Waste Isolation Pilot Plant

Compliance Certification Application

Reference 535

Rechard, R.P., Stockman, C.T., Sanchez, L.C. Liscum-Powell, J., and Rath, J.S. 1996. Nuclear Criticality in Near Feild and Far Field. Summary memo of Record for RNT-1, SWCF-A:1.2.07.3:PA:QA:TSK:RNT-1. Sandia National Laboratories, Albuquerque, NM. WPO 40818.

WPO 40818

Sandia National Laboratories

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Sandia Corporation

Albuquerque, New Mexico 87185-1328

INFORMATION ONLY

date: August 22, 1996

to: Freddie Davis, 6848, MS 1328
Tim Hicks, Galson Sciences Ltd.

D. R. Anderson

from: Rip Anderson, 6849, MS 1328

For Review
8/22/96

subject: Technical Review for FEP RNT-1

Please provide a technical review of the attached FEP RNT-1. Reviewer comments must be completed by mid-September. Documentation of the review, at a minimum, will consist of completing a *FEP Technical Review Sheet* and *Document Review and Comment Form* (form 430-A from QAP 6-3). As a reminder, reviewer comments and their resolution will be documented on form 430-A. The *Technical Review Sheet* should be completed after all reviewer comments have been resolved between the lead staff and technical reviewers. Guidance for the FEP technical review and a copy of the Technical Review Sheet may be found in *Features, Events, and Processes (FEPs) Screening Analysis Plan, Version 5-4.* A copy of the analysis plan is available electronically under the NWMP Applications Icon.

Attachments: as stated

Copy to (w/o attachments):
MS 1328 Rip Anderson, 6849
MS 1328 Kathy Economy, 6849
MS 1328 Mert Fewell, 6849
MS 1328 Al Schenker, 6849
MS 1335 Margaret Chu, 6801
MS 1337 Wendell Weart, 6000
MS 1341 Peter Swift, 6821
MS 1395 Les Shephard, 6800
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Dan Galson, Galson Sciences Ltd.
SWCF-A:1.2.07.3:PA:QA:MGT:PLN (2 copies)

WPO 40818

Sandia National Laboratories
Operated for the U.S. Department of Energy by
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Albuquerque, New Mexico 87185-1328

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date: September 12, 1996

to: David Bennett, Galson Sciences
Tim Hicks, Galson Sciences

for Rip A.

from: Rip Anderson, 6849, MS 1328

subject: Technical Review for FEPs RNT-1

The technical review assignment for RNT-1 is changed from Tim Hicks to David Bennett. This is due to Tim Hicks' having an unavoidable schedule conflict. David Bennett is assigned the responsibility for the RNT-1 technical review. Please provide a technical review of the attached FEPs RNT-1. Reviewer comments should be completed by September 18, 1996, to allow for comment resolution by the end of September. Documentation of the review, at a minimum, will consist of completing a *FEP Technical Review Sheet* and *Document Review and Comment Form* (form 430-A from QAP 6-3). As a reminder, reviewer comments and their resolution will be documented on form 430-A. The *Technical Review Sheet* should be completed after all reviewer comments have been resolved between the lead staff and technical reviewers. Guidance for the FEP technical review and a copy of the Technical Review Sheet may be found in *Features, Events, and Processes (FEPs) Screening Analysis Plan, Version 5-4*. A copy of the analysis plan is available electronically under the NWMP Applications Icon.

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FEP Qualitative Screening Argument

RNT-1: Nuclear Criticality in Near Field and Far Field
SWCF-A: 1.2.07.3:PA:QA:TSK:RNT-1

For Review
D. R. Anderson

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Recommended Screening Decision

Nuclear criticality can be eliminated from performance assessment calculations for the Waste Isolation Pilot Plant (WIPP) based on low consequence and low probability. However, because conditions in the repository and Culebra Dolomite Member of the Rustler Formation (hereafter referred to as Culebra) are different, the arguments for low probability and low consequence are presented by location.

The possibility of a nuclear criticality in the repository is eliminated from performance assessment calculations based on low probability because of the dispersed emplacement of the fissile material and no credible mechanism to concentrate the fissile material. The possibility of a nuclear criticality in the Culebra is eliminated from performance assessment calculations based on low probability (1) when the plutonium solubility is less than 10^{-3} mM, based on general reasoned arguments, and (2) because of lack of a credible mechanism (for all plutonium solubilities) to concentrate fissile material in the Culebra.

In the repository, the consequences of a criticality of ^{239}Pu are actually beneficial because fissioning, followed by about 100 years of emplacement, produces fission products with fewer EPA units (a measurement designated by the Environmental Protection Agency [EPA] in 40 CFR 191, which serves as a surrogate for health risk) than those initially emplaced. In addition, the maximum fissions (energy) possible in the WIPP repository are four orders of magnitude less than the fissions represented by the proposed 70,000-MTHM (metric tons of heavy metal) repository at Yucca Mountain, Nevada. In the Culebra, the situation is similar: the consequences are low because (1) the maximum fissions (energy) are three orders of magnitude less than those that occurred from the natural reactor approximately 1.7 to 2 billion years ago at the Oklo site, in Gabon, Africa, and six orders of magnitude less than those represented by the proposed 70,000-MTHM repository at Yucca Mountain, and (2) the maximum power output from fissions is two orders of magnitude less than that of the remotely handled (RH) and contact-handled (CH) transuranic (TRU) waste initially placed in the repository.

Screening Issue

In any risked-based analysis of a nuclear facility, nuclear criticality safety is an important issue. This issue is of prime importance for worker safety prior to closure. However, it is of less importance after closure because, assuming that a criticality could occur, it would have to either (1) degrade the ability of the disposal system to contain nuclear waste before it would have the potential to affect human health or (2) produce more hazardous waste than originally present. Performance assessment calculations are concerned with post-closure performance of the disposal system and thus examine the probability or consequences of a criticality only after repository closure.

Overall Argumentative Approach

The general approach in this screening is to use arguments of both low probability and low consequence to eliminate the criticality process (or event) from consideration. The arguments depend on the subsurface location; hence specific arguments are grouped by repository (near field) and Culebra (far field). However, the arguments are similar for each location. For example, each location lacks a credible means to concentrate the fissile mass. In addition, the argument for low probability of a criticality in the Culebra is also supported by the low solubilities of the fissile material there. Rechard et al. (1996a) used a reasoned qualitative argument followed by a more quantitative argument in their report on the probability and consequences of a criticality in a repository containing spent nuclear fuel and high-level waste in volcanic tuff. The same method for evaluating the probability and consequences of a criticality in the WIPP disposal system is adopted here.

Information Used in Screening Decision

Two pieces of information are important as the basis for the recommended screening decision: (1) the ranges of solubility and partition coefficient and (2) the limits on critical concentration.

Ranges of Solubility and Partition Coefficient

Because the range of the solubility and partition coefficient for plutonium in various brines is crucial to this screening discussion, the following text briefly describes these values. More detail on these ranges will be presented in the Compliance Certification Application (CCA) for the WIPP.

Range of Matrix Partition Coefficients for Plutonium

The adsorption on mineral surfaces is frequently modeled through a simple partition coefficient (K_D). For Pu(III), the partition coefficient (K_D) in the Culebra is assumed to be uniformly distributed between 0.02 to 0.4 m^3/kg. For Pu(IV), K_D is assumed to be uniformly distributed between 0.7 and 10 m^3/kg (Table 1). As explained by Brush (1996), the maximum and minimum K_D values for Pu(III) were established by assuming that batch experiments with crushed Dolomite for Pu(V) bound the values. The maximum and minimum K_D values for Pu(IV) were obtained primarily from batch experiments with Th(IV).

Type of Brine Assumed for Solubility

The range of solubility is dependent upon the type of brine. A distinction is usually made between a brine from the pores in the Salado Formation (hereafter referred to as the Salado), which is the formation in which the repository is located, and brine from the Castile Formation (hereafter referred to as the Castile), which is the formation directly below the Salado. In the Salado, minute amounts of brine can be found, which are thought to be the very concentrated remnants left after the original brine precipitated away from the Salado. The brine from the Castile is thought to resemble more closely the type of brine that would be produced if one were to dissolve material from either the Castile or the Salado with fresh water. Assuming that brine from the Culebra (a member of the Rustler, which is directly above the Salado) enters the Salado, the brine formed by the dissolution of the Salado by the dilute brine (relative to Castile or Salado brines) of the Culebra would likely be similar to the brine from the Castile brine reservoir. Furthermore, in most situations, the volume of Castile and Culebra fluid (rather than Salado brine) would likely dominate in the repository. Hence, the solubility for the Castile brine is used primarily in the following discussion on solubility limits, but the values for the Salado brines are presented here also.

Solubility Limit for Plutonium

For actinides, the solubility is highly dependent upon the oxidation state. As discussed in the CCA (Sections 6.4.3.4 through 6.4.3.6 and Appendix SOTERM, Section SOTERM.4), the WIPP Project has assumed plutonium would exist in only a +3 [Pu(III)] or +4 state [Pu(IV)]. Furthermore, the WIPP Project has assumed that only one oxidation state will dominate in solution and thus oxidation state is sampled in each vector of sampled parameters in the 1996 calculations. In addition, an apparent solubility is calculated that is the sum of the dissolved species and four types of colloids: humic, microbial, intrinsic, and mineral. The mineral type colloids are minute minerals with adsorbed plutonium; the intrinsic colloids are minute particles of PuO_2; the microbial colloids are organic microbes that have absorbed Pu; and the humic colloids are humic material that has complexed the plutonium. For Pu(III), the solubility of the dissolved species dominates (65%) the calculated apparent solubility in Salado brine, but colloids dominate in Castile brine (70%). Approximately 25% of the apparent solubility for Pu(III) (microbial and mineral col-

Table 1. Ranges of K_Ds (m^3/kg) for Pu, Am, U, Th, and Np (probability distribution assumed to be <u>uniform</u> between range) (after Brush, 1996, Table 1).

	Element				
Oxidation State	**Pu**	**Am**	**U**	**Th**	**Np**
VI	NA	NA	**3×10^{-4} to 0.02[a,c]** 0 to 0.06[b,c]	NA	NA
V	NA	NA	NA	NA	**0.002 to 2[a,c]** **0.001 to 2[b,c]**
IV	**0.7 to 10[a,d]** NE	NA	**0.7 to 10[a,e]** NE	**0.7 to 10[a,c]** NE	**0.7 to 10[a,g]** NE
III	**0.02 to 0.4[a,h]** 0.009 to 4[b,h]	**0.02 to 0.4[a,i]** 0.009 to 4[b,i]	NA	NA	NA

a range for deep (Castile and Salado) brine only
b range for Culebra brines only
c experimentally obtained range
d experimentally obtained range for Th(IV) applied to Pu(IV) by oxidation-state analogy
e experimentally obtained range for Th(IV) applied to U(IV) by oxidation-state analogy
f experimentally obtained range for Th(IV) and deep brines applied to Th(IV) and Culebra brines
g experimentally obtained range for Th(IV) applied to Np(IV) by oxidation-state analogy
h experimentally obtained range for Pu(V) applied to Pu(III)
i experimentally obtained range for Pu(V) applied to Am(III)

loids) can be filtered. The filtration would probably occur at the point at which they were formed within the repository (Attachment A) and thus their inclusion in the apparent solubility is suspect; nonetheless, to be consistent with the conditions specified by the CCA, the microbial and mineral colloids are included here. For Pu(IV), the colloids are 80% and 90% of the calculated apparent solubility in the Salado and Castile brines, respectively. Approximately 7% and 43% of the calculated apparent solubility in the Salado and Castile brines, respectively, can be filtered. In all cases for the solubility limits, the values used have assumed a MgO backfill in the repository (Table 2).

In Castile brine, the apparent solubility for Pu(III) is assumed to range from 10^{-5} to 10^{-2} mM with a median of 2×10^{-4} mM. In Salado brine, the apparent solubility for Pu(III) is assumed to range from 3×10^{-5} to 3×10^{-2} mM with a median of 7×10^{-4} mM. In Castile brine, the apparent solubility for Pu(IV) is assumed to range from 10^{-5} to 3×10^{-3} mM with a median of 6×10^{-5} mM. In Salado brine, the apparent solubility for Pu(IV) is assumed to range from 3×10^{-4} to 4×10^{-1} mM with a median of 2×10^{-2} mM (Figure 1). The very high solubility for Pu(IV) in Salado brine assumed in the 1996 CCA is higher than the solubility assumed for U(VI). As explained in the CCA, the distribution was calculated with the software code, FMT, and required extrapolation of Pitzer coefficients.* Because of the extrapolation, the solubility values in this distribution are possibly much higher than believed reasonable. It is also interesting to note that speculative modeling of the Salado brine *increases* the solubility of Pu(IV) by 2.5 orders of magnitude although expert opinion, based on extrapolation experiments, maintains the solubility of U(VI) as con-

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* Currently the Pitzer Model is considered the best model for explaining and predicting behavior of various species in solutions of high ionic strength. However, to provide accurate results, the model requires a number of parameters that must be measured or reasonably estimated.

Table 2. **Example Showing Calculation of Median Apparent Solubility of Pu(III) and Pu(IV) in Castile and Salado Brines.**

Salado with MgO							Fraction	Fraction	Log
	Dissolved	Humic	Microbe	Intrinsic	Mineral	Total	Colloid	Mic & Min	Conc.
Am(III)	4.73E-7	8.99E-8	1.70E-6	0	2.60E-8	2.29E-6	0.79	0.75	-5.64
Pu(III)	4.73E-7	8.99E-8	1.42E-7	1.00E-9	2.60E-8	7.32E-7	0.35	0.23	-6.14
Pu(IV)	3.58E-6	1.10E-5	1.07E-6	1.00E-9	2.60E-8	1.57E-5	0.77	0.07	-4.80
U(IV)	3.58E-6	1.10E-5	7.51E-9	0	2.60E-8	1.46E-5	0.76	0.00	-4.84
U(VI)	7.07E-6	8.49E-7	1.49E-8	0	2.60E-8	7.96E-6	0.11	0.01	-5.10
Th(IV)	3.58E-6	1.10E-5	1.11E-5	0	2.60E-8	2.57E-5	0.86	0.43	-4.59
Np(IV)	4.40E-6	1.10E-5	5.28E-5	0	2.60E-8	6.82E-5	0.94	0.77	-4.17
Np(V)	2.30E-6	2.09E-9	2.76E-5	0	2.60E-8	2.99E-5	0.92	0.92	-4.52
Castile with MgO							Fraction	Fraction	Log
	Dissolved	Humic	Microbe	Intrinsic	Mineral	Total	Colloid	Mic & Min	Conc.
Am(III)	5.30E-8	7.26E-8	1.91E-7	0	2.60E-8	3.42E-7	0.85	0.63	-6.47
Pu(III)	5.30E-8	7.26E-8	1.59E-8	1.00E-9	2.60E-8	1.69E-7	0.69	0.25	-6.77
Pu(IV)	4.88E-9	3.07E-8	1.46E-9	1.00E-9	2.60E-8	6.41E-8	0.92	0.43	-7.19
U(IV)	6.00E-9	3.78E-8	1.26E-11	0	2.60E-8	6.98E-8	0.91	0.37	-7.16
U(VI)	7.15E-6	3.65E-6	1.50E-8	0	2.60E-8	1.08E-5	0.34	0.00	-4.96
Th(IV)	6.00E-9	3.78E-8	1.86E-8	0	2.60E-8	8.84E-8	0.93	0.50	-7.05
Np(IV)	6.00E-9	3.78E-8	7.20E-8	0	2.60E-8	1.42E-7	0.96	0.69	-6.85
Np(V)	2.20E-6	1.63E-8	2.64E-5	0	2.60E-8	2.86E-5	0.92	0.92	-4.54

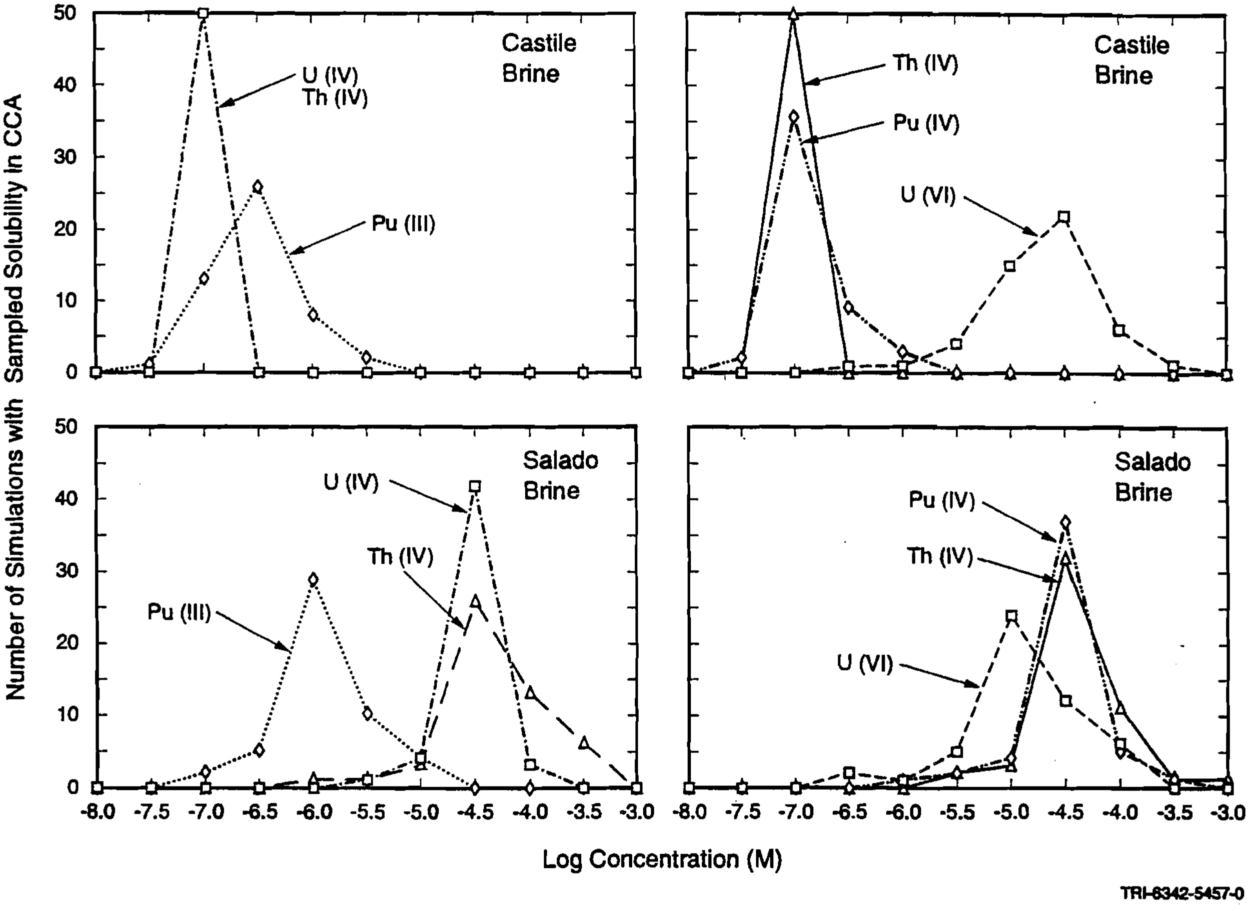

Figure 1. Probability histograms for solubility limit for Pu(III), Pu(IV), U(IV), U(VI), and Th(IV) in Salado and Culebra brines obtained from sampling used in 1996 CCA.

stant.[*] However, the distribution used in the CCA will be used herein for consistency. Note, however, that the use of such high solubility values represents a conservative assumption and increases the difficulty of demonstrating a low probability for a criticality.

Limits on Critical Concentration

A self-sustaining fission chain reaction (critical condition) depends on the chain-carrying neutrons and thereby on their interaction with matter; hence a critical condition depends not only on the quantity of fissile material but also on its concentration and shape and any other material surrounding the fissile material either as a solid (e.g., containment vessel), liquid (e.g., solvent), or gas that reflects or absorbs the neutrons. As thoroughly demonstrated by Clayton (1979), the interaction of neutrons with different types, shapes, and masses of material can produce results that are hard to categorize. The heterogeneous mixture (i.e., one with specified shapes and masses of fissile and other material) is particularly complex. However, standard limits below which criticality is impossible do exist for homogenous mixtures of fissile material with one or more other materials and can help guide analysis.

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[*] Though not significant, the solubility of U[VI] actually decreases by 0.5 order of magnitude.

Limits Based on Homogeneous Spherical Shapes

As with heterogeneous mixtures, the limits below which criticality is impossible in a homogeneous mixture do depend upon the materials. However, the amount of ^{239}Pu mass in a unit volume of material is often near 7 kg/m^3 when water is the primary interactive substance and the other substances are fairly transparent to neutrons (i.e., very ideal conditions). For a mixture of ^{239}PuO$_2$ /Culebra dolomite ($\phi = 16\%$) and brine, this limit is ~3 kg/m^3 (the same as calculated for a ^{239}Pu/tuff mixture by Sanchez et al. [1995]) and will be used herein (Figure 2). Note the concentration of plutonium must reach levels (>1000 ppm) that are considered to be economically mineable ore bodies (at least for uranium) when located near the surface. This limit was evaluated with MCNP (Version 4a, a general Monte Carlo code for neutron and photon transport) (Briesmeister, 1986). For a ^{239}Pu/Salado salt/brine mixture, this value is very conservative because the chlorine in the salt is very effective in absorbing neutrons. However, because of the effectiveness of chlorine, an important variable is the extent to which the plutonium and salt are mixed. Rather than assume various mixture values, the extremely conservative limit of 3 kg/m^3 will be used in the following discussions for the repository as well as the Culebra.

Geometric Constraints on Deposition of Fissile Radionuclides

The following discussion primarily uses the limit on homogenous, spherical mixtures because the results are more general; however, in the Culebra a geometrical constraint may be possible, which leads to

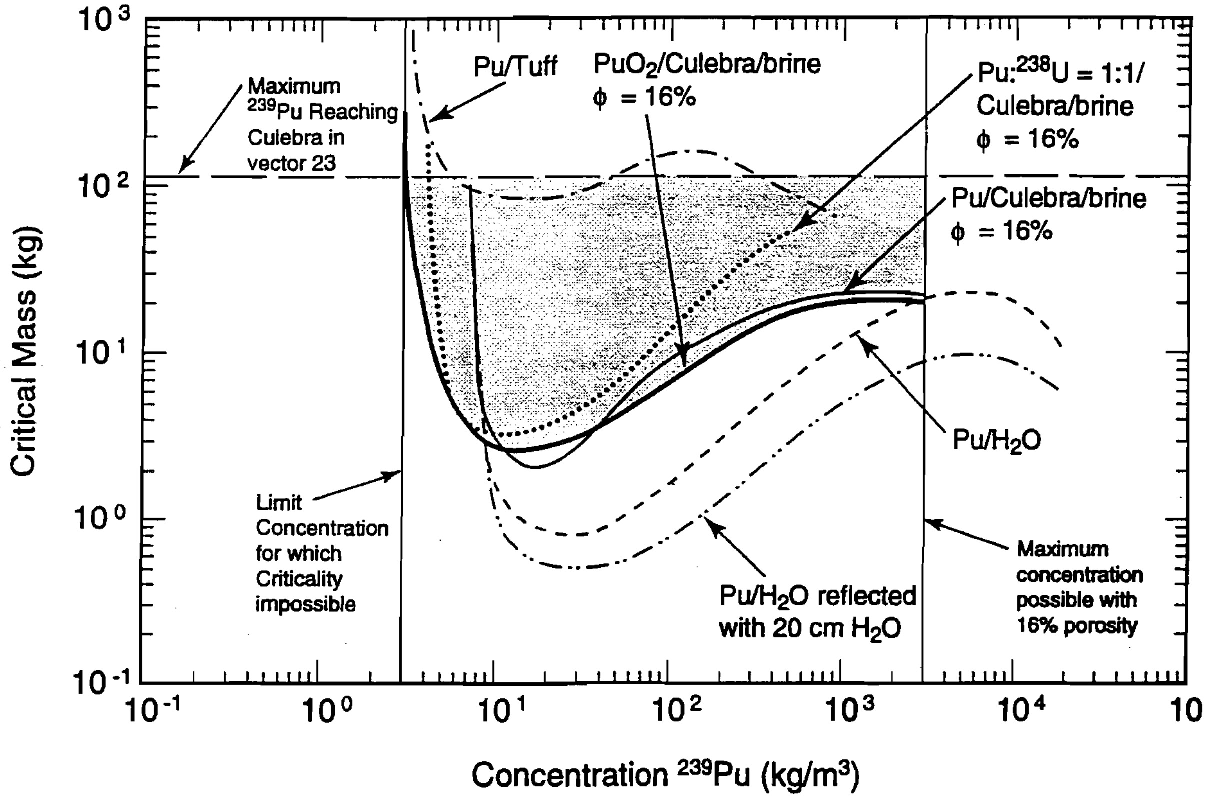


Figure 2. Critical masses of plutonium in a spherical shape as a function of plutonium solid concentration when mixed with various substances. The curves corresponding to ^{239}Pu/H$_2$O and ^{239}Pu/H$_2$O with 20 cm H$_2$O reflection are reproduced from Clayton and Reardon (1980). The curve corresponding to ^{239}Pu/tuff was calculated herein but is similar to that shown in Sanchez et al. (1995).

