

EPA Comment**G-10 Ground water basin modeling and ground water chemistry**

Since DOE submitted the original certification application (CCA), new information has become available on the Culebra hydrology and potential recharge related to potash mining. The possibility of potash mining as a potential source of recharge could affect previous interpretations of the ground water chemistry and ground water basin modeling that was done for the CCA. DOE must update the ground water basin modeling and ground water chemistry to accommodate the possibility that potash mining is a potential source of recharge. DOE must also provide discussion on how this new information would or would not affect the current performance assessment.

DOE Response

The purpose of the basin-scale modeling performed by DOE was to provide a conceptual framework for how the hydrologic system around the WIPP site has evolved with time and will continue to evolve in the future (Corbet and Knupp 1996). The modeling examined how the system might have evolved from near the end of the last glacial period (14,000 years ago) through the present to the end of the regulatory period 10,000 years from now. It was not calibrated to present-day heads, and was never intended to provide any more than a qualitative match to current conditions. Because the model grid cells were 2 km on a side, the model could not capture the smaller scale heterogeneity known to exist in the Culebra.

Revising the basin-scale model to include potential recharge related to potash mining would not be appropriate for several reasons:

1. The recharge source would be present for only about 100 years, which is insignificant on the time scale of the basin modeling and for the purposes of that modeling.
2. Model gridding is so coarse and poorly detailed that only qualitative conclusions could be drawn. These conclusions can be known in advance—heads in all units would rise temporarily and then decrease with the largest effect occurring at the location of the recharge and decreasing with distance. The amounts of rise would depend on the hydraulic properties used in the model; but again, the model is not sufficiently detailed to allow comparison of the simulated results to actual observations of water-level change.
3. Features such as the Intrepid East Tailings Pile create an elevated water table, as evidenced by the encounter of brine at a depth of 36 ft while drilling SNL-1 a few hundred yards south of the tailings pile (Powers and Richardson 2004). The Intrepid East Tailings Pile would occupy less than a single grid cell in the basin-scale model. Raising the water table to the surface in a single grid cell for only the 100 years potash mining is expected to occur (or even a century or two longer to allow continued drainage from the tailings pile) would have much less effect on the Culebra than raising the water table globally for longer periods of time as has already been done in the basin-scale modeling.

Recharge related to potash mining has, if anything, a conservative effect on compliance calculations. Globally raising the water table to the surface causes the maximum gradient through the Culebra, and the results of this modeling formed the basis for the Climate Index used in PA to increase velocities through the Culebra. The CRA T fields are calibrated to heads from

2000, 35 years after brine disposal at the Intrepid East Tailings Pile began. If the present-day heads used in CRA modeling have already been raised by potash-mining-related recharge (which is inherently temporary in nature), applying the Climate Index to these heads is redundantly conservative.

With regard to groundwater chemistry, the DOE's conceptual model at the time of the CCA already included the idea that potash mining was responsible for the facies D groundwaters found in Nash Draw (Siegel et al. 1991). Twice-yearly sampling at the WQSP wells on the WIPP site conducted since 1995 (DOE 2004) has shown no changes in hydrochemical facies at these wells (Figure 1). Culebra groundwater samples have recently been collected, or will be collected in 2005, at wells between the Intrepid East Tailings Pile and the WIPP site (SNL-1, 2, 3, 5, and 9 and WIPP-30), as well as in Nash Draw (WIPP-25 and 26), to determine if potash brine is affecting hydrochemical facies elsewhere.

In any case, Culebra water quality enters into PA calculations only with respect to selection of K_d values for radionuclides. Culebra K_d s were evaluated for four brines: a Castile brine like that found at ERDA-6, a Salado brine (Brine A), and two Culebra brines (from the Air Intake Shaft and H-17) (Brush and Storz 1996). To be conservative, two ranges of K_d values were calculated for each radionuclide, one for the two Culebra brines and one for the Salado and Castile brines, and the lower of the ranges are used in PA calculations. K_d s were found to generally decrease with increasing ionic strength, hence the K_d s determined for Castile and Salado brines were used in PA calculations for all radionuclides except Np(V), for which the uncertainty range for Culebra brines was 1 to 200 mL/g, while the range for Salado and Castile brines was 2 to 200 mL/g (Brush and Storz 1996). Brine from the Intrepid East tailings pile (as sampled at SNL-1 (Powers and Richardson 2004)) is similar in ionic strength to Salado and Castile brines (Table 1). As it migrated over seven miles to the WIPP site, it would be significantly diluted with less saline Culebra brine. Therefore, the K_d s determined for the higher ionic strength Salado and Castile brines would be lower (more conservative) than K_d s determined for the mixed potash-Culebra brine. Consequently, any change in Culebra groundwater chemistry at the WIPP site resulting from potash mining would have no impact on compliance calculations.

In summary, recharge related to potash mining has, if anything, a slightly conservative effect on the current performance assessment because it provides a temporarily elevated gradient upon which the Climate Index redundantly builds. No changes in groundwater chemistry have been observed at the WIPP site and, in any case, the K_d values used in PA calculations are already more conservative than K_d s that might result from mixing potash and Culebra brines.

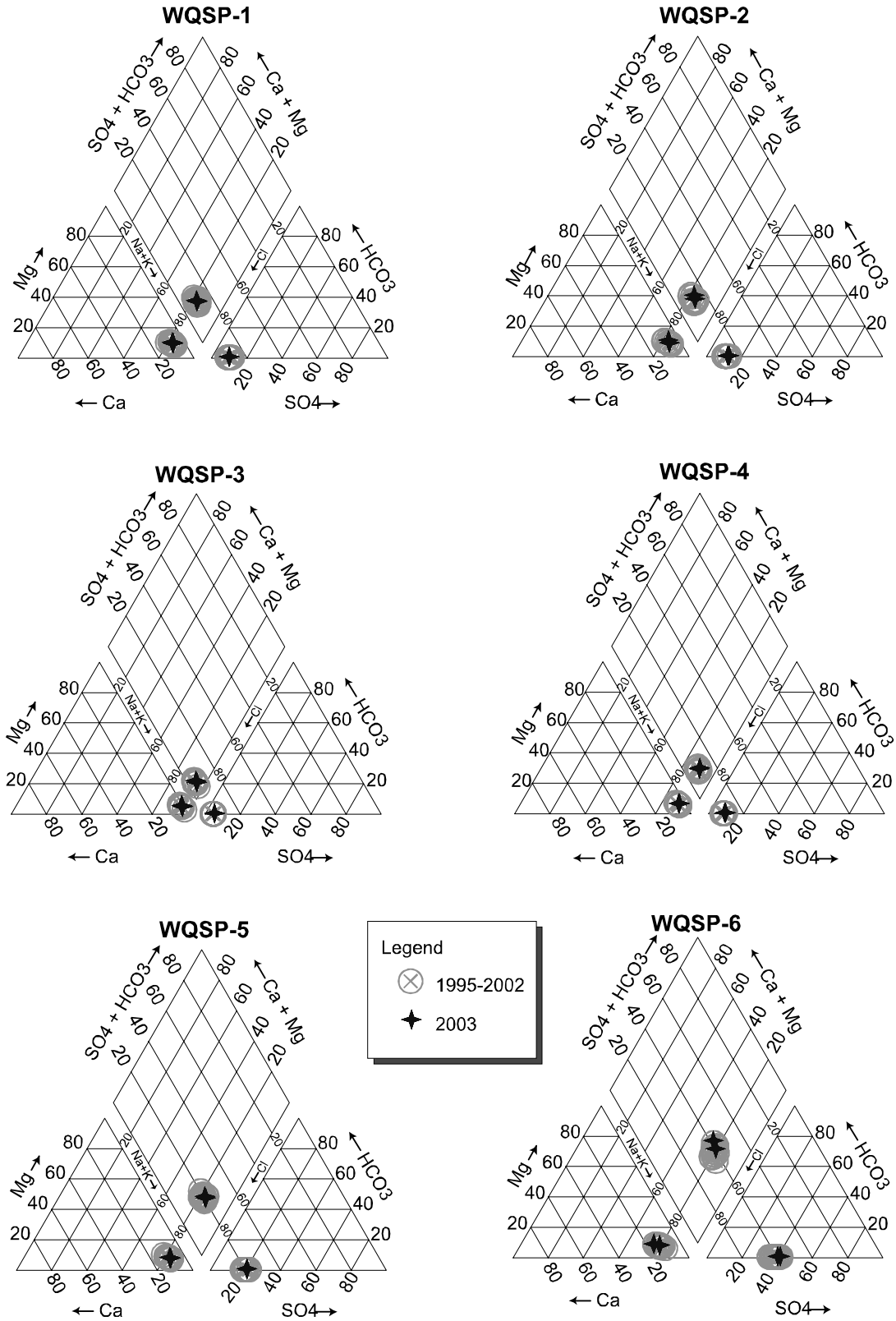


Figure 1. Ternary diagrams for samples collected from WQSP Culebra wells from 1995 through 2003 (2003 results highlighted).

Table 1. Comparison of Salado, Castile, and Potash Brine Ionic Strengths

Solute	Brine A (Salado)	ERDA-6 (Castile)	SNL-1 (Potash)
Cl (M)	5.35	4.8	5.36
Br (mM)	10	11	5.51
SO ₄ (mM)	40	170	156
Ca (mM)	20	12	13.5
Na (M)	1.83	4.87	3.96
K (mM)	770	97	537
Mg (M)	1.44	0.019	0.185

References:

Brush, L.H., and L.J. Storz. 1996. Revised Ranges and Probability Distributions of K_{ds} for Dissolved Pu, Am, U, Th, and Np in the Culebra for the PA Calculations to Support the WIPP CCA. Memorandum to M.S. Tierney, July 24, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS# 241561.

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EPA Comment**G-12 Potential Effects of Heterogeneous Waste Loading on Chemical Conditions**

DOE has continued to assume that chemical conditions will be homogeneous (evenly distributed) throughout the waste disposal region. Current information regarding Panel 1 loading has indicates [sic] that waste is unlikely to be homogeneously (evenly) distributed throughout the repository. In addition, tight panel seals are likely to limit mixing of brine between panels in an inundated repository.

DOE must address the potential effects of heterogeneous (not evenly distributed) waste loading on the assumption of homogeneous chemical conditions throughout the entire repository as opposed to assuming homogeneous chemical conditions that exist only on a panel-by-panel basis.

DOE Response

Due to the inherent uncertainties and complexities of performance predictions of this type, it is sometimes necessary to make simplifying assumptions within performance assessment models. Therefore, where realistic approaches to incorporating uncertainty are unavailable or impractical, or where the impact of the uncertainty on performance is small, the DOE has chosen to simplify the analysis by implementing reasonable and conservative assumptions. The assumption of random emplacement of waste as directed in 40 CFR 194.24(d) is consistent with the assumption of homogeneous chemical conditions in the repository.

This request is closely related to the question asked in 1997 by the EPA in their March 19, 1997 Request for Information (EPA 1997) where the DOE was asked to, "...analyze the effect of non-random loading" where the DOE demonstrated that the simplifying assumption of homogeneity has a small impact on performance (DOE 1997). In this request, however, the EPA asks more specifically about the effects of heterogeneous chemical conditions in the repository.

It is correct that Panel 1 contains more Pu than would be expected based on the homogeneous emplacement of this radioelement throughout the 10-panel WIPP repository. The only potentially significant effect of this higher-than-expected loading of Pu in Panel 1 is that, due to higher-than-expected alpha radiolysis, this radioelement might speciate as Pu(V) and/or Pu(VI) in this panel. However, the DOE maintains that there is more than enough metallic Fe in the waste containers, especially the pipe overpacks, and the waste in Panel 1 to reduce any Pu(V) and Pu(VI) that might occur to Pu(III) or Pu(IV). Furthermore, microbial consumption of cellulosic materials, or of cellulosic, plastic, and rubber materials, assumed to have a probability of 0.5 in the CCA PA and the CRA-2004 PA, would also reduce any oxidized Pu that might form in Panel 1.

Predictions of Pu oxidation-state speciation are important because: (1) the order of importance of the radioelements in TRU waste from the standpoint of their potential effects on the long-term performance of the WIPP is $\text{Pu} \cong \text{Am} \gg \text{U} > \text{Th} > \text{Np}$; and (2) these actinides have higher solubilities and lower K_{ds} (and are thus more mobile) when they speciate in their higher oxidation states (Pu(V), Pu(VI), Am(V), U(VI), Np(V), and Np(VI)) than they do in their lower oxidation states (Pu(III), Pu(IV), Am(III), U(IV), and Np(IV)). (The K_{ds} for these actinides

under conditions expected during transport in the Culebra Member of the Rustler Formation are much less important than their solubilities in WIPP disposal from the standpoint of PA because the Culebra is a much less important off-site transport pathway than direct brine releases from the repository.)

