

#### Department of Energy

Carlsbad Area Office P. O. Box 3090 Carlsbad, New Mexico 88221

February 24, 1998



Ms. Mary Kruger WIPP Program Manager Office of Radiation Programs U.S. Environmental Protection Agency 401 M. Street SW Washington, DC 20460

# **MAIL ROOM COPY**

Dear Ms. Kruger:

On December 31, 1997, the Environmental Evaluation Group (EEG) transmitted a letter to the EPA docket that presented an extended list of issues which it had assembled at EPA's request in a meeting between the two organizations held December 10, 1998. The Department of Energy (DOE) has elected to respond to these issues in the belief that they can be resolved by open and frank exposition of the basis for the DOE's position on each issue. The accompanying attachment presents DOE's response.

As you are aware, most of the issues presented in EEG's December 31, 1997, letter have been repeated from earlier comments made on DOE's Compliance Certification Application (CCA). In some cases, the DOE response provided herein simply directs the reader to where and when that information was previously provided, but apparently not considered by EEG. In most of the responses provide herein, DOE has recast its arguments in an attempt to very clearly explain its position, and elucidate the reasoning that should resolve each issue.

The DOE continues to believe that it has met both the spirit and intent of 40CFR194 in its CCA (and supplementary material provided in response to requests by EPA for additional information). We hope that the accompanying material will help EPA resolve the issues. We also hope that it will help EPA's process of issuing the final certification rule in a timely manner. If you have any questions about this information, please contact me at (505) 234-7400.

Sincerely,

Manage



Attachment

cc:

Larry Weinstock (EPA) Frank Marcinowski (EPA) Robert Neill (EEG) Chris Wentz (NMEMNRD)

UNIQUE NO. 9800859

## DOE's Response to Comments Made by EEG to Docket A-93-02, dated 12/31/97

For convenience in formulating focused responses, the DOE has divided the EEG areas of concern into specific technical topics. For example, the EEG's single extended comment on solubility is considered to contain five principal technical concerns, and is therefore addressed in five separate responses.

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#### EEG Comment #1: Solubility - FMT Model and the database

#### Text of EEG Comment:

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

#### **DOE Response:**

The FMT model, not unlike the chemical conditions which exist at the WIPP, is indeed unique. However, FMT has never yielded calculations with the solubility (with all other geochemical conditions being the same) differing between Castile and Salado brine by 19 (nineteen) orders of magnitude as inferred in EEG's comment. Slight differences in the actinide solubilities between Castile and Salado brine are expected in that the concentrations of solubility influencing constituents in the brine (e.g.  $CO_3^{2^2}$ ,  $Mg^{2^+}$ ) vary significantly in these two brines. EEG's unsubstantiated assertion of 19 orders of magnitude difference in solubility is perhaps the result of some typographical error.

The FMT code has undergone extensive validation. This included a comparison of problem solutions by FMT with the solutions to the same problem as provided by PHRQPITZ and EQ3/6. The code PHRQPITZ was utilized instead of PHREEQE (the use of PHREEQE was suggested by EEG) since PHRQPITZ includes the Pitzer formalism (which is used by FMT) whereas PHREEQE does not. These validation efforts are extensively documented in FMT Version 2.0 Validation Document Version 1.0. This validation document was placed in the Sandia WIPP Central Files under WPO# 28121 on 11/17/95.



#### **EEG Comment Issue #2: Solubility - Oxidation State Analogy**



#### **Text of EEG Comment:**

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

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

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

#### **DOE Response:**

Numbered references in this response are listed at the end of the response.



The oxidation state analogy, as used in the WIPP CCA, states that actinides in the same oxidation state exhibit similar trends and behaviors. SNL used this similarity along with theoretical and observed trends in behavior to establish bounding cases for the actinide solubility. The NAS in its WIPP Committee Report appropriately recognized that there are documented cases where the actinide oxidation state analogy is not an appropriate assumption. The key to the oxidation state analogy then lies in understanding the chemical conditions where it is and is not applicable, and also understanding the appropriate use, including limitations, as applied to a real problem.

