release from air drilling) comes very close to the EPA limit at 10^{-3} probability for the actinide solubilities assumed in the CCA, and violates the standard at the "no backfill" and "nesquehonite" solubilities.

Fluid Injection Scenario

The petroleum reservoirs surrounding and underlying the WIPP are potential candidates for fluid injection to recover a substantial amount of crude oil reserves. For oil field operations in

southeastern New Mexico, the problem of water migrating from the intended injection zone, through the Salado Formation, and onto adjacent property has long been recognized. In fact, concerns about unexplained water losses due to solution mining, potential oil field development, or future oil field waterflooding has helped eliminate other sites from consideration as documented in an EEG report on fluid injection (Silva 1996; EEG-62). The EPA proposes to accept the DOE position that fluid injection can be ruled out as a potential scenario and, hence, need not be considered in the performance assessment calculations.

For fluid injection activities on leases adjacent to the site, the DOE argues that such events can be eliminated from further consideration on the basis of low consequence. The EPA raised questions regarding DOE's consequence analysis and "concluded that regardless of the consequence argument, the probability of such an injection event that affects WIPP is very low, and so this FEP can be eliminated on the basis of low probability"(CARD 32, p.42). The DOE chose to examine consequence rather than probability, as noted by Stoelzel and O'Brien, "[because certain petroleum practices are hard to define in a probabilistic sense (for example, the quality of the cement and/or casing and its ability to withstand leaks over time)..."(Stoelzel and Obrien 1996, 8). Nonetheless, EPA assigned probabilities to certain petroleum practices, such as an undetected leak occurring in the annulus, and multiplied the probability of each event and calculated that the *realistic* probability of a injection well impacting the repository was only one in 667 million (EPA, III-B-22, Table Q). But this value appears to be based on an optimistic view of future injection well performance and does not reflect the actual experience of documented waterflows in the Salado Formation in water flood areas throughout southeast New Mexico.

In the final analysis, for the low consequence argument, the EPA has accepted the modeling results of Stoelzel and O'Brien (1996) and Stoelzel and Swift (1997) for DOE, and has rejected the modeling results of Bredehoeft (1997) for the New Mexico Attorney General. The DOE maintains that a leaking injection well in the vicinity of WIPP is a low consequence event. But a very fundamental question remains. Can the DOE codes model a documented high consequence event? In other words, can the DOE codes take the injection data and geologic data from the highly visible Hartman case and reproduce what is believed to have happened at the Bates Lease? Can these codes model the migration of substantial amounts of water through a single zone of the Salado Formation, two miles in the up dip direction, in about 12 years? That has yet to be shown. Unless the code is verified with actual field data, the low consequence conclusion will remain a speculation at best.

The EPA does not anticipate that CO₂ injection for oil recovery will be a widespread practice in the future near WIPP (EPA CARD-23, p. 131). However, EPA's reasons do not have supporting references and appear to be at odds with the published literature. The EPA technical support document (III-B-22) states "at this time, the only examples of CO₂ injection enhanced recovery techniques are some distance from the WIPP site and under much different geologic conditions

(Magruder 1990; Trash 1979)". But an examination of the current and relevant literature strongly suggests that the Delaware Mountain Group sands are excellent prospects for future CO₂ flooding. First, CO₂ flooding has been demonstrated to be quite successful in mature fields in the Delaware Basin such as the TwoFred's (Silva, 1996, pp. 142-145). Second, the DOE continues to sponsor university research on Delaware Basin oilfields, such as the Geraldine Ford and the West Ford, aimed at optimizing infill drilling and CO₂ flooding throughout the Delaware Basin. Third, oil and gas companies continue to purchase mature fields, such as the El Mar in the Delaware Basin, specifically for carbon dioxide flooding. Fourth, the recently drilled reservoirs surrounding the WIPP such as Cabin Lake, Livingston Ridge, Los Medanos, and Lost Tank have oil and reservoir characteristics that easily qualify them as potential candidates for future CO₂ flooding using the enhanced oil recovery (EOR) screening criteria.

EPA maintains that "there are no natural gas storage horizons in the Salado Formation" (EPA CARD-32, p.71). As shown on a map presented to EPA by EEG on October 10, 1996, there are eight gas storage underground facilities in southeast New Mexico, three of which are in the Salado Formation in which the salt was "washed out to create a cavern", according to entry in a State document.

There are other fluid injection issues that have either not been fully addressed or in which there appears to be a misunderstanding of the issue including, for example, the yet to be explained water level rises in the Culebra Aquifer, the likely expansion of solution brine wells in the Delaware Basin, and the likely initiation of solution mining activities in maturing potash mines.

SUMMARIES OF THE ISSUES NOT PRESENTED ON 12/10/97

The following are the summaries of the other important issues related to the CCA and the Draft Rule that were not presented to your staff on December 10, but have been previously presented to the EPA.

Waste Issues

EEG has concerns about some EPA conclusions regarding: (1) waste inventory and waste form; (2) waste characterization; and (3) waste repository limits.

Waste Inventory and Waste Form:

The EPA has concurred with the DOE's contention that there is no uncertainty in the waste inventory. EEG's view is that: (1) there is considerable uncertainty in the stored inventory; (2) there is uncertainty in the volume of newly generated waste and the processes at the generating sites have changed significantly since the stored waste was generated; and (3) DOE plans to treat most of the waste at INEEL and the RFETS (residues) and repackage, and treat for size reduction, at other facilities. These plans are not reflected in the CCA inventory.

EPA should recognize this uncertainty and either not accept the DOE inventory and Waste Material Parameter (WMP) values or not permit DOE to bring in waste that differ significantly from the values in the CCA until more accurate inventory data have been developed and used in the PA calculations.

Waste Characterization:

DOE has concluded that a maximum repository limit of 2×10^7 kg of cellulose, rubber, and plastic (CRP) should be set in order to prevent production of more CO₂ than can be controlled by the MgO backfill. EPA has concurred in this recommendation. The expected amount of CRP in the repository is 2.1×10^7 kg (see CARD 24-38).

EEG is concerned about the ability to measure CRP in the waste with enough accuracy to ensure that this limit will be met. Visual Examination (VE) is a method that is capable of good precision on those containers measured if all internal containers are emptied and their contents identified and weighed. However, the preferred method of characterization is real time radiography (RTR) which is only semi quantitative (WMP weights are estimated by determining the void space and weight of waste in the drum which is not very accurate even if there is only one WMP in the container). EEG has not found a reference to the uncertainty in determining the weight of CRP in waste containers in either the DOE or the EPA reports. The EPA needs to point out where this uncertainty has been addressed, if it has been, or address the issue at this time.

Waste Repository Limits:

DOE has concluded that all repository limits need to be controlled only for the full repository. EPA has concurred in this recommendation and concluded that DOE's WIPP Waste Information System (WWIS) is capable of controlling repository limits.

There are two concerns that do not appear to have been addressed:

- (1) An excess of CRP in a waste panel could overload the MgO in that panel and since no interchange of brine between panels is assumed, it is questionable how much benefit would incur from excess MgO in another panel. Estimated concentrations of CRP do vary significantly between generating sites (e.g. at INEEL the average is 1.8 times the total inventory average);
- (2) A management plan that allows emplacement of repository limited parameter quantities that vary significantly from the required average could result in a situation where the required limits could not be met by emplacing the remainder of the inventory. This is a potential problem because the actual content of waste containers will be known only as the individual containers are characterized and may be much different than the current estimates.

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EEG believes that the case for controlling limits on a repository basis has not been justified. We recommend control on a per panel basis, at least, until the inventory is known with more certainty.

Retardation Coefficient

The EEG has submitted the following four documents to the EPA on this issue:

- Copy of November 14, 1996 letter from R.H. Neill to J. Salisbury, with attachments;
- February 7, 1997 letter from R.H. Neill to F. Marcinowski, with attachment "Chemical Retardation";
- Copy of May 23, 1997 letter from R.H. Neill to J. Salisbury, with attachments; and,
- Copy of August 29, 1997 letter from R.H. Neill to G.E. Dials, with attachments.

The August 29, 1997 letter and the attachments (docket # II-D-117) contained the EEG position on this issue based on the July 30, 1997 meeting in Albuquerque, which was organized by the EEG. Copies of this letter with the attachments were mailed to several EPA officials and the EPA WIPP docket. The DOE also sent a copy of their impressions of the July 30 meeting (Dials to Neill 8/25/97 letter with attachments, docket # II-D-115) to the EPA on August 25, 1997, four days before the EEG letter.

The EPA draft rule discusses this issue in the Technical Support Document, "Assessment of K_d S Used in the CCA", docket # III-B-4. This document makes extensive references to the DOE's August 25, 1997 letter, but no mention of the EEG's August 29, 1997 letter. Because the issue was raised by the EEG, and the July 30, 1997 meeting was organized by the EEG, it is difficult to understand why the EPA's analysis makes no mention of the EEG's summary of the July 30 meeting and the recommendations.

As described in the EEG's August 29, 1997 letter, the EEG has recommended conducting both batch and column tests for at least the actinides Pu(III), Pu(IV), and Am(III) in the Culebra brine; setting the lower end of K_d for U(VI) to be zero; conducting sensitivity analysis for potential impact of organic ligands; extending performance assessment calculations beyond 10,000 years to see how long the chemical retardation delays the releases to the environment; investigating the potential impact of nonlinear sorption on radionuclide transport; and, checking the validity of the K_d values derived from the column tests by examining the cores to identify whether the Pu and Am are present in adsorbed or crystalline solid phase.

The EEG recommends that the EPA consider the EEG submissions to the docket before reaching a final conclusion on the issue.

Brine Reservoir Probability

The EEG raised a number of issues related to the Castile Formation brine reservoirs (see R.H. Neill letters to F. Marcinowski, dated 2/7/1997 and 3/14/1997, attachments "Brine Reservoir Assumptions"). The EPA has accepted all of the EEG suggestions except the one related to the assumption of the probability of encounter of brine reservoirs, and we disagree with the EPA on this issue. The CCA assumed 8% probability on the basis of faulty assumptions. The EEG recommended 100% probability on the basis that the WIPP-12 brine reservoir was large enough to most likely extend under the repository, a conclusion also confirmed by geophysical testing directly above the repository. The EPA has sampled on a range of 1 to 60%, but has provided no basis for assuming less than 60%. Based on the arguments that the geophysical (Time-domain electro-magnetic survey) data may be interpreted to indicate the brine to be under 60% of the repository, and that some boreholes adjacent to the brine producing boreholes are known to be dry, the EEG is willing to accept the assumption of a fixed 60% probability of encounter, and recommends that a new performance assessment calculation be run with this fixed value.

Assurance Requirement/Engineered Barriers

The EEG believes that in allowing the resource disincentive requirement of the EPA standards (40 CFR 191.14 e) to be satisfied if the numerical containment requirements (40 CFR 191.13) are satisfied (through 40 CFR 194.45), the EPA deviated from the basic philosophy of the "belt-and-suspender" approach inherent in the assurance requirements of the standards. Faced with the *fait accompli* of promulgation of 40 CFR 194, the EEG recommended (EEG-61, May 1996) that at least the actual conditions at the site related to the presence of natural resources be fully and conservatively assumed in projecting compliance with the numerical containment requirements. This does not appear to have been done in the CCA, judging from the DOE resistance to consideration of fluid injection, air drilling, and mining scenarios. The other suggestion made by the EEG (in EEG-61) is to compensate for siting the repository in a mineral resource rich area by incorporating robust engineered barriers in the WIPP's design. The DOE has proposed Magnesium Oxide backfill as an engineered barrier, but that is needed for assuming low actinide solubility to show compliance with the containment requirement. The "containment" and the "assurance" requirements of the EPA standards thus have not been kept separate, as was intended by the EPA standards, 40 CFR 191.

The EEG recommends that additional confidence in predicting the behavior of the waste over 10,000 years can be obtained by processing the waste. Hence, EPA should encourage the DOE to process the waste before shipment to WIPP. TRU waste is highly heterogeneous and there are no limits on the allowable particle size of the waste. The Nuclear Regulatory Commission requires a 300 year waste-form or container longevity for class B or class C *low-level* waste, whereas there are no requirements for the TRU containers or the waste-form in 40 CFR 191. Moreover, the DOE proposed action in the WIPP 1997 Environmental Impact Statement only commits to meeting the Waste Acceptance Criteria for acceptance of waste at WIPP. The DOE

preferred alternative, published in the 1997 Final Waste Management Programmatic Environmental Impact Statement for Managing, Treatment, Storage and Disposal of Radioactive and Hazardous Waste, is to **treat** and store at the sites where it is generated prior to shipment to WIPP.

The recommendation to treat the waste before shipping to WIPP should be easier to accomplish because several of the DOE's waste generator sites are planning to process and/or repackage the waste before shipping to WIPP anyway, for other reasons, as described below. The EPA's directive will result in an orderly and coordinated decisions on this matter throughout the DOE weapons complex, and will make WIPP safer.

- According to the September 1997 WIPP Final Supplemental Impact Statement (DOE/ES-0026-S-2), 27,000 m³ of alpha emitting low level waste at INEEL will be processed to convert it to TRU waste.

The information for the following processing and repackaging plans is derived from the National TRU Waste Management Plan, DOE/NTP.-96-1204, Rev.1.

- INEEL plans to process all the existing and projected TRU waste except for 15,000 drums (3,000 m³) to meet the INEEL/State of Idaho agreement, which amounts to processing 79,600 m³ - 3,000 m³ = 76,600 m³ of waste.
- ANL-E plans to treat and stabilize all the 203 m³ existing and newly generated CH-TRU waste.
- Hanford plans on repackaging most of its 16,127 m³ of CH-TRU waste.
- Rocky Flats Plant will process the plutonium residues and the scrap alloy since plutonium concentrations exceed the DOE limits. About half the other TRU waste will be processed and repackaged.
- The Plutonium-238 heat source wastes at Savannah River exceed the hydrogen gas limits imposed by NRC and will require treatment or an easing of the regulations for a less stringent flammable limit or the use of hydrogen getters in the transportation containers.
- All the 1097 m³ CH-TRU waste at ORNL will be processed with a 50% volume reduction.
- SRS plans to process and repackage 9,525 m³ of the existing 11,725 m³ of CH-TRU waste.

Mr. Frank Marcinowski
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In summary, of the existing 104,400 m³ of CH-TRU waste, DOE has plans to treat or repackage 88,900 m³ or 85%. Of the 15,500 m³ not being processed, 3,000 m³ is intended for shipment to meet a scheduled commitment between DOE and the State of Idaho. The EPA should recognize DOE's efforts in stabilizing the waste and encourage DOE to also fix the yet-to-be generated waste.

We look forward to continuing the dialogue with you to resolve these and other issues.

Sincerely,

Robert H. Neill
Director

RHN:js
Enclosures

cc: Mr. Richard Wilson, EPA
Mr. Larry Weinstock, EPA
Ms. Mary Kruger, EPA
Mr. Chuck Byrum, EPA
Mr. Tom Peake, EPA
Mr. George Dials, DOE
Mr. Chris Wentz, NMEMNRD
Mr. Lindsay Lovejoy, Jr., NMAG
EPA Docket for WIPP (A-93-02)

Issue: Solubility Modeling

The modeling of solubility changes to the PAVT started with the re-running of the ‘Source Term’ files. The Latin Hypercube Sampling (LHS) generated a range of solubilities in the CCA that were 2.0 and 1.4 orders of magnitude below and above the median values, respectively. For the present model the range of solubilities were reduced to a constant value, based on solubilities of ‘No Backfill’ from Van Bynum (1997), and Nesquehonite in Novak (1997). The parameters of SOLSIM (solubility factor for Salado) and SOLCIM (solubility factor for Castile) (DOE, 1996-Appendix PAR) were changed for the oxidation states of +3, +4, and +6.

Table 1 shows the values used to replace SOLSIM and SOLCIM for all the actinides for the different mineral types. Again, the range from -2.0 to 1.4 with a cumulative continuous distribution was changed to the values below with a cumulative discrete distribution. One hundred vectors were created for all six scenarios of the first replicate with the new LHS file.

Once Source Term files were created, PANEL was rerun with the new solubilities using BRAGFLO files of the PAVT. The BRAGFLO files supply the velocity information for PANEL to use in the transport equations. The PANEL ‘concentration’ simulations were ran for 100 vectors of S1 and S2 scenarios. The PANEL ‘time’ simulations were reran for 100 vectors of S6 for times 100, 350, 1000, 4000, 6000 and 9000 years postclosure.

Lastly, the PANEL files were incorporated into the CCDFGF to create CCDF curves for comparison with 40 CFR Part 194. In addition to the Nesquehonite and No Backfill simulations with PANEL to create the new CCDFs, the CCA PANEL files containing CCA solubilities were used with PAVT releases of direct brine release, cuttings, spallings, and transport through the Culebra. Figure 1 shows the CCDF results of the different solubilities.

The figure shows that none of the curves violate the standard. The CCA solubility model has an estimated release of 0.45 EPA units at the 10^{-3} probability level. This is slightly higher than the 0.37 EPA units of the PAVT model and 0.22 EPA units of the CCA. The releases are shown to increase to 6 EPA units for Nesquehonite solubilities and to 7.5 EPA units for ‘No Backfill’ solubilities. The EPA compliance limit for the 10^{-3} probability level is 10 EPA units, or 3500 Ci for Plutonium, Uranium, Thorium, and Americium.

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U.S. Department of Energy, 1996. Title 40 CFR 191 Compliance Certification Application. DOE/CAO-1996-2184.

	Nesquehonite		No Backfill	
	SOLCIM	SOLSIM	SOLCIM	SOLSIM
SOLAM3	1.51616	-.27709	4.48678	3.83714
SOLPU3	1.51616	-.27709	4.48678	3.83714
SOLPU4	5.23242	2.15588	4.06695	2.05552
SOLU4	n/a	2.15588	n/a	2.05552
SOLU6	0.95861	0.96357	0.95861	0.96357
SOLTH4	5.23242	2.15588	4.06695	2.05552

Table 1. Solubility Factors for SOLCIM and SOLSIM

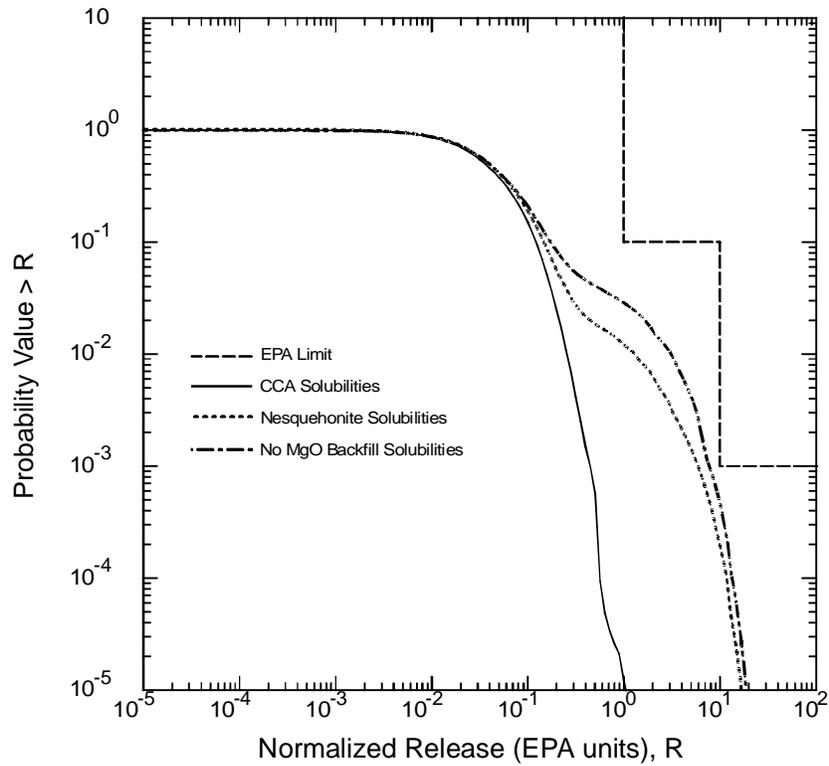


Figure 1. CCDF Overall Mean for Solubility Modeling with the CCA, Nesquehonite, and 'No Backfill' Values.

Issue: Three Dimensional Processes and Boundary Conditions

Problem Description

The EEG first brought this issue to the EPA's attention as an attachment titled ABrine Inflow From Salado: 2-D versus 3-D Geometry in BRAGFLO to the 3/14/97 letter from R.H. Neill to F. Marcinowski. The DOE submitted a response as an attachment to the 6/27/1997 letter from G.E. Dials to L. Weinstock. The Draft Rule includes this issue as Issue F in CARD #23. The EEG position is summarized as Comment #553 on page 115 of CARD #23, and the EPA response is provided on page 116. This issue was presented by the EEG to the EPA on December 10, 1997 as 2D/3D Modeling in BRAGFLO.

The FEP Screening Analysis titled S1: Verification of 2D-Radial Flaring Using 3D Geometry (*Vaughn et al.*, 1996) compared the two dimensional radial flaring model of BRAGFLO used in the CCA performance assessment to a three dimensional BRAGFLO model of the repository. The 3-D model calculated a large flow of brine into the repository after the pressure reached the anhydrite fracturing pressure. The large flow did not occur in the 2-D model. Figure 1 shows the pressure history for the two models. The scenario used for the investigation included a drilling intrusion at 1,000 years, accounting for the large drop in pressure at that time. Our concern is the difference in behavior of the two models after the pressures reach 12.7 MPa but prior to 1,000 years.

Figure 2 depicts the calculated brine inflow and outflow rates. The figure shows a large difference in calculated inflows of the two models during the period of 700 to 1,000 years. Figure 3 reinforces the perception that the brine inflow in the 3-D model is large. As shown in Figure 3, during the 700 to 1,000 years period the 3-D model shows a decrease in gas saturation of 0.05. Our concern is that if the brine inflow calculated in the 3-D model persists for thousands of years then the 2-D model calculations significantly under-predict repository saturation at high pressures.

Greater saturations could lead to much larger direct brine release calculations. Figure 4 (Figure 5.1.5 of *Helton*) is the basis of this contention. Figure 4 depicts the relationship of calculated direct brine releases to repository conditions at three separate times. The average repository brine saturation and repository pressure are plotted for each vector on the horizontal plane. A vertical line connects the plane to a small circle at the level of the vertical axis corresponding to the volume of brine calculated to reach the surface. Calculated releases greater than one cubic meter are highlighted using a filled circle.

Figure 4 indicates that there were few calculated direct brine releases when the calculated repository pressures exceeded 12.7 MPa and almost none when the pressure exceeded 14 MPa. Almost all of the larger calculated direct brine releases occurred when brine saturations were above 0.5, a condition never calculated at pressures above 14 MPa. The FEP S-1 analysis suggests that the potential for many of the vectors with great repository pressure to also have large brine saturations. Thus calculated direct brine releases might have both larger volumes and greater frequency in the performance assessment.

EEG Assessment of DOE Response to Comment # 553

The major concern of the EEG is that the 3-D modeling of the repository system indicates the potential for large brine inflow to the repository at high pressure which leads indirectly to the potential of larger direct brine releases than calculated in the CCA. The DOE has presented three independent lines of reasoning to indicate that the EEG's concern is unwarranted. If convinced that any of these lines of reasoning are correct then the EEG will concur with DOE's assessment that the issue is of little concern.

DOE's three arguments are: 1) Additional brine will be consumed by corrosion and the resultant gas generation will not cause greater repository pressures. 2) The difference in the two dimensional and three dimensional models only occurs at pressures above those calculated during the performance assessment for CCA. 3) The changes in the repository consistent with the three dimensional model are of little consequence to the performance assessment.

At this time, the first two of the lines of reasoning appear to be flawed. The third argument relies on the CCA values of actinide solubility that the EEG is not convinced are correct.

1. *Additional brine will be consumed by corrosion and the resultant gas generation will not cause greater repository pressures.*

That additional brine inflow will lead to more gas generation is not questioned. The flaw in this argument is that the potential brine inflow is too large to be consumed in a short period and could lead to large enough amounts of additional gas to significantly effect the pressure. The result could be both larger brine saturations and higher pressures. Figure 1 indicates that lower pressures are also possible. In the FEP S-1 the rate of gas generation was assumed to be constant. Thus, there was no feedback between brine inflow and gas generation in the FEP S-1 study.

The DOE cites the amount of iron remaining in the repository (Figure 5; *DOE*, 1996 Figure 12-13) as support for the argument that more brine inflow will lead to more gas generation not higher saturations. Figure 6 (Figure 2.2.9 of *Helton*) shows less iron remaining

in the lower (waste) panel, presumably due to relatively more brine inflow to the lower panel (Pg 2-18 of Helton, 1996). Figure 7 (Figure 2.2.7 of Helton, 1996) shows that at most 30,000 cubic meters of brine are predicted to be consumed through iron corrosion. In most vectors, the calculated brine consumption was less than 15,000 m³. In many, brine consumption continues through-out the 10,000 year compliance period. Other vectors show a secession of brine consumption after less than 2,000 years, presumably due to exhaustion of available brine (See Section 2.2 of Helton). Figure 2 suggests that brine inflow from fracturing may be on the order of 10 m³ / year or more and continue for hundreds to thousands of years. Drawn on the Figure 7 is a line with a slope of 10 m³ / year. Comparing the brine consumption with this slope indicates that the potential brine flow is large compared to the rate of brine consumption. The potential brine inflow is greater than 10,000 m³. Most of this flow would likely be into the lower panel. The maximum amount of brine consumed in the lower panel was 6,000 m³ (Figure 8, Figure 7.2.1-10 of Bean et al.).

2. *The difference in the two dimensional and three dimensional models only occurs at pressures above those calculated during the performance assessment for CCA.*

DOE cites Figure 9 (Figure 2.3.2 of Helton), showing the 10, 50 and 90 percentile pressures for each replicate for the 10,000 years, as demonstration that pressures will not increase greatly above 12.7 MPa. In fact, Figure 10 (Figure 2.3.1 of Helton), which depicts the pressure history of each vector of replicate 1, indicates that many of the calculated pressures were greater than 13 MPa and that for one vector the calculated pressure reached close to 16 MPa. 16 MPa is less than 2 MPa below the 17.5 MPa peak pressure of the 2-D simulation of the FEP S-1 analysis (Figure 1). The DOE has offered no explanation of what happens between 16 and 17.5 MPa to cause such large brine inflow in the 3-D simulation but not the 2-D simulation. A believable explanation is that the change occurs at initiation of anhydrite fracturing not just above 16 MPa.

3. *The changes in the repository behavior consistent with the three dimensional model are of little consequence to the performance assessment.*

There are two obvious potential impacts on the performance assessment calculations from greater pressure and brine saturations in the repository. Greater pressures would lead to larger calculated releases from the spillings model. If the spillings model described in Hansen et al. is correct then it is unlikely that the volumes brought to the surface because of greater pressures would approach those calculated in the CCA.

Either greater pressures or saturations could lead to much larger direct brine release calculations. Figure 4 indicates that there were very few calculated direct brine releases when the calculated repository pressures exceeded 12.7 MPa and almost none when the pressure exceeded 14 MPa. Almost all of the larger calculated direct brine releases occurred when brine saturations were above 0.5, a condition never calculated at pressures above 14 MPa. The FEP S-1 analysis suggests that the potential for many of the vectors with great repository pressure to also have large brine saturations. Thus calculated direct brine releases might have both larger volumes and greater frequency in the performance assessment.

Direct brine release was a minor component of the total calculated radionuclide releases in the CCA (Figure 11; Figure 6-41 of the CCA). The volumes of direct brine release would have to be two orders of magnitude greater to have an impact on agreement with the containment requirements which is large in relation to a possible increases in the calculated volumes of brine brought to the surface through direct brine release. However, the radionuclide content of brine brought to the surface may be underestimated in the CCA which would make direct brine release of greater significance to the performance assessment (See EEG comments on solubility).

EEG Response to EPA's Resolution of Comment # 553.

The EPA's resolution of this comment relies on the fact that brine and gas saturations are inversely related. This relationship does not necessarily lead to higher brine saturations indicating lower pressures or less gas in the repository. The statement that the 2-D model may overestimate gas saturation by underestimating brine saturations will lead to the prediction of higher gas pressures than those that would have been predicted with the 3-D configuration and this will result in more conservative estimates of releases. This is a conclusion that the 3-D modeling results may indicate is not valid.

Consider Figure 4. This figure provides a plot of calculated brine saturation and pressure conditions in the repository at three separate times for undisturbed performance. This figure shows a correlation of brine saturation with repository pressure. There are at least three mechanisms that may lead to such a correlation:

A) Faster corrosion rates lead to more gas generation, less brine and greater pressures. Table 1 (Table 2.3.1 of Helton) lists the parameters most closely correlated with pressure in the lower waste panel. The list results from a step wise rank regression of the sampled parameters with pressure. The parameter that correlates the most pressure is listed first. The table lists the microbial degradation of cellulose and rubber and plastics (WMICDFLG) as the most important factor with halite porosity (HALPOR) next. Table 1 indicates that sampled corrosion rate (WGRCOR) is not a dominant factor in repository pressure. Halite porosity is a reasonable surrogate for brine availability (see Figure 2.1.5 of Helton).

Table 2 (Table 2.2.2 of *Helton*) lists halite porosity as by far the most important controlling factor over iron consumption. The second most important factor is the corrosion rate. Other parameters identified as slightly correlated with repository pressure and fraction of steel remaining are: ANHPRM (unfractured anhydrite permeability), SALPRES (Far field pressure in the Salado Formation), SHRGSSAT (residual gas saturation in the shaft seal), and WASTWICK (the parameter describing the tendency of brine to be pulled above the lower part of a room by capillary forces)

Figure 12 (Figure 2.4.3 of *Helton*) provides important supporting evidence. The figure presents the fraction of iron remaining in the lower waste panel (FEREM_W) or in the rest of the repository (FEREM_R) with respect to halite porosity, microbial degradation, steel corrosion rate. The plots of remaining iron and halite porosity suggest that a sufficient supply of brine is needed for iron consumption but other factors also limit corrosion. The main factor is probably corrosion rate. Figure 12 shows that low corrosion rates limit iron consumption, but that predicted iron consumption is not strongly dependent on corrosion rate. The comparison of iron remaining to microbial degradation is important because its strong correlation with repository pressure (Table 1). These plots show that the fraction of iron remaining in the repository is only weakly correlated with microbial degradation and that the correlation is positive e.g. microbial degradation, hence pressure, is inversely correlated with iron consumption. This inverse correlation is probably linked to the availability of brine.

B) Less brine flows into the repository at high pressures, at least in the 2-D BRAGFLO model used for the CCA performance assessment.

C) The repository inflates as the pressure rises (Figure 13; Figure 2.3.5) leading to more void space and lower saturations per unit volume of brine. Figure 13 indicates that the calculated void space in the repository is twice as large at 12 MPa than at 5 MPa and nearly three times at 16 MPa. Thus, the correlation of brine volume to pressure is much weaker than the correlation of saturation to pressure seen in Figure 4.

The FEP S-1 screening analysis concluded that the increased brine inflow to the repository in the 3-D simulation did not increase release to the accessible environment through the marker beds. The EEG agrees with this conclusion. It has not been demonstrated, however, that the increased flow into the repository predicted using the 3-D geometry will not lead to much greater releases from human intrusion. The 3-D modeling indicates that there is a potential for the combination of high pressure and relatively high brine saturation in the repository at the same time. This combination did not occur in the performance assessment modeling for the CCA and thus conclusions of the impact on radionuclide releases due to human intrusion can not be assessed using the CCA performance assessment.

The DOE has not yet demonstrated that the performance assessment modeling for the CCA accurately represents the potential repository conditions. The results of FEP S-1 screening analysis suggest that the two dimensional BRAGFLO model used in the CCA calculations may be misrepresenting repository performance at pressures above the anhydrite fracture pressure.

Recommendations for Resolving the Issue

To resolve this issue, the EEG recommends that a few 3D BRAGFLO simulations of the repository should be performed using the parameter values of vectors used in the CCA performance assessment. The 3D BRAGFLO simulations should be used to provide repository conditions for the normal suite of direct brine release calculations. The calculations should also be assessed in terms of impact on spillings calculations. Spallings simulations are probably not required to assess the impact. The following criteria may be used to select the CCA vectors for running the 3D simulations to bound the magnitude of the problem:

- Since the discrepancy occurs above the fracture initiation pressure, the simulations should be limited to parameter vectors that result in pressures above 12.7 MPa at some time during the 10,000 year time frame.
- Direct brine release calculations should be sensitive to increased brine saturations above the waste residual brine saturation. Vectors that had either large brine saturations or a mobile brine component (saturations above the residual saturation) are more likely to be sensitive to increased brine inflow. Figure 5.1.5 of the preliminary sensitivity analysis report (Helton, 1996) indicates one vector with a 10,000 year pressure above 14 MPa and a brine saturation above 0.4. This is a likely candidate.
- The potential for brine consumption by corrosion should be assessed. Vectors with both slow and fast corrosion rates that also meet the above two criteria should be run.
- If the first simulations indicate a large change in saturation, then assess whether the 3D BRAGFLO simulations indicate a much larger number of significant direct brine releases than those calculated in the CCA. Simulations using brine saturations on the order of 0.1 and 0.3 should be performed.

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Bean, J.E., M.E. Lord, D.A. McArthur, R.J. MacKinnon, J.D. Miller, and J.E Schrieber, , 1996, Analysis Package for the Salado Flow Calculations (Task 1) of the Performance Assessment Analysis Supporting the Compliance Certification Application (WPO # 40514).

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Vaughn, P., T. Hadgu, D. McArthur, and J. Schreiber, FEP Screening Analysis S1: Verification of 2-D Radial Flaring Using 3D Geometry, Memorandum to D.R. Anderson, January 26, 1996, WPO 30840, Sandia National Laboratory, Attachment 4-1 to Appendix Mass of the Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, DOE/CAO-1996-2184, December, 1996.

Figures

Figure 1: Average Pressure in Repository, FEP S-1 Analysis
From Vaughn et al, 1996.

Figure 2: Cumulative Net Brine in and outflow at Repository, FEP S-1 Analysis
From Vaughn et al, 1996.

Figure 3: Average Gas Saturation in Repository, FEP S-1 Analysis
From Vaughn et al, 1996.

Figure 4: Three dimensional scatter plots for volume of brine reaching the surface due to direct brine release for a drilling intrusion into the lower panel.
From Helton, 1996.

Figure 5: Fraction of Initial Iron Remaining in Repository
From: DOE, 1996.

Figure 6: Remaining Fraction of Steel Inventory in Waste Panel
Modified from Figure 2.2.9 in Helton, 1996.

Figure 7: Cumulative Volume of Brine Consumed by Corrosion in the Repository
Modified from: Helton, 1996.

Figure 8: Cumulative Volume of Brine Consumed in the Waste Panel
From Bean et al., 1996

Figure 9: Percentile curves for three replicated LHSs for pressure in waste panel
From: Helton, 1996.

Figure 10: Pressure in waste panel
Modified from Figure 2.3.1 of Helton, 1996.

Figure 11: Mean CCDFs for Specific Release Modes, Replicate 1.
From DOE, 1996.

Figure 12: Scatter Plots of the Fraction of Iron Remaining in the Waste Panel (Right Frames) and Rest of the Repository (Left Frames) for Undisturbed Conditions at 10,000 Years.
From Helton, 1996.

Figure 13: Scatter plot of pressure versus total pore volume in the repository.
From Helton, 1996.

Tables

Table 1: Stepwise Regression Analysis with Rank-Transformed Data for Pressure in the Waste panel at 10000 years. From Helton, 1996.

Table 2: Stepwise Regression Analysis with Rank-Transformed Data for Fraction of Steel Remaining and Total Gas Generation in Upper and Lower Waste Panels at 10000 years.
From Helton, 1996.

FULL TEXT OF ORIGINAL EEG COMMENT

Environmental Evaluation Group Review of the WIPP-CCA, 3/14/97

BRINE INFLOW FROM SALADO: 2-D VERSUS 3-D GEOMETRY IN BRAGFLO

The 2-D geometry used in the BRAGFLO appears to have caused an under-prediction of brine inflow to the repository and thus may have resulted in a significant under-prediction of the direct brine release. This assumption may also have effected the amount of releases predicted by the spillings scenario.

The justification for modeling the repository in a pseudo 3-D manner (2-D radial flaring) rather than in a full 3-D geometry has been provided through evaluation of FEP S-1. The summary memo of record for the FEP S-1 screening analysis¹ discusses the impact of the 2-D assumption on 1) brine flow through the anhydrite layers to the 2.4 km boundary, 2) flow to the top of the shaft, 3) brine flow up the borehole, and 4) the repository pressure. This memo does not consider the effects of the 2-D assumption on the inflow of brine to the repository, and on the spillings or direct brine releases.

The amount of projected inflow of brine in the repository directly effects the gas pressure in the repository. Table 5.5.3 of the sensitivity analysis report² lists the residual gas saturation as the parameter with the strongest influence on the projected direct brine releases. This is also shown in Figure 5.1.5 of the sensitivity analysis report (the attached Figure 1). In addition, brine inflow is important to the spillings release estimates through increased gas generation. This dependence is made clear in Table 4.4.3 of the sensitivity analysis report which lists halite porosity, a large source of brine, as the second most important parameter to spillings releases.

The screening analysis compared 2-D simulations of the repository to 3-D simulations of the repository. For computational efficiency, the calculations were performed for half the repository. Two sets of simulations were conducted for the analysis. One set of calculations used a gas generation rate below the level that would cause anhydrite bed fracturing. The second used twice the gas generation rate to ensure anhydrite bed fracturing. In both sets, less brine-inflow occurred in the 2-D case compared to the 3-D geometry. No dependency of gas generation on brine inflow to the repository was included in the calculations; gas generation was prescribed as a function of time, ending after 1,000 years in the screening calculations.

The largest impact of 2-D geometry occurs with anhydrite bed fracturing. The 3-D model predicts the flow into the repository to significantly increase if the anhydrite beds fracture, while the 2-D model predicts the flow to decrease in relation to calculations without anhydrite fracturing.

Figure 15 of the FEP S-1 analysis (Figure 2) shows the cumulative brine inflow to the repository for the high gas generation calculations. The flows calculated using the 3-D model indicate that once anhydrite bed fracturing occurs roughly 2×10^6 kg ($1,600 \text{ m}^3$) of brine enters the repository in a period of 200 to 300 years and that this flow rate was continuing unabated at the time of drilling intrusion. Another 4×10^6 kg ($3,200 \text{ m}^3$) flowed into the repository shortly after the drilling intrusion. Figure 2 shows differences of 4×10^6 to 6×10^6 kg ($3,200$ to $6,500 \text{ m}^3$) for much of the 10,000 years. The brine inflow differences listed above should be doubled for the full repository. Virtually no flow enters the repository as a result of anhydrite bed fracturing in the 2-D geometry. In fact, the net flow over the 10,000 year simulation is less with anhydrite fracturing compared the simulation without the beds fracturing. Figure 2.1.4 of the sensitivity analysis report² (Figure 3) indicates very little marker bed inflow with microbial gas generation of plastics and

¹Vaughn, P., T. Hadgu, D. McArthur, and J. Schreiber, FEP Screening Analysis S1: Verification of 2-D-Radial Flaring Using 3D Geometry, Memorandum to D.R. Anderson, January 26, 1996, WPO 30840, Sandia National Laboratory, Attachment 4-1 to Appendix Mass of the Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, DOE/CAO-1996-2184, December, 1996.

²Helton, Jon, Preliminary Summary of Uncertainty and Sensitivity Analysis Results Obtained in Support of the 1996 Compliance Certification Application for the Waste Isolation Pilot Plant, Memo, Sandia National Laboratories, December, 1996.

rubber, supporting the findings of the FEP analysis. Figure 5.1.5 of the sensitivity analysis report reveals the importance to direct brine release of these low brine inflows. The highest pressures are correlated with brine saturations below the residual brine saturation of the waste. The low saturations are due partly to increasing repository pore space with increasing pressure and partly to lower brine inflow.

Table 2.5.13 of the sensitivity analysis report indicates that the potential for anhydrite bed fracturing is high. As a crude approximation, consider the undisturbed scenario of a total fracture-enhanced flow of 20,000 m³ over a period of 2,000 years. The highest repository pressure in the FEP S-1 calculations was 13 MPa [Correct value is 16.5 MPa]. This corresponds to a repository pore space of 85,000 m³ (Figure 2.3.5 of the sensitivity analysis report)[at 13 MPa]. The increased brine flow would increase the average brine saturation by 0.23. The CCA calculations do not include simulations of both very high pressure and brine saturations above the residual brine saturation of the waste. Inspection of Figure 5.1.5 suggests a significant impact from a 0.23 saturation shift at high pressures.

The simulations without anhydrite fracturing show a decrease of 1x10⁶ to 2x10⁶ kg (800 to 1,600 m³) in predicted brine inflow in the 2-D simulations compared to the 3-D simulations(Figure 4; Figure 10 of the FEP S-1 memo). These flows are doubled for the full repository. The differences are most likely from differences in marker beds flows to the repository.

To put these brine inflow differences in perspective, note that average brine inflow to the repository in the CCA calculations of the similar S5 scenario was almost 40,000 m³, with an average 8,000 m³ from the marker beds². Marker bed brine flows in the S5 scenario are dominated by flows under low pressure conditions. The marker bed flows are a more significant concern in the S1 undisturbed scenario. An average of roughly 3,000 m³ flowed into the repository from the marker beds in the S1 CCA calculations. To approximate the brine flow error in the undisturbed calculations for pressures below the anhydrite fracture threshold, we ratio the FEP S-1 differences by 3,000/8,000 - resulting in the range of 600 to 1,200 m³ less brine inflow to the full repository. If 1,200 m³ of brine were distributed throughout the entire repository it could increase the average saturations by 0.015 to 0.03 (0.04 to 0.08 in the S5 scenario and 0.16 to 0.32 after anhydrite fracturing in an S5 scenario). It is more likely that much of the additional brine would be consumed through increased gas generation, leading to higher repository pressures.

There are indications in the sensitivity analysis report that the computational grid effects the distribution of brine within the repository in addition to the overall magnitude of brine. One indication is the statement on page 2-26 that "Due to the computational grid in use (Fig. 1.2.1), the lower panel receives more brine inflow from the marker beds relative to its size than the upper waste panels (Fig. 2.1.2)." Another indication may be the importance of the residual gas saturation of the shaft seals to flow through the marker beds (Table 2.1.1 of the sensitivity analysis report). As stated in the report, "its selection may be due to effects related to brine and gas movement across the part of the computational grid that corresponds to the shaft in the repository and DRZ (i.e., regions 10,11 in Fig. 1.2.1)." As a result, the upper waste panels receive roughly one ninth of the brine inflow from the marker beds per panel as the lower waste panel. In a large fraction of the sampled vectors, gas generation stops in the upper panels because of limited brine availability for steel corrosion. Thus, the CCA calculations are under-predicting repository pressure as well as brine saturation.

The EEG concludes that the use of a 2-D geometry in the BRAGFLO may introduce significant non-conservatism into the CCA calculations. The FEP S-1 needs to be re-examined with appropriate consideration of the impact of increased brine saturation on calculated release estimates.

DOE Response to the EEG Comments

Attached to Letter by GE Dials to L. Weinstock, *DOE Response to Comments made to EPA by EEG on the DOE's CCA Dated March 14, 1997.*, June, 27, 1997.

Brine inflow to the repository

Vaughn et al. justified the use of the 2-D radial-flaring BRAGFLO model by comparing the results of the 2-D model with those of a corresponding 3-D model. However, the limits of the analysis exceeded the highest predicted pressures in the repository by approximately 4 to 5 MPa.