The oxidation-state distributions of these radioelements implemented in the CCA PA and the CRA-2004 PA comprised a probability of 0.5 that Pu, Am, U, Th, and Np will speciate entirely as Pu(III), Am(III), U(IV), Th(IV), and Np(IV), respectively; and a probability of 0.5 that they will speciate entirely as Pu(IV), Am(III), U(VI), Th(IV), and Np(V). The DOE has acknowledged that Pu(V) and Pu(VI) could occur in isolated microenvironments in the WIPP. However, the DOE has also maintained that any Pu(V) and Pu(VI) would not persist in significant quantities because diffusive and, especially in the event of human intrusion, advective transport of dissolved Pu(V) and Pu(VI) would expose this oxidized Pu to the reductants that will be present in the repository. Because the pipe overpacks in which the Pu residues are emplaced in Panel 1 contain large quantities of steel relative to 55-gal drums and other steel waste containers, there is more than enough metallic Fe in Panel 1 to reduce any oxidized Pu that might form as a result of the higher Pu loading in this panel.

References

DOE (Department of Energy) 1997. Second Set of Responses to EPA's March 19, 1997 Letter. EPA Comment 18, Enclosure 1. EPA Rulemaking Docket II-I-28. May 2, 1997.

EPA Comment**G-13 Ligands Potentially Produced as Aqueous Metabolites**

Recent experimental investigations of microbial degradation of CPR have indicated that potentially significant amounts of acetic and other organic acids may be formed as aqueous metabolites under inundated conditions (Gillow and Francis, 2003). The formation of these organic acids could be significant because these acids dissociate to form ligands capable of complexing actinides (for example, acetic acid dissociates to form acetate). However, the potential effects of the formation of organic acids during microbial degradation on the concentrations of ligands that could be present in the repository has not been considered.

DOE must assess the experimental evidence developed since the CCA to determine if significant amounts of ligands could be produced as aqueous metabolites during microbial degradation of cellulose.

DOE Response***Introduction***

Some of the microbial gas-generation experiments at Brookhaven National Laboratory (BNL) yielded acetic acid and lactic acid as microbial metabolites (Gillow and Francis (2003). "Both acetic acid and lactic acid are relatively weak complexants relative to some of those already included in the FMT thermodynamic database used for the speciation and solubility calculations for the CRA-2004 PA. However, an extensive literature review (see below) yielded numerous references to studies that showed that microbes, including those expected in the WIPP (e.g., sulfate reducers) will consume these organic acids as rapidly as they are produced.

Furthermore, the EPA has specified that the DOE assume that all of the organic carbon in cellulose, plastic, and rubber (CPR) materials would be converted to carbon dioxide in the event of microbial consumption of all of these materials (EPA 2004). Addition of microbially produced acetate and/or lactate to the acetate and lactate dissolved from the waste by brine would be inconsistent with the specification that all organic carbon be converted to carbon dioxide. To the extent that acetate and/or lactate are assumed to be produced by microbial activity, there would be more carbon present in the repository than that present originally in the CPR materials if it were also assumed in the PA calculations that all carbon present in the CPR materials is converted to carbon dioxide. This would violate the condition that the masses of chemical elements initially present in a chemical system be preserved unless they are lost by radioactive decay, or gained or lost by transport into or out of the system.

Therefore, it is appropriate to calculate the concentrations of acetate, citrate, EDTA, and oxalate in WIPP brines by assuming that all of these organic ligands in the waste will dissolve in 29,841 m³ of brine, the quantity used by the DOE for the CCA and the CRA. However, it would be inappropriate to increase the concentration of these ligands to simulate their production as aqueous metabolites.

Background

Posttest analysis of some of the long-term, microbial gas-generation experiments at BNL (Gillow and Francis, 2003) has yielded acetic acid concentrations of “none detected” to 6.99×10^{-3} M, and lactate concentrations of “none detected” to 3.03×10^{-3} M. The mean and median concentrations of acetate observed by Gillow and Francis (2003) were 2.84×10^{-3} M and 1.81×10^{-3} M, respectively; and the mean and median concentrations of lactate were 4.8×10^{-4} M and 2.8×10^{-4} M (Trone, 2004). (All these results are from the experiments without bentonite, the WIPP relevant BNL experiments).

For comparison, the concentrations of acetate and lactate used in the Fracture-Matrix Transport (FMT) calculations of +III, +IV, and +V actinide speciation and solubilities for the CRA-2004 PA were 5.05×10^{-3} M and 0, respectively (Brush and Xiong, 2003a); and the current (post-CCA) concentrations of these ligands are 3.56×10^{-3} M and 0 (Brush and Xiong, 2003b). FMT (Babb and Novak, 1995; 1997 and addenda; Wang 1998) is a geochemical, thermodynamic speciation and solubility code similar to the EQ3NR component Wolery, 1992b) of the EQ3/6 geochemical software package (Wolery, 1992a). The lactate concentration was set to zero because no lactate has ever been identified in the inventory of TRU waste to be emplaced in the WIPP.

CCA Position on Microbial Consumption and Production of Organic Ligands

The DOE stated that one of the ways in which microbial consumption of CPR materials could influence actinide solubilities is “consumption of solubilizing organic ligands” (U.S. DOE, 1996, Appendix SOTERM, page SOTERM-4, line 26).

The DOE also stated (U.S. DOE, 1996, Appendix SOTERM, page SOTERM-19, lines 1-5) that one of the “four effects of microbial degradation of [CPR] materials is:

“Consumption of organic ligands. While some microbes are known to consume some organic ligands, there is uncertainty as to the presence or viability of these particular microbes within the repository environment. Therefore, no credit has been taken for the microbial degradation of organic ligands. Other mechanisms for reducing the effect of organic ligands are discussed in Section SOTERM.5.”

The U.S. DOE (1996, Appendix SOTERM, page SOTERM-37, Table SOTERM-4) calculated the concentrations of acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate in WIPP brines by assuming that all of these organic ligands in the waste will dissolve in 29,841 m³ of brine, “the smallest quantity of brine required to be in the repository [for] transport away from the repository” (Larson, 1996). The DOE did not decrease the concentrations thus obtained to simulate microbial consumption, or increase them to simulate microbial production of these organic ligands. Therefore, the CCA concentrations were consistent with the assumption that there will be no significant microbial consumption or production of these or other organic ligands (i.e., lactate), or that the quantities consumed will be equal to those produced.

Additional Information Obtained Since the CCA

If organic acids such as acetic acid, citric acid, lactic acid, and oxalic acid are formed during the degradation of CPR materials in the WIPP wastes, a multitude of microbial species can and will degrade these compounds and their by-product organic ligands (e.g., acetate, citrate, lactate, and oxalate). The formation of organic ligands would potentially lead to organo-metallic complexes (radionuclides complexed onto organic molecules) and these complexes would increase the radionuclide solubilities used in the CRA-2004 PA. Abundant halophilic organisms, including sulfate-reducing bacteria and Archaea, will be present in the WIPP and would effectively reduce the accumulation of these organic acids during the waste degradation process. Halophilic microbes, specifically sulfate reducers that consume acetate and lactate, may contribute significantly to the consumption of these organic acids; this may become particularly important in the consumption of organic acids once anoxic conditions prevail in the repository and oxygen and nitrate have been exhausted as electron acceptors.

Relatively recent studies (Canfield and Des Marais, 1991; Jorgensen and Bak, 1991; Marschall et al., 1993; Minz et al., 1999; Okabe et al., 1999; Santegoeds et al., 1998; Sass et al., 1997; Teske et al., 1996; 1998) indicate that, in fact, the consumption of acetic and other organic acids may occur even under oxic or near-oxic conditions. Therefore, it is not unrealistic to expect significant consumption of organic acids produced during the decomposition of CPR materials in the repository by sulfate-reducing organisms before anoxic conditions prevail in the WIPP. However, for the purposes of the PA calculations the DOE assumes that sulfate-reducing microbes actively consume organic acids only after anoxic conditions have been attained and all nitrate has been consumed. Additionally, it is likely that the decomposition of CPR materials will progressively decrease through time as the nitrogen contents in the organic materials are consumed (i.e., nitrogen-limited decomposition). Thereafter, further decomposition will be greatly limited after the readily metabolized substrates have been consumed and only the more resistant organic compounds remain.

A consortium of microorganisms converts reduced carbon of methane (methane produced by Archaea during the decomposition of organic materials) into organic foodstuffs (e.g., acetate) that are ultimately oxidized by other microorganisms to form carbon dioxide. The carbon dioxide produced by the combined action of methane and sulfate consumers is free to cycle back into the methane pool through methane-producing microbes.

Acetate is a key intermediate in the breakdown of organic matter during anaerobic digestion. Both sulfate reducers and methanogens consume acetic and other organic acids in anaerobic reactors treating sulfate-rich wastewaters, such as paper mill and food oil industry wastewaters (Oude Elferink et al., 1994). Generally, acetate is utilized by methanogens, but in some reactors it is mainly utilized by sulfate reducers (Visser et al., 1993). Consequently, it is clear that competition exists between the dissimilative sulfate reducers (i.e., "*Desflo*" spp.) and methanogens for the consumption of these organic substrates. In aquatic environments, where sulfate is abundant, the methanogens generally lose the competition. An additional advantage of the dissimilative sulfate reducers over the methanogens as a group is that the sulfate reducers have a greater affinity for molecular hydrogen.

Sulfate-reducing organisms are universally distributed in marine sediments and microbial mats and have been observed in highly saline environments (Teske et al., 1998). Sulfate reduction is the dominant anaerobic biomineralization pathway in marine sediments and has been documented to be quantitatively equivalent to or greater than aerobic respiration in this respect (Jorgensen, 1982). It has been documented that in the presence of high sulfate concentrations, both sulfate-reducing organisms and methanogens will consume available acetate (Isa et al., 1986). Sulfate respiration may contribute to as much as 50 percent of the total organic carbon oxidized in some marine sediments and it has been reported that sulfate-reducing bacteria are the dominant anaerobes in hypersaline cyanobacterial mat communities (Jorgensen, 1982).

Evidence has been mounting that both methanogens and sulfate reducers play a significant role in the consumption of acetate in anaerobic bioreactors. It has been traditionally assumed that because of their higher growth rates, methanogens would play a larger role in acetate consumption (Yoda et al., 1987). Oude Elferink et al. (1998) investigated the kinetic parameters of acetic acid oxidation for the sulfate reducers *Desulforhabdus amnigenus* and *Desulfobacca acetoxidans* and reported that *D. acetoxidans* had a higher growth rate than most *Methanosaeta* spp. The growth rate of *D. amnigenus* was in the same range as that of *Methanosaeta soehngenii*. Acetate-degrading sulfate reducers from bioreactors seemed to have only a slight kinetic advantage over *Methanosaeta* spp. However, some reactor studies concluded that acetate-degrading methanogens may have predominated over sulfate reducers only because the duration of the competition study was not long enough to allow sulfate reducers to become dominant (Isa et al., 1986; Visser et al., 1993). For example, studies by Visser (1995) showed that it can take more than a year before sulfidogens have out-competed methanogens for acetate. In the case of the WIPP, since we are considering a long time period (10,000 years) for regulatory compliance, it is likely that sulfate-reducing microbes would eventually out-compete methanogenic microbes for acetate.

Additional Evidence for Consumption of Organic Acids by Sulfate-Reducing Microbes

Oude Elferink et al. (1998) evaluated the kinetic parameters of acetate oxidation for the sulfate reducers *Desulforhabdus amnigenus* and *Desulfobacca acetoxidans*. Their study suggested that both sulfate reducers seem to be able to out-compete *Methanosaeta* spp. for acetate in acetate-fed anaerobic bioreactors. Mixed-substrate studies showed that *D. amnigenus* degraded acetate and hydrogen simultaneously but preferred lactate, propionate, and ethanol over acetate.