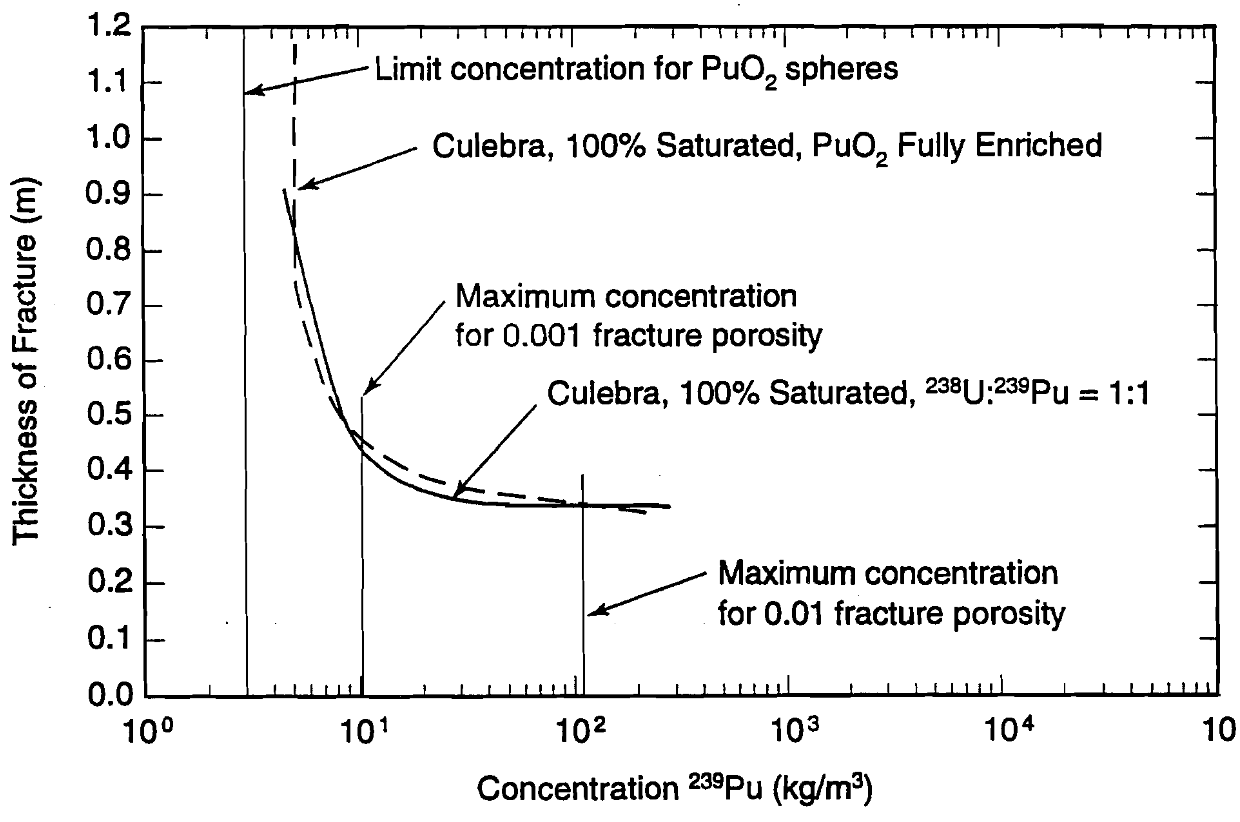
less restrictive criticality limits. The porosity in the dolomite consists of intergranular porosity, vugs, microscopic fractures, and macroscopic fractures. The WIPP Project believes that advected flow occurs mostly through macroscopic fractures (Section 6.4.6.2 of the CCA and Appendix MASS). For those situations where the flow is along a few discrete fractures, any potential deposition through sorption, colloidal filtering, or precipitation can be only along surfaces lining the fracture. This situation places an important constraint on the geometry of the fissile material and eliminates the possibility of a criticality in regions with flow predominately in discrete fractures because of the thickness required. Idealized criticality analysis of flat plates in dolomite show that the deposited thickness of fissile material must exceed ~0.45 m before criticality is possible (Figure 3). This aperture size is improbable for one discrete fracture and is a considerable thickness even for a series of closely spaced fractures.

Possibility of Criticality in the Repository

Within the repository, five mechanisms could exist to cause a concentration of fissile material in one location: compaction, concentrated solution, adsorption on mineral surfaces (e.g., ion exchange or surface complexation), filtration of colloid material, and precipitation. However, in the repository, no special features exist to make these mechanisms feasible, as discussed below.

Compaction

Pre-closure criticality concerns are addressed elsewhere; however, we note here that the radioactive waste to be emplaced at the WIPP contains very low concentrations of fissile material (primarily ^{239}Pu);



TRI-6342-5479-0

Figure 3. Critical thickness of plates of plutonium and uranium as a function of plutonium solid concentration in the Culebra.

thus, the possibility of a criticality is remote prior to closure. Just as important, the possibility is also remote after closure because a criticality requires that this emplaced fissile mass be substantially concentrated. To elaborate, the solid concentration below which an infinite volume of a homogeneous mixture of $^{239}PuO_2$, Culebra dolomite, and brine will *not* go critical is taken conservatively as 3 kg/m^3. This limit is 30 times larger than the emplaced density of 0.12 kg/m^3 based on a total fissile gram equivalent (FGE) mass scheduled to be placed in the WIPP of 21 Mg (Table 3) and a waste volume of 1.756×10^5 m^3 ($6. \times 10^6$ ft^3). This density could be increased somewhat through compaction; however, assuming a compaction to one fourth the thickness (0.69 m), without any salt creep into the waste layer, the fissile mass density is still only 0.48 kg/m^3.

Table 3. Fissile gram equivalent of ^{239}Pu in the WIPP inventory (as evaluated from DOE, 1995)

Time (yr)	TRU Inventory (Curies)			Computed TRU Waste Values				
				Heat Load (Watts)	**^{239}Pu (kg)**	**^{239}Pu FGE (kg)**	**^{238}U (kg)**	**Mass (kg)**
	CH	**RH**	**Total**	**Total**	**Total**	**Total**	**Total**	**Total**
0	6.42E+06	1.02E+06	7.44E+06	1.37E+05	1.28×10^4	2.11E+04	1.49×10^5	1.81E+05
100	2.65E+06	1.07E+05	2.76E+06	8.60E+04	1.28×10^4	2.11E+04	1.49×10^5	1.81E+05
125	2.40E+06	7.02E+04	2.47E+06	7.81E+04	1.28×10^4	2.11E+04	1.49×10^5	1.81E+05
175	2.04E+06	3.80E+04	2.08E+06	6.63E+04	1.28×10^4	2.10E+04	1.49×10^5	1.81E+05
350	1.45E+06	2.19E+04	1.47E+06	4.65E+04	1.28×10^4	2.11E+04	1.49×10^5	1.81E+05
1,000	1.06E+06	1.71E+04	1.08E+06	3.36E+04	1.28×10^4	2.11E+04	1.49×10^5	1.81E+05
3,000	8.87E+05	1.38E+04	9.01E+05	2.78E+04	1.28×10^4	2.10E+04	1.49×10^5	1.81E+05
5,000	8.15E+05	1.27E+04	8.28E+05	2.55E+04	1.28×10^4	2.10E+04	1.49×10^5	1.81E+05
7,500	7.41E+05	1.15E+04	7.52E+05	2.31E+04	1.28×10^4	2.10E+04	1.49×10^5	1.81E+05
10,000	6.76E+05	1.05E+04	6.87E+05	2.11E+04	1.28×10^4	2.10E+04	1.49×10^5	1.81E+05

If salt creeps into and mixes with the waste or if plutonium moves into the salt, then the mass of plutonium and the diameter of the sphere required to go critical are quite large indeed. For example, the mass of plutonium FGEs required is 10 times greater than exists in any one room (~21 MT FGE of ^{239}Pu exist, and the repository has 118 rooms or only ~178 kg FGE of Pu per room). Also, spherical diameters the same or greater than the original height of the waste (2.76 m) are required for a criticality in Salado salt (as calculated by MCNP, assuming a homogeneous mixture of Salado salt with a porosity of 1.28% and the pores filled with pure ^{239}Pu and Salado brine). These arguments do not even consider the massive amount of ^{238}U also present in the repository (149 Mg), which lowers the possibility of a criticality even further because, when ^{238}U is considered, the total *fissile* radionuclides make up less than 14% of the total radionuclide inventory (14% enrichment).

Concentrated Solution of Plutonium

A solution of the fissile material at a concentration of 3 kg/m^3 (Figure 2) corresponds to 12 mM, a concentration 30 times greater than the anticipated maximum solubility of Pu(IV); consequently, a solution of dissolved plutonium cannot go critical in the repository or elsewhere.

Adsorption of Plutonium

Special features to lead to the mechanism of adsorption of plutonium do not exist in the repository. First, the waste contains nothing that is found in only one or a few drums that would adsorb great quantities of plutonium and thereby cause a critical concentration. Second, although the adsorption (or precipitation) of the actinides onto backfill is a possibility, current backfill schemes involve a fairly uniform distribution of the backfill throughout the repository. Thus preferential concentration in one area is unlikely. This assumption of general uniform mixing is consistent with the general conceptual model of the WIPP repository in the 1996 CCA. Finally, even if localized concentration of backfill were a possible backfill scheme, separation of plutonium to the exclusion of the large amounts of the other radionuclides (e.g.,^{238}U) is very unlikely. If a facile technique was known, it would have been used in place of the expensive PUREX method to separate plutonium from other radionuclides when purifying plutonium for weapons. Likewise a difficulty in proposing an adsorptive backfill as an engineered alternative is that the adsorption on proposed backfills is not usually specific and so large masses of adsorptive backfill are required to ensure enough adsorptive sites for all of the different types of material that will adsorb in the TRU waste. For example, large amounts of iron, nickel, and lead exist in the waste, but handling these large amounts of potential adsorbates would require using more space for a highly effective adsorbent backfill, such as hyroxyapatite, than is available (unless space needed for waste is used).

Filtering of Colloid Material

Because of their high ionic strength, the colloids generated in the waste matrix region (Salado) agglomerate in a dispersed manner within the vicinity in which they were generated. Because the waste matrix region becomes compressed/consolidated in the vertical dimension due to lithostatic stress of the host rock with time and because the permeability of that region is small, the colloids would be entrained in (i.e., restricted to) the waste matrix region. (Permeability is a measure of filter penetration efficiency for actinide transport either in solution or as colloids.) The overall result is that there is no credible mechanism to increase the partial density/concentration of ^{239}Pu or FGE of other fissile radiouclides (Attachment A).

Precipitation of Fissile Material

Of the mechanisms to concentrate actinides, only precipitation is known to have occurred to form large ore deposits. Precipitation of fissile material requires a change in the water chemistry from one area to another in the repository. (Usually the change is in Eh or pH.) Generally, the deposition of uranium occurring as soluble U(VI) (e.g. uranium as a uranyl polycarbonate) is reduced by organic material, iron pyrite, or H_2S (Figure 4). However, the repository is conceptually thought to behave as a fairly well mixed cell without large differences in water chemistry. In addition, the repository will be extremely reducing because the source of hydrogen gas is the reduction of water (i.e., the repository will lie along the lowest line, which defines the stability of water as shown in Figure 4). Hence, soluble hexavalent uranium or plutonium is not anticipated in the repository. Rather, the already fairly insoluble U(IV) or Pu(III) are anticipated, which limits further reduction of the fissile material. Based on these arguments, large amounts of precipitation in a localized area of the repository are not credible.

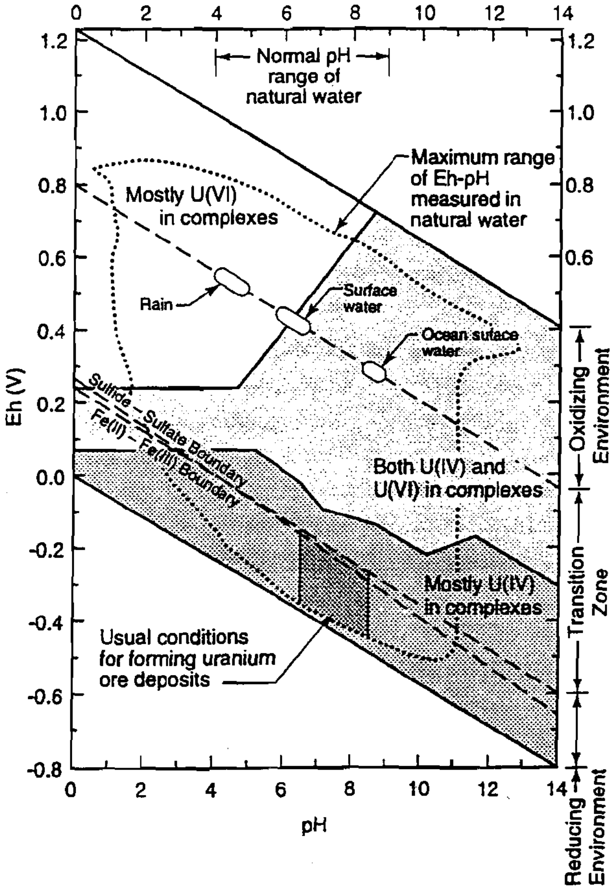


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Figure 4. General Eh-pH diagram of uranium formed by superimposing Eh-pH diagrams from several systems (U-C-O-H, U-O-H, U-Si-C-O-H, U-Si-O-H) (after Brookins, 1988, Figs. 1, 87, 88, 89, 90, and 91). Uranium ore deposits typically form when massive amounts of waters with small amounts of dissolved U(VI) species encounter a reducing environment (e.g., hydrocarbons) that reduces the uranium to U(IV) and precipitates uraninite (UO_2).

Possibility of Criticality in the Culebra

Once the fissile mass leaves the repository, the general tendency is for the radionuclides to disperse rather than concentrate. However, the first general arguments put forth below follow the general approach of Rechard et al. (1996a) in which the difficult question of how fissile material is concentrated is ignored and, for purposes of the argument, concentration is simply assumed. This first approach avoids discussion of dissolution, transport, and reconcentration of fissile material. Following this first argument, stronger arguments are posed that refute the probability of methods existing that would concentrate fissile material in the Culebra.

Scenario Development with Criticality as an Event

In the following arguments, the criticality condition (C) is treated as an event along with human intrusion by exploratory drilling (HI) (see Rechard et al., 1996a, Figure 6). All other events, processes, and features are treated either as certainties or impossibilities. The elementary probability of at least one human intrusion in the first 10,000 yr ($P\{n>0\}$) is taken as $1-e^{\lambda\Delta t}$ assuming a Poisson discrete analytic distribution function for exploratory drilling with a drilling rate (λ) and period Δt of 10,000 yr. The elementary probability of the criticality is less than 10^{-4} for concentrations of plutonium that are less than 1.4×10^{-3} mM in the Culebra. The calculation of this probability is explained in the next section. The important item to note in this section is that scenarios involving a criticality are less than 10^{-4} and can be neglected by virtue of EPA guidance in 40 CFR 191 that allows omission of categories of features, events, and processes with probabilities of occurrence of less than 10^{-4} in 10,000 yr.

Elementary Probability of the Criticality Event

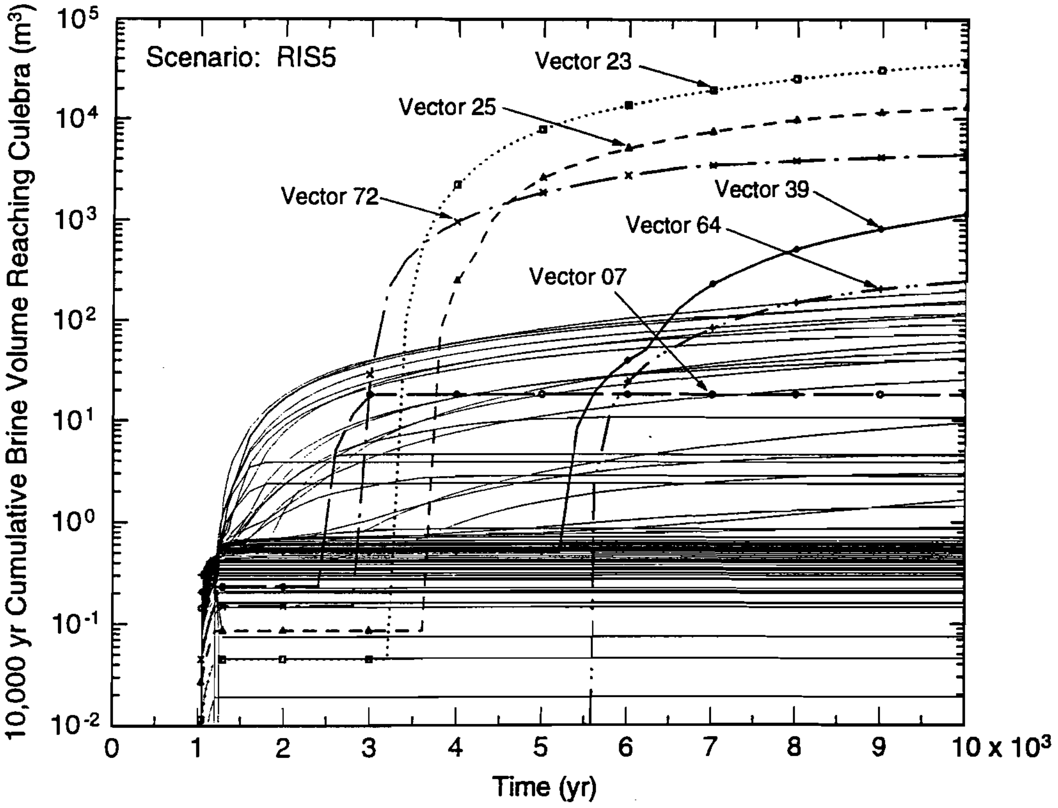
The occurrence of a criticality in the far field is analogous to the natural reactor in uranium ore deposits in Gabon, Africa (Rechard et al., 1996a). The Oklo ore, which contains 17,000 Mg (17,000 metric tonnes), consists mostly of a low grade ore (0.2% to 1% uranium); however a very high grade ore (20% to 60%) is located at faults where hydrocarbons had been trapped. Of the 16 reactors, data were available for the first six. Based on this data, researchers have estimated that 6 Mg of ^{235}U was consumed out of ~800 Mg of high grade uranium associated with the natural reactors. Thus, the Oklo natural reactors provide a basis for determining a rate and probability of forming a criticality. Basically, 6 events occurred per 800 Mg of uranium.

The rate of accumulation of plutonium in the far field is dependent upon the fissile material solubility and the flow rate of brine through the repository; in turn, the flow through the repository is dependent upon the type of human intrusion scenario selected. 1996 CCA calculations show that 4×10^4 $m^3/10^4$ yr (one-fourth of the volume of the underlying brine reservoir) is likely an upper bound for one borehole intrusion (Figure 5). (Although other conditions have changed from the E1E2 scenario used in the 1992 WIPP PA, the commonly used maximum flow rate through the repository was similar, i.e., 10^5 $m^3/10^4$ yr [Rechard et al., 1996b, Attachment B].) For a constant plutonium liquid concentration of 1.4×10^{-3} mM, ~13.4 kg of plutonium (1.4×10^{-3} mM • 4×10^4 m^3) could be brought to the Culebra (and in this section is assumed to be deposited "miraculously" as an ore body) over 10^4 yr. This fact, combined with information from the Oklo natural reactors, produces a rate (r(t)) for criticalities of 10^{-8} events/yr [(6 events/800 Mg) × (0.0134 Mg/10^4 yr)].

Next, we determine the probability in the first 10^4 yr. The probability model is based on the failure-rate function defined by $r(t) = -d/dt \ln[1-F(t)]$ where t is the time elapsed since the disposal system was closed and F(t) denotes the cumulative distribution function for the first time, T, when failure occurs (i.e., $F(t) = P\{T \le t\}$). This expression can be integrated to give

$$F(t) = 1 - \exp[-\int r(t)dt]. \quad [1]$$

As argued above, here r(t) is a constant and equal to 10^{-8} events/yr. Over a period of 10^4 yr, Equation 1 gives a probability of 10^{-4} for a plutonium liquid concentration of 10^{-3} mM = 3×10^{-4} kg/m^3. If solubility is used as a surrogate for concentration, then, as seen in Table 2, the median solubility of plutonium does not remain below 3×10^{-4} kg/m^3 (except for Pu(IV) in Castile brine). If, however, the 1996 CCA concentrations are used (Figure 6), then only one simulation has concentrations of plutonium above this value and remains above the concentration threshold long enough to result in a sufficient amount of mass reaching the Culebra (Figure 7). Even for this simulation however, the criticality event can be neglected based on arguments as presented in the following sections.



DISK$TINA_CCA2[JSRATH.R1S5]SPL_BRAG_VOL_R1_S6.COM:4

SPLAT_PA96 1.01 07/22/96 09:59:19

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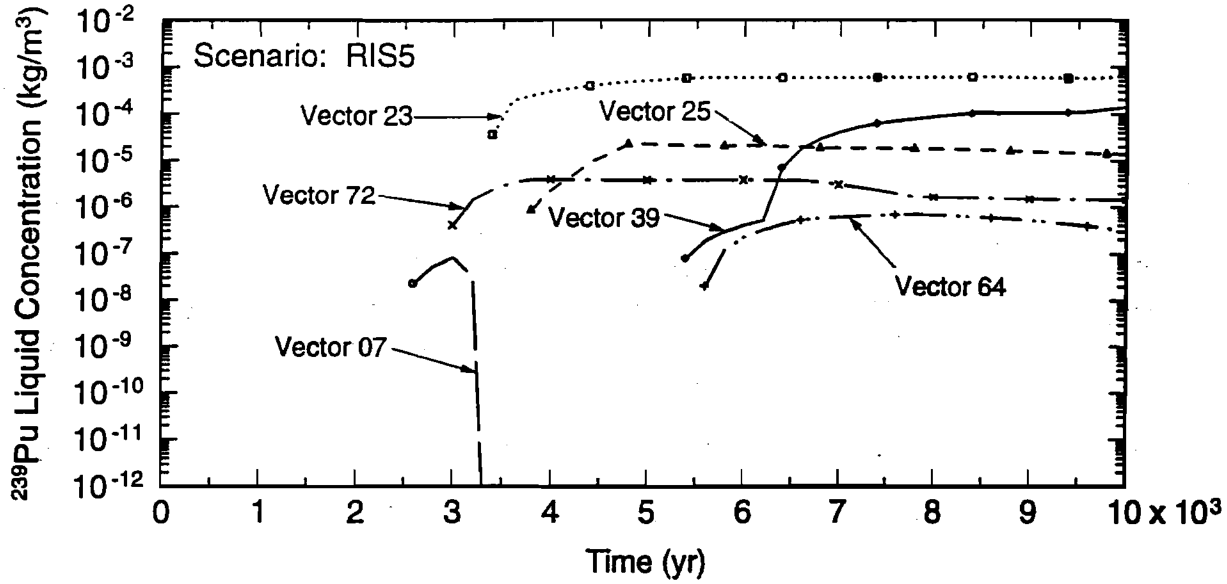
Figure 5. Cumulative brine flow up an intrusion borehole over 10,000 yr after an intrusion that occurs 1000 yr after closure of the repository for the E2 scenario (intrusion without hitting a brine reservoir) in the first replication of the 1996 CCA calculation (R1S5).



DISK$TINA_CCA2[JSRATH.R1S5]SPL_PU239_CONC_R1S5.COM:7

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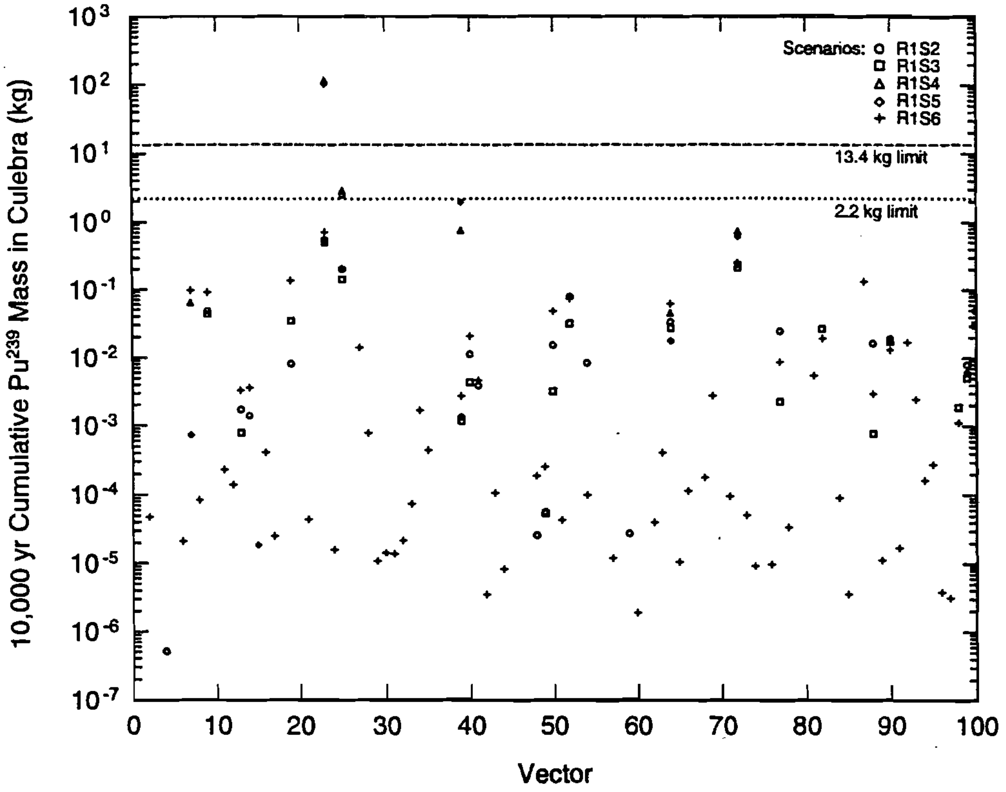
Figure 6. Liquid concentrations of plutonium in brine reaching Culebra in R1S5.