The 2-D and 3-D model results show reasonable agreement, except under conditions where fracturing of the anhydrite beds occurs (at pressures above 12.7 MPa). The 3D model predicted a greater flow of brine into the repository than the 2-D model when the pressure in the repository was sufficient to increase porosity in the fractured anhydrite beds. However, the high constant gas generation rate assumed in the *Vaughn et al.* analysis resulted in peak average pressures in the repository of about 17.5 MPa (2-D BRAGFLO) and 16.5 MPa (3-D BRAGFLO) (*Vaughn et al.*, Figure 11) (not 13 MPa as stated by the EEG), which are greater than the highest pressures expected in the repository (see *Helton*, Figure 2.3.2). Thus, the large increases in average anhydrite porosity and associated brine inflow predicted by 3DBRAGFLO are not likely to occur in the repository.

Vaughn et al. assumed constant gas generation rates with no brine consumption. In reality, any additional brine entering the repository would likely be consumed by gas generation processes, which would limit brine saturation. PA calculations show that significant

amounts (at least 409G of the initial inventory) of uncorroded iron will persist throughout the 10,000 year regulatory period under conditions of undisturbed performance (CCA Figure 9-10). The extent of corrosion is limited by the amount of brine available, and the iron inventory will not be exhausted as a result of the increase in brine flow to the repository predicted by 3D-BRAGFLO. Subsequent to an intrusion the pressure within the repository is relieved and remains below the fracture initiation pressure. EEG acknowledges that higher brine saturations would not necessarily occur as a result of increased brine flow to the repository, but that increased brine flow would lead to increased gas generation. Increased volumes of gas generated at high pressures (above 12.7 MPa) would tend to result in increased porosity in the fractured anhydrite rather than significant increases in pressure. Helton (Figure 2.3.1) showed that repository pressures do not increase greatly above 12.7 MPa (after fracturing has occurred).

Pressures sufficiently high to cause fracturing (12.7 MPa) tend to occur at low brine saturations (Helton Figure 5.1.5) due to the consumption of brine by corrosion. If brine inflow occurs at the high pressures suggested by the 3-D BRAGFLO analysis (in excess of 16.5 MPa), then brine saturation in the repository could increase. The EEG suggests that brine saturation could increase by as much as 23 % at such pressures. However, as discussed above, this value of pressure is unrealistically high given that gas generation processes could consume most of any additional brine entering the repository. Nonetheless, even with the unrealistic assumption that brine saturation increases by 23%, Figure 5.1.5 of Helton shows that the number of simulations in which direct brine release resulting from a drilling intrusion occurs would not increase significantly. Although accounting for higher brine saturations could increase cumulative direct brine releases, the overall CCDFs from all release pathways would be little changed because of the relatively minor contribution of direct brine release to overall releases (CCA Figure 641).

In summary, the set of conditions where the 3D-BRAGFLO and 2D-BRAGFLO do not show good agreement (average pressures above 16 MPa) are not expected to occur in the repository. Even if such pressures did occur, resulting in anhydrite fracturing and porosity increase, the brine inflow predicted by 3D-BRAGFLO would have little effect on direct brine release during a drilling intrusion.

EPA Response to Comment # 553

EPA disagrees with the comment. The work that is most relevant to this concern is the FEP Screening Analysis titled S1: Verification of 2D-Radial Flaring Using 3D Geometry, WBS No. 1.1.6.3, SANDIA WIPP CENTRAL FILES-A: 1.2.07.3: PA:QA:TSK:S1, ERRATA - February 19, 1996 (SNL WPO #30840). In this work, a simplified version of the two dimensional CCA PA grid was tested against a corresponding three-dimensional (3-D) model. BRAGFLO was used in both two-dimensional (2-D) and 3-D simulations, and TOUGH28W was used to model the 3-D simulations only. Simulation results were compared for cases with an average repository gas generation rate, and a gas generation rate that was double the average. The results of the second case, in which the gas generation rate was doubled, indicates that a combination of pressure induced fracturing and the 1-degree dip cause flow paths which are different for the 2-D and 3-D grids. Once fracturing of the interbeds occurs, the 3-D model displays an immediate migration of gas primarily out of the west side of the repository into the anhydrite layers, accompanied by brine inflow to the repository. This phenomenon is not seen in the results from the 2-D model, in which the west side of the repository is a no flow boundary, which demonstrates that the 2-D and 3-D simulations show local variations. However, the results also show that the predictions of brine flow to the accessible environment are similar for both 2-D and 3-D grids. With respect to increased brine saturation, Figures 7 and 12 of the FEPs Screening Analysis referenced above (WPO# 30840), shows the average gas saturations calculated with the 3-D simulations of TOUGH28 and both the 2-D and 3-D versions of BRAGFLO. Simulation results are compared for the base case and twice the base case generation rates, respectively. These curves indicate that gas saturations are higher in the 2-D simulations (WPO# 30840, page 27). Since brine and gas saturations are inversely related a similar trend would be observed for the brine saturations. In the Performance Assessment Verification Test (PAVT) , it was determined that the greatest potential releases could be attributed to those associated with spallings and direct brine releases. Furthermore, these releases are pressure controlled and will not occur if repository pressures are below 8 MPa. The fact that the 2-D model may overestimate gas saturation by underestimating brine saturations will lead to the prediction of higher gas pressures than those that would have been predicted with the 3-D configuration and this will result in more conservative estimates of releases. Based on this, EPA believes that the 2-D geometry used in the BRAGFLO CCA PA calculations is a reasonable simplification and that the predicted results are conservative.

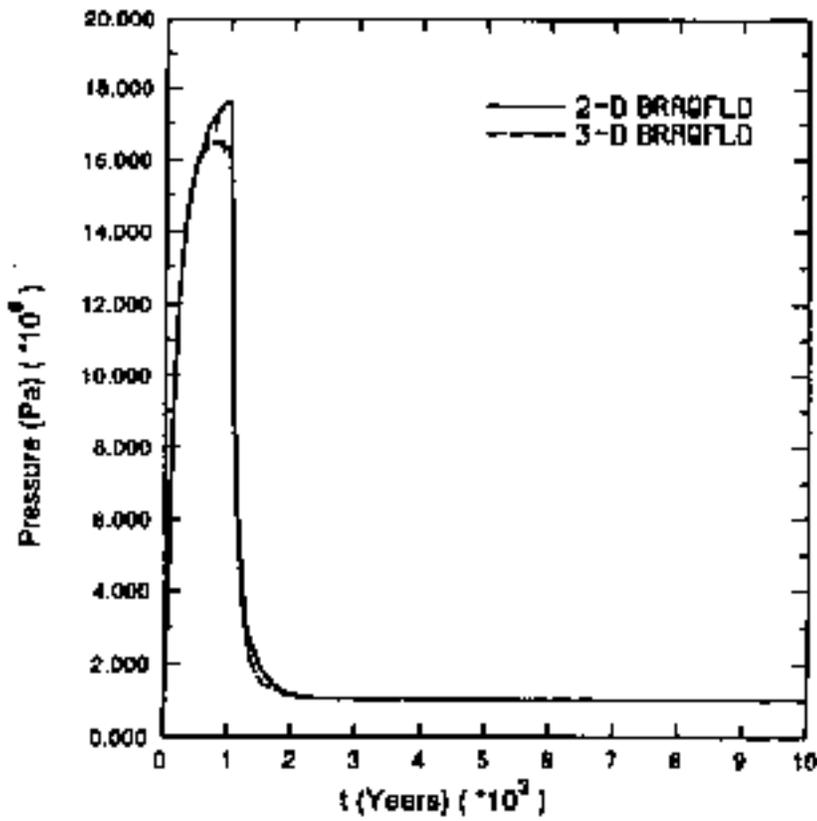


Figure 1: Average Pressure in Repository, FEP S-1 Analysis From Vaughn et al, 1996.

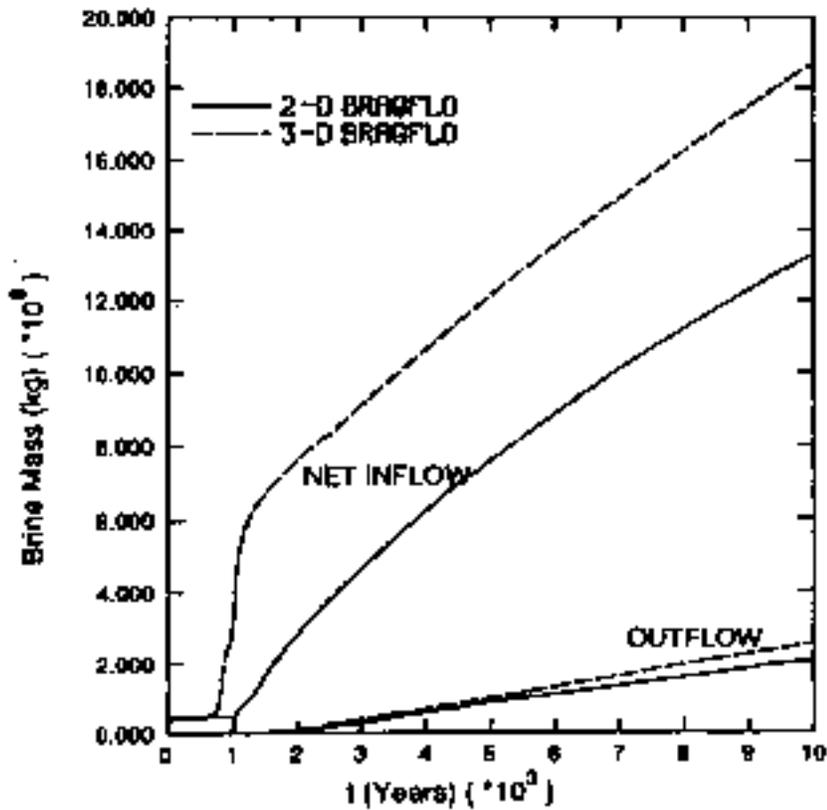


Figure 2: Cumulative Net Brine in and outflow at Repository, FEP S-1 Analysis From Vaughn et al, 1996.

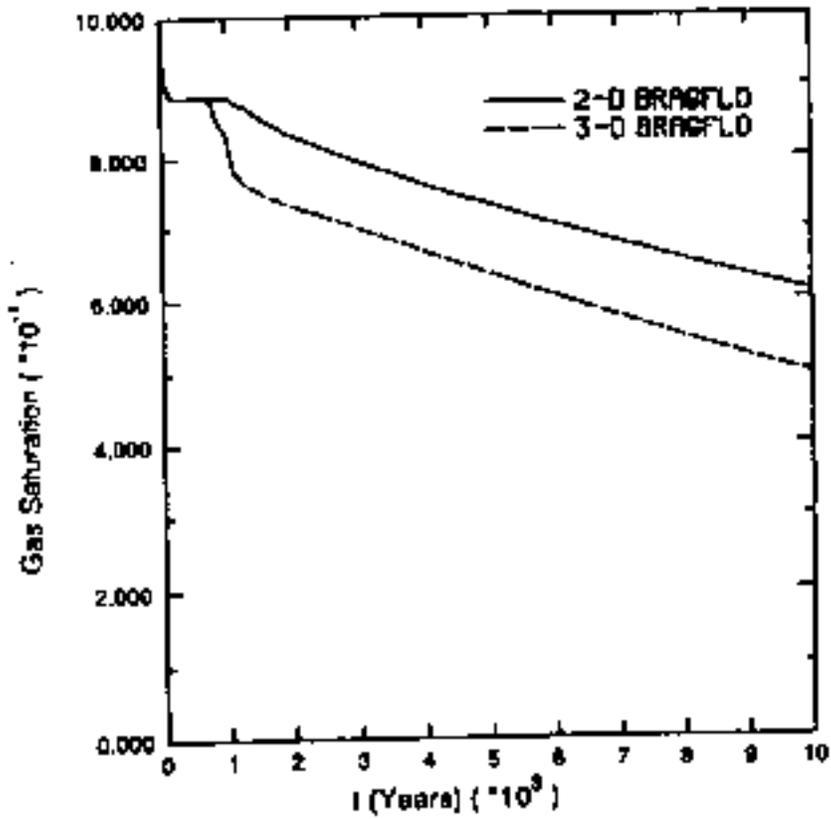


Figure 3: Average Gas Saturation in Repository. FEP S-1 Analysis
 From Vaughn et al, 1996

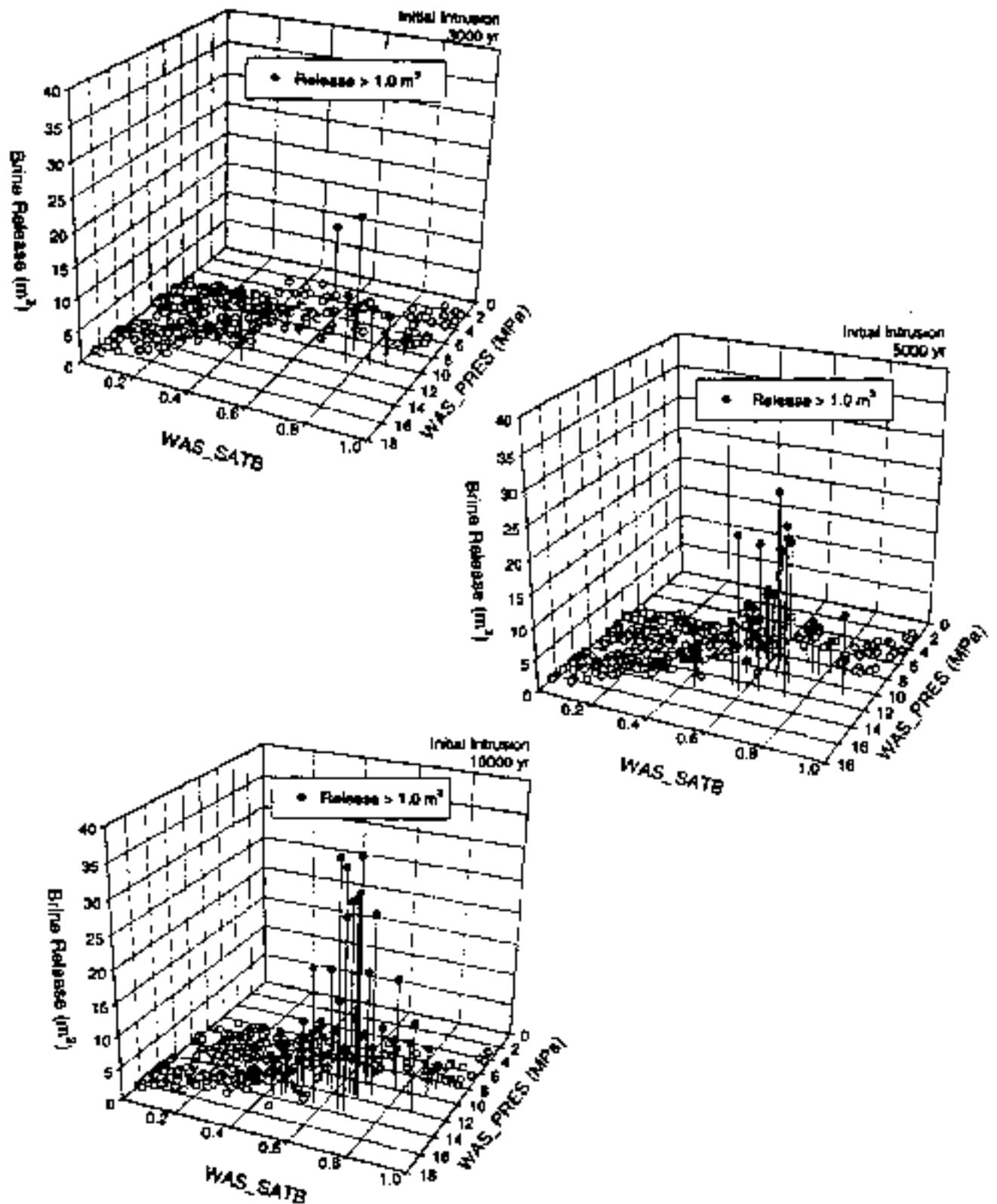


Figure 4: Three dimensional scatter plots for volume of brine reaching the surface due to direct brine release for a drilling intrusion into the lower panel. From Helton, 1996.

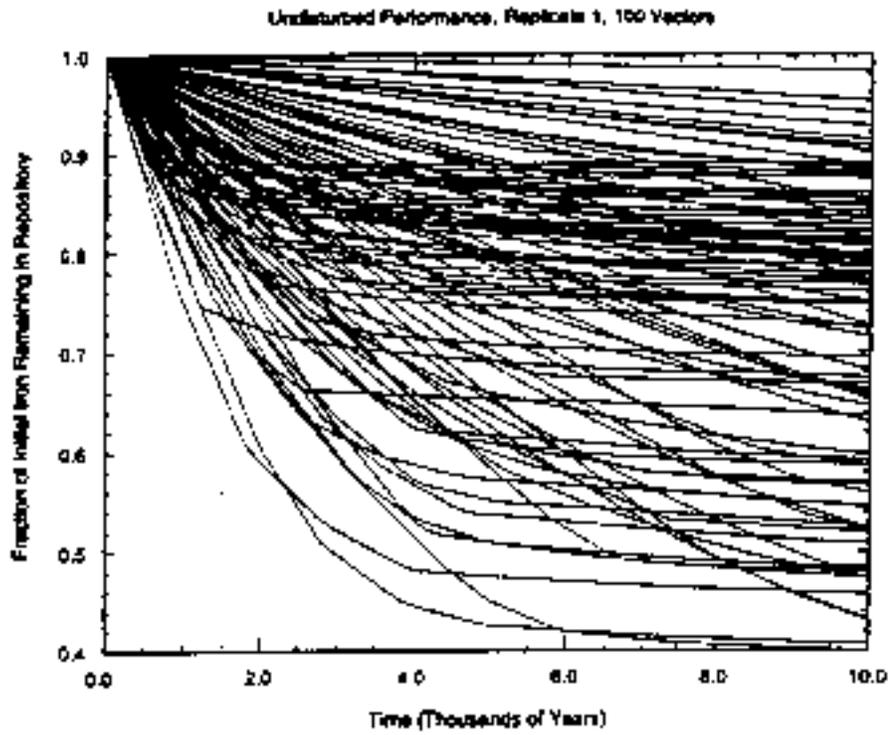


Figure 5: Fraction of Initial Iron Remaining in Repository
From: DOE, 1996.

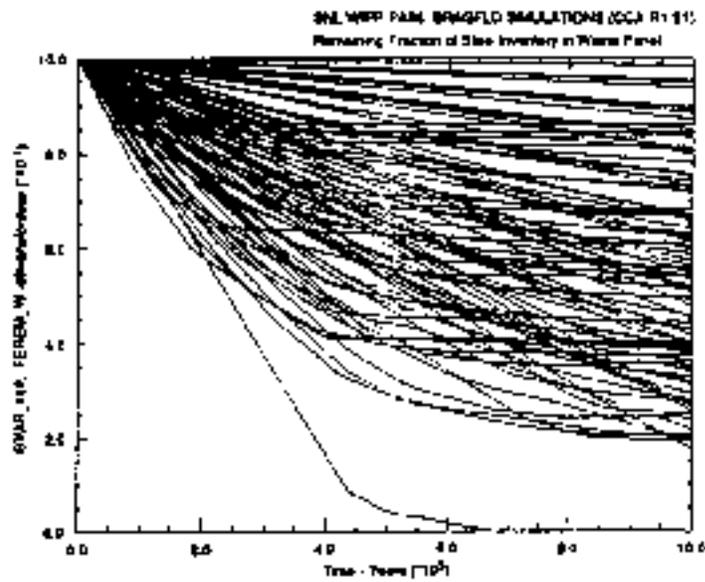


Figure 6: Remaining Fraction of Steel Inventory in Waste Panel
Modified from Figure 2.2.9 in Helton, 1996.

Brine Consumed

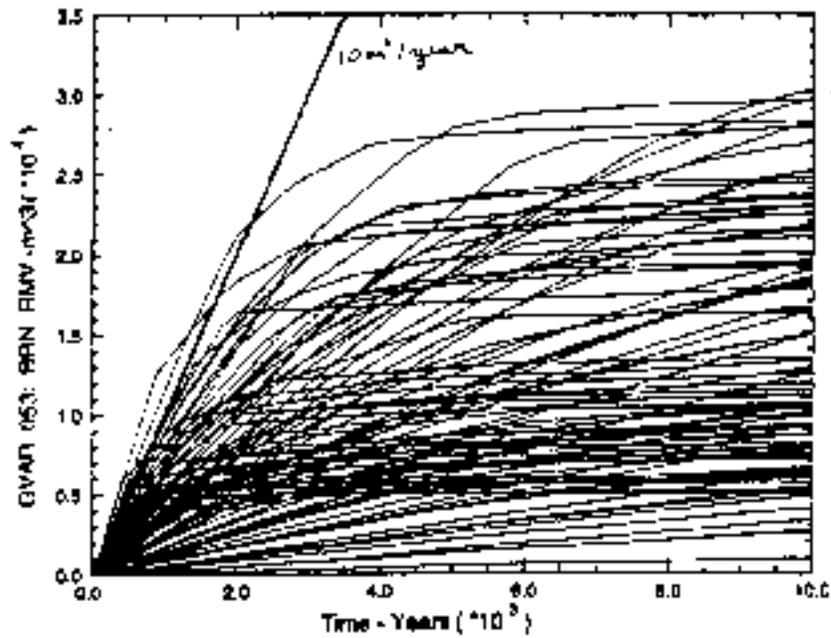


Figure 7: Cumulative Volume of Brine Consumed by Corrosion in the Repository Modified from: Helton, 1996.

Brine Consumed in Waste Panel

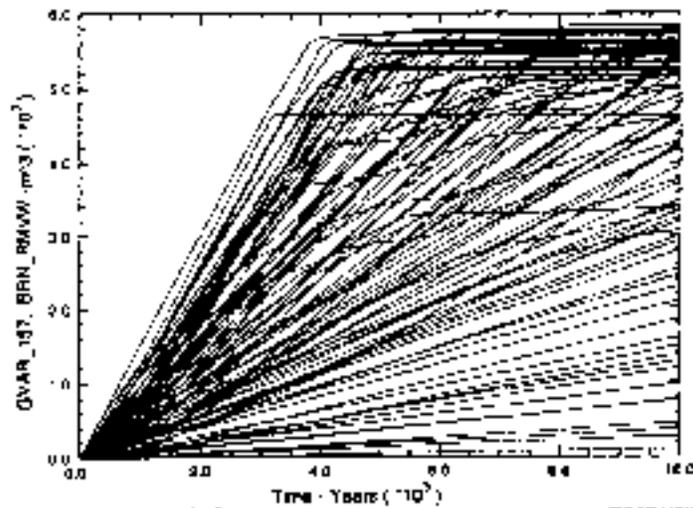


Figure 8: Cumulative Volume of Brine Consumed in the Waste Panel From Bean et al., 1996

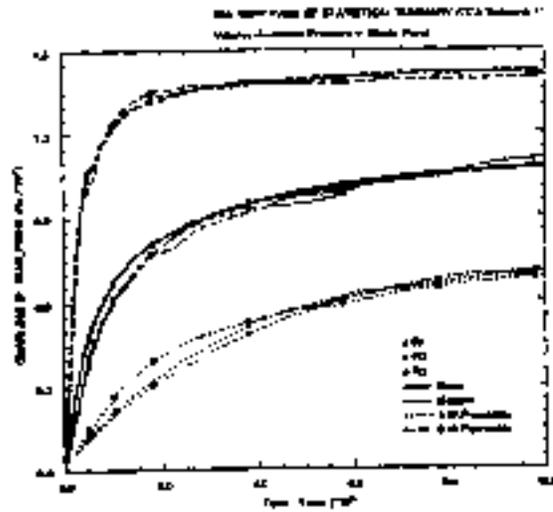


Figure 9: Percentile curves for three replicated LHSs for pressure in waste panel
From: Helton, 1996.

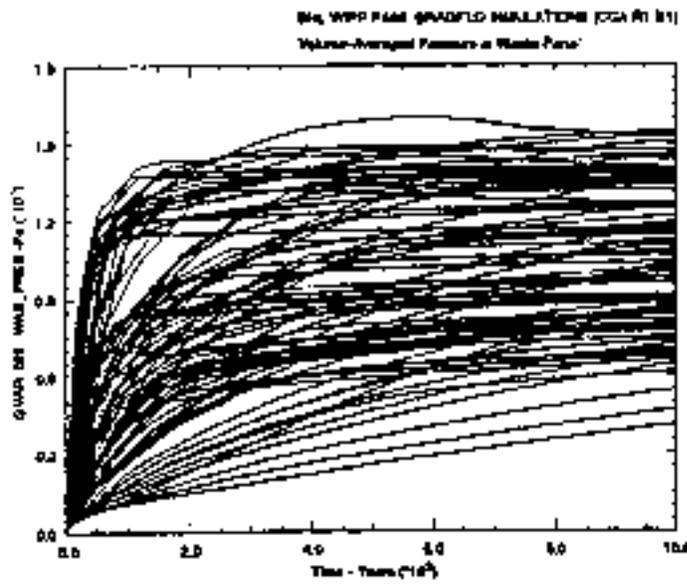
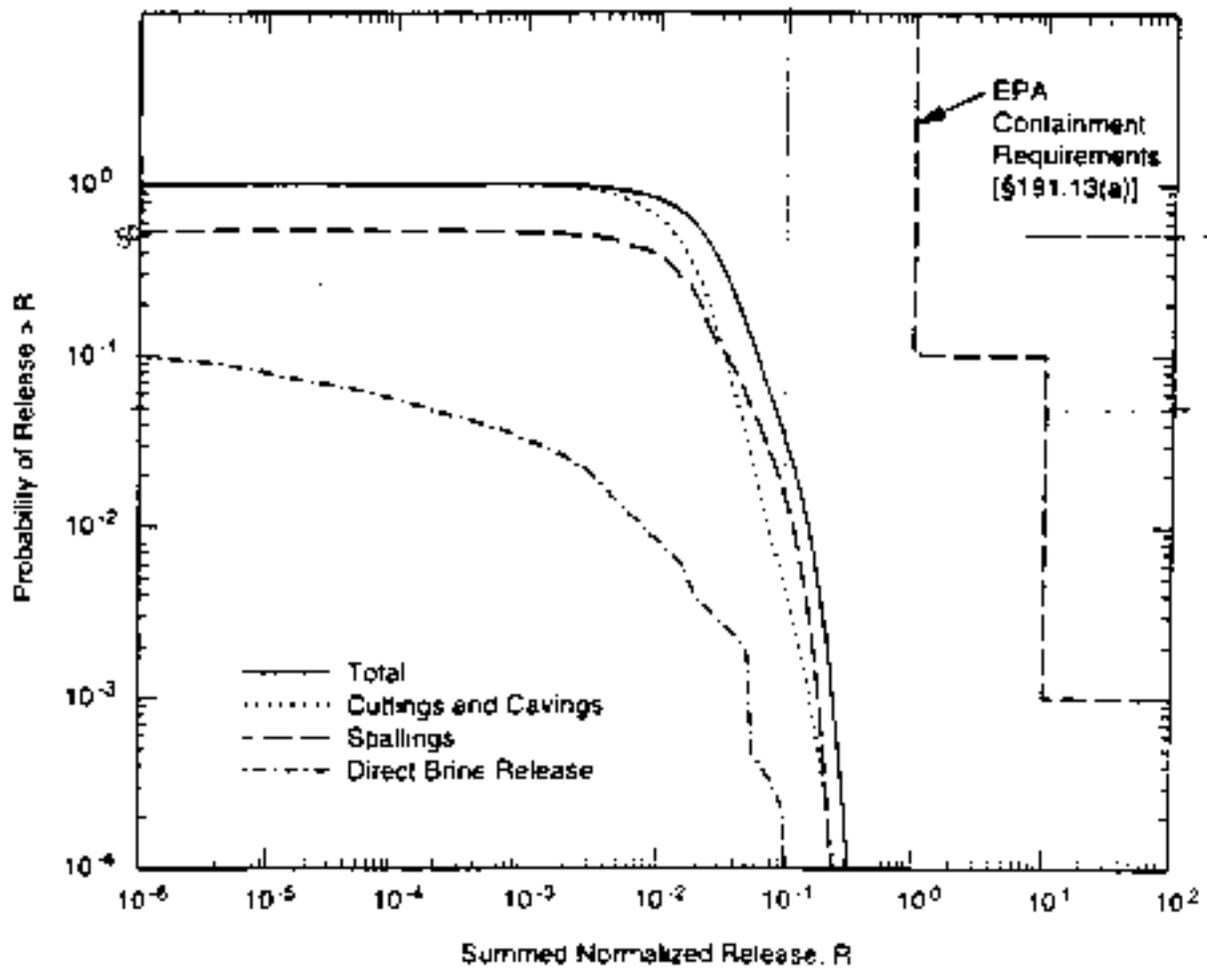


Figure 10: Pressure in waste panel
Modified from Figure 2.3.1 of Helton, 1996.



CCA-140-3

Note: Mean CCDFs are shown for the total normalized release (this curve is also shown in Figure 6-40 and is the mean of the family shown in Figure 6-35) and for the normalized releases resulting from cuttings and cavings, spallings, and direct brine release. The mean CCDF for subsurface releases resulting from groundwater transport is not shown because these releases were less than 10⁻⁶ EPA units and the CCDF cannot be shown at the scale of this figure.

Figure 11: Mean CCDFs for Specific Release Modes, Replicate 1.
From DOE, 1996.

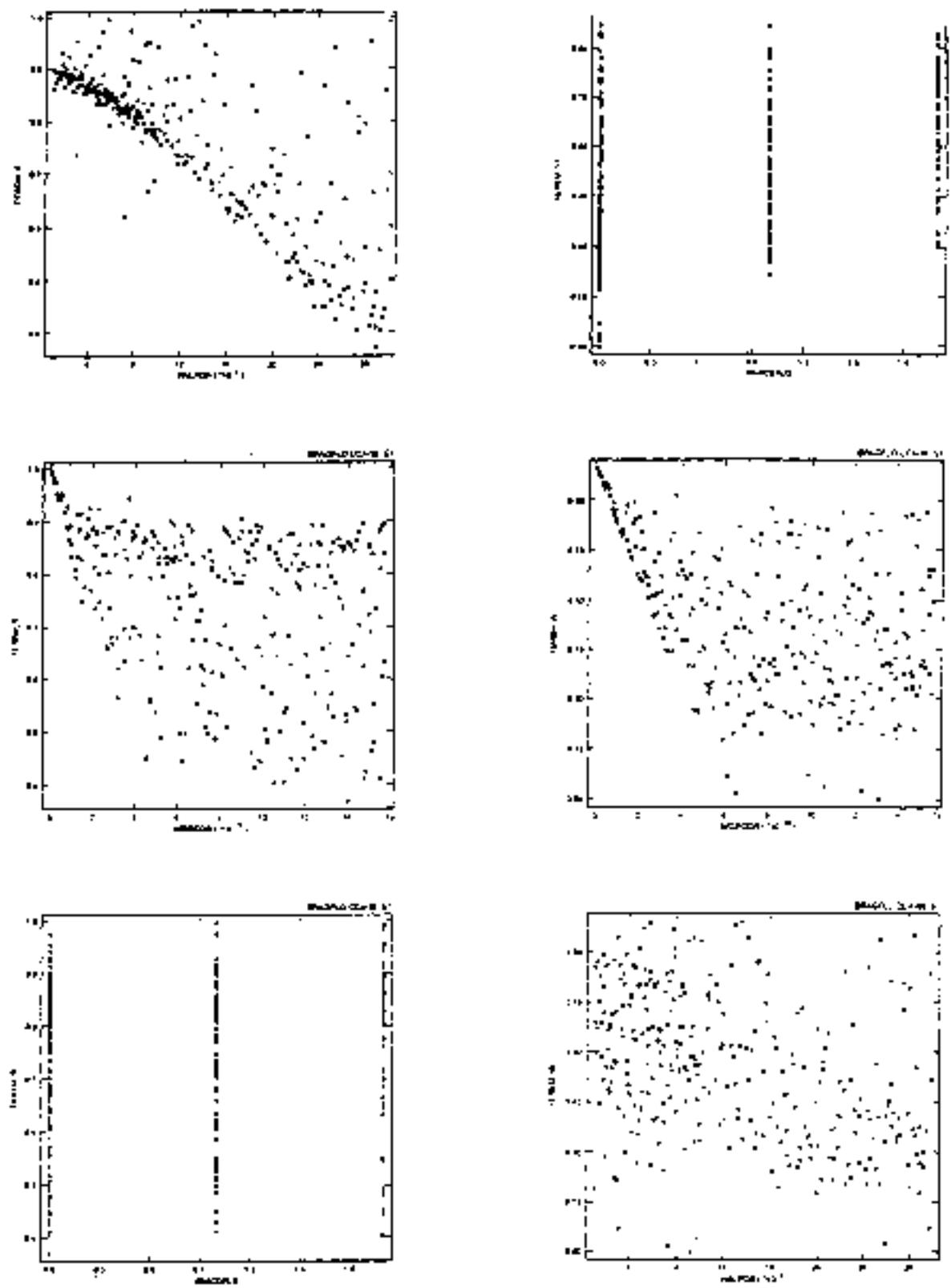


Figure 12: Scatter Plots of the Fraction of Iron Remaining in the Waste Panel (Right Frames) and Rest of the Repository (Left Frames) for Undisturbed Conditions at 10,000 Years. From Helton, 1996.

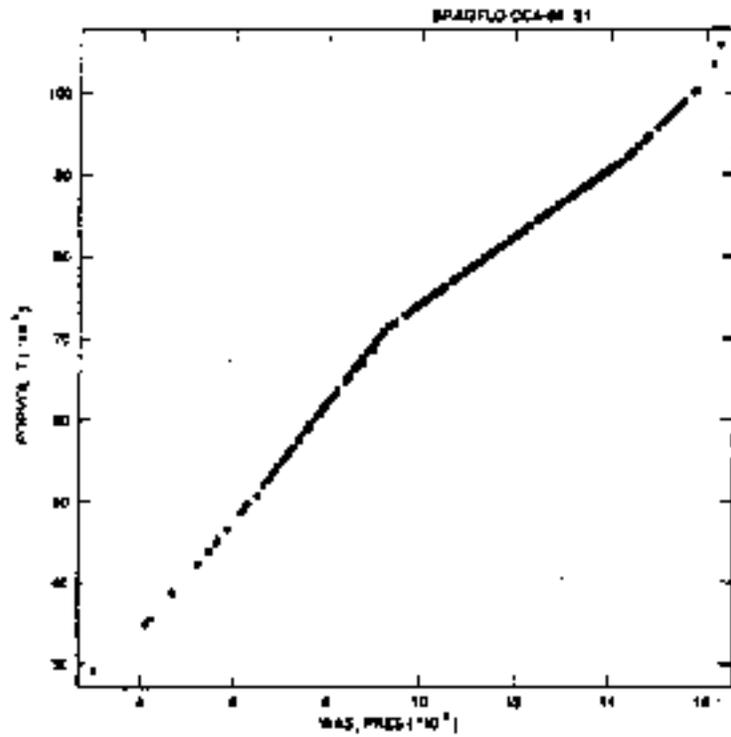


Figure 13: Scatter plot of pressure versus total pore volume in the repository. From Helton, 1996.

Table 1: Stepwise Regression Analysis with Rank-Transformed Data for Pressure in the Waste panel at 10000 years. From Helton, 1996.

Step ^a	Variable ^b	SRRC ^c	R ^{2d}
1	WMICDFLG	0.71	0.52
2	HALPOR	0.45	0.73
3	WGRCOR	0.23	0.79
4	ANHPRM	0.11	0.80
5	SALPRES	0.07	0.80
6	SHRGSSAT	0.06	0.81

^a Steps in stepwise regression analysis.

^b Variables listed in order of selection in regression analysis with ANHCOMP and HALCOMP excluded from entry into regression model.

^c Standardized regression coefficients in final regression model.

^d Cumulative R² value with entry of each variable into regression model.

Table 2: Stepwise Regression Analysis with Rank-Transformed Data for Fraction of Steel Remaining and Total Gas Generation in Upper and Lower Waste Panels at 10000 years. From Helton, 1996.

Step ^a	Fraction Steel Remaining Upper Waste Panels			Fraction Steel Remaining Lower Waste Panels			Total Gas Generation Upper Waste Panels			Total Gas Generation Lower Waste Panels		
	Variable ^b	SRRC ^c	R ^{2d}	Variable	SRRC	R ²	Variable	SRRC	R ²	Variable	SRRC	R ²
1	HALPOR	-0.78	0.63	WMICDFLG	0.46	0.20	WMICDFLG	0.65	0.43	WGRCOR	0.47	0.23
2	WGRCOR	-0.35	0.75	WGRCOR	-0.45	0.41	HALPOR	0.58	0.77	HALPOR	0.45	0.44
3	WMICDFLG	0.12	0.76	HALPOR	-0.38	0.56	WGRCOR	0.24	0.83	ANHPRM	0.33	0.55
4	WASTWCK	-0.10	0.77	ANHPRM	-0.25	0.63	WASTWCK	0.07	0.83	WMICDFLG	0.17	0.58
5	SHRGSSAT	-0.08	0.78	HALPRM	-0.09	0.67	SHRGSSAT	0.06	0.83	HALPRM	0.12	0.59
6	RPINTPRS	-0.06	0.78	SHRGSSAT	-0.09	0.64				SHRGSSAT	0.08	0.60

^a Steps in stepwise regression analysis.

^b Variables listed in order of selection in regression analysis with ANHCOMP and HALCOMP excluded from entry into regression model.

^c Standardized regression coefficients in final regression model.

^d Cumulative R² value with entry of each variable into regression model.

Issue: Compliance Failure as a Result of Spalled Material Reaching the Accessible Environment

Introduction

The issue of spalled material reaching the accessible environment at the WIPP has undergone much research within the past few years (Berglund, 1994; DOE, 1996; Hansen et al., 1997). Spall is the mechanical failure of waste due to high repository gas pressures that could be induced by a drop in pressure from a drilling intrusion. This process of waste removal has been included in the Performance Assessment calculations of the CCA. Yet, the amount that will actually reach the surface it is still unclear. Spallings are very important to the compliance of the disposal system, because the large release of radionuclides in the spalled material may prove the repository to be unsafe to future generations.

The three mechanisms of spall include blowout, stuck pipe and gas erosion, with the latter two being eliminated from calculations at the WIPP. It has been estimated that stuck pipe and gas erosion could bring more waste to the surface than blowout (Berglund (1994)). Blowout is the removal of the drilling fluid from the wellbore from a high influx of gas into the spalled cavity. The gas will cause some of the waste material on the cavity walls to fail in tension and be transported to the surface. High repository pressures and high waste permeability are general repository conditions for blowout.

Stuck pipe is a process of spall that, due to relatively low permeability and high repository pressures, may cause failed waste to press against the drill string sufficiently hard to prevent normal drilling. The solution of a jammed bit is to pull the drill string up and start drilling again. If the pressures remain high, the driller may have to bring the bit up several times, thus allowing significant quantities of waste to be brought to the surface. Gas erosion describes spall that is eroded by the drilling mud and may occur due to high repository pressures and low waste permeability. The rate of spall is slower than stuck pipe due to slightly lower pressures than stuck pipe (just above hydrostatic), and may release waste into the drilling mud at a rate undetectable by the driller. Gas erosion could continue until the repository pressure is in equilibrium with the drilling fluid, and may also bring significant quantities of waste to the surface. Stuck pipe and gas erosion releases would occur if the waste permeability is less than 10^{-16} m^2 , a permeability threshold defined in Berglund (1994) that is currently under question, and repository pressures are greater than the pressure exerted by the drilling mud.

As part of the performance assessment, blowout calculations were performed, and volumes of failed waste material were estimated for the CCA, which ranged from 0.5 m^3 to 4 m^3 . However, these calculations were found to be faulty by the DOE's Conceptual Model Peer Review Group (Wilson et al., 1997), and a new model for blowout was developed (Hansen et al., 1997). The new model showed that the CCA predicted blowout releases were conservative, by estimating a maximum release of only 0.27 m^3 at the worst conditions of repository behavior.

Through an investigation of permeability of the new spallings model, it is questionable whether the calculations of blowout is sufficient in estimating releases to the surface. The model was run with a range of permeability values consistent with Hansen et al., (1997), and was found to have high volumes of failed material in the repository cavity when gas influx was insufficiently large to cause blowout. Though blowout had not occurred, the failed waste in the borehole cavity would be introduced into the drilling mud and be carried to the surface with other cuttings and cavings from borehole drilling activity. This defines gas erosion and was not considered in Hansen et al., (1997).

More important to the question of the amount of waste released to the surface that will be expelled from the pressurized repository, is the amount of spalled material that will cause the repository to fail compliance. The performance assessment calculations of the CCA (DOE, 1996) and PAVT (DOE, 1997) demonstrated that any combination of spalled releases from blowout from 0.5 m^3 to 4 m^3 will demonstrate compliance. However, no one, as of yet, looked at the issue of failure. This report investigates the amount of spalled material that would result in failure to meet the EPA compliance standards.

Discussion

For the performance assessment calculations of the PAVT, the EPA decided to sample blowout releases on a range from 0.5 m^3 to 4.0 m^3 with a uniform distribution assigned to that range. The result was an increase in the overall mean of releases for spallings in the CCDF from 0.04 EPA units at the 10^{-1} probability in the CCA to 0.08 EPA Units in the PAVT. The increase was also due to the number of vectors that exhibited pressures above hydrostatic. The spallings and cuttings portions of the CCDF contribute equally to the overall mean of the CCDF.

For a more complete view of spallings and its contribution to the overall mean of the CCDF, the values of 0.5 to 4 m^3 used in the PAVT calculations were increased by a factor until it was shown that there was failure of compliance. The factor ranged from 2 to 16, and was a very simple adjustment to the PAVT values.

The results of increased spall reaching the surface can be seen in Figure 1. The increase in spall was accomplished by multiplying the PAVT generated releases by a factor of 2, 4, 8, and 16. These curves are seen in Figure 1, and are compared to the CCA releases. The figure suggests that a maximum of 16 times the amount of spallings will cause the repository to fail at the 10^{-1} probability, which corresponds to spallings releases between 8 m^3 and 64 m^3 .

Conclusion

The questions raised on the amount of spalled material that will cause the disposal system to fail compliance is addressed here. The concern of additional spalled material that may reach the surface, by either a stuck pipe / gas erosion process, or through air drilling can be seen in Figure 1. The figure shows that a maximum of 16 times the PAVT spalled release can be brought to the surface before compliance of the disposal system is compromised if other modes of releases are held constant.

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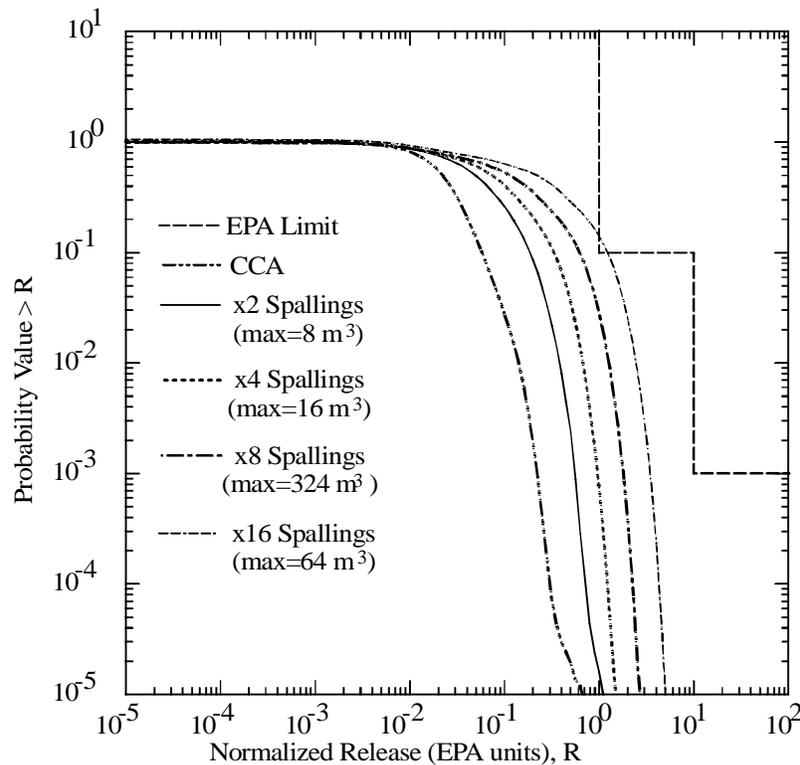


Figure 1: Overall Mean For PAVT Increased Spallings

Issue: Modeling the Air Drilling Scenario through a Direct Brine Release at the WIPP

Introduction

The practice of drilling with air as the circulation fluid in wells has been established in the Delaware Basin. On April 2, 1991 the Lincoln Federal Well No. 1 in Section 26, T21S, R32E, NMPM, in Lea County, New Mexico was drilled with air after 11 days of drilling with mud brine (Silva, 1994; EEG-55 p.63-64). The CCA did not consider the practice of drilling with air as a possible method for well development.