The importance of sulfate reduction in marine sediments is well documented (Canfield and Des Marais, 1991; Jorgensen, 1982; Jorgensen and Bak, 1991). Sulfate reduction is generally considered to be an anaerobic process, occurring only after more energetically favorable electron acceptors such as oxygen, nitrogen, and metal oxides have become depleted. However, evidence that the abundance and activity of sulfate reducers may be higher in oxic zones than in neighboring anoxic zones has been accumulating (Canfield and Des Marais, 1991; Jorgensen and Bak, 1991; Marschall et al., 1993; Minz et al., 1999; Okabe et al., 1999; Santegoeds et al., 1998; Sass et al., 1997; Teske et al., 1996; 1998). The metabolic ability of sulfate reducers, especially *Desulfobulbus* and *Desulfovibrio* species, to tolerate oxygen (Cypionka et al., 1985; Marschall et al., 1993) and to effectively utilize nitrate (Dannenberg et al., 1992; Widdel and Pfenning, 1982) or even oxygen (Dannenberg et al., 1992; Marschall et al., 1993) instead of sulfate⁻ as a terminal electron acceptor has been reported.

Okabe et al. (2002) concluded that their study findings on the activity of sulfate-reducing organisms in an activated sludge immobilized agar gel clearly suggested the production of sulfide near the oxic/anoxic interface. The presence and proliferation of *Desulfobulbus* spp. was unequivocally supported.

In summary, it is becoming increasingly apparent the sulfate-reducing microbes can effectively participate in the degradation of organic substrates, specifically acetic and other organic acids. Therefore, a significant portion of the organic acids formed as by-products of the decomposition of CPR materials in the WIPP repository could effectively be consumed by sulfate reducers and methanogens. The literature cited above suggests that this process could become significant and, in fact, even play a role in the decomposition of the degradation products of CPR materials such as acetate and lactate immediately following the closure of repository panels.

Decomposition of organic materials is not a constant linear process. On the contrary, the rate of decomposition is variable over time and highly influenced by environmental factors that control the microbial consumption of the organic substrates. Therefore, as the decomposition process proceeds within the WIPP, the degradation of CPR materials, as well as the formation of decomposition products (e.g., carbon dioxide, methane, and organic acids), should progressively decrease as the remaining organic substrates become increasingly resistant to further decomposition.

Organic matter properties that influence decomposition rates include the carbon:nitrogen ratio, lignin content, and to some extent surface area of the substrate (Tate, 1987, p. 100). It is evident that increased exposure of the surfaces of CPR materials would result in greater decomposition by microbes and this phenomenon has been well documented. For example, Cheshire et al. (1974) evaluated the impact of surface area in a study of hemicellulose decomposition in soil and found a significant increase in carbon dioxide evolution after fine grinding the hemicellulose prior to incorporation into soil. Thus, one would expect that those CPR materials with the greatest effective surface area exposed to microbial populations would be subject to greater and more rapid decomposition.

Inhibition of biodecomposition by lignin in organic materials has long been appreciated (Reeve and Norman, 1948). The slow decomposition rates of woody plant materials is due, in large part, to the high lignin content of the external cellular structure which protects the readily decomposed internal compounds. Specifically, the mechanism of biodecomposition inhibition by lignin primarily involves steric hindrance of microbial and enzymatic interaction with the more readily metabolized molecules (Tate 1987, p.100).

Fogel and Cromack (1977) investigated the contributions of both lignin content and carbon:nitrogen ratio in the decomposition of various plant parts (needles, female cones, branches, and bark within four mature vegetation types in western Oregon). This study found that the highest correlation with net decomposition (as measured by carbon dioxide evolution) was the carbon:nitrogen ratio.

Knapp et al. (1983a; 1983b) in their study of microbial decomposition of wheat straw (*Triticum aestivum* L. var *Nugaines*) observed that decomposition was nitrogen limited during the initial decomposition period when the microbes are metabolizing carbon rich/nitrogen poor substrates,

such as carbohydrates. Straw metabolism was stimulated by amendment with mineral nitrogen at this stage in the decomposition process. As the readily decomposed carbon pool was exhausted and the microbial metabolic rate declined, sufficient nitrogen was contained in the substrate for continued microbial catabolism of the more resistant plant components, albeit at a slower rate. The microbes at that point became carbon-limited because of the greater energy expenditures necessary to metabolize these resistant substrates. However, amendment of the soil with a carbon source once again stimulated microbial respiration indicating a renewed enhancement in decomposition. The results of this study support our assumption that CPR materials emplaced in the WIPP will initially degrade rapidly and the rate of decomposition will then drop off significantly after the nitrogen levels to consuming microbes become limiting. Thereafter, the process of organic matter degradation will likely become carbon limited and decomposition rates should decline to very low levels as only the more resistant carbon substrates remain. The production of organic acids, including acetate, is therefore expected to decrease substantially after the initially high mineralization rates of CPR materials level off when low nitrogen contents limit further microbial degradation. A substantially longer period characterized by even lower decomposition rates can then be expected when carbon availability finally becomes the limiting factor to further decomposition.

CRA-2004 Position on Microbial Consumption and Production of Organic Ligands

Brush and Xiong (2003a) calculated the concentrations of acetate, citrate, EDTA, and oxalate in WIPP brines by assuming that all of these organic ligands in the waste will dissolve in 29,841 m³ of brine, the same quantity used by the DOE for the CCA. Brush and Xiong (2003a) did not decrease their concentrations to simulate microbial consumption, or increase them to simulate microbial production of these organic ligands. Therefore, their results were consistent with the assumption that there will not be any microbial consumption or production of these or other organic ligands, or the assumption that the quantities consumed and produced will be equal. This is consistent with the CCA, and is probably conservative in view of the information obtained since the CCA (see above). The corrected concentrations of organic ligands calculated by Brush and Xiong (2003b) were also calculated in the same way as the concentrations presented in the CCA.

The concentrations calculated by Brush and Xiong (2003a) are also consistent with the method specified by the EPA to calculate the MgO safety factor. The EPA has specified that the DOE assume that all of the organic carbon in CPR materials would be converted to carbon dioxide in the event of microbial consumption of all of these materials. Addition of microbially produced acetate and/or lactate to the acetate and lactate dissolved from the waste by brine would be inconsistent with the specification that all organic carbon be converted to carbon dioxide. To the extent that acetate and/or lactate are assumed to be produced by microbial activity, there would be more carbon present in the repository than that present originally in the CPR materials if it were also assumed in the PA calculations that all carbon present in the CPR materials is converted to carbon dioxide. This would violate the condition that the masses of chemical elements initially present in a chemical system be preserved unless lost by radioactive decay, or gained or lost by transport into or out of the system. The mass-balance constraint is universally accepted and is typically used in the geochemical speciation and solubility calculations implemented in codes such as the EQ3/6 geochemical software package and FMT.

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EPA Comment**C-23-12 Documentation for Chemical Benefit of MgO Emplacement**

The CRA introduces a statement about the methodology for MgO emplacement and a particular chemical benefit, “(3) minimizes the exposure of periclase, the main, reactive constituent of MgO, to atmospheric carbon dioxide (CO₂) and water prior to rupturing of the supersacks”. This information was not part of the original CCA and no reference or justification for the statement is provided in the CRA. DOE must provide summary information in the CRA and cite references, which explain and support the statement.

DOE Response

The DOE addressed this issue in its response to a similar EPA comment during their review of the CCA. The EPA asked, *“In Appendix BACK, the Department states that bags of cellulose or plastic will protect the MgO from premature exposure to the atmosphere without providing supporting evidence. The Department needs to provide evidence that CO₂ will not diffuse through or otherwise penetrate the bags during the operational phase and reduce the post-closure capability of the MgO.”* The DOE’s response is contained in EPA Docket A-93-02, II-I-10, and consists of an analysis that demonstrates the bags will protect the MgO during the operational phase from atmospheric water and CO₂.

The DOE provided a reference in the CRA-2004 to a requirement in an MgO specification document that is intended to minimize exposure of MgO to the atmosphere prior to closure. (U.S. DOE, Appendix BARRIERS, page 4, lines 33-36):

“WTS (2003) provides detailed specifications for the supersacks. In particular, WTS (2003) specifies that the supersacks ‘shall provide a barrier to atmospheric moisture and carbon dioxide (CO₂) ... equivalent to or better than that provided by a standard commercial cement bag’ and ‘must be able to retain [their] contents for a period of two years after emplacement without rupturing from [their] own weight.’”

In summary, the WTS (2003) specification that MgO be packaged in polypropylene supersacks “equivalent to or better than ... a standard commercial cement bag” ensures that the supersacks will effectively prevent atmospheric CO₂ and H₂O from reacting with periclase and lime prior to creep closure of the repository and concomitant rupture of the supersacks. This is because standard commercial cement bags are routinely used to prevent atmospheric CO₂ and H₂O from reacting with lime, which reacts with CO₂ and H₂O much more readily than periclase, prior to use of the cement in construction and other applications. Additionally, the analysis captured within the A-93-02 Docket provides justification that the bags will minimize reaction of the MgO with atmospheric water and CO₂.

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EPA Comment**C-23-13 Organic ligand complexation on (V) and (VI) oxidation state actinides**

DOE discusses the effects of organic ligand complexation on the (III) and (IV) actinides, given the new data on organic ligand complexation developed since the CCA (Choppin et al., 2001). However, DOE does not address the predicted effects of organic ligand complexation on the (V) and (VI) actinides, given these new data. DOE must provide this discussion.

DOE Response***Introduction***

The results of FMT speciation and solubility calculations (see below) demonstrate that acetate, citrate, EDTA, and oxalate increase An(V) solubility significantly. However, this increase has essentially no effect on the long-term performance of the WIPP because: (1) Np is the only actinide expected to speciate in the +V oxidation state (see above), (2) the probability that Np will speciate as Np(V) is 0.5, and (3) from the standpoint of its potential effects on long-term performance, Np is much less important than Pu, Am, U, or Th.

The DOE has not developed a thermodynamic speciation-and-solubility model for U(VI) in brines. Therefore, speciation and solubility calculations cannot be carried out to determine the effects of acetate, citrate, EDTA, and oxalate on the solubility of U(VI) in WIPP brines. However, an analysis by Wall and Wall (2004) showed that these organic ligands do not significantly impact the solubility of U(VI) under expected WIPP conditions.

Background

Acetate, citrate, oxalate, and EDTA are capable of forming soluble complexes with the actinides, and have been identified in the WIPP inventory. The predicted concentrations of organic ligands are presented in the Table SOTERM-4 of the Compliance Recertification Application (CRA) (DOE, 2004). The database describing the interaction of the organic ligands with the actinides was not complete at the time of the Compliance Certification Application (CCA) (DOE, 1996), but since 1996 both stability constants and Pitzer parameters have been determined, allowing inclusion of the organic ligands in the FMT speciation and solubility calculations.

U(IV) and Np(IV) are likely to be the most stable oxidation states of these two actinides under the mildly basic pH and chemically reducing conditions that will exist within the WIPP. However, in order to address potential issues surrounding uncertainties of the prevailing oxidation states of these two actinides, the WIPP PA models uranium as U(IV) in approximately half of the PA vectors, and as U(VI) in the other half. Likewise, Np is modeled as Np(IV) in half of the PA vectors, and as Np(V) in the other half. The solubility of U(VI) remains, as was the case for the CCA, based upon a literature survey carried out by Hobart and Moore (1996). Speciation and solubility calculations for Np(V) are carried out by FMT, the database of which now includes parameters for acetate, citrate, oxalate, and EDTA. Plutonium is not modeled either as Pu(V) or Pu(VI) in any of the PA calculations.

Effect of the organic ligands on An(V)

Pitzer parameters that describe the interactions of organic ligands and complexes with brine components, along with stability constants, have been entered into the FMT database for calculation of speciation and solubility of Np(V). The influence of organic ligands upon the speciation and solubility of the +III, +IV, and +VI actinides is mitigated by the susceptibility to hydrolysis of Pu(III), Am(III), Th(IV), U(IV), Np(IV) Pu(IV) and U(VI). However, Np(V) is much less influenced by hydrolysis, even at the mildly basic pH of the MgO buffered WIPP brines. As a result, Np(V) is free to participate in complex formation with organic and inorganic ligands. For that reason, Np(V) speciation may be expected to be more greatly influenced by the presence of organic ligands than the other oxidation states of the actinides. Results of the FMT speciation and solubility calculations in absence and presence of organic ligands for Np(V) are reproduced in Table 1.

Table 1. Comparison of An(V) Solubilities Calculated for the PAVT and the CRA-2004 PA. From Brush and Xiong (2003), Downes (2003a, 2003b).