DISK$TINA_CCA2[JSRATH.ROB_CR]SPL_PU239_R1S23456.COM;5

SPLAT_PA96 1.01 08/05/96 06:05:17

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Figure 7. Cumulative mass of ^{239}Pu reaching the Culebra through intrusion borehole over 10,000 yr for R1S2, R1S3, R1S4, and R1S5.

Concentration Mechanisms to Deposit Fissile Material in the Culebra

The process that might cause the "miraculous" deposition and concentration of the fissile material was not explored in the previous section. However, an exploration of possible concentration mechanisms is pursued here because it provides additional support for the low probability argument. First, it should be noted that material leaving a disposal site tends to disperse, not concentrate. A practical consideration is to note that, if concentration of material in a geologic setting were the general tendency, the mining of contaminate plumes outside of disposal sites would be a common practice to cheaply recover purified precious materials originally mixed with waste. Or specifically, rather than throw away trash that was contaminated with plutonium, engineers (here in the U.S. or anywhere in the world) would simply design facilities that made use of such mechanisms for concentration to purify the fissile material. In reality, concentrating and purifying plutonium mixed with the trash is extremely difficult.

The same five mechanisms that existed in the repository to concentrate fissile material in one location could exist in the Culebra. However, further compaction of the Culebra after plutonium deposition is not credible, and increased solubility beyond the already excessively high solubility is also assumed to be not reasonable. Therefore, three mechanisms could exist in the Culebra to cause a concentration of fissile material in one location: adsorption on mineral surfaces (e.g., ion exchange or surface complexation), filtration of colloid material, and precipitation. However, in the Culebra, no special features exist to make use of these mechanisms, as discussed below.

No instance of a uranium ore body being created by means of adsorption on material is described in the literature; thus, adsorption appears an unlikely mechanism for concentrating actinides. More important, as noted above in the arguments related to a criticality in a repository, sorption would also occur for other constituents in the brine, particularly actinides, which would greatly decrease the likelihood of a criticality. However, several quantitative arguments are presented below to support this general reasoned argument. As noted above, the current K_D for Pu(IV) in the Culebra ranges between 0.7 to 10 m^3/kg (Table 1). The maximum solubility of Pu(IV) is 4.3×10^{-1} mM (Figure 1). If the maximum solubility were combined with the maximum K_D for Pu(IV) (which is not a realistic occurrence), plutonium densities are greater than 3 kg/m^3. (The same is true for Pu(III) but only by a factor of 2.) However, when the actual calculated concentrations of plutonium (rather than solubility limit) are combined with the sampled K_D in the CCA, potential adsorbed solid concentrations are less than 3 kg/m^3 in all but two cases (Figure 8).

These two situations can be eliminated for two reasons: (1) the density of sorption sites on dolomite would have to be on the same order of magnitude as the sorptive sites on synthetically prepared goethite and (2) fracture flow constrains the deposition of fissile radionuclides and thus geometry of the critical mass (discussed below in "Precipitation of Fissile Material"). With regard to the density of sorption sites (Item 1), the amount of sorption that can occur on a small volume of Culebra dolomite is limited and explains why adsorption has not been found to produce mineable ore bodies. (Note, however, that these details are not included in the linear sorption model.) A concentration of 3 kg/m^3 corresponds to 7.6×10^{24} $atoms/m^3$ of dolomite. The measured surface area on an acid-washed sample of dolomite from the Air Intake Shaft (sample #VBX-27-9), as evaluated by BET surface area analysis, was 620 m^2/kg dolomite and corresponds to 1.5×10^6 m^2 of surface area per m^3 of dolomite (assuming a porosity of 16% and dolomite grain density of 2820 kg/m^3). Dividing the concentration by the surface area requires a site density of ~5 $atoms/nm^2$, which is of the same order of magnitude as adsorptive minerals (about 2 $sites/nm^2$) (Davis and Kent, 1990). Furthermore, even synthetically prepared goethite (a-FeOOH) has a site density of less than

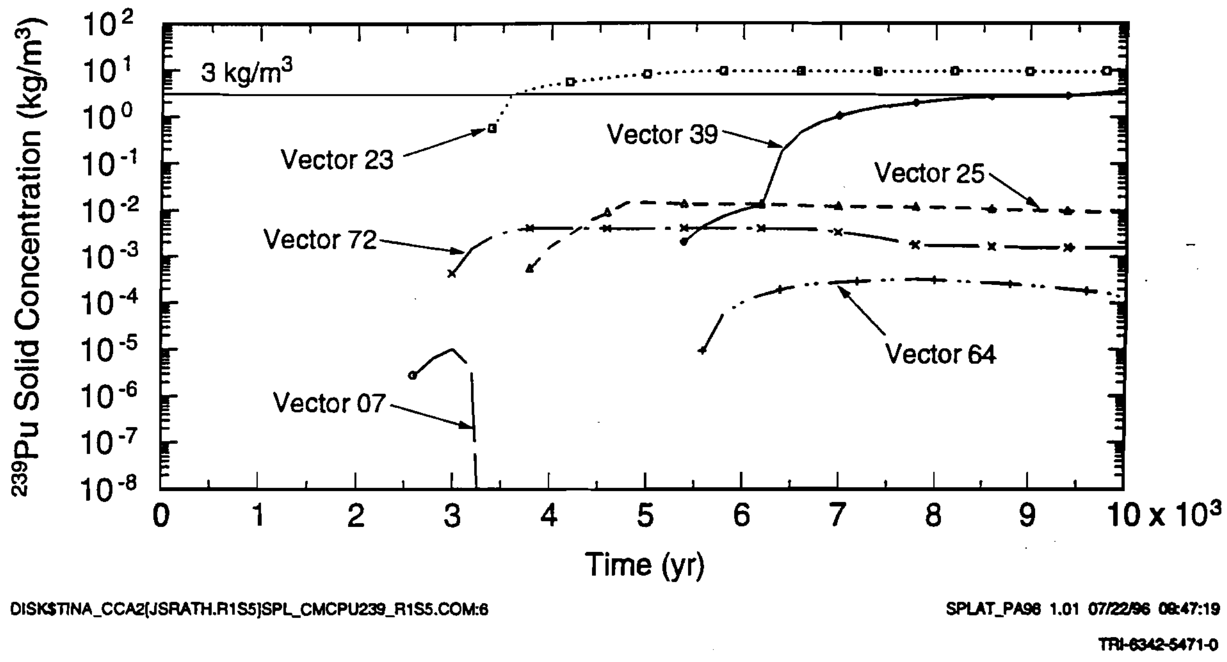

Figure 8. Solid concentration of plutonium from adsorption for R1S5 (replication 1, scenario 5).

17 sites/nm^2 (Kent et al., 1988, Table 3-1); these values are not reasonable for the sorptive capacity of the dolomite in the Culebra. Also, the Pu(IV) would be competing for the limited number of sorption sites with other radionuclides (e.g., Th[IV], which is assumed to behave identically to Pu[IV]) and other constituents in the waste, and thus would need to dislodge already sorbed material present in the Culebra brine reservoir.

Filtering of Colloid Material

Because the current solubilities of Pu(IV) and U(IV) are due partially to assumed adsorption on humic and biologic colloids and subsequent colloid mobility, the possible means of plutonium deposition in the Culebra (if the colloids escape from the repository) could be colloidal filtering. (A similar but related phenomenon would be de-adsorption from mineral colloid and diffusion and possible adsorption on minerals in the Culebra dolomite matrix; however mineral colloids are a small fraction of the total apparent solubility.) There is no reason to assume that colloids susceptible to filtering would remain unhindered during transit through salt pores within the repository or the borehole (see section on colloid filtering in the repository); however, to be consistent with the assumptions for the 1996 CCA, mineral and biologic colloids are assumed to have escaped and then be trapped in the Culebra. For the cases in which large releases of plutonium are calculated, the speculative high Pu(IV) solubilities in Salado brine were used. In these cases, mineral and biologic colloids form only 7% of the solubility. Perfect filtering of 7% of the maximum 100 kg results in 7.7 kg that must be filtered in less than 2.6 m^3. Although 7.7 kg is larger than the 2.2-kg minimum for spheres, it is less than the 13.4-kg limit suggested by the arguments presented in the section above (Figure 7). Therefore, colloidal filtering is unlikely to cause criticality by itself.

Precipitation of Fissile Material

Of the three mechanisms to concentrate actinides, only precipitation is known to have occurred to form large ore deposits. However, precipitation of fissile material is not at all ensured. Normally, precipitation requires a change in the water chemistry (i.e., the Eh or pH) from the existing chemistry. The existing chemistry in the repository will be extremely reducing, because the source of hydrogen gas is the reduction of water, as argued previously (i.e., the repository will lie along the line defining the stability of water in Figure 5). Therefore, the normal situation in which uranium ore bodies are formed through reduction of a soluble species does not apply, and more unusual situations must be hypothesized. One such situation is one in which a slightly soluble Pu(III) species (reduced by the conditions in the repository) reaches the Culebra and is oxidized to a slightly less soluble Pu(IV) species (i.e., either a Castile- or Salado-dominated brine is diluted and oxidized by the Culebra brine). The possibility of this situation occurring is remote, however, for several reasons. First, the Culebra brine does not contain many reductants or oxidants, which is consistent with the general inaccessibility over short times of trace iron and sulfate reductants in the dolomite. Thus, the water chemistry (Eh and pH) of the Culebra tends to equilibrate to the water chemistry of the solution added, even when the solution is greatly diluted (at least up to 100 to 1 dilution) (Figure 9). Furthermore, the change in solubility of the modes and medians of the distributions (Figure 1 and Table 2) is less than 0.5 order of magnitude. Finally, the solubility of Pu(III) is sufficiently low that a critical mass never reaches the Culebra in 10,000 yr.

A second situation is the dilution of Pu(IV) in a Salado-dominated brine to a Culebra-dominated brine (Figure 1).* In this case, the maximum calculated discharge of ^{239}Pu(IV) over 10,000 yr as calculated in the CCA must be considered, which is about 110 kg (simulation 23 in Figure 7). Therefore, to obtain a

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* A similar but noncredible situation is the reduction of Pu(IV) to Pu(III) in a Salado-dominated brine. The source of any reduction would be the Culebra brine, but the reduction could not occur without changing the fluid chemistry to a Castile-like brine.

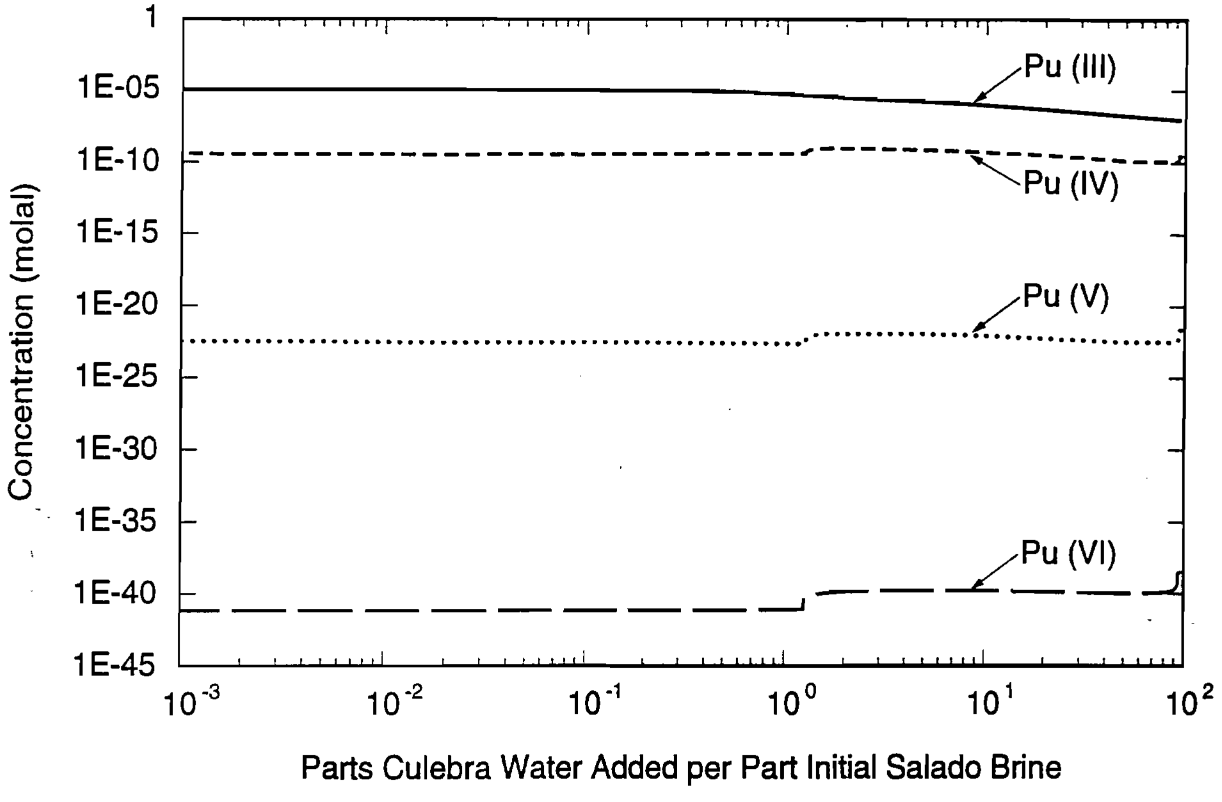

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Figure 9. Concentration of plutonium species in each oxidation state at various dilutions of Salado with Culebra brine as calculated by EQ3/6 assuming sufficient dilution so that Pitzer coefficients were not required (i.e., Brine A, which was used to conservatively model the Salado because of its high Mg concentration, was diluted in half.)

plutonium concentration of 3 kg/m^3 or greater (see Figure 2), assuming a single porosity medium, the volume of deposition of all the plutonium reaching the Culebra in 10,000 yr must be less than 37 m^3 (a sphere of about 4 m or an 8.25-m^2 area, assuming deposition throughout the 4-m thickness of the Culebra dolomite). When the Culebra is represented as a fractured medium, a small volume is also required because the fracture space available for precipitation of fissile radionuclides in the Culebra is limited near the WIPP repository. Assuming a fracture zone 0.8 m thick, the volume must be 22 m^3 or 27.5 m^2 to obtain a plutonium concentration of 5 kg/m^3 or greater (see Figure 3). Because the calculated flow fields for radionuclides migrating through the Culebra over 10,000 yr do not show a tendency to concentrate into a small area except at the intrusion borehole (Figure 10), once plutonium is dispersed into the Culebra it will be impossible to reconcentrate the 110 kg of plutonium. Thus, the only area in which a criticality may occur is at the borehole. Also, as seen in Figure 10, the zone in which dilution and potential precipitation could occur is too large for a critical concentration of fissile radionuclides after only 100 yr of discharge into the Culebra.* A simple conservative estimate of the volume of the dilution zone as two concentric circles results in a solid concentration an order of magnitude lower than the 3 kg/m^3 limit even for a total of 110 kg (over 10,000 yr) in vector 23.

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* Note that it takes more than 130 yr to release more than 2.2 kg of ^{238}Pu in vector 23.

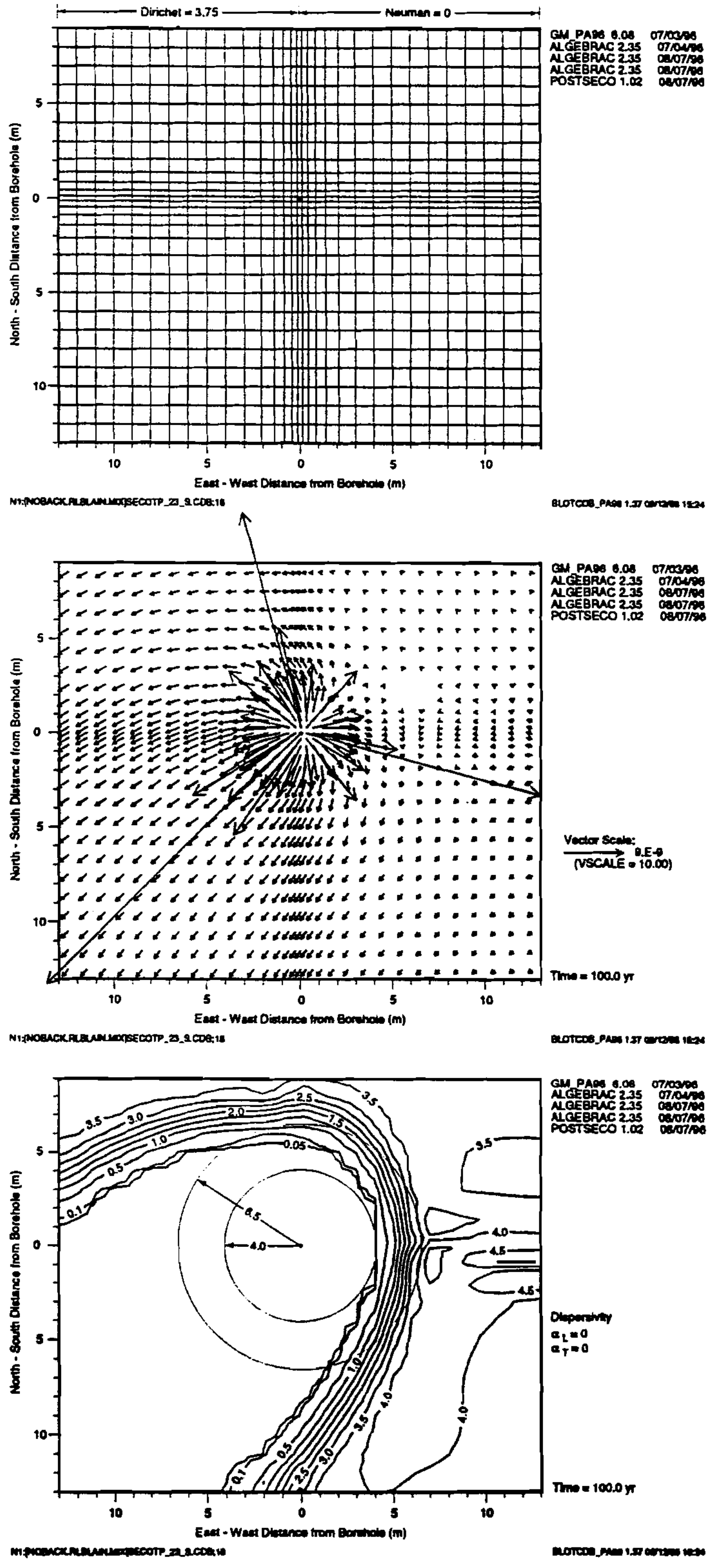

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Figure 10. *Mixing of brine from Culebra with liquid from borehole using discharge and flow field from vector 23 (a) refined numerical mesh, (b) calculated velocity field, and (c) concentration contours assuming background concentration in Culebra of 3.75 kg/kg.*

Another reason against radionuclides precipitating in a sufficient concentration concerns porosity. Along the flow path, the fraction porosity averages 10^{-3} as interpreted from tracer tests at the H-3 and H-11 hydropads (Sandia WIPP Project, 1992, Vol. 3). This fracture porosity, in combination with the density of the likely PuO_2 precipitate $\rho = 11{,}370$ kg/m^3) and the required minimum concentration of the plutonium* (5 kg/m^3, Figure 3), requires at least 44% of all minerals precipitated out of the solution to be PuO_2—unreasonably pure given the ionic strength of the Salado brine† and all the other constituents brought up from the repository along with the plutonium. Specifically, Th(IV) is assumed to behave identically to Pu(IV). Consequently, any change in the water chemistry or dilution of the solution of contaminated brine reaching the Culebra from the repository would occur over volumes larger than those that would permit a criticality. (That is, if precipitation occurred at all, it would be gradual over large areas and so significant, localized precipitation at a critical solid concentration would not occur.)

Consequences of a Criticality in the Repository

In general, the consequences of a ^{239}Pu criticality is actually beneficial because, after about 100 years following waste emplacement, the fissioning produces fission products with fewer EPA units (which are a surrogate for health risk) than those initially emplaced (Table 4). This is the reasoning behind the desire to use plutonium in nuclear reactors (or even transmute without extraction energy) by means of particle accelerators. In addition, the extent of fissioning is small compared to other situations. For example, the initial heat load of 137 kW from the CH and RH TRU waste (Table 3) gives a rough indication of the fission products in the waste and can be used to estimate an equivalent number of fissions represented by the waste. A heat load of 137 kW corresponds to ~28 MTHM of pressurized water reactor (PWR) spent fuel. Furthermore, 28 MTHM of PWR spent fuel with a burnup of 40,000 MWd/MTHM represents a total of 3×10^{27} fissions (Figure 11). The fissions (energy) possible from the 21 MTHM FGE in the WIPP repository are also ~10^{27} fissions. Furthermore, these values are four orders of magnitude less than the number of fissions represented by a 70,000-MTHM repository at Yucca Mountain.

Damage to Salt

The possibility of a nuclear explosion in a geological repository such as the WIPP, which will contain an average of only 14% fissile enrichment (Table 3), is far below the theoretical minimum of 35% enrichment (Murry, 1957, p. 182). In addition, the potential damage to the salt from a sudden assembly of fissile material is minor. The maximum energy release from prompt neutrons for aqueous accidents, as calculated by BetheTait analysis, is 6×10^{17} fissions or 18.7 MJ (Rechard et al., 1996a). This small amount of rapidly produced energy release per event would be unlikely to cause any significant damage either to the immediate rock, situated 655 m (2100 ft) below the surface at the repository horizon. Potential voids (camouflets) of <1.3 m radius would occur in the salt (Rechard et al., 1996a).

Consequences of a Criticality in the Culebra

The consequences of a criticality in the Culebra (far field), should one occur, would be analogous to the consequences of the Oklo natural reactor. These consequences include (a) generation of heat and (b) generation of additional fission products above those already being released from the repository.

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* The limit for pure PuO_2 is used rather than the limit for a 1:1 mixture of PuO_2 and UO_2 because in this hypothetical situation—in which a high Pu(IV) solubility in Salado brine is diluted to Pu(IV) in Castile-like brine—uranium solubility increases with dilution and would not be precipitated.

† Salado brine is used because the solubility of Pu(IV) is assumed to be so high in the Salado. In turn, this situation is responsible for the largest amounts of plutonium reaching the Culebra.

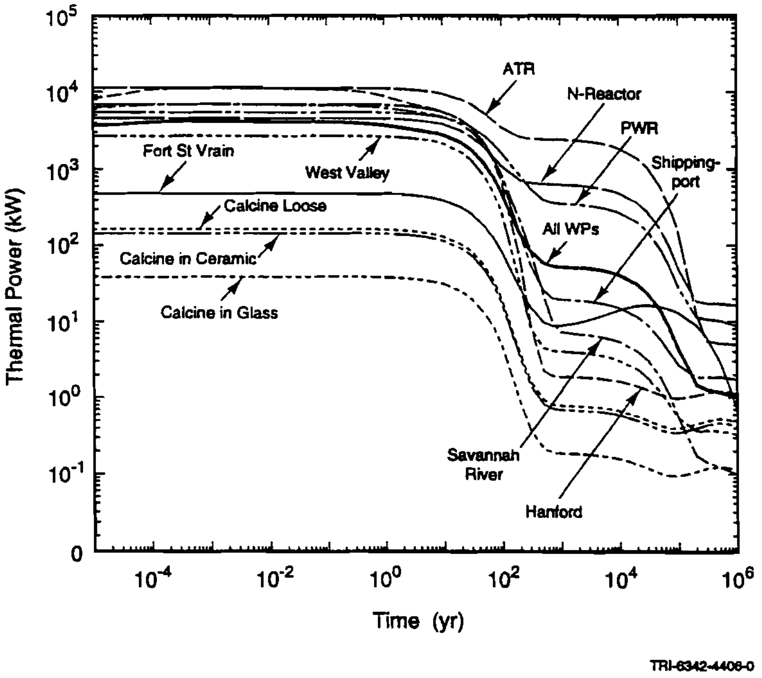

Figure 11. Thermal power decay history for spent nuclear fuel owned by the U.S. Department of Energy (DOE) (after Rechard, 1995, Figure 4-11, Vol. 2).

Amount of Heat Potentially Generated

The maximum amount of plutonium carried to the Culebra is 110 kg (Figure 7). The volume occupied by 110 kg of plutonium at a density of 3 kg/m^3 is ~37 kg. The amount of heat generated at Oklo has been estimated as 0.1 kW/m^3 in the natural reactors. Consequently, the power produced would amount to 3.7 kW. Consequently, the power produced would be much less than the initial heat load—137 kW—from the CH and RH TRU waste (Table 3).

Number of Fissions Possible in the Far Field over 10,000 yr

As described earlier, the initial heat load of 137 kW from the CH and RH TRU waste (Table 3) gives a rough indication of the fission products in the waste and can be used to estimate an equivalent number of fissions represented by the waste: 3×10^{27} fissions (Figure 11). The number of fissions from 28 MTHM of equivalent spent fuel roughly estimated above for the WIPP repository is two orders of magnitude greater than the 110 kg potentially transported to the surface because, if 110 kg undergo a similar 40,000-MWd/MTHM burnup, then ~10^{25} fissions would have occurred. Furthermore, the number of fissions is two orders of magnitude less than the number that occurred at Oklo and six orders of magnitude less than that represented by 70,000 MTHM of spent nuclear fuel for disposal in a commercial repository, e.g., the proposed Yucca Mountain site (Rechard et al., 1996a).