The modeling of air drilling was first raised by Bredehoeft (1997). Bredehoeft addressed the concern of spalled (solid) material that would reach the accessible environment through an air drilling scenario. His results show that a large amount of material could reach the surface, thus breaking the compliance standards set in 40 CFR Part 194 (EPA, 1997). This is the first report to address the issue of contaminated brine released after drilling with air. The issue is studied here, by applying a model to the release of brine through an inadvertent drill intrusion into the WIPP repository.

Discussion

An air drilling scenario is investigated using the Sandia developed code for a brine release through an intruding borehole. The code, BRAGFLO_DBR, is used along with the same assumptions as the Performance Assessment Verification Test (PAVT), including the BRAGFLO output files, and CUTTINGS_S files, but changing the boring fluid from a brine mud to air. The change in boring fluid would decrease the pressure at the bottom of the borehole, thus allowing a higher release of brine to escape to the surface.

For blowout to occur, the pressure of the repository must be higher than the borehole pressure at the repository depth. For brine mud, the pressure is assumed to be hydrostatic, or 8 MPa. For the air column, the air pressure will be very low, and was assumed to be approximately 2 MPa for this model, thus allowing higher and more frequent blowout occurrences than higher pressures. The 2 MPa is assumed to approximate the pressure exerted by a foam/air mixture at the depth of the WIPP repository. Air alone would exert pressures far below that of foam/air combination. However, this cutoff is reasonable due to the extremely low number of vectors that are expected to fall below the 2 MPa cutoff. One additional change from the PAVT for modeling with air includes the density of the drilling fluid from 1215 kg/m³ for brine to 1.161 kg/m³ for air.

The model was run for an initial E1 intrusion at 350 and 1000 years, and subsequent E2 intrusions at 550, 750, 1200, 1400, 2000, 3000, 4000, 5000, and 10000 years post closure (S2 and S3 scenarios). The results, shown in Figure 1, demonstrates the danger of drilling with air into the repository. The figure shows the results of 100 vectors for time 1200 years for S3, Replicate 1 using air as the drilling fluid. A single realization is shown to release as much as 2400 m³ of brine to the surface at a second intrusion time of 1200 years. This is the highest brine release seen for all vectors at all times. The mean value for all releases at 1200 years is 436 m³. The PAVT results show a maximum of 76 m³ at 1200 years postclosure (DOE, 1997), and the CCA predicted a maximum release of 15 m³ (DOE, 1997).

The high volumes of release seen in Figure 1 can be attributed to the high pressures of the repository. At 1200 years postclosure, the repository pressure of vector 51, which has the highest releases, exceeds most other vectors at 13.3 MPa, and is ranked 4th out of 100 vectors for highest repository pressure. Also contributing to its high release is the waste saturation. Vector 51 has a saturation of 0.67, which has been seen in past sensitivity analyses (See Figure 5.1.5. of Helton, 1996) to be an ideal saturation for release.

Inherently, there are problems with using the BRAGFLO_DBR code this way. The model assumed an incompressible fluid in the wellbore. Air is compressible, and the effects of incompressibility on the releases are not known. There are also some questions of whether the drilling fluid density change affected the whole repository or just the wellbore. This was a quick experiment, and these questions will be investigated further by the EEG. However, the results seen in Figure 1 are believed to provide an indication of the magnitude of potential releases.

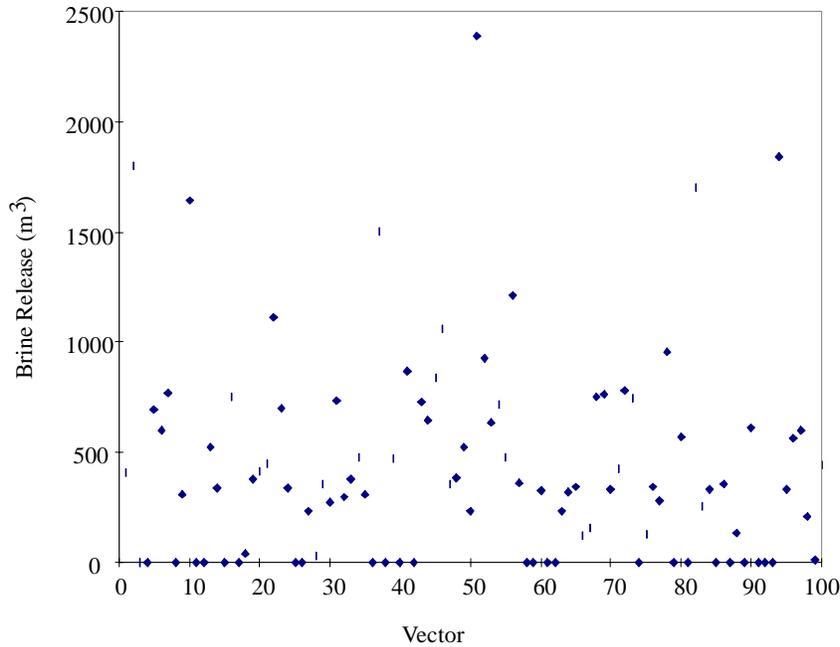


Figure 1. Air Drilling Results for 100 vectors of an S3 scenario at 1200 years postclosur

The carrying capacity of the brine to transport radionuclides to the surface depends on the solubility of the actinides in solution. The CCA’s median value of solubility for a +4 actinide (Plutonium (IV), Uranium (IV), or Thorium (IV)) in Salado brine is approximately $4e-6$ M. Thus, calculating the number of grams of Plutonium-239 (IV) for 2400 m^3 of brine is 2300 g. The grams can be converted to activity, and the 2400 m^3 of brine can be calculated to carry 140 Ci, or 0.4 EPA units. Higher solubility values will result in higher releases to the surface.

The CCDF curves, using the results of air drilling, can be seen in Figure 2. The code, which produced the curves, used the releases from PAVT and solubilities from the CCA. The direct brine release results of air drilling were then substituted for the results of the PAVT. Again, it should be noted that the CCDF results use spillings releases calculated in the PAVT. Spallings releases due to an air drilling event were not incorporated into the results. These curves assume a worst case scenario, in which all the drilling from an E1E2 drilling event would be using air as the drilling fluid.

In addition to the CCA solubilities, actinide solubilities with different mineral species were included. The solubilities were from median values using Nesquehonite, a mineral phase of the magnesium carbonate system, and from no MgO backfill. The ‘No Backfill’ case does not suggest that MgO should not be present in the repository, but gives an upper bound on solubility and how it affects compliance to the EPA standards. Table 1 shows the values used for each actinide oxidation state.

The CCDF curves for CCA solubility values do not exceed the EPA standard at the 10^{-1} or 10^{-3} probability level. Yet, the issue should not be readily dismissed. The problem was run on the scenarios of S2 and S3 only. The other three scenarios assumed brine mud as the drilling fluid. Furthermore, solubility values are shown to be greater in other mineral species of the magnesium carbonate system, and if the repository is breached during a time when these minerals will dominate the repository, then there may be sufficient releases to the accessible environment to cause the repository to fail compliance. This example can be seen in the curve for the Nesquehonite solubility. Again, this is a worst-case scenario in which all vectors for the simulation of air drilling uses the median values for Nesquehonite solubility, which can be seen in Table 1. The curve for Nesquehonite crosses the EPA compliance limit at the 0.02 probability level. This relates to a 1 in 50 chance of releasing more than 3500 Ci to the surface. The curve drops to a 1 in 500 chance of releasing more than 35000 Ci to the surface.

Salado	+3 (M)	+4 (M)	+6 (M)
Nesquehonite	3.17e-7	6.3e-4	NA (used No Backfill)
No Backfill	4e-3	5e-4	8e-5
Castile			
Nesquehonite	2.4e-6	1.04e-3	NA (used No Backfill)
No Backfill	2e-3	7e-5	8e-5

Table 1. Solubility values used in PANEL for generation of CCDF curves.

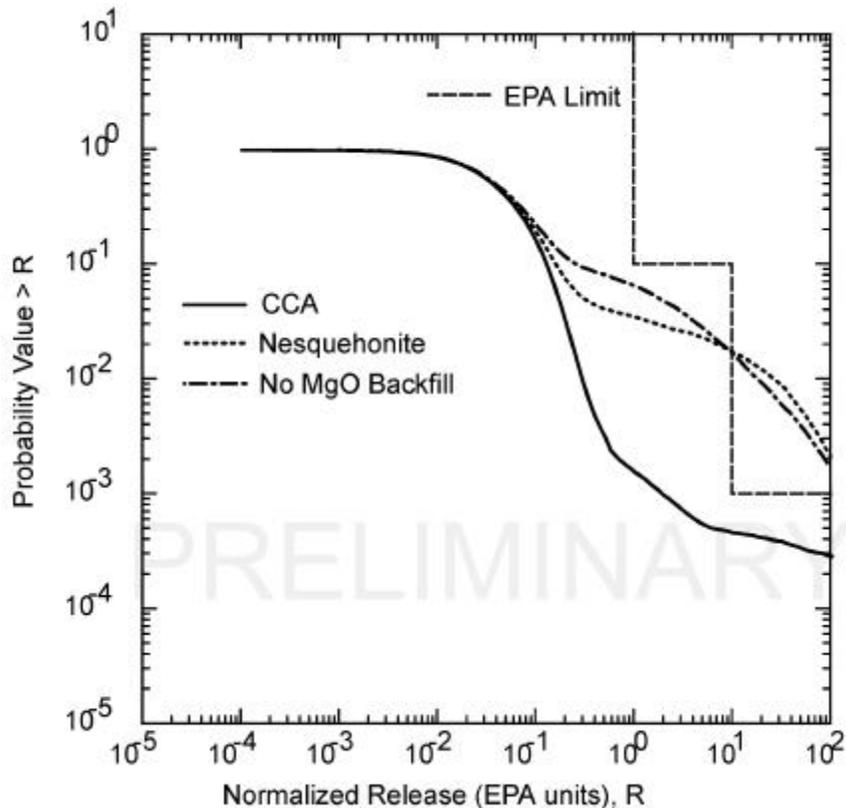


Figure 2. CCDF for Air Drilling with different solubilities. Air Drilling Modeling only included Direct Brine Releases for S2 and S3. Cuttings, spallings, and transport through the Culebra results are from PAVT, with actinide solubility values from the CCA, formation with Nesquehonite, and no MgO backfill.

The third curve on the CCDF plot shows the response of the disposal system for solubility values from 'No MgO Backfill'. The releases for probabilities greater than 1 in 50 are much higher than the other two curves. However, at lower probabilities the 'No MgO Backfill' has lower releases than the solubilities with Nesquehonite. This is due to the difference in solubility values at the +4 oxidation state for both Salado and Castile brine. In conclusion, the CCDF curves are shown to cross the EPA Release limits for higher solubility values, and the issue of air drilling must be taken more seriously than previous evaluations.

Recommendations

- 1) The EPA should look more closely at the issue of air drilling to determine the probability of such an event occurring in the 10000 year projected history of the disposal system.
- 2) EPA needs to assess the appropriateness of using the BRAGFLO direct brine release model for air drilling.
- 3) Depending on EPA's resolution of the solubility issue, the EPA may need to calculate CCDFs for air drilling.

Reproducibility

To reproduce the results of this experiments, the summarized files (*.TBL) of CUTTINGS_S, BRAGFLO_DBR, and SECOTP2D from PAVT, and the summarized files of NUTS, PANEL, and ST (Source Term) from the CCA are needed for the input for CCDFGF. In addition, the BRAGFLO_DBR files from an air drilling scenario will replace some of the BRAGFLO_DBR of the PAVT. Attachment 1 shows the input for the preprocessor of CCDFGF. The Direct Brine Release summarized files begin with: 'SUM_BF4_CCGF_AIR'.

The simulation of drilling with air with BRAGFLO_DBR was accomplished by changing the inputs to the preprocessor of the model. The ALGEBRA file 'ALG_BF4_CCA_PRE_DIR_REL_S3_DIST.INP' was modified to allow a lower threshold of pressure from the drilling fluid for time stepping. The file sets the time step for the BRAGFLO_DBR to 0 if the flowing bottomhole pressure (FBHP) is less than the pressure of the drilling fluid column, and to a maximum 1000 time steps if the pressure is greater. The FBHP was established in the preprocessor by a 3D curve fit from the Poettmann-Carpenter correlation (DOE, 1996). The ALGEBRA file was also modified for drilling fluid density. Attachment 2 lists the file and highlights the areas of change. The original ALGEBRA file used 8 MPa as the cutoff for timestep configuration. The new model sets the cutoff at 2 MPa.

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Attachment 1: Input for CCDFG Preprocessor Mode for Air Drilling

```

$!
$! MODULE:   PREPROC.COM
$! PURPOSE:  RUN PREPROCESSOR CODE TO CREATE CUTTINGS, SPALLINGS
$!          BLOWOUT, NUTS, AND SECUTP INPUT TABLES FOR USE BY
$          CCDFG PREPROCESSOR OPTION
$! ---
$! AUTHOR:   JAY D. JOHNSON
$! DATE:     11/22/96
$!
$! Date      Changes
$! 11/10/97  Solubility -D. Rucker
$!          CCA denotes CCA Solubilities
$!          EEG2 denotes Nesquehonite Solubilities
$!          EEG1 denotes No Backfill Solubilities
$!
$! 12/3/97   Air Drilling -D. Rucker
$!          Direct Brine Releases 'SUM_bf4_ccgf_dir.tbl'
$! ---
$! Setup for run
$ SET NOON
$ REP := "R:"
$!
$ TESTDIR1 := "14:\dfucke\ccdfgf"
$ TESTDIR2 := "14:\dfucke\ccdfgf\nput_REP"
$ TESTDIR2a := "14:\dfucke\pav"
$ TESTDIR3 := "14:\dfucke\ccdfgf\nput_REP"
$ TESTDIR3a := "14:\dfucke\pav"
$ TESTDIR4 := "14:\dfucke\ccdfgf\input_REP"
$ TESTDIR5 := "14:\dfucke\ccdfgf\input_REP"
$ TESTDIR6 := "14:\dfucke\panel\cbr"
$ TESTDIR6a := "14:\dfucke\panel\lme"
$ TESTDIR7 := "14:\dfucke\cusp"
$ TESTDIR8 := "14:\dfucke\dr"
$ TESTDIR9 := "14:\dfucke\nuts"
$ TESTDIR0 := "14:\dfucke\sl"
$ CULDIR := "14:\dfucke\ccdfg"
$! ---
$! Define CUTTINGS file names
$! ---
$ DEFINE/NOLOG HT_FRAC$INP          TESTDIR1\CCGF_CCA_HT_FRAC.DAT
$ DEFINE/NOLOG EPAUN_CCH$INP       TESTDIR1\EPU_CCGF_CCA_CCH.DAT
$ DEFINE/NOLOG EPAUN_CRHE$INP       TESTDIR1\EPU_CCGF_CCA_CRH.DAT
$ DEFINE/NOLOG SUM_CUSP_CCGF_CCA$INP TESTDIR2a\SUM_CUSP_C97_rep_51_L_T5000.TBL
$ DEFINE/NOLOG CCGF_CUTTINGS$OUT   OUTDIR\CUTTING.TRN
$! ---
$! Define SPALLINGS file names
$! ---
$ DEFINE/NOLOG CH_TRU$INP           TESTDIR1\CCGF_CCA_CH_TRU.DAT
$! ---
$ DEFINE/NOLOG CUSP_51_L_T100$INP   TESTDIR2a\SUM_CUSP_C97_REP_51_L_T100.TBL
$ DEFINE/NOLOG CUSP_51_L_T350$INP   TESTDIR2a\SUM_CUSP_C97_REP_51_L_T350.TBL
$ DEFINE/NOLOG CUSP_51_L_T1000$INP  TESTDIR2a\SUM_CUSP_C97_REP_51_L_T1000.TBL
$ DEFINE/NOLOG CUSP_51_L_T3000$INP  TESTDIR2a\SUM_CUSP_C97_REP_51_L_T3000.TBL
$ DEFINE/NOLOG CUSP_51_L_T5000$INP  TESTDIR2a\SUM_CUSP_C97_REP_51_L_T5000.TBL
$ DEFINE/NOLOG CUSP_51_L_T10000$INP TESTDIR2a\SUM_CUSP_C97_REP_51_L_T10000.TBL
$! ---
$ DEFINE/NOLOG CUSP_51_U_T100$INP   TESTDIR2a\SUM_CUSP_C97_REP_51_U_T100.TBL
$ DEFINE/NOLOG CUSP_51_U_T350$INP   TESTDIR2a\SUM_CUSP_C97_REP_51_U_T350.TBL
$ DEFINE/NOLOG CUSP_51_U_T1000$INP  TESTDIR2a\SUM_CUSP_C97_REP_51_U_T1000.TBL
$ DEFINE/NOLOG CUSP_51_U_T3000$INP  TESTDIR2a\SUM_CUSP_C97_REP_51_U_T3000.TBL
$ DEFINE/NOLOG CUSP_51_U_T5000$INP  TESTDIR2a\SUM_CUSP_C97_REP_51_U_T5000.TBL
$ DEFINE/NOLOG CUSP_51_U_T10000$INP TESTDIR2a\SUM_CUSP_C97_REP_51_U_T10000.TBL
$! ---
$ DEFINE/NOLOG CUSP_52_L_T550$INP   TESTDIR2a\SUM_CUSP_C97_REP_52_L_T550.TBL
$ DEFINE/NOLOG CUSP_52_L_T760$INP   TESTDIR2a\SUM_CUSP_C97_REP_52_L_T760.TBL

```



```

5 DEFINE/NOLOG BF4_S2_L_T4000$INP
$ DEFINE/NOLOG BF4_S2_L_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S2_U_T550$INP
$ DEFINE/NOLOG BF4_S2_U_T750$INP
$ DEFINE/NOLOG BF4_S2_U_T2000$INP
$ DEFINE/NOLOG BF4_S2_U_T4000$INP
$ DEFINE/NOLOG BF4_S2_U_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S3_L_T1200$INP
5 DEFINE/NOLOG BF4_S3_L_T1400$INP
$ DEFINE/NOLOG BF4_S3_L_T3000$INP
5 DEFINE/NOLOG BF4_S3_L_T5000$INP
5 DEFINE/NOLOG BF4_S3_L_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S3_U_T1200$INP
5 DEFINE/NOLOG BF4_S3_U_T1400$INP
$ DEFINE/NOLOG BF4_S3_U_T3000$INP
$ DEFINE/NOLOG BF4_S3_U_T5000$INP
$ DEFINE/NOLOG BF4_S3_U_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S4_L_T550$INP
$ DEFINE/NOLOG BF4_S4_U_T750$INP
$ DEFINE/NOLOG BF4_S4_U_T2000$INP
$ DEFINE/NOLOG BF4_S4_L_T1400$INP
$ DEFINE/NOLOG BF4_S4_L_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S4_U_T550$INP
$ DEFINE/NOLOG BF4_S4_U_T750$INP
$ DEFINE/NOLOG BF4_S4_U_T2000$INP
$ DEFINE/NOLOG BF4_S4_U_T4000$INP
$ DEFINE/NOLOG BF4_S4_U_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S5_L_T1200$INP
$ DEFINE/NOLOG BF4_S5_L_T1400$INP
$ DEFINE/NOLOG BF4_S5_L_T3000$INP
$ DEFINE/NOLOG BF4_S5_U_T5000$INP
$ DEFINE/NOLOG BF4_S5_L_T10000$INP
$! ---
$ DEFINE/NOLOG BF4_S5_U_T1200$INP
$ DEFINE/NOLOG BF4_S5_U_T1400$INP
$ DEFINE/NOLOG BF4_S5_U_T3000$INP
$ DEFINE/NOLOG BF4_S5_U_T5000$INP
$ DEFINE/NOLOG BF4_S5_U_T10000$INP
$! ---
$ DEFINE/NOLOG CCGF_BLOWOUT$OUT
$! ---
$ Define NUTS file names
$! ---
$ DEFINE/NOLOG ALG_ST_CCGF_CCA_S1$INP
$ DEFINE/NOLOG ALG_ST_CCGF_CCA_S2$INP
$! ---
$ DEFINE/NOLOG SUM_NUTS_S1$INP
$! ---
$ DEFINE/NOLOG SUM_NUTS_S2_100$INP
$ DEFINE/NOLOG SUM_NUTS_S2_350$INP
$ DEFINE/NOLOG SUM_NUTS_S3_1000$INP
$ DEFINE/NOLOG SUM_NUTS_S3_3000$INP
$ DEFINE/NOLOG SUM_NUTS_S3_5000$INP
$ DEFINE/NOLOG SUM_NUTS_S3_7000$INP
$ DEFINE/NOLOG SUM_NUTS_S3_9000$INP
$! ---
$ DEFINE/NOLOG SUM_NUTS_S4_100$INP
$ DEFINE/NOLOG SUM_NUTS_S4_350$INP
$ DEFINE/NOLOG SUM_NUTS_S5_1000$INP
$ DEFINE/NOLOG SUM_NUTS_S5_3000$INP
$ DEFINE/NOLOG SUM_NUTS_S5_5000$INP
$ DEFINE/NOLOG SUM_NUTS_S5_7000$INP
$ DEFINE/NOLOG SUM_NUTS_S5_9000$INP
$! ---
TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_L_T4000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_L_T10000.TBL

TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_U_T550.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_L_T750.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_U_T2000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_L_T4000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S2_U_T10000.TBL

TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_L_T1200.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_L_T1400.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_L_T3000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_L_T5000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_L_T10000.TBL

TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_U_T1200.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_U_T1400.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_U_T3000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_U_T5000.TBL
TESTDIR8\SUM_bf4_ccgf_ar_REP_S3_U_T10000.TBL

TESTDIR3a\SUM_dbr_C97_REP_S4_Lower_T550.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Upper_T750.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Lower_T2000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Upper_T4000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Lower_T10000.TBL

TESTDIR3a\SUM_dbr_C97_REP_S4_Up_T550.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Up_T750.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Up_T2000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Up_T4000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S4_Up_T10000.TBL

TESTDIR3a\SUM_dbr_C97_REP_S5_Lower_T1200.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Upper_T1400.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Lower_T3000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Lower_T5000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Lower_T10000.TBL

TESTDIR3a\SUM_dbr_C97_REP_S5_Up_T1200.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Up_T1400.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Up_T3000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Up_T5000.TBL
TESTDIR3a\SUM_dbr_C97_REP_S5_Up_T10000.TBL

'OUTDIR\BLOWOUT.TRN

TESTDIR0\SUM_ST_CCGF_ang1_REP_S1.TBL
TESTDIR0\SUM_ST_CCGF_ang1_REP_S2.TBL

TESTDIR4\SUM_NUT_CCGF_CCA_REP_S1.TBL

TESTDIR4\SUM_NUT_CCGF_CCA_REP_S2_100.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S2_T550.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S3_1000.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S3_T3000.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S3_5000.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S3_7000.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S3_9000.TBL

TESTDIR4\SUM_NUT_CCGF_CCA_REP_S4_1100.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S4_T350.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S5_T1000.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S5_T3000.TBL
TESTDIR4\SUM_NUT_CCGF_CCA_REP_S5_T5000.TBL

```

```

$ DEFINE/NOLOG SUM_NUTS_SE_7000$INP          'TESTDIR4\SUM_NUT_CCGF_CCA_'REP'_S6_7000.TBL
$ DEFINE/NOLOG SUM_NUTS_SE_9000$INP          'TESTDIR4\SUM_NUT_CCGF_CCA_'REP'_S6_9000.TBL
$! ---
$ DEFINE/NOLOG SUM_PNL_SE_100$INP            'TESTDIR6a\SUM_PANEL_CCDf_eeq1_'REP'_S6_100.TBL
$ DEFINE/NOLOG SUM_PNL_SE_350$INP            'TESTDIR6a\SUM_PANEL_CCDf_eeq1_'REP'_S6_350.TBL
$ DEFINE/NOLOG SUM_PNL_SE_1000$INP           'TESTDIR6a\SUM_PANEL_CCDf_eeq1_'REP'_S6_1000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_4000$INP           'TESTDIR6a\SUM_PANEL_CCDf_eeq1_'REP'_S6_4000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_6000$INP           'TESTDIR6a\SUM_PANEL_CCDf_eeq1_'REP'_S6_6000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_9000$INP           'TESTDIR6a\SUM_PANEL_CCDf_eeq1_'REP'_S6_9000.TBL
$! DEFINE/NOLOG SUM_PNL_SE_100$INP           'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_100.TBL
$! DEFINE/NOLOG SUM_PNL_SE_350$INP           'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_350.TBL
$! DEFINE/NOLOG SUM_PNL_SE_1000$INP          'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_1000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_2000$INP           'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_2000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_4000$INP           'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_4000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_6000$INP           'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_6000.TBL
$ DEFINE/NOLOG SUM_PNL_SE_9000$INP           'TESTDIR4\SUM_PANEL_CCDf_eeq1_'REP'_S6_9000.TBL
$! ---
$ DEFINE/NOLOG SUM_CCDFRF_CCA_CAVGE00$INP    'TESTDIR5\SUM_PANEL_eeq1_CON_'REP'_S1.tbl
$ DEFINE/NOLOG SUM_CCDFRF_CCA_CAVGE10$INP    'TESTDIR6\SUM_PANEL_eeq1_CON_'REP'_S2.tbl
$! ---
$ DEFINE/NOLOG CCGF_NUTS$OUT                 'OUTDIR\NUTS.TRN
$! ---
$! Define SECQTP file names
$! ---
$ DEFINE/NOLOG ST2D3_CCA_PMS$INP             'TESTDIR2a\SUM_ST2D3_c97_R*_pm.TBL
$ DEFINE/NOLOG ST2D3_CCA_FM$INP             'TESTDIR2a\SUM_ST2D3_c97_R1_fm.TBL
$ DEFINE/NOLOG CCGF_SECQTP$OUT              'OUTDIR\SECQTP.TRN
$! ---
$ DEFINE/NOLOG CCGF_MISC$INP                 'TESTDIR1\CCGF_MISC_PRE_CCA.INP
$ DEFINE/NOLOG CCGF_SDB$INP                  'TESTDIR1\CCGF_SDB
$ DEFINE/NOLOG CCGF_PRT$OUT                  'OUTDIR\CCGF_CCDFRF_CCA_'REP'.OUT
$ DEFINE/NOLOG CCGF$OUT                      'OUTDIR\CCGF_cca_'REP'.OUT
$! ---
$! Define release summary tables file name
$! ---
$ DEFINE/NOLOG CCGF_REF TAB$OUT              'OUTDIR\eeq1_refab_eeq1_'REP'.DAT
$! ---
$! Execute CCDFRF with preprocessor option
$! ---
$ CCDFRF
$! ---
$ EXIT
$! ---

```

Attachment 2: ALGEBRA file for Air Drilling Scenario

TITLE:BRAGFLO 1996 DCA CALCULATIONS: REPOSITORY SCALE BLOWOUT

ANALYST: Dan Stoezel, SNL

ICREATED: NOV 2, 1995

PURPOSE: ALGEBRA file computes properties that can not be obtained from CAMDAT and/or assigns properties to element blocks.

THIS FILE PREPARES A CDB FILE FOR PREBRAG TO READ

IMPORTANT: This file originates from J.E. Bear's algebra file for his FEP model. The methodologies to calculate dip were copied from his file with minor changes made to account for the differences in the meshes.

ALGEBRA TO CALC. DIP IN REPOSITORY - SCALE BLOWOUT MODEL.
new version of bragto

MODIFIED:

MARCH 26, 1996

BLOWOUT MODEL STRUGGLING IN PANEL SEAL REGION TURNED OFF
CAP PRESSURE IN PANEL SEAL AND HALITE BY SETTING EQUAL TO
CAP PRESSURE IN WASTE REGION

MAY 17, 1996

ADDED BOUNDARY CONDITION WELL CALCULATION FOR E1-E2 SCEN
NEW CHANGES FOR LATEST DCA ANALYSIS

MAY 20, 1996

WELL 2 INPUT FILE TO ACCOUNT FOR E1-E2 SAME PANEL BOUNDARY
COND.

MAY 30, 1996

ADDED LOGIC TO ACCOUNT FOR CHANGES IN ABANDONED WELLBORE PERM
FOR BOUNDARY CONDITION WELL.
SCENARIO 2 AND 4 FILE FIRST INTRUSION AT 350 YEARS

December 1, 1997

Charged Cutoff for pressure in the repository to allow Air Drilling
Dale Rucker, EEG

=====

CHAPTER 0: DEFINE NEW VARIABLE NAMES AND SOME NEEDED CONSTANTS

=====

! SET CONSTANTS AND PUT IN WASTE REGION

LIMIT BLOCK 1

THETA1 = MAKEPROP(DIP_DEG[B:8]*2.0*PI[B:8])/360.0;

THETA2 = MAKEPROP(0.0)

!

PERM_X = 10**PRMX_LOG

PERM_Y = 10**PRMY_LOG

PERM_Z = 10**PRMZ_LOG

SB_MIN = SAT_RBRN * 1.05

POR_COMP = COMP_RCK/POROSITY

! CALCULATE PROPERTIES FOR DRZ & HALITE

LIMIT BLOCK 2 3

PERM_X = 10**PRMX_LOG

PERM_Y = 10**PRMY_LOG

PERM_Z = 10**PRMZ_LOG

SB_MIN = SAT_RBRN * 1.05

! NOW ADJUST POROSITY AND PORE COMPRESSIBILITY TO EQ. PORE VOL WITH CRUSHED

! ROOM HEIGHT

POROSITY = HEIGHT * POROSITY / HEIGHT*(10:1)

POR_COMP = COMP_RCK/POROSITY

! CAP PRESSURE MODEL CHANGES HERE:

```

CAP_MOD = CAP_MOD(ID:1)
PCT_A = PCT_A(ID:1)
PCT_EXP = PCT_EXP(ID:1)
! CALC PROPERTIES FOR PANEL SEALS
LIMIT BLOCK 4
PERM_X = 10**PRMX_LOG
PERM_Y = 10**PRMY_LOG
PERM_Z = 10**PRMZ_LOG
SE_MIN = SAT_RBRN*1.05
! NOW ADJUST POROSITY AND FRC COMPRESSIBILITY TO EQ. PORE VOL WITH CRUSHED
! ROOM HEIGHT
POROSITY = HEIGHT*POROSITY/HEIGHT(ID:1)
POR_COMP = COMP_RCK/POROSITY
! CAP PRESSURE MODEL CHANGES HERE
CAP_MOD = CAP_MOD(ID:1)
PCT_A = PCT_A(ID:1)
PCT_EXP = PCT_EXP(ID:1)

```



```

! SET WELLBORE PROPS
LIMIT BLOCK 7
SEBRINE1 = MAKEPROP(0.0)
SEGAS1 = MAKEPROP(0.0)
KRW1 = MAKEPROP(0.0)
KRG1 = MAKEPROP(0.0)
SEBRINE2 = MAKEPROP(0.0)
SEGAS2 = MAKEPROP(0.0)
KRW2 = MAKEPROP(0.0)
KRG2 = MAKEPROP(0.0)
SEBRINE3 = MAKEPROP(0.0)
SEGAS3 = MAKEPROP(0.0)
KRW3 = MAKEPROP(0.0)
KRG3 = MAKEPROP(0.0)
SEBRINE4 = MAKEPROP(0.0)
SEGAS4 = MAKEPROP(0.0)
KRW4 = MAKEPROP(0.0)
KRG4 = MAKEPROP(0.0)
! DEFINE CONSTANTS FOR THE THREE EQUATIONS TO BE USED TO CALCULATE FBHP
! EQUATION 1: (FOR BRINE FLOW ONLY, KRG = 0)
! FBHP = (A+BX+CY)/(1+DX+EY)
! X = LOG10(BRINE CONST) LOG M3/μA-S
! Y = PANEL PRESSURE (Pa)
1.8,022,373 Pa < FBHP < 8.038,390 Pa
EQ1_A = MAKEPROP(8002577.4)
EQ1_B = MAKEPROP(62.137575)
EQ1_C = MAKEPROP(0.024918096)
EQ1_D = MAKEPROP(0.10254807)
EQ1_E = MAKEPROP(5.1235777E-9)
! EQUATION 2: (FOR LOG10(KRG/KRW) < 0 BRINE DOMINATED FLOW)
! FBHP = (A+BX+CX2+DX3+EY)/(1+FX+GX2+HY)
! X = LOG10(KRG/KRW)
! Y = PANEL PRESSURE (Pa)
225,452 Pa < FBHP < 8,028,643 Pa
EQ2_A = MAKEPROP(947082.85)
EQ2_B = MAKEPROP(2788147.8)
EQ2_C = MAKEPROP(3451058.3)
EQ2_D = MAKEPROP(-54864.382)
EQ2_E = MAKEPROP(-0.017079483)
EQ2_F = MAKEPROP(0.8953587)
EQ2_G = MAKEPROP(0.54041537)
EQ2_H = MAKEPROP(-4.9369107E-9)
! EQUATION 3: (FOR LOG10(KRG/KRW) > 0 GAS DOMINATED FLOW)
! FBHP = EXP(A+BX+CX*0.5+DE-X+EY*0.5)
! X = LOG10(KRG/KRW)
! Y = PANEL PRESSURE (Pa)