Actinide Oxidation State, and Brine	Solubility, PAVT, All Vectors, No Organics (M)	Solubility, CRA PA, Nonmicrobial Vectors, No Organics (M)	Solubility, CRA PA, Nonmicrobial Vectors, Organics (M)	Solubility, CRA PA, Microbial Vectors, No Organics (M)	Solubility, CRA PA, Microbial Vectors, Organics (M)
An(V), GWB	Not calculated	2.30×10^{-7}	9.72×10^{-7}	2.36×10^{-7}	1.02×10^{-6}
An(V), ERDA-6	4.8×10^{-7}	1.07×10^{-6}	2.13×10^{-5}	5.38×10^{-7}	5.08×10^{-6}

Effect of the organic ligands on U(VI)

The only actinide predicted to exist in the hexavalent oxidation state in the WIPP is U(VI). As stated in Attachment SOTERM of the Appendix PA of the CRA, “The actinide(VI) speciation and solubility model for brines under basic conditions has not been developed sufficiently for use in FMT. The hydrolysis behavior of U(VI) is quite complicated and no satisfactory predictive models applicable to WIPP conditions are available.” As a result, no database was developed to include An(VI) in the FMT calculations. The An(VI) solubility in systems containing no acetate, citrate, oxalate, or EDTA was estimated for the CCA, based on literature data (Hobart and Moore, 1996). The solubility of U(VI) in the presence of these organic ligands was assumed to be equal to that in the absence of organic ligands. Wall and Wall (2004) presented calculations to show that organic ligands do not significantly impact the solubility of U(VI) under the conditions described by the FMT runs.

Table 2. Comparison of An(VI) Solubilities Estimated for the PAVT and the CRA-2004 PA. The original data expressed in molal units are from Hobart and Moore (1996).

Actinide Oxidation State, and Brine	Solubility, PAVT, All Vectors, No Organics (M)	Solubility, CRA PA, Nonmicrobial Vectors, No Organics (M)	Solubility, CRA PA, Nonmicrobial Vectors, Organics (M)	Solubility, CRA PA, Microbial Vectors, No Organics (M)	Solubility, CRA PA, Microbial Vectors, Organics (M)
An(VI), GWB	Not estimated	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}
An(VI), ERDA-6	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}

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EPA Comment**C-23-14 Identification of Relevant Non-WIPP Actinide Solubility Data**

DOE does not discuss whether additional, potentially relevant actinide solubility data developed outside the WIPP program has become available since the CCA. DOE must address whether additional solubility or other data have been developed that may be relevant to the solubility calculations.

DOE Response***Introduction***

The DOE used new (post-CCA), non-WIPP actinide-solubility data from several sources for the An(III) speciation and solubility model, some new, non-WIPP data for the An(IV) model, and no new, non-WIPP data for the An(V) model.

Detailed Response

The DOE provided references for the version of the FMT thermodynamic database used for the speciation and solubility calculations for the CRA-2004 PA calculations (U.S. DOE, 2004, Appendix PA, Attachment SOTERM, page 19, lines 35-37):

“The FMT database currently used to predict the solubilities of the +III, +IV, and +V actinides is documented in Giambalvo (2002a, 2002b, 2002c, 2002d, 2002e, 2003).”

These memoranda describe in detail the establishment of the FMT database used for the CRA-2004 PA. This version replaced the version developed by Novak (1997) for the 1997 PAVT. The current database features: (1) improved implementation of previously obtained laboratory data, (2) results of lab studies carried out at Florida State University and Pacific Northwest National Laboratory (PNNL) from the time of the PAVT through 1999, and (3) results of recent lab studies carried out for applications other than the WIPP, especially the German radioactive waste management program.

Giambalvo (2002a) used the following non-WIPP sources of data for the CRA-2004 An(III) speciation and solubility model: Fanghänel and Kim (1998), Fanghänel et al. (1994), Fanghänel et al. (1995), Fanghänel et al. (1999), Könnecke et al. (1997), Morss and Williams (1994), Paviet et al. (1996), Runde and Kim (1995), and Silva et al. (1995).

Giambalvo (2002c) used non-WIPP data from Ryan and Rai (1987) for the CRA-2004 An(IV) model (this work was not carried out for the WIPP Project).

Giambalvo (2002d) made only minor changes to the An(V) speciation and solubility model used for the 1997 PAVT, and did not include any additional non-WIPP data.

After the FMT calculations for the CRA-2004 PA, Xiong (2004a) modified the CRA-2004 database, and Xiong (2004b) released the current version of the FMT database. Xiong (2004a) corrected the molecular weight of oxalate in the version used for the CRA-2004 PA, and added

calcium (Ca) oxalate(solid) to this database. To add Ca oxalate(solid), Xiong (2004a) used the mean of three values of the normalized standard chemical potential (μ^0/RT) of whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). All three of these values were obtained from non-WIPP sources (Nancollas and Gardner, 1974; Tomažič and Nancollas, 1979; and Streit et al., 1998).

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EPA Comment**C-23-17 Metal/Organic Ligand Competition for Actinides and Solution Ionic Strength**

DOE presents calculations performed for the CCA to estimate the effects of other metals competing with actinides for organic ligands, which were carried out using parameters obtained at low ionic strengths. At the time of the CCA, parameters were not available for WIPP-relevant high-ionic-strength solutions. However, additional data have become available since the time of the CCA.

DOE must address whether the low-ionic-strength calculations discussed in this section are still valid in light of the high-ionic-strength data that have been developed for organic ligands.

DOE Response***Introduction***

The results of FMT speciation and solubility calculations carried out for the CRA-2004 PA demonstrate that acetate, citrate, EDTA, and oxalate have essentially no effect on An(IV) solubility. This conclusion is completely consistent with the CCA conclusions that nickel (Ni) will render “EDTA unavailable for complexation with the actinides,” which means that “complexation of actinides by organic ligands inconsequential” (U.S. DOE, 1996, Appendix SOTERM, SOTERM-38).

The results of the FMT calculations carried out for the CRA-2004 PA also show that acetate, citrate, EDTA, and oxalate have a modest effect on An(III) solubility, a conclusion inconsistent with the results of the low-ionic-strength hand and HYDRAQL calculations conducted for the CCA. However, because dissolved brine releases (DBR) are at least about one order of magnitude lower than the mean Complementary, Cumulative Distribution Function (CCDF) and are typically much less than this, the overall effects of organics on the long-term performance of the repository are negligible.

Furthermore, the FMT calculations performed for the CRA-2004 PA show that acetate, citrate, EDTA, and oxalate increase An(V) solubility significantly. However, this increase has essentially no effect on the long-term performance of the WIPP because: (1) Np is the only actinide expected to speciate in the +V oxidation state, (2) the probability that Np will speciate as Np(V) is 0.5, and (3) from the standpoint of its potential effects on long-term performance, Np is much less important than Pu, Am, U, or Th.

Therefore, based on the effects of organics on the solubilities of the +III, +IV, and +V actinides, the overall effects of organics on the long-term performance of the repository are still negligible.

Revision of Attachment SOTERM for the CRA-2004 PA

The DOE stated in the CCA that, based on low-ionic-strength calculations with the HYDRAQL code, nickel (Ni) will render “EDTA unavailable for complexation with the actinides,” and – thus - that “complexation of actinides by organic ligands [will be] inconsequential” (U.S. DOE, 1996, Appendix SOTERM, page SOTERM-38). The DOE also stated that, based on low-ionic-

strength hand calculations, “complexation of the organic ligands with actinides will be negligible” (U.S.DOE, Appendix SOTERM, page SOTERM-41).

Similar statements were made in U.S. DOE (1996, Appendix WCA, page WCA-33, line 17, through page WCA-34, line 32), and in U.S. DOE (1996, Appendix WCL, page WCL-6, line 38, through page WCL-7, line 9).

The DOE removed these statements and the accompanying table from Attachment SOTERM of the CRA-2004 (U.S. DOE, 2004, Appendix PA, Attachment SOTERM, page 42, line 27, through page 43, line 26; and Table SOTERM-7) to indicate that it had replaced these hand and HYDRAQL calculations with FMT speciation and solubility calculations that included the effects of dissolved acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate on the solubilities of the +III, +IV, and +V actinides (An(III), An(IV), and An(V)) in the WIPP brines ERDA-6 and GWB. ERDA-6 is a synthetic brine representative of fluids in brine reservoirs in the Castile Formation (Fm.) (Popielak, et al., 1983). GWB is synthetic brine typical of intergranular (grain-boundary) fluids from the Salado Formation at or near the stratigraphic horizon of the repository (Snider 2003). The concentrations of the organic ligands used in the FMT calculations for the CRA-2004 PA were: acetate: 5.05×10^{-3} M; citrate: 3.83×10^{-4} M; EDTA: 3.87×10^{-6} M; and oxalate: 2.16×10^{-2} M. Brush and Xiong (2003a) calculated these concentrations based on estimates by Crawford (2003) of the total masses of these organics to be emplaced in the WIPP. However, after Crawford and Leigh (2003) corrected these estimates of the masses of these organics, Brush and Xiong (2003c) obtained the following corrected concentrations: acetate: 3.56×10^{-3} M; citrate: 2.71×10^{-4} M; EDTA: 2.73×10^{-6} M; and oxalate: 1.53×10^{-2} M. Because the corrected concentrations are about 70% of those used in the FMT calculations for the CRA PA, the results described below overestimate to some extent the effects of these organics on the solubilities of the +III, +IV, and +V actinides in WIPP brines.

Table 1 shows the effects of acetate, citrate, EDTA, and oxalate on An(III), An(IV), and An(V) solubilities in the WIPP brines GWB and ERDA-6 (Brush and Xiong, 2003b; Downes, 2003a; 2003b).

The results in Table 1 demonstrate that acetate, citrate, EDTA, and oxalate have essentially no effect on An(IV) solubility. This conclusion is completely consistent with the CCA conclusions that “The [low-ionic-strength HYDRAQL] calculations showed that under these conditions 99.8 percent of the EDTA was complexed by Ni, thus effectively rendering the EDTA unavailable for complexation with the actinides and rendering complexation of actinides by organic ligands inconsequential” (U.S. DOE, 1996, Appendix SOTERM, SOTERM-38, lines 31-34); and “The results [of low-ionic-strength hand calculations] indicate more than 97 percent of the total EDTA is complexed by the transition metals. Thus the excess of nonradioactive metals present in the repository will overwhelm the complexation sites of the organic ligands and complexation of the organic ligands with actinides will be negligible” (U.S. DOE, 1996, Appendix SOTERM, SOTERM-41, lines 5-8). The conclusion that organics do not affect An(IV) solubility is important because: (1) the order of importance of the radioelements in TRU waste from the standpoint of their potential effects on the long-term performance of the WIPP is $\text{Pu} \cong \text{Am} \gg \text{U} > \text{Th} > \text{Np}$; (2) the oxidation-state distributions of these radioelements implemented in PA consisted of a probability of 0.5 that Pu, Am, U, Th, and Np will speciate entirely as Pu(III), Am(III), U(IV), Th(IV), and Np(IV), respectively; and a probability of 0.5 that they will speciate

entirely as Pu(IV), Am(III), U(VI), Th(IV), and Np(V); and (3) therefore, the +IV oxidation state is one of the two most important oxidation states expected in the WIPP. The results in Table 1 also show that acetate, citrate, EDTA, and oxalate have a modest effect on An(III) solubility, a conclusion inconsistent with the results of the low-ionic-strength hand and HYDRAQL calculations carried out for the CCA. The conclusion that organics affect An(III) solubility to some extent is significant because the +III oxidation state is the other important oxidation state expected in the WIPP (see above). However, it is noteworthy that comparison of the mean CCDF and the CCDF for DBR shows that DBR are at least one-half order of magnitude lower than the mean CCDF, and are typically much less than this (U.S. DOE, 2004, Chapter 6, Figure 6-39). Therefore, based on the effects of organics on the solubilities of the +III and +IV actinides (the two most important oxidation states expected in the WIPP), the overall effects of organics on the long-term performance of the repository are negligible.

Table 1. Comparison of Actinide Solubilities Calculated for the PAVT and the CRA-2004 PA. From Brush and Xiong (2003b), Downes (2003a, 2003b).