Damage to Dolomite

For a nuclear explosion to be feasible, many important thresholds must be reached. One such threshold is that the enrichment of fissile radionuclides must exceed 35% (Murry, 1957, p. 182). The fissile content in the repository is 14%; thus the fissile content must more than double between the repository and its entry into the Culebra. Consequently, an explosion is not considered feasible. Furthermore, the potential

Table 4. EPA units of fission products for ^{239}Pu after criticality in the repository*

EPA Unit	1.0000E+00
Release Limit	1.0000E+02
Activity (Ci)	1.0000E+02
Halflife (s)	7.5940E+11
No. of Atoms	4.0537E+24
Mass (kg)	1.6091E+00

Time (yr)	Sum EPA Unit**
0	1.1179E+01
10.	8.8538E+00
20.	7.0142E+00
30.	5.5583E+00
40.	4.4061E+00
50.	3.4940E+00
60.	2.7720E+00
70.	2.2003E+00
80.	1.7475E+00
90.	1.3888E+00
100.	1.1047E+00
110.	8.7943E-01
120.	7.0085E-01
130.	5.5921E-01
140.	4.4681E-01
150.	3.5757E-01
160.	2.8668E-01
170.	2.3031E-01
180.	1.8547E-01
200.	1.2127E-01
300.	1.8810E-02
400.	5.2756E-03
500.	2.2820E-03
1000.	3.9943E-04
2000.	3.5926E-04
3000.	3.5790E-04
4000.	3.5666E-04
5000.	3.5546E-04
6000.	3.5431E-04
7000.	3.5317E-04
8000.	3.5206E-04
9000.	3.5095E-04
10000.	3.4986E-04

* Calculation corresponds to initial quantity of 1 EPA unit of fissile material, ^{239}Pu

** Corresponds to sum of EPA units for all fission yield products damage to the dolomite from a sudden assembly of fissile material is minor. The maximum energy release from prompt neutrons for aqueous accidents, as calculated by BetheTait analysis, is 6×10^{17} fissions or 18.7 MJ (Rechard et al., 1996a). This small amount of rapidly produced energy release per event (~4.5 kg TNT [10 lbs]) would be unlikely to cause any significant damage to the dolomite 300 m below the surface in the Culebra. If tuff were used as an analog for dolomite, the potential void would have a radium less then 0.8 m (Rechard et al., 1996).

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Attachment A: Sanchez, 1996 (WIPP PA Meeting Minutes- July 19, 1996)

Attachment B: Rechard et al., 1996b (SAND96-0866) Influence of Backfill on Chemical Behavior within the Waste Isolation Pilot Plant (WIPP) Repository under Simplified Conditions

Sandia National Laboratories

Managed and Operated by Sandia Corporation
a Lockheed Martin Corporation
Albuquerque, New Mexico 87185-1328

date : July 22, 1996
to : Memo of Record
from : L.C. Sanchez, Org 6848, MS-1328, PH-(505)848-0685, Fax-848-0705

subject : **WIPP PA Meeting Minutes -- July 19,1996**

A meeting was held on July 19, 1996 / 1:00 pm with H.W. Papenguth (Org. 6832), K.M. Economy (Org. 6848), L.C. Sanchez (Org. 6848), J. Rath (Org. 6849) and S. Schremmer (Org. 6849). The topic of discussion was colloid transport and key comments at this meeting include the following:

Hans Papenguth indicated that as colloids are generated in the WIPP TRU-waste matrix region, they agglomerate in a dispersed manner within the vicinity at which they were generated. Since the TRU-waste matrix region becomes compressed/consolidated in the vertical dimension due to lithostatic stress of the host rock with time, they would be entrained (restricted to) in the TRU-waste matrix region because the TRU-waste matrix permeability (which is a measure of filter penetration efficiency for actinide transport [in solution, or as colloids] through the porous media) is very small.

The overall results is that there is no credible mechanism to increase the partial density/concentration of Pu239 or FGE (fissile gram equivalent) of other fissile radionuclides.

LCS:6848:lcs/(96-2117)

Copy to:
MS-1341, H.W. Papenguth [Dept. 6832]
MS-1328, K.M. Economy [Dept. 6848]
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Influence of Backfill on Chemical Behavior within the Waste Isolation Pilot Plant (WIPP) Repository under Simplified Conditions

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Abstract

One assurance measure under consideration for the Waste Isolation Pilot Plant (WIPP) is backfill. This report describes a parametric analysis of the conditions under which backfill would provide a possible means of changing the chemical environment to reduce solubility and provide sorptive media for radioisotopes. Although this study does not assume that backfills are necessary to meet compliance requirements, it does analyze the aspects of disposal system performance that could lead to unacceptable releases as a method for determining when backfill would be helpful (i.e., the most sensitive parameters are set at extremes or parametrically varied between extremes). In general, the report identifies possible "ok" and "marginal" conditions below a solubility of 10^{-7} *for plutonium,* 10^{-8} *for americium, and* 10^{-4} *for uranium at maximum values of the model parameters assumed for transport within the Culebra and the volume of brine from the hypothetical brine reservoir. The report also identifies backfill characteristics likely to mitigate potentially unacceptable releases. In general, a chemical backfill can reduce the solubility of the actinides by reducing the oxidation state, increasing the pH of the brine solution above 7, adding anions that form insoluble compounds, and removing organic chelators that tend to increase actinide solubility. While several chemicals or combinations of chemicals can produce these phenomena, this report examined the influence of lime, CaO or* $Ca(OH)_2$*. Collaborating previous studies, CaO and* $Ca(OH)_2$ *are successful, in theory, in raising the pH and thereby lowering the solubility of americium and neptunium (and, presumably, plutonium and uranium). This study concludes by identifying additional investigations for consideration.*

1. Introduction

The Waste Isolation Pilot Plant (WIPP) is a proposed underground disposal facility for transuranic waste located near Carlsbad, New Mexico. To comply with the Environmental Protection Agency's (EPA) regulation, *40 CFR Part 191—Environmental Radiation Protection Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes; Final Rule* (EPA, 1993), assurance measures may be incorporated into the design of the WIPP disposal system as a means of improving confidence in long-term compliance. Current assurance measures include DOE land ownership, proposed markers, and shaft seals. An additional assurance measure under consideration is the engineered barrier alternative, backfill. The remainder of this introduction describes the relationship of this study to previous work and the general approach of this study. In Chapter 2, the report describes the current behavior of the WIPP disposal system, based on simplified models, to identify possible "ok," "marginal," and "cautionary" conditions for which backfill with certain characteristics can improve confidence in long-term compliance of the WIPP. In Chapter 3, qualitative predictions are provided on the ability of a lime backfill to modify chemical conditions within the repository to reduce solubilities of the radioisotopes and provide a sorptive medium to inhibit migration. This study concludes by identifying additional investigations needed to provide a defensible basis for backfill performance (Chapter 4.)

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1.1 Background of Study

1.1.1 Previous Findings from Performance Assessment

Performance assessments (PAs) have been conducted for the WIPP since 1989. Although preliminary, the results have generally shown compliance of the WIPP disposal system with the EPA regulation, 40 CFR 191. In a sensitivity analysis of the results from these assessments, the solubility of the radioisotopes has been among the top ten most important parameters (Table 1). For example, in the 1992 performance assessment, solubility (of the six radioisotopes sampled) was ranked fifth in overall importance (WIPP PA Dept., 1993, Table 9-3). Hence, engineered alternatives that reduce radioisotope solubility can help to provide significant improvement in the performance of the disposal system.

Table 1. Ranking As Related to 40 CFR 191 of Parameters Sampled in 1992 Performance Assessment. Results apply only to human intrusion scenarios (from WIPP PA Dept., 1993, Table 9-3)

Critically important parameters (listed in order of importance)
- 1. Intensity of drilling in Poisson analytic function (λ)
- 2. Permeability of intrusion borehole (K_{bore})

Very important parameters (listed in order of importance)
- 3. Permeability of halite in Salado Formation (K_{halite})
- 4. Permeability of anhydrite in Salado Formation ($K_{anhydrite}$)
- 5-10. Solubility of radioisotopes (S_{Am}, S_{Np}, S_{Pu}, S_{Ra}, S_{Th}, and S_U)
- 11. Spacing of fractures in Culebra dolomite (B)
- 12-17. Adsorption coefficients of radioisotopes in Culebra matrix (Kd_{Am}, Kd_{Np}, Kd_{Pu}, Kd_{Ra}, Kd_{Th}, and Kd_U)

Important parameters (listed in order of importance)
- 18. Transmissivity field of the brine aquifer in the Culebra dolomite
- 19. Porosity of Culebra dolomite matrix (ϕ_m)

Less important parameters (rank approximately equal)
- a. Fracture porosity in Culebra Dolomite (ϕ_f)
- b. Adsorption coefficients of radioisotopes in hypothesized clay of fractures in Culebra dolomite
- c. Porosity of hypothesized clay lining fractures in Culebra dolomite
- d. Fraction of space occupied by hypothesized clay in fractures of Culebra dolomite
- e. Recharge from climatic change
- f. Pressure of hypothesized brine reservoir in Castile Formation
- g. Storativity of hypothesized brine reservoir in Castile Formation
- h. Area of repository underlain by hypothesized brine reservoir in Castile Formation
- i. Initial water saturation of waste
- j. Volume fraction of metals and glass in waste
- k. Volume fraction of combustibles in waste
- l. Gas-generation from corrosion under humid conditions
- m. Gas-generation from corrosion under inundated conditions
- n. Gas-generation from biodegradation under humid conditions
- o. Gas-generation from biodegradation under inundated conditions
- p. Stoichiometry of corrosion
- q. Stoichiometry of biodegradation
- r. Porosity of anhydrite layers in Salado Formation
- s. Porosity of disturbed halite in Salado Formation
- t. Far-field brine pressure in Salado Formation
- u. Residual brine saturation in Salado Formation
- v. Exponent on Brooks-Corey relative permeability model
- w. Index for choosing between Brooks-Corey and van Genuchten-Parker relative permeability model
- x. Residual gas saturation in Salado Formation in Brooks-Corey relative permeability model

In the 1992 performance assessment for the WIPP, a backfill of crushed salt was included in the baseline condition. However, because later data indicate that crushed salt as a material not only does not significantly improve the disposal system performance but also generates some operational concerns (such as salt dust, which can disrupt radiation monitors), the current baseline condition does not include backfill. This report, however, is proposing that conditions might exist in which other backfill materials, such as lime, be considered as an engineered alternative because of their potential for improving performance by reducing solubility of actinides.

1.1.2 Previous Supplementary Backfill Studies

Historically, the policy of backfill at the WIPP has been subject to debate and has changed as the understanding of the long-term performance of the disposal system has evolved. Several investigations evaluating the long-term performance and short-term operational aspects of the use of backfill at the WIPP have been conducted. Key investigations dealing with the long-term performance aspects of backfill include

- Preliminary Evaluation of Potential Engineered Modifications for the WIPP (Butcher, 1990)
- Final Report of the Engineered Alternatives Task Force (DOE, 1991).

In the following two sections, these investigations are summarized with respect to their consideration of backfill.

Preliminary Evaluation of Potential Engineered Modifications for the WIPP. Butcher (1990) discusses potential effects of the addition of backfill and backfill additives on long-term performance, but no analyses are presented in the report. The discussions include the use of clay for brine absorption and radioisotope adsorption. Lime was considered as a backfill additive for its ability to react with microbially generated CO_2 to form calcite ($CaCO_3$), thus removing CO_2 from the gas phase.

Engineered Alternative Task Force Report (EATF). The Engineered Alternative Task Force (DOE, 1991) evaluated the effects of backfill on long-term performance using a simplified performance model that simulated undisturbed and human intrusion scenarios. The model calculated changes in normalized cumulative releases offered by engineered alternatives relative to the baseline repository design that was current at the time. Specific backfill options considered by the EATF included crushed salt (baseline case), no backfill, cementitous grout, and a salt aggregate grout. One alternative incorporated salt backfill as barriers to flow to provide compartmentalization of the waste.

Results indicated that crushed salt had only a minor effect on the pressurization history of the storage rooms, and also had only a minor effect on the consequences of human intrusion by providing a slight reduction in the permeability of the room contents. Cementitous grout backfill had a more substantial effect on consequences of human intrusion by reducing permeability. Concerns were raised regarding the longevity of a cementitous grout in the repository environment. These concerns with longevity were eased by the use of a salt aggregate grout (a cementitous grout with a very high percentage of crushed Salado salt aggregate) that would maintain plasticity. This material was assumed to consolidate under lithostatic load to maintain very low permeability without fracturing, and assumed to be chemically compatible with the repository environment.

The most favorable alternative was the compartmentalization option. The objective of this option was to segregate a known quantity of curies in an isolated compartment and (1) set a limit on the maximum quantity of curies that could be released from any single human intrusion event and (2) significantly reduce the probability of an E1E2 event.*

The report noted, but did not model, that Portland-type grouts would raise the pH of brine which, in turn, would reduce radioisotope solubilities. Positive attributes associated with lime that were noted (but not modeled) included its ability to (a) remove CO_2 from the gas phase (as noted previously by Butcher [1990]), (b) absorb brine by hydration reactions, and (c) reduce microbial gas generation and radioisotope solubilities by raising the pH.

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* The E1 scenario represents a borehole through the repository into a pressurized brine pocket; the E2 scenario represents a borehole through the repository but not into a pressurized brine pocket; and the E1E2 scenario represents a borehole through the repository into a pressurized brine pocket and a second borehole into the repository.

1.1.3 Engineered Alternatives Cost/Benefit Study (EACBS)

Section 14 (d) of 40 CFR 191 states "Disposal systems shall use different types of barriers to isolate the wastes from the accessible environment. Both engineered and natural barriers shall be included." To date, the WIPP disposal system includes engineered seals in all shafts to meet this engineered barrier requirement. As mentioned in Section 1.1.1, this prudent barrier has been sufficient to demonstrate compliance.

While 40 CFR 191 requires the use of engineered barriers, it does not specify how many or what kinds of engineered barriers must be used. In the draft version of 40 CFR 194 (EPA, 1995), which is the regulation that the EPA has proposed to implement 40 CFR 191, the EPA suggested that the following criteria be considered when evaluating engineered barrier alternatives (40 CFR 194, Section 44):

1. Ability to prevent or delay movement of water or radioisotopes
2. Public and worker exposure
3. Ease of removing waste from the WIPP repository
4. Transportation risk
5. Reduction of uncertainty in the WIPP compliance assessment
6. Public confidence in the WIPP disposal system performance
7. Total system costs and estimates of schedule impact to U.S. Department of Energy (DOE) complex
8. Impacts on other DOE waste disposal programs
9. Effects on mitigation consequences of human-initiated processes or events.

Hence, EPA included other factors for consideration in addition to performance. For example, an alternative that improves the performance of the site but drastically affects the health of workers and is very costly would not necessarily be chosen. At the request of the U.S. Department of Energy, Carlsbad Area Office (DOE/CAO), the Westinghouse Waste Isolation Division (WID) examined various engineered alternatives against the above criteria.

In October 1995, WID reported on an evaluation of a set of engineered barrier alternatives for the WIPP in the Engineered Alternatives Cost/Benefit study (EACBS) (WID, 1995a). In this study, a set of 14 engineered alternatives (EAs) was evaluated with respect to the nine criteria listed above. An original list of 109 alternatives had been first narrowed to 53 by the Engineered Alternatives Screening Working Group (EASWG), which used a screening process based on regulatory and technical feasibility (WID, 1995b). This list was further reduced to the working set of 14 alternatives, based on a prioritization process (WID, 1995c), and included backfills, supercompaction, shred and clay, and plasma arc processing. This prioritization process examined effectiveness in four categories: gas generation, actinide solubility, permeability, and shear strength.

For each of the 14 engineered alternatives, the EACBS produced a mix of quantitative and qualitative information as a response to the nine factors. Simulations of the long-term performance of the disposal system were performed using an updated version of the same model that was used for the EATF (DOE, 1991). In its comparisons, the EACBS did not use all properties of the engineered alternatives in question; for example, the sorptive capacity of clay was not used (and so was explored in this report). Moreover, the results of the EACBS study suggested that a number of criteria were non-discriminatory (Figure 1-1 and Appendix A). Specifically, the alternatives' effect on public acceptance, public health risks, worker health at the generator sites, final closure schedule, waste removal capability, transportation costs, and impact on other waste programs did not differ significantly among the options, and so all could be removed as primary decision factors. The final primary discriminating factors were long-term compliance confidence (as measured by cuttings and water release scenarios), worker health at the WIPP site, storage and treatment system costs, placement and backfill system costs, and first waste placement schedule. Given these results, DOE/CAO decided that backfill could be considered as a preferred alternative in its submission for the compliance application. However, because the EACBS study did not define all of the backfill options in detail, a further study of backfill characteristics and its effect on repository performance was recommended. This document reports on a portion of the recommended study.

Identification		Engeneered Alternatives		Decision Criteria In Draft 40 CFR 191								
Seq. No.	Engineered Alternative Case #	Additional Waste Processing?	Waste Backfill?	Cuttings Scenarios Confidence	Water Scenarios Confidence	Public Health Risk	Worker Health Risk	Disposal System Costs	Other Disposal System Impacts	WIPP Schedule	Waste Removal Capability	Public Acceptance
1	Baseline-1	None	None	○	○	○	○	○	○	○	○	○
2	33-1		Sand+Clay	○	○	○	○	○	○	○	○	○
3	35a-1		Salt Grout	◓	○	○	○	○	○	○	○	○
4	35b-1		Cement Grout	◓	○	○	○	○	○	○	○	○
5	111-1		Clay	○	○	○	○	○	○	○	○	○
6	83-1		Lime (CaO)	○	◓	○	○	○	○	○	○	○
7	1-1	Supercompaction of all waste, except sludges	None	◓	○	○	◒	◒	◒	●	◓	○
8	77a-1		Salt Grout	◓	○	○	◒	◒	◒	●	◓	○
9	77b-1		Clay	◓	○	○	◒	◒	◒	●	◓	○
10	77c-1		Sand+Clay	◓	○	○	◒	◒	◒	●	◓	○
11	77d-1		Lime (CaO)	◓	◓	○	◒	◒	◒	●	◓	○
12	6-1	Shred & compaction	None	○	○	○	◒	◒	◒	●	◓	○
13	94a-1	Sludges cemented, other wastes shredded and packaged with clay	None	◓	○	○	◒	●	◒	●	○	○
14	94b-1		Sand+Clay	◓	○	○	◒	●	◒	●	○	○
15	94c-1		Cement Grout	◓	○	○	◒	●	◒	●	○	○
16	94d-1		Salt Grout	◓	○	○	◒	●	◒	●	○	○
17	94e-1		Clay	◓	○	○	◒	●	◒	●	○	○
18	94f-1		Lime (CaO)	◓	◓	○	◒	●	◒	●	○	○
19	10-1	Plasma	None	◎	◎	○	◒	●	◓	●	○	○

◎ Performance is significantly better than the corresponding baseline performance.

◓ Performance is marginally better than the corresponding baseline performance.

○ Performance is approximately the same as the corresponding baseline performance.

◒ Performance is marginally worse than the corresponding baseline performance.

● Performance is significantly worse than the corresponding baseline performance.

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Figure 1-1. General results of the Engineered Alternatives Cost/Benefits Study (WID, 1995a, after Figure 5-4).

1.2 Scope of Report

The general purpose of the proposed backfill studies, of which this report is a part, is to examine the conditions under which an engineered barrier might be helpful and how backfill materials might contribute. The primary decision criterion for "helpful" in this study was enhanced performance. Enhanced performance might mean that the backfill could fulfill one or more of the following functions:

1. Reduce the solubility of the radioisotopes.
2. Increase the retention of radioisotopes in the repository through sorption on backfill.
3. Impede brine flow through the repository.
4. Increase the shear strength of the waste.

Furthermore, a complete decision analysis of a backfill as an engineered alternative would consider the following alternatives, alone or in combination:[†]

1. Type of backfill material, e.g., crushed salt, concrete, cement grout, lime (CaO or $Ca[OH]_2$), magnesium (Mg or $Mg[OH]_2$), phosphates (Na_3PO_4), vanadium, or clay.
2. Design configuration, i.e., how the waste is emplaced. For example, the backfill could (a) be placed in the drums, (b) be placed simply on the floor, (c) surround the drums, or (d) serve as an outer barrier layer to each room or panel in which waste is emplaced. The placement could be a monolithic structure, such as a dike, or individual blocks.

Because of time considerations, however, this initial report focuses primarily on the first aspect of performance, solubility. The report also focuses on one type of backfill material, lime, either as CaO or $Ca(OH)_2$ because of the data in the EACBS regarding its ability to improve performance for situations involving groundwater releases (see Figure 1-1). However, a small effort was made to determine the influence of a clay backfill on retention of radioisotopes in the repository. Hence, the purpose of this report is to confirm, through chemical modeling, the positive role of lime and clay as a chemical backfill.

The first step in this report was to define a baseline condition to establish current behavior of the WIPP disposal system, along with potential deviations from this baseline condition. The performance metric was the cumulative release of three radioisotopes, ^{239}Pu, ^{241}Am, and ^{233}U, which represented the 10 radioisotopes normally considered important with regard to releases over the long term. The result, the predicted release, is expressed as the fraction of the EPA release limits, as defined in 40 CFR 191, Appendix A, and presented as 0.01, 0.1 and 1 contours in Chapter 2. These contours define "ok" "marginal," and "cautionary" regions with regard to radioactive release.

The second step in this report was to define the solubility of the radioisotopes in the repository in the presence of a lime backfill and the benefits of sorption on a clay backfill. As explained in Chapter 3 and Appendix B, actinide solubility was evaluated semi-theoretically using the software currently in place for the WIPP compliance calculations and the items of data currently available from the experimental program on the actinide solubilities. Because the experimental data are far from complete, this aspect of the study is far more qualitative than quantitative.

The identification of these conditions, together with the characterization of the performance of backfill, provides information about whether backfill can benefit compliance. Further analysis that can be conducted as more data become available and additional investigations that may be needed to provide a defensible basis for backfill performance are discussed in Chapter 4. Continued studies of this type, together with simple experiments, would likely be sufficient to identify the optimum chemical or chemicals for performance and operational safety issues, should the backfill be used solely as an assurance measure. However, if backfill would be considered essential to the compliance certification application because of possible new requirements, more extensive experiments would be required to provide a defensible basis for backfill performance.

[†] Waste form, i.e., the waste either as is (untreated) or treated (where cementing sludges, supercompaction, or vitrification are examples of treated waste forms) was examined in the EACBS, as described in Section 1.1.3.

2. Results of Parametric Analysis

The results from determining releases from a median baseline condition and several deviations from this condition are presented below. The results show the influence of solubility on releases for various transport conditions in the Culebra. Appendix B provides details on the models used.

2.1 Methodology of Study

Potential radioisotope releases from a geologic repository are a function of the physical, chemical, and geohydrologic characteristics of the natural barriers of the disposal system and the waste inventory. Waste acceptance criteria and engineered barrier alternatives influence calculated releases, and both can be used to limit releases if the existing disposal system is at some risk of failing to meet release requirements. For this study, the waste acceptance criteria (and thereby the waste inventory) is assumed fixed, and the emphasis is on an engineered backfill alternative.

While a formal performance assessment of the WIPP for the compliance application will use many sophisticated submodels of the disposal system in a stochastic simulation, only two simplified conceptual models were developed in this parametric study, based on the codes PANEL and SECOTP (see Appendix B). For the two models, four different groups of parameters from Table 1 (Chapter 1) were considered to dominate releases:

1. Uncertainty in the range of solubilities for actinides in the disposal room (Items 5-10).
2. Volume of brine that could flood the disposal system on intrusion (Items 2-4, f, g, r, s, and t).
3. The relationship of advection and diffusion between in situ fractures and the dolomitic matrix (Items 11, 18, 19, a, and e).
4. Degree to which actinides will be sorbed in the Culebra if released from the disposal room (Items 12-17).

As described further in the next two sections, the first two groups apply to parameters for PANEL and the last two groups apply to parameters for SECOTP2D.

2.1.1 Parameter Sets for PANEL

The entire repository was modeled as the accessible volume, and the pore volume was a constant of 40,000 m^3 (9% of initial unfilled volume) that was conservatively assumed to be filled with brine at time zero. The brine flow through the repository was varied in the study, being a constant of 0.1, 1, and 10 m^3 per year. These data resulted in integrated releases of brine of 1000, 10,000, and 100,000 m^3 over the 10,000-year period. These correspond to a small E2 flow, a large E2 or small E1 flow, and a large E1E2 flow, respectively.

Other important inputs are the inventory of the radioisotopes and their corresponding solubility. The inventory is from the draft of the second revision of the Transuranic Waste Baseline Inventory Report (TWBIR) as described in Appendix B. Solubilities were varied parametrically from 10^{-8} to 10^{-3} moles per liter (M). This solubility range includes solubilities of interest. At a solubility > 10^{-9} M, violation of the release limits of 40 CFR 191 was thought to be unlikely, based on earlier performance assessments. At solubility > 10^{-2} M (for all actinides), violation of the release limits was felt to be fairly certain using the simplified models.

2.1.2 Parameter Sets for SECOTP2D

In this report, five model sets were used to represent conditions in the Culebra to reflect current uncertainty in data ranges. The models include conditions that reflect (1) the median values from the 1992 WIPP PA calculations, (2) reduced matrix porosity to observe the effect of low matrix diffusion, (3) reduced number of fractures, (4) reduced porosity and number of fractures, and (5) prevention of diffusion. The hydrologic transport parameters are shown in Tables 2 and 3. Each of the five parameter sets was run with the actinide concentrations obtained from PANEL and retardation values in the Culebra dolomite calculated from K_ds ranging from 10^{-2} to 10^{2} (ml/g).