```

```

I 153,271 Pa = FBHP = 385,493 pA
EQ3_A = MAKEPROP(8.9214835)
EQ3_B = MAKEPROP(-0.2274279)
EQ3_C = MAKEPROP(1.3680586)
EQ3_D = MAKEPROP(1.8350386)
EQ3_E = MAKEPROP(0.0045726223)

! CALCULATE SKIN FROM SPALL REMOVED, & WELL PRODUCTIVITY INDEX
! ELEMENT 59 IS LOCATION OF WELL 2 (2ND INTRUSION DOWN DIP)
WELLRAD = BITSIZE/2
DRAINRAD = SORT(DEL_X[E:59]*DEL_Y[E:59]/PI[B:B])
SKIN = -1.0*LOG(SQRT(AREA_TOT/PI[B:B])/WELLRAD)
SKIN = IFLT0(SKIN,SKIN,0)
! CHECK TO BE SURE WELLP1 IS NOT 0 OR NEG. & SET TO 1.0 IF IT IS
WELLP1 = PERM_X[ID:1]*HEIGHT[ID:1]/(LOG(DRAINRAD/WELLRAD)+SKIN-0.5)
WELLP1 = IFLT0(LOG(DRAINRAD/WELLRAD)+SKIN-0.5,PERM_X[ID:1]*HEIGHT[ID:1] &
    / (LOG(DRAINRAD/WELLRAD)+SKIN-0.5),1.0)
! CALCULATE CONSTANTS NEEDED FOR WELLBORE MODEL
! CALCULATE EFFECTIVE SATURATION USING KRP = 4 (BROOKS-COREY MODIFIED,
! WITH LAMBDA (PORE DIS) = 2.89, NO CAP PRESSURE). DO FOR 4 COUPLED REGIONS
! REGION NO 1 (PANELS 1 & 8)
BRINE1 = IFLT0(BSATPAN1[ID:1]-SAT_RBRN[ID:1],SAT_RBRN[ID:1],BSATPAN1[ID:1])
SEBRINE1 = (BRINE1 - SAT_RBRN[ID:1])/(1.0 - SAT_RBRN[ID:1])
SEGAS1 = (BRINE1 - SAT_RBRN[ID:1])/(1.0 - SAT_RBRN[ID:1]-SAT_RGAS[ID:1])
SEGAS1 = IFLT0(1.0 - SEGAS1,1.0,SEGAS1)
KRW1 = SEBRINE1**((2+3*PORE_DIS[ID:1])/PORE_DIS[ID:1])
KRG1 = (1.0-SEGAS1)**2*(1.0-SEGAS1)**(2 + PORE_DIS[ID:1])/PORE_DIS[ID:1])
! NOW CALCULATE CONSTANT FOR BRINE AND GAS
CONBR1 = WELLP1 * KRW1 / VISC0[ID:5]
CONGAS1 = WELLP1 * KRG1 / VISC0[ID:6]
! NOW TAKE LOG BASE 10 OF PARAMETERS NEEDED FOR FBHP EQUATIONS
LOG_B1 = IFEQ0(KRW1-10,LOG10(CONBR1+1E-24))
LOG_KR1 = IFEQ0(KRW1,10,LOG10((KRW1+1E-24)/(KRW1+1E-24)))
! CALCULATE FBHP'S AND SET WITHIN LIMITS
PR1_EQ1 = (EQ1_A+EQ1_B*LOG_B1+EQ1_C*PRES PAN1[ID:1]) &
    (1.0+EQ1_D*LOG_B1+EQ1_E*PRES PAN1[ID:1])
PR1_EQ1 = IFLT0(8036090.0 - PR1_EQ1,IFLT0(8036090.0 - PR1_EQ1,8036090.0, &
    PR1_EQ1),8036090.0)
PR1_EQ2 = (EQ2_A+EQ2_B*LOG_KR1+EQ2_C*LOG_KR1**2+EQ2_D*LOG_KR1**3 &
    EQ2_E*PRES PAN1[ID:1])/(1.0+EQ2_F*LOG_KR1+EQ2_G*LOG_KR1**2 &
    EQ2_H*PRES PAN1[ID:1])
PR1_EQ2 = IFLT0(225453.0 - PR1_EQ2,IFLT0(8028643.0 - PR1_EQ2,8028643.0, &
    PR1_EQ2),225453.0)
PR1_EQ3 = EXP(EQ3_A+EQ3_B*LOG_KR1+EQ3_C*ABS(LOG_KR1)**0.5 &
    EQ3_D*EXP(-1.0*ABS(LOG_KR1))+EQ3_E*PRES PAN1[ID:1])**0.5)
PR1_EQ3 = IFLT0(153271.0 - PR1_EQ3,IFLT0(385493.0 - PR1_EQ3,385493.0, &
    PR1_EQ3),153271.0)
! RESET FBHP TO 0 IF NO BRINE BLOWOUT (KRW = 0 OR PRESSURE < 2 MPa (300 psi))
IF (KRW1 = 0 OR PRES PAN1 < 2) FBHP = 0
! IF NO BLOWOUT, SET NUMBER OF BRAGFLO STEPS TO 1, ELSE 1000
NUMSTEP1 = MAKEPROP(IFEQ0(FBHP,1,1000))
! REGION NO 2 (PANELS 2 & 7)
BRINE2 = IFLT0(BSATPAN2[ID:1]-SAT_RBRN[ID:1],SAT_RBRN[ID:1],BSATPAN2[ID:1])
SEBRINE2 = (BRINE2 - SAT_RBRN[ID:1])/(1.0 - SAT_RBRN[ID:1])
SEGAS2 = (BRINE2 - SAT_RBRN[ID:1])/(1.0 - SAT_RBRN[ID:1]-SAT_RGAS[ID:1])
SEGAS2 = IFLT0(1.0 - SEGAS2,1.0,SEGAS2)
KRW2 = SEBRINE2**((2+3*PORE_DIS[ID:1])/PORE_DIS[ID:1])
KRG2 = (1.0-SEGAS2)**2*(1.0-SEGAS2)**(2 + PORE_DIS[ID:1])/PORE_DIS[ID:1])
! NOW CALCULATE CONSTANT FOR BRINE AND GAS
CONBR2 = WELLP1 * KRW2 / VISC0[ID:5]
CONGAS2 = WELLP1 * KRG2 / VISC0[ID:6]
! NOW TAKE LOG BASE 10 OF PARAMETERS NEEDED FOR FBHP EQUATIONS
LOG_B2 = IFEQ0(KRW2-10,LOG10(CONBR2+1E-24))
LOG_KR2 = IFEQ0(KRW2,10,LOG10((KRW2+1E-24)/(KRW2+1E-24)))
! CALCULATE FBHP'S AND SET WITHIN LIMITS
PR2_EQ1 = (EQ1_A+EQ1_B*LOG_B2+EQ1_C*PRES PAN2[ID:1]) &
    (1.0+EQ1_D*LOG_B2+EQ1_E*PRES PAN2[ID:1])
PR2_EQ1 = IFLT0(8036090.0 - PR2_EQ1,IFLT0(8036090.0 - PR2_EQ1,8036090.0, &

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PR2_EQ1 = (EQ2_A+EQ2_B*LOG_KR2+EQ2_C*LOG_KR2**2+EQ2_D*LOG_KR2**3+ &
EQ2_E*PRES PAN2(ID:1))/(1.0+EQ2_F*LOG_KR2+EQ2_G*LOG_KR2**2+ &
EQ2_H*PRES PAN2(ID:1))
PR2_EQ2 = IFLT0(225453.0 - PR2_EQ2,IFLT0(8028643.0 - PR2_EQ2,8028643.0, &
PR2_EQ2),225453.0)
PR2_EQ3 = EXP(EQ3_A+EQ3_B*LOG_KR2+EQ3_C*ABS(LOG_KR2)**0.5+ &
EQ3_D*EXP(-1.0*ABS(LOG_KR2))+EQ3_E*PRES PAN2(ID:1)**0.5)
PR2_EQ3 = IFLT0(153271.0 - PR2_EQ3,IFLT0(385493.0 - PR2_EQ3,385493.0, &
PR2_EQ3),153271.0)
* RESET FBHP TO 0 IF NO BRINE BLOWOUT (KRW = 0 OR PRESSURE < 2 MPa)
PR2_FBHP = 0
! IF NO BLOWOUT, SET NUMBER OF BRAGFLO STEPS TO 1, ELSE 1000
NUMSTEP2 = MAKEPROP(IFEQ0(FBHP2,1,1000))
! REGION NO 3 (PANELS 3 & 5)
BRINE3 = IFLT0(BSATPAN3(ID:1)-SAT_RBRN(ID:1),SAT_RBRN(ID:1) BSATPAN3(ID:1))
SEBRINE3 = (BRINE3 - SAT_RBRN(ID:1))/(1.0 - SAT_RBRN(ID:1))
SEGAS3 = (BRINE3 - SAT_RBRN(ID:1))/(1.0-SAT_RBRN(ID:1)-SAT_RGAS(ID:1))
SEGAS3 = IFLT0(1.0 - SEGAS3),0,SEGAS3)
KRW3 = SEBRINE3**(2+3*PORE_DIS(ID:1))/PORE_DIS(ID:1)
KRG3 = (1.0-SEGAS3)**2/(1.0-SEGAS3)**(2 + PORE_DIS(ID:1))/PORE_DIS(ID:1))
! NOW CALCULATE CONSTANT FOR BRINE AND GAS
CONBR3 = WELLP1 * KRW3 / VISC0(ID:5)
CONGAS3 = WELLP1 * KRG3 / VISC0(ID:6)
! NOW TAKE LOG BASE 10 OF PARAMETERS NEEDED FOR FBHP EQUATIONS
LOG_B3 = IFEQ0(KRW3,-10,LOG10(CONBR3+1E-24))
LOG_KR3 = IFEQ0(KRW3,10,LOG10((KRG3+1E-24)/(KRW3+1E-24)))
! CALCULATE FBHP'S AND SET WITHIN LIMITS
PR3_EQ1 = (EQ1_A+EQ1_B*LOG_B3+EQ1_C*PRES PAN3(ID:1)) &
(1.0+EQ1_D*LOG_B3+EQ1_E*PRES PAN3(ID:1))
PR3_EQ1 = IFLT0(8002373.0 - PR3_EQ1,IFLT0(8036090.0 - PR3_EQ1,8036090.0, &
PR3_EQ1),8002373.0)
PR3_EQ2 = (EQ2_A+EQ2_B*LOG_KR3+EQ2_C*LOG_KR3**2+EQ2_D*LOG_KR3**3+ &
EQ2_E*PRES PAN3(ID:1))/(1.0+EQ2_F*LOG_KR3+EQ2_G*LOG_KR3**2+ &
EQ2_H*PRES PAN3(ID:1))
PR3_EQ2 = IFLT0(225453.0 - PR3_EQ2,IFLT0(8028643.0 - PR3_EQ2,8028643.0, &
PR3_EQ2),225453.0)
PR3_EQ3 = EXP(EQ3_A+EQ3_B*LOG_KR3+EQ3_C*ABS(LOG_KR3)**0.5+ &
EQ3_D*EXP(-1.0*ABS(LOG_KR3))+EQ3_E*PRES PAN3(ID:1)**0.5)
PR3_EQ3 = IFLT0(153271.0 - PR3_EQ3,IFLT0(385493.0 - PR3_EQ3,385493.0, &
PR3_EQ3),153271.0)
! RESET FBHP TO 0 IF NO BRINE BLOWOUT (KRW = 0 OR PRESSURE < 2 MPa)
PR3_FBHP = 0
! IF NO BLOWOUT, SET NUMBER OF BRAGFLO STEPS TO 1, ELSE 1000
NUMSTEP3 = MAKEPROP(IFEQ0(FBHP3,1,1000))
! REGION NO 4 (PANELS 4 & 5)
BRINE4 = IFLT0(BSATPAN4(ID:1)-SAT_RBRN(ID:1),SAT_RBRN(ID:1) BSATPAN4(ID:1))
SEBRINE4 = (BRINE4 - SAT_RBRN(ID:1))/(1.0 - SAT_RBRN(ID:1))
SEGAS4 = (BRINE4 - SAT_RBRN(ID:1))/(1.0-SAT_RBRN(ID:1)-SAT_RGAS(ID:1))
SEGAS4 = IFLT0(1.0 - SEGAS4),0,SEGAS4)
KRW4 = SEBRINE4**(2+3*PORE_DIS(ID:1))/PORE_DIS(ID:1)
KRG4 = (1.0-SEGAS4)**2/(1.0-SEGAS4)**(2 + PORE_DIS(ID:1))/PORE_DIS(ID:1))
! NOW CALCULATE CONSTANT FOR BRINE AND GAS
CONBR4 = WELLP1 * KRW4 / VISC0(ID:5)
CONGAS4 = WELLP1 * KRG4 / VISC0(ID:6)
! NOW TAKE LOG BASE 10 OF PARAMETERS NEEDED FOR FBHP EQUATIONS
LOG_B4 = IFEQ0(KRW4,-10,LOG10(CONBR4+1E-24))
LOG_KR4 = IFEQ0(KRW4,10,LOG10((KRG4+1E-24)/(KRW4+1E-24)))
! CALCULATE FBHP'S AND SET WITHIN LIMITS
PR4_EQ1 = (EQ1_A+EQ1_B*LOG_B4+EQ1_C*PRES PAN4(ID:1)) &
(1.0+EQ1_D*LOG_B4+EQ1_E*PRES PAN4(ID:1))
PR4_EQ1 = IFLT0(8002373.0 - PR4_EQ1,IFLT0(8036090.0 - PR4_EQ1,8036090.0, &
PR4_EQ1),8002373.0)
PR4_EQ2 = (EQ2_A+EQ2_B*LOG_KR4+EQ2_C*LOG_KR4**2+EQ2_D*LOG_KR4**3+ &
EQ2_E*PRES PAN4(ID:1))/(1.0+EQ2_F*LOG_KR4+EQ2_G*LOG_KR4**2+ &
EQ2_H*PRES PAN4(ID:1))
PR4_EQ2 = IFLT0(225453.0 - PR4_EQ2,IFLT0(8028643.0 - PR4_EQ2,8028643.0, &

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PR4_EQ3,225453.0)
PR4_EQ3 = EXP(EQ3 A+EQ3 B*LOG_KR4+EQ3 C*ABS(LOG KR4)**0.5 + &
EQ3_D*EXP(-1.0*ABS(LOG_KR4))-EQ3_E*PRESAN4[10]**0.5)
PR4_EQ3 = IFLT0(153271.0 - PR4_EQ3,IFLT0(385493.0 - PR4_EQ3,385493.0, &
PR4_EQ3),153271.0)
I RESET FBHP TO 0 IF NO BRINE BLOWOUT (KRW = 0 OR PRESSURE < 2 MPa)
IF (KRW = 0 OR PRESSURE < 2) FBHP = 0
IF NO BLOWOUT, SET NUMBER OF BRAGFLO STEPS TO 1, ELSE 1000
NUMSTEP4 = MAKEPROP(IFEQD(FBHP4,1,1000))
DELETE BRINE1, BRINE2, BRINE3, BRINE4
=====
!SET UP BOUNDARY CONDITIONS FOR PREVIOUS INTRUSIONS HERE
=====
!SFT (IF NEEDED CONSTANT) S (NOTE: BOREHOLE LENGTH FROM PANEL TO CAST) (E.B.P.
! IS 247 METERS - USED IN CON_SAND & CON_CREP)
! MODIFICATIONS MADE 5/30/9E
LEN_BC = MAKEPROP(247.0)
DRAIN_BC = MAKEPROP(SQRT(DEL_X[E:15]*DEL_Y[E:19])/PI[3:8])
WELLP_BC = PERM_X[10:1]*HEIGHT[10:1]/(LOG(DRAIN_BC/WELLRAD)+0.01-0.5)
RHO_G_H = MAKEPROP(DNSFLUID[10:5]*GRAVACC[10:5]*LEN_BC)
CON_OPEN = MAKEPROP((PRM_CAST*THICK_CAST[10:5]*(LOG(DRAIN_BC/WELLRAD)-0.5)) &
/(PERM_X[10:1]*HEIGHT[10:1]*LOG(RE_CAST[10:5]/WELLRAD)-0.5))
CON_SAND = MAKEPROP((PRM_SAND**[10:8]*WELLRAD*WELLRAD* &
(LOG(DRAIN_BC/WELLRAD)-0.5))/(PERM_X[10:1]*HEIGHT[10:1]*LEN_BC)
CON_CREP = MAKEPROP((PRM_CREP**[10:8]*WELLRAD*WELLRAD* &
(LOG(DRAIN_BC/WELLRAD)-0.5))/(PERM_X[10:1]*HEIGHT[10:1]*LEN_BC)
! SOLVE FOR OPEN BOREHOLE TO CASTILE B.C. (WITHIN 200 YEARS AFTER FIRST INTR.)
! USE FBHP4 SINCE BOUNDARY CONDITION WELL IS ASSUMED TO BE IN PANEL 5 (DOWN-
! DIP) FOR ALL SUBSEQUENT INTRUSIONS
BHP_OPEN = (FBHP4+CON_OPEN*(CAST_H-RHO_G_H))/(1.0+CON_OPEN)
! SOLVE FOR SAND-FILLED BH CONDITION (200 TO 1200 YEARS AFTER 1ST INTRUSION)
BHP_SAND = (FBHP4+CON_SAND*(CAST_WB-H-HO_G_H))/(1.0+CON_SAND)
! SOLVE FOR CREEP CLOSED BH CONDITION (< 200 YEARS AFTER 1ST INTRUSION)
BHP_CREP = (FBHP4+CON_CREP*(CAST_WB-H-HO_G_H))/(1.0+CON_CREP)
ASSIGN ABANDONED BH PRESSURE BASED ON INTRUSION TIME
PREV_TME = MAKEPROP(1000.0)
DELT_TME = INTR_TME/YRSEC[10:8] - PREV_TME
BHP_ABAN = IFGT0(DELT_TME - 200.1,IFGT0(DELT_TME - 1200.1,BHP_CREP,BHP_SAND) &
BHP_OPEN)
=====
=====
!CHAPTER 3. COMPUTE DIP IN REPOSITORY
=====
=====
LIMIT ELEMENT OFF
!COMPUTE THE GRID BLOCK ELEVATIONS ACCOUNTING FOR 1 DEGREE DIP IN SALADO
!DEFINE GRID BLOCK ELEVATIONS DUE TO DIP
!USE ELEVATION OF SHAFT AT MID-REPOSITORY
ZORIGIN = 382.871
YORIGIN = 1000.0
ELEVN = MAKENODE(COS(THETA1[10:1])*(Z-ZORIGIN) &
-SIN(THETA1[10:1])*(Y-YORIGIN))
ELEV = NODEELE(ELEVNI + ZORIGIN)
!COMPUTE GRID BLOCK POTENTIAL ASSUMING BRINE IS INCOMPRESSIBLE (APPROXIMATELY)
POTE = PRESEL(DNSFLUID[10:5]*GRAVACC[10:5]) + ELEV
! NOW SET GRID THICKNESS FOR ALL ELEMENTS TO CRUSHED PANEL HEIGHT
THICK = MAKEATTR(HEIGHT[10:1])
!
DELETE ELEVNI, YORIGIN, ZORIGIN
EXIT

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**8.4a. Solubility of Plutonium as Expected Under Conditions
in the WIPP Repository (V.M. Oversby, 1997)**

THE SOLUBILITY OF PLUTONIUM UNDER CONDITIONS EXPECTED IN THE WIPP REPOSITORY

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This report was prepared for the Environmental Evaluation Group, Albuquerque, New Mexico. Every attempt has been made to make the report as complete as possible within the time available for its preparation; however, the author cannot guarantee that all relevant work is included in the discussion. The author is not responsible for the subsequent use of information and opinions contained in this report.

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Introduction

The Waste Isolation Pilot Plant (WIPP) is located in southeastern New Mexico. It is designed to be a final disposal site for transuranic wastes (TRU) produced from defense-related activities in the USA. The repository site is 655 meter below ground surface in a bedded salt formation (Salado Fm.) of Permian age. The planned inventory of wastes includes 850,000 canisters of relatively low activity, contact-handled, TRU, and about 7500 canisters of higher activity, remote-handled, TRU (Chaturvedi et al., 1997). The remote handled TRU canisters will contain about 15% of the total activity in the repository and, thus, can be expected to contain the highest concentrations of Pu and Am, the main actinide constituents in the waste.

The Environmental Evaluation Group (EEG) conducts independent technical evaluations of the impact of the WIPP project on public health and on the environment. In October, 1996, the US Department of Energy submitted their Compliance Certification Application (CCA) to the US Environmental Protection Agency. During their independent review of the CCA, EEG identified a number of concerns (Chaturvedi et al., 1997). They determined that an additional review of the factors that influence the solubility of plutonium under the conditions that will pertain at WIPP would assist them in their evaluation of the CCA. The work covered by this report was initiated in response to EEG's request. Some specific questions were proposed as important to their evaluation:

Is there enough experimental evidence to rigorously conclude that plutonium will be in the Pu(III) and Pu(IV) states in the repository environment, rather than the potentially more soluble Pu(V) state?

Is there something that has not been considered in the CCA that might result in higher Pu solubility?

What is the effect on the solubility of Pu of the compounds formed by the MgO backfill interactions with brine?

What, specifically, are the scientific shortcomings of the DOE arguments in the CCA and what needs to be done to address these shortcomings in terms of calculations and experimental work?

This report attempts to answer those questions by discussing the most likely redox state for Pu based on published experimental work, the effect of brine composition on solubility of actinides in the (IV) valence state, the influence of solution species formed by reaction of the MgO backfill on An(IV) solubility, and the influence of other potential ligands present in the waste itself on actinide solubility. An analysis of the calculational path used as a result of the scenario adopted for the calculations suggests that there are means of forming significant

amounts of soluble Pu as citrate complexes or as complexes with the chemical degradation products of cellulose. A new scenario for calculations to test the sensitivity of the results to pathway is proposed. In addition, some inconsistencies in the calculated results reported in the CCA are discussed and issues are identified that need resolution.

Factors controlling solubility

There are four major factors that will determine the effective solubility of plutonium in the WIPP environment. These are (1) the redox conditions, (2) the brine composition, (3) the availability of ligands through degradation of the waste, and (4) the effects of slow kinetics of reaction due to lack of lability of species (i.e., persistence of metastable species). The brine composition, itself, will be affected by the persistence of metastable reaction products, especially those formed by the MgO backfill. Each of these factors is discussed in the sections that follow.

Redox state

Plutonium can exist in several oxidation states in natural waters depending on the availability of oxygen and complexing agents. Under normal atmospheric carbon dioxide pressure ($p_{\text{CO}_2} = 3.2 \times 10^{-4}$ atm), but in the absence of other complexing ligands, the expected oxidation states of Pu are PuO_2^{2+} , PuO_2^+ , and Pu^{4+} under oxic conditions and Pu^{4+} and Pu^{3+} under reducing conditions. PuO_2^+ disproportionates into PuO_2^{2+} and Pu^{4+} , but the rate of the reaction depends on the 4th power of the H^+ concentration and on the square of the PuO_2^+ concentration so that at low concentrations of Pu in neutral solutions the reaction rate is negligible (Choppin, 1990). This suggests that PuO_2^+ , once present, may persist outside of its stability field because of slow reaction kinetics.

During the operational period of the WIPP repository, oxygen will be present in the storage rooms. This oxygen will be trapped in the salt formation after repository closure and will be available to react with the waste materials and their containers. Void space in the repository will be reduced by salt creep, and the encroaching salt will eventually crush the waste drums. The residual oxygen can react with the drum material or with the waste itself, producing soluble corrosion products, such as Fe^{2+} , and possibly PuO_2^+ . Radiolysis of water inside the waste drums can also result in oxidation of plutonium to produce PuO_2^+ . If there are organic complexing agents present, the PuO_2^+ will be rapidly reduced to Pu(IV) and stabilized in solution as soluble complex ions (AlMahamid et al., 1996). It is reasonable to conclude that PuO_2^+ will not be able to coexist with organic ligands for any significant period of time, and that solubility calculations should consider either transient presence of PuO_2^+ or presence of Pu(IV) with or without organic ligands.

Weiner et al. (1996) discuss the possible oxidation states of Pu under WIPP conditions. They conclude that Pu(IV) is expected to be the stable state, but include Pu(III) based on observations by Felmy et al. (1989). These experiments used Pu(III) maintained in that redox state by adding Fe powder to the solutions. The solubility of Pu(OH)₃ was measured in dilute solutions and brines. The redox state of Pu was verified by using chemical extraction methods; however, the method used measured Pu(III) + Pu(IV), so there is not positive identification of Pu(III) content. At pH 9 and above, the concentration of Pu was below detection limits (Felmy et al., 1989). This would suggest that Pu(III) needs to be considered up to pH 9 in modelling calculations if metallic Fe is present, which it will be in the form of WIPP disposal drums. Above pH 9, the upper limit for Pu(III) is set by the detection limit in the Felmy et al. (1989) experiments as 10⁻⁹ M.

Pu(V) has been observed in a number of experiments conducted in brines. Weiner et al. (1996) discuss some of these results in Appendix A to their report and conclude that Pu(V) will not be important because it disappears with time. This conclusion would be perfectly valid for cases where release from the repository is assumed to occur through flow mechanisms that take long periods of time to reach the accessible environment; however, for human intrusion scenarios where the brine may reach the surface directly via a borehole, it is probably more valid to include transient species that have been shown to have long lifetimes. Since any Pu(V) is likely to react with dissolved Fe(II), the steady-state amount of Pu(V) should be small and not lead to a large increase in calculated total mobile Pu species in the repository.

Brine composition

Brine composition can affect solubility in two principal ways. The first is through the effect of ionic strength, which will generally lead to higher actinide solubilities for high ionic strength. Most of the effect of ionic strength increase is seen by the time a solution concentration of 2M NaCl is reached, with little change in effective activity coefficients expected as ionic strength increases further. The second means of affecting solubility is through the formation of complex ions. Carbonate ion and hydroxyl ion are the main inorganic ligands that will cause increased solubility of Pu in the WIPP brines. Novak and Moore (1996) calculated that sulfate complexes are important for some cases; see Appendix B for discussion.

In this section we will consider experimental evidence that can be used to evaluate the expected effects of brine composition on the solubility of Pu. The conclusions that can be drawn from the experimental evidence will be useful in assessing the validity of model calculations. Most measurements using Pu have

been done with oxygen present in the system, either with normal atmospheric composition together with carbon dioxide, or under argon glove box conditions with 18 to 30 ppm oxygen in the gas. While the latter amount may seem very small, it is enough to provide for oxidation of Pu from Pu(IV) to Pu(V) in solution. Once Pu(V) is formed, it may be long-lived if there is not an active reductant present.

DePablo et al. (1995) conducted experiments using unirradiated crystalline UO_2 (s) in synthetic brines. Both oxidizing and reducing conditions were studied; reducing conditions were maintained using a hydrogen flux and a Pd catalyst. Carbon dioxide was not present in the experiments. Brine compositions (molal concentrations) were

Species	NaCl-brine	MgCl ₂ -brine
Na ⁺	6.036	0.48
K ⁺	0.037	0.57
Mg ²⁺	0.018	4.21
Ca ²⁺	0.021	0
Cl ⁻	6.036	8.84
SO ₄ ⁼	0.058	0.32
Ionic Str.	6.25	14.00
pH	7.7	4.7

The UO_2 (s) had an initial surface condition that was very oxidized, $\text{UO}_{2.7}$ as measured by XPS. This led to an initial rapid dissolution of the oxidized surface even when the solution was maintained with reducing conditions. The solution concentrations in both brines gradually decreased and settled after 20 to 25 days at steady-state values of 2.8×10^{-7} mol/kg in the NaCl brine and 3.1×10^{-7} mol/kg in the MgCl₂-brine. At the end of the experiments the Eh was measured to be 0 to 60 mV (compatible with the stability of UO_2) and the surface of the dissolving solid was measured to have a composition of $\text{UO}_{2.1}$ as measured by XPS. A model calculation was done using the PHRQPITZ code (the PHREEQE equilibrium code with Pitzer parameters added) and gave quite good agreement of the concentrations predicted by the calculations with those measured in the experiments. The calculated concentrations for zero ionic strength solutions were about a factor of 3 lower than those calculated for the brines.

The experiments of DePablo et al. (1995) show that for UO_2 (s), there is very little variation in solubility that can be attributed to the combined effects of increasing the brine ionic strength by a factor of more than 2 and simultaneously increasing sulfate by a factor of 5. In addition, changing the dominant cation from Na⁺ to Mg²⁺ did not seem to have a large effect. From the modelling calculations, the effect of high ionic strength on solubility of the UO_2 (s) was limited to an increase of a factor of 3.

The effect of carbonate ion on the solubility of Th was measured in solubility and speciation experiments by Östhols et al. (1994). They measured the solubility of a freshly precipitated thorium oxide/hydroxide with low crystallinity as a function of pH with an atmosphere of 10% carbon dioxide. They analyzed the data and deduced speciation with $\text{Th}(\text{OH})_3\text{CO}_3^-$ as the dominant species from pH 5 to slightly greater than 7 and with $\text{Th}(\text{CO}_3)_5^{6-}$ beginning to occur at pH just under 7 and taking over from the hydroxycarbonate complex after pH 7.4. The total solubility of Th(IV) at pH 7 was 10^{-5} M. Östhols et al. (1994) also calculated stability constants for these species and the solubility product for amorphous ThO_2 for their experimental solution conditions of 0.5 M NaClO_4 and for the extrapolated values at zero ionic strength.

Rai et al. (1995) measured the solubility of U(IV) and Th(IV) freshly precipitated oxides under inert atmosphere conditions as a function of carbonate/bicarbonate concentration in solution. For the U experiments, Fe powder was added to the solutions to ensure that no U(VI) formed. At low carbonate concentration, the uranium solubility was about 10^{-8} M. (This is about a factor of 10 lower than the value calculated by DePablo et al. (1995) for low ionic strength and no carbonate. See above). Two data points at a carbonate content of 0.1 molal also had a solubility of 10^{-8} M for Th(IV). The Th solubility increased to be 10^{-5} M at a sodium carbonate content of about 0.3 m, which is similar to the carbonate content that one would expect with a partial pressure of CO_2 of 0.1 atmosphere. For U, a carbonate concentration about a factor of 4 higher was needed to achieve the same solubility of 10^{-5} M. It should be noted that for both U and Th, the concentration of carbonate had to exceed 0.1 molal before a dramatic increase in solubility was observed.

From the results presented above, we may derive two important conclusions concerning the effect of brine composition on Pu(IV) solubility.

- (1) The detailed composition of the brine will probably not be important in determining Pu(IV) solubility in the absence of organic ligands and at low carbonate concentrations.
- (2) Carbonate ion concentrations will only have a large effect on Pu(IV) solubility if they are above 0.1 molal.

These conclusions should be valuable in assessing the reliability of modelling calculations for WIPP long-term performance predictions.

Experimental studies of Th and Pu solubility were supported by the WIPP Project in FY 1997 to determine what the effects of the MgO backfill would be on solubility and to validate the model assumption that Th data could be used to model Pu behavior. Preliminary results are available in the annual report for

FY97 (Rai et al., 1997). All experiments were done with nitrogen atmosphere. The concentrations of Th in the presence of MgO after 5 days exposure in two brines was between $10^{-7.3}$ and 10^{-8} M, while with hydromagnesite present the solubility was much higher (10^{-5} and $10^{-6.5}$ M). The solubility of amorphous plutonium dioxide in the brines in the presence of Fe powder was measured to be $10^{-6.5}$ M at pH 7.5 and $10^{-7.5}$ M at pH 8. Solubility changes when hydromagnesite was present were +/- a factor of 10 with increase in pH of 0.5 units in both brines. The presence of $\text{Na}_2\text{S}_2\text{O}_4$, a strong reducing agent, resulted in higher Pu solubility in all cases. This was interpreted to indicate the possible presence of Pu(III) species that were more soluble than the Pu(IV) species. Pu(V) was also considered as a possible species to explain some of the higher-than-expected concentrations found.

The solubilities for Pu in the absence of carbonate found by Rai et al. (1997) are quite similar to those found by DePablo et al. (1995) for UO_2 . Solubilities for Pu and Th depend to a large degree on the "age" of the solid and its degree of crystallinity. This factor is less important for UO_2 . Since the preliminary results for Pu in brines seem to be consistent with those for UO_2 solubility in brines, the UO_2 solubility data measured in brines would seem to represent a sounder basis for performance prediction than those calculated from a model based on Th with Pitzer parameters. This conclusion is strengthened by the fact that the solubilities of Th measured by Rai et al. (1997) in the presence of hydromagnesite are much higher than those calculated by Novak (1997 - see discussion in the next section and in Appendix A).

Phases controlling brine composition

The brine compositions assumed for the WIPP performance assessment conditions are either the Salado brine or the Castile brine or a mixture of these brines. To assess the solubility of actinides in the brines, Novak and Moore (1996) further assumed that the brines became saturated with halite and anhydrite, the major minerals in the associated salt formations. The effective pH of the brines under these conditions was about 5.6 to 5.8, which was thought to be lower than desirable. Actinide solubility goes down with increasing pH, at least until pH of 11 or 12 is reached; for this reason, addition of a backfill material was considered to buffer the pH at about 10 and to absorb CO_2 gas that might be generated by microbial action. (See Appendix A for a more detailed discussion of this issue.)

The MgO from the backfill was thought to produce brucite and magnesite as its stable reaction products and that these materials would be those responsible for conditioning the brine chemistry. During experiments with alteration of MgO with the brines, it was found that other phases formed. These phases are (or, at least, may be) metastable with respect to magnesite and brucite; however, they

may persist for extended periods of time under the WIPP disposal conditions. The draft report on the MgO alteration shows evidence for the formation of reaction products that are predominantly nesquehonite ($MgCO_3 \cdot 3H_2O$) with the later appearance of a phase that could not be positively identified, but was tentatively identified as $MgCO_3 \cdot 3H_2O \cdot MgCl(OH)$ (PDF7-278) (no name given). The chemistry of this phase is quite different from that of hydromagnesite [$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 4H_2O$]. Despite this, the draft report claims on page 30 that “we observed that hydromagnesite, with a loose platy habit, is the favored metastable phase in our experiments, rather than nesquehonite” (Sandia, 1997).

The identity of the Mg-carbonate phase that forms with alteration of MgO is important because this phase will control the carbonate and bicarbonate concentrations in the brines. High concentrations of carbonate in the brines can increase the solubility of Pu via complex ion formation with carbonate. Calculations in the Sandia, 1997, draft manuscript reported only the effect of hydromagnesite on expected actinide solubility. Hydromagnesite, however, was never identified in the experiments described in the draft manuscript. In other materials available from Sandia, it was seen that calculations were also done with nesquehonite (C. F. Novak memo to R. Vann Bynum dated 21 April 1997, “Calculation of actinide solubilities in WIPP SPC and ERDA6 brines under MgO backfill scenarios containing either nesquehonite or hydromagnesite as the $MgCO_3$ solubility-limiting phase.”) Since the results with nesquehonite were quite different for the (IV) actinides, they are reproduced here together with the results reported in the draft manuscript.

Conditions	+4 act., molar Salado (SPC)	+4 act., molar Castile	log fugacity (CO_2)
CCA calc.	4 E-6	6 E-9	-6.9
No backfill	5 E-4	7 E-5	0 to 2
5424 hydromag.	1 E-8	4 E-8	-5.5
4323 hydromag.	2 E-8	5 E-8	-5.39
Nesquehonite	6.3 E-4	1.0 E-3	-3.8

Note that with nesquehonite present, the solubility of the +4 actinides is calculated to be higher than it is with no backfill present. pCH for Salado conditions is calculated to be 9.4 and for Castile, 9.9.

The predictions of solubility in the presence of hydromagnesite are lower than the experimental results for Th discussed above, but are similar to the results found for Pu in the presence of hydromagnesite and Fe. No experimental data on the solubility of Th or Pu in the presence of nesquehonite is yet available.

Complex ion formation

Discussions in the previous sections have shown that the inorganic anions most likely to affect actinide (IV) solubility through complex ion formation under WIPP brine conditions are hydroxide and carbonate ions. Sulfate ion has been shown in experiments with U(IV) to have no significant effect on overall solubility over the range of variation in sulfate content expected for the WIPP.

The remaining possibility for complex ion formation comes from the waste materials, themselves. Citrate, which forms a very stable complex ion with Th, is present in large amounts in the waste inventory. The solubility calculations for the actinides in brines with and without MgO are discussed in Appendix B. These calculations assume homogeneous equilibria, which for actinides in the absence of complexing ligands from the waste is probably an adequate estimate. For the case where organics are present, the organics are also treated by SOTERM as if they were homogeneously dissolved in 29,841 m³ of brine.

To model the behavior of Pu with citrate, we must consider heterogeneous equilibria for organic complexation with the actinides. The main difficulty arises because the Pu in the waste is probably located in the same drums as the citrate, which is the dominant organic ligand. This is because these wastes arise from chemical separations of Pu and are not the type of waste described in the general descriptions of TRU waste as contaminated equipment, clothing, etc. To get an accurate estimate of the effect of organic ligands on Pu solubility, one must calculate the concentration of Pu as citrate complex inside a waste drum that has been breached, but can still provide a hindrance to mixing of the brine inside the drum with a larger pool of brine outside the drum. This will give a high concentration of Pu in solution as the citrate complex. Other ions will not compete with Pu sufficiently to prevent complex formation because the stability for (IV) actinide complexation - as shown by the stability constant for Th(IV) on p. 39 of the SOTERM appendix- is orders of magnitude larger than that for other ion complexes with citrate.

Another possible ligand for increasing Pu(IV) solubility comes from the degradation of cellulose. Work in England has shown that degradation of cellulose can occur both through chemical processes at high pH and by radiation effects. The degradation products have been shown to increase the solubility of plutonium dramatically (Cross et al., 1989; Greenfield et al., 1992).

To obtain a more accurate estimate of the effect of citrate and cellulose degradation products on Pu solubility in the event of human intrusion, calculations that use Pu complexes formed inside a waste drum and model the mixing of that relatively concentrated brine with the average repository brines must be done, taking into account the time scales for mixing and the possibility that the intrusion event may release some brine from waste drums that has not

had an opportunity to mix with the average repository brines. The development of an appropriate scenario is discussed further in the next section.

The conclusion given in the CCA SOTERM appendix that EDTA complexes will not increase actinide solubility is probably correct, since the amount of EDTA is small and the Ni and Fe complexes have stability constants that are similar to those for the actinides. It is not shown, and is probably not true, that the more abundant citrate inventory will not increase actinide solubility, especially for Pu.

Scenarios for dissolution of plutonium

Analyses of the long-term performance of the WIPP repository have shown that the only likely cause for significant releases of radioactivity would come as the result of human intrusion into the repository. One pathway for release involves drilling into the repository level, flooding of the repository with brine, and then flow of the brine through the overlying Culebra dolomite aquifer. This pathway would require considerable time before radionuclides would reach the accessible environment and, in this case, the model of homogeneous brine compositions averaged over the whole repository at the time of the release is probably appropriate. For this scenario, the large volume of brine (29,841 m³) discussed in the SOTERM calculations is probably needed.

Another human intrusion release scenario involves drilling through the repository and reaching the underlying Castile formation, in which there are pockets of pressurized brine. If a pocket of pressurized brine were to be encountered during drilling, it is possible that it might rise up the drill hole, through the repository, and up to the surface very rapidly. The only waste encountered in this case might be that in a few drums that were in the immediate path of the drill hole. These drums might contain low Pu concentrations and little or no citrate ions or cellulose degradation products, or they might contain the maximum allowed Pu concentration and sufficient citrate or cellulose degradation products to fully complex the Pu. The brine composition would be determined by the local, internal environment in the waste drum, rather than by the grand average of the repository.

As an illustration, the volume of brine that would be associated with this release scenario may be estimated by assuming a small diameter exploratory drill hole of about 0.01 m² area (a bit over 10 cm diameter drill core) and a hole depth of about 900 m. The volume to fill this hole would be 9 m³. A reasonable volume for the release of brine before it was capped off would be about 100 m³, or about 10,000 liters of brine. This brine could be assumed to contain the contents of two waste drums, each containing 10g Pu and 10 moles of citrate. The brine inside a crushed waste drum with these inventory amounts could be modelled assuming the drum material was actively corroding to provide Fe(II) at equilibrium

concentration with appropriate citrate complexation as well as the Pu(IV) citrate complex. The amount of such brine could be quite small (< 1 L) or moderate (10-30 L). This assumed concentrated brine could then be intercepted by the drill hole and the brine rising from the Castile formation, providing dilution of the concentrated brine, but probably not a major change in speciation. The appropriately diluted brine would then be the material that would be assumed to reach the surface.

The construction of the CCDF for assessment of compliance with 40 CFR 191 would then involve a selection of model realizations with the release from a pressurized brine and a probability distribution of whether the drums that might be intersected by the drill hole were those with high Pu or with low Pu. This method for handling heterogeneous waste distributions and heterogeneous equilibria in the repository would be rather simple to implement, at least on the level of exploratory calculations.

Suggestions for future work

Experimental work

Performance predictions for WIPP are currently done using equilibrium thermodynamic modelling of brine chemistry and with Th as the representative of the (IV) actinides. The calculated Th concentrations have internal inconsistencies (described in Appendix B) with respect to both the total solubility and the speciation of Th under conditions with similar brine composition. Experimental work on systems that contain Pu itself, rather than Th as a surrogate, have been started and should be continued. Results from these and future experiments should be compared with existing experimental results on U(IV) compounds.

If MgO will be used in the repository to control pH and to attempt to control carbon dioxide fugacity, experiments using brines with nesquehonite and brines with hydromagnesite should be conducted. Carbon speciation should be measured in these experiments as a function of reaction progress, as well as the evolution of the brine chemistry. These parameters will be needed if the longer term solubility of Pu in these systems is to be modelled. Redox state of Pu in solutions should be measured; methods that might be used are direct spectroscopy at relatively high concentrations and valence-specific solution extraction methods at low concentrations.

The stability constant for formation of citrate complex ions with Pu(IV) should be determined. The sensitivity, if any, of the value of the stability constant on brine composition should be evaluated. Experiments in systems that contain abundant citrate and Pu together with metallic iron and iron corrosion products formed under WIPP-relevant conditions should be done to evaluate the ability of

Fe(II) in solution to compete for citrate ion in complexes. Sequential dilution of brine with Pu-citrate complexes in solution by adding samples of that brine to solutions containing brine with metal and corrosion products should be conducted to provide validation of the calculations suggested below.

Thermodynamic properties and models

Use of Th to model the behavior of all actinide (IV) elements requires that (1) the chemistry of all actinide (IV) elements in brines is closely similar and (2) that the data base for species formation and solubility as well as for activity coefficients of Th(IV) species in brines is sufficiently well known. The differences found between Th concentrations calculated by Novak and Moore (1996) and those measured by Rai et al. (1997), and the differences between the calculations for Th and the experimental data for U(IV) indicate that one or both of those requirements is not met.

Several work areas need to be undertaken in order to improve the reliability of the calculations. First, the calculations should be done using data for Pu and the values for solubility and complex ion formation contained in the peer-reviewed data compilation prepared by OECD/NEA. This work has been underway for about 10 years and has had many man-years of effort from the members of the specialist review committee. Even though small changes may be made between the current draft document and its final publication, it is likely that a significant improvement in the consistency of the calculated results and the findings in solubility and speciation experiments could be found if this source were used for the basic thermodynamic data.

DePablo et al. (1995) reported calculations of U(IV) solubility in brines using an equilibrium thermodynamic modelling code developed by the US Geological Survey. It would be instructive to compare the results of calculations of Th solubility using the same code and data base to the reported results of Novak and Moore (1996). In particular, a comparison of the calculated activity coefficients for dissolved species using each code would be useful. For highly charged species such as $\text{Th}(\text{CO}_3)_5^{6-}$ it is extremely difficult to estimate the activity coefficient using calculational methods. Comparison of the species included in the calculations as well as the results of speciation and solubility predictions for Th would be interesting and might give an insight into the uncertainties that exist in the calculation of solubilities for these systems.

A sensitivity analysis should be conducted to determine the effects of uncertainties in both the solubility measurements and stability constant determinations as well as the estimation of Pitzer parameters on the final calculated solubility. This would involve a "Monte Carlo" type of sampling procedure that selects a value within the range of +/- appropriate to the solubility

product for a given compound and then values for each of the complex ion stability constants within their range of data uncertainties. A similar process would be used for the calculation of the Pitzer coefficients. Results of 30 to 40 calculations using this type of sampling method should give a reasonable indication of the real range of combined uncertainty in the calculations.

Release scenario calculation

A scenario for release via human intrusion that involves release of brine with concentrated Pu-citrate content via mixing with a larger volume of brine and transport through the Culebra aquifer should be done. This calculation can be done as a simple, sequential dilution model in which 10 liters of initial Pu-citrate-containing brine is mixed with 10 liters of Salado brine equilibrated with appropriate minerals and Fe(II) corrosion products. The second calculation would then mix this 20 liter volume of brine with another 20 liters of Salado brine. Ten steps of mixing would give a brine volume of 10,000 liters. The pattern of speciation changes in Pu and the overall Pu solubility calculated could then be compared to the sequential dilution experiments discussed above. If the results agree, a level of validation is achieved for the calculations. If the results disagree, insight into requirements to improve the data base and calculational methods should be gained.

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Appendix A

Review of “Chemical Conditions Model: Results of the MgO Backfill Efficacy Investigations”, Sandia National Laboratories (no author names), April 23, 1997, Draft.

This paper describes some experiments in which MgO in the form of small pellets (2 to 4 mm in size) or MgO “fines” (0.5 to 1.0 mm) were reacted with Castile and Salado brines (presumably synthetic, but the text does not address this point).

The experiments produced reaction products that are predominantly nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) with the later appearance of a phase that could not be positively identified, but was tentatively identified as $\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \cdot \text{MgCl}(\text{OH})$ (PDF7-278) (no name given). The chemistry of this phase is quite different from that of hydromagnesite [$(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$]. Despite this, the paper claims on page 30 that “we observed that hydromagnesite, with a loose platy habit, is the favored metastable phase in our experiments, rather than nesquehonite.” (See comment 4 below for a more detailed discussion.)

The concentration of an element in solution is the sum of all of the species concentrations in which that element is present. Usually, one species predominates as the most soluble for a given element under a given set of conditions, and the concentration of that species is determined by the solubility of the most soluble solid phase that results in that species being formed. That phase will continue to control the solubility so long as it is present in the system, even if other, more stable, phases are also present. For the set of possible conditions with MgO backfill present, and assuming the absence of ligands for the actinides that result in even higher solubility species, the phase that results in highest (IV) actinide solubility is nesquehonite. So long as nesquehonite may be present in the WIPP repository, the solubility of (IV) actinides must be modelled using calculations that include it as a member of the phase assemblage. Since the production of CO_2 is assumed to persist over periods of thousands of years, and since nesquehonite is observed to be formed early in the sequence of phases formed when carbon dioxide reacts with MgO in the backfill, we must assume that nesquehonite will be present over thousands of years, even if it can be shown that the conversion of a particular amount of nesquehonite to a less soluble phase occurs over a time scale of a few hundred years.

As shown in item 7 of the detailed comments, the solubility of (IV) actinides with nesquehonite present is even higher than that calculated for the case with no MgO present. If nesquehonite must be considered as present for most of the performance period of the repository, it would seem that the addition of MgO does not enhance the performance of the repository, but rather adds to the uncertainties to be considered, if our attention is limited to the case of the (IV) actinides. For the (III) and (V) actinides, the MgO does seem to reduce the solubility considerably, even with nesquehonite present (data in Novak,

21 April 1997 memo). Since Pu is the dominant actinide, and since (IV) is the most likely oxidation state for Pu under WIPP conditions, there might be good cause to reconsider the inclusion of MgO as backfill in the repository.

Detailed comments:

1. p. 5, bottom. “There is evidence in the literature that MgO can exhibit a bactericidal characteristic. However, there [*sic*] studies supporting this assertion were performed under conditions far removed from those expected in the WIPP and no direct correlation could be drawn from the literature conditions to those expected at WIPP. Therefore, no beneficial credit was taken for the potential bactericidal effect of MgO and the microbial gas generation rates were left unchanged.”

The microbes are assumed to decompose cellulose to CO₂ and methane. If the microbes are not present, chemical degradation of cellulose at high pH is likely to result in compounds that can form complexes with actinide elements and increase their solubility. See, for example, the paper by J. E. Cross, F. T. Ewart, and B. F. Greenfield in *Mat. Res. Soc. Symp. Proc.* Vol. 127, W. Lutze and R. Ewing, eds., pp. 715-722, 1989. Absence of microbes may provide negative as well as positive contributions to the potential performance of the repository.

2. p.2, middle. “Arrhenius plots assembled with laboratory synthesis of magnesite at 60°C for 7 years and at higher temperatures suggest that magnesite will form within several hundred years in the WIPP.” And, p. 19, “Nesquehonite is also temperature sensitive, but is stable well within the temperature range anticipated at the WIPP; it will convert to hydromagnesite above about 60°C (Lippmann, 1973).” The extrapolations using Arrhenius plots are discussed in more detail on pages 35-6.

The use of data obtained outside of the field of temperature stability of a phase to estimate kinetics of conversion of that phase to another phase is invalid. In addition, the phase into which nesquehonite converts is stated on p. 19 to be hydromagnesite, not magnesite.

3. p. 13. The pH curves vs reaction time show Salado brine with both the “coarse” and “fine” MgO with pH about 6, and the Castile samples to have pH about 6.8. In the figure caption, it is claimed that “The difference between the Salado and Castile curves reflects differences in the mineralogy of the coatings formed in these two brines.”

This statement seems to conflict with the reaction product discussion in the manuscript on page 20 ff.

4. p. 30. “As describe [*sic*] in Section 4, we observed that hydromagnesite, with a loose platy habit, is the favored metastable phase in our experiments, rather than nesquehonite.”

This statement conflicts with the content of section 4. Hydromagnesite was never identified in any of the experiments. Nesquehonite was described as the abundant and identifiable phase in most of the experiments.

The reaction sequence observed is described on p. 20 ff. in the draft manuscript. There is no clear difference in the phase assemblage claimed in the two brine