In designing the dissolved actinide source term program, it was recognized that the combination of several actinides (e.g., Am, Pu, U, Np, Th), the potential for some of these actinides to exist in multiple oxidation states, and the extremely broad range of chemical conditions that existed prior to the implementation of the MgO backfill would make for an untenably large and unnecessary experimental program. The oxidation state analogy provided a means to focus the work while DOE's Response to 3

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providing a reasonable, bounding prediction of the actinide behavior. To develop this reasonable model of actinide behavior under WIPP conditions, two general trends were taken advantage of:

- 1. the tendency of actinides in the same oxidation state to exhibit similar behaviors under similar conditions (i.e., the oxidation state analogy), and
- 2. the general trend of increasing stability of the actinide solid phases progressing across the series.

The tendency of actinides in the same oxidation state to exhibit similar behaviors is well recognized (see for example Cotton and Wilkinson<sup>1</sup>, 1980, page 1012), as demonstrated by the fact that similar compounds in the same oxidation state have similar crystal structures, differing only in the structure parameters (Cotton and Wilkinson<sup>1</sup>, 1980, page 1009). The basis for this tendency is firmly rooted in the fundamental electronic structure of the actinides themselves, and is one of the building blocks of chemistry that forms the periodicity upon which the periodic table of the elements is based. The chemistry of any element is primarily dominated by the outer sphere electron environment. In the case of the actinides in the same oxidation state this outer sphere electron environment tends to be the same, for example  $5f^n7s^2$  or  $5f^{n-1}6d7s^2$ . The loss of electrons usually occurs from an inner electron shell which typically has only a minor impact on the chemistry of the element. This phenomena manifests itself in the radii of the elements <sup>2</sup>(Cleveland, 1979, p. 6), Table 1, which demonstrates that the radii for the species in the same oxidation state are essentially the same.

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Metallic, ionic, and covalent radii

Element	Meta	llic rad	ii, Å		Ion	ic radii	, Å		Single coval	e-bond ent rad	ii, Å
Oxidation State	+3	+4	+5	+6	+3	+4	+5	+6	+4	+5	+6
Uranium	1.92	1.74	1.61	1.54	1.03	0.93	0.87	0.83	1.62	1.5	1.42
Neptunium	1.89	1.72	1.6	1.52	1.01	0.92	0.88	0.82	1.6	1.49	1.41
Plutonium	1.86	1.70	1.59	1.51	1.00	0.90	0.87	0.81	1.58	1.48	1.40
Americium	1.84	1.69	1.58	1.5	0.99	0.89	0.86	0.80	1.57	1.47	1.39

The trend for the analogous lanthanides in the same oxidation state to exhibit similar behaviors is further borne out by experimental results, as shown in Figure  $1^3$ .

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**Figure 1.** Aqueous concentrations in 0.0018- $\mu$ m filtrates from nonphosphate-glass/water suspensions equilibrated under Ar(g) atmosphere. The solid line represents predicted solubility of Nd(OH)<sub>3</sub> (gl)

The second trend, the general trend of increasing stability of the actinide solid phases progressing across the series, follows the same well established trend of the lanthanides and actinides. As shown both in Table 1 and Table  $2^4$ , progressing across the lanthanide or actinide series, the ionic radii tend to decrease. This decrease in radii is commonly referred to as the lanthanide (or actinide) contraction. One result of this contraction is an increased stability of complexes of these metals with increasing atomic number, which manifests itself through decreased solubility products for analogous compounds with an increase in atomic number (see Figure  $2^5$ ).