Table 2. Culebra Hydrological Transport Parameters

	Set 1	Set 2	Set 3	Set 4	Set 5
One-half fracture spacing, [B]	20 cm	20 cm	2800 cm	200 cm	400 cm
Fracture porosity, $[\phi]_f$	0.001	0.001	0.001	0.001	0.05
Matrix porosity, $[\phi]_m$	0.139	0.01	0.139	0.04	0.005

Table 3. Other Culebra Hydrologic Transport Parameters Kept Constant at Median Values

Longitudinal dispersivity	100 m
Transverse dispersivity	10 m
Tortuosity	0.12

The transport conceptual model used a uniform velocity field with a transport distance equal to the average of distances transversed in the 1992 WIPP PA. Uniform Darcy velocities of 10^{-8}, 10^{-9}, and 10^{-10} m/s were used. (These velocities are converted in the code to an average linear velocity by dividing by the fracture porosity—0.001 in the first four models.) These values of velocity were chosen as representative of the average of the velocities used in the 1992 WIPP PA calculation and a bounding velocity obtained when screening the features, events, and processes (FEPs). The average velocity along the travel path of a particle released from the source injection point to the land-withdrawal boundary for the 1992 WIPP PA calculation ranges from 10^{-9} to 10^{-10} for the 70 transmissivity realizations. The value of 10^{-8} for Darcy velocity was used as a bounding case. This number was obtained from information acquired through the FEP screening process to evaluate the effect of climate on the flow field in the Culebra, FEP NS-8B (SWCF-A:1.1.6.3; PA; QA:TSK:NS-8B). In this FEP, the maximum climate condition applied produced a flow rate of about 3×10^{-8} m/s along the path of a particle released for the source injection point.

2.1.3 Caveats on Baseline Modeling

Although this study used models based on those for the WIPP performance assessment (described in Appendix B), several important changes in the models and analysis occurred that should be restated. First, the simulation is not stochastic; also, parameter values that cause adverse conditions are combined, irrespective of the probability that this combination will occur, to produce severe conditions in order to determine if a backfill could moderate the severe conditions. For example, a high solubility and a high brine volume velocity through the repository were combined (Parameter Set 5) even though the solubility could be lowered by the pH of the high volume of brine flowing through the repository. Furthermore, no accounting was made of the amount of CO_2 generated.

Second, the conceptual model for fluid flow in the Culebra dolomite was changed to uniform flow. Furthermore, the maximum fracture velocity used was 10^{-5} m/s (~300 m/yr), which is an extreme velocity as noted above. For the purposes of this analysis, which is to make relative comparisons, these changes to Culebra transport are not important, but the changes are very important for making absolute comparisons. Thus, evaluations as to whether the WIPP disposal system complies with the EPA Standard, 40 CFR 191, cannot be made from these results.

2.1.4 Description of Variables and Graphs

In this analysis, the following parameters were varied: volume of brine flowing through the repository, solubility of radioisotopes in the repository, spacing of fractures in the Culebra, and porosity of the fractures and the matrix in the Culebra. After these values were parametrically varied, the calculated releases of three isotopes (^{239}Pu, ^{241}Am, and ^{233}U) were normalized by the release limits in 40 CFR 191. For this analysis, the resulting space of radioisotope releases were displayed versus solubility and adsorption partition coefficient in the Culebra, with all other parameters held constant. Solubility and adsorption partition coefficient were selected because they are currently being evaluated in experimental programs; in addition, solubility is a parameter that can be directly affected by backfill.

Because the isotope releases are normalized by the release limits in 40 CFR 191, the results are shown as contours that are a fraction of the release limits (Figures 2-1 through 2-5). To avoid cluttering the graphs, three contours are plotted: 1, 0.1, and 0.01 (i.e., 100%, 10% and 1% of the EPA release limit for that radioisotope) that roughly define regions that are "cautionary," "marginal," and "ok." (The terms "compliance" and "noncompliance" are avoided because the conceptual models, as explained above under Caveats and further in Appendix B, are greatly simplified versions of the models that will be used in the final WIPP PA and, more important, the probability of adverse combinations of modeling parameters was not evaluated here.) Thus, these plots show which combinations of solubility and K_d will be "ok" (white) meaning the fraction is low enough that an engineered alternative is not needed for assurance, and which combinations are "cautionary" (dark grey), meaning an engineered alternative such as a backfill might provide additional assurance. For the "cautionary" cases, a backfill can provide additional assurance by changing the solubility or providing additional sorption, thus reducing the predicted release. Note that this predicted release measure is somewhat similar to the Measure of Relative Effectiveness[‡] used in the EACBS study; however, the ratios are not summed over all radioisotopes in this study because there is significant difference in the release percentages among the different radioisotopes.

2.1.5 Discussion of Results

In general, Figures 2-1 through 2-5 identify "ok" and "marginal" conditions in almost all cases if the solubility of plutonium remains below 10^{-7} M, the solubility of americium remains below 10^{-8} M, and the solubility of uranium remains below 10^{-4} M. Because the solubility limit for uranium is so high and because such a high proportion of the uranium present is ^{238}U, uranium solubility is not likely to be critical in meeting the release limits and is not discussed further here.

The probability of reaching the extreme conditions (e.g., maximum climatic change to obtain maximum fracture velocities in the Culebra combined with maximum solubility) is likely low. Figures 2-1 through 2-5 show that a high but more reasonable bound on fracture velocity of 10^{-6} m/s (30 m/yr) raises the solubility limit for "ok" and "marginal" conditions by an order of magnitude for both Pu and Am while still using the E1E2 discharge of 10^4 m^3 per 10^4 yr. The solubility raises another order of magnitude to 10^{-5} M and 10^{-6} M for Pu and Am, respectively, for a discharge of 10^4 m^3 per 10^4 yr, and solubility raises another order of magnitude for both Pu and Am for a discharge of 10^3 m^3 per 10^4 yr. Based on these results, the goal for the backfill was set to maintain the solubility for plutonium and americium below 10^{-5} M for use in the next step of the study, as described in Chapter 3.

Although not directly applicable to the backfill, the curves show "ok" and "marginal" conditions for a partition coefficient (K_d) in the Culebra greater than 100 for plutonium, a K_d of 1 for americium, and K_d of 10^{-2} for uranium, regardless of other transport parameters of the Culebra and the solubility of the actinides, and provided the fracture velocity in the Culebra remained below 10^{-6} m/s (~30 m/yr). Hence, for a large discharge through the repository, adsorption in the Culebra is of far less influence than solubility.

[‡] The EACBS used the Measure of Relative Effectiveness as a performance measure, which was defined as the ratio of the cumulative release of radioisotopes for an engineered alternative to the release under baseline conditions. Thus, a smaller number is better. The MRE was measured for each engineered alternative, under E1, E2, and E1E2 scenarios, for both groundwater and cuttings pathway releases. The backfill options had MREs mostly in the 40%-95% range, indicating marginal improvements.

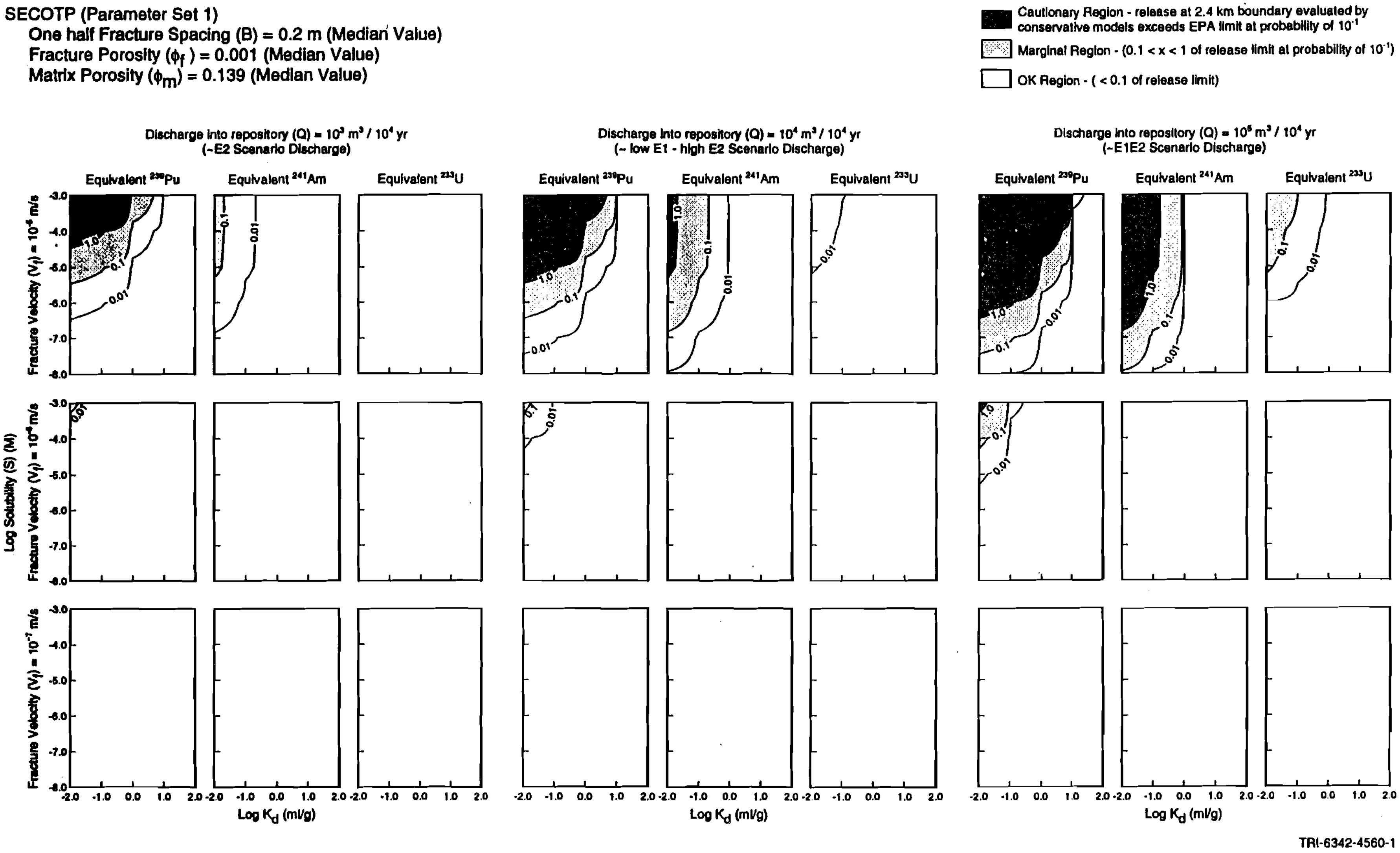

Figure 2-1. Variation of normalized releases of plutonium, americium, and uranium as their solubility and adsorption in Culebra dolomite, and fracture velocity vary for Parameter Set 1 (a one-half fracture spacing of 0.2 m, a fracture porosity of 0.001, and a matrix porosity of 0.139), with a repository discharge of (a) 10^3 m^3/10^4 yr, (b) 10^4 m^3/10^4 yr, and (c) 10^5 m^3/10^4 yr.

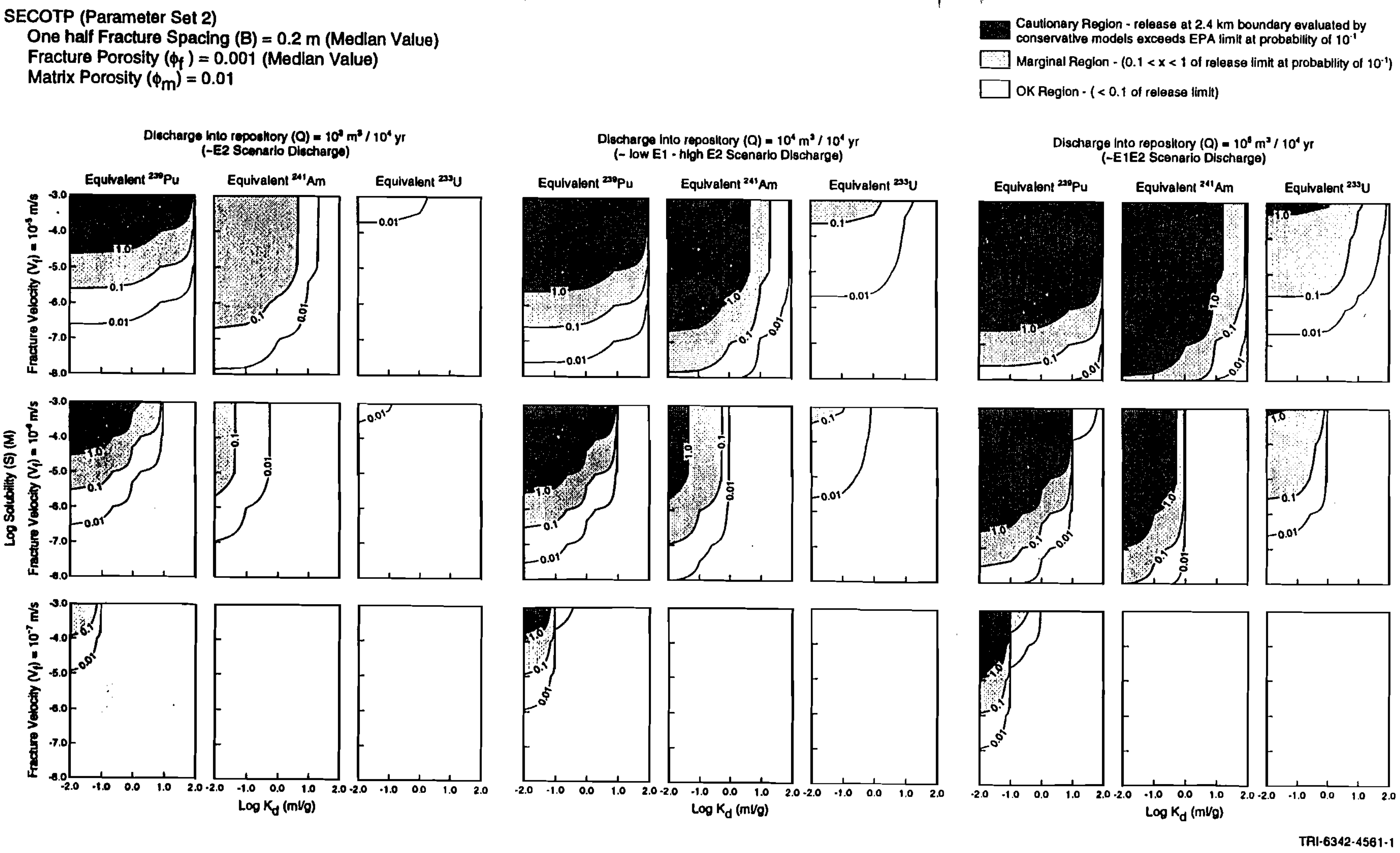

Figure 2-2. *Variation of normalized releases of plutonium, americium, and uranium as their solubility and adsorption in Culebra dolomite, and fracture velocity vary for Parameter Set 2 (a one-half fracture spacing of 0.2 m, a fracture porosity of 0.001, and a matrix porosity of 0.01), with a repository discharge of (a) 10^3 m^3/10^4 yr, (b) 10^4 m^3/10^4 yr, and (c) 10^5 m^3/10^4 yr.*

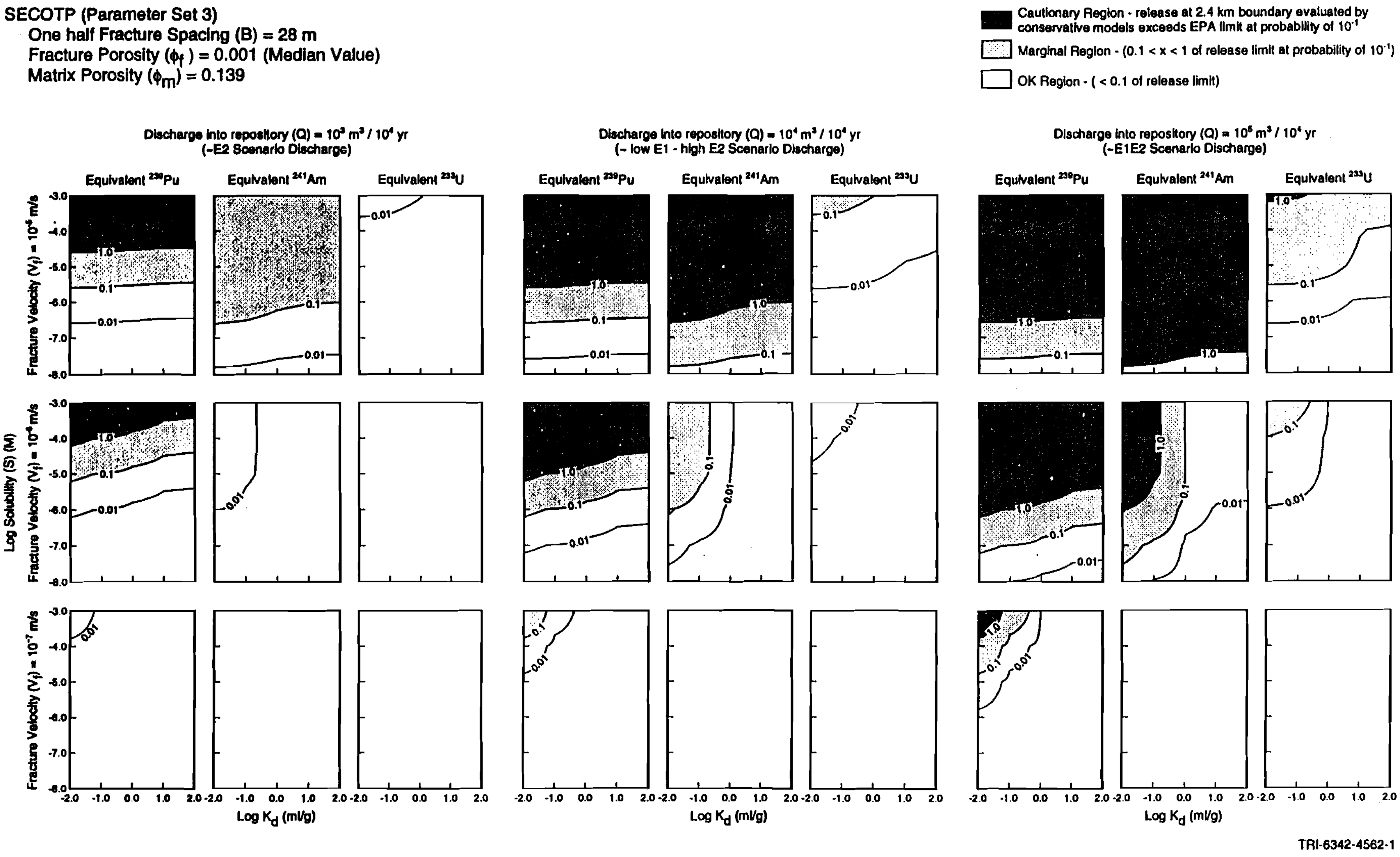

Figure 2-3. *Variation of normalized releases of plutonium, americium, and uranium as their solubility and adsorption in Culebra dolomite, and fracture velocity vary for Parameter Set 3 (a one-half fracture spacing of 28 m, a fracture porosity of 0.001, and a matrix porosity of 0.139), with a repository discharge of (a) 10^3 $m^3/10^4$ yr, (b) 10^4 $m^3/10^4$ yr, and (c) 10^5 $m^3/10^4$ yr.*

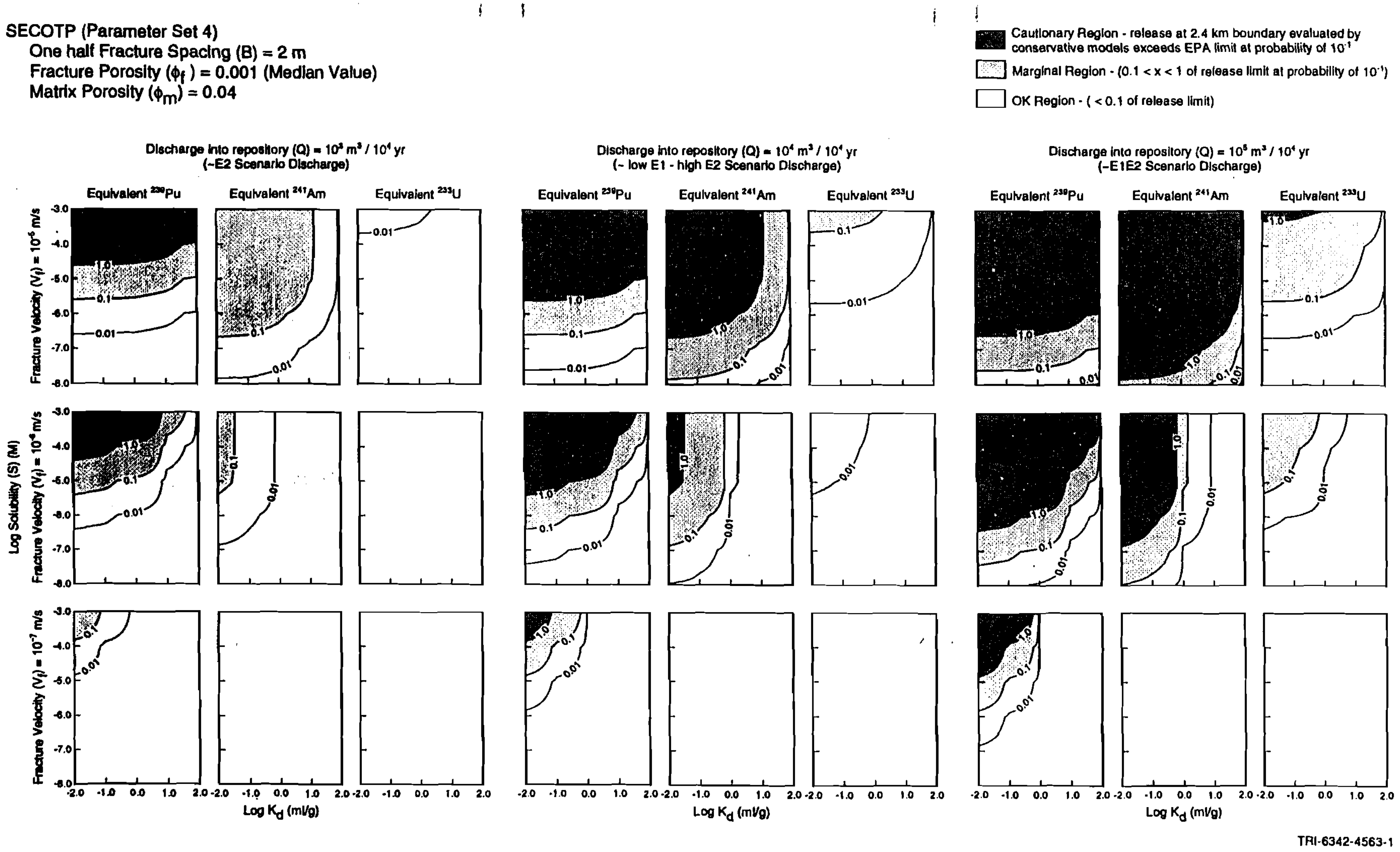

Figure 2-4. Variation of normalized releases of plutonium, americium, and uranium as their solubility and adsorption in Culebra dolomite, and fracture velocity vary for Parameter Set 4 (a one-half fracture spacing of 2 m, a fracture porosity of 0.001, and a matrix porosity of 0.04), with a repository discharge of (a) 10^3 m^3/10^4 yr, (b) 10^4 m^3/10^4 yr, (c) 10^5 m^3/10^4 yr.

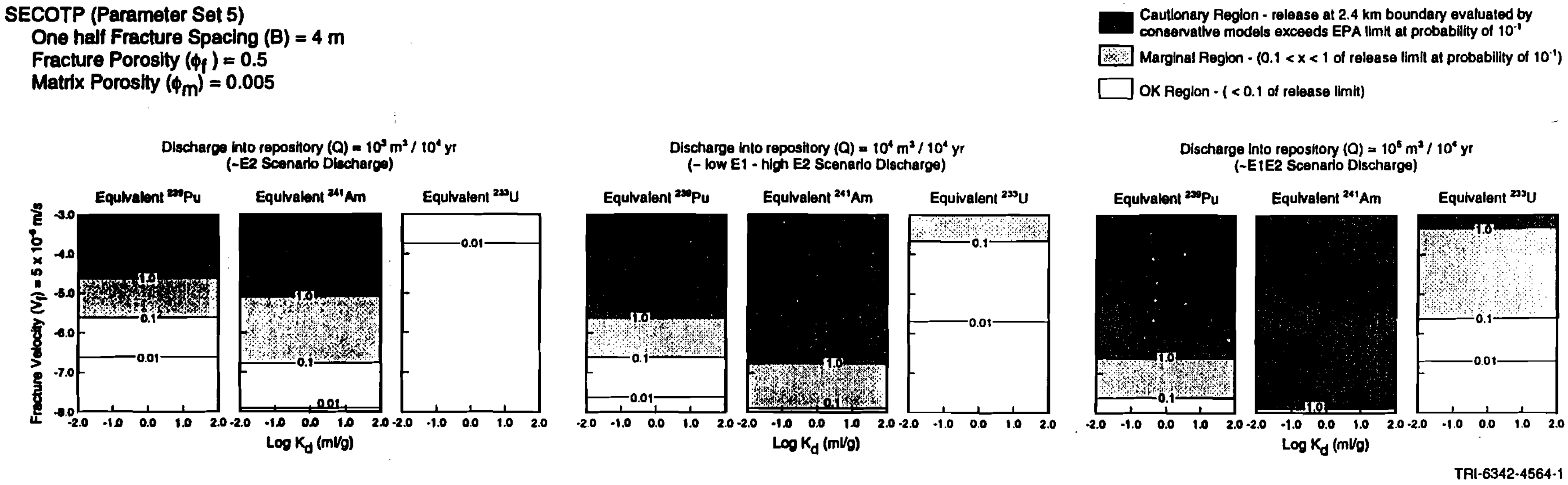

Figure 2-5. Variation of normalized releases of plutonium, americium, and uranium as their solubility and adsorption in Culebra dolomite vary for a uniform fracture velocity of 1×10^{-5} m/s, and Parameter Set 5 (a one-half fracture spacing of 4 m, a fracture porosity of 0.5, and a matrix porosity of 0.005), with a repository discharge of (a) 10^3 m^3/10^4 yr, (b) 10^4 m^3/10^4 yr, and (c) 10^5 m^3/10^4 yr.