systems, only in the morphology of the phases; see p. 27 top in the draft manuscript. From what can be seen in the text, nesquehonite, once formed, persists in the system even if a new, unidentified phase also forms later.

The first phase observed (at point c in the model of reaction progress) is stated to contain C, O, and Mg, with very little Cl. It is interpreted to be protohydromagnesite on p. 21, top. Note: protohydromagnesite is not the same phase as hydromagnesite.

“For the coarse fraction samples, nesquehonite formation had become the dominant alteration process by day two for the Salado fraction and day three for the Castile fraction.” (p. 21)

For the fines, at day four there was no nesquehonite observed in either brine, but the original alteration product (noted above as point c) was thicker and is now referred to as “hydromagnesite-like”. At day ten, the Salado brine sample with MgO fines showed nesquehonite as a mat over a Cl-rich version of the “hydromagnesite-like” material. (p. 21, middle and Fig. 4-5).

At stage f in the reaction progress model, the samples (not stated whether it is coarse fraction, fine fraction, or both) develop an interlocking mesh of fine, platy crystals, which is interpreted to be protohydromagnesite containing a detectable amount of Cl.

On p. 27, the appearance of the new phase is claimed to be related to the presence of a high Mg concentration. The phase identification was tentative. “Although the SEM photographs show the material to be crystalline, the small crystal size has made it very difficult to get positive identification by x-ray diffraction. The best, though still highly tentative, identification arises from the comparison of the fines recovered from a 10-day treatment. In the case of the Castile coarse sample, a very clean pattern for pure nesquehonite was obtained. The dominant peaks in the Salado coarse sample were also nesquehonite, but a comparison with the Castile pattern showed that a few very small new peaks were present. These could be indexed to the material $\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \cdot \text{MgCl}(\text{OH})$ (PDF7-278).” Six lines later, the manuscript claims “The parallel between this new material and hydromagnesite is quite evident. Both this phase and hydromagnesite $[(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ consist of mixtures of magnesium carbonate, magnesium hydroxide, and waters of hydration.” This analogy would imply that most of the other phases listed on page 18 would also be equally closely related to the new material. The presence of Cl in the new material is, apparently, not considered to be important.

On p. 29, the results of the “tea-bag” experiments are discussed. The samples with longest reaction times were for 19 days. “In the 19-day samples, masses of nesquehonite needles are readily observable in the pore spaces between the grains.”

5. p.32. “Given the extremely slow precipitation rate detailed by the low pCO₂ in the repository, we expect that nesquehonite will not form. The favored metastable phase is hydromagnesite.”

It is difficult to reconcile this claim with the experimental evidence presented in Section 4 of the manuscript, especially since hydromagnesite has not been seen to form in any of the experiments described in that section.

6. In the figure caption for Fig. 5-5, it is stated “In our experiments, nesquehonite, [*sic*] is initially formed but converts to hydromagnesite, probably through the protohydromagnesite intermediary.”

This statement misrepresents the experimental results. The only phase that was positively identified was nesquehonite, which was found in abundance in nearly all of the experiments discussed in the draft manuscript. The reaction path described at the top of page 37 as “possible” is just that - possible, not definitive.

7. p. 38. “As shown previously, hydromagnesite has been observed and predicted to be the metastable phase possibly formed in the repository which then ages to form magnesite. Model predictions were performed to predict the actinide solubilities which could occur during these transient periods. To perform the model predictions, hydromagnesite had to be added to the actinide solubility database.”

As stated above, hydromagnesite was never identified in the experiments described in the draft manuscript. In other materials available from Sandia, it was seen that calculations were also done with nesquehonite (C. F. Novak memo to R. Vann Bynum dated 21 April 1997, “Calculation of actinide solubilities in WIPP SPC and ERDA6 brines under MgO backfill scenarios containing either nesquehonite or hydromagnesite as the Mg-CO₃ solubility-limiting phase.”) Since the results with nesquehonite were quite different for the (IV) actinides, they are reproduced here together with the results reported in the draft manuscript.

Conditions	+4 act., molar Salado (SPC)	+4 act., molar Castile	log fugacity (CO ₂)
CCA calc.	4 E-6	6 E-9	-6.9
No backfill	5 E-4	7 E-5	0 to 2
5424 hydromag.	1 E-8	4 E-8	-5.5
4323 hydromag.	2 E-8	5 E-8	-5.39
Nesquehonite	6.3 E-4	1.0 E-3	-3.8

pH for Salado conditions is calculated to be 9.4 and for Castile, 9.9.

Note that with nesquehonite present, the solubility of the +4 actinides is higher than it is with no backfill present. This suggests that the addition of MgO backfill may

not provide clear improvement in performance, but may add significant uncertainty in performance predictions.

Appendix B

Comments on SNL Tech Memo by C. F. Novak and R. C. Moore dated March 28, 1996, "Estimates of Dissolved Concentrations for +III, +IV, +V, and +VI Actinides in a Salado and a Castile Brine under Anticipated Repository Conditions." (Referenced in US DOE Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Appendix SOTERM, October 1996. Stated to be on file in Sandia WIPP Central File A: WBS 1.2.0.7.1; WBS 1.1.10.1.1: WPO 36207.)

This memo describes the general method used to calculate the solubilities of actinides for use in the CCA and gives the results for several sets of calculations. The database used is cited, but not included in the memo.

Solubilities were calculated using an equilibrium thermodynamic speciation code "FMT", which employs Pitzer-type interaction parameters to obtain activity coefficients for dissolved species.

Equilibrium thermodynamics for solution chemistry requires the use of the activity, a , of species in equations that describe solubility or complex ion formation. The activity of a species is related to its concentration in solution by the relationship

$$a = \gamma m \quad \text{where } \gamma \text{ is the activity coefficient and } m \text{ is the concentration of the species in moles per kg of solution.}$$

The solubility product, K_{eq} , of the salt AB in an aqueous solution can then be written as

$$K_{eq} = a_{A^+} a_{B^-} / a_{AB} = (\gamma_{A^+} m_{A^+}) (\gamma_{B^-} m_{B^-})$$

The term a_{AB} is eliminated because the activity of a pure solid is unity. The terms such as γ_{A^+} are the activity coefficients of the dissolved ionic species. For an ideal solution, which generally means solutions near infinite dilution (very little solute), these terms approach unity and the solubility may be approximated by the product of the molal concentrations. At low total dissolved solids for aqueous solutions, molal concentration (m) approaches molar concentration ($M = \text{moles/liter}$).

When solubilities are calculated for systems with many components, a group of equilibrium solubility equations must be solved simultaneously with a group of association relationships that describe formation of complex ions in solutions. The association relationships generally are limited to the attachment of an anionic ligand, L, to a cation, A^+ .

$$\beta_{1,1} = a_{AL} / a_L a_{A^+} \quad \text{where the subscript 1,1 indicates that the complex consists of 1 cation and 1 ligand.}$$

To solve the system of equations, data are needed for the equilibrium solubility constants, the association constants for ligands with cations, and the activity coefficients for all solution species.

What is available from direct measurements is the equilibrium solubility of compounds under various conditions at a fixed ionic strength in some noncomplexing electrolyte such as 0.5M NaClO₄ and similar data for association reactions for ligands and cations. These data must first be extrapolated back to zero ionic strength to get true equilibrium values for infinite dilution and then extrapolated up to the ionic strength of the actual solution. For dilute natural groundwaters, the zero ionic strength data are generally used directly. For brines, the use of some scheme such as Pitzer parameters is needed to provide the activity coefficients for the calculations.

Chemical solutions with many components are routinely modelled using computer codes such as EQ3, or, in the case of the WIPP project, FMT. These codes use a database of equilibrium, zero ionic strength data for solubility and complex ion formation, a method to calculate activity coefficients as a function of solution chemistry and solution ionic strength, and a numerical method to solve a large number of simultaneous equations. Errors and uncertainties can enter the calculations from any and all of these areas. In addition, since the codes are for equilibrium conditions, when systems occur with long-lived metastable species the code user must select which species will be suppressed in the calculations. This means that the suppressed species are eliminated from the calculations so that less stable species can control solution concentrations. For example, if hydromagnesite is to be allowed to be present, the more stable magnesite phase must not be included in the calculations. The user of the code must select the phases that will not be allowed to form.

The types of difficulties that can be encountered in using computer modelling of solution chemistry are

- (1) Data for solubility or complex ion formation are not available for the species needed or are incorrect.
- (2) Insufficient data exist to allow accurate estimation of ion interactions at high ionic strength. (Activity coefficients cannot be accurately estimated.)
- (3) Data for solubility or for complex formation are known, but are not included in the data base used by the code in question.
- (4) Incompatible thermodynamic properties data are included in the data base. (This can cause erratic results in calculations.)

(5) Computational problems related to the algorithms used to solve the simultaneous equations. (This can result in errors from accumulation of rounding errors in calculations or from multiplication of uncertainties through use of a convoluted calculational path.)

It is rare that the accuracy of computer calculations of thermodynamic equilibria for complex systems can be determined directly. In most cases, one must examine the results of calculations for consistency with experiments on related, but not identical, systems. It is also important to examine the results of calculations for internal consistency, i.e., when large changes occur in the calculated concentration of a solution species, are these accompanied by other changes in the solution species that would be expected.

When I examined the calculational results in the memo by Novak and Moore, I found inconsistencies both internally and with respect to relevant published work. These are discussed below.

Novak and Moore did a series of calculations in which they stepwise equilibrated a brine composition with selected solids, actinides, more selected solids, and organics in the solution phase. The sequence of calculations was

- (1) Brine alone
- (2) Brine plus halite and anhydrite
- (3) Brine from step 2 plus Am(III) + Th(IV) + Np(V) until an actinide solid phase precipitated for each actinide
- (4) Brine from step 3 plus brucite and magnesite
- (5) Brine from step 4 plus organic ligands.

In addition, steps 4 and 5 were done with saturation with portlandite and calcite instead of with brucite and magnesite.

Selected calculation results are presented in Table 1 as element concentrations and in Table 2 as species concentrations in mol/kg. The changes in major solutions chemistry in going from step 1 to step 3, which is the first result shown in Tables 1 and 2, were

ERDA brine: sodium increased from 5.63 m to 6.22 m, and pmH decreased from 6.74 to 5.84, accompanied by changes in carbon dioxide and carbonate species related to pH and complex ion formation.

Salado brine: sodium increased from 2.06 m to 2.9 m, and pmH increased from 4.11 to 5.63, again with changes in carbon dioxide and carbonate species.

We will discuss only the calculations for Th solubility and speciation here. For the case with actinides plus brine plus saturation with halite and anhydrite, two sulfate complexes with thorium appear as the sole reason for high solubility in the Salado brine case and are significant contributors to high solubility in the ERDA brine case. The abundance of these

calculated species does not appear to be strongly affected by the factor of 4 difference in sulfate ion concentration in the two brines. When calculations are then done for addition of brucite and magnesite, the sulfate ion concentrations in solution remain about the same, but the Th sulfate complexes become insignificant. This occurs together with a calculated decrease in total Th solubility. Since the only major change in brine chemistry for the ERDA case is an increase in pH and accompanying changes in carbonate equilibria, the Th sulfate solution complexes should remain dominant. Their absence in the speciation results for the step 4 cases suggests that there are major calculational problems with the FMT code and its data base.

Experimental data for the solubility of UO_2 in brines of NaCl with similar ionic strength (pH = 7.7) and MgCl_2 with higher ionic strength (pH = 4.7) under reducing conditions in the absence of carbon dioxide gave U^{4+} concentrations of 2.8×10^{-7} m and 3.1×10^{-7} m, respectively (DePablo et al., 1995). These results are compared to calculations for thorium by Novak and Moore in the following table. (See Tables 1 and 2 at the end of this appendix for detailed results.)

Table B-1: Comparison of experimental determination of solubility for U with calculated solubility for Th.

Brine type	Experimental value UO_2 , DePablo et al.	Calculated value ThO_2 , Novak and Moore
NaCl/ERDA	2.8×10^{-7} m	3.9×10^{-3} m
MgCl_2 /Salado	3.1×10^{-7} m	4.4×10^{-4} m

The Th solubility in the ERDA brine was calculated to be dominated by the pentacarbonate complex; however, the amount of soluble Th sulfate complexes was calculated to be 7×10^{-4} m. For the Salado brine, the calculated Th solubility was due almost completely to the soluble sulfate complexes. Since DePablo et al. had no carbon dioxide in their system, the soluble species should be present as hydroxy or sulfate complexes only. The experimental results are three and four orders of magnitude lower than those calculated by Novak and Moore for Th. Since the WIPP project bases their model for (IV) actinide solubility on the assumption that all (IV) actinide solubilities can be calculated using Th as the model, this discrepancy between calculations and experiments under similar conditions is significant.

The Th sulfate complexes used in the calculations were proposed by Felmy and Rai (1992) when they reinterpreted data published originally in 1963; they do not consider the monosulfate complex. Data for sulfate complexes of Pu being considered for use in the international compendium of thermodynamic data for Pu and Np under preparation by OECD/NEA contains recommended values for a mono-sulfate, $\text{Pu}(\text{SO}_4)^{2+}$, and a di-

sulfate, $\text{Pu}(\text{SO}_4)_2$, complex, rather than the di- and tri-sulfate complexes, $\text{Th}(\text{SO}_4)_2$ and $\text{Th}(\text{SO}_4)_3^-$, used in the Novak and Moore calculations (K. Spahiu, personal communication). This suggests that either (1) the complexes used to model Th were incorrect, or (2) that Th is not a good surrogate for Pu in its behavior with respect to sulfate complexes. In either case, the calculations done for Th would not be valid for use in estimating Pu solubility.

Another problem that is evident in the Novak and Moore calculations concerns the carbonate species calculations. At low pH in the Castile brine, the dominant soluble Th species is calculated to be $\text{Th}(\text{CO}_3)_5^{6-}$ with very minor amounts of $\text{Th}(\text{OH})_3\text{CO}_3$. At higher pH (9.9), the two species are calculated to be about equal in importance in Castile brine, but with the solubilities in the 2 to 4×10^{-9} range. In Salado brine, the pentacarbonate complex is absent at pH 5.6 (nearly the same pH as for the equivalent Castile calculation, which shows this complex present at 3×10^{-3} m), but appears at 3 orders of magnitude higher than Castile calculated concentrations at pH 9.4, with similar total dissolved carbonate species in the two cases. These internal inconsistencies in calculated results point to problems in the calculational methods used and/or the data base parameters selected. In addition, the species predominance at low pH should be the opposite of that calculated for the Castile brine. The stability constants for these species were determined by Östhols et al. (1994); a graphic display of the progression of species as a function of pH is given in their paper. The pentacarbonate complex is dominant at high pH, while the hydroxycarbonate species is important at lower pH.

An additional problem with the calculated carbonate species for Th is that the pentacarbonate complex is predicted to exist in solutions with only micromolar carbonate concentrations. In general, this species is not important until carbonate concentrations are above 0.1 molal. See, for example, Rai et al. (1995). Discussion with K. Spahiu confirmed that behavior of Pu carbonate complexes could be expected to be similar to Th and to require concentrations in the > 0.1 m carbonate range.

It should be noted that conclusions drawn by Novak and Moore concerning the lack of importance of organic complexation in the determination of Th solubilities are invalidated since their basic calculations for Th solution species appear to contain a number of significant errors.

References

J. DePablo, J. Giménez, M. E. Torrero, and I. Casa (1995) Mechanism of unirradiated UO_2 (s) dissolution in NaCl and MgCl_2 brines at 25°C, Mat. Res. Soc. Symp. Proc. 353, T. Murakami and R. C. Ewing, eds., 609-615.

E. Östholms, J. Bruno, and I. Grenthe (1994) On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO₂ in CO₂-H₂O media, *Geochim. Cosmochim. Acta* 58, 613-623.

A. R. Felmy and D. Rai (1992), An aqueous thermodynamic model for a high valence 4:2 electrolyte Th⁴⁺-SO₄²⁻ in the system Na⁺- K⁺- Li⁺-NH₄⁺- Th⁴⁺- SO₄²⁻ - HSO₄⁻ - H₂O to high concentrations, *J. Soln. Chem.* 21, 407-423.

D. Rai, A. Felmy, D. A. Moore, and M. J. Mason (1995) The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaHCO₃ and Na₂CO₃ solutions, in *Mat. Res. Soc. Symp. Proc.* 353, T. Murakami and R. C. Ewing, eds., 1143-1150.

Table 1: Results of model calculations by Novak and Moore(1996) in concentrations of moles/kg brine. Equilibrations of Castile-like brine (ERDA) and Salado-like brine with anhydrite and halite plus actinides with and without MgO or CaO.

Element	ERDA-HA-An		Salado-HA-An		with CaO
	no MgO	with MgO	no MgO	with MgO	
Hydrogen	111	111	111	111	111
Oxygen	56.5	56.5	55.8	55.9	55.6
Sodium	6.22	6.2	2.9	4.69	3.5
Potassium	0.11	0.11	0.865	1.05	1.06
Magnesium	0.0214	0.0443	1.62	0.51	5.0 E-6
Calcium	0.0112	0.0133	0.0305	0.0331	1.31
Chlorine	5.98	5.97	6.95	6.67	7.12
Sulfur	0.189	0.191	0.0529	0.06	0.002
Carbon	1.86 E-2	3.15 E-5	1.15 E-2	4.08 E-5	5.87 E-6
Boron	0.0709	0.0708	0.0225	0.0272	0.0244
Bromine	0.0124	0.0124	0.0112	0.0136	0.0122
Th(IV)	3.88 E-3	6.78 E-9	4.37 E-4	4.98 E-6	1.16 E-9
Am(III)	4.49 E-4	4.12 E-7	2.57 E-4	4.39 E-6	1.25 E-9
Np(V)	1.74 E-4	2.53 E-6	1.78 E-5	2.64 E-6	4.85 E-6
pH	5.843	9.893	5.63	9.366	12.124
Solid phases	halite anhydrite	halite anhydrite brucite magnesite glauberite	halite anhydrite	halite anhydrite brucite magnesite Mg-oxychloride	halite anhydrite brucite portlandite calcite Ca-oxychloride
	Am(OH)CO ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ ·2H ₂ O(s)	Am(OH)CO ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ ·2H ₂ O(s)	Am(OH)CO ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ ·2H ₂ O(s)	Am(OH) ₃ ThO ₂ (am) KNpO ₂ CO ₃ ·2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) NpO ₂ (OH)(aged)

Table 2: Solution species concentrations in brines (from Novak and Moore, 1996) in moles/kg
 Only species involving major ions, sulfate, carbonate, and actinides are given.

Species	Castile		Salado		SPC-HA-An-Mg		SPC-HA-An-Ca	
	ERDA-HA-An	ERDA-HA-An-Mg	SPC-HA-An	SPC-HA-An-Mg	SPC-HA-An-Mg	SPC-HA-An-Mg	SPC-HA-An-Ca	SPC-HA-An-Ca
Na+	6.22	6.2	2.9	2.9	4.69	4.69	3.5	3.5
K+	0.11	0.11	0.865	0.865	1.05	1.05	1.06	1.06
Ca++	0.011	0.011	0.03	0.03	0.032	0.032	1.29	1.29
Mg++	0.071	0.039	1.67	1.67	0.495	0.495	1.6 E-6	1.6 E-6
MgOH+	2.1 E-8	4.2 E-4	1 E-6	1 E-6	1.7 E-3	1.7 E-3	4.4 E-6	4.4 E-6
H+	1.4 E-6	1.3 E-10	2.3 E-6	2.3 E-6	4.3 E-10	4.3 E-10	7.5 E-13	7.5 E-13
Cl-	5.98	5.97	5.93	5.93	6.67	6.67	7.12	7.12
SO4=	0.187	0.191	5.16 E-2	5.16 E-2	6.02 E-7	6.02 E-7	1.97 E-3	1.97 E-3
HSO4-	4 E-6	3.6 E-10	8 E-7	8 E-7	3 E-10	3 E-10	1 E-14	1 E-14
HCO3-	8.1 E-4	7.1 E-6	2.39 E-3	2.39 E-3	1.78 E-6	1.78 E-6	1.4 E-10	1.4 E-10
CO3=	8.0 E-8	8.0 E-6	6.4 E-7	6.4 E-7	8.3 E-7	8.3 E-7	3.1 E-7	3.1 E-7
CO2(aq)	1.4 E-3	1.2 E-9	9.1 E-3	9.1 E-3	1.2 E-9	1.2 E-9	6 E-16	6 E-16
NpO2+	1.7 E-4	1.7 E-6	1.7 E-5	1.7 E-5	2.4 E-6	2.4 E-6	7.3 E-8	7.3 E-8
NpO2OH(aq)	1.9 E-9	2.1 E-7	1.5 E-10	1.5 E-10	1.2 E-7	1.2 E-7	2.4 E-6	2.4 E-6
NpO2(OH)=	NEGL.	1.0 E-9	NEGL.	NEGL.	1.8 E-10	1.8 E-10	2.4 E-6	2.4 E-6
NpO2CO3-	6.6 E-7	6.3 E-7	4.2 E-7	4.2 E-7	1.2 E-7	1.2 E-7	1 E-9	1 E-9
Am+++	3.4 E-4	7.8 E-11	1.94 E-4	1.94 E-4	3.2 E-9	3.2 E-9	1.4 E-17	1.4 E-17
AmOH++	1.1 E-4	7.7 E-7	5.6 E-5	5.6 E-5	3.8 E-6	3.8 E-6	1.2 E-11	1.2 E-11
Am(OH)2+	5.0 E-9	1.4 E-7	1.8 E-9	1.8 E-9	5.7 E-7	5.7 E-7	1.1 E-9	1.1 E-9
AmCO3+	3.2 E-6	7.2 E-11	7.3 E-6	7.3 E-6	2.9 E-10	2.9 E-10	3 E-19	3 E-19
Th(SO4)2(aq)	1.35 E-5	9 E-22	1.4 E-5	1.4 E-5	1 E-20	1 E-20	0	0
Th(SO4)3=	5.9 E-4	4 E-20	4.2 E-4	4.2 E-4	8 E-20	8 E-20	0	0
[Th(CO3)5]6-	3.27 E-3	3.7 E-9	0	0	5 E-6	5 E-6	0	0
Th(OH)3CO3-	2.0 E-7	1.8 E-9	6.9 E-7	6.9 E-7	5 E-10	5 E-10	1 E-13	1 E-13
Th(OH)4(aq)	1.3 E-9	1.3 E-9	1.1 E-9	1.1 E-9	1.2 E-9	1.2 E-9	1.2 E-9	1.2 E-9

APPENDIX C

Comments on Appendix SOTERM to the Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant dated October 1996.

Comments will be confined to those sections of the Appendix that deal with estimation of the dissolved actinide portion of the source term as it applies to plutonium. Most attention will be focused on Pu(IV), which is the most probable oxidation state under WIPP conditions. The section concerning the potential for colloidal transport (6) is quite thorough and, if anything, overestimates the amount of actinide that might be transported as the result of the presence of colloids in the brine.

The solubility calculations for the actinides in brines with and without MgO are discussed in Appendix B. These calculations assume homogeneous equilibria, which for actinides in the absence of complexing ligands from the waste is probably an adequate estimate. For the case where organics are present, the organics are also treated by SOTERM as if they were homogeneously dissolved in 29,841 m³ of brine. There are some inconsistencies in the table of inventories and molal concentrations (see item 8 below); however, this problem is small when compared to the failure to consider heterogeneous equilibria for organic complexation with the actinides.

The main difficulty arises because the Pu in the waste is probably located in the same drums as the citrate, which is the dominant organic ligand. This is because these wastes arise from chemical separations of Pu and are not the type of waste described in the general descriptions of TRU waste as contaminated equipment, clothing, etc. To get an accurate estimate of the effect of organic ligands on Pu solubility, one must calculate the concentration of Pu as citrate complex inside a waste drum that has been breached, but can still provide an hindrance to mixing of the brine inside the drum with a larger pool of brine outside the drum. This will give a high concentration of Pu in solution as the citrate complex. Other ions will not compete with Pu sufficiently to prevent complex formation because the stability for (IV) actinide complexation - as shown by the stability constant for Th(IV) on p. 39 - is orders of magnitude larger than that for other ion complexes with citrate.

To obtain a more accurate estimate of the effect of citrate on Pu solubility in the event of human intrusion, calculations that use the Pu citrate formed inside a waste drum and model the mixing of that relatively concentrated brine with the average repository brines must be done, taking into account the time scales for mixing and the possibility that the intrusion event may release some brine from waste drums that has not had an opportunity to mix with the average repository brines.

The conclusion that EDTA complexes will not increase actinide solubility is probably correct, since the amount of EDTA is small and the Ni and Fe complexes have stability constants that are similar to those for the actinides. It is not shown, and is probably not

true, that the more abundant citrate inventory will not increase actinide solubility, especially for Pu.

Specific comments:

(1) p.2 and later discussions of the same topic. The authors appear to believe that degradation of organic waste can only occur by microbial action and that the most detrimental product will be carbon dioxide gas. Work in England has shown that degradation of cellulose can occur both through chemical processes at high pH and by radiation effects. The degradation products have been shown to increase the solubility of plutonium dramatically (Cross et al., 1989; Greenfield et al., 1992).

(2) p. 17 Figure caption seems to be incorrect. This should be the Castile Brine.

(3) p. 19 The corrosion equation at the bottom of the page is not balanced. If the corrosion is envisaged to occur through the action of water, rather than dissolved oxygen, it should be written as



(4) p. 20, near bottom “Therefore, radiolysis is not expected to affect the reduction-oxidation state of the repository.” This is probably true on the scale of the entire repository, averaged over time; however, radiation effects within a waste canister that contains up to 10 g of ²³⁹Pu could be quite significant on the local scale.

(5) p. 26 The selection of species for Th solubility includes Th(SO₄)₂ (aq.) and Th(SO₄)₃⁻. The data base being prepared by OECD/NEA for recommended thermodynamic properties for Pu and Np includes sulfate complexes for Pu with one and two sulfate ligands and none with 3 sulfate ligands. In addition, the calculations of speciation with sulfate complexes for Th appear to give erratic results. See appendix B for further discussion.

(6) P. 29 The small range in uncertainties estimated for the calculation of solubilities seems to be at odds with the differences in calculated results for brines with rather similar chemistry and the difference between the calculated results and those measured for solubility of uranium dioxide in brines. See Appendix B for details.

(7) p. 35 bottom and 36 top. “Neretnieks (1982) has shown that when dissolved actinides in moving groundwater came in contact with Fe(II), the actinides were reduced to a much less soluble state and precipitated.” Actually, Neretnieks did not show that reduction occurred; he did a model calculation that predicted the process should occur. His calculations, of course, have the same limitations concerning the adequacy of the data base used as do those done by Novak and Moore.

(8) p. 37, Table SOTERM-4. This table gives organic ligand inventories and calculated molal concentrations in a brine that is stated to be 29,841 m³, being the smallest volume of brine that could escape from the repository. Converting to kg of brine using a density of 1.125 kg/L gives a total of 3.35 x 10⁷ kg of brine. Using the inventory amounts in grams and converting to moles, one finds

Ligand	Mol. Wt.,g	Inventory, g	Inventory, moles
Acetate	60	1.3 x 10 ⁶	2.2 x 10 ⁴
Oxalate	126	1.6 x 10 ⁶	1.3 x 10 ⁴
Citrate	192	1.4 x 10 ⁸	7.3 x 10 ⁵
EDTA	372	2.3 x 10 ⁴	62

(Mwt. as Versenate)

Dividing the inventory in moles by the brine amount in kilograms gives the molal concentration of the organics. The table below compares the results of my calculation with the values given in Table SOTERM-4

Ligand	Molal conc. from Inventory calc. above	Molal conc. from SOTERM
Acetate	6.6 x 10 ⁻⁴	5.2 x 10 ⁻⁴
Oxalate	3.9 x 10 ⁻⁴	2.3 x 10 ⁻⁴
Citrate	2.2 x 10 ⁻²	3.6 x 10 ⁻³
EDTA	1.8 x 10 ⁻⁶	2.0 x 10 ⁻⁶

The differences in calculated concentrations range from 10% for EDTA to a factor of 6 for citrate.

References

J. E. Cross, F. T. Ewart, and B. F. Greenfield (1989) Modelling the behaviour of organic degradation products, *Mat. Res. Soc. Symp. Proc.* 127, W. Lutze and R. C. Ewing, eds., 715-722.

B. F. Greenfield, A. D. Moreton, M. W. Spindler, S. J. Williams, and D. R. Woodwar (1992) The effects of the degradation of organic materials in the near field of a radioactive waste repository, in *Mat. Res. Soc. Symp. Proc.* 257, C. G. Sombret ed., 299-306.

Appendix D: Summary of relevant articles used in preparation of this report

D. Rai, A. Felmy, D. A. Moore, and M. J. Mason (1995) The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaHCO_3 and Na_2CO_3 solutions, in Mat. Res. Soc. Symp. Proc. 353, T. Murakami and R. C. Ewing, eds., 1143-1150.

Measurements of the solubility of U(IV) and Th(IV) in carbonate and bicarbonate solutions of various concentrations, in some cases with added NaOH. Both solubilities increase dramatically as carbonate concentrations increase beyond 0.1 M. In general, Th(IV) hydrous oxide was about 1000 times more soluble at a given carbonate concentration than U(IV). Solubilities of Th in Na_2CO_3 solutions decreased with added hydroxide ion at fixed carbonate concentration (1M).

U(IV) experiments were conducted in inert atmosphere (Ar chamber) and with Fe powder present in the experiments to ensure absence of U(VI). Th(IV) experiments were also conducted in an Ar atmosphere, but without Fe powder present. Solubility limits were approached from undersaturation by suspending freshly precipitated amorphous hydrous oxides in the appropriate solutions.

Th(IV) solubility increases from $10 \text{ E-}8 \text{ M}$ at 0.1 M Na_2CO_3 concentration to $> 10 \text{ E-}3 \text{ M}$ at 1 M Na_2CO_3 . U(IV) shows the same behaviour, but the steep increase starts at 1 M Na_2CO_3 and finishes at 6 M. Species responsible for this increase is most likely $\text{An}(\text{CO}_3)_5^{6-}$. Similar behavior is observed in bicarbonate solutions, but the increase in solubility begins at lower concentrations - 0.01 M for Th and about 0.08 M for U.

G. R. Choppin (1990) Actinide Speciation in Spent Fuel Leaching Studies, in Mat. Res. Soc. Symp. Proc. 176, V. M. Oversby and P. W. Brown, eds., 449-456.

Results from SKB's spent fuel testing program, in which LWR fuel is leached at room temperature in deionized water or in dilute sodium bicarbonate (synthetic) groundwater were used as the basis for deciding the expected speciation of U and Pu in these liquids under oxic conditions.

Figure 2 (p. 452) is a Pourbaix diagram for plutonium redox states under atmospheric CO₂ pressure and including carbonate complexes and hydrolysis reactions. The stable conditions shown are PuO₂²⁺, PuO₂⁺, and Pu⁴⁺ for oxic conditions and Pu⁴⁺ and Pu³⁺ for reducing conditions. It is noted that PuO₂⁺ disproportionates into PuO₂²⁺ and Pu⁴⁺ but that the rate of the reactions depends on the 4th power of the H⁺ concentration and on the square of the PuO₂⁺ concentrations so that at low concentrations of Pu in neutral solutions the reaction rate is negligible. As an example of this lack of disproportionation, a table is given listing the redox state of Pu in natural waters and showing more than 50% Pu(V) in most cases. (Note that at high pH this would also be expected. This may explain the relative long life of Pu(V) in some of the speciation experiments done in brines.) Choppin concludes that in oxic conditions with Pu concentrations of 10⁻⁶ M and lower, the dominant species may be PuO₂⁺.

The relative strengths of complexation for plutonium cations is Pu⁴⁺ > PuO₂²⁺ > Pu³⁺ > PuO₂⁺, which is the same order of relative stability as for U cations. (Complexes of Pu(IV) are not discussed, since the paper limits itself to oxic conditions.)

Under oxic conditions, the spent fuel leaching studies showed apparent solubility for Pu of 5-10 ppb in DIW and 0.3 to 1 ppb in synthetic groundwater (0.002 M carbonate). The redox states present are interpreted to be Pu(V) as PuO₂⁺ and Pu(IV) as precipitated Pu(OH)₄ or PuO₂ · xH₂O present as the solid phase that limits total Pu solubility. The ratio of Pu(V) to Pu(IV) in the solution phase is predicted to be extremely large: 10²³ in DIW and 10^{26.6} in the synthetic groundwater at pH 8.2. (Note: There is no reason to believe that this mechanism for solubility control under oxic conditions would not also work in brines.)

H. Nitsche (1991) Basic research for assessment of geologic nuclear waste repositories: what solubility and speciation studies of transuranium elements can tell us. Mat. Res. Soc. Symp. Proc. 212, T. Abrajano, jr. and L. H. Johnson, eds., 517-528.

Discusses experimental results for NpO_2^+ , Pu^{4+} , and $\text{Am}^{3+}/\text{Nd}^{3+}$ in J-13 well water, a natural dilute sodium bicarbonate groundwater, at pH 6, 7, and 8.5 and at $T = 25, 60,$ and 90°C . The experimental results are compared to modelling calculations using EQ3/6. Tables of stability constants for solution species used in the calculations are given and may be useful for comparison with those used in calculations for WIPP.

Plutonium was added to the groundwater as Pu(IV). The solubility controlling species were found to be polymeric plutonium(IV) and lesser amounts of plutonium carbonates. At pH 7 and 8.5, Pu solubility at 25°C was about 5×10^{-7} M. The Pu used was Pu-239 isotope. Calculations that assumed crystalline PuO_2 predicted solubility at 25°C of 10^{-12} M. Use of amorphous $\text{Pu}(\text{OH})_4$ in the calculations overestimated the solubility limit to be 10^{-4} M at 25°C . The oxidation state distribution found in the pH 8.5 experiments for species in solution was about 70% Pu(V) and 25% Pu(VI) with minor amounts of Pu(IV) and Pu(III)+polymer. (Note, this agrees with Choppin's predictions that the solid phase under oxic conditions contains Pu(IV), while the solution species would be Pu(V).)

J. E. Cross, F. T. Ewart, and B. F. Greenfield (1989) Modelling the behaviour of organic degradation products, Mat. Res. Soc. Symp. Proc. 127, W. Lutze and R. C. Ewing, eds., 715-722.

Research into the effect of alkaline degradation of organic materials that might be found in low and intermediate level radioactive wastes showed that the degradation of cellulose produced products that greatly increased the solubility of Pu. The details of the experimental results can be found in a report by J. D. Wilkins, UKAEA Report AERE R 12719 (1987).

The specific ligands responsible for the enhanced solubility could not be identified. Also, attempts to reproduce the effect using possible ligands with Pu did not produce as high a solubility. This shows the importance of examining actual waste mixtures to ensure that symbiotic effects are included.

Experiments were conducted with cement equilibrated with water with and without organic materials and with Pu added as a separate acid solution. The precipitated Pu was separated and the solution concentrations were measured. The results were

Cement alone + Pu	[Pu] = 5×10^{-10} M
Cellulose chemical degradation	[Pu] = 7×10^{-6} M
Cellulose, radiation degradation	[Pu] = 5×10^{-6} M

The effect of other organics was much less.

New experiments were done with separated organic acids. The closest results were found with D-saccharic acid $\text{HOOC} \cdot (\text{CHOH})_4 \cdot \text{COOH}$, which at pH 12 gave Pu solubility of 7.2×10^{-6} M at 10^{-5} organic acid concentration, 7.3×10^{-6} M at 10^{-4} M organic acid, 8.2×10^{-6} M at 10^{-3} M organic acid, and 9.3×10^{-6} M at 10^{-2} M organic acid. This behaviour pattern, with little change in Pu solubility even though large changes were made in organic acid concentration, was successfully described so long as one considered complexation involving hydroxyl groups as well as carboxylic acid groups.

Both experiments and modelling were done for conditions at a redox potential of + 200 mV.

B. F. Greenfield, A. D. Moreton, M. W. Spindler, S. J. Williams, and D. R. Woodwar (1992) The effects of the degradation of organic materials in the near field of a radioactive waste repository, in *Mat. Res. Soc. Symp. Proc.* 257, C. G. Sombret ed., 299-306.

A number of different solid organic materials were degraded in the presence of Portland cement and blast furnace slag (representing the concrete components in the proposed UK Nirex low and intermediate level radioactive waste repository) at 80°C under anaerobic conditions. Generally the experiments contained 10% organic and 90% cement. Samples of liquid were taken periodically, cooled to room temperature, pH adjusted to 12 (if necessary), and then spiked with a small volume of radioactive elements in acid solution to measure their solubility in the leachates. After 2 days samples were taken and filtered, and then the radioelement concentrations were measured.

Results found for Pu(IV) solubility in leachates produced from 500 days of degradation of the organics were

Cellulose or wood fiber	10 E-3 M
Cotton wool	10 E-5 M
Bakelite	6 x 10 E-6 M
PVC	10 E-9 M
Polystyrene	5 x 10 E-10 M
Nylon, Polythene, and Pure cement leachate	10 E-10 M

Degradation of cellulose under aerobic conditions resulted in a lower solubility for Pu(IV), namely 10 E-4 M, and solubilities of 10 E-5 M for Th(IV) and U(IV). Am(III) and Np(IV) in these leachates had apparent solubilities of 10 E-6 M.

The effect of varying cellulose to cement ratio was tested under anaerobic degradation conditions. The Pu (IV) solubilities found were 4 x 10 E-10 M at 0.1% cellulose, 4 x 10 E-9 M at 0.5% cellulose, but 1 x 10 E-6 M at 1% cellulose.

The product of cellulose degradation that is most likely to explain the enhanced Pu solubility is isosaccharinic acid (ISA); other possible degradation products are produced in lesser amounts and have less effect on Pu solubility than ISA. If ISA is exposed to cement, it will sorb onto the cement surface, thus diminishing its effect on Pu solubility. This is thought to explain the results found at low cellulose loadings in cement.

Modelling calculations were able to reproduce the effects seen in the experiments. It was concluded that the solubility enhancement for Pu was achieved through complexation that involved 4 deprotonated hydroxyl groups in the bonding.

I. AlMahamid, K. A. Becraft, N. L. Hakem, R. C. Gatti, and H. Nitsche (1996) Stability of various plutonium valence states in the presence of NTA and EDTA, *Radiochimica Acta* 74, 129-134.

Experiments were conducted using solutions of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) with all four soluble plutonium oxidation states - III, IV, V, and VI - at macroscopic (10^{-3}M) and microscopic (10^{-7}M) concentrations. Experiments were performed at room temperature in an argon atmosphere. Pu was prepared by dissolving PuO_2 electrochemically in 1 M HClO_4 and then adjusting to produce the desired oxidation states.

NTA was added to an acidic solution of Pu and the pH adjusted to 5 with NaOH. Final ionic strength of the solutions was about 0.01 M. At the higher Pu concentrations, the final species is a Pu(IV)-NTA complex, regardless of the initial oxidation state of the Pu, at NTA/Pu ratios of 6. At higher NTA amounts, the Pu(IV) polymeric form can even be dissolved. With EDTA, only Pu(III) was studied. This oxidized to produce an EDTA-Pu(IV) complex.

Studies with the lower Pu concentrations with NTA resulted in mainly Pu(IV) if the starting valence was III or IV. For initial Pu(V), about 65% of the Pu persisted as V, with a little becoming VI and most of the rest present as IV. For initial Pu(VI) at NTA/Pu of 100, 48% of the Pu was IV after 10 days and 31% was V, with 21% remaining as VI. Very high NTA/Pu ratios reduced essentially all of the Pu(VI), producing 38% Pu(IV) and 61% Pu(V). Experiments with EDTA at ligand to Pu ratios of 100 and of 1 also showed persistence of Pu(V) if the starting materials were VI or V, but little or no Pu(VI). It is expected that the Pu(V) will reduce to Pu(IV) with time. These solutions had low ionic strength (as low as 10^{-5}M) and no active reducing agents other than the organic ligands themselves.

J. DePablo, J. Giménez, M. E. Torrero, and I. Casa (1995) Mechanism of unirradiated UO_2 (s) dissolution in NaCl and MgCl_2 brines at 25°C, Mat. Res. Soc. Symp. Proc. 353, T. Murakami and R. C. Ewing, eds., 609-615.

Experiments using unirradiated crystalline UO_2 (s) with 1 mm particle size and BET surface area of $0.0016 \text{ m}^2/\text{g}$ were done in synthetic brines. Both oxidizing and reducing conditions were studied. Reducing conditions were maintained using a hydrogen flux and a Pd catalyst.

Brine compositions: molal concentrations

Species	NaCl-brine	MgCl_2 -brine
Na ⁺	6.036	0.48
K ⁺	0.037	0.57
Mg^{2+}	0.018	4.21
Ca^{2+}	0.021	0
Cl ⁻	6.036	8.84
SO_4^-	0.058	0.32
Ionic Str.	6.25	14.00
pH	7.7	4.7

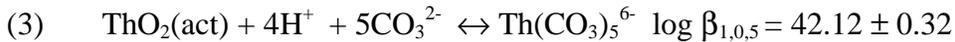
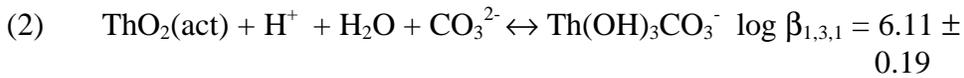
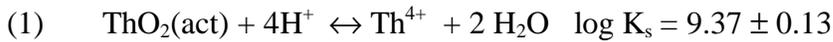
The UO_2 (s) had an initial surface condition that was very oxidized, $\text{UO}_{2.7}$ as measured by XPS. This led to an initial rapid dissolution of the oxidized surface even when the solution was maintained with reducing conditions. The solution concentrations in both brines gradually decreased and settled after 20 to 25 days at steady-state values of 2.8×10^{-7} mol/kg in the NaCl brine and 3.1×10^{-7} mol/kg in the MgCl_2 -brine. At the end of the experiments the Eh was measured to be 0 to 60 mV (compatible with the stability of UO_2) and the surface of the dissolving solid was measured to have a composition of $\text{UO}_{2.1}$ as measured by XPS. A model calculation was made using the PHRQPITZ code (the PHREEQ equilibrium code with Pitzer parameters added) and gave quite good agreement of the predicted concentrations with those measured in the experiments. The predicted concentrations at zero ionic strength were about a factor of 3 lower than those predicted for the brines.

Under oxidizing conditions, the final uranium concentration in the MgCl_2 -brine was about $10 \text{ E-}5.7$, and still slowly rising, while that in NaCl brine was considerably lower ($10 \text{ E-}6.4$) and was constant. Modeling calculations for oxidizing conditions overestimated the solubility of U in the Mg-brine by about a factor of 1000, while modeling of the NaCl brines was able to produce compatible results by using a schoepite solubility of 6.2×10^{-7} mol/kg as the solid controlling the final solution concentrations.

E. Östhols, J. Bruno, and I. Grenthe (1994) On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO₂ in CO₂-H₂O media, *Geochim. Cosmochim. Acta* 58, 613-623.

The solubility of microcrystalline ThO₂ was measured in 0.5M NaClO₄ at 25°C and 1 atm. as a function of pH and partial pressure of CO₂ to determine the stability of carbonate complexes of Th⁴⁺. The following species and stability constants were proposed to explain the results:

For 0.5 M NaClO₄ conditions,



Note: For mass balance, equation (3) should have 2 H₂O added to the right hand side. This will not affect the calculated log β_{1,0,5}.

Extrapolation of these constants to zero ionic strength gave

$$(1) \log K_s = 7.31 \pm 0.3$$

$$(2) \log \beta_{1,3,1} = 6.78 \pm 0.3$$

$$(3) \log \beta_{1,0,5} = 39.64 \pm 0.4$$

The solid used in these experiments was a freshly prepared precipitate of thorium oxide/hydroxide, which was of low crystallinity, and the atmospheres were mixtures of 97% CO₂ in N₂, 10% CO₂ in N₂, and pure N₂.

For the experiments at 0.1 atm carbon dioxide, the crossover between the Th-hydroxycarbonate and Th-pentacarbonate species as dominant in solution occurred at pH = 7.5. Above pH 8, essentially all of the dissolved Th was present as the pentacarbonate complex.

F. L. Sayles and W. S. Fyfe (1973) The crystallization of magnesite from aqueous solution, *Geochim. Cosmochim. Acta* 37, 87-99.

In the introduction section of this paper, evidence is presented to show that the oceans are supersaturated with respect to magnesite and dolomite, and that their formation is controlled by kinetic rather than thermodynamic considerations. Natural occurrences of magnesite are generally in hypersaline environments, with salinity much greater than seawater.

Reagent grade basic magnesium carbonate (hydromagnesite) was reacted with saline solutions that had been equilibrated with atmospheric pressure carbon dioxide at 25°C. The solid and solutions were sealed into Pyrex ampules and reacted at 126°C to produce magnesite, which was detected using X-ray diffraction. The experiments showed that there was a long induction period prior to the production of any detectable magnesite. After crystallization of magnesite started, conversion to pure product proceeded fairly rapidly. The conversion rate increased with ionic strength and partial pressure of carbon dioxide, but decreased with Mg concentration. Nucleation of magnesite occurred on hydromagnesite surfaces (seen in SEM images).

M. P. Neu, D. C. Hoffman, K. E. Roberts, H. Nitsche, and R. J. Silva (1994) Comparison of chemical extractions and laser photoacoustic spectroscopy for the determination of plutonium species in near-neutral carbonate solutions, *Radiochimica Acta* 66/67, 251-8.

Experiments were conducted to investigate the solubility and speciation of ^{242}Pu in a 1.93 mM total carbonate solution of 0.100M NaClO_4 at pH = 6.0 and 30°C. The isotope ^{242}Pu was chosen to minimize the radiolysis effects that occur. The experiments were conducted in a controlled atmosphere argon glove box in which the oxygen concentration was typically 18 to 30 ppm. The Pu solution was added to a 0.100M NaClO_4 solution that had been pre-equilibrated with 5.71% CO_2 in Ar gas together with an amount of base needed to neutralize the acid from the Pu stock solution.

Experiments with a starting solution of Pu(V) with an initial concentration of 2.51×10^{-5} M had a soluble Pu concentration of $2.1 \pm 1 \times 10^{-5}$ M after 53 days. The speciation was determined by spectroscopy to be PuO_2^+ at the level of $95 \pm 5\%$. When the Pu solution was initially Pu(VI) as PuO_2^{2+} at $2.4 \pm 1 \times 10^{-4}$ M, the concentration of soluble Pu after 120 days was $3.1 \pm 5 \times 10^{-6}$ M, or only 1.3% of the initial concentration. This was also 7 times lower than the final concentration when Pu(V) was the initial valence state for the Pu, even though it is Pu(V) as PuO_2^+ that represents the soluble Pu after 28 days of the experiment. If Pu(VI) disproportionates to produce Pu(IV) at pH =6, polymeric Pu-hydroxide will precipitate. This may explain the lower final concentrations found when Pu(VI) was the starting valence.

Speciation inferred from chemical extraction agreed with that measured directly from spectroscopy.

H. Nitsche, K. Roberts, R. Xi, T. Prussin, K. Becraft, I. Al Mahamid, H. B. Silber, S. A. Carpenter, R. C. Gatti, and C. F. Novak (1994) Long term plutonium solubility and speciation studies in a synthetic brine, *Radiochimica Acta* 66/67, 3-8.

This paper describes solubility studies of ^{239}Pu in a synthetic brine (H-17) conducted with a gas phase overpressure of 0.26% CO_2 and 20.75% O_2 in argon. Five separate experiments were conducted using initial species of Pu as Pu^{3+} , Pu^{4+} , PuO_2^+ , PuO_2^{2+} , and Pu(IV) polymer at concentrations high enough to ensure supersaturation. The brine composition was