#### Table 2.

М	M <sup>3+</sup> ionic radius, Ū	Unit cell vol, Å <sup>3</sup>	log K <sub>sp</sub> (equilib)	
La	1.160	141.8	-21.7	
Ce	1.143	139.8	-22.1	
Pr	1.126	135.9	-22.1	
Nd	1.109	133.6	-23.1	
Pm	1.093	130.1	(-24)	
Sm	1.27	129.3	-25.2	
Eu	1.25	127.8	-26.5	
Gd	1.053	126.0	-26.9	
Tb	1.040	124.1	-26.3	15
Dy	_ 1.027	122.2	-25.9	
Ho	1.015	120.5	-26.5	( t <u>a</u>
Er	1.004	119.2	-26.6	And They
Tm	0.994	117.8	-26.6	
Yb	0.985	117.3	-26.6	
Lu	0.977		-27.0	
Pu	1.115			
Am	1.09	132.8	-30	
			-23.3	
			-24.2	

Reported and est	imated values	of structural	and thermody	namic proper	ties of
$I_{n}(OU)$	and An(OU)	(antrias in n	aranthacas ara	actimates)3	

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-25.7



**Figure 2.** Variation of solubility products of actinide dioxides. (A) Hydrous oxides, experimental errors are within the point diameters, (B) Crystalline oxides, error bars represent reported accuracy in the experimental thermodynamic measurements.

Figure 2 demonstrates that the trend of increasing stability, with a concomitant decrease in solubility is reasonably accurate for a number of the +4 actinide oxides, which will be a dominant contributor to the WIPP disposal room chemistry. Additionally, Table 3<sup>6</sup> demonstrates the wide applicability under conditions which may exist at the WIPP.

#### Table 3.

Selected Stability Constants of +4 Carbonate and Hydroxycarbonate Species (from Moriyama et al.<sup>7</sup> and references therein)

<u>Species</u>	<u>log β</u>
$Np(CO_3)_2$	<27.9
$Pu(CO_3)_2$	30.0
$Np(CO_3)^{2+}$	<22.5
$Pu(CO_3)^{2+}$	17.0
$Np(CO_{3})_{3}^{2}$	<33.2
$Pu(CO_3)_{3}^{2}$	39.1
$Np(CO_{3})_{4}^{4}$	<38.5
$Pu(CO_3)_4^{4}$	42.9
Np(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	<41.6
$Pu(CO_3)_3^{2}$	44.5
$Np(OH)_{2}(CO_{1})_{2}^{2}$	45.69
$Pu(OH)_2(CO_3)_2^{2}$	46.4
$Np(OH)_{4}(CO_{3})_{3}^{4-}$	53.07
$Pu(OH)_4(CO_3)_2^{4-}$	51.84

Comparative Data of Oxidation Analogs

The similarity in behavior also extends to the solution species. As shown in Table 4<sup>8</sup>, the complexation constants for the analogous systems tend to be very similar.

Comparadi	o Data or	Onidation	141050				
	III			IV		VI	
	Sm	Am	Th	Np	U	Pu	
Inorganic	$\log \beta_1$		log ß,		$\log \beta_1$		$=$ $\langle \rangle \sim \langle \rangle$
SO4 <sup>2-</sup>	1.3	1.4	3.3	3.5	1.7	1.9	/ ··· · · · · · · · · · · · · · ·
OH-	-7.3	-7.5	-3.2	-1.5	-5.8	-6.0	
F-	3.1	2.9	4.5	4.7	4.7	4.3	
Organic	$\log \beta_1$		$\log \beta_1$		$\log \beta_1$		
Acetate	2.0	2.0			2.4	2.2	
EDTA	16.2	16.4	23	24			

The use of analogues for the actinides has been extensively used, while recognizing its limitations, and is well accepted within the scientific community.<sup>9</sup> In developing the Actinide Source Term Dissolved Species Model, the limitations of the oxidation state analogy were a

Table 4.