3. Potential Benefits of Backfill

The results of the parametric analysis, as described in Chapter 2, indicate that certain combinations of brine flow, actinide solubility, hydrologic connection between Culebra matrix and fracture, and actinide retardation values define regions that can be considered "cautionary" with regard to possible WIPP compliance. In this section, the potential of backfill to affect repository behavior in these "cautionary" regions is discussed. The discussion begins with an overview of the hypothesized behavior of the WIPP repository, including conditions before and after intrusion, followed by possibilities for improving performance using a backfill.

3.1 Hypothesized Repository Behavior

3.1.1 Prior to Intrusion

The sequence of episodes that leads to so-called "undisturbed conditions" is as follows. Initially, panels of the repository would be filled with waste. All shafts would be backfilled and sealed. No free brine would likely be present in the repository at that time, although the fractures in Marker Bed (MB) 139 might be filled with brine from the Salado Formation (Figure 3-1a). During the first 50 to 200 yr after decommissioning, creep would first collapse the room and then compress the voids around the waste to encapsulate it. Any brine in the salt would likely flow into the disturbed rock zone or remain in pockets within the waste and panel rooms. Crystallization of NaCl from the brine onto waste surfaces would also aid in encapsulating the waste (Figure 3-1b).

The presence of brine in the disposal rooms would promote corrosion of the steel containers and of steel wastes within them. Initially this corrosion would consume oxygen. However, rather quickly, the oxygen would be consumed and only anoxic corrosion would occur, which generates hydrogen gas if brine is present. The rate of corrosion depends upon whether the waste was fully saturated with brine or not. Furthermore, encapsulation of the containers through salt creep and NaCl crystallization would significantly delay the corrosion rate. In the sequence of events described here, room closure is assumed to be nearly complete before much anoxic corrosion of the containers has occurred. Sandia typically assumes microbial degradation of organic materials in the wastes has a probability of about 50% and would produce carbon dioxide. Gases (H_2 and CO_2) generated in the room would fill interstitial voids. The gas could also migrate into anhydrite layers above the room (Figure 3-1c).

In the undisturbed condition, the amount of brine from the Salado Formation is limited. Hence, in undisturbed conditions for a salt repository, the solution chemistry in the repository is determined by the possible carbon dioxide, the waste chemistry (e.g., steel), and the water chemistry of the brine in the Salado Formation. No radioisotopes are released to the accessible environment in this gas-filled pressurized state, even without backfill (Figure 3-1d). For releases to occur, intruders must drill into the repository, as discussed in the next section.

3.1.2 After Intrusion

As is readily seen in Figure 3-2, a hypothetical human intrusion is represented by a drilling event that initiates a complicated interaction of phenomena within the disposal room. The episode described here is the drilling intrusion scenario E1 in which a borehole is drilled through a disposal room and then into a hypothetical pressurized brine pocket beneath the repository in the Castile Formation. Usually, the most important part of the event is the short-term result, namely the entrainment of wastes into the drilling fluid and their immediate release at the surface during drilling operations. However, releases through groundwater flow into the overlying Culebra can also be important when the solubility of the actinides is high and are discussed further here.

In the drilling intrusion scenario E1, the initial breakthrough into a repository panel quickly depressurizes a disposal room. According to 40 CFR 191, the intruders "soon"** realize the area is "incompatible" with their purposes. The drillers seal the borehole using present-day technology and abandon it. Sealing would permit the room to repressurize as the result of on-going gas generation from corrosion and microbial degradation, if steel, cellulosics, and rubber were still available. These conditions are not certain because, for example, using the maximum microbial degradation rates, the total CO_2 gas would be produced in ~140 yr and thus might not be present after the initial intrusion released this gas.

** "Soon" is the term used in the guidance for 40 CFR 191. However, it is not defined quantitatively. The authors take it to mean less than a month.

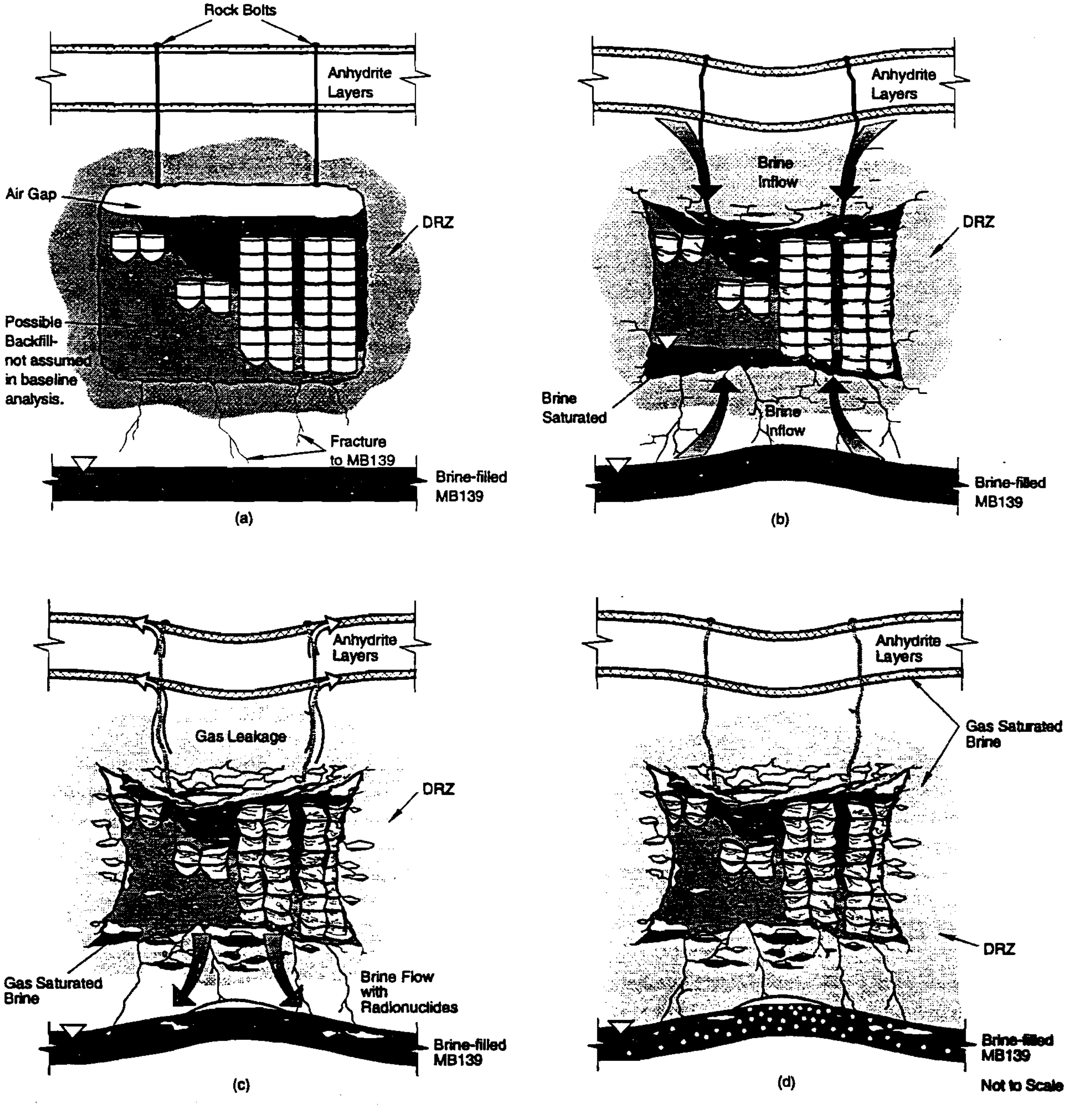

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Figure 3-1. Hypothesized episodes in the disposal area leading to an undisturbed state of the WIPP disposal system. This drawing shows (a) initial conditions after disposal, (b) room creep closure and brine inflow, (c) gas generation and brine outflow, and (d) undisturbed conditions with repository chemistry controlled by carbon dioxide in gas-filled room, waste properties (assuming no backfill) and water chemistry of brine in Salado Formation (after Rechard et al., 1990).

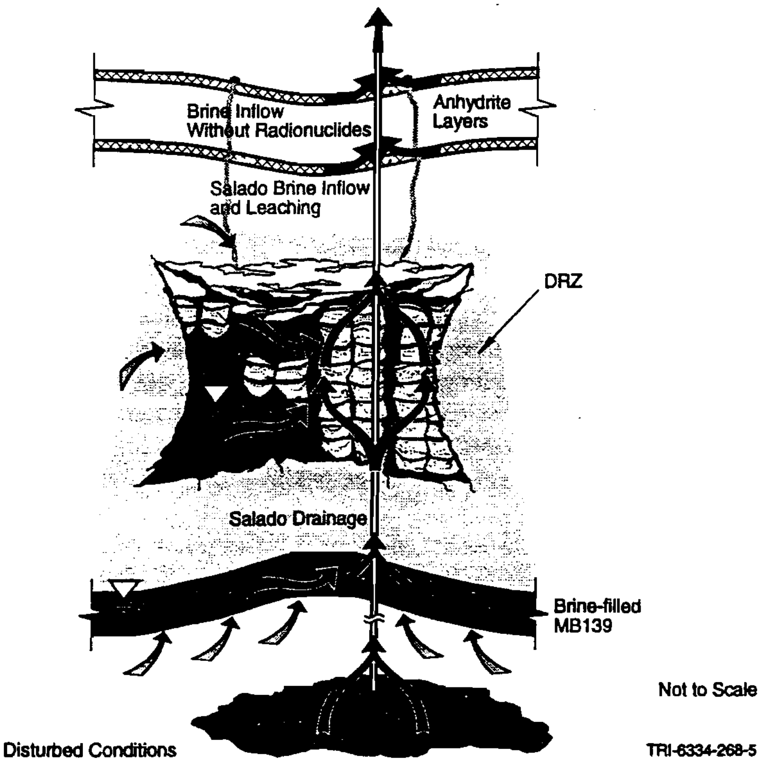


Figure 3-2. Hypothesized situation in the disposal area after human intrusion (E1 scenario). The massive amount of brine flowing into the repository greatly influences the chemistry within the repository (after Rechard et al., 1990).

Following abandonment, hypothesized degradation of the borehole plug throughout its length allows gases to migrate out of the room, with brine refilling any remaining voids. Depending on (a) pressure differences, (b) whether borehole plugs above or below the repository degrade first, and (c) the depth of drilling, brine could flow down from the repository into underpressurized formations below the repository. However, in the cases usually considered in PA calculations, brine flow from the Salado Formation and from the brine pocket beneath force the liquid through the repository up into the Culebra Dolomite Member of the Rustler Formation (Figure 3-2). The pore volume of the repository (40,000 m^3), the panel (4230 m^3), and the room (340 m^3) all relate to the anticipated maximum discharge through a portion of the repository in the E1E2 scenario (10 to 20 m^3/yr) (see Section 2.1.1). Hence, the theoretical detention times in the repository, panel, and room are 4000 yr, 420 yr, and 34 yr, respectively. As noted above, with fast microbial degradation rates, all CO_2 might be produced prior to intrusion. However, with slow rates of microbial degradation, and thus CO_2 generation, CO_2 gas would continue to be generated after intrusion and would have ample time to influence the solution chemistry. But it must be noted that the maximum effect would be reduced because the maximum CO_2 gas pressure would be slightly above hydrostatic pressure (~10 MPa) rather than lithostatic pressure (~14 MPa).[††]

3.2 Possibilities for Improved Performance with Backfill

An advantage of backfill is its potential for altering the chemical environment in the repository especially prior to intrusion. Provided below is a general overview of the pertinent chemical principles involved, followed by the specific questions that needed to be examined for this report.

3.2.1 Overview of Pertinent Chemical Principles

An important issue in the behavior of the repository is whether compounds of the actinide elements (e.g., americium, plutonium, uranium, and neptunium) will have the opportunity to dissolve or mobilize as colloids in brine; if so, these actinides will be transported by any brine flowing through the repository sometime after a hypothetical intrusion, as described above. The equilibrium concentration of an actinide dissolved in solution is called its *solubility*. Solubility of an actinide depends on the chemical environment, and the two aspects of that chemical environment considered here are (1) its oxidizing (or reducing) nature and (2) its acidity or alkalinity (pH[‡‡]), as discussed further below.

Solubility of an actinide depends heavily on the oxidation or valence state of that actinide, with lower oxidation states being generally much less soluble than higher oxidation states. The actinides can exist in the +3, +4, +5, or +6 oxidation states, e.g., plutonium can be present as either Pu^{+3}, Pu^{+4}, Pu^{+5}, or Pu^{+6}, or as a combination of several of these oxidation states. The chemical behavior of an actinide element often depends more on the oxidation state than on what actinide it is. For example, there is experimental evidence that actinide elements in the same oxidation state can be considered to exhibit the same chemical behavior. Within the WIPP Project, this behavior is called the *oxidation state analogy* and is considered to describe the solubility behavior of actinides in the WIPP with sufficient accuracy.

As described in Section 3.1.2, conditions in the WIPP will be anaerobic after a relatively short period, so that movement to a higher oxidation state would be highly unlikely. However, reduction to lower oxidation states is quite possible. Some chemical substances like powdered iron, when added to brine, reduce dissolved actinides to lower, less soluble oxidation states, and could be considered in future work, as noted in Chapter 4.

For an actinide in a particular oxidation state, the solubility depends also on the pH of the solution (of the brine, in this case). The actinides appear to exhibit a minimum solubility in a particular pH range. Maintaining the pH at the minimum solubility by an added backfill provides added assurance of compliance. However, the solubility minima can occur at a somewhat different pH range for the different oxidation states.[***]

[††] This is pressure pan produced and is approximately an order of magnitude drop in solubility, as seen in Figure 3-3, described in Section 3.2.2.

[‡‡] pH is defined as the negative $\log_{10}$ of the hydrogen ion concentration, so that pH 5 means a hydrogen ion concentration of 10^{-5} moles/liter. pH <7 is acidic; pH >7 is basic.

[***] We note that maintaining the pH within a particular range (from 8 to 12, for example) is not the same as buffering; a solution is buffered to a specific pH (e.g., pH 7.8) and retains that specific pH unless overwhelmed by the addition of hydronium or hydroxyl ion.

Various anions may form complexes with actinide ions that enhance actinide solubility. For example, complexing agents like citrate and oxalate are present in the WIPP waste and, if dissolved in brine, could act to increase actinide solubility. However, if there is microbial activity, microbes may consume those agents first before they digest less biodegradable materials such as cellulosics. Although some organic compound will be derived as the intermediates of metabolism processes, there is no reason to assume that all chelating agents initially present in the waste will still be available to complex with actinides after all biodegradable cellulosics and rubbers are consumed. In addition, carbonic acid formed by dissolution of CO_2 acts both to complex and dissolve actinides and to acidify the solution to a point at which actinide solubility is increased. Carbonic acid is formed by the dissolution of gaseous carbon dioxide in brine and further disassociates to eventually form the carbonate ion $\left(CO_3^{-2}\right)$ (Snoeyink and Jenkins, 1980, p. 156):

$$
\begin{array}{lll}
CO_{2(g)} & <=> CO_{2\,(aq)} & K = 10^{-1.5} \\
CO_{2(aq)} + H2O & <=> H_2CO_3 \text{ (carbonic acid)} & K = 10^{-2.8} \\
H_2CO_3 & <=> H^+ + CO_3^- & K = 10^{-3.5} \\
HCO_3^- & <=> H^+ + CO_3^{-2} & K = 10^{-10.3}
\end{array}
$$

At atmospheric pressure, the amount of carbonic acid in the brine would be quite small. But at the elevated pressures in the repository, the amount can be quite large. The resulting lower pH can increase the solubilities of the actinides.

Thus two questions with regard to solubility that needed to be examined were

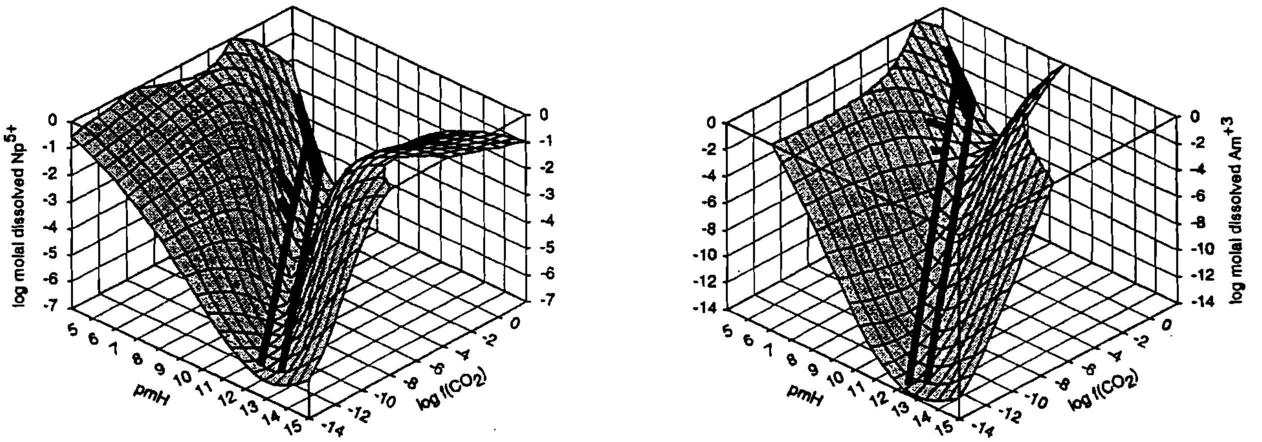
1. Which backfills can move the brine pH into the appropriate range?
2. Can a backfill act as a carbon dioxide "getter" without otherwise adversely affecting the repository?

Because lime (CaO or $Ca[OH]_2$) appears to perform some of these functions very well, the remainder of this study focused primarily on lime, although clay was included in one study case. The use of lime as backfill was prompted in large part by continued reference to its potential in previous backfill studies (see Section 1.1.1), engineers' familiarity with it because of its common use in industry and water treatment, and by knowledge gained from the ongoing experimental program in actinide chemistry. As this experimental program progresses and further literature searches continue, other backfill materials with similar capabilities (e.g., MgO) or other properties with potential to improve performance may emerge, as discussed in Chapter 4.

3.2.2 Effect of Lime on Brine Solution in Repository

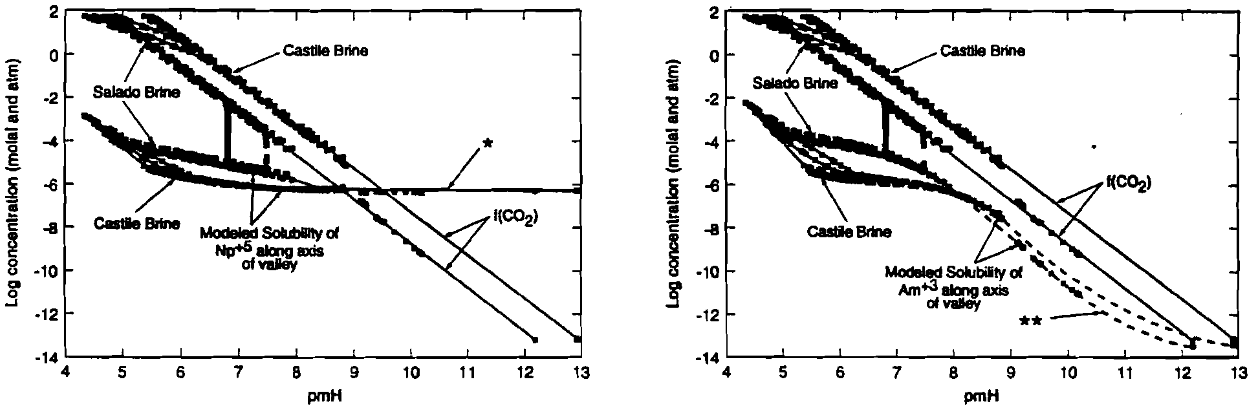
Evaluating the variation of radioisotope solubility with pH and concentration of CO_2 of the brine solution within the repository makes use of *preliminary* work from a large development effort to incorporate results from the ongoing actinide source-term experiments into the performance assessment calculations that will be done for the compliance certification application of the WIPP with 40 CFR 191. It is also important to emphasize that the results are based on a model that may not account for all chemical interactions. For example, the work that was completed for this study did not include the effect of chelating agents in the brine solution.

As explained more thoroughly in Appendix B, the chemistry model in the performance assessment will evaluate the concentration of each oxidation state of an actinide through some calculational results provided by the thermodynamic equilibrium codes FMT and EQ3/6. (The chemistry model will also use WIPP-specific data on speciation of actinides at various conditions from the experimental program, but could not here because the data are not yet available.) Specifically, the code FMT was used to produce a table of concentrations of Np^{+5} and Am^{+3} in Castile brine solution as a function of pH and partial pressure of CO_2. (Actually because of the high ionic strength of brines, the activity of carbon dioxide $f(CO_2)$ and the molal pH (pmH) were used.) For these tables, equations were fit to the calculational results and the surface defined by the equation plotted (Figures 3-3a and 3-3c). In both plots, the surface is basically a valley with the minimum solubility at various values of pmH and $f(CO_2)$ located along the axis of the valley.



Np^{+5}
(a)

Am^{+3}
(c)



Np^{+5}
(b)

Am^{+3}
(d)

* Pitzer coefficients verified experimentally in low calcium systems.

** Effects of ion interactions with hydrolysis species are not included in this preliminary model. The solubility of Am^{+3} for pH > 8 is most likely higher than shown (possibly > 10^{-10}m).

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Figure 3-3. Variation of thermodynamically modeled neptunium (V) and americium (III) solubility with molal ph (pmH) and activity of carbon dioxide $f(CO_2)$ (a) preliminary results from FMT modeling of Np^{+5} in Castile brine, (b) path followed on surface "a" by titrating a brine solution of Np^{+5} with $Ca(OH)_2$ and CO_2, using EQ3/6, (c) preliminary results from FMT modeling of Am^{+3} in Castile brine, and (d) path followed on surface "a" by titrating a brine solution of Am^{+3} with $Ca(OH)_2$ and CO_2, using EQ3/6.

The code EQ3/6 was used to calculate the equilibrium $f(CO_2)$ and pmH for various amounts of CO_2 and $Ca(OH)_2$ added to Salado and Castile brines in order to define the actual area of interest on the surfaces in Figures 3-3a and 3-3c. This area, shown as a line, is plotted in Figures 3-3b and 3-3d.[†††] From this area of interest, the solubilities of interest were evaluated using the surfaces; these solubilities in Salado and Castile brines are also plotted in Figures 3-3b and 3-3d and in black on the surfaces. Taking the results of Am^{+3} as an example, it is seen that the solubility of Am^{+3} (and all other actinides in the +3 oxidation state using the oxidation state analogy mentioned in the previous section) is $10^{-4.7}$ M in virgin Salado brine and $10^{-7.5}$ M in virgin Castile brine. The solubility of the +3 actinides in Salado brine is slightly above the target solubility of 10^{-5} selected based on the results from Chapter 2. It is clear that avoiding a pH lower than 7 will keep the solubility of the +3 actinides below the target solubility of 10^{-5}. This may be readily achieved if enough $Ca(OH)_2$ is added to the system to neutralize any carbonic acid formed by the dissolution of CO_2 gas and/or precipitate carbonates ($CaCO_3$).

Figures 3-3b and 3-3d show that Np^{+5} and Am^{+3} (and presumably all +3 and +5 actinides) decrease as the pH increases. Furthermore, Np^{+5} and Am^{+3} have moderate and very similar solubilities in both Castile and Salado brines at least up to pH 8.

These modeling results establish, with the calculational tools being used for the compliance certification application for the WIPP, that a lime backfill can lower the solubility of the actinides and, in cautionary regions as reported in Chapter 2, provide assurance that the WIPP will meet the EPA limits. However, attention to side reactions that may adversely affect the repository could not be studied in the limited time available.

3.2.3 Mass of Lime Required

According to Revision 2 of the Baseline Inventory Report (DOE, 1995), the inventory of the WIPP is 11-kg cellulosics per drum. This value is equivalent to 400 moles of carbon in cellulosics per drum. Adding plastics and rubbers gives a total of 720 moles of carbon in each drum for CH-TRU waste; for RH-TRU waste, the value could be smaller. If we assume that we have 145 moles of NO_3 and 23 moles of SO_4 per drum, the complete degradation of organic carbon materials will produce 473 moles of CO_2 per drum. Because one mole $Ca(OH)_2$ is needed to consume one mole CO_2, we need a total of 473 moles of $Ca(OH)_2$ or CaO (i.e., 35 kg of $Ca(OH)_2$ or 26 kg of CaO) in each drum to neutralize the effect of CO_2 on pH. If we further assume the density of $Ca(OH)_2$ to be 2300 kg/m^3, about 10% of a container volume will be occupied by $Ca(OH)_2$. This amount is likely enough to react with any CO_2 produced even though kinetic effects have not been modeled, because 100% conversion of all organic carbon in the water to CO_2 has been assumed.