Ca^{2+}	0.029 M/L	Cl^-	2.482 M/L
Mg^{2+}	0.074	SO_4^{2-}	0.075
Na^+	2.397	Br^-	0.00095
K^+	0.031	TIC	0.00082 (Total inorganic C as HCO_3^-)
B^{3+}	0.004		

pH = 7.0, $\text{pCO}_{2(\text{g})} = 10 \text{ E-}2.56 \text{ ATM}$
Ionic strength = 3.0 molal
Density = 1.10 g/cm^3

This brine is similar chemically to the Castile simulant brine ERDA-6 diluted by a factor of 2.

Solids that precipitated from the samples that originally contained Pu(III), Pu(IV) or Pu(IV) polymer appeared to be identical and consist of Pu(IV) polymer. Solids recovered from the experiments that initially contained Pu(V) and Pu(VI) effervesced when dissolved in HCl, indicating that they contained carbonate. Similarities of the x-ray patterns for these solids with those of $\text{KPuO}_2\text{CO}_3(\text{s})$ suggested that the solid was $\text{NaPuO}_2\text{CO}_3(\text{s})$, for which no reference powder pattern was found, since there is so much more Na than K in the brine.

Steady state concentrations found range from $2 \times 10^{-7} \text{ M}$ for solutions that originally contained soluble Pu(III) and Pu(IV), to $3.6 \pm 0.8 \times 10^{-7} \text{ M}$ for Pu(V) solution, and $7.6 \pm 2.3 \times 10^{-7} \text{ M}$ for initial Pu(VI). The predominant oxidation state of the solution species at the end of the experiments was (VI) with lesser amounts of (V), found mainly in those experiments that began with Pu as VI and V. Eh measured in solution at the end of the experiments was +400 to +500 mV vs. the normal hydrogen electrode.

D. T. Reed, S. Okajima, and M. K. Richmann (1994) Stability of plutonium (VI) in selected WIPP brines, *Radiochimica Acta* 66/67, 105-111.

States that the predominant actinide in TRU waste will be plutonium-239 at the level of up to 10 grams per waste drum.

Studies were done in two synthetic brines - brine A (similar to Salado conditions) and ERDA-6, which represents expected conditions in the Castile formation brines - and in two brines collected from the WIPP site. The natural brines had a composition that was between those of the synthetic brines with the exception of sulfate, which was a factor of two higher than ERDA brine for one of the natural brines. The pH was about 6 in all cases.

Pu(VI) was stable in Brine A, which contained carbonate. In the ERDA brine, which had no intrinsic carbonate (other than that which would dissolve from contact with normal air), the predominant species was a Pu(VI) hydrolytic form, with the possibility of some Pu(V) forming over time. In the natural brines, the Pu(VI) species disappeared from spectra after 6 days and no peak attributable to Pu(V) was observed. Final concentrations in these brines for Pu were about $5 \times 10^{-5}M$, which would make direct observation of Pu(V) doubtful; however, the authors conclude that the Pu has been reduced further to an unidentified species, possibly polymeric plutonium.

**8.4b Solubility Issues Raised by Dr. Rodney C. Ewing
After the February 20, 1998 Meeting Between the EEG and Sandia.**

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Rodney C. Ewing

February 22, 1998

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Environmental Evaluation Group
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Dear Bob,

Thank you for inviting me to attend the technical exchange meeting between DOE contractors and the EEG on the subject of the actinide source term (AST) held this past February 20th. Since the time of the last meeting of the National Research Council's Committee on the Waste Isolation Pilot Plant (May, 1997), I have not had the opportunity to follow the progress of the AST program. I should also emphasize that I am no longer on the NRC WIPP Committee, and these brief comments represent my own views. I am not a representative or consultant for any committee or agency regarding the WIPP.

I want to emphasize my view of the importance of the actinide source term work. Although the NAS (1996) report on WIPP arrived at a positive evaluation of the potential for the WIPP as a repository for transuranic waste, the same report clearly identified outstanding technical issues, prominent among them was the issue of actinide solubilities in brine (page 5). Unfortunately, there was little of substance to review concerning the AST program at the time the WIPP committee completed its report in October of 1996. We concluded (page 62):

"Overall, the scientific program outlined by DOE for study of the source term is adequate, provided that the program is carried to completion. Because the program at this time consists largely of work planned or in progress, it has not been possible to critically review experimental results or to judge whether these results are used appropriately in the PA analysis."

Thus, I believe the review of this topic by EEG and EPA is essential to establishing confidence in the data and models used for the AST in the performance assessment. I note that the most recent PA analysis suggests that the actinide solubilities in brine are of lesser importance; however, this conclusion is based on the new and revised view of transport in the Culebra and the introduction of the MgO backfill. In the event, either or both of these issues

change with further analysis or experimental results, then the role of actinide solubilities may again become important.

My general observations and comments include:

1. The oxidation state analogy and the FMT calculations appear to predict trends in actinide solubilities; however, this work still requires important experimental verification. The NAS (1996) report concluded (page 63),

"Although some aspects of its geochemical behavior can be estimated by studies of other actinides using the oxidation state model, ideally, data for each oxidation state should be followed by experiments with plutonium."

The presentations this past week only emphasized and confirmed the need for such experiments. Particularly important were the points made by the EEG consultant, Dr. Virginia Oversby, which were based on a critical review and use of data in the published scientific literature. It seems to me that the credibility of the project would be greatly enhanced by the comparison of FMT results to experimental results obtained outside of the project, as an example, studies of actinide solubilities in spent fuel or UO_2 corrosion experiments.

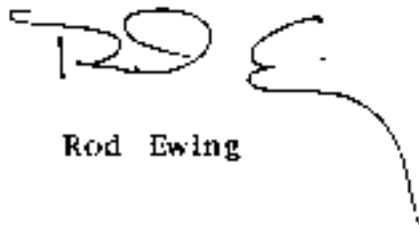
2. It certainly appears to be an opportune time to review the results and analysis of the source term test program (STTP) at LANL. The limited results presented, were used to conclude that the predicted actinide concentrations in brine are "conservative". In my view, the data only suggest that there are processes (not identified) that affect the actinide concentrations, and these processes, in general, lower the actinide concentrations.

There was some mention of discontinuing some of these tests; however, considering the time, effort and expense required to begin and sustain these experiments, such a decision should be made only after careful review and analysis of the data from the STTP experiments. Although some of the experiments may have no present applicability to the WIPP project, DOE may want to consider the experiments in a wider context, as an example the interaction of actinides and clays may be important to other DOE projects; thus, there may be value to continuing even those experiments which are not now considered to be relevant to WIPP.

3. The project still is not in a position to present and discuss models of the longer term evolution of the chemistry of the WIPP system. In this regard, well constrained, simple, experiments with relevant actinides (e.g., Pu) that are designed to run for years are still much needed. I see no reason that such experiments cannot be initiated and run through the operational phase of the repository, and their results may be utilized in the recertification process. This is consistent with the recommendations of the NAS (1996) study (page 64). Similar experiments to study retardation in the Culebra would also be of value.
4. Concerning the report and comments by the EEG consultant, Dr. V. Oversby, I believe that some of the issues she raised can be rather directly addressed by the exchange of recent and relevant results, straightforward calculations, and/or limited additional experimental work. However, her approach to the review of the CCA, particularly in the areas of verification and validation, merit careful attention. I believe that she very commendably demonstrated the real meaning of a *critical* review by:
 - i.) comparison of project results to the published literature (e.g., use of the NEA data base; UO_2 and spent fuel corrosion studies);
 - ii.) comparison of results from project codes and models to more generally used and accepted geochemical code results.

I hope that these brief comments are of use to the project. You may give copies to this letter to DOE and EPA.

Sincerely,



Rod Ewing

cc: John Garrick, chair, NRC WIPP Committee
Thomas Kiess, staff officer, NRC WIPP Committee

**8.4c Solubility Issues Raised by Dr. Virginia Oversby
After the February 20, 1998 Meeting Between the EEG and Sandia.**

Issues related to solubility of Pu at WIPP

1) Heterogeneous vs homogeneous equilibria

Calculations of solubility of actinides under WIPP conditions have been done assuming that before any release the repository will contain 29,841 cubic meters of brine that is well equilibrated. This assumption is doubtful and other models should be investigated to determine the effects of local variations in brine compositions and actinide speciation and concentration. After closure, the repository salt formation will creep and close up void spaces. Subsequent intrusion of brine, either as drilling fluid during an intrusion event or as intrusion of pressurized brine following penetration to layers below the repository, will add concentrated - if not saturated - brine solutions to the repository horizon. After fluid is added, the resulting physical state of the repository should still be one of rather low total porosity and have a high proportion of solids relative to fluids. In that case, equilibration of fluid compositions over large distances is unlikely, since the mechanism of mixing would be diffusion rather than advection. Local pockets of solutions with chemical compositions representative of the range of potential waste container soluble actinide inventory should be considered, rather than the grand average of the actinide inventory and brine compositions. This is particularly important for issues such as the complexation of Pu by citrate and/or cellulose degradation products, as well as the changes in solubility that may accompany presence of different alteration products of MgO.

2) MgO alteration products

The CCA calculations of solubility of actinides assumed that MgO backfill would alter to produce an equilibrium assemblage of brucite and magnesite. Later investigations indicated that the first phase formed from reaction of MgO with aqueous carbon dioxide dissolved in the brine would be nesquehonite. Calculations of actinide solubility in the presence of nesquehonite resulted in estimates of Th solubility (and, thus, other actinide (IV) elements) that were in the range of those calculated for the case without backfill. While it was argued that the longer-term phase would be hydromagnesite, nesquehonite might persist for rather long times.

At the meeting between WIPP staff and EEG on February 20, 1998, it was stated that the reason nesquehonite had been found in the previously reported experiments was that a high pressure of carbon dioxide had been used. New experiments, with lower carbon dioxide pressure, produced an unidentified phase, persistent over at least 200 days, that was thought to be hydromagnesite.

Two issues remain to be resolved: 1) what is the identity of the phase in the new experiments, and 2) what is the effect of heterogeneous repository conditions on the pressure of carbon dioxide in local regions of the repository. Gas generation rates will depend on the local abundance of bacteria and microbes as well as the local abundance of materials that can degrade to produce carbon dioxide. An analysis of maximum gas generation rates in local areas is needed before it can be assumed that nesquehonite can not form.

3) Relative solubility of Th versus other actinides

As part of the rationale for using Th as an analog to estimate the solubility of other actinides in the (IV) oxidation state, the WIPP staff claim that Th always shows higher solubility than U(IV) and Pu(IV). While this has been shown to be the case for freshly precipitated Th and U hydroxides, it is not the case for the vast majority of materials that contain U and Th in natural settings - i.e., minerals containing U and Th. A vast body of geochemical data pertaining to the U-238 decay series shows that U leaches from minerals in preference to Th.

Th (and Pu) forms an amorphous solid when freshly prepared from solution by precipitation of the hydrous oxide. The solubility of this amorphous hydrous oxide can be quite high. With time, Th and Pu precipitates of hydrous oxides age into materials that have increasing degrees of crystallinity. As crystallinity increases, the measured solubility of the materials decreases. This is the major reason for the very large range of reported solubility data for Th and Pu oxides in the literature.

4) Solution speciation in solubility calculations

In order to evaluate the potential validity of calculated actinide solubilities one must closely inspect the identity of the solid phases assumed to control the brine composition and the speciation of the actinides in solution. As conditions change (e.g., identity of solids assumed to be present, or chemistry of the brine), the speciation of the actinides should change in a manner consistent with the changes in assumed solids and fluid compositions. Changes in speciation between two successive calculation that cannot be explained by rational chemical arguments are symptomatic of problems in the chemical data base or the calculational methods. An example of this type of problem was seen in the CCA calculations, where Th solubility was dominated by di- and tri-sulfate complexes in the no backfill case, but these species were calculated to be insignificant in the case where Mg was added. Detailed examination of the solution speciation did not indicate any reason for this drastic change in calculated speciation.

5) Calculations and measurements for pyrochemical salts

Tests underway at LANL using actual waste samples have produced conditions for which the calculated solution concentrations for Pu were greater than 0.001 M. The details of these calculations have not been presented. If the pH of the brines in contact with the pyrochemical salts is near neutral or higher, the high calculated solubility should not be greatly affected by the assumption of adding MgO to the system. Measurements of Pu-239 in these tests gave concentrations of about 1×10^{-5} , which is higher than the concentration used in the CCA for demonstration of compliance with release limits. These high calculated and measured solubilities need to be investigated, particularly in light of the fact that inventories of Pu contained in chloride salts at Rocky Flats exceed 1 ton.

6) Direct estimates of solubility for U(IV) and Pu(IV)

The Nuclear Energy Agency (NEA) of the OECD has published a compendium of recommended values for the thermodynamic properties of U. Data from this volume (I. Grenthe, ed.) should be used to provide a direct estimate of the solubility of U(IV) in brines similar to those expected at WIPP. Also, data on U solubility in brines published in the open literature should be used as a means to estimate solubilities for U(IV) under WIPP conditions.

The NEA is also preparing a compendium of recommended values for the thermodynamic properties of Np and Pu (R. Lemire, ed.). This volume is in the final stages of preparation, so that any changes in the recommended data between the present draft and the final issued volume should be small. This volume could provide a sound basis for estimation of Pu solubility in WIPP brines.

7) Needs for additional experimental work

Direct measurements of solubilities of actinides under conditions that are assumed to be relevant for WIPP are needed. Some examples of the types of experiments needed are measurements of the solubility of Pu in brines in the presence of Fe, direct measurement of Pu speciation in brines, and solubility of actinides in the presence of the alteration phases of MgO, both at low and high carbon dioxide concentrations.

8.5 WIPP Related Geological Issues (Chaturvedi, 1993)

WIPP-RELATED GEOLOGICAL ISSUES

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Abstract The Waste Isolation Pilot Plant (WIPP) is a proposed repository for disposal of defense transuranic (TRU) radioactive waste. Located in southeastern New Mexico, 25 mi (40 km) east of Carlsbad, the repository has been excavated in the Salado Formation bedded salt at a depth of 2150 ft (655 m) below the surface. The concept of geologic isolation of radioactive waste, with the half-life of the radionuclides measured in tens of thousands of years, is to primarily rely on the geologic barriers to keep the radionuclides from leaking to the biosphere. Several geologic features and processes have been identified during the site characterization of the WIPP site that could impact the performance of the repository for the 10,000 year regulatory period. These include salt dissolution, brine chimneys, brine reservoirs, Salado Formation hydrology, hydrology of the overlying Huastler Formation water-bearing units, disturbed rock behavior and natural resources. These geologic factors are being considered in the analysis of breach scenarios from the WIPP repository for the next 10,000-year period.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is being excavated and constructed to be a geologic repository for permanent disposal of defense transuranic (TRU) waste. It is located 25 mi (40 km) east of Carlsbad, New Mexico. In addition to support facilities on the surface to provide

office space to workers and to receive and handle radioactive waste (Fig. 1), there are four shafts (waste handling, construction and salt loading, air intake and air exhaust shafts) that connect the surface to the underground facilities. The project is being administered by the U.S. Department of Energy (DOE), with Sandia National Laboratories



FIGURE 1. An aerial view of the WIPP (courtesy U.S. Department of Energy)

in charge of site characterization and most of the experiments and Westinghouse Electric Corporation as the managing contractor.

The repository is excavated at a depth of 2150 ft (655 m) below the surface and consists of an experimental area to the north and the main repository to the south of the shafts (Fig. 2). The experiments carried out in the northern part of the facility include mechanics of closure of excavations; effect of heat on closure and brine migration; development of plugs and seals to be used to plug the excavations, shafts and bore holes; and the effect of salt creep on the waste drums. The repository itself will consist of 56 "rooms," each 300 ft long, 33 ft wide and 13 ft high (91.5 m x 10 m x 4 m), divided in eight panels of seven rooms each. The seven rooms of the first panel were excavated between 1986 and 1988, since the DOE had planned to start shipping radioactive waste to WIPP in 1988 for an "operational demonstration." Excavation for the other seven panels of the repository has not yet begun.

Transuranic waste consists of various kinds of trash including paper, rubber, wood, metals and sludges, contaminated with radionuclides heavier than uranium with half-lives greater than 20 years and a level of contamination exceeding 100 nanocuries per gram. The waste has resulted as a by product of nuclear weapons production in the United States during the past 50 years. Only waste retrievably stored since 1970 is presently planned to be shipped to WIPP. Two-thirds of the planned capacity of waste for WIPP is yet to be produced. Two categories of the TRU waste are currently stored at DOE-managed national laboratories and will be disposed at WIPP. The contact-handled (CH-TRU) waste is contained in 55 gallon (0.21 m³) mild carbon-steel drums that have a maximum surface-dose rate of 200 millirem per hour. The remote-handled (RH-TRU) waste will be disposed of in 0.85 m³ capacity cylindrical canisters with unshielded surface dose rates higher than 200 millirem per hour and up to a maximum of 1000 rem per hour. The 50 hectare WIPP repository has been designed to hold 850,000 drums (176,000 m³) of CH-TRU waste containing 9 million curies of radioactivity and 7,500 canisters (7100 m³) of RH-TRU waste containing 5

million curies. The CH-TRU waste drums will be stacked three high in 56 "rooms" to be excavated in salt. The RH-TRU canisters will be disposed in 36 in. (0.91 m) diameter and 10 ft (3 m) deep horizontal holes.

The TRU waste to be disposed at WIPP consists of both hazardous chemical waste and radionuclides. Its disposal should therefore be according to the requirements of the Environmental Protection Agency (EPA) Standards for the handling and permanent disposal of transuranic radioactive materials (U.S. CFR, 1985), as well as the requirements of the Resource Conservation and Recovery Act (RCRA) (U.S. CFR, 1991). The idea of permanent disposal of the radioactive waste is to isolate it from the environment for a very long period of time. The EPA Standards for radiation protection specify a time of 10,000 years for containment of the waste and require probabilistic risk analyses to assure that potential releases to the environment will have a low probability and not allow more than a specified amount of various radionuclides. The RCRA regulations require assurance of no releases of hazardous materials beyond a specified "net boundary," which in the case of WIPP has been accepted to be the 2.5 mi by 2.5 mi (4 km x 4 km) WIPP site laterally and up to the top of the Salado Formation vertically.

A geological repository relies primarily on the geology of the site to provide containment of waste for thousands of years. This is especially true for the WIPP project, because there is no commitment to use ritual engineered barriers for disposal of the TRU waste. Ninety seven percent (by volume) of the waste to be disposed at WIPP will be contained in ordinary mild carbon steel 55 gallon drums with an expected life of only 20 years, or in Standard Waste Boxes made of plywood or metal. The containers are expected to get crushed and corroded in a few years in the corrosive briny environment of a repository in salt beds and salt creep is expected to close the openings and form a cocoon around the waste. Geologic integrity and the absence of geologic and geohydrologic conditions or processes that may breach the integrity of the repository are, therefore, critical issues in assessing the suitability of the WIPP site for use as a permanent geologic repository for radioactive waste.

The purpose of this paper is to describe and discuss the geological features and processes that potentially may have an impact on the integrity of the WIPP site. Most of the geologic and hydrogeologic investigations pertinent to the WIPP have been performed by the scientists of the U.S. Geological Survey, Sandia National Laboratories, other contractors of the DOE and university researchers. The Environmental Evaluation Group (EEG) has analyzed the importance of various geologic issues and controversies as they have come to light from time to time and has proposed mechanisms and further investigations to resolve them. The EEG is affiliated with the New Mexico Institute of Mining and Technology and has offices in Albuquerque and Carlsbad. It was established in 1978 as an interdisciplinary group of scientists and engineers to provide an independent technical evaluation of various aspects of the WIPP project to protect the health and safety of the people of New Mexico. The group is funded 100% by the DOE.

GEOLOGICAL SETTING OF WIPP

The WIPP site is situated in the northern part of the Permian Delaware Basin. The repository is located at a depth of 2150 ft (655 m) from the surface in the Salado formation of the Permian Ochoan Series. The Salado Formation is about 1975 ft (602 m) thick at the center of the WIPP site and the repository is situated at a depth of 1300 ft (396 m) from the top of the formation (Fig. 3). The Delaware Basin is bounded by the Permian Capitan Reef (Fig. 4). The basin contains about 15,000 ft (4572 m) of Paleozoic sedimentary rocks overlying the Precambrian basement. The formations of interest with respect to the WIPP project, from the oldest to the youngest, are the Bell Canyon Formation of the Delaware Mountain Group, the Castle, Salado, Rustler and Dewey Lake Formations of the Permian Ochoan Series, the Upper Triassic Santa Rosa Sandstone Formation that tapers from the east to the west across the WIPP site and the Pleistocene Guffin Formation. A caliche layer known as the Mesalero caliche is consistently encountered underlying the surficial sands at the WIPP site.

The site lies on a generally flat plain covered with sand, caliche and

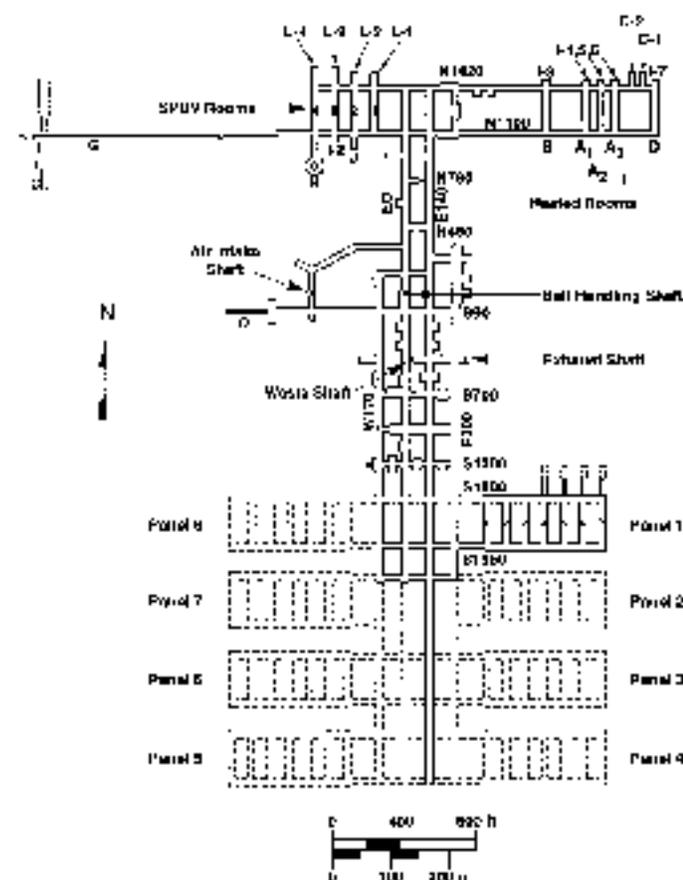


FIGURE 2. Underground layout of the WIPP repository.

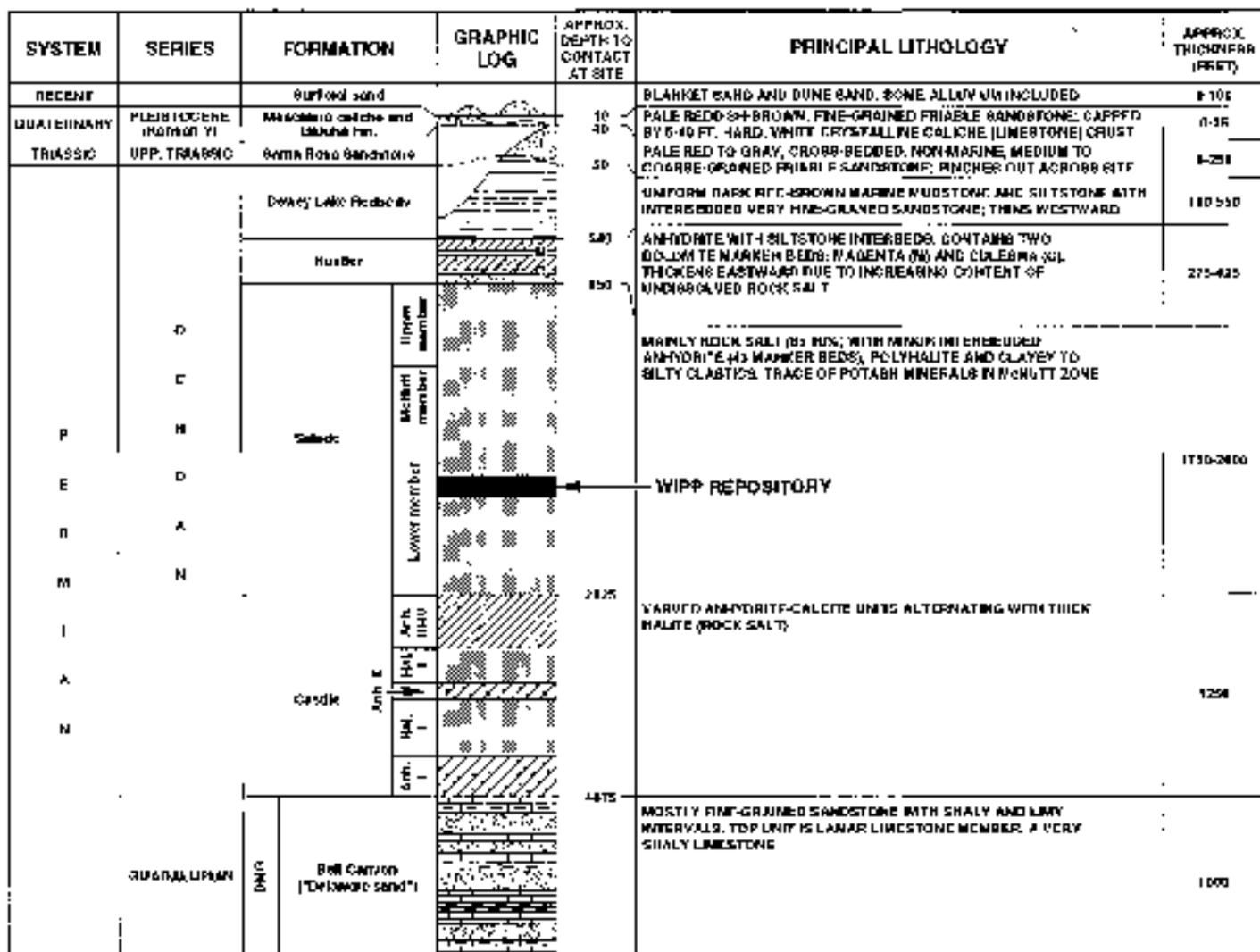


FIGURE 3. General stratigraphy at the WIPP site, including the complete Permian section and overlying state, plus underlying Quaternary Bell Canyon Formation (adapted from Fig. 4-7 of Powers et al., 1998).

desert bushes. It is located in a gypsum karst region. A subsidence landform feature called Nash Draw lies about 3 mi (5 km) west of the WIPP site. It is 6-7 mi (10-12 km) wide in the east-west direction, about 18 mi (30 km) long in the north-south direction and has resulted from erosion by solution and fill (Lee, 1925) of soluble rocks, a process that has occurred in the past and which is also presently active. The Peeps River flows from northwest to southeast, about 12 mi (20 km) west of the WIPP. Based on the presence of saline seeps along the Malaga Bend of the Peeps River (14 mi southwest of WIPP repository), a marked increase in the salinity of the river south of the bend and the general flow direction of the water-bearing beds of the Rustler Formation, the Malaga Bend has been identified as an area of discharge of the Rustler water from Nash Draw and perhaps even from the WIPP site.

All the formations shown on Fig. 3 are geohydrologically significant. Ground water occurs in the upper part of the Bell Canyon Formation in poorly cemented sandstone stringers (Fiss., 1976). The Castile Formation is about 1500 ft (470 m) thick at the WIPP site and overlies the Bell Canyon. It consists of alternating layers of anhydrite and halite, with four anhydrite and three halite members. The uppermost anhydrite member contains pressurized brine reservoirs that have been encountered by two of the boreholes drilled for the WIPP project and by several oil and gas exploratory wells. The Salado Formation overlies the Castile Formation and the repository is located in its lower part (Fig. 3). The

Salado consists primarily of halite with a zone of potassium- and magnesium-bearing minerals (sylvite, langbeinite) and thin (<3 ft) seams of clay, anhydrite and polyhalite. Before 1986, thick salt beds, as in the Salado Formation, were considered essentially dry and impermeable. Observations from the WIPP excavations, however, indicate that the salt beds may be saturated with brine and the salt may exhibit Darcian flow, albeit at very low permeability.

The Rustler Formation overlies the Salado and contains the most important geohydrologic units in the region. The thickness of the Rustler varies between 275 ft to 425 ft (84 m to 130 m) in the northern Delaware Basin and is approximately 310 ft (95 m) at the WIPP site. Sedimentology of the Rustler Formation was described by Lowenstein (1987) and Powers and Holz (1990). The formation contains three recognized fluid-bearing zones: in ascending order the Rustler-Salado contact reservoir, the Culebra dolomite and the Magenta dolomite. The transmissivity of the Culebra is the highest, followed by the Magenta and the Rustler-Salado contact. The water quality is highly variable within each unit. The total dissolved solids concentration is lowest in the Magenta and highest in the Rustler-Salado contact zone. Nearly all the water in the Rustler Formation at the WIPP site has total dissolved solid (TDS) concentrations greater than 10,000 mg/l.

All three Rustler hydrologic units probably discharge into the Peeps River, 14 mi (22 km) to the southwest near the Malaga Bend. The recharge areas are identified rather imprecisely as being upgradient of

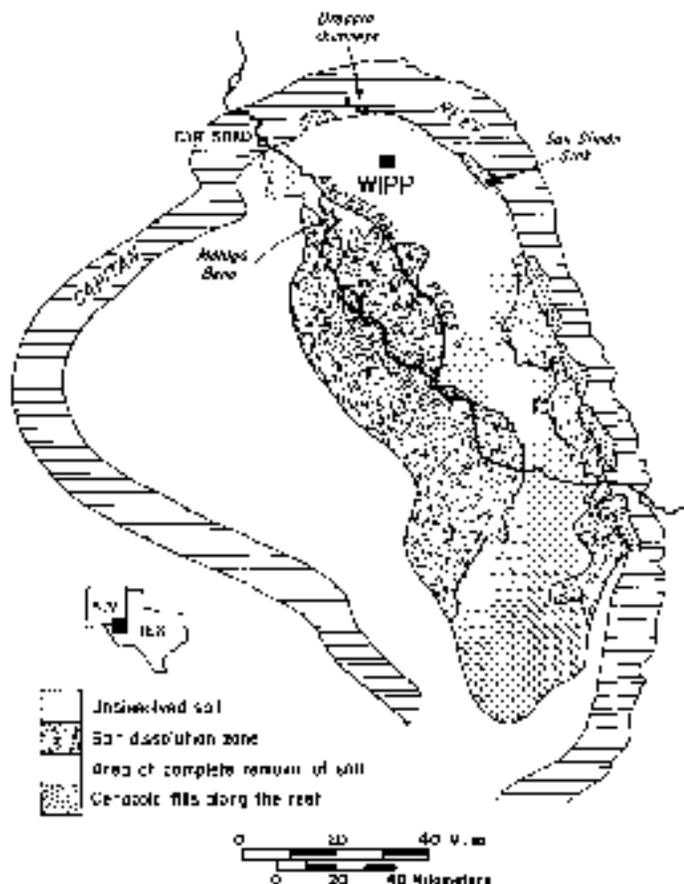


FIGURE 2. Regional extent of removal of salt from the Salado Formation.

the measured hydraulic heads, about 10 to 15 mi (16–24 km) north of the WIPP site. At the WIPP site, the lower units are separated but are probably interconnected in Nash Draw, west and southwest of the site. Of the three Rustler units, the Magenta and the Culebra are of prime concern because they extend over the WIPP site, whereas the Rustler-Salado contact zone mainly produces water west of the WIPP site (Mercer, 1983). The majority of testing in the Rustler has concentrated on the Culebra because it is more transmissive than the Magenta and therefore better suited for analyzing bounding breach scenarios.

Results of several single hole and multihole flow tests (Happin, 1988) at the site indicate that the transmissivities of the Culebra aquifer at and near the WIPP site range from $1000 \text{ ft}^2/\text{day}$ ($10^{-5} \text{ m}^2/\text{s}$) in Nash Draw to $10^7 \text{ ft}^2/\text{day}$ ($10^{-1} \text{ m}^2/\text{s}$) east of the WIPP site. Generally, transmissivity increases from east to west across the WIPP site. High transmissivity zones occur in the southeastern part of the site, in the area of boreholes DOE-1 and H-11 and in the north-central and northwestern parts in the vicinity of boreholes WIPP-13, DOE-2 and H-6 (Fig. 5).

Chemical composition of ground water from the Culebra aquifer varies widely within short distances at and near the WIPP site (Chapman, 1988). Three miles south of the WIPP site, the Culebra water typically contains 3000 mg/l of total dissolved solids (TDS). At the site itself, TDS varies from $12,500 \text{ mg/l}$ at H-2 (Fig. 5) to $130,500 \text{ mg/l}$ at H-5. Extreme variation in the chemistry of the Culebra water within short distances is illustrated by the TDS at H-2 ($12,500 \text{ mg/l}$), H-3 ($124,500 \text{ mg/l}$) and DOE-1 ($118,000 \text{ mg/l}$), within a distance of less than 2 mi.

The WIPP is situated in a mineral-rich area. Potash minerals are mined around the WIPP site from the McNitt potash zone in the upper part of the Salado Formation, approximately 1500 ft (450 m) below the surface. Oil and gas are produced around the WIPP site from the Permian Delaware Mountain Group and Pennsylvania Antrim and Marcellus strata.

STATUS OF WIPP-RELATED GEOLOGICAL ISSUES

History of WIPP site characterization

The geological site characterization for the WIPP began in 1974, following the abandonment of the Lyons, Kansas site in 1972. A 2 mi by 1.5 mi (3.2 km \times 2.4 km) rectangular site was selected by the Oak Ridge National Laboratory (ORNL) about 7 mi (11.2 km) northeast of the present site. Cores from two boreholes (AEC-7 and AEC-8, Fig. 3) penetrating through the Salado Formation drilled at the northeast and the southwest corners of that site indicated acceptable geology. Sandia National Laboratories (SNL) was given the responsibility for site characterization for WIPP in 1975. A third borehole (ORDA-6), drilled by SNL in the northwest corner of that original site in 1975, encountered a pressurized brine reservoir and intense structural disturbance in the fractured upper anhydrite of the Castile Formation at a depth of 2709 ft (826 m). The present site was selected by the SNL and the U.S. Geological Survey (USGS) and a stratigraphic borehole (ERDA-9) was drilled in 1976 through the Salado Formation at the center of the new 2.5 mi by 2.5 mi (4 km \times 4 km) WIPP site.

Early site characterization activities focused on obtaining basic data on the stratigraphy, hydrology and geoch resources of the WIPP site. As these studies progressed, several geologic features or processes that were potentially deleterious to a radioactive waste repository were identified. The EEO organized a meeting of geoscientists in January 1980, and a field trip in June 1980, to discuss these geologic issues (EEO, 1980; Chattervedi, 1980). Based on the recommendations from these meetings and independent analyses by the EEO scientists, the EEO imposed preparation of a number of topical reports to address the geological issues that had surfaced at that time. These recommendations were accepted by the DOE and a Stipulated Agreement between the State and the DOE was signed on 1 July 1981, that included the DOE commitment to prepare eleven "topical reports" and six "additional investigations." As a part of additional investigations, the DOE deepened the borehole WIPP-12, located 1 mi north of the center of the WIPP site, from its 1978 completed depth of 2737.5 ft (834.5 m) at the top of the Castile, to a total depth of 3927.5 ft (1197.4 m). Pressurized brine associated with hydrogen sulfide gas was encountered at a depth of 3046 ft (929.5 m). As a result, the DOE, following the EEO recommendation, again relocated the repository about 1.25 mi (2 km) north of the planned location that would have brought the repository within a few hundred feet of the WIPP-12 borehole.

The WIPP topical studies were published in 1983 and the DOE claimed that the geologic site characterization issues were resolved. The EEO reviewed the reports and concluded (Neill et al., 1983) that the site characterization work completed until then warranted confidence in the site, but work still remained to be done to answer the remaining questions. Underground excavation began in 1982 and additional issues came to light from the observations underground.

The more important geologic issues relevant to WIPP are described below and the status of their resolution is discussed.

Dissolution of Salado salt

There is indisputable evidence that the Cretaceous evaporite deposits (Castile, Salado, Rustler and Dewey Lake formations) have undergone erosion and blanket dissolution in the Delaware Basin. The edges of the Castile and the Salado halite can be traced west of the Pecos River essentially running parallel to it in a north-west-southeast direction (Anderson, 1981).

Based on a 600,000 year dating of the Pearlrite O ash layer exposed at the ridge on the 200 ft (61 m) deep Nash Draw margin, Buchanan (1980, 1981) calculated an average rate of 330 ft (100 m) per million years for the vertical dissolution. Assuming that the edge of the Salado salt has moved from the Capitan Reef front to its present location during the past 7 to 8 Ma (since Ogalala time), Bachman and Johnson (1973) concluded that the horizontal rate of movement of the blanket dissolution front is about 6 to 8 miles per million years. These are, of course, very rough average rates of movement; the front itself may have moved faster under less arid climatic conditions. Also, an advancing "tongue" of the front may reach a point faster than the front itself. Using the

of the BEG, the DOE drilled a 4325 ft (1319 m) deep corehole (DOE-2, Fig. 5) to investigate the origin of this feature, which was identified as a structural depression on the basis of observed depression in the anhydrite clay marker-beds in the potash industry boreholes.

The core from the DOE-2 borehole confirmed the existence of the structural depression but showed no indication of this being due to dissolution at depth. The absence of any dissolution residue and a thickened halite section can best be interpreted as due to gravity-driven salt flow in the area (Borns, 1987). The WIPP repository is no longer considered to be threatened by the effects of the Salado salt dissolution at depth.

Breccia chimneys

A breccia chimney is a solution-subsidence structure formed by dissolution of an evaporite layer at depth that results in collapse of the overlying layers, thus forming a brecciated chimney up to several thousand feet in diameter with its base in the collapsed cavity. These features are found in many evaporite basins of the world. With respect to the WIPP, the concern was that a breccia chimney may form under the WIPP repository sometime in the future, thereby providing a potential pathway for breach of the repository.

Vine (1960) identified as possible breccia chimneys several domal structures in the Delaware Basin that have been explored during the investigations for WIPP. After extensive investigation, the existence of only two chimneys (Hills A and C) was confirmed. Geophysical and geological studies show that two others (Hills B and Hills-Weaver) are also likely breccia chimneys, although they were not cored. All of these features appear to be situated over the Capitan Reef limestone, which is a prolific aquifer in the area. Davies (1983) pointed out that the Hill "C" breccia pipe is located at the southern edge of the buried Capitan Reef and since the borehole WIPP-16, drilled to explore this chimney, was drilled only to the level of the McNitt potash zone of the Salado formation, it is not clear whether the Hill "C" breccia chimney roots in the Capitan aquifer.

Besides boreholes WIPP-31 and WIPP-16, which were drilled at Hills A and C, respectively, to investigate the breccia chimneys, three other boreholes were drilled at suspected breccia chimney locations in the basin. Borehole WIPP-32 was drilled in a small topographic high in Nash Draw, which had been described by Vine (1963) as a domal karst feature. These features (domal karst) have been extensively studied by Bachman (1980, 1984). Boreholes WIPP-13 and WIPP-15 were also drilled to explore for possible breccia chimneys. There is a marked electrical resistivity anomaly at WIPP-13 and a prominent topographic depression exists at the location where WIPP-13 was drilled. Collapsed breccia was not found at either of the wells.

Anderson and Kirkland (1980) described the occurrence of collapse breccia in a borehole in Culberson County, Texas, about 55 mi south of the WIPP site. Anderson (in Chaturvedi, 1980) described occurrences of "castles," which are mounds of brecciated rock that crop out a few miles south of the New Mexico-Texas border, south of the WIPP site. Both occurrences are in the eroded western part of the Delaware Basin, which has already undergone extensive dissolution.

Snyder and Gard (1982) studied the known occurrences of breccia chimneys in the Delaware Basin. They studied in detail the Hill "C" breccia chimney, which is also encountered at the McNitt potash zone of the Salado Formation in the Mississippi Chemical Company potash mine, 1200 feet (366 m) below the surface. From study of this exposure, the core of WIPP-16 drilled in this chimney and the core of WIPP-31 drilled in the Hill "A" breccia chimney, Snyder and Gard (1982) concluded that the breccia chimneys are formed by collapse of the overlying rocks in solution cavities in the Capitan Reef aquifer. Bachman (1980) hypothesized that the location of all the known breccia pipes in a small area over the reef is due to the presence of an old submarine canyon in the reef in this area. On the basis of the presence of Mesocera calcite over the breccia pipes, Bachman (1980) also concluded that the collapse occurred prior to the deposition of this calcite layer, i.e., more than 0.5 Ma.

Davies (1984) also studied chimneys A and C and concluded that they were produced by salt dissolution at the base and within the low-

ermost portion of the Salado formation, through incremental subsidence rather than catastrophic collapse of the overlying strata. The BEG concluded (Neill et al., 1983) that the probability of a breccia chimney forming under the WIPP site was fairly remote and that this phenomenon did not appear to pose a threat to the WIPP repository.

Brine reservoirs

Within a few miles of the WIPP site there are at least sixteen reported encounters of pressurized brine in the upper anhydrite layer of the Castile Formation (Fig. 6). Two of these encounters (ERDA-6 and WIPP-12, Fig. 5) were in the WIPP project boreholes and the rest have been reported by oil and gas drilling companies. When borehole WIPP-12, located 1 mi (1.6 km) north of the center of the WIPP site, hit brine at a depth of 3016 ft (919.5 m), brine started flowing out of the well at a rate of 350 gallons per minute (22 liters/sec) and more than 1.14 million gallons (4.3 million liters) of brine flowed out before the well was controlled. Based on an extensive series of flow tests, the brine reservoirs penetrated by the WIPP-12 and ERDA-6 boreholes were estimated to contain 17 million barrels (2.7 billion liters) and 630,000 barrels (100 million liters) of brine, respectively (Popielak et al., 1983). The different pressure potentials and geochemical data from the two encounters suggested a lack of communication between the ERDA-6 and WIPP-12 brine reservoirs. There was no consensus on the origin and the age of the brine reservoirs.

The planned configuration of the WIPP repository and the WIPP experimental areas would have brought the waste within 460 ft (140 m) south of the WIPP-12 borehole. The BEG recommended moving the repository in 1982 and the DOE rotated the repository configuration to relocate the nonwaste experimental area to the north and the repository 1.2 mi (2 km) south of WIPP-12. In 1983, BEG formally proposed geophysical investigations to delineate the extent of pressurized brine in the Castile Formation underlying the WIPP site and particularly under the new location of the repository. The work was performed in 1987, and the results gave a clear indication of the presence of brine under parts of the WIPP repository (Earth Tech. Corp., 1988).

The presence of brine reservoirs in the Castile Formation is a major geological issue affecting the anticipated performance of the repository. Since there are good geophysical indications of the presence of brine in the Castile Formation, 800 ft (244 m) or so below the repository, the inadvertent drilling to a brine reservoir through the repository is a scenario that the WIPP project has to evaluate. Such a drilling sometime during the next 10,000 years would allow pressurized brine to flow into the repository. Several pathways for migration of such contaminated brine into the Rustler Formation or directly to the surface have been postulated.

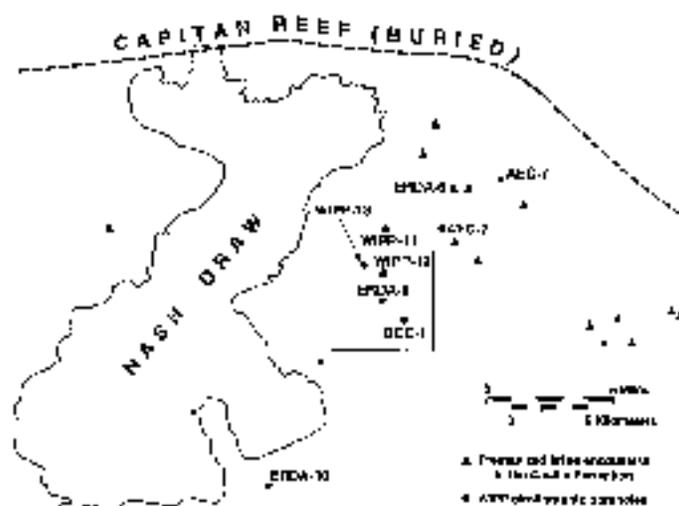


FIGURE 6. Pressurized brine encounters in the Castile Formation in the vicinity of the WIPP site.

Salado brine

A reason for selecting bedded salt deposits for isolating radioactive waste was the assumption that salt would be essentially dry. One of the surprises encountered by in situ underground studies at the WIPP is that the Salado salt yields a fair amount of water. A large percentage of boreholes drilled down from the WIPP excavations fill up with brine and the walls are covered with efflorescences and encrustations resulting from brine inflow from salt into the excavation and drying up by vented air. Several boreholes completed in the Salado Formation indicate fluid pressure buildup (Merrett, 1987). In situ Salado salt has low (10^{-21} m²), but measurable, permeability.

Bredemuhl (1988) proposed that the Salado salt is saturated with brine and exhibits Darcian flow. Nowak et al. (1988) calculated that for salt permeabilities of 10^{-21} to 10^{-20} m² (1 to 10 nanodarcies), between 4 m³ to 43 m³ of brine would accumulate in a typical WIPP repository room with dimensions of 300 ft × 33 ft × 13 ft (91.5 m × 10 m × 4 m). Since the WIPP CH TRU containers are ordinary 55-gallon mild carbon steel drums that are not expected to last much beyond their 20-year design life, the brine would mix with the TRU waste and may form a slurry. Sandia National Laboratories (1987) calculated that if someone drills into such brine slurry and inadvertently brings a part of it to the surface, EPA Standards may be violated.

Corrosion of the metal containers and metal in the waste would produce hydrogen. Microbiological degradation of the organic material in the waste would produce carbon dioxide and methane. These processes require water to produce gas and the Salado brine inflow will satisfy that need. The rate of brine inflow in the repository is therefore a very important parameter for assessing breach scenarios. DOE has been monitoring and sampling the Salado brine from 13 boreholes in the WIPP underground since 1984 (Deal et al., 1991). After five years of observation, five 50 ft (15 m) deep holes have remained steady producers of brine, one showing increased brine production and five showing decreasing rates. One stop in the floor has produced between 0.15 to 0.2 gallons (0.5 to 0.75 liters) of brine per day for five years. Several holes in the roof and in the walls also have been producing brine.

Hydraulic testing of the Salado Formation at the WIPP repository horizon (Beauheim et al., 1993) shows the brine flow in the Salado salt to be Darcian in nature because the Darcy flow models are able to replicate the flow and the pressure behavior observed during the entire testing sequences involving different types of tests. The estimation of brine inflow by Nowak et al. (1988) appears to be on sound theoretical basis. Estimation based on actual inflow observation for a long time, under progress now, would provide confirmatory evidence of this calculation.

Rustler Formation hydrology

The Culebra dolomite member of the Rustler Formation, being the most prolific of the three water-bearing zones underlying the WIPP repository, is the most likely pathway for transport of radionuclides after a breach of the repository. Based on three multiwell flow tests, several single-well flow tests and absorbing tracer tests at four hydrologs, LaVerne et al. (1990) performed ground water flow modeling of the Culebra at the WIPP site. The flow model suggests that if radionuclides are injected into the Culebra directly above the repository panels near the center of the WIPP site, the fastest flow path out of the WIPP area would be to the south-southeast past the boreholes H-3 and H-11 (Fig. 5).

The calculated travel time for contaminant transport along this pathway, however, is very sensitive to assumptions of fracturing in the Culebra dolomite and distribution of contributing porosity between the rock matrix and the fractures. If double-porosity flow is assumed, with diffusion of contaminants in the rock matrix, the shortest travel time from the center of the WIPP site to the southern boundary is 14,000 years. If, on the other hand, transport is assumed through fractures only (single porosity), then the travel time would be less than 100 years. Additional multiwell flow tests are required to better define the transmissivity field at the WIPP site. Additional tracer tests designed to better define the fracture vs. matrix porosity flow are also needed. The

breach scenario calculations have identified radionuclide retardation during contaminant transport through the Culebra as one of the sensitive parameters that control the magnitude and timing of the postulated releases of radioactivity to the environment. Field and laboratory experiments are required to provide reliable and justifiable numbers for physical and chemical retardation. Laboratory experiments are being set up and initial results are expected in 1993 or 1994.

The WIPP site is situated in a gypsum karst area. The subsidence feature called Nash Draw has been formed by the karstic process of solution and dissolution (Lee, 1925; Bachman, 1960, 1984). The depression in which borehole WIPP-33 (Fig. 5) was drilled is a karst sink. No positively identified karst feature has been encountered east of WIPP-23 in the WIPP area, but hydrologic tests in the area detected any channelized flow. Breach scenario calculations have not considered potential releases through channelized flow or through narrow transmissive layers due to vertical heterogeneity. Such conceptual models would result in greater releases, as shown by Chattervedi and Channell (1985).