Actinide Oxidation State, and Brine	Solubility, PAVT, All Vectors, No Organics (M)	Solubility, CRA PA, Nonmicrobial Vectors, No Organics (M)	Solubility, CRA PA, Nonmicrobial Vectors, Organics (M)	Solubility, CRA PA, Microbial Vectors, No Organics (M)	Solubility, CRA PA, Microbial Vectors, Organics (M)
An(III), GWB	Not calculated	2.27×10^{-7}	3.07×10^{-7}	2.26×10^{-7}	3.07×10^{-7}
An(III), ERDA-6	1.3×10^{-8}	9.14×10^{-8}	1.77×10^{-7}	8.67×10^{-8}	1.69×10^{-7}
An(IV), GWB	Not calculated	1.24×10^{-8}	1.24×10^{-8}	1.19×10^{-8}	1.19×10^{-8}
An(IV), ERDA-6	4.1×10^{-8}	5.80×10^{-9}	5.84×10^{-9}	2.50×10^{-8}	2.47×10^{-8}
An(V), GWB	Not calculated	2.30×10^{-7}	9.72×10^{-7}	2.36×10^{-7}	1.02×10^{-6}
An(V), ERDA-6	4.8×10^{-7}	1.07×10^{-6}	2.13×10^{-5}	5.38×10^{-7}	5.08×10^{-6}

Finally, Table 1 shows that acetate, citrate, EDTA, and oxalate increase An(V) solubility significantly. However, this increase has essentially no effect on the long-term performance of the WIPP because: (1) Np is the only actinide expected to speciate in the +V oxidation state (see above), (2) the probability that Np will speciate as Np(V) is 0.5, and (3) from the standpoint of its potential effects on long-term performance, Np is much less important than Pu, Am, U, or Th. Therefore, based on the effects of organics on the solubilities of the +III, +IV, and +V actinides, the overall effects of organics on the long-term performance of the repository are still negligible.

U is the only actinide expected to speciate in the +VI oxidation state, and the probability that U will speciate as U(VI) is 0.5. A thermodynamic speciation-and-solubility model for U(VI) in brines was not developed. Because a model is not available for U(VI), speciation and solubility calculations were not carried out to determine the effects of acetate, citrate, EDTA, and oxalate on the solubility of U(VI) in WIPP brines. However, an analysis was conducted to estimate the effects of these organics on the solubility of U(VI) (Wall and Wall, 2004).

The DOE believes that FMT predictions of the effects of acetate, citrate, EDTA, and oxalate on the solubilities of An(III), An(IV), and An(V) in WIPP brines are much more defensible than the hand calculations, or even the HYDRAQL calculations, carried out for the CCA because: (1) both of these approaches used data for low-ionic-strength solutions, and (2) the hand calculations did not include all of the reactions that could affect actinide solubilities. (A computer code such as FMT is required to simultaneously consider all possible reactions that could occur in a multicomponent geochemical system such that expected in WIPP disposal rooms.)

Revision of Appendix TRU-WASTE for the CRA-2004 PA

The DOE removed statements about the effect of complexing agents on actinide solubility that were present in CCA Appendix SOTERM when it was prepared for CRA-2004 to indicate that the low-ionic strength hand and HYDRAQL calculations had been redone for CRA-2004 with FMT using high-ionic-strength data. The FMT calculations indicate that complexing agents have no effect on the solubility of +IV actinides, a modest effect on +III actinides, and increase the solubility of +V actinides. However, the DOE did not revise the corresponding text in Appendix TRU-WASTE. Therefore, Appendix TRU-WASTE of CRA-2004 contained information about the effect of complexing agents on actinide solubility that was consistent with the CCA but was not updated to reflect DOE's current understanding as stated in Attachment SOTERM of CRA-2004. Appendix TRU-WASTE will be revised so that it is consistent with DOE's current position about the effect of complexing agents on actinide solubility (as stated above).

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EPA Comment**C-24-5 Inclusion of information on complexing agents, nitrates and phosphates**

The CRA states that a summary of complexing agents, nitrates, phosphates and cements is included in Appendix DATA Attachment F. However, Appendix F does not include summary information on these components, just the detailed data sheets. The detailed waste stream descriptions in Annexes I, J and K of Attachment F contain volume information for cements. However, it does not appear that complexing agents, nitrates or phosphates were specifically included in these profiles.

The specified summary information as well as the waste stream specific quantities for complexing agents, nitrates, and phosphates must be included in the CRA; DOE needs to provide this summary and waste stream detail information, including justification as to why the occurrence of complexing agents, etc., was limited to solidified waste forms.

DOE Response

The waste stream specific information on complexing agents, nitrates, and phosphates is presented in Tables 1 and 2 below. This information was obtained from calculations performed on data from the *Transuranic Waste Baseline Inventory Report (TWBIR) Revision 3* (DOE 1996) and updated Inventory data that was obtained for CRA-2004 (Crawford and Leigh 2003 and Crawford 2004) that describe the complexing agent composition of waste streams at Rocky Flats Environmental Technology Site (RFETS), Idaho National Engineering and Environmental Laboratory (INEEL), Los Alamos National Laboratory (LANL) and Hanford Office of River Protection (Hanford-RP). One additional analysis was also performed in order to determine the oxyanion content of waste streams at INEEL, LANL, Lawrence Livermore National Laboratory (LLNL), RFETS, and Hanford-RP (Leigh and Sparks-Roybal 2003). The information reported does not indicate that the waste streams are only solidified waste forms. Various waste forms are reported as provided in the following summary information.

There are a total of eighteen waste streams that contain complexing agents as shown in Table 1. Thirteen of the waste streams identified are homogeneous solids and five of the LANL waste streams are combustible waste streams; therefore, the complexing agents are not limited to solidified waste forms. Waste stream RF-MT0541 consists of liquid residues from laboratory operations. The remaining seven waste streams were determined to result from saltcrete at RFETS and are described in detail in Crawford (2004).

Table 1 - Complexing Agents in TRU Waste by Waste Stream

Waste Stream Identifier	Acetic Acid (kg)	Sodium Acetate (kg)	Citric Acid (kg)	Sodium Citrate (kg)	Oxalic Acid (kg)	Sodium Oxalate (kg)	EDTA (kg)
IN-W218.909	1.27×10^2	1.07×10^3	8.64×10^1	3.84×10^2	8.64×10^1	0.00	2.21×10^1
RF-MT0007	4.87×10^{-2}	4.09×10^{-1}	3.32×10^{-2}	1.47×10^{-1}	3.32×10^{-2}	0.00	8.48×10^{-3}

Waste Stream Identifier	Acetic Acid (kg)	Sodium Acetate (kg)	Citric Acid (kg)	Sodium Citrate (kg)	Oxalic Acid (kg)	Sodium Oxalate (kg)	EDTA (kg)
RF-MT0541	0.00	0.00	0.00	0.00	0.00	0.00	2.6×10^0
RF-MT0803	1.40×10^{-1}	1.18×10^0	9.54×10^{-2}	4.24×10^{-1}	9.54×10^{-2}	0.00	2.44×10^{-2}
RF-MT0807	5.12×10^0	4.31×10^1	3.49×10^0	1.55×10^1	3.49×10^0	0.00	8.92×10^{-1}
RP-W013	0.00	0.00	0.00	0.00	0.00	2.60×10^4	0.00
RP-W016	0.00	7.40×10^3	0.00	0.00	0.00	6.49×10^3	0.00
RP-W754	0.00	0.00	0.00	0.00	0.00	1.45×10^3	0.00
LA-TA-50-17	3.31×10^{-1}	0.00	3.65×10^1	0.00	4.54×10^2	0.00	0.00
LA-TA-50-10	1.53×10^{-3}	0.00	1.69×10^{-1}	0.00	2.10×10^0	0.00	0.00
LA-TA-50-19	1.81×10^0	0.00	1.99×10^2	0.00	2.48×10^3	0.00	0.00
LA-TA-55-38	1.30×10^0	0.00	1.43×10^2	0.00	1.78×10^3	0.00	0.00
LA-TA-55-41	6.69×10^{-2}	0.00	7.36×10^0	0.00	9.17×10^1	0.00	0.00
LA-TA-55-19	4.97×10^0	0.00	5.46×10^2	0.00	6.81×10^3	0.00	0.00
LA-TA-55-20	9.64×10^{-1}	0.00	1.06×10^2	0.00	1.32×10^3	0.00	0.00
LA-TA-55-43	9.94×10^{-2}	0.00	1.09×10^1	0.00	1.36×10^2	0.00	0.00
LA-TA-55-44	3.53×10^{-1}	0.00	3.89×10^1	0.00	4.84×10^2	0.00	0.00
LA-TA-55-62	1.13×10^{-1}	0.00	1.24×10^1	0.00	1.54×10^2	0.00	0.00

The thirty-eight waste streams containing oxyanions are shown in Table 2. These waste streams include four debris waste streams, and two salt waste streams. The remaining waste streams are homogeneous solids waste streams. There are seven solidified organic waste streams and the remaining twenty-five waste streams are solidified inorganic waste streams.

Complexing agents, nitrate, sulfate and phosphate salts were used for various stages of Pu purification including separations, stabilization, sequestration and extraction and therefore are found in a number of the solidified waste streams in the inventory. Liquid-liquid extractions involved both organic and aqueous phases. When process clean-outs occurred many of these compounds were placed in tanks and settled as sludges with metal oxides that were present in the process or were evaporated and are now included in evaporator bottoms or salt cakes. Some process salts are identified in pure salt waste streams and other salts may be included in debris waste along with various sample residues.

Table 2 - TRU Waste Streams Containing Oxyanions for Disposal at WIPP

Waste Stream Identifier	Nitrate (kg)	Sulfate (kg)	Phosphate (kg)
IN-W164.153	0.00×10^0	5.41×10^2	0.00×10^0
IN-W216.98	5.11×10^5	7.02×10^3	0.00×10^0
IN-W218.909	8.37×10^4	2.09×10^2	0.00×10^0
IN-W220.114	3.80×10^4	5.22×10^2	0.00×10^0
IN-W228.101	1.47×10^5	2.03×10^3	0.00×10^0
IN-W315.601	1.82×10^3	0.00×10^0	0.00×10^0
LA-TA-03-28	5.68×10^2	9.04×10^1	0.00×10^0
LA-TA-03-30	7.08×10^1	6.59×10^1	0.00×10^0
LA-TA-21-13	1.58×10^3	2.51×10^2	0.00×10^0
LA-TA-21-15	3.35×10^2	6.48×10^1	0.00×10^0
LA-TA-21-16	3.75×10^3	3.49×10^3	0.00×10^0
LA-TA-21-43	1.26×10^5	2.00×10^4	0.00×10^0
LA-TA-48-01	2.32×10^0	4.49×10^{-1}	0.00×10^0
LA-TA-50-15	1.76×10^3	3.41×10^2	0.00×10^0
LA-TA-50-17	1.56×10^4	2.49×10^3	0.00×10^0
LA-TA-50-18	7.64×10^3	1.22×10^3	0.00×10^0
LATA-50-19	5.80×10^4	5.40×10^4	0.00×10^0
LA-TA-55-30	1.65×10^4	1.52×10^4	0.00×10^0
LA-TA-55-32	3.46×10^2	3.18×10^2	0.00×10^0
LA-TA-55-33	6.48×10^2	1.25×10^2	0.00×10^0
LA-TA-55-34	3.11×10^5	0.00×10^0	0.00×10^0

Waste Stream Identifier	Nitrate (kg)	Sulfate (kg)	Phosphate (kg)
LA-TA-55-38	0.00 x 10 ⁰	2.09 x 10 ⁵	0.00 x 10 ⁰
LA-TA-55-41	4.21 x 10 ³	3.92 x 10 ³	0.00 x 10 ⁰
LA-TA-55-44	1.22 x 10 ³	1.14 x 10 ³	0.00 x 10 ⁰
LA-TA-55-49	1.23 x 10 ³	1.14 x 10 ³	0.00 x 10 ⁰
LA-TA-55-53	5.93 x 10 ³	5.52 x 10 ³	0.00 x 10 ⁰
LL-W019	0.00 x 10 ⁰	1.22 x 10 ³	0.00 x 10 ⁰
RF-MT-0001	2.74 x 10 ²	3.80 x 10 ⁰	0.00 x 10 ⁰
RF-MT0007	0.00 x 10 ⁰	5.78 x 10 ⁻²	0.00 x 10 ⁰
RF-MT0541	8.51 x 10 ¹	8.51 x 10 ¹	8.51 x 10 ¹
RF-MT0800	3.22 x 10 ³	4.43 x 10 ¹	0.00 x 10 ⁰
RF-MT0801	0.00 x 10 ⁰	5.54 x 10 ⁴	0.00 x 10 ⁰
RF-MT0803	1.51 x 10 ²	2.07 x 10 ⁰	0.00 x 10 ⁰
RF-MT0807	5.55 x 10 ³	7.63 x 10 ¹	0.00 x 10 ⁰
RP-W013	4.40 x 10 ⁵	1.43 x 10 ⁴	1.80 x 10 ⁴
RP-W016	5.05 x 10 ⁵	1.35 x 10 ⁴	1.29 x 10 ⁴
RP-W754	7.31 x 10 ⁴	7.47 x 10 ²	1.12 x 10 ⁴
RP-W755	1.22 x 10 ⁵	6.86 x 10 ³	6.33 x 10 ⁴

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EPA Comment**C-24-7 Impact of waste loading within TDOP containers**

The CRA did not include any discussion of waste loading within TDOP containers and what impact that may have on the PA. DOE is currently loading TDOPs with a combination of drums that when averaged meets the required composition for disposal of TRU waste at the WIPP. The TDOPs could contain combinations of different waste classifications (low-level, TRU, dunnage) and the impact of the variability of radionuclide concentrations and waste materials within the TDOP is not addressed in the CRA. DOE must address the potential impact of waste loading management within TDOPs on the PA. Although this activity was not fully implemented until after the Sept 2002 cut-off date, it was clearly being planned for use prior to this date and so should be recognized as an activity in the CRA.