3.2.4 Effect on Radioisotope Sorption

Another possible advantage of backfill is its potential for sorbing of radioisotopes or complexing agents that in turn can substantially increase retention of actinides in the waste within the repository. Lime as backfill can either tie up complexants, react with other waste constituents to release metals that can preferentially tie up complexants, or can hydrolyze or otherwise destroy the complexant molecule. However, because the adsorption of actinides on mineral surfaces strongly depends on the aqueous speciation of the elements and the pH of the solution, and because sorption might decrease with the high pH caused by adding lime, only sorption of radioisotopes on clay (without any lime backfill) was briefly investigated here. For one brine discharge case (10^5 m^3/10^4 yr), 10^7 kg of backfill that adsorped radioisotopes (~100 kg/7-pack drums of waste) was assumed to be placed in the repository. The EPA normalized releases *from the repository* for several radioisotope solubilities are plotted in Figure 3-4. A K_d for the backfill of ~3000 is necessary to retain plutonium in the repository regardless of its solubility. Because the influence of the Culebra has *not* been included in these figures, these results most resemble results using Parameter Set 5 (where the Culebra has little influence on releases). Lower K_ds would be helpful for the parameter sets that represent more likely conditions.

[†††] The curve for Am+3 was generated by FMT without adequate hydrolysis constants for hydroxyl complexes at pHs above 7 and so could change in shape in the final analysis. In Figure 3-3d, this region is shown as a dashed line.

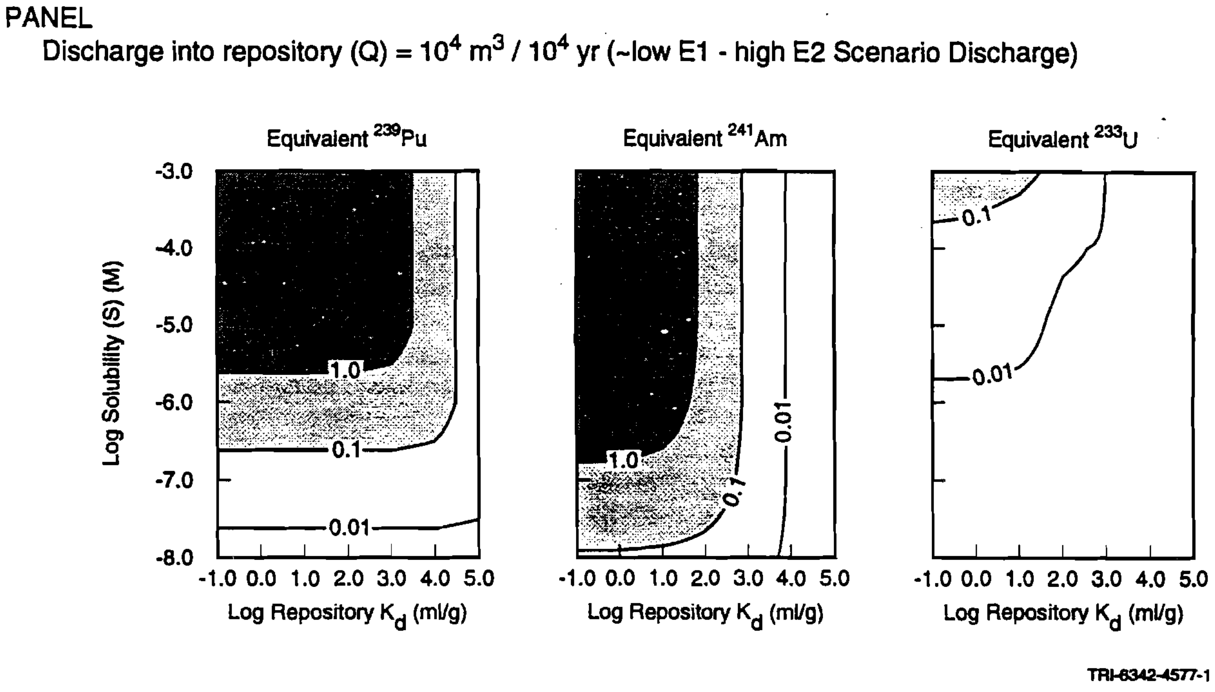

Figure 3-4. Variation of normalized releases of plutonium, americium, and uranium as solubilities and adsorption in repository vary for a repository discharge of 10^4 $m^3/10^4$ yr.

4. Summary and Additional Considerations

4.1 Summary

This report can be considered as a part of the general backfill study that was recommended following the Engineered Alternatives Cost Benefit Study (EACBS), which concluded that backfill, if required, was the preferred addition to the assurance requirements already in place or considered for the WIPP disposal system. This report confirms the positive role for a chemical backfill such as lime (CaO or Ca[OH_2]),which had been discussed, but not modeled, in previous backfill studies (i.e., Butcher, 1990; EATF, 1991; EACBS, 1995). Specifically, this report describes how the computational tools proposed for use in the compliance certification application were used to show that backfill will affect releases, i.e., through the chemical equilibrium code EQ3/6 that lime will combine with carbon dioxide (CO_2) to raise the pH of the brine solution in the repository to as high as 13. Because the solubility of the actinides is very important in determining the releases as shown in the 1992 PA (WIPP PA Dept., 1993) and the solubility is reduced as pH increases, as shown by calculations with the thermodynamic equilibrium code FMT, the addition of lime to the repository can provide more assurance that WIPP will comply with the Containment Requirements of 40 CFR 191.

One mole of lime is required for each mole of CO_2 produced by biodegradation of the waste. The amount of CO_2 that will be generated is uncertain but assuming the maximum possible based on the inventory of organic material reported in Revision 2 of the WIPP Baseline Inventory Report, the maximum amount necessary is 26 kg (57 lb) of CaO or 35 kg (77 lb) of $Ca(OH)_2$ per each drum of waste. (The amount of cement already added to the sludge wastes could be included in this amount.) This amount is very large, but not excessive, and could be placed in bags throughout each room, spread in pellet form, or placed as concrete. If no large operational concerns are presented regarding a lime backfill by the repository operator, Westinghouse's Waste Isolation Division (WID), lime could be used as an additional engineered barrier at the WIPP. Furthermore, lesser amounts of lime can be added and still provide a benefit. For example, enough lime might be added to combine with the mean or median amount of CO_2 that might be generated. Alternatively, and at a minimum, assurance credit could be taken for the amount of cement already added to the sludge waste. However, we recommend continuing with a general backfill study, including several other analyses, as discussed in the next section, before adopting this approach or settling on lime as the backfill.

Prior to this study, the exact actinide solubility below which compliance was fairly certain was not known. Earlier sensitivity studies done as part of the 1992 WIPP PA were of only qualitative use because (1) early results from a new tracer test done on the Culebra potentially modifies the conceptual model and, more important, (2) 40 CFR 194 may require that DOE assume extensive human disruption of the Culebra through mining of potash as part of the performance assessment analysis. Hence, as part of this study, an analysis was done to provide a better boundary for the influence of solubility on compliance of the repository. In general, the report found that compliance is fairly certain below a solubility of 10^{-7} for plutonium, a solubility of 10^{-8} for americium, and a solubility of 10^{-3} for uranium. These limits can be raised several orders of magnitude as various extreme flow conditions are removed; under these conditions, a target solubility for plutonium of 10^{-5} M seems reasonable for a backfill to maintain. Using the results from the chemical modeling, this finding corresponds to maintaining the solution pH above ~7.

This report also conducted a small parallel effort on the sorptive benefit of a backfill. In the case examined, 10^7 kg of sorptive backfill (100 kg per 7-pack of drums) was added to the repository. To benefit compliance, the partition coefficient (K_d) of the sorptive backfill needed to stay above ~3000 for plutonium and 60 for americium, regardless of the disruption assumed for the Culebra.

4.2 Additional Evaluations of Backfill

Backfill has been previously considered as an engineered barrier in the WIPP disposal system (e.g., Butcher, 1990; EATF, 1991), but until now has been rejected because of uncertainty concerning the backfill performance (usually fears that the backfill would not perform as well as thought) and a few drawbacks, especially during the operational phase of the repository. For example, the beneficial effect of minimizing structural damage to the host rock (i.e., reducing the size of the disturbed rock zone) or subsidence of overlying strata or the surface by using a crushed-salt backfill has not been considered great enough to offset drawbacks such as fouling of radiation monitors, difficulty of emplacement, or use of storage space. Even when earlier studies noted the benefits of enhancing the control of the room chemistry through the additions of chemicals, previous studies concluded that backfill was not warranted. However, recent proposed changes in the implementation of 40 CFR 191, as described in the draft 40 CFR 194, as well as new results from the experimental program that have increased the understanding of the disposal room chemistry, may override previous concerns about adding a backfill in the WIPP repository.

This report has taken a step in addressing the first concern (i.e., uncertainty concerning backfill performance) by quantifying the performance of one chemical function, pH control, of a specific backfill material, lime. Additional work in quantifying other potential functions of backfill should also be performed, as described in the following sections. In addition, potential drawbacks of this chemical backfill in terms of long-term performance and operational safety must be quantified Possibly, simple modifications to a chemical control system can be made to counter any drawbacks.

4.2.1 Additional Options to Evaluate for Chemical Backfills

This report selected pH control as the backfill function to evaluate first because the computational tools were already in place to make a quantitative evaluation. However, before focusing on just one chemical function for the backfill (such as pH control as discussed in this report) other chemical functions need to be explored, at least cursorily, to evaluate the advantages and disadvantages before selecting one function to optimize. Other functions for a chemical backfill include (1) forming insoluble compounds (e.g., phosphates), (2) sorption (this report did begin looking at this backfill function), (3) reducing the oxidation state of the actinides, and (4) preventing colloid formation.

Many chemical candidates for backfill can perform well in one of the functions but often adversely affect other functions or areas of the repository. For example, a drawback already mentioned for using lime to control the pH is the very large mass needed to combine with all the CO_2 potentially produced. Although the controlled release of the heat of reaction would not likely heat the repository by more than 1 K after closure, another drawback is that lime, CaO, is very reactive with water and thus possibly causes unacceptable worker hazards during operations. Simple modifications are as follows. First, the hydrated form of lime, $Ca(OH)_2$, is much less reactive and could be used instead of CaO. Unfortunately, it is heavier, bulkier, and water is produced as $Ca(OH)_2$ combines with CO_2. Hence an alternative to consider is MgO. It has the characteristics of maintaining the pH above 7 but below 9. This upper pH range of 9 (rather than 13 for CaO) could be an additional advantage if experimental work failed to confirm that the solubility of the actinides remains low at very high pH values as concurrently predicted by equilibrium modeling. However, a possible disadvantage of MgO is that fewer data may be available on its behavior. Consequently, another modification to consider would be to interperse among the waste backfill in the form of concrete blocks that had been cast on the surface. As the concrete disintegrated in the repository, lime would be released. This use of concrete would actually increase the volume of backfill required and so another type of backfill might need to be added to the concrete. For example, phosphates (or possibly vanadium) tend to combine with the actinides to form insoluble compounds regardless of the oxidation state. Addition of anions like phosphates might greatly reduce the volume of lime needed. Alternately, the function of the backfill might be changed from primarily pH control to primarily insoluble compound formation; thus the backfill might consist only of compounds such as phosphates. However, adding nutrients such as phosphates, might increase the probability that microbes would degrade cellulose and rubber in the waste to produce CO_2. Hence the benefit would need to be quantified to understand the implication of this negative aspect of phosphate.

The issues presented in this example are at the heart of what must be examined in order to design a backfill that would provide benefits without significant drawbacks. Furthermore, the biggest challenge is often not the qualitative evaluation through literature searches and examination of early results from experiments on-going at the WIPP, but rather the effort needed to quantify the effect such that the positive aspects of the backfill option can be evaluated against any negative aspects.

4.2.2 Evaluation of Other Functions for Backfills

Besides chemical functions, a backfill can provide a physical function such as resisting brine flow. The EATF (1991) found that compartmentalizing the waste was beneficial. The effective permeability of the repository is increased by adding barriers; thus the amount of brine flowing through the repository is reduced and thereby the amount of actinides. The computational tools to be used in the WIPP application were not available during the time frame of this report, but should be available in the near future in order to quantify this influence.

4.2.3 Future Evaluations of Proposed Systems

Continued studies similar to the one documented here would likely be sufficient to identify good chemical(s) for performance and operational safety issues should the backfill be used as an assurance measure. However, some simple experiments should be conducted. Simple experiments include conducting titration experiments to verify qualitatively the behavior of adding lime to waste-contaminated brine because the chemical calculations with EQ3/6 and FMT are complex. In addition, the project might consider adding lime at the conclusion of experiments that are currently being done to evaluate actinide chemistry. This addition would allow the experimentalists to qualitatively evaluate the calculations presented here. We are not suggesting extensive quantification of the benefit provided by the backfill (i.e., only minimal assurance is necessary for an engineered barrier alternative to meet "assurance requirements" in 40 CFR 191, because it is assumed that the WIPP disposal system already complies with a very conservative standard).

However, if backfill would be considered essential to the compliance certification application, more extensive experiments and analysis would be required to provide a defensible basis for backfill performance. The development of potential backfill options would need to be more thorough starting with a careful literature search and review of data currently available on the WIPP disposal system. The more detailed analysis would greatly benefit from reports such as this one, but should optimize aspects of long-term performance (physical barrier, pH control, sorption, insoluble compound formation, complexation, etc.) simultaneously with other criteria such as cost, impact on schedule, worker health, etc. To include these additional criteria would require a multiple objective optimization method with defined preferences, tradeoffs, and interactions among the various criteria provided by DOE/CAO and WID, but would allow a more thorough evaluation of the positive and negative characteristics of various backfill options. Additional experiments beyond those already occurring would also be necessary to provide information and/or confirm analysis results.

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Appendix A
Engineered Alternatives Cost/Benefit Study

The results of the Engineered Alternatives Cost/Benefit Study (EACBS) for the Waste Isolation Pilot Plant (WIPP) were analyzed graphically to (a) identify the options that dominated in each of three subsets of alternatives (backfill, supercompaction, and shredding/repackaging with clay) and (b) screen out the factors that do not discriminate. According to Tables 5-3 and 5-4 from the EACBS report (WID, 1995) prepared for the Westinghouse Electric Corporation's Waste Isolation Division (WID), factors that do not discriminate are public acceptance and waste removal capability, so these were removed as primary decision factors. Also, public health risk is a secondary factor, because all alternatives rank as the same except the plasma arc processing option, which is significantly worse. Thus, the final primary decision factors are long-term compliance confidence (as measured by cuttings and water release scenarios), worker health risks, disposal system costs, and the impact on the schedule for emplacing waste at the WIPP.

As seen on Figure A-1, none of these options clearly dominates, i.e., one engineered alternative is not better than another on all factors. When an option improves on one factor, another factor degrades. The options are grouped into three subsets in Figure A-1 to show the dominance within each subset.

Within the set of backfills examined, the performance did not vary significantly; backfills were expected to improve performance of releases only marginally.* The cost and health risks associated with backfill options also did not differ significantly (Figure A-2). Note that processing costs and transportation costs are exactly the same across the backfills; the only difference in total costs is due to differences in the costs of materials for the backfills. The health risks to both workers and the public were also the same across backfill options. The major differentiator of backfills according to the EACBS is performance as measured by Measure of Relative Effectiveness (MRE). Salt and cement grout backfills appear to be better than clay or lime backfills because of modeling assumptions used. Thus, part of the purpose of the general backfill study and this report in particular is to better understand and discriminate between the performance of various backfills.

Reference

WID (Westinghouse Waste Isolation Division). 1995. *Engineered Alternatives Cost/Benefit Study Report.* DOE/WIPP 95-2135. Carlsbad, NM: U.S. Department of Energy, Carlsbad Area Office.

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* The EACBS used the Measure of Relative Effectiveness as a performance measure, which was defined as the ratio of the cumulative release of radioisotopes for an engineered alternative to the release under baseline conditions. Thus, a smaller number is better. The MRE was measured for each engineered alternative, under E1, E2, and E1E2 scenarios, for both groundwater and cuttings pathway releases. The backfill options had MREs mostly in the 40%-95% range, indicating marginal improvements.

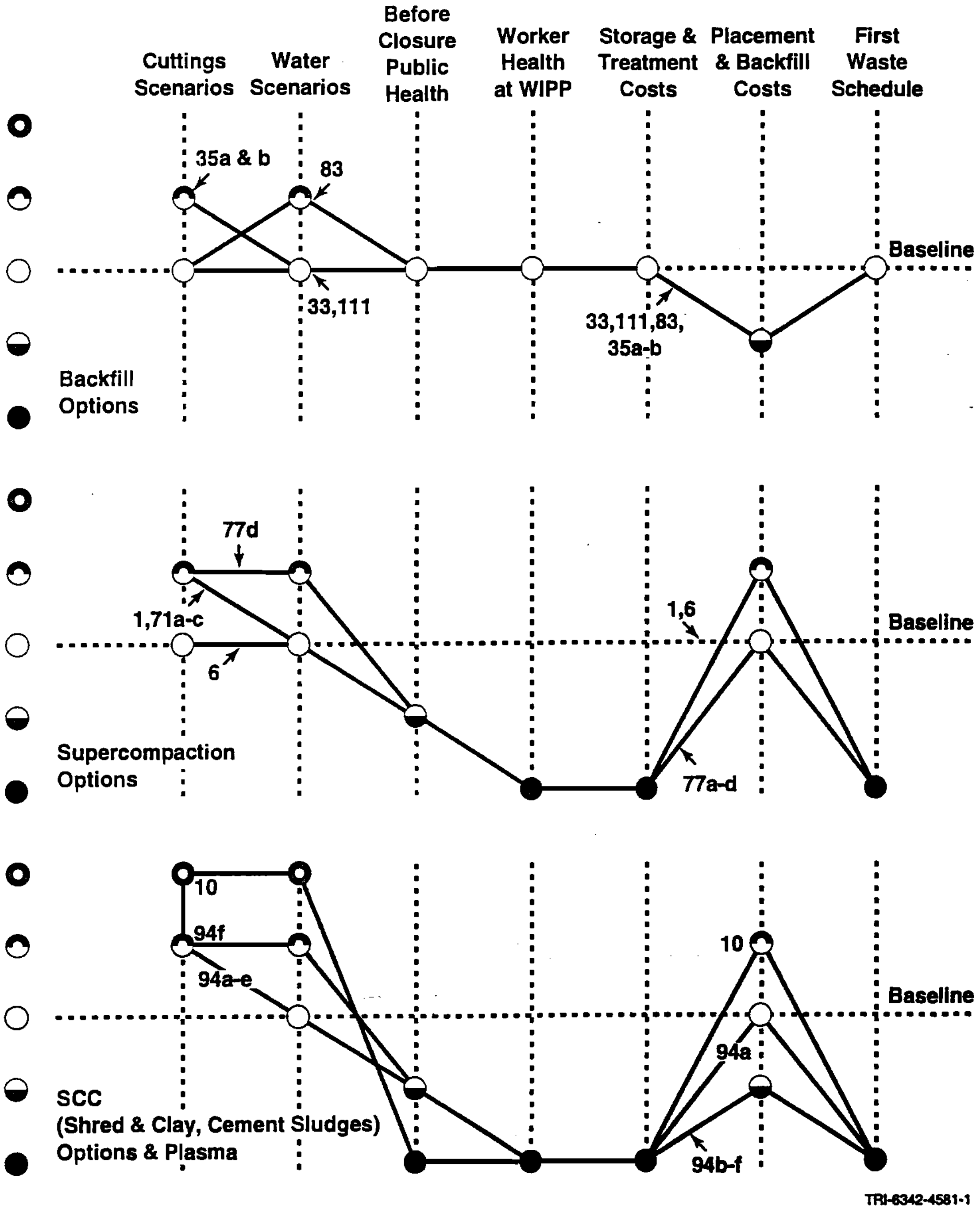

Figure A-1. Graphical display of change in qualitative ranking of engineered barrier alternatives for performance criteria listed in draft of 40 CFR 194 (based on Figure 5-4, WID, 1995, reproduced as Figure 1 in this report).

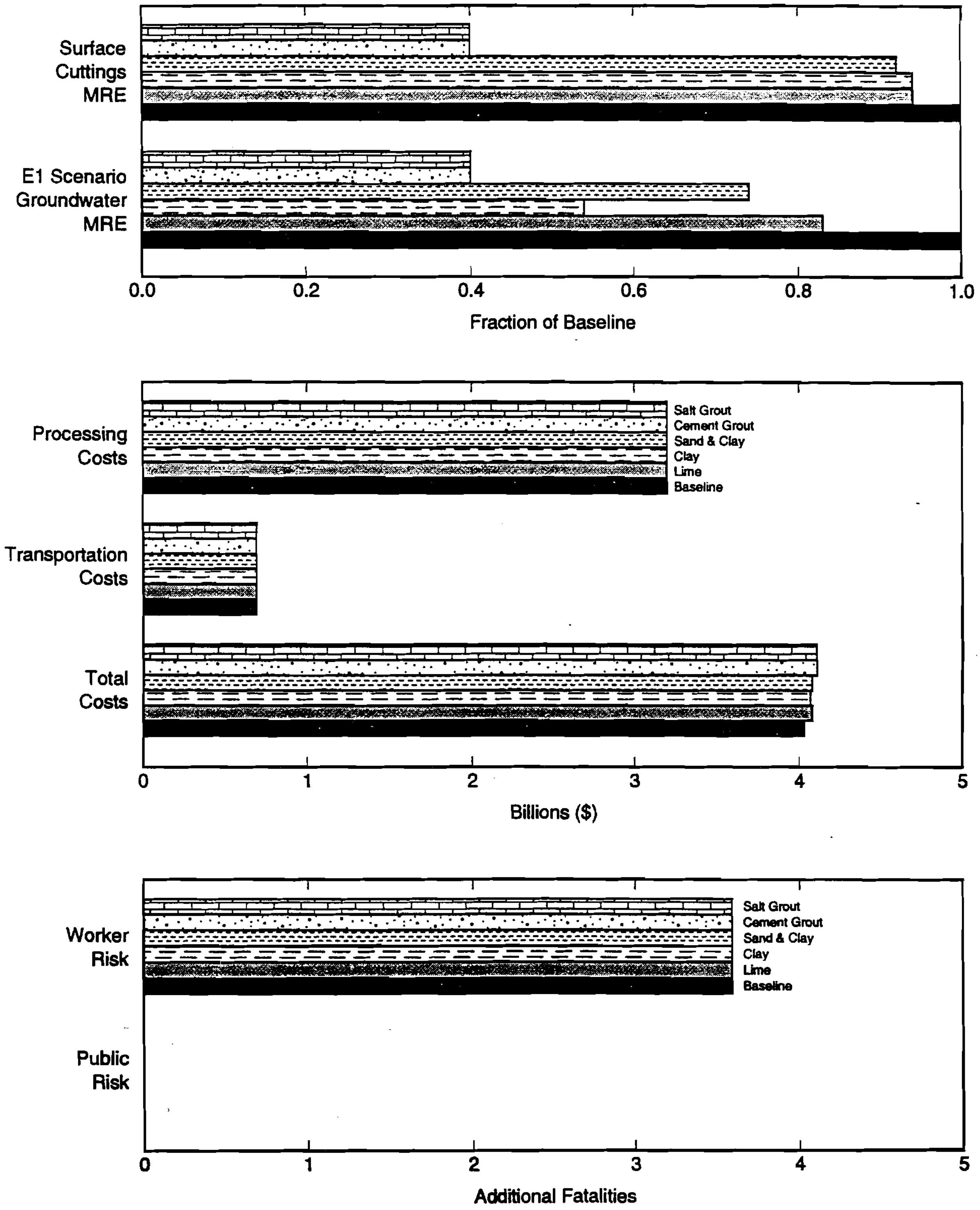

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Figure A-2. Bar graphs of qualitative performance for various performance criteria (based on Figure 5-3, WID, 1995).

Appendix B
Data and Models for Parametric Analysis

This section describes the models and data that will be used in the performance assessment of the Waste Isolation Pilot Plant (WIPP) and the simplifications done to establish baseline conditions in this report.

B.1 Baseline Behavior

B.1.1 Models Selected for WIPP Performance Assessment Baseline

To evaluate scenario consequences, numerous computer codes are used in the performance assessment to simulate relevant features of the disposal system. The major computer codes planned for the compliance certification application for the WIPP and the flow of information among them are illustrated in Figure B-1. This information is presented as a means of showing the models that will be used in the compliance calculations, which represent the technical baseline from which the models for this report were simplified. Several new codes (FMT, EQ3/6, and NUTS) have been added since the last performance assessment in 1992 (WIPP PA Dept., 1992) and are included in the general discussion below. Further discussion of the use of FMT and EQ3/6 in the chemistry model is also included in Section B.3, because preliminary results from these codes are used in this report.

In a complete performance assessment, the performance assessment codes are executed sequentially. BRAGFLO calculates the overall movement of gas and brine in the repository and the Salado Formation; this gas and brine movement forms the basis for estimating radioisotope releases to the accessible environment. BRAGFLO also contains subsystem models for estimating gas generation in the repository, disposal room closure and consolidation, and interbed fracturing. BRAGFLO does not calculate the movement of radioisotopes.

NUTS calculates the movement of radioisotopes in the Salado Formation. NUTS uses the same geometry as BRAGFLO and the brine and gas flow fields calculated by BRAGFLO. The radioisotope concentrations are derived from a source-term model that includes calculational results from FMT and EQ3/6. The concentration of radioisotopes in that brine, calculated by NUTS, are used to determine the quantity of radioisotopes released to the Culebra dolomite. In addition, PANEL calculates radioisotope decay and can be used in place of NUTS to also establish the radioisotope source term for use in codes modeling the Culebra dolomite, SECOFL2D and SECOTP2D, as was done for this report and in the 1992 WIPP PA. Although not considered in the backfill study, reported here, CUTTINGS, BRAGFLO, and PANEL are used to evaluate the immediate consequences of inadvertent human intrusion through exploratory drilling.