Beauheim and Davies (1992) have proposed a sewer-well flow and tracer test to be fielded between H-3 and DOE-1. This test is designed to address the questions of vertical heterogeneity and matrix diffusion and would provide data to better characterize the flow mechanism. It is also intended to use the instruments for a field seeping tracer test for providing data on chemical retardation processes and properties within the Culebra. This test is planned to begin in 1993.

Disturbed rock behavior

Before underground excavation at WIPP began in 1982, DOE scientists performed calculations to predict the closure history of the excavations. These calculations used the geomechanical properties of the rock strata at the selected WIPP repository horizon obtained from testing of the rock cores from boreholes. The calculations predicted that a WIPP room would "close slowly in a stable manner as the salt creeps" and "relative closure values of 0.21 m (8.25 in.) in the vertical direction and 0.28 m (11 in.) total in the horizontal direction are seen for the isothermal room after 10 years" (Miller et al., 1982). The WIPP excavations have behaved very differently than predicted. Vertical closure in the WIPP test rooms has varied between 3 in. (75 mm) and 4 in. (100 mm) per year and horizontal closure has ranged between 2 in. (50 mm) and 3 in. (75 mm) per year. A "disturbed rock zone" consisting of fractured rock surrounds all the excavations. In less than eight years after excavation, the roof of the first of the four test rooms fell in February 1991, due to fractures propagating above the roof and creating an up to 7 ft (2 m) wide unstable trapezoidal beam between the roof and a thin layer of anhydrite above the roof.

The difference between the predicted and measured closure rates has been explained on the basis of use of the wrong geomechanical models and not taking into account the details of the stratigraphy (Munson et al., 1989). While the faster closure rate will help emboss the waste sooner, it creates problems during operations. The WIPP repository rooms should be excavated just before they are needed for waste emplacement and backfilled soon thereafter. It will also create problems in maintaining retrievability of the waste. Due to its interaction with brine inflow and gas pressure from gases produced by the waste, the room closure rate also affects long-term performance of the repository.

Natural resources

The WIPP site is located in a region that contains substantial amounts of potash, natural gas and petroleum resources. Therefore, breach scenarios involving inadvertent drilling by future generations must be considered. The EPA Standards 40 CFR 191 (EPA, 1985, App. B) prescribed a limit of assuming 50 boreholes/km²/10,000 years, which was based on the drilling frequency in the WIPP site vicinity in 1970s. Judging by the number of producing wells, drilling activity around the WIPP site in 1992 and the number of applications to the U.S. Bureau of Land Management for new drilling permits, the oil and gas resources in the WIPP area are much more prolific than previously considered. This fact must be taken into account in the assessment of the WIPP's compliance with the EPA Standards.

CONCLUSIONS

Since the WIPP repository is designed to rely on geologic isolation for 10,000 years, consideration of the various geologic features and processes are very important to assess the capability of the site to keep the waste isolated from the environment. The impact of the potentially deleterious geologic factors on the repository will be judged on the results of consequence analyses of potential breach scenarios.

ACKNOWLEDGMENTS

Without John Hawley's persuasive talent and enormous patience, this paper would not have been written. Carol Hill and Thomas Corbet reviewed the paper and made many useful suggestions. Betsy Krueger prepared the list of references in the correct format in a short notice and also provided review comments. Jill Shortenberger patiently and competently typed the manuscript.

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8.6 Letter Reports of EEG Consultants on the K_o Issue

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August 5, 1997

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Dear Bob:

Following are some thoughts based on my attendance at the DOE/BEG Meeting on Chemical Retardation in Albuquerque on July 30, 1997, and on related reading. I have ordered the discussion topics as they were set forth by Dr. Lokesh Chaturvedi of BEG in his introductory presentation.

Transferability of Lab K_d Data to Field

Transferability has always been an issue of concern. My understanding is that a consensus now exists that groundwater flow in the Culebra is slow enough to guarantee that important diffusion of the groundwater into rock matrix will occur. If this is the case then the radionuclides in groundwater will have ample opportunity to access mineral surfaces in pores in the dolomite, making laboratory measured batch K_d values applicable to the field.

The Limited K_d Data Base

The limited K_d data base remains a serious problem. We can all agree that K_d values for the important actinides Pu, Am and U, regardless of oxidation state, probably equal or exceed 1 ml/g in Culebra groundwaters, which is necessary for compliance. However, the hydrologic model for the Culebra and associated groundwater flow mechanisms and travel times in the formation have non-zero uncertainties. It is unclear how much these hydrologic uncertainties contribute to the uncertainty of assigning a minimum compliance K_d value of 1 ml/g. Given this additional hydrologic uncertainty, if I were a regulator, I would be much more confident that the site was in compliance if the DOE's recommended K_d 's for the important actinides were at least 10 to 100 times greater than 1 ml/g. As discussed below, the approach used by the DOE for estimating unmeasured K_d values involves questionable assumptions.

K_d Estimation Methods used by the DOE

The DOE proposes that K_d values for actinide cations of the same charge should be roughly the same. This approach has been used by many others. (See discussion below). Its weakness lies in the fact that such approximations assume that differences in the speciation behavior of the cations does not affect their adsorption and can be neglected.

The second assumption used by the DOE to estimate K_d values, is that predictable trends exist among the K_d 's of actinide cations of different charge. The DOE assumed that such trends

identified by Canepa (1992)¹ in dilute, J-13 groundwaters at Yucca Mountain would apply to WIPP brines. Canepa (1992) proposed that K_d values for actinides in J-13 groundwater should decrease in the same order as their solubilities increased in the same groundwater. The reported solubility data for U(VI), Np(V), Pu(IV)² and Am(III) plotted linearly, seeming to support her contention. This led to the proposal that K_d values should decrease in the order Am(III) > Pu(IV) > Np(V) > U(VI). The DOE has suggested that the same order of K_d values should apply in groundwaters at the WIPP site. However, recent solubility measurements performed at LANL indicate that Np(V) solubility is about 10 times lower than assumed by Canepa (1992). The computed solubility of Np in J-13 groundwater is in fact as low as 10^{-7} mol/L (Langmuir, 1997, p. 534)³, about 10^3 less than suggested by Canepa (1992). Similarly, the solubility of U(VI) in J-13 groundwater may also be about 10^{-7} mol/L, 10^1 to 10^2 times lower than proposed by Canepa (cf. Langmuir, 1997, p. 533). Assuming as did Canepa (1992), that the actinide solubilities in J-13 groundwater should be inversely proportional to their K_d values, these changes suggest that the order of decreasing K_d 's in J-13 and in WIPP groundwaters should be Am(III) > U(VI) > Pu(IV) > Np(V).

In fact, in general K_d values are probably not inversely proportional to the solubilities of the actinides. Thus, in a summary of adsorption trends among the actinides, Langmuir (ibid, p. 536) reports that K_d 's decrease in the order Th(IV) > Am(III) > Np(V) for the adsorption of these actinides by Al_2O_3 , as evidenced by respective pH values of 2.4, 5.8, 7.3 at 50% of each species adsorbed. Similarly, as pH is increased, goethite has adsorbed 50% of Pu(IV), U(VI) and Np(V) at pH values of 3.2, 4.2 and 7.0, respectively. This is therefore also the order of their decreasing K_d 's (Langmuir, ibid, p. 537). Also, based on a literature survey, Silva and Nitsche (1996)⁴ propose a general order of decreasing K_d 's for the adsorption of actinides (An elements) by the same sorbents, of An(IV) > An(III) > An(VI) > An(V), in general agreement with the abbreviated adsorption series listed previously. Based on the plot of Canepa (1992), the DOE argues in the CCA, that estimated K_d values for Am(III) and Pu(III) should be greater than the measured K_d for Pu(V). Although their conclusion is based on the questionable data and assumptions in Canepa (1992), the same trend of K_d values for these species is fortuitously observed within the adsorption trends for the actinides reported by Langmuir, (1997) and Silva and Nitsche, (1996).

Availability and Reliability of Measured K_d Values

At the July 30, 1997 meeting in Albuquerque, the DOE presented the results of adsorption measurements performed in both column and batch tests. Results of the intact core column tests are probably of questionable value for determining Am(III) and Pu(V) (Pu(IV)?) adsorption K_d 's, in that the Am and Pu input concentrations to the cores were high and so close

¹Los Alamos National Laboratory

²The oxidation state of Pu may have been a mixture of IV, V, and VI.

³Aqueous Environmental Geochemistry, Prentice Hall, Upper Saddle River, NJ, 600 pp.

⁴Actinide Environmental Chemistry, Radiochim. Acta, in press.

to saturation with solids, that precipitation rather than adsorption may have occurred. The Pu(IV) column adsorption experiments and their results were not discussed at the meeting.

Useful batch adsorption results have been reported for Pu(V), U(VI), Th(IV) and Np(V). Performance assessment indicates that the important actinides at WIPP are Pu and Am, with U of tertiary importance. Based on oxidation state predictions, Pu(III) and Pu(IV) are the dominant Pu oxidation states in WIPP brines. Unfortunately, Am(III) batch adsorption experiments have given inconclusive results, and batch adsorption of Pu(III) and Pu(IV) has not been measured. Thus, the K_d values for the most important actinides in WIPP brines have had to be estimated.

K_d Values Chosen for the CCA

In the CCA, it was conservatively assumed that the lowest K_d values measured in the Culbren Dolomite or deeper Castle or Salado brines would be assumed for performance assessment (PA). Ranges of K_d values for the actinide cations proposed in the CCA are given in Table 1.

Table 1. K_d values used by DOE in the WIPP 1996 Compliance Certification Application (CCA) (assumes uniform distribution). Bold values are based chiefly on batch adsorption measurements discussed by L.H. Brush in his June 10, 1996 memo to M.S. Tierney of Sandia Natl. Laboratories. The probable order of decreasing K_d 's in column 7 is based on earlier discussion in the text.

Oxidation State	Am	Pu	U	Th	Np	Probable Order of Decreasing K_d 's
III	20-500 (no data)	20-500 (no data)				2
IV		900-20,000 (no data)	900-20,000 (no data)	900-20,000	900-20,000 (no data)	1
V		20-500			1-200	4
VI			0.03-30			3

The DOE reported a measured batch K_d of 20-500 ml/g for Pu(V), a species not expected in WIPP brines. Based on adsorption trends, the K_d for Am(III) and Pu(III) should be greater than its value for Pu(V). Given this assumption, the DOE conservatively assumes the K_d for Am(III) and Pu(III) equals the range measured for Pu(V). One could as well argue that the lower measured K_d range of 1-200 ml/g for Np(V) adsorption could instead have been assumed conservatively for Am(III) and Pu(III).

In summary, the most important actinides in WIPP brines are Pu(III), Pu(IV) and Am(III). The DOE has used the Canepa (1992) report and limited batch adsorption data to estimate K_d values for these actinides in WIPP brines. Although the estimated K_d values used in the CCA are probably conservative, it is most unfortunate that Am(III), Pu(III) and Pu(IV) adsorption has not

been measured. I understand that batch adsorption experiments designed to obtain K_d values for these actinides would not be particularly difficult to perform, and might be completed in a few months. It is also possible that accelerated intact column tests could be run in a few months using an ultracentrifuge. Admittedly, resultant K_d 's can be predicted to exceed 1-3 ml/g. However, having measured instead of estimated values for the key actinide species would greatly improve confidence that K_d values for the most important actinides are in compliance with regulations.

Solubility Controls on Am, Pu, U and Np Concentrations in WIPP Brines

According to an unpublished July 6, 1996 Sandia report by Stockman and Stockman, titled "Constraints on Actinide Oxidation State in the Culebra: Reaction Path Mixing Calculations", the Culebra Dolomite contains an average of 0.17% FeO. These authors also note that 20 polished sections of the Culebra from 9 WIPP-area boreholes contained pyrite (FeS_2) in every section. The redox state of the rock will ultimately control redox conditions in the WIPP brines. In the absence of a source of free oxygen, reducing conditions are likely to dominate groundwaters away from the waste. Ferric iron staining is common in the Culebra. Eh values in the brines are thus likely to be poised by reactions between either ferroan dolomite and the Fe(III) oxyhydroxides, or pyrite and the Fe(III) oxyhydroxides.

In the vicinity of the waste, iron and nickel metal and organic matter will also tend to deplete any oxygen introduced with the waste. Reduced Fe, S and C in the waste and the rock are likely to cause reduction not only of Pu(V) to Pu(IV) and Pu(III), but may also lead to reduction of U(VI) to U(IV) and Np(V) to Np(IV). If these reductions take place, then maximum concentrations of Pu, U and Np may be limited by the solubilities of their quadrivalent oxides or hydroxides to values of 10^{-8} mol/L or less. If maximum concentrations of Pu and U are so limited, then the adsorption behavior of higher oxidation states may be irrelevant to performance assessment.

In carbonate-rich groundwaters, the concentration of Am(III) is limited by the solubility of Am(III) hydroxy-carbonate to values below 10^{-4} mol/L between about pH 7.5 and 9 (Langmuir, *ibid*). In WIPP brines at high pH's in the presence of MgO to scavenge the carbonate, Am(III) solubility may limit Am(III) concentrations at similarly low concentrations.

Limited solubility data for these actinides in WIPP brines is available. However, those of An(IV) species in particular are likely to be well below 10^{-8} mol/L in the presence of MgO and in the absence of carbonate. It would be useful for the DOE to evaluate and report on the available solubility data for these actinides measured in WIPP brines and in similar brines. The brine solubilities of analog rare earth cations and analog actinides such as Th(IV) would also shed light on the probable behavior of Am(III), Pu(III) and Pu(IV) in WIPP brines.

Non-Culebra Dolomite

The K_d 's for U(VI) adsorption by Norwegian dolomite are within the range of values for U(VI) adsorption by Culebra Dolomite. This is reasonable. That this pure dolomite adsorbed more U(VI) than some Culebra Dolomites that contain other sorbing minerals, does not strike me as an issue of concern.

Effect of Organic Ligands on Actinide Complexing and Adsorption

It seems probable as argued by Vann Bynum, that organic complexing of actinides does not significantly increase their solubilities or adsorption behavior in the vicinity of the waste. This reflects the competition of more abundant cations such as Ni^{2+} , Ca^{2+} and Mg^{2+} for organic ligands such as EDTA. Also important is the fact that actinides such as Th(IV), Pu(IV) and Np(IV) form strong OH complexes at neutral to alkaline pH's so that their free ion concentrations are many orders of magnitude lower than the free ion concentrations of Ni^{2+} , for example. Van Bynum made his calculations ignoring hydrolysis of the actinide cations, and still found less than 1% of Th(IV) complexed with EDTA, the strongest organic complexer. If he had corrected for Th-OH complexing, orders of magnitude less Th would have been complexed by EDTA.

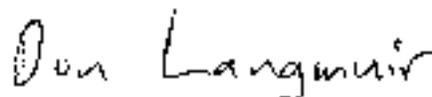
It would be most convincing if the actinide complexation reaction calculations were rerun, but including OH and other inorganic actinide complexing, and varying (increasing) the amount of EDTA in the waste within possible ranges, to more rigorously disprove the importance of actinide-organic complexing near the WIPP waste.

K_d's Based on the Intact Column Test Results

As noted earlier, the Pu(V) and Am(III) column test results are of dubious value for determining K_d values for these actinides. Because of the high concentrations of Pu(V) and Am(III) in intake solutions, they could have been precipitated as solids rather than been adsorbed in the columns. If so, their concentrations in the rock cannot be used to define K_d values. In order to prove or disprove this concern, if possible, it is recommended that the core materials that have been drilled out be examined to identify whether the Pu and Am are present in adsorbed or 3-D solid phase form. It is also unclear whether the Pu is adsorbed as Pu(V) or as a lower oxidation state such as Pu(IV). The similar K_d values for Pu(V) and Th(IV) found in batch tests with ERDA-6 brines (about 10^3 and $10^{3.5}$ ml/g) suggest that the Pu may be adsorbing as Pu(IV). We were never shown tomographic results of the Th(IV) column tests and resultant K_d values. If these tests were run at Th(IV) concentrations below saturation with Th(IV) solids, the test results could be used to estimate the K_d for Pu(IV) adsorption. Finally, as noted earlier, it is possible that K_d values for the important actinides could be obtained in a few months from accelerated intact core experiments performed in an ultracentrifuge.

I hope my comments and suggestions have been useful to you.

Yours truly,



Donald Langmuir, PhD

PLN
8/19

REPORT ON CHEMICAL RETARDATION DATA FOR CULEBRA AQUIFER

To: Environmental Evaluation Group (EEG)
7007 Wyoming Blvd, NE
Albuquerque, NM

From: Mark L. Brusseau

Date: 11 August 1997

I have reviewed the documents supplied to me before and during the July 30 meeting, and have considered the presentations and comments provided during the meeting. My comments and recommendations are presented below.

I. Analysis of Original EEG Concerns

1. Use of batch K_d data: EEG originally expressed concern with the use of K_d values determined from batch experiments for the field-scale modeling. The major question was the representativeness of batch K_d values for the field scale. It appears that at least some (the more recent) batch experiments were conducted under well defined and controlled conditions. The results obtained from these experiments may thus provide an accurate data set for evaluating the "sorpitivity" of the specific radionuclides used in the experiments.

However, there remains the basic question of whether or not K_d values obtained under static batch conditions are an accurate measure for dynamic field conditions. I do not believe that this question has been answered for the Culebra system. To help address this issue, I recommend that additional analyses be made of the column experiments (to be discussed in greater detail below).

2. Use of Oxidation State Analogy: EEG expressed concern with the use of the oxidation state analogy for estimating K_d values. This approach appears to have merit in some cases (when it is definitively conservative), but appears to have large uncertainty for other cases. It is not clear why batch experiments were not conducted for the most critical radionuclides. An opinion was expressed by a DOE employee that the K_d values for at least some of the unmeasured radionuclides could be measured relatively easily. I recommend that such experiments be conducted for as many of the critical radionuclides as is feasible.

3. Use of Uniform Distribution: EEG expressed concern with the use of an uniform distribution for representing the K_d data. The reasoning provided by DOE for the use of an uniform distribution appears to be valid. As they noted, the experiments were not designed to provide a statistically representative sample of all possible field conditions. Thus, the uniform distribution should be the one to use. I recommend that this approach be accepted.

4. Organic Ligands and Facilitated Transport: EEG expressed concern regarding the potential of organic ligands to complex the radionuclides and thereby facilitate their transport. There were three subconcerns associated with this topic--

A) There was concern regarding the varied sources of complexation-coefficient data used in the original DOE analyses. The DOE mentioned new data at the meeting that may negate this concern. The DOE now appears to have a consistent set of measured complexation-coefficient data specific to the Culebra/WIPP system.

B) There was concern regarding the amount of EDTA DOE assumed would be present in the waste. I agree that there is great uncertainty in the concentration of EDTA that may be present in the WIPP system, and that the value used by DOE may be too small.

C) There was concern regarding the potential for other organic ligands, which were not included in the DOE analysis, to facilitate the transport of radionuclides. I agree with this concern.

To help resolve both B and C, I recommend that the DOE conduct a formal sensitivity analysis of the potential impact of organic ligands on the aqueous concentrations of the radionuclides. The concentrations of the ligand should be varied by several orders of magnitude, and the full list of ligands provided by EEG should be used. Based on the preliminary analysis presented by DOE personnel at the meeting, it is quite possible that the results from this study will indicate that complexation by the organic ligands may have minimal impact on radionuclide behavior. A formal sensitivity analysis will provide greater confidence in the results.

5. Other Concerns of EEG: EEG expressed concern with the application of the Norwegian dolomite study results to the Culebra system, and with the use of different CO₂ concentrations in the batch experiments. After the meeting, EEG commented that these were of minor concern, and I concur.

II. Additional Concerns

1. Potential Nonlinear Sorption: The data I reviewed indicates that the sorption of many of the radionuclides is most likely nonlinear. This is to be expected given the sorption mechanism stated by DOE (exchange reaction). As is well known, nonlinear sorption can cause retardation to vary as a function of solute concentration. In addition, it is possible that the initial representative retardation factor operative during field-scale transport may not be the same as that calculated using the batch K_d data. Thus, not accounting for nonlinear sorption may under or over predict retardation, depending on the initial solute concentrations used in the analyses. It is not clear if the range of K_d values reported by DOE take into account the concentration dependency of sorption. I recommend that the potential impact of nonlinear sorption be addressed.

2. **Use of a K_d Approach versus a more Complex Approach:** The transport model used by DOE is based on the simple K_d approach, which is based on linear, instantaneous sorption. It is clear that the fluid-solid interactions influencing radionuclide transport at the WIPP site are more complex, potentially involving inorganic/organic complexation, precipitation/dissolution, competitive sorption, and varying pH and ionic strength effects. The simplicity of the K_d approach makes its use understandable. However, some analysis of the potential impacts of more complex fluid-solid interactions on radionuclide transport would be useful.
3. **Spatial Variability of Sorption:** The current modelling analysis is based on a homogeneous K_d field. It is highly likely, however, that sorption is spatially variable at the site. The potential impact of spatially variable sorption on radionuclide transport should be evaluated.

III. Conclusions and Recommendations

Several questions and concerns were addressed satisfactorily at the meeting. However, some issues remained unresolved. The majority of these could potentially be resolved with relatively minimal additional effort. Recommendations for additional activities are as follows:

1. It is recommended that additional analyses be made of the column experiments. This includes additional analysis of the completed experiments and additional analysis of the ongoing experiments. The latter should involve an attempt to determine if precipitation is occurring during the column experiments, which appears to be a major uncertainty influencing the applicability of the column results. Would it be possible to sample the column material at the completion of the experiment and analyze for precipitated forms of the radionuclides?
2. I recommend that additional batch experiments be conducted to measure K_d values for the critical radionuclides, at least Pu^{III} and Pu^{IV} .
3. I recommend that a formal sensitivity analysis be conducted to examine the potential impact of organic ligands on the aqueous concentrations of the radionuclides. The concentrations of the ligand should be varied by several orders of magnitude, and the full list of ligands provided by EEG should be used.
4. If the potential impact of nonlinear sorption is not incorporated in the range of K_d values used by DOE, I recommend that the potential impact of nonlinear sorption on radionuclide transport be addressed. This could be accomplished by calculating effective K_d values for pertinent C_0 values, using the nonlinear isotherm data available. These values could then be compared to the existing K_d range.
5. I recommend that the potential impact of spatially variable sorption on radionuclide transport be evaluated. This could be done by conducting a series of model simulations using spatial distributions of K_d s based on the conceptual site models.

August 12, 1997

Dr. Robert Neill
Director
Environmental Evaluation Group
7007 Wyoming Blvd, N.E., Suite F-2
Albuquerque, New Mexico 87109

Dear Bob,

In this letter I provide my viewpoint on chemical retardation in the Culebra dolomite. The opinions expressed reflect my consideration of the reports and correspondence supplied to me prior to the meeting, the material presented by EEG and DOE at our meeting on July 31, and the ensuing discussions that day. I will not comment directly on the issues concerning the amount of EDTA in the waste inventory, the potential for EDTA to facilitate transport of thorium, or the data presented by DOE to justify their application of the oxidation state analogy.

The Probability Distribution for K_d

I accept the DOE position that it is appropriate to adopt a uniform probability distribution to represent the uncertainty in the K_d values for the CCA calculations. The use of a log-uniform distribution, as required of DOE in the EPA verification tests, has the primary benefit of placing considerably more weight on the lower end of the proposed range for K_d . The EPA verification test suggests that the conclusions drawn from the CCA calculations with respect to transport in the Culebra are not sensitive to this marked change in the form of the distribution.

The probability distribution for K_d can be interpreted in terms of the likelihood that a value sampled from the distribution will correspond to an effective K_d value for sorption in the matrix blocks. This value must be applicable for transport times greater than 100 years, and transport distances of approximately 3 km. I see the attempt to quantify this likelihood as an issue related to, but distinct from, the distribution of K_d values obtained in the replicate batch tests. It is not feasible to obtain a set of field data, applicable at the scale of the transport predictions, that would allow one to equate the distribution of measurements with an appropriate sampling distribution in the CCA. One is forced to adopt a more subjective viewpoint in representing the uncertainty in the K_d value, with the consequence that the distribution of the data from the batch tests need not correspond to the distribution describing the likelihood for the effective K_d value. This approach is the most reasonable way to account for the spatial variability in K_d , and the influences of brine type and pH conditions inside a plume migrating through the Culebra.

The position taken by DOE that the sorption experiments (batch, mechanistic, and column tests) should be used to define a range for the K_d parameters, rather than its distribution in probability space, is reasonable.

I have used decision models that adopt uniform distributions to characterize the uncertainty in the key model parameters (eg. Bugai, Smith, Beckie; Environmental and Engineering Geoscience, 1996). We took this approach because we were faced with a sparse data base, and there were confounding uncertainties in future system behavior. A uniform distribution is appropriate when there is no strong basis for deciding if one value in the range is more likely than any other. It is my opinion that this is the case we face when selecting an effective K_d value for radionuclide transport in the Culebra. This is a slightly different spin on the DOE statement that "the uniform distribution is appropriate when all that is known about a parameter is its range".

In more recent work, I have adopted truncated exponential distributions to represent uncertainty in model parameters (Smith and Gaganis, Environmental and Engineering Geoscience, submitted). This latter model for representing parameter likelihood includes the uniform distribution as a special case, if the prior estimate of the mean is midway between the specified lower and upper bounds of the distribution. There is a sound basis in theory for choosing a truncated exponential distribution to represent parameter uncertainty, when the data base is sparse. Qualitatively, the log-uniform distribution is similar to the truncated exponential distribution, when the estimate of the mean is closer to the lower bound than the upper bound.

The more important issue to debate, in my opinion, is the values that DOE has selected for the lower and upper bounds of the probability distribution, and how these bounds are defined relative to the type of brine used in the batch experiments. I agree with the approach taken by DOE in choosing a range for K_d relative to brine type that will give a conservative estimate of retardation. I was somewhat bothered by DOE's decision to select this range based on the average value of the sample distribution. It is possible to criticize the sampling range for Pu^V in this regard (and by their extrapolation, the sampling ranges for Pu^{III} and Am^{III}). The recommended range used in the CCA calculations was 20 - 500 ml/g, which reflects values from the batch tests using deep brines. Batch tests for Pu^V with Culebra brines had a higher mean value for K_d , but the lower bound was smaller (9.8 ml/g). Therefore, the sampling distribution in the CCA does not encompass all the measured values from the batch tests for a Culebra brine, at the low end of possible values. A more conservative sampling distribution would have ranged from 10 - 500 ml/g. However, because I would not expect the lowest value from a set of small-scale batch tests to equal the lower bound for a single, effective K_d value along a 3 km flow path, the consequence of their approximation is not likely to have a significant impact on the reliability of the CCA calculations. The analogy here is that the smallest value of hydraulic conductivity measured in a set of slug tests is not a reasonable lower bound on the estimate of a larger-scale effective hydraulic conductivity. A similar approximation did not emerge in selecting the sampling range for Th^{IV} because data are only available for the deep brine.

The DOE data base indicates U^{VI} will be the most mobile radionuclide of concern in the Culebra. The low end of the sampling range for U^{VI} is 0.03 ml/g, if we ignore the negative K_d values. This lower bound is obtained from the observed breakthrough of U^{VI} in the column tests. If we accept the interpretation of Bob Holt that the column test for U^{VI} measures retardation tied to the advective porosity, then this lower bound should be a conservative value for the compliance calculations when matrix diffusion plays a major role in retardation. The value from the column test is lower than any of the values in the batch tests (Tables D-1 through D-4 of the Brush memo, June 10, 1996). This sampling range for U^{VI} introduces the possibility that the EPA standard could be violated in an undetermined number of observations in the CCA calculations, if alternate scenarios were considered for the release of the uranium inventory from a disposal panel (i.e. a K_d less than 1 ml/g, using the DOE benchmark for Pu^{III} and Am^{III}). We do not know how robust the CCA calculations are to a violation of the assumptions on the uranium release to the Culebra. Several factors need to be considered. A lower bound for K_d more reflective of matrix sorption than the value obtained in the column tests is not well-defined because of uncertainties in the batch tests (eg. the negative values). The zero values assigned to the negative K_d values for the batch tests with the Culebra brine did not get passed into the CCA calculation because of a lower average value of K_d for the batch tests using deep brines. This issue may be worth pursuing if BEG has concerns about the scenario assumed in characterizing the release of uranium to the Culebra.

An alternate interpretation in adopting the log-uniform distribution is that it de-emphasizes the importance of the K_d value that defines the upper bound of the distribution. Given the results of the EPA verification test, I have concluded that the questions regarding the relevance of the mechanistic K_d tests on pure dolomite from Norway are not a significant issue. These tests only make their way into the final sampling distributions once, in determining the upper bound for U^{VI} at high pH conditions.

The Sparse K_d Data Base

I disagree with the characterization made by M. McFadden in his opening presentation that K_d values used in the CCA are well-founded on experimental data. This simply is not the case, given the lack of experimental data for some radionuclides. The real issue is whether there is an adequate data base, and evidence to support the application of the oxidation state analogy, in assigning conservative bounds for radionuclides where measurement are not available from batch or column experiments. While I found the arguments presented by DOE to be compelling, they are not based on experimental data specific to the Culebra. It is still reasonable to ask if it would be more expedient, in a project of this magnitude and duration, and given the importance to DOE of a public demonstration of their commitment to ensuring the safe disposal of radioactive wastes, to complete a set of batch experiments on Pu^{III} , Am^{III} , and Pu^{IV} . DOE could then avoid the arguments and indirect support that must be linked to the oxidation state analogy. I understand from informal comments made at our meeting that these experiments could be carried out without great technical difficulty. My expectation from all that I have

heard is that these tests would serve to confirm that DOE has used a suitable range of values in the CCA calculations.

Batch Tests

BEG has accepted the viewpoint that the batch tests have relevance in determining K_d values for the CCA calculations. After considering the geologic and hydrologic descriptions in the report by Bob Holt on a conceptual model for multi-rate transport in the Culebra, I am persuaded the batch tests can provide a basis for defining K_d values that characterize matrix sorption. The approach is subject to uncertainty (which should be balanced by conservative approximation), and I would not necessarily expect a one-to-one correspondence between a batch test and a long-term column test in a core from the same sample location (and interpreted with a dual porosity model). However, I am now of the opinion that the batch tests can be used to identify the sampling range in the CCA calculations. This sampling range applies only to the matrix porosity. It is inappropriate to use these batch test values to characterize retardation in the fracture system (advective porosity).

Column Tests

It is my impression that the latest analyses of the column tests do not move us much further along in reducing the uncertainty in the appropriate sampling range of K_d for Pu^{III} and Am^{III} . The attempt was worthwhile, but we now see there are limitations in the experimental design, because of issues tied to solubility. I agree that if it is technically feasible, it would be worthwhile to request that DOE try to determine if a mineral phase is present, that would confirm if the migration distance cannot be interpreted strictly in terms of a K_d estimate. It is not apparent to me what else could be done with the column experiments to gain further insight to the magnitude of K_d for Pu^{III} and Am^{III} .

Tom Clement has raised the important issue that the only batch test data available for Th^{IV} (and, by DOE extrapolation U^{IV} and Pu^{IV}) are for the ERDA-6 brine. His statistical analysis suggests that the mean K_d 's measured in ERDA-6 brine are greater than the values determined using the other 3 brines. It is my understanding that the column tests on the B core were carried out using Culebra brine. The estimated K_d value from tomographic analysis on the B-core is reported to be approximately 400 ml/g. Although this value is lower than the sampling range from batch tests that was used in the CCA calculations (900-20,000 ml/g), the value is sufficiently beyond 1-3 ml/g (the DOE benchmark) to suggest that Th^{IV} will not be of concern. Whether this same conclusion can be drawn for Pu^{IV} and U^{IV} depends upon the acceptability of the oxidation state analogy in setting conservative bounding values for their sampling distributions.

Beyond 10,000 Years

In our discussion after the meeting with DOE, we considered whether the CCA calculations should be extended beyond the mandated 10,000 year time frame. This topic

is akin to an issue of full disclosure. There has been considerable informed debate on the regulatory time frame, and the advantages / limitations of looking beyond 10,000 years. My personal bias, influenced by reviewing projects under Canadian regulations, is to base siting decisions on a 10,000 year time frame, but to examine system behavior from a more qualitative perspective over a longer time horizon. Perhaps there is a role to be played here by EEG, in representing the interests of the State of New Mexico. It could be informative to look at the probability of radionuclide release along the pathway through the Culebra for time frames of 20,000 or 30,000 years, using the sampling distributions adopted by DOE.

Closure

EEG should continue to press DOE to refine and verify their calculations and modeling assumptions used in the CCA. Comments made by Sandia and LANL staff at the meeting suggest that this process is ongoing, if informal. For example, Vann Bynum described his latest calculations on the effects of the amounts of organic ligands on transport, and we heard that measurements of the EDTA β for nickel under WIPP conditions have recently been completed. Efforts to update the performance assessment should continue as time and computational tools become available.

Sincerely,



Leslie Smith

**8.7 Walter Gerstles' Responses to Anhydrite Fracturing Issues
Raised on February 17, 1998**

Memo

Feb. 24, 1998

To: Lokesh Chaturvedi
Environmental Evaluation Group
Albuquerque, NM
Fax: (505) 828-1062
Phone: (505) 828-1003

From: Walter Gerstle
Dept. of Civil Engineering
University of New Mexico
Albuquerque, NM 87131

I have had a few days to digest Norm Warpinski's presentation at our meeting last week. I make the following observations.

I. Estimate of Crack Opening Displacements in Bragflo Model.

The Bragflo model "smears" cracks in the anhydrite layers, using the porosity model. Assuming 200,000 m³ of gas is stored in these cracks, and assuming n layered cracks, with radius R=1000 m, it is possible to calculate the average crack opening displacement, w. Figure 1 shows the situation.

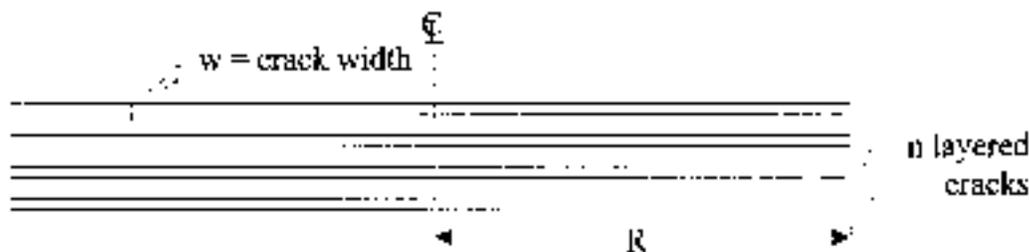


Figure 1. Cross Section Along Crack Diameter

The area, A, of each crack is $A = \pi R^2 = \pi(1000 \text{ m})^2 = 3.14 \times 10^6 \text{ m}^2$.

$$\text{Volume} = V = n w A; w = \frac{V}{n A} = \frac{200,000 \text{ m}^3}{n(3.14 \times 10^6 \text{ m}^2)} = \frac{6.37 \text{ cm}}{n}$$

So the average crack opening displacement is 6.37 cm divided by the number of layered cracks.

The following table shows the average crack width for various numbers of cracks.

<u>n</u>	<u>W, cm.</u>
1	6.37
5	1.27
10	0.64
20	0.32

So the consequence of the Bragflo porosity model is many cracks with wide openings. However, anhydrite is relatively fine grained, and certainly cannot transmit stresses across crack openings of larger than approximately 0.001 cm. Consequently, it is reasonable to assume that all but one of the cracks would close up, but that single crack would extend in radius, as both the Gerstle and Bredehoeft 1997 and the Geertsma and Deklerk 1969 models assume.

II. Geertsma and Deklerk 1969 "Industry" Model

Warpinski made reference to the Geertsma and Deklerk 1969 model as being both an industry standard model and as being more consistent with the Bragflo model than with the LEFM model. In fact, the Geertsma and Deklerk model is an LEFM model, with fracture toughness assumed to be negligible, and it predicts even longer crack radii than the Gerstle and Bredehoeft 1997 model, contrary to Warpinski's assertions. I agree with Warpinski that the Geertsma and Deklerk model is basically reasonable, in that it assumes a single, localized, discrete crack.

A quote from Geertsma and Deklerk 1969 illustrates the fundamental difference between this model and the Bragflo model: "it is found that p_w (pressure at the well bore) decreases with increasing fracture length and approaches S (overburden stress) for large values of L (crack length). Such pressure behavior is in agreement with reported field observations." It is noted that the Gerstle and Bredehoeft 1997 model also demonstrates this pressure behavior, while the Bragflo model demonstrates the opposite pressure - crack length behavior. The decreasing pressure vs increasing crack length behavior also is indicative of a single, localized hydrofracture, which is in contrast with Bragflo's assumption of widely dispersed cracks forming simultaneously in multiple anhydrite layers.

Warpinski in his presentation predicted a crack radius of $R = 366$ m using Geertsma and Deklerk's formula:

$$R = \frac{1}{\pi} \frac{Q^2 t}{C^2} \quad (24)$$

Where R = fracture radius
 Q = rate of flow into hydrofracture
 t = time
 C = fracturing fluid coefficient, $C = u\sqrt{\Delta t}$
 u = rate of filtration loss per unit of exposed surface of the fracture.

I do not know what numbers Warpinski used, but I used the following numbers and arrived at a much larger predicted radius, R .

$$u = \frac{4499m^3}{2\pi(750m)^2(1000yrs)} = 1.27 \times 10^{-6} \frac{m^3}{m^2 \cdot yr}$$

$$C = u\sqrt{\Delta t} = 1.26 \times 10^{-6} \frac{m^3}{m^2 \cdot yr} \times \sqrt{1000yr} = 4 \times 10^{-5} \frac{m^3}{m^2 \cdot \sqrt{yr}}$$

$$Q = \frac{200,000m^3}{1000yrs} = 200m^3/yr$$

$$\text{So } R = \frac{1}{\pi} \left[\frac{(200m^3/yr)^2(1000yr)}{(4 \times 10^{-5} m^3/m^2 \cdot \sqrt{yr})^2} \right]^{1/4} = 4003 \text{ m.}$$

Obviously, there is room for debate upon precisely what values of C , Q , and t are reasonable, but Sandia has not performed any calculations using the Geertsma and Deklerk model or any other standard hydrofracture model. This should be done.

III. Warpinski's claim that Gerstle and Bredehoeft model is incorrect

Warpinski claimed that Gerstle and Bredehoeft's 1997 model is incorrect because it contained no explicit flow equation and no leakoff equation. In fact, calculations in (Gerstle, Mendenhall, and Wawcisik 1996) show that leakoff is negligible - and therefore does not need to be explicitly included in the LEFM model. Warpinski also claimed that our model would require flow rates of $Q = 1.85 \times 10^6 \text{ m}^3/\text{yr}$, using the equation

$$Q = \frac{\pi w^3 \Delta P}{6\mu \ln [R/r]}$$

In fact, use of this equation is inappropriate because we assumed identical pressure ($\Delta P=0$) everywhere within the crack, and thus flow Q would be negligible. Our LEFM model neither assumes nor requires high flow rates.

IV. Conclusions

It is essential for the WIPP facility that a credible gas-driven hydrofracture model be used. I believe that the (Gerstle and Bredehoeft 1997) model is essentially correct despite Warpinski's observations about it. Warpinski's comments appear to be spurious.

I would suggest that Sandia present calculations of hydrofracture extent using Geertsma and Dekker 1969 model, fully documenting all inputs to the model. I believe they will arrive at conclusions similar to those I have presented.

**8.8 Ncill to Kruger letter dated 8/11/97 with attachment,
“EEG comments on CCA Chapter 5”**



ENVIRONMENTAL EVALUATION GROUP

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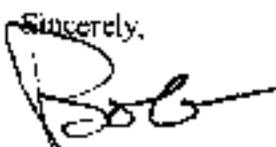
August 11, 1997

Mary Kruger
U.S. Environmental Protection Agency
Office of Radiation and Indoor Air
401 M Street SW (6602J)
Washington, DC 20460

Dear Ms. Kruger:

Enclosed please find the *EEG Review of the WIPP/CCA (DOE/CAO-1996-2184), Chapter 5 (Quality Assurance)*.

Sincerely,


Robert H. Neill
Director

RHN:js

cc: EPA Docket

EEG REVIEW OF WIPP/CCA (DOE/CAO-1996-2184) CHAPTER 5 (QUALITY ASSURANCE)

The DOE's Carlsbad Area Office (CAO) has successfully focused on developing a quality assurance (QA) program which implements the Nuclear Quality Assurance (NQA) standards required by 40 CFR 194 over the last few years. Chapter 5, Quality Assurance (QA), in the DOE's Compliance Certification Application (CCA), is, however, of lesser quality than the QA program it attempts to describe. The chapter fails to show compliance with most of the requirements of 40 CFR 194.22, Quality Assurance, and ignores most of the expectations for QA published in EPA 402-R-95-014, Compliance Application Guidance for 40 CFR 194 (the CAG).

In a chapter which should provide specific responses to clearly delineated requirements and expectations Chapter 5 offers a diffuse scattering of relevant information, provides generalized information without examples or details, and references other documents which are no more specific (and were not intended to address the QA requirements for the CCA). The chapter contains what seems to be extraneous information (some of which is found elsewhere in the CCA), glosses over past QA problems rather than explaining how they were resolved, and fails to include information explicitly required by 40 CFR 194.22. In many cases the CAO QA program and process has adequately covered the area, yet the chapter fails to fulfill the responsibility of describing how it was done.

Parts of Chapter 5 are also misleading. For example, "the CAO QAPD" is referenced throughout much of the chapter and is initially identified as appearing in CCA Appendix QAPD. The version in the Appendix QAPD is Revision 1, dated April 22, 1996, though it was not officially transmitted to, or required to be implemented by, subsidiary organizations until after June 13, 1996--when essentially all QA-related activities for the CCA had already been completed. Revision 1 is a substantial rewrite of Revision 0, among other things establishing the CAO QAPD as a requirements document for all CAO subsidiary programs for the first time, and adding elements of NQA standards previously not included. To state that