primary consideration. For example, the oxidation state analogy applied to +3 actinides trends very closely and provides for a very good predictive model, including when a model based on americium<sup>10</sup> data is used to predict neodymium behavior (Figure 3) or a model based on curium<sup>11</sup> is used to predict americium (Figure 4) and neodymium data (Figures 5 and 6). For the +5 actinides, neptunium is the only actinide of concern to the repositories performance and the +5 model was based upon neptunium data, with no necessity for imposing the oxidation state analogy. Although not utilized in the CCA, it is noteworthy that the oxidation state analogy holds very well for the +6 state with the log of the solubility product for  $UO_2CO_3(s)$  being -13.35  $\pm$  0.14 and the corresponding plutonium compound being -13.98  $\pm$  0.12.<sup>12</sup> The area being questioned for utilizing the oxidation state analogy is thus the +4 actinides. The +4 oxidation state exhibits the greatest variations of the actinide oxidation state analogy. These variations are principally due to the proximity of the electron orbitals in the +4 state and the ability of various electronic configurations to exist. However, the general trends that form the basis of the oxidation state analogy still exist, but vary in magnitude in relation to the stability of the various species. The trend of increasing stability progressing across the series is manifested in the +4 actinides and was used to develop a bounding predictive model. As shown previously in Figure 2, thorium has the least stable oxide phase and thus exhibits the highest solubility. Therefor the model for the +4 actinides was developed primarily based on thorium data, confident that the solubilities of any other actinides which may exist in the +4 state (i.e. Pu, Np, and U) will have lower solubilities due to the greater stability of the solid phase.



Figure 3. Prediction of Nd solubilities utilizing Am parameters.

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**Figure 4.** Solubility of  $Am(OH)_3$  in 5.61 molal NaCl solution as a function of pmH. The experimental data are from Runde and Kim.<sup>13</sup>



**Figure 5.** Experimental and calculated solubilities in the system NaCl-NdCl<sub>3</sub>-H<sub>2</sub>O. The experimental data are from Shevtsova et al.<sup>14</sup>





**Figure 6.** Experimental and calculated solubilities in the system  $CaCl_2$ -NdCl\_3-H<sub>2</sub>O. The experimental data are from Shevtsova et al.<sup>14</sup>

The trend of increasing solid phase stability resulting in lower solubilities holds true except for the case where there are exceptionally stable solution species formed. Only in the case that the stability of the solution species is more pronounced then the difference in the solid phase stabilities of the actinides will the conservatism of the predictive model come into question. During the course of the investigations into the expected chemistry in WIPP, several ligands and their ability to form stable solution species were investigated (to varying degrees). These ligands include:  $OH^-$ ,  $Cl^-$ ,  $CO_3^{-2}$ ,  $HCO_3^{-2}$ ,  $and PO_4^{-3-2}$ .

Of all the ligands studied, only sulfate  $(SO_4^{2-})$  (see Table 5<sup>15</sup>) can begin to exert a discernible impact on the relative solubility as a result of forming a stable solution species. However, 1) this effect is not strong enough to overcome the differences in the stability of the solid phases, 2) sulfate will be present only in very low concentrations in the repository (i.e., the expected concentrations are not high enough to cause any significant impact), and 3) sulfate is very readily consumed in the event of any microbial action.



with Su	lifate in 2.0 M Pe	rchlorate Media at	<u>25°C</u>	
Metal ion	$\log \beta_1^*$	$\log \beta_2^*$	Reference	
Th⁴⁺	2.22	3.56	Zielen <sup>16</sup>	
	2.20	3.45	Zebroski et al. <sup>17</sup>	
	2.26	3.56	Patil and Ramakrishna <sup>18</sup>	(M)
U <sup>4+</sup>	2.42	3.73	Sullivan and Hindman <sup>19</sup>	$\bigcirc$
	2.52	3.87	Day et al. <sup>20</sup>	
	2.53	4.93	Betts and Leigh <sup>21</sup>	
Np⁴⁺	2.43	3.47	Sullivan and Hindman <sup>22</sup>	
	2.53	4.04	Bagawde et al. <sup>23</sup> .	
	2.50	4.03	Patil and Ramakrishna <sup>24,25</sup>	

Table 5.	Values of Complexation Constants of Tetravalent Actinides (a)
	with Sulfate in 2.0 M Perchlorate Media at $25^{\circ}$ C

(a)  $\log \beta_n^*$  for  $M^{4+} + nHSO_4^- = M(SO_4)_n^{4-2n} + nH^+$ .