SECOFL2D and SECOTP2D together calculate the detailed movement of radioisotopes in the Culebra that occurs if radioisotopes are introduced by flow up the shafts or through a degraded exploratory borehole. SECOFL2D calculates regional Culebra flow fields using an assumption that flow occurs in a single-porosity medium. SECOFL2D uses the transmissivity fields calculated by GRASP-INV (one field in each simulation). SECOTP2D calculates radioisotope transport in a double-porosity medium, accounting for advection in fractures, matrix diffusion, retardation, and decay.

Two of the above mentioned submodels, PANEL and SECOTP2D, were simplified and used in the parametric study reported here.

B.1.2 PANEL Model Used in Parametric Analysis

As described above, PANEL calculates radioactive decay, using source concentrations. PANEL is based on a simple conceptual model that treats the entire room, panel, or repository as a continuously mixed cell (Figure B-2). In this study, the entire repository was modeled as the accessible volume, and the pore volume was a constant of 40,000 m^3 that was filled at time zero. The brine flow through the repository was varied in the study, being a constant of 0.1, 1, and 10 m^3 per year. These data resulted in integrated releases of brine of 1000, 10,000, and 100,000 m^3 over the 10,000-year period. These compare with a small E2 flow, a large E2 or small E1 flow, and a large E1E2 flow, respectively.

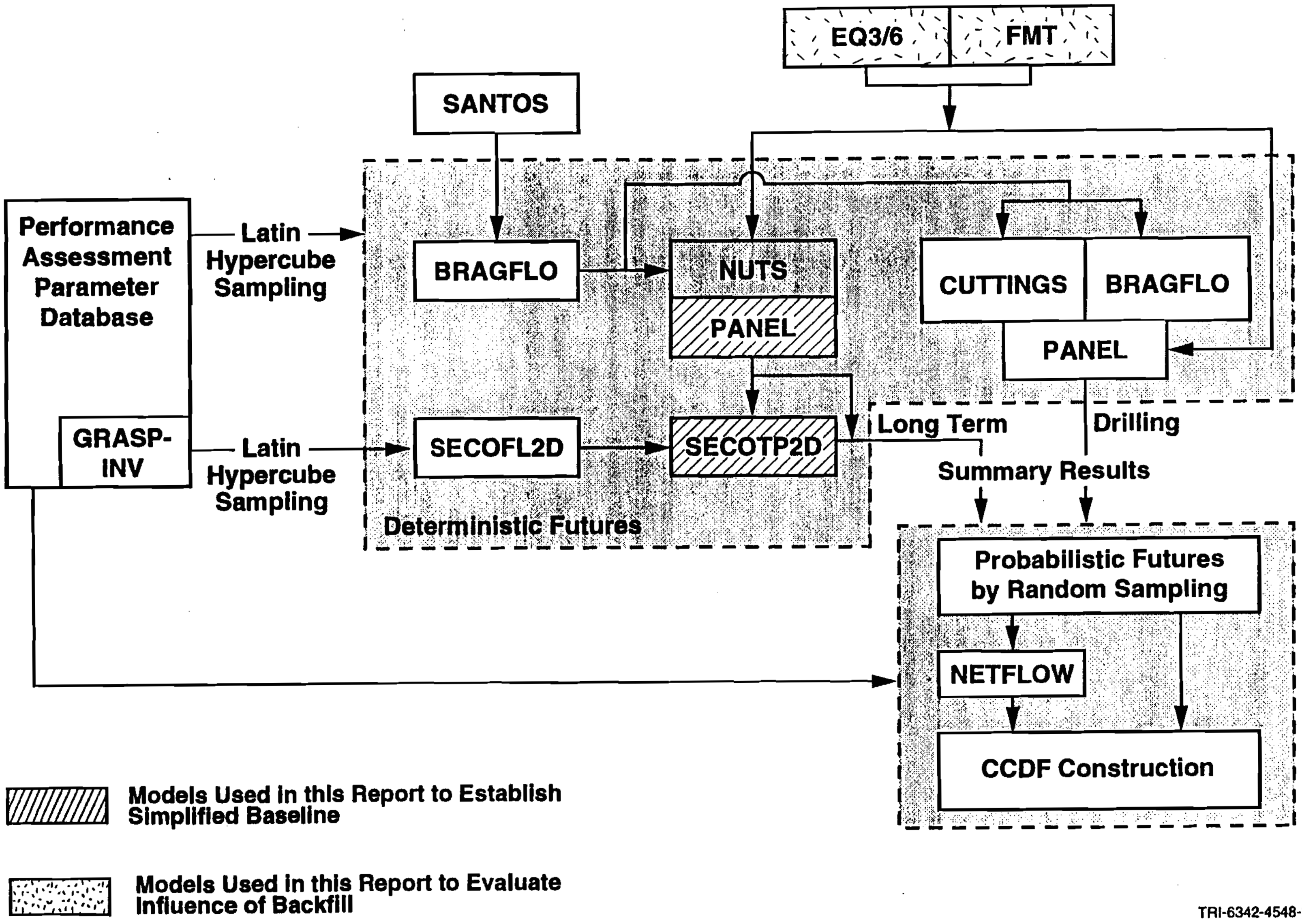

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Figure B-1. Models used in WIPP Performance Assessment.

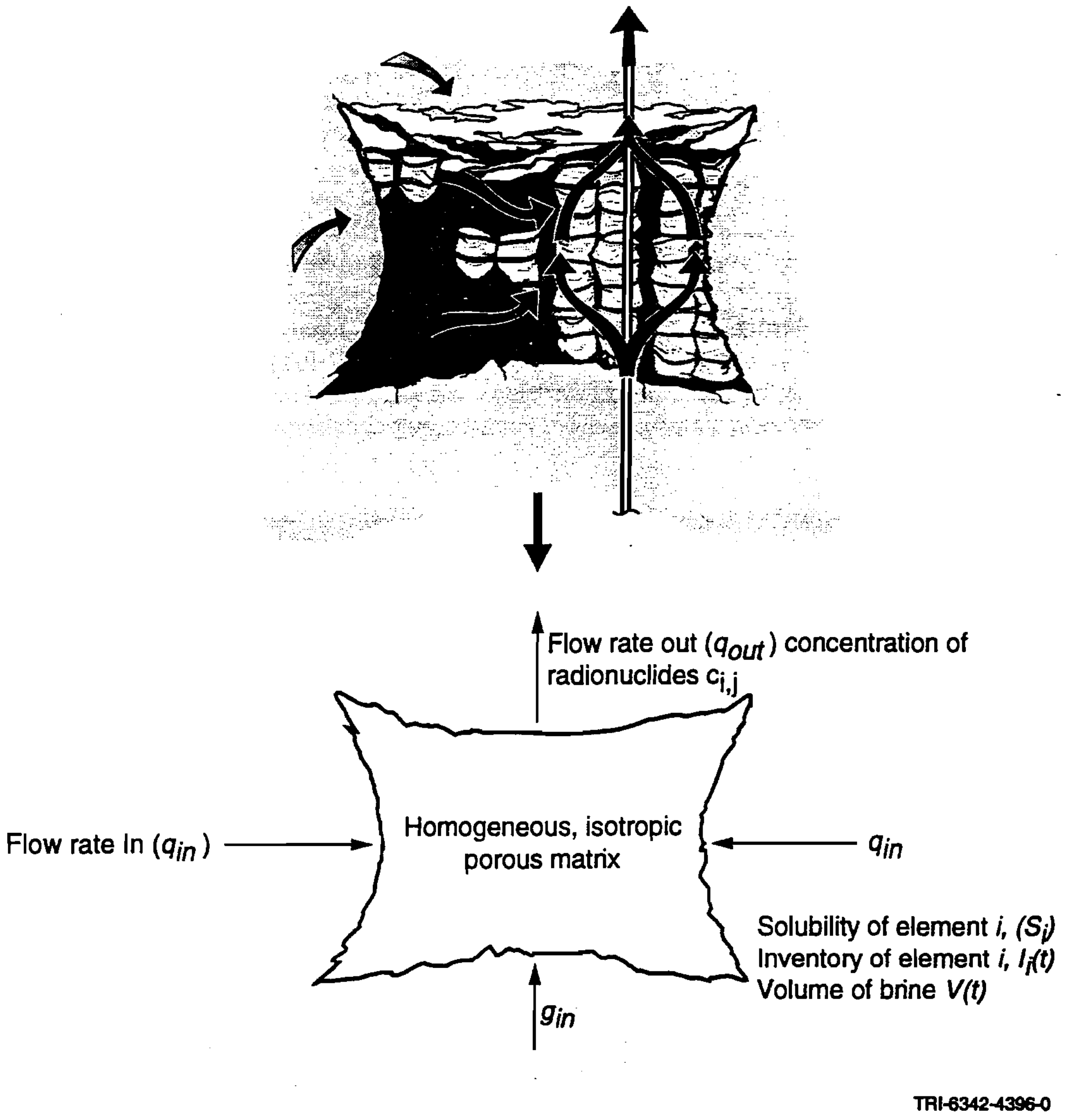

Figure B-2. Idealization of the WIPP repository for evaluating concentration (or mass discharge) of radioisotopes leaving a panel.

Other important inputs are the inventory of radioisotopes and their corresponding solubility. The inventory is from the Transuranic Waste Baseline Inventory Report (TWBIR) as described below (DOE, in preparation). Solubilities were varied parametrically from 10^{-8} to 10^{-3} moles per liter (M). This solubility range includes solubilities of interest: the greatest actual anticipated solubility is 10^{-3} M. At 10^{-8} M, violation of the release limits of 40 CFR 191 would be extremely unlikely.

Inventory of Radioisotopes. The inventory was calculated as 6.65 million curies of alpha emitters with a half-life greater than 20 years (EPA scale factor), based on the draft of Revision 2 of the TWBIR (DOE, 1995). The TWBIR reports all DOE TRU waste, including wastes intended for the WIPP and non-WIPP wastes. The TWBIR supports many WIPP program needs, including the WIPP Land Withdrawal Act, WIPP transportation studies, the WIPP No-Migration Variance Petition, and the Sandia National Laboratories performance assessment processes. The TWBIR reports all of the DOE complex TRU waste at the waste stream level expected to be disposed of in the WIPP.

The WIPP baseline inventory is estimated using waste streams identified by the DOE TRU waste generator/storage sites. Each waste stream is defined in a waste stream profile and has been assigned a Final Waste Form by the DOE TRU waste generator/storage site. The sites provided and/or authorized all information in the Waste Stream Profiles.

Waste Stream Profiles with similar physical and chemical properties can be combined into the same Final Waste Form and, if so, the combination is documented in a site-specific waste profile for each TRU waste generator/storage site. To derive a WIPP waste profile, a particular site-specific waste profile, with a specific Final Waste Form, can be combined with other site-specific waste profiles having Final Waste Forms from the TRU waste generator/storage sites.

The anticipated inventory of TRU waste is defined as the sum of retrievably stored waste plus currently projected TRU waste volumes. The anticipated inventory for CH-TRU waste is not sufficient to fill the maximum CH-TRU disposal inventory for WIPP (calculated to be 5,950,000 ft^3 or approximately 168,500 m^3). Therefore, scaling has been developed as a means for Sandia to model the impacts of a full repository (175,000 m^3). Scaling has not been applied to the RH-TRU inventory because the sites have reported sufficient RH-TRU waste to fill the RH-TRU disposal inventory (250,000 cubic feet or approximately 7,080 cubic meters).

Additionally, there is uncertainty about and a current lack of data on wastes produced from decontamination and decommissioning (D&D) and environmental restoration (ER) activities, so D&D and ER projections are not included in the TWBIR.

This TWBIR represents the second revision of the inventory. Major differences between Revision 1 and Revision 2 are

1. Changes in the plan at Rocky Flats Environmental Technology Site (RFETS) for the processing of plutonium residues for actinide separation have been incorporated. Recently it was decided that the plutonium residues will be repackaged/processed to meet WIPP Waste Acceptance Criteria. This decision increased the WIPP waste inventory by approximately 1320 cubic meters in volume and increased the radioisotope inventory by approximately 1.35 million curies.

2. The volume and radioisotope inventory of RH-TRU waste have been substantially increased. At present, reported numbers identify more anticipated (i.e., stored and projected) RH-TRU waste than volume capacity will allow at the WIPP site.

3. The major waste sites (Savannah River Site, Idaho National Engineering Laboratory, Hanford Site, and RFETS) have divided their waste streams into the Local Identification level, which not only provides greater detail on the waste forms, but also causes the total number of waste streams to increase from 360 to approximately 970.

For the WIPP performance assessment, data used for the anticipated CH-TRU and RH-TRU waste include total radioisotopes, as scaled by volume for the WIPP, and waste matrix composition. Five general categories of waste characteristics are used in the performance assessment: (1) source-related parameters, such as mass of ferrous metals; (2) hydrologic-related parameters, such as porosity and permeability; (3) chemical-related parameters, such as stoichiometry for corrosion and biodegradation; (4) mechanical-related properties/parameters, such as mass of non-ferrous metals; and (5) other waste characteristics, such as surface area of ferrous metals.

Grouping of Elements. In this report, the released radioisotopes were lumped by curies into ^{241}Am, ^{239}Pu, and ^{233}U to reduce calculational time. These three radioisotopes (^{239}Pu, ^{241}Am, and ^{233}U) represented the 10 radioisotopes considered to be important with regard to long-term releases: ^{241}Am, ^{240}Pu, ^{239}Pu, ^{238}Pu, ^{237}Np, ^{234}U, ^{233}U, ^{230}Th, ^{229}Th, and ^{226}Ra (WIPP PA Dept., 1992). To obtain the three groups, the following steps were taken:

1. Only ^{241}Am, ^{239}Pu, and ^{233}U were transported.
2. For radioisotope $^{\#\#\#}$Nn, M$^{\#\#\#}$Nn was defined as the mass to transport, and P$^{\#\#\#}$Nn was defined as the mass from PANEL.
3. M^{241}Am = P^{241}Am + P^{241}Pu.
   (Note that ^{241}Pu decays to ^{241}Am with a 14.4-yr half-life.)
4. M^{239}Pu = P^{239}Pu + P^{240}Pu * 3.7E0 + P^{242}Pu * 6.4E-2[†]
5. M^{233}U = P^{233}U + P^{234}U * 6.5E-1 + P^{238}Pu * 6.5E-1 + P^{235}U * 2.3E-4 + P^{238}U * 3.5E-5 + P^{236}U * 6.8E-3 + P^{237}Np * 7.4E-2[†]
   (Also note that ^{238}Pu decays to ^{234}U with a half-life of 87.7 yr; ^{237}Np decays to ^{233}U, but the half-life is 2.1E6 yr. This substitution is equivalent to Np being transported like U.)
6. Each radioisotope was assumed to be a single chain.
7. The half-life of ^{233}U was assumed to be infinite (which helped to account for the daughters of U by assuming that they were transported the same as U).

B.1.3 SECOTP2D Model Used in Parametric Analysis

Releases of radioisotopes from the WIPP repository to the accessible environment might occur along liquid pathways through the Culebra Dolomite Member of the Rustler Formation. The conceptualization of the Culebra consisted of two continuums: one continuum associated with the intact dolomite matrix with an original porosity and one continuum associated with secondary porosity through the dolomite matrix that is modeled as fractures. For the WIPP performance assessment, and based on available field evidence at the time (Reeves et al., 1991), a dual porosity model of contaminant transport in the Culebra was used, that is, transport of contaminants was advected by fluid flow through the fracture continuum but diffusion of contaminants into the matrix continuum surrounding the fracture could occur.

B.2 Predicting Influence of Backfill

As partially described in Chapter 3, it is assumed that the water chemistry (primarily pH) within the repository prior to an intrusion will be controlled by generation and pressurization with carbon dioxide (CO_2) that will be released from the biodegradation of cellulosics and rubber in the WIPP waste. This CO_2, in turn, affects the solubilities of the radioisotopes. Performance assessments up through 1992 used solubilities elicited from an expert panel and included radioisotopes with the high solubilities obtained in an oxic environment. Since that time, an experimental program has been measuring radioisotopes in a WIPP-like environment. To use these experimental results, several changes to the chemistry model, which was originally entirely embedded in PANEL, have been proposed and some work completed.

[†] The activity conversion factors are used to determine the number of curies, because curies are the units of the 40 CFR 191 release limits.

To accurately understand the influence of any chemical backfill in the repository, this report drew upon this partially completed work. Thus, a brief description of the new chemistry model is included here.

B.2.1 Mechanistic Description of Chemistry Model

The proposed chemistry model consists of evaluating two types of information as follows (Figure B-3). The model itself remains quite simple but some sophisticated calculational information is provided by the codes EQ3/6 and FMT. Also, WIPP-specific speciation of actinides at various conditions is used from the experimental program.

Evaluating the Concentration of Each Actinide Oxidation State. An oxidation state analogy is assumed (i.e., for a given oxidation state all five actinides are assumed to have the same solubility). The first step therefore is to provide the tables from which the chemistry model could extract the appropriate oxidation state concentration in solution.

1. Amounts of the complexants EDTA and citrate, and possible oxalate, lactate, and acetate, will be derived from the BIR. The ratio of the amounts of the five possible complexants (EDTA, acetate, citrate, oxalate, lactate) will be fixed at the ratio in the BIR. Three different amounts of total complexant, and the condition of no complexant present, will be considered.

2. Brine flow will be calculated by BRAGFLO. In the undisturbed case, the brine will be presumed to be Salado brine. For the E2 intrusion scenario (a borehole through the repository but not into a pressurized brine pocket), the brine will be also assumed as Salado brine. For the E1 intrusion scenario (a borehole through the repository into a pressurized brine pocket) and the E1E2 intrusion scenario (a borehole through the repository into a pressurized brine pocket and a second borehole into the repository), the brine will be assumed as Castile brine after intrusion. Mixing of Salado and Castile brine will not be modeled. Concentrations of actinides in solution depend on brine composition (Salado or Castile).

   BRAGFLO will be used with the average stoichiometric model. BRAGFLO currently calculates the gas pressure, brine mass, gas volume, and mass of remaining Fe and cellulosics for each time step and for each computational cell. All will be output to the computational database.

3. An estimate of the total CO_2 in the repository, as well as of dissolved $Ca(OH)_2$, will be evaluated from output of BRAGFLO based on the amount of steel corroded, cellulosics and plastics biodegraded, $Ca(OH)_2$ inventory, and $Ca(OH)_2$ dissolution rate.

   From the BRAGFLO output and from other parameters retrieved from the database, the new chemistry model will calculate the parameters needed to extract pH and $f(CO_2)$ from lookup tables, for each time step.

4. EQ3/6 will be used to construct lookup tables for pmH and $f(CO_2)$ as a function of gas volume $\{V/A\}$, $\{(\text{moles of } CO_2)/A\}$, and $\{Ca(OH)_2/A\}$. The entire possible range for each independent variable will be covered.

5. FMT will produce tables of concentrations of actinide in solution as a function of pH (actually pmH), $f(CO_2)$, complexant, brine composition, and oxidation state. Each individual table has pmH and $f(CO_2)$ as independent variables (axes) and concentration of an actinide oxidation state as a dependent variable. For each actinide oxidation state (III, IV, V, VI), there will be two sets (for Salado and Castile brine) of four tables (one for each complexant concentration). There will thus be $4 \times 4 \times 2 = 32$ tables for oxidation state concentration. For each table, an equation will be fit to the data and included in the PA code.

Providing an Actinide Concentration in the Repository to NUTS. The new chemistry model extracts a concentration in solution of each oxidation state from Step 5 above. The concentrations thus extracted must now be combined with an oxidation state distribution to provide an actinide concentration.

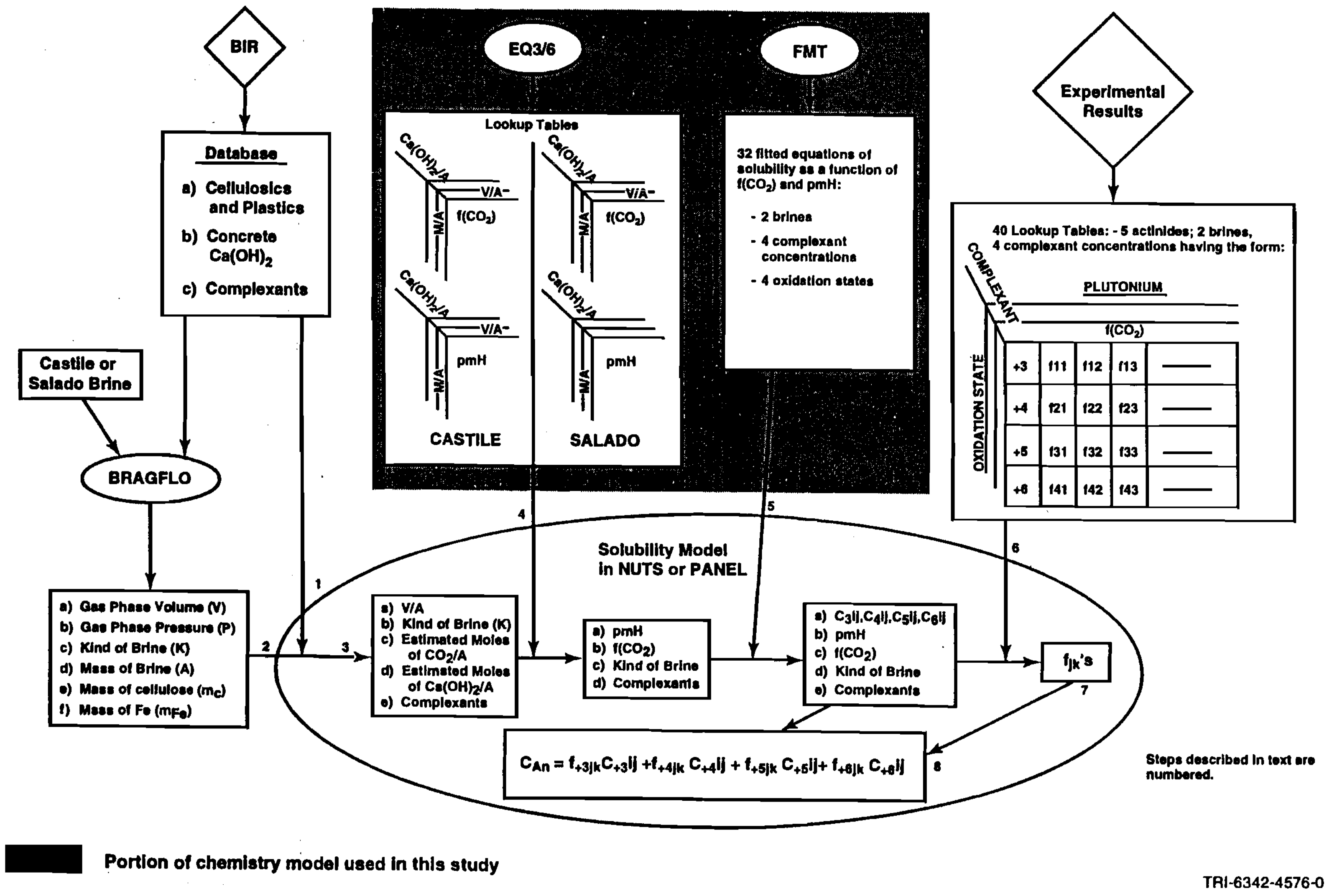

Figure B-3. Proposed chemistry model.

6. Experimental data will result in tables, for each of the five actinides (Th, U, Np, Pu, Am), of fractions of each dissolved actinide in each oxidation state as a function of $f(CO_2)$, and complexant. Each lookup table will have the four oxidation states (+3, +4, etc.) and $f(CO_2)$ as independent variables (axes) and the fraction of the actinide in each oxidation state as a dependent variable. For each actinide there will be two sets (for Salado and Castile brine) of four lookup tables (one for each complexant concentration). There will thus be $5 \times 4 \times 2 = 40$ lookup tables for oxidation state concentration. For Th, Np, and Am, only one oxidation state may predominate. Considerable degeneracy among these tables is expected.

7. The numbers designated f_j in Figure B-3 are the experimentally determined fractions of the total concentration of the actinide in oxidation state +3, +4, +5, and +6, respectively. The detection limit of the experimental determinations is expected to be about 10^{-9} M.

8. The solubilities obtained from the fitted equations will be combined with the fractions of each oxidation state to yield the maximum concentration of each actinide under a particular set of repository conditions as shown in Eq. 1.

$$C_{An} = f3{*}C_3 + f4{*}C_4 + f5{*}C_5 + f6{*}C_6 \qquad \text{(Eq. 1)}$$

where C_3, C_4, C_5, and C_6 are the dissolved concentrations (solubilities) of the "pure" oxidation states of the actinide in question and are calculated from the equations fit to the FMT models outputs, and f_j is the fraction of the actinide in each oxidation state.

In addition, the amount of an actinide dissolved cannot exceed the inventory of that actinide, so that

$$C_{An} = \min\{I_{An}/V_{brine}, C_{an}\} \qquad \text{(Eq. 2)}$$

where I_{an} is the inventory of that actinide remaining in the repository, and V_{brine} is the brine volume within the repository.

B.2.2 Use of FMT and EQ3/6 in this Study

Because the production of carbon dioxide and the subsequent pressurization of the room has such a strong influence on the pH (and thereby actinide solubility) in the repository prior to intrusion, a backfill that can combine with the carbon dioxide can have a profound influence. Lime or cement can indeed combine with the carbon dioxide. Furthermore, excess lime or cement will raise the pH to around 13 where radioisotope solubilities are typically low. To more quantitatively evaluate this predicted effect, the ranges of pH and carbon dioxide partial pressure used in FMT and EQ3/6 had to be extended greatly from those originally anticipated by the Salado or Castile brines.

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