DOE Response

Appendix E of the Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant (DOE 2004) dictates the manner in which the DOE implements payload management. Appendix E requires that ten-drum overpacks (TDOPs) be loaded with drums that originated from the same TRU waste stream in order to be compliant. The comment incorrectly states that a TDOP may contain both low-level and TRU waste, only waste managed as TRU waste may be placed into the payload container. Load management of drums from a TRU waste stream ensures that the final payload container (in this case the TDOP) meets the WIPP WAC criteria of greater than 100 nCi/g.

For the purposes of the CRA performance assessment (PA), radionuclide concentrations and waste material parameters are assumed to be homogeneous within each waste stream and variations in concentration are only considered between waste streams. In addition, the radionuclide concentration and waste material parameter values used by PA are expressed in units of radioactivity (or EPA units) and mass per “emplaced volume”. Emplaced volume is the volume that the waste stream will occupy in the repository and is based on payload container volume. Each generator site supplies the project with the concentration and volume of each waste stream based on the combination of containers they have shipped or plan to ship to the WIPP. The sites have provided estimates of the volume and numbers of containers in their respective waste streams and when planning to use TDOPs, provided estimates of the number of TDOPs they are expecting to ship to WIPP for the inventory update (Wells 2003).

In the case of waste emplaced inside a TDOP, the final volume used for the concentration calculation is that of the TDOP container, which is greater than the total volume of the ten 55-gallon drums inside. The emplacement of waste inside TDOP containers will tend to dilute the radionuclide concentration in the waste stream relative to the concentration that would be calculated if the waste were to be emplaced as seven-packs of 55-gallon drums.

For the calculation of cuttings and cavings, it is assumed that if an intrusion encounters waste, releases are derived from a waste stack consisting of three randomly sampled waste streams. None of the release mechanisms considered by the PA accounts for the possibility that one or more of the drums may be empty or that radionuclide concentrations within a specific waste stream may vary from drum to drum. Even if concentration variability were included within

waste streams the effect of this variability on the mean CCDF curve would be minor because the mean CCDF is based on approximately six million separate intrusions [(100 vectors) x (10,000 futures) x (6 intrusions per future on average)]. Given the large number of intrusions, variability within waste streams will tend to be obscured. Furthermore, there is a bound to the amount of variability that is possible for waste being shipped to WIPP. First, waste must meet acceptance criteria that include a requirement that the radioactivity must exceed 100 nanocuries per gram (LWA 1992). Second, shipping regulations provide an upper bound on the Fissile Gram Equivalents (FGEs) and the wattage that can shipped for each container (NMED 2002). This controls the radionuclide concentration of each container and shipment that is sent to WIPP. For these reasons, waste-loading management within TDOP containers will have no significant impact on WIPP performance.

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EPA Comment**C-53-1 Reference to support NUTS code tracer exercise**

There is no reference provided to support the NUTS code tracer exercise which is used to scale the anticipated releases of ²²⁶Ra and ²²⁸Ra since they are not calculated by NUTS. The scaling factor has changed from 2.5E-7 kg/m³ to 1.025E-7 kg/m³, but a new tracer exercise is not referenced to support the change in the scaling factor. It is not clear if the reference associated with the maximum concentration of Ra in the accessible environment (Wagner, 2003) also discusses the scaling factor. In addition, the reference for Table 8-6 is incorrectly cited: the author is Fox, not Leigh, and the reference only discusses activities, not mass loadings—these have been calculated from activities—but there is no reference or documentation cited.

DOE Response

A new tracer exercise was run to derive a new scaling factor for the 2004 CRA. In Wagner 2003, Garner 2003 is referenced as the source for the scaling factor derived from a NUTS tracer exercise (attached).

The mass loading in CRA Chapter 8, Table 8-6 was determined by dividing the Ra inventories by the isotopes specific activity. The specific activity for ²²⁶Ra is 9.89 x 10² curies per kilogram and for ²²⁸Ra is 2.72 x 10⁵ curies per kilogram (see CCA Appendix GENII, Appendix E to PREGENII Users Manual).

EPA has correctly determined that the listed author for ERMS 530992 reference in Table 8-6 was incorrect. Fox is the correct author for Revision 1 of the document, Leigh (ERMS 528748) was the original author of the document. ERMS 530992 was supplied with the CRA.

References

Garner, J. W. 2003. "CRA Marker Bed Concentrations," Memo to Record, ERMS 532402, Sandia National Laboratories, Carlsbad NM, October 16, 2003.

Revised Response**EPA Comment****C-23-1 Ch 6, pg 6-3, section 6.0.2**

The previous baseline for DOE's compliance (from the initial certification decision completed in 1998) is the Performance Assessment Verification Test (PAVT) set of CCDFs and releases at the regulatory limits. To provide context for understanding the changes from the previous baseline, DOE must provide a comparison of the CCA PAVT results to the results of the CRA PA in a tabular form with columns/rows for 0.1 and 0.001 probabilities. For the table, use as an example the table submitted as part of the review of super compacted waste (Comparison of AMW and PAVT Results with CRA Results by C.W. Hansen, March 19, 2004. ERMS 534241 and EPA Docket A-98-49, Item II-B2-34).

DOE Response

This document supersedes "Response to EPA C-23-1, Rev. 0" (Dunagan 2004).

This revision of the results reflects the changes introduced by correcting an error in the CCDFGF code and three errors in the inputs to PRECCDFGF. First, there was an omission in the code for CCDFGF Version 5.00 of a correction of spillings releases for the volume fraction of contact handled waste in the repository. Second, an error in the input control files for SUMMARIZE used for the CRA incorrectly listed the variable representing spillings area where the variable representing spillings volume was required. These problems are documented in Kirchner and Vugrin (2004). Third, the incorrect LHS transfer files were used as input to PRECCDFGF for replicates 2 and 3. Finally, an error in the input control files to SUMMARIZE resulted in reading the ²³⁴U colloid mobilization fraction as representing ²³⁰Th and vice versa (Vugrin and Kirchner, 2004). These errors had relatively little impact on the results and no significant impact on the conclusions of the CRA.

The following is from Vugrin (2004a). Vugrin (2004b) documents the run control that created the files for this analysis.

As requested by EPA in a letter on May 20, 2004 (C-23-1, EPA 2004), Table 1 compares total releases at probabilities of 0.1 and 0.001 for the CRA PA and CCA PAVT.

Table 1. CRA PA and CCA PAVT Releases at Probabilities of 0.1 and 0.001, All Replicates Averaged

Probabilities	Analysis	Mean Total Release	90th Quantile Total Releases
0.1	CRA PA	0.095651	0.157114
	CCA PAVT	0.123713	0.191564
0.001	CRA PA	0.507010	0.858232
	CCA PAVT	0.381863	0.390739

The CRA PA total releases at probabilities of 0.1 are smaller than the CCA PAVT total releases (Figure 1) at the same probabilities due to a decreased contribution of spall at this probability. The typical spall release in the CRA PA at a probability of 0.1 is smaller than the typical spall release in the PAVT CCA at the same probability (Figure 2).

The CRA PA total releases at probabilities of 0.001 are larger than the CCA PAVT total releases (Figure 1) due to the presence of several small volume, high activity waste streams in the new inventory that cause an increase in the cuttings and cavings releases at very low probabilities (Figure 3). Additionally, the typical spill release in the CRA PA at a probability of 0.001 is larger than the typical spill release in the PAVT CCA at the same probability (Figure 2).