The TWBIR was prepared in compliance with the CAO QAPD...

(p. 5-3) implies that the data from the TWBIR used in the CCA (first published in December 1995) was prepared according to the requirements in Revision 1. It wasn't, and the distinction should have been clearly made. Similar statements are found elsewhere Chapter 5:

The WAC was written and reviewed in compliance with the CAO QAPD [p. 5-3]...The TRU QAPP was written and reviewed in compliance with the CAO QAPD requirements [p. 5-4]...NDA software is controlled in accordance with the requirements of the CAO QAPD [p. 5-9]...

Versions of the WAC and TRU QAPP current at the time the CCA was submitted were written under Revision 0; the NDA (Non-Destructive Assay) software is, of course, currently controlled under Revision 1, but any NDA data used in the CCA would clearly predate the issuance of Revision 1.

The chapter contains an important misinterpretation of the intent of 40 CFR 194.22(a)(2). This paragraph requires the compliance application to demonstrate that a QA program adhering to the 1989 edition of the Nuclear Quality Assurance (NQA) standards has been established and executed for eight specific areas considered by the EPA to be critical to the compliance application. In Chapter 5, this is interpreted (p. 5-3, line 28) as:

40 CFR Part 194 stipulates that the DOE apply QA controls to eight areas.

Under this interpretation Chapter 5 fails to clearly demonstrate that the requirements of the NQA standards have been executed for any of the eight areas, though discussions under specific headings for each of the eight areas immediately follows. In some of these discussions virtually no QA information is supplied at all.

The EEG, in a preliminary commentary (Neill-to-Dials letter dated July 22, 1996; see Attachment I) on what now must be considered a draft of the final Chapter 5, pointed out several clearly erroneous statements in the text. Most of these have been removed from this October version, but the chapter still includes a curious concept that since the EPA had reviewed site selection and site characterization QA programs during examination of the 1989 No-Migration Variance Petition (NMVP), the QA for site selection and characterization is considered satisfactory by the DOE (p. 5-8). The EEG's comment pointed out that the argument was untenable, in that (among other reasons) compliance with NQA standards was not a part of the 1989 NMVP. The DOE response (enclosure to undated Dials-to-Neill letter received August 9, 1996; see Attachment II, enclosure p. 4) stated that the DOE agreed with the comment, and "We have updated this portion of Chapter 5". The updating is not apparent--the argument is still the same, and still an obvious error (see line-by-line review of p. 5-6, lines 6-13 for more discussion).

The EEG's July 1996 letter concerning Chapter 5 (see Attachment I) recommended that the DOE rewrite the chapter to meet the published EPA requirements and expectations for QA. The DOE has not substantially rewritten the document (though material was added and removed), and this final CCA Chapter 5 and associated materials arguably fails to demonstrate fulfillment of the requirements in 40 CFR 194.22, Quality Assurance.

The following sections consist of 1) a comparison of Chapter 5 to the CAG expectations; 2) a comparison of Chapter 5 to the requirements for QA in 40 CFR 194.22; and 3) a line-by-line review of the document.

OCTOBER '96 CCA CHAPTER 5 (QA) AND THE CAG

The DOE has previously (see Attachment II, letter p. 2, and enclosure p. 7) informed the EEG that, as a guidance document, the Compliance Application Guidance (CAG) expectations need not necessarily be included in the CCA. However, the CCA begins with the statement that:

This application has been developed to be fully responsive to the requirements of 40 CFR Part 191, the criteria in 40 CFR Part 194, and the guidance in the *Compliance Application Guidance for 40 CFR Part 194*, EPA 402-R-95-014. [p. EXEC-1;

emphasis in the original]

Chapter 5 is not fully responsive to the CAG expectations. The chapter seems to address the CAG requirements for QA only occasionally, and by accident, rather than design. Below are listed some of the CAG expectations for §194.22, Quality Assurance, and the results of EEG's attempts to find the data in Chapter 5. This is not an exhaustive list, as it is intended only to show that the CAG expectations for QA were not addressed by the DOE.

CAG §194.22(a)(1) Expectations (p. 18 of CAG):

1. *DOE top tier QA documents will be included in the CCA.*

The DOE included only the CAO QAPD. The TRU Waste Characterization Quality Assurance Program Plan, Revision 0 (QAPP; CAO-94-1010) would also seem to be a DOE top-tier document, and much of it would enhance the DOE's claim to having implemented a QA program in accordance with the NQA statutes. The TRU-Waste Characterization QAPP (Section 1.0, p. 1.1) does contain an important statement that the CAO QAPD Revision 1 lacks:

This QAPP addresses all of the basic requirements, and their supplements, of ASME NQA-1.

Section 1.9.3, Computer Hardware and Software, of the Waste Characterization QAPP also supplies a clear statement requiring the use of the successor document to the 1989 NQA-2 Subpart 2.7, "Quality Assurance Requirements of Computer Software for Nuclear Facility Applications", which would seem to address the specifications for software QA as required by 40 CFR 194.22(a)(1). The CAO QAPD Revision 1 contains no comparable direct statement of compliance with the requirements found in §194.22(a)(1)--that is, adherence to a QA program which implements the requirements of NQA-1, NQA-2 Part 2.7, and NQA-3.

Nor, in fact, does Chapter 5 contain a direct statement of compliance to the requirements of NQA-1, NQA-2 Part 2.7, or NQA-3.

2. *DOE principal contractor top tier QA documents, and a list of all non-principal contractor or sub-contractor top tier QA documents will be included in the CCA.*

SNL QA top-tier documents were not included, nor any listing of QA documents for non-principal contractors or subcontractors for WTD or SNL.

CAG §194.22(a)(2) expectations are that, for each of 8 defined critical areas, the CCA will (among many other expectations):

1. *Provide a list of quality affecting activities and items important to a demonstration of compliance.*

Lists seem to be incomplete. For instance, the bulk of field measurements of geological factors

were performed by SNL, yet SNL activities are described as "None" in the section concerning measurement of geological factors (5.1.3; p. 5-6, line 26). Other examples: Section 5.1.1 identifies the WIPP Waste Information System (WWIS; p. 5-4, lines 2-3) and the Performance Demonstration Program PDP (p. 5-4, lines 22-23) as elements of the waste characterization system, but doesn't show them as activity for any of the organizations involved. Section 5.1.2 doesn't include a discussion of QA on the current WID environmental monitoring program; Section 5.1.3 doesn't mention QA of the current WID meteorological monitoring program, or past SNL meteorological programs. These two sections have "environmental monitoring" and "meteorological" in their titles.

2. *Describe the selection of applicable NQA requirements for each of the areas.*

No descriptions are included.

3. *Provide dates of QA implementation conforming to NQA for each item or activity, and the nature and location of objective evidence which supports this determination.*

No dates are provided.

CAG §194.22(b) expectation (other expectations were also not met, though some were met in part):

1. *Provide the QED governing documents that include procedures and management plans for independent review, peer review...*

QED governing documents were not included in the CCA (CAO MP 10.5, SNL QAP 20-3).

OCTOBER '96 CCA CHAPTER 5 (QA) AND §194.22 REQUIREMENTS

§194.22(a)(1) Requirement: *As soon as practicable after April 9, 1996, the DOE will adhere to a program that implements the requirements of the NQA standards.*

The CAO QAPD Revision 1 (in CCA Appendix QAPD) does not require full implementation of NQA standards for all activities, but only for those listed in §194.22(a)(2), other radioactive materials handling, and processes related to transportation containers. This is established in the CAO QAPD in section 1.1.2.3, Applicability of QAPD Requirements, where the difference between general requirements and additional requirements is introduced, and subsections A through J list the areas that fall under the additional requirements. The additional requirements generally seem to be those which are found in the NQA standards, but not in DOE Order 5700.6C, the DOE's internal QA requirements document (which follows 10 CFR 830.120). For compliance with 40 CFR 194.22(a)(1), the NQA standards may need to be the primary criteria.

There is no indication in §194.22(a)(1), or anywhere else in the criteria, that some WIPP activities can be granted a variance from the requirements of the NQA standards.

§194.22(a)(2) Requirement: *The compliance application will demonstrate that the QA program adhering to the NQA standards has been established and executed for the following activities: waste (i) characterization activities and assumptions; (ii) environmental monitoring, monitoring of the disposal system performance, and sampling and analysis activities; (iii) field measurements of geologic factors, ground water, meteorologic, and topographic characteristics; (iv) computations, computer codes, models and methods used to demonstrate compliance; (v) expert elicitation procedures used to support compliance; (vi) design of the disposal system and actions taken to ensure compliance with design specifications; (vii) collection of data used to support the compliance application; (viii) other systems structures, components, and activities important to containment of waste.*

The requirement is misinterpreted in Chapter 5 as "40 CFR 194 stipulates that the DOE apply QA controls to eight areas" (p. 5-3, line 28). The misinterpretation is essentially an echo of page 5-2, lines 6 and 7. This statement is far from presenting evidence that the program has been established and executed. Demonstration of execution would presumably be by citing independent assessments (audits and surveillances) for the different areas.

The chapter does provide separate sections for each of the eight activities, but demonstration of establishment and execution of adherence to the NQA standard requirements is weak or nonexistent in these sections and references from these sections (see line-by-line review below).

§194.22(b) Requirement: *The compliance application shall include information which demonstrates that data collected prior to establishment of adherence to the NQA standards has been qualified by a methodology approved by the EPA.*

Chapter 5 offers no demonstration of EPA approval of any of the methods used. While the EEG understands that the EPA has not provided approval/disapproval to the DOE for the various methods the DOE has utilized, §194.22(b) clearly requires information demonstrating approval to be in the CCA. The CCA should at least contain a statement concerning qualification of the methodology by the EPA.

§194.22(c) Requirement: *The compliance application shall provide, to the extent practicable, information which describes how data in support of the application have been assessed for data quality characteristics, including precision, accuracy, representativeness, completeness, and comparability (PARCC).*

The application provides an argument that it is not practicable to apply the PARCC characteristics to "most scientific investigations used to support performance assessment in which there is uncertainty in conceptual models and the resultant ranges of parameters" (section 5.21.1, lines 40-42). The characteristics are not provided as required. While it may be that evaluation of these characteristics did not take place at the sampling level, some assessment should have been made to establish how much uncertainty in models and parameters would be not only practicable, but necessary. Note also that apparently some of the scientific investigations are not covered by the argument, and information which

describes how PARCC was assessed for these, at least, should have been included. For example, the argument states specifically that the PARCC requirements would apply to waste characterization and environmental monitoring activities, yet provides no information as to how data from these areas were assessed for PARCC.

§194.22(d) Requirement: *The application shall provide information which demonstrates how all data are qualified for use in the demonstration of compliance.*

Section 5.4.2.1 of the CCA does provide a description of the programs for qualifying data.

LINE-BY-LINE REVIEW OF CHAPTER 5

Introductory Material

Page 5-1, Lines 17-18: *...see Table 1-5 in Chapter 1.0 for a list of appendices that provide additional information supporting this chapter...*

Table 1-5 lists only Appendices QAPP and AUD, but other appendices are referenced in Chapter 5 (MON, p. 5-5 line 38; EMP, p. 5-6 line 20); SEAL, p. 5-12 line 24)

These additional appendices should have been included in Table 1-5.

Page 5-1, Lines 29-31: *A comprehensive series of assessments has determined that the DOE, SNL, and WID QA programs are adequate and effectively implemented.*

The overall CAO assessment of SNL QA (May 1996) and WID QA (June 1997) previous to the publishing of the CCA found the SNL program to be marginal both for adequacy and implementation, and the WID program marginally effective (see CCA p. 5-39, lines 6-13 for definitions of these terms.). It is the later resolution of issues raised during the assessment by which the CAO determined SNL and WID QA to be adequate and effectively implemented (see Section 5.4.2, p. 5-45 ff, and section 5.4.3, lines 24-29). The text of this portion of Chapter 5 should reflect that the resolution of concerns raised by the assessments were performed before the SNL and WID QA programs was determined to be adequate and effectively implemented.

5.1. Applicability

Page 5-2, Line 6: *These NQA requirements form the basis of the CAO QAPD.*

Revision 1 of the CAO QAPD may incorporate the requirements in the NQA standards, but they are split between general requirements (for all activities) and additional requirements (applied to activities in which radioactive materials, shipping packages, or the eight compliance activities specified by §194.22(a)(2) are involved). This division indicates that DOE Order 5700.6C is the basis of the CAO QAPD rather than the NQA requirements, as DOE Order 5700.6C is covered by the general requirements, and the additional requirements are those NQA requirements not covered in the DOE Order.

There is no variance granted in §194.22(a)(1) for activities in the QA program, and Chapter 5 presents no evidence of any agreement for such a variance. The intent of the regulation seems to be that the WIPP will adhere to NQA standards for at least all disposal-related activities, and arguably for the entire QA program.

This statement is, however, as close as Chapter 5 gets to a clear statement of compliance with §194.22(a)(1), which requires that the DOE

...shall adhere to a quality assurance program that implements the requirements of [the NQA standards].

Page 5-2, Lines 6-7: *Additionally, 40 CFR § 194.22 requires that QA programs be applied to the following eight items or activities:...*

§194.22(a)(2) does not require the application of QA programs to the areas described in its eight subparagraphs. The requirement is for the compliance application: the CCA must demonstrate that the requirements of the NQA standards have been applied for each of the eight subparagraphs. The regulation is:

Any compliance application shall include information which demonstrates that the quality assurance program required pursuant to paragraph (a)(1) of this section has been established and executed for [the eight activities].

Demonstration of execution of the requirements of the NQA standards would presumably be by describing QA assessments which confirm adherence to the NQA standards for each of the areas.

The difference in approach to the requirement is critical. Chapter 5 describes the general QA program which includes the eight critical area specified by §194.22(a)(2), but is ineffective in demonstrating that the QA program has been established and executed for each of them.

This misinterpretation of the regulatory requirement is repeated on page 5-3, line 28 (see below). The chapter should address the requirements as stated.

Page 5-2, lines 33-39: *The CAO QAPD establishes two primary categories of requirements, identified as general requirements and additional requirements. The sections of the CAO QAPD that do not identify specific applications are general requirements that apply to all items, activities, and processes under the cognizance of the DOE. The requirements of the CAO QAPD sections identified as additional requirements apply to the eight key areas identified above.*

See comment for page 5-2, line 6. These statements imply that the NQA standards in the CAO QAPD Rev. 1 additional requirements are to be applied only to the eight key areas, omitting the radioactive materials handling and NRC packaging included in Revision 1 of the CAO QAPD (sections 1.1.2.3.A and 1.1.2.3.J; pp. 1-10 and 1-11).

Page 5-2, line 41, to page 5-3, line 8: *Additionally, the use of a graded approach supports the proper implementation of QA program requirements...*

The discussion of the graded approach offers no tie of the graded approach to the compliance application requirements. A statement that NQA-1 does allow the graded approach (with reference) would seem appropriate, and perhaps necessary.

40 CFR 194.22(a)(1) specifically excludes those portions of NQA-3 (which addresses QA for site characterization data collection activities), that refer to the graded approach. Having raised the "graded approach" issue, Chapter 5 should provide evidence (even a single statement) that the site characterization data was not collected or processed using a graded approach to QA.

Page 5-3, lines 11-14: *The CAO QAPD requirements are further supported and amplified by the next tier of QA program documents which include the DOE TRU Waste Characterization Quality Assurance Program Plan (TRU QAPP), the SNL Implementing Procedures, and the WTD Quality Assurance Program Description.*

The first CAG expectation (p. 18) is that the DOE top tier QA documents be included in the application; the second is that the top tier QA documents of principle contractors also be included in the application. This first mention of these documents should also state where they can be found. CCA Appendix QAPP contains the CAO QAPD Rev. 1 and the WTD QAPD Rev. 16, but the TRU QAPP, SNL's procedures, and QAPjPs from the generator sites are not included.

It is important to note that the CAO QAPD Revision 1 became the sole "top tier" DOE QA document after June 13, 1996 (the CAO transmittal letter dated June 13, 1996 requires it to be implemented within 60 days after receipt). There was no requisite condition previously that programs other than the CAO itself adhere to the CAO QAPD. Revision 0 states that the QA programs of WTPP participants are expected to be "guided" by the CAO QAPD only (p. 1-1), and the DOE has informed the EEG that guidance documents need not be followed (Neill-to-Dials letter received August 9, 1996).

Revision 0 also did not place an emphasis on the NQA standards as requirements for WTPP QA programs, instead stating that (p. 1-1):

WTPP participants develop, implement, maintain, and document their quality assurance programs either in accordance with DOE Order 5700.6C or 10 CFR Part 830.

Page 5-3, line 28: *40 CFR Part 194 stipulates that the DOE apply QA controls to eight areas.*

The requirement (§194.22(a)(2)) is that the compliance application demonstrate that a QA program adhering to the NQA standards has been established and executed for the eight areas (see comment for page 5-2, lines 6-7).

Section 5.1.1, Waste Characterization Activities and Assumptions

Page 5-3, lines 34-39: *The Transuranic Waste Baseline Inventory Report (TWBIR) (see Appendix BIR) is the inventory source document that provided the waste data used in the performance assessment and is presented in tabular form in Chapter 4.0...*

Chapter 5 is titled "Quality Assurance", but is noticeably incomplete in discussing QA for the TWBIR.

The TWBIR has been published separately as Revision 0 (June 1994), Revision 1 (February 1995), and Revision 2 (December 1995), and some of the radionuclide data varies widely between the different versions. CCA Appendix BIR data is from Revision 2, with additional material requested by the EPA after Revision 2 was published (included in TWBIR Revision 3, according to the Executive Summary).

None of the data in any of the TWBIR versions seems to have been gathered under the NQA standards as required by §194.22(a)(2)(i). Sources of information included extrapolations from, among other sources, safety documentation and interviews with workers (TWBIR 2 p. 1-21; DOE/CAO-95-1121). EEG-61, Review of the WIPP Draft Application To Show Compliance with EPA Transuranic Waste Disposal Standards (EEG; March, 1996) on page 4-5 quotes a 1995 ORNL report that "TRU waste streams at ORNL are not as yet fully characterized...waste sludge...physical data such as particle size, hardness, viscosity and particle distribution are unknown".

The bulk of the source data may be more reliable, but is based primarily on acceptable knowledge (TWBIR 2, p. 1-20), which is in turn predominantly process knowledge. Use of process knowledge to quantify components in waste, which is how the TWBIR data is used in the CCA, is required by §194.24(c)(3) to conform to the NQA standards, also. There is no evidence in the CCA that any of the process knowledge activities were conducted under the requirements of the NQA standards.

The Waste Characterization Analysis Peer Review Report (p. 4-3) mentions both cost and time restraints as justification for the lack of QA on the TWBIR. The NQA standards contain no variances for cost and time considerations.

Page 5-3, lines 36-38. *The TWBIR was prepared in compliance with the CAO QAPD and this activity was audited by the DOE QA Program on September 5 and 6, 1995.*

Chapter 5 is offering incomplete and misleading data here. Note that the data (taken from Revision 2) used for the CCA was published months after the single assessment (a surveillance by one auditor, not an audit) cited, and QA of the additional data requested by the EPA (in 1996) included in CCA TWBIR was certainly not assessed during the surveillance. The surveillance issued one significant finding, which essentially stated that there was no analysis or data collection plan to assess the TWBIR against, as is required by the NQA standards.

The implication is that the waste characterization data used in the CCA has not undergone sufficient QA assessment. Given that both §194.22(a)(2) and §194.24(c)(3) required a demonstration in the CCA that QA has been performed on the TWBIR data, it would seem that a QA assessment should have been conducted of the TWBIR data used in the CCA.

Page 5-3, lines 38-39: *Quality assurance of the use of those waste data (by SNL) for performance assessment is addressed in Sections 5.1.4 and 5.1.7.*

The referenced sections are brief generalized statements which include no specific discussion of waste characterization data from the TWBIR. The data in section 5.1.4 is, in fact, misleading when applied to TWBIR data--it does contain a brief paragraph on the use of NDA (non-destructive assay) QA, which in part states that:

NDA software is controlled in accordance with the requirements of the CAO QAPD.

NDA software used to gather data in the TWBIR, Revision 2, was not controlled by the requirements of the CAO QAPD (see earlier discussion).

Page 5-3, line 41 - page 5-4, line 12: *The Waste Acceptance Criteria (WAC) serve as the primary directive for ensuring that only waste that can be transported, handled, and disposed of in the WIPP are shipped and/or ensuring that these wastes are certified by the generator and storage sites....The TRU QAPP describes the QA and quality control requirements for characterization....*

The requirement from §194.22(a)(2) is for a demonstration that a QA program in conformance with the NQA standards has not only been established, but also executed for waste characterization activities. Presumably, demonstration of execution would be accomplished by citing QA assessment reports on the generator sites. The EFG is unaware of any demonstration that compliance with the WAC criteria has been officially met for any waste container, so it seems unlikely that the NQA requirements can be said to have been "executed".

It may be argued that establishing the QA of the WAC, the TRU QAPP, and site QAPjPs and procedures as documents shows that the NQA standards have been "executed". One counter to this argument is provided on page 4-9 of EFG-61 (cited above): 58% of a WAC-certified population of 80 drums at INEL were miscertified according to a 1993 DOE report (DOE/WIPP 93-062).

The DOE now has a strict program for certification of generator sites before waste characterization can take place. Information on a demonstration of a full execution of the requirements of the NQA standards at the generator sites, including the certification audits, should have been provided in the CCA.

Page 5-4 line 14-16: *The DOE verifies program implementation at participating sites through audits and assessments to ensure that WIPP waste characterization activities comply with*

applicable QAPjPs and standard operating procedures.

The first three sites to ship waste to WIPP will be INEEL, Rocky Flats, and LANL. The three CAO formal assessments of waste characterization QA at these sites previous to CCA publication found that at INEEL (August 1995; INEL at the time), that ANL-W QA was inadequate; at Rocky Flats (September 1995), that the program was marginal; at LANL (August 1996), that software QA had only just begun. LANL waste characterization has not yet been formally audited by CAO to the NQA standards, though several surveillance-type activities have taken place. None of these would qualify as a demonstration that a QA program adhering to the requirements of the NQA standards had been established and executed for waste characterization activities and assumptions.

Page 5-4 Lines 25-42: *The following identifies the applicable quality-affecting activities, QA documents, and examples of subcontractors for the principal participants. DOE Activities: ...DOE QA Documents: ...*

The list of documents does not include some that would seem to be applicable. For instance, documentation used in design of the TWBIR (which should have addressed QA), the TRU Waste Characterization QAPP, the WWTS Software Quality Assurance Plan, and Performance Demonstration Program documentation should be listed, as these activities are all mentioned in the preceding text.

The "examples of subcontractors for the principal participants" does not include the subcontractor that assembled the TWBIR, which is the principal waste characterization activity that had taken place at the time the CCA was published.

Page 5-5 Lines 3-25: *Generator Site Activities: 1. Characterize TRU waste. Generator Site QA Documents: The following sites have Generator Site QAPjPs that have been approved by the DOE...*

The DOE should show that the QAPjPs were in force for the collection of data for the TWBIR. It is likely that the approval of at least some of the QAPjPs by CAO post-dates the accumulation of the TWBIR data.

The CAG (Compliance Application Guidance for 40 CFR Part 194; EPA 402-R-95-014) states (p. 18-19) that the EPA expects much more information on waste characterization activities and assumptions than is included in this section. Among these expectations are several that relate to objective evidence for various QA activities; a listing of dates when conformation to the NQA standards for each activity became effective; a description of not only DOE but principal contractor QA assessment activities; and the schedules for these activities. None of these are supplied in the CCA, though Appendix AUD lists by title (which is not a description) and date a general list of assessments that includes CAO's waste characterization assessments. The list does not however, show assessments by "principal contractors", which for waste characterization would be the generator site QA programs.

Section 5.1.2 Environmental Monitoring, Monitoring of the Performance of the Disposal System, and Sampling and Analysis Activities.

Page 5-5, Lines 30-38: *The monitoring plans required by 40 CFR § 194.42 detail the disposal system monitoring program that will be implemented during pre-and postclosure of the WIPP. This program will be implemented by the WID under the QA program described in this chapter. SNL Activities: None. WID Activities: Conduct performance monitoring. WID Documents: Reference Appendices MON and EMP.*

Lines 30-38 are the complete section. The section offers no demonstration that the "monitoring plans" have been established in accordance with the NQA standards; the "monitoring plans" are not even identified, though one can infer that the appendices may contain them. The section itself offers no demonstration that a QA program adhering to the requirements of the NQA standards has been established and executed for the titular areas--no QA documents specific to the activities are listed, no procedures that would demonstrate QA requirements at the working level.

Environmental monitoring activities, and associated sampling and analyses activities, have been conducted for years by the WID but no mention is made of QA for this effort.

The referenced appendices do not contain information which demonstrates execution of the NQA standards, even for the pre-closure activities that have been in operation for years. The QA section in CCA Appendix MON simply states (p. MON-62) that future work will be controlled by the CAO QAPD Rev. 1, and that the DOE has "agreed to adopt QA and quality control guidance" from the NQA standards (the DOE opinion is that guidance for QA is not a requirement, and therefore need not be addressed). CCA Appendix EMP describes in general terms the QA program for environmental monitoring but does not demonstrate that it has been executed. The description is in terms of 10 CFR 830.120 (from which DOE Order 5700.6C was derived), not the NQA standards, though a table (Table 8-1 on p. 8-2) attempts a cross-reference to NQA-1 requirements.

The mapping of 10 CFR 830.120 or DOE Order 5700.6C requirements to the NQA standards is not a satisfactory process--nor a quality one. NQA-1 alone contains about 30 pages of basic and supplemental requirements (not counting definitions or suggested practices); the §830.120 requirements cover about 2 pages. To find 30 pages of requirements in 2 pages of information would seem to require an exceedingly imaginative approach.

It appears that 40 CFR 194.22(a)(2)(ii) requirement for demonstration in the CCA that a quality assurance program in conformance with the NQA standards has been established and executed for monitoring has at best only been partially met.

The CAG expectations seem to have been ignored completely, unless "conduct performance monitoring" can be considered a "list" of quality affecting activities.

Section 5.1.3 Field Measurements of Geological Factors, Groundwater, Meteorologic, and

Topographic Characteristics

Page 5-5, Lines 43 to page 5-6, line 4: *The current WIPP activities related to field measurements are conducted by the WID and include several areas. Measurements of geologic factors include...*

No statements related to QA are attached to the description of measurement of geological factors.

Page 5-6, lines 6-13: *In 1989, the EPA reviewed and commented on much of the data collected by the DOE during the site selection and site characterization program. After this review by EPA geologists, hydrologists, and other scientists, the EPA reached conclusions regarding the adequacy of the DOE's site characterization program and the reasonableness of the site characterization activities. The EPA's independent reviews and conclusions regarding the adequacy of the data were supplemented by the independent reviews conducted by the National Academy of Sciences. Therefore, the DOE considers the adequacy of the QA program and the data collected during site selection and characterization to be satisfactory.*

Substantially the same argument was included in the earlier version of Chapter 5 that EEG commented on (Neill to Dials letter dated July 13, 1996). The EEG comment (p. 3 of the enclosure) noted that:

This is untenable on several grounds, not the least of which is that the NMVP is for compliance with 40 CFR 268.6, which has no requirement that QA programs must comply with the 1989 versions of NQA-1, NQA-2 Part 2.7, and NQA-3, as is found in 40 CFR 194.

The DOE's response (p. 4 of the enclosure to Dials-to-Neill letter received August 9, 1996) was as follows:

We agree with the comment on the No Migration Variance Petition (NMVP) and had already noted this. We have updated this portion of Chapter 5.

The only substantive differences between the two presentations of the argument is that 1) in the most recent version, a statement that the EEG also conducted an independent review and was in agreement with the EPA and NAS conclusions has been dropped; and 2) references to the source document were dropped.

The argument is ludicrous in a document written to show compliance with 40 CFR 194. A large part of site characterization data included in the CCA has been performed since 1989; the NMVP is concerned with disposal of chemical wastes, not the radiological component that is the §194 concern, and the major concern at WIPP (plutonium is not on the list of 40 CFR 268 hazardous components); QA approaches and philosophies have changed in the intervening years; the regulation to be complied with is different for the CCA (40 CFR 191 and 194) than it was for the NMVP (40 CFR 268); and a demonstration of establishment

and execution of a QA program that adheres to the NQA standards was not a requirement for the 1989 NMVP.

Neither the "References" nor the "Bibliography" at the end of Chapter 5 contain an entry for either an EPA document, or an NAS document, concerning the 1989 NMVP. The accuracy of the DOE interpretation cannot be verified without proper referencing of the source documents.

The May 31, 1996 draft of Chapter 5 (p. 5-6) included the statement that:

These conclusions were issued in a document titled Background Document for the U.S. Environmental Protection Agency's Proposed Decision on the No-Migration Variance for the U.S. Department of Energy's Waste Isolation Pilot Plant.

No further information on this document was provided in the bibliography of the May 31, 1996 draft Chapter 5. One of the EEC's comments on this draft was that documents were not referenced in a manner which allowed traceability.

Page 5-6, lines 15 and 17: *Topographic characteristics were characterized early in the site characterization phase of the WIPP project, and the QA of data from that period is addressed in detail in Section 5.4.2.2.*

Section 5.4.2.2 discusses in very generalized terms the Qualification of Existing Data (QED) process (for data that was not collected under an NQA program) and includes no commentary specific to measurements of topographic characteristics. Reference to this section implies that a demonstration of adherence to NQA standards for topographic characteristics as required by §194.22(a)(2) cannot be performed.

Page 5-6, lines 20-21: *See Appendix EMP for QA controls applied to monitoring activities of groundwater well levels.*

The section of Appendix EMP concerning groundwater (Section 5.4.3, p. 5-12) does not include any QA information; the QA section of Appendix EMP does not discuss establishment and execution of NQA requirements (see comments to p. 5-5, lines 30-38 above for additional data on the QA section of Appendix EMP).

Page 5-6, lines 23-35: *The following identifies the applicable quality-affecting activities, QA documents, and examples of subcontractors for the principal participants. SNL Activities: None.*

SNL was responsible for most of the measurements of geologic factors, including the "site selection and characterization program" mentioned in this section. To state that there were no SNL activities, QA documents, or subcontractors is ludicrous.

WIPD Activities:

No mention is made of the WID meteorological measurements or associated QA efforts.

The WID has measured meteorologic characteristics at the WIPP for many years; Section 2.5.2 (p. 2-178 ff) of the CCA indicates that data was used in the CCA from WID environmental monitoring reports from 1991-1995. This section of Chapter 5 should demonstrate that a QA program adhering to the requirements of the NQA standards was established and executed for these data and reports.

Appendix EMP also contains a section on meteorological monitoring (section 5.4.1, p. 5-11) which states that:

A Quality Assurance Project Plan (QAPJP) is being developed for the collection of meteorological data use [sic] for regulatory purposes.

This QAPJP may be necessary before demonstration of establishment and execution of a quality assurance program that adheres to the NQA requirements can be made.

Appendix EMP section 5.4.1 lists the requirements documents for the QAPJP. Those listed do not include 40 CFR 194, the NQA standards, or the CAO QAPD Revision 1.

Page 5-6, lines 36-39: *WID QA Documents...WP 02-1 WIPP Groundwater Monitoring Quality Assurance Plan*

The title of this document since March 3, 1996 (eight months before the CCA was published) has been "Groundwater Surveillance Program Plan, Revision 3"; it is not a "Quality Assurance Plan", but five of the 25 pages (pp. 5-9) have brief sections addressing each of the 18 NQA-1 Basic Requirements.

The QAPJP for collecting meteorological data described in Appendix EMP is not listed among the WID QA documents.

5.14. Computations, Computer Codes, Models, and Methods to Demonstrate Compliance

Page 5-7, lines 9-10: *Computations and computer codes used to demonstrate compliance with 40 CFR Parts 191 and 194 are controlled as described in Section 5.3.20.*

Section 5.3.20 is a general description of computer software QA for the WIPP. It does not address computations (which are not always performed on a computer) and does not demonstrate the establishment and execution of a QA program which adheres to the requirements of the NQA standards for computer codes. It also does not describe the process for controlling the most important of computer codes for the CCA, those related to performance assessment (PA).

None of these PA codes were properly qualified (as prescribed by NQA-2 Part 2.7) for use at the time the PA calculations used in the CCA were performed (see p. 1 in Attachment 1 of the EEG July 11, 1996 Walker-to-Neill memorandum, "CAO Audit of SNL PA June 17-

21, 1996", included here as Attachment III, for a more complete discussion). Some of the important documentation for perhaps the most important computer code, BRAGFLO, had still not been completed in December, 1996—two months after the CCA was submitted, and several more months after the PA for the CCA was ran.

Page 5-7, lines 11-16: *Software supporting compliance fall into one of three categories... Table 5-1 lists the compliance software according to category.*

It is unclear why the three categories are described, as no information on the differences in QA among the various categories is supplied. Were these three categories graded differently for QA purposes?

The statement implies that all software supporting compliance is to be found in Table 5-1 (which lists only SNL's PA-related software). Other software (data acquisition, WWIS, facility design, NDA) are discussed later in this section (p. 5-9, lines 14-30), but these are not identified in Table 5-1, which is titled "Computer Software and Codes".

Page 5-7, lines 19-37: *SNL QAP 9-2, Quality Assurance Requirements for the Selection and Documentation of Parameter Values Used in WIPP Performance Assessment... The four parameter categories that are used in current compliance calculations are... 1. parameters derived from experimental data... 2. parameters representing inventory of the waste... 3. parameters representing physical constants... 4. parameters that are model configuration parameters or that are assigned based on assumed correlation of properties between similar materials.*

It is unclear why the description of the four categories of parameters is included in a section that should be discussing QA for computations, computer codes, models, and methods. Discussion of parameter categories are not a part of the requirements of either 40 CFR 191, §194, the CAG, or the NQA standards. The categories are more properly described in Appendix PAR (p. PAR. 1).

Since SNL's QAP 9-2 and parameter categorization is mentioned, however, it should be pointed out that parameters of the 4th type are divided into type 4a and 4b in the version of QAP 9-2 current at the time of publication of the CCA (Revision 2, effective 09-12-96; see p. 3).

It should also be pointed that various groups of parameters are not required to comply with the complete QAP 9-2. None of the parameters entered into the PA database before 11-28-95 are required to comply with the quality-affecting portions of 9-2 according to Revision 2 (see p. 3), which was current when the CCA was published. Revision 1 did not require any of the type 4 parameters to comply with QAP 9-2, though 9-2 could be used at the discretion of the Parameters Task Leader (Rev 1, p. 3). Type 4b in the current Revision 2 are the "model configuration parameters", and are excluded from the requirements of QAP 9-2 (p. 3 of Revision 2).

...as they are not used in current compliance calculations and therefore are not

subject to this procedure.

QAP 9-2 requires, among other things, that the need and intended use of a parameter be documented; that the rationale for the parameter choice (the value range) be documented; and that documentation of the parameter development be referenced or attached to the Form 464 (which is a form essential to tracing of parameters). These requirements are unique to QAP 9-2, and should be required of all parameters used. Assuming that the PA is considered a scientific investigation, the CAO QAPD Rev. 1 would seem to require use of QAP 9-2 for all but the excluded type 4b parameters under the dictates of Section 5.1.B, 5.1.C, 5.1.D, 5.1.E, and 5.1.H (other sections may also apply).

Finally, it seems useful to note that parameter data in the CCA (in Appendix PAR) is not necessarily the same values as was used in the running of the PA codes for the CCA. For example, Parameter # 3148, a concrete compressibility parameter, is listed in Appendix PAR as having a value of $1.2e-9/\text{Pa}$, but is shown in the code listings for the CCA (not in the CCA; at SNL) as $2.64e-9/\text{Pa}$. This difference is apparently due to Appendix PAR being taken from a later database than the one used by the PA codes for the CCA. The information and data in the CCA should be the same data that was used to demonstrate compliance.

Page 5-7, line 39, to page 5-9, line 2: *A set of screening efforts, comprised of calculations and reasoned arguments, has been identified to help define and build confidence in assumptions, data sets, and conceptual and numerical models on which the performance assessment in this application is based. Assessing the effects of features, events, and processes (FEPs) on system performance is a primary component in conceptual model development...*

No explanation as to the definition or purpose of "screening efforts" is supplied, and the terminology is rather obscure. The calculations and reasoned arguments are used to determine whether or not to include consideration of a FEP in a model, but this is not explained in the text.

The connection between screening efforts and the requirements of 40 CFR 194.22 or the NQA standards is not made clear in this section. As with the parameter categorizations, this is not a QA description but a description of an operational process.

No screening efforts other than those for FEPs are identified.

Page 5-9, lines 4-10: *FEP screening is phased. Phase I FEPs are those that could potentially affect conceptual and/or numerical models. Phase II FEPs are those that could impact parameter input to the numerical models. FEP screening analysis plans for Phase I and Phase II FEPs were developed and controlled in accordance with SNL QAP 9-1...*

Phase I and II screening were only performed separately so that SNL could meet deadlines, and under SNL QAP 9-1 could have easily been written as a single analysis plan. The necessity for describing them in the CCA chapter on QA is not apparent.

FEPs screening is an area of controversy all its own, as 40 CFR 194.32(e) requires that the CCA include documentation of the reason for excluding any identified processes or events that may affect the disposal system during the regulatory time frame. The DOE originally developed a list of nearly 1200 FEPs; the draft CCA (DOE/WIPP/CAO-2056, March 31, 1995) considered about 900 FEPs; of the 900, about 30% were addressed by Phase I and II screening plans for the CCA, and 89 of these were "screened in" to the CCA. No documentation, or screening analysis plans, were developed for the reduction of the vast majority of the nearly 1200 FEPs to the approximately 240 included in the CCA.

The FEPs which were to be addressed by Phase I and II analysis plans were not all adequately documented. The EEG asked for information on 31 of these FEPs (Neill-to-Dials letter dated July 11, 1996) and the response (McFadden-to-Dials letter dated August 2, 1996) was that screening information would be supplied only in the CCA--though the analysis plans indicate screening decision packages were to be kept for each FEP. All FEP screening decisions should have been performed according to a reviewed plan, and be adequately documented. §194.32(e) requires the CCA to include documentation of why those screened out were not included in the PA results. This was not done.

Page 5-9, lines 10-11: *Additionally the DOE and SNL have provided oversight of the FEPs screening process in the form of detailed audits and surveillances.*

Failure of the DOE and SNL detailed audits and surveillances to discover and require resolution to the FEP screening problems described above does not establish confidence in the application of the quality assurance process to FEPs.

Page 5-10, lines 20-23: *WID Documents...WP 16-117 WIPP Computer Software Quality Assurance*

This document was replaced by WP16-IT3117, Revision 0, which has the same title, on 9/26/96 (a month before publication of the CCA).

5.1.5 Expert Judgment Elicitation

This section simply states "No expert judgment activities have been identified" (p. 5-10, line 31). There have been many expert judgment activities; the question is whether or not any of these should have been performed under the formal elicitation process regulated by 40 CFR §194.26.

Some examples of expert judgment activities used in the CCA follow. Expert judgment is a part of the passive institutional control development process according to the WIPP Passive Institutional Control Peer Review Report (p. 4-3 and 4-4). Numerous parameters used in the performance assessment are justified by "investigator judgment" or "professional judgment". A November 14, 1995 RE/SPEC Inc. memorandum (RE/SPEC's Profile to SNL's Diane Hurtado) outlines as part of a task plan "solicitation of expert opinion" for establishing seals parameter values, and execution of this task plan would seem to fall directly under the §194.26, Expert Judgment requirements.