In addition to the sound theoretical basis for the oxidation state analogy, direct experimental demonstration under WIPP relevant conditions has been performed. These studies have included ThO<sub>2</sub>(am)/UO<sub>2</sub>(am) in 6.0 m NaCl (Figure 7)<sup>26</sup>, ThO<sub>2</sub>(am)/UO<sub>2</sub>(am) in various MgCl<sub>2</sub> solutions (Figures 8 and 9)<sup>26</sup>, Th(IV)/U(IV) in 0.1M sulfate (Figure 10)<sup>27</sup>, Th(IV)/U(IV) as a function of NaHCO<sub>3</sub> (Figure 11)<sup>27</sup>, Th(IV)/U(IV) in 0.01m NaOH as a function of CO<sub>3</sub><sup>2-</sup> (Figure 12)<sup>27</sup>, and Th(IV)/U(IV) as a function of pcH in 0.03m to 6 m NaCl (Figure 13)<sup>27</sup>.





Figure 7. Solubility of  $UO_2(am)$  and  $ThO_2(am)$  in 6.0 m NaCl at different equilibration periods. Solid lines represent predicted concentrations.





**Figure 8.** Solubility of  $UO_2$  (am) in 1.0 and 2.0 m MgCl<sub>2</sub> and of ThO<sub>2</sub> (am) in 1.0 and 1.82 m MgCl<sub>2</sub> at different equilibration periods. Solid lines represent predicted concentrations.





Figure 9. Solubility of  $UO_2$  (am) and of  $ThO_2$  (am) in 3.0 m MgCl<sub>2</sub> at different equilibration periods. Solid lines represent predicted concentrations.

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Figure 10. Solubility of  $UO_2$  (am) and of  $ThO_2$  (am) in 0.1 M sulfate at different equilibration periods.





Figure 11. Solubility of  $UO_2$  (am) and of  $ThO_2$  (am) as a function of bicarbonate concentration.



Figure 12. Solubility of  $UO_2$  (am) and of ThO<sub>2</sub> (am) in 0.01 m NaOH and either Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>.

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Without exception, these WIPP relevant data demonstrate that the actinide oxidation state analogy applied to thorium for constructing a predictive model for the +4 actinides provides a conservative prediction (i.e. it will over-predict by orders of magnitude) of the solubility of the other actinides which could exist in the +4 oxidation state. Based on the sound theoretical basis, which has been confirmed with direct, WIPP relevant observations, the use of the oxidation state analogy for the construction of the Actinide Source Term Dissolved Species Model was appropriate and prudent.

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### EEG Comment #3: Solubility - Organic Ligands

#### Text of EEG Comment:

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

#### **DOE Response:**

The EEG incorrectly asserts that the "CCA inappropriately discounts the role of organic ligands on plutonium solubility." This assertion is based on the false premise that the impact of an organic ligand is dependent only on its abundance. EEG appropriately concludes that citrate complexes with the +4 actinides are stronger than with the other major cations expected to be in the WIPP brines (e.g., Ca<sup>+2</sup>, Mg<sup>+2</sup>, Fe<sup>+2</sup>, Ni<sup>+2</sup>) as was stated in the CCA. The formation of stronger complexes by a bare, highly charged (+4) ion as compared to a lower charged ion (+2) is what would be expected based on the chemical theory and is borne out by experimental data.

As described to the EEG on numerous occasions, the most recent being the Technical Exchange on  $K_ds$  held on July 30, 1997<sup>28</sup> (see attachment 8), the degree of impact of any ligand depends on several factors. These factors include:

- concentration of actinides
- concentration of ligands
- concentrations of other metals
- speciation of actinides
- speciation of ligands
- speciation of other metals
- complexation constants of ligands with actinides
- complexation constants of ligands with other metals

The EEG's stated issue is based on a single one of the above listed factors, and is simply not appropriate.





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In the CCA, the DOE performed bounding calculations which demonstrated that EDTA, with a complexation constant over six orders of magnitude greater than that of any of the other organic ligands with a +4 actinide, will not have sufficient interaction with the actinides to have any appreciable impact on the dissolved actinide source term. These calculations were based on demonstrating that the organic ligands were essentially tied up by complexation with the numerous other metallic species which will exist in the disposal room environment. These calculations and their underlying assumptions were reviewed by the Waste Characterization Independent Peer Review Panel (the Panel). The Panel included in their Supplementary Peer Review Report:

"The Panel agrees that under the conditions of MgO backfill, chelating agents will have a negligible effect on repository performance. The Panel notes that, even at the basic pH in the repository, the availability of transition metals may be enhanced due to the formation of soluble halo complexes, making an even stronger case that base metals control ligand chemistry."