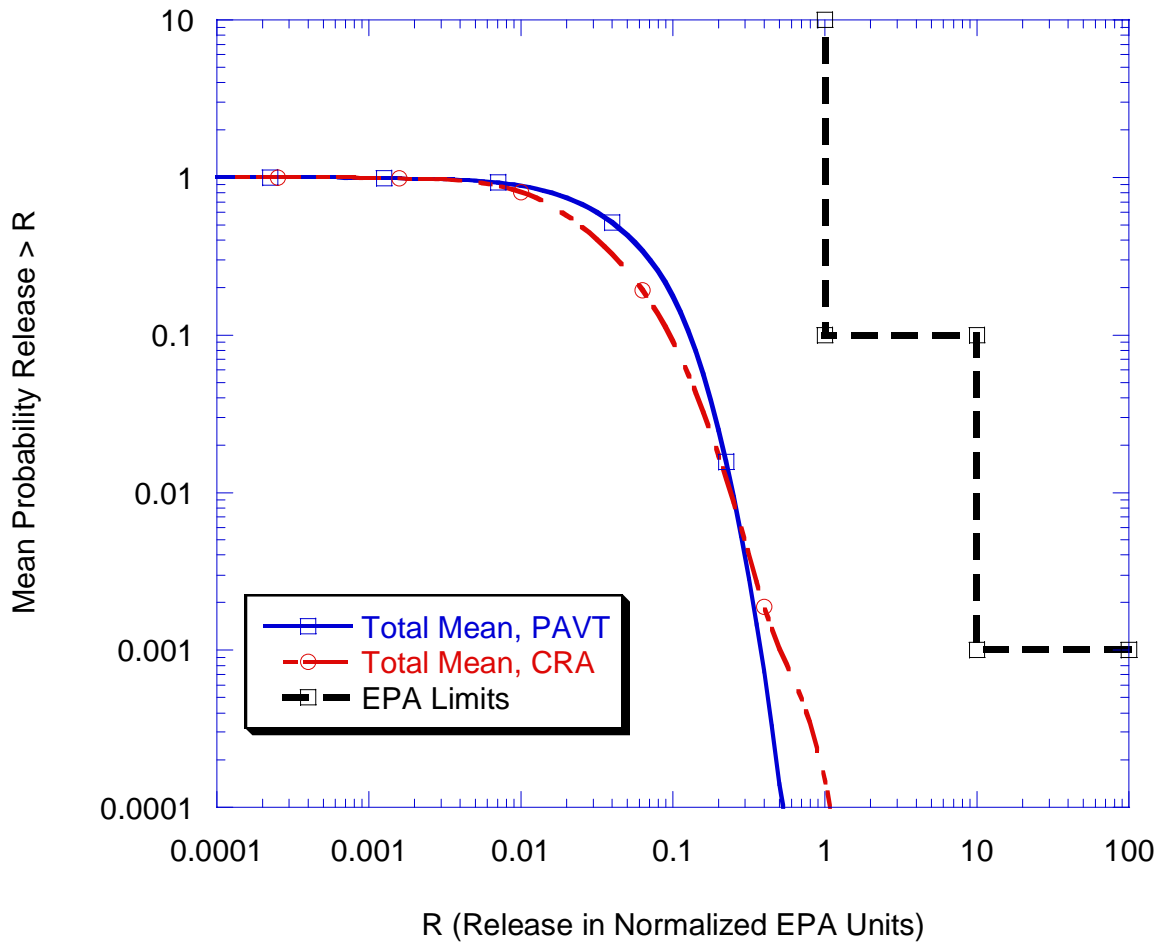


Figure 1. CRA PA and CCA PAVT Total Release Means, All Replicates Averaged

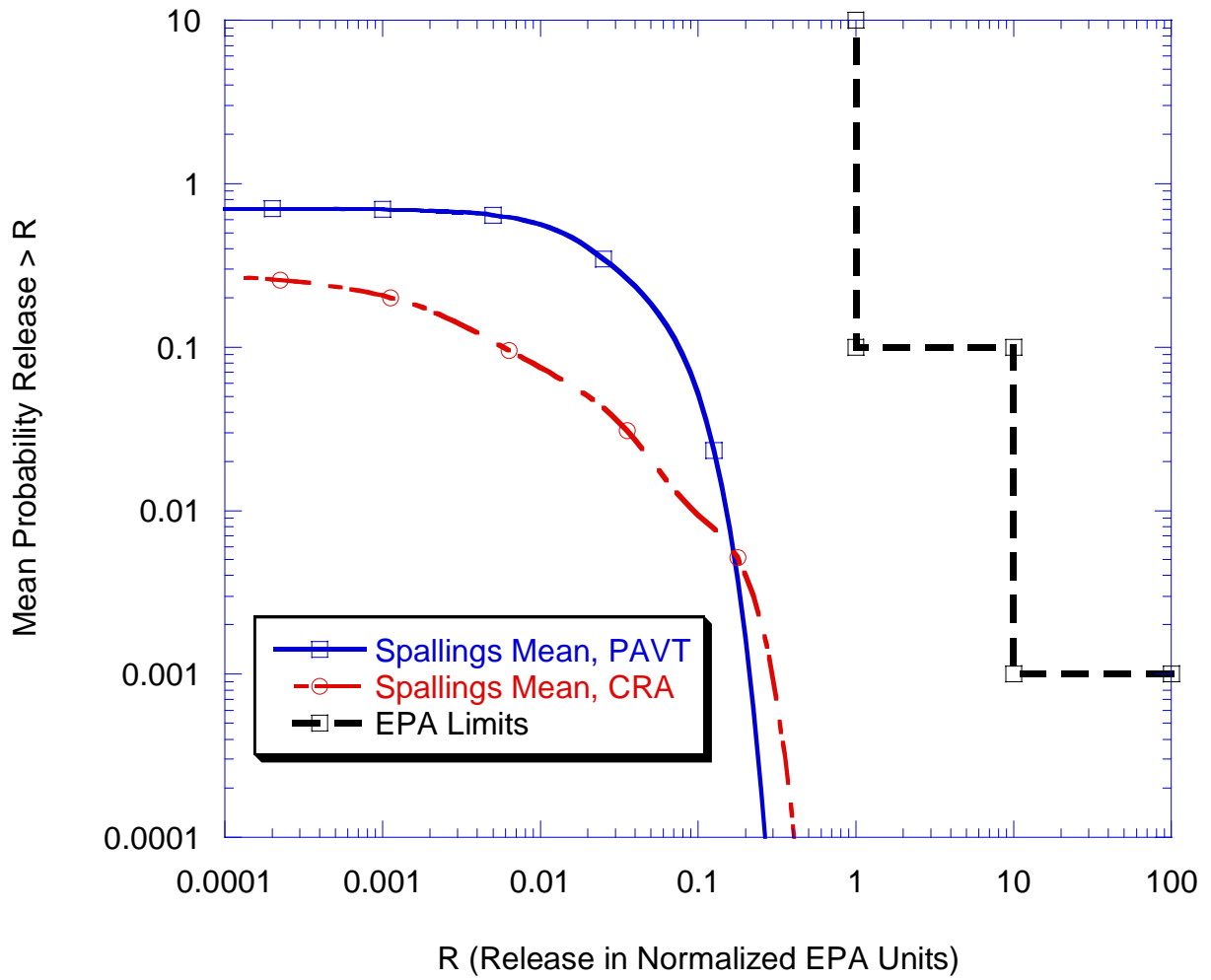


Figure 2. CRA PA and CCA PAVT Spallings Release Means, All Replicates Averaged

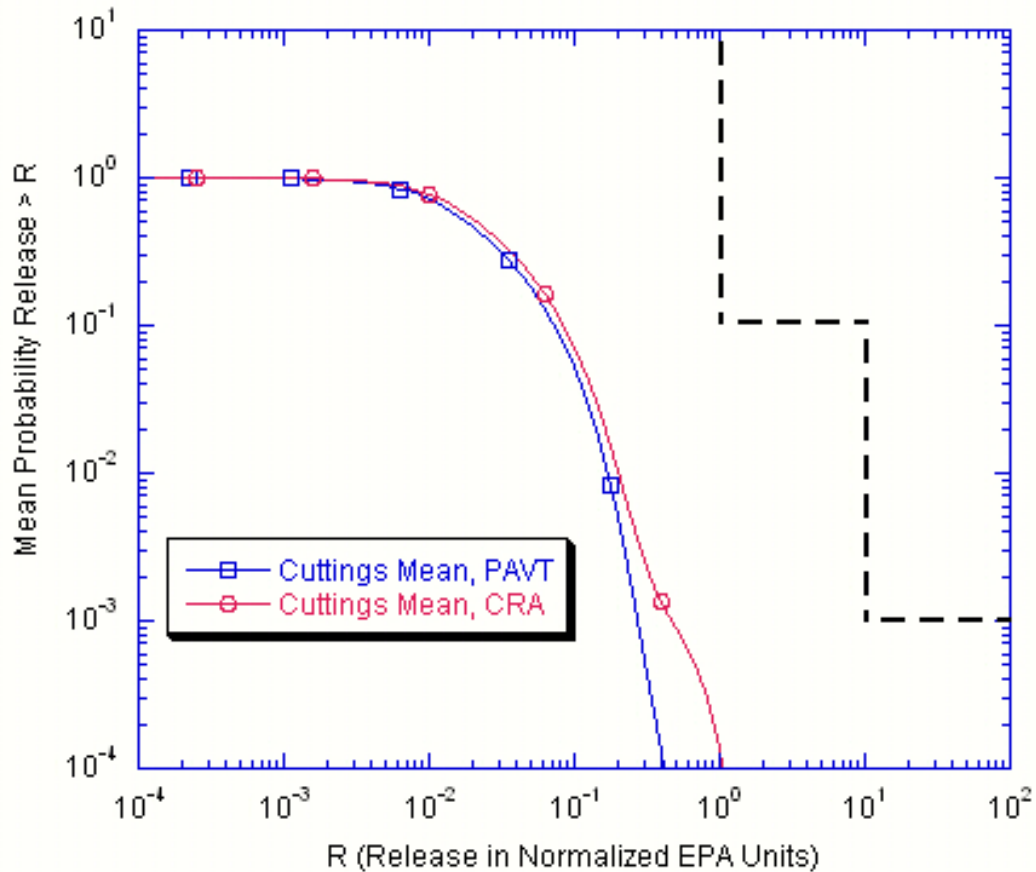


Figure 3. CRA PA and CCA PAVT Cuttings and Cavings Release Means, All Replicates Averaged

References

Dunagan, S. 2004. Response to EPA C-23-1, Rev. 0. Sandia National Laboratories, Carlsbad, NM. ERMS #535939.

Kirchner, T. B. and E. D. Vugrin. 2004. "Errors Affecting Spallings Releases." Memorandum to David Kessel. November 10, 2004. Sandia National Laboratories. Carlsbad, NM. ERMS# 537852.

U. S. Environmental Protection Agency (EPA). 2004. Letter from Elizabeth Cotsworth to Dr. R. Paul Detwiler. May 20, 2004. ERMS# 535554.

Vugrin, E. D. 2004a. "Comparison of CRA PA and CCA PAVT for probabilities of 0.1 and 0.001 in response to C-23-1, Revision 2." Memorandum to David Kessel. December 3, 2004. Sandia National Laboratories. Carlsbad, NM. ERMS# 537990.

Vugrin, E. D. 2004b. "Run Control for Correction of Releases for the CRA." Memorandum to David Kessel. December 3, 2004. Sandia National Laboratories. Carlsbad, NM. ERMS# 537987.

Vugrin, E. D. and T. Kirchner. 2004. "Incorrect LHS and SUMMARIZE Input Files for PRECCDFGF." Memorandum to David Kessel. December 1, 2004. Sandia National Laboratories. Carlsbad, NM. ERMS# 537965.

**Revised Response
EPA Comment C-23-10****Ch 6, pg 6-166, lines 23 to 24**

The CRA states that “spallings are assumed to be derived from a sufficiently large volume of waste that container-scale variability can be neglected.” While we accepted this assumption in the original certification decision, since then DOE has used a number of different container configurations—such as ten drum overpacks and supercompacted waste—with greater frequency than estimated earlier. In addition, the new DRSPALL code generally predicts much lower release volumes. For these reasons, neglecting container-scale variability may not be a valid assumption.

DOE must fully justify the existing waste spall model given the changes in waste container since the CCA and the new spallings model results or must rerun the CRA PA with assumptions that better reflect the container variation.

DOE Response

This document supersedes “Response to EPA C-23-10, Rev. 0” (Vugrin 2004b).

This revision of DOE’s response to Comment C-23-10 reflects the changes introduced by correcting an error in the spallings releases. An error in the input control files for SUMMARIZE used for the CRA incorrectly listed the variable representing spallings area where the variable representing spallings volume was required. This issue is documented in Kirchner and Vugrin (2004).

EPA’s comment contains two related, but separate PA issues; waste variability and container variability. The statement quoted from the CRA primarily relates to waste variability.

The DOE models spallings using the volume-averaged activity of CH-TRU waste because the processes involved operate on a physical scale larger than the local, drum-specific scale of the cuttings and cavings releases. Cuttings and cavings releases are calculated assuming random emplacement of drums of CH-TRU waste, with releases coming only from a single stack of three drums. The distance from which spalled material may move toward the borehole is uncertain. If spallings releases were assumed to include at a minimum, material only from the drums immediately surrounding penetrated stack, the activity of the released material might appropriately be assumed to be drawn from a random combination of up to 21 different CH-TRU waste streams (depending on the emplacement geometry), plus backfill. If the radius of the effect of spall is larger, the number of CH-TRU waste streams potentially involved becomes larger. The appropriateness of this assumption is discussed in CRA Appendix PA, Attachment MASS where it states:

“...Because spallings may release a relatively large volume of material (exceeding 4 m³), spallings releases for intrusions into CH-TRU waste are computed by multiplying the volume of spalled material with the average concentration of radioactivity in the waste at the time of the intrusion. A separate PA (Hansen et al. 2003a) compared spallings releases computed using the average concentration of radioactivity in the waste to spallings

releases computed by using the radioactivity of a single, randomly selected single waste stream. The analysis determined that the assumption had only a minor effect on the mean CCDF for releases. For more details on the analysis, see Section MASS-21.0.

To further evaluate the impact of waste variability on the spallings model, a recent analysis (Vugrin 2004a) randomly sampled three waste streams for each spallings event, and releases were calculated using the average of these three waste streams. Three waste streams were chosen to be sampled because waste containers are typically stacked three high in the repository. Vugrin (2004c) documents the run control that created the files for this analysis.

Figure 1 shows the 100 complementary cumulative distribution functions (CCDFs) for CRA Replicate 1 spallings releases that were computed using the average radioactivity across all CH waste streams. Fifty-eight of the 100 vectors fall off-scale with values too low to plot. Figure 2 shows the 100 CCDFs for CRA Replicate 1 spallings releases that were computed using the randomly sampled waste streams. Fifty-seven of the 100 vectors fall off-scale.

Figure 3 shows the mean and 90th percentile curves for both the spallings releases calculated using the average radioactivity of all the waste streams and the spallings releases calculated using the radioactivity of the randomly selected waste streams. The two mean CCDFs are nearly identical everywhere except at very low probabilities. The 90th percentile curve calculated using the randomly selected waste streams shows higher releases than the 90th percentile curve calculated using the total average radioactivity, but the largest deviations occur at low probabilities. It is not surprising that the 90th percentile curves differ somewhat because the second method of computing spallings releases introduces greater variability. Thus, we expect the 90th percentile curve for the random sampling method to show higher releases than the 90th percentile curve for the average radioactivity method shows. Therefore, spallings releases are not significantly affected by waste variability.

With regard to container variability, the addition of new container types do not impact calculated spall releases (or cuttings and cavings) because PA conservatively assumes that the containers are not present. In Appendix PA, Attachment SCR, both features, events, and processes (FEPs) associated with container type (W4 Container Form and W34 Container Integrity) are screened out due to beneficial consequences.¹ That is, the containers are assumed to instantaneously fail, making the waste material immediately available to cuttings, cavings, spallings, or other transport and release mechanism. The emplacement of additional container types in the repository can only impact the performance of the WIPP if it is assumed that they maintain some of their structural integrity. In the case of spallings, a robust container that would persist over time would at least delay or decrease the movement of radionuclides towards the intrusion borehole, and may, in an extreme case, isolate the waste material from spalling altogether. In either case, the releases would decrease if the physical properties of waste containers were included in performance assessment calculations. Because PA takes no credit due to the physical aspects of the container, container variability does not impact calculated spall releases.

¹FEPs may be screened out of PA calculations because they have a beneficial effect on performance. Because accurate representation of such beneficial effects may be quite difficult and uncertain, such beneficial FEPs may not be represented (screened-out) in PA models. Not accounting for such beneficial effects is considered to be conservative.

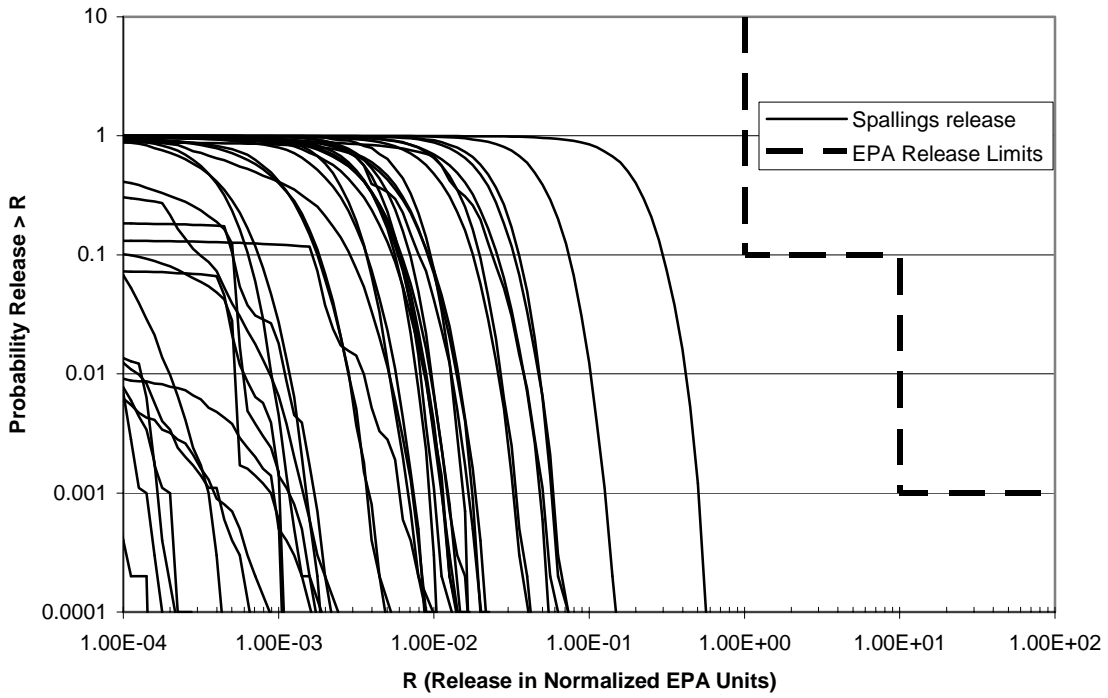


Figure 1. Spallings Releases Calculated Using the Average Radioactivity Over All CH-TRU Waste Streams

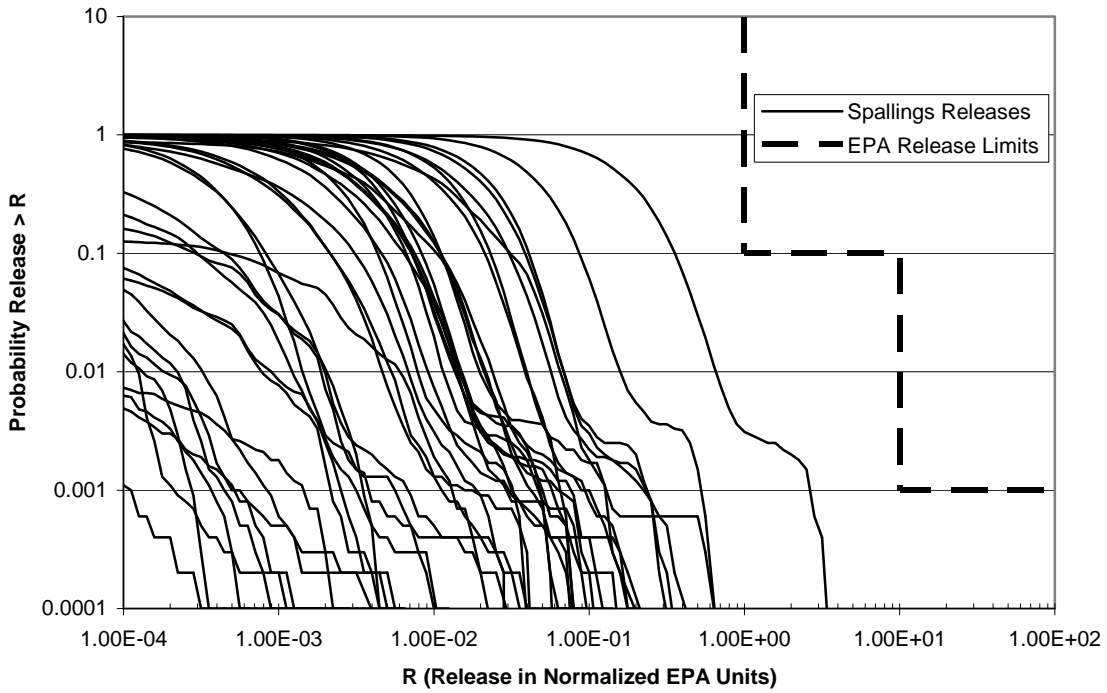


Figure 2. Spallings Releases Calculated Using the Average Radioactivity of 3 Randomly Sampled CH-TRU Waste Streams

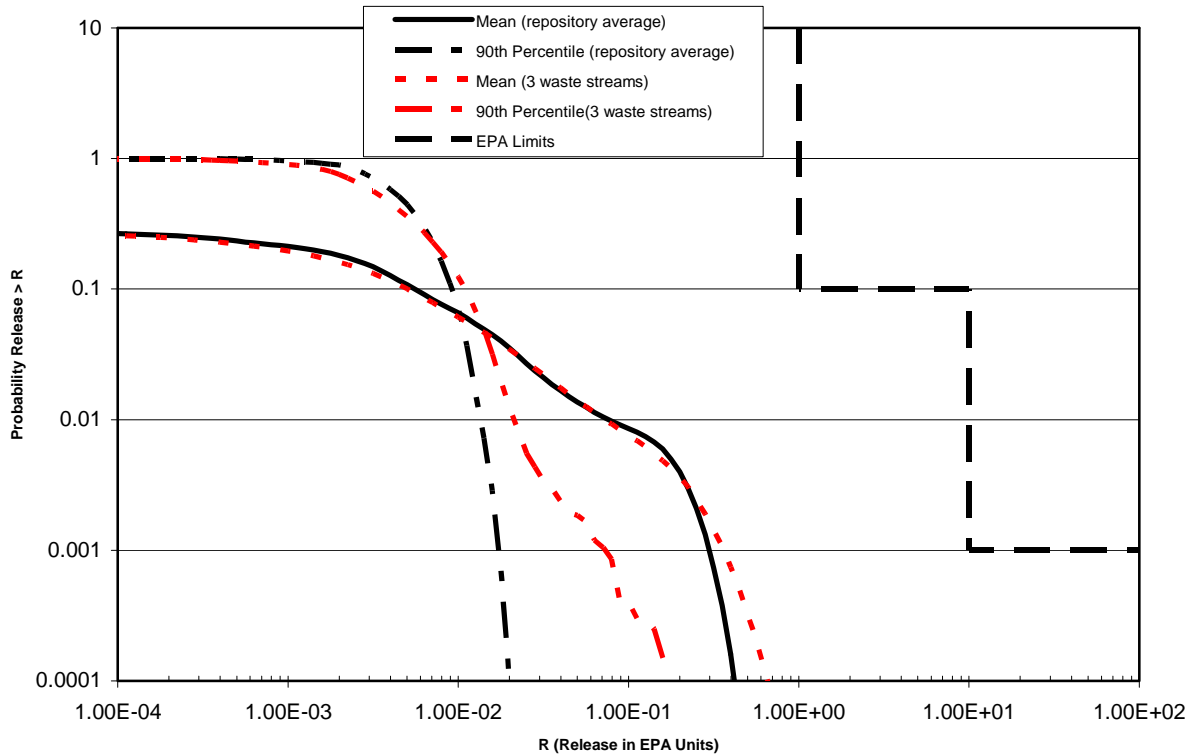


Figure 3. Sensitivity of Spallings Releases to Assumptions About Container-Scale Variability: mean spallings release calculated using the repository average activity vs. mean spallings release calculated using three waste streams

References

- Kirchner, T. and E. Vugrin. 2004. Errors affecting spallings releases, Rev. 0. Sandia National Laboratories, Carlsbad, NM. ERMS #537852.
- Vugrin, E. D. 2004a. "Container-Scale Variability and DRSPALL in response to C-23-10, Rev 1." Memorandum to David Kessel. November 15, 2004. Sandia National Laboratories. Carlsbad, NM. ERMS# 537870.
- Vugrin, E. D. 2004b. Response to EPA C-23-10, Rev. 0. Sandia National Laboratories, Carlsbad, NM. ERMS #536339.
- Vugrin, E. D. 2004c. "Run Control for Correction of Calculation of Spallings Releases." Memorandum to David Kessel. November 19, 2004. Sandia National Laboratories. Carlsbad, NM. ERMS# 537897.
- U. S. Environmental Protection Agency (EPA). Letter from Elizabeth Cotsworth to Dr. R. Paul Detwiler. May 20, 2004. ERMS# 535554.

EPA Comment

In an email from Betsy Forinash of EPA to Lloyd Piper of DOE, EPA requested assistance in addressing a question raised by several stakeholders regarding how increases in drilling rate might eventually affect WIPP's compliance with the release limits. The increase, of course, is due to the fact that drilling rates in the PA are based on a rolling 100-year average of drilling activities in the Delaware Basin. So every five years, one would basically expect to drop five years of no drilling (or almost no drilling, based on the early 1900's) from the average, and include five years of present-day rates. Thus, for each recertification up until the end of WIPP's operating lifetime, the drilling rate for PA would be expected to rise.

EPA initially requested that DOE extrapolate the drilling rate at WIPP to 30 years from now (i.e., 2034), use the drilling rate increase from the last thirty years to project the drilling rate increase over the next thirty years, then estimate the releases from cuttings and cavings, and assess how the difference would affect compliance.

In a subsequent phone conversation with Tom Peake of EPA, it was determined that the stakeholders were interested in seeing how doubling the drilling rate would affect WIPP repository performance,

DOE Response

Sandia National Laboratories (SNL) has prepared the enclosed document (Kanney and Kirchner 2004) that analyzes the impact on predicted repository performance of increasing the drilling rate used in PA calculations.

SNL performed an analysis of using two drilling rates. One drilling rate is the doubling of the 2004 CRA rate requested by the stakeholders. The other rate was determined by using data collected by the Delaware Basin Drilling Surveillance Program and a 100-year window anchored at the closure date (1934 through 2033). For the interval in which there is no drilling activity data (2005 through 2033), SNL assumed that the total number of deep boreholes during the period is equal to that observed in the previous 29 years (1976 through 2004). This was preferable to the EPA suggestion because extrapolation forward using the last 30 years of drilling data actually results in a *decrease* in the drilling rate. The drilling rates used are shown in Table 1.

Table 1. Drilling rates used in Kanney and Kirchner (2004)

Description	Drilling Rate ($\text{km}^{-2} \text{yr}^{-1}$)
projected drilling rate in 2033	8.30×10^{-3}
double the 2004 CRA drilling rate	1.05×10^{-2}

The results presented in Kanney and Kirchner (2004) show that doubling the drilling rate used in WIPP PA relative to the current rate has only a modest impact on mean total releases, and releases continue to be well within regulatory limits under this modeling assumption. Mean total releases increase almost linearly with increases in the drilling rate, which is reasonable

considering that direct releases to the surface such as drill cuttings dominate releases in PA calculations.

References

Kanney, J. F. and T. B. Kirchner. 2004. Impact of Potential Drilling Rate Increases on WIPP Repository Performance. Technical Memorandum ERMS 538262. Sandia National Laboratories. Carlsbad, NM.