The EEG has ignored the conclusions of this independent, technically qualified panel, which performed a thorough review of the data, assumptions, and conclusions.

To reiterate what has previously been presented to the EEG, a simplified representation of the complexation of a metal cation by an anionic ligand proceeds according to equation 1.

$$M^{n+} + L^{m-} \leftrightarrow ML^{(n+m)}$$
 (eq. 1)

And the complexation relationship is described by a complexation constant (commonly referred to as  $\beta$ ) as shown in equation 2.

$$\beta_{M} = [ML^{(n+m)}]/[M^{n+1}][L^{m-1}] \qquad (eq. 2)$$

It is important to note that the concentration of the metal cation is for an uncomplexed metal cation. Hydrolyzed species, due to the strong hydroxyl to metal bond, do not effectively participate in the complexation. The inability of the hydrolyzed species to effectively participate in complexation was one of the drivers behind the decision to measure the complexation constants in a region where hydrolysis is not predominant (i.e., in a more highly acidic region than will be experienced in WIPP). When using the measured constants in a region where hydrolysis is likely to\_predominate (i.e., conditions reflective of those to be found in the WIPP), an extremely conservative calculation results because the concentration of the free metal cation is grossly overstated. For example, only the first hydrolysis constant of plutonium has been reliably measured due to either the formation of a highly insoluble precipitate (the solubility product of  $Pu(OH)_4$  is estimated to be approximately 7 x  $10^{-56}$ )<sup>29</sup>, or the formation of an insoluble polymeric species.

The calculations performed were also highly conservative due to the exclusion of the possibility of any degradation of, or alternate pathways for, the organic materials. For example, Rocky Flats

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Environmental Technology Site (RFETS) assumed for the purposes of the Transuranic Waste Baseline Inventory Report (TWBIR) that all of the EDTA that had ever been brought onto the site ended up in the WIPP TRU waste inventory. This assumption was utilized in the TWBIR and CCA calculations despite there being documented evidence<sup>30</sup> that most, if not all, of the K. W. Cleaner (the principal source of the EDTA) was used in Building 881. Building 881 is a very small contributor to the total TRU inventory at RFETS (on the order of 8 drums out of the currently stored approximately 6000 drums).

The CCA calculations were performed with EDTA and extended to the other organic ligands of interest based on EDTA being the most impactive. Equation 1 can be rearranged to show that, given the metal concentration to be the same for each calculation (which will be the case in the WIPP), the amount of metal existing as the complexed species is dependent on the product of the complexation constant (B) and the concentration of the ligand (equations 3 and 4).

$$[ML^{(n+m)}] = \beta_{M} [M^{n+}][L^{m-}]$$
 (eq. 3)

and where  $[M^{n+}]$  is the same for all cases

$$[ML^{(n+m)}] \propto \beta_{M} [L^{m}]$$
 (eq. 4)

Calculating the products of  $\beta_M$  [L<sup>m-</sup>] utilizing the average complexation constant for each of the organic ligands with Th<sup>+4</sup> from the CCA Appendix SOTERM Table SOTERM-5 and the ligand concentrations Table SOTERM-4, provides the data presented below in Table 6.

Table 6.

Complexation Constant/Ligand Concentrations Products

acetate oxalate

citrate EDTA







These data demonstrate that the calculations performed for EDTA constitute a bounding case and validate that the use of the EDTA calculations to dismiss the contributions from other organic ligands which may be in the waste was appropriate. The validity of the determination of lack of impact due to complexation with other metallic species is supported by independent data from the Paul Scherrer Institut (PSI)<sup>31</sup> and from Keiling and Marx<sup>32</sup>. Keiling and Marx investigated the influence of organic complexing agents, including EDTA, citrate, and oxalate in relatively simple brine systems (either saturated NaCl or Q-brine pre-equilibrated with either cement or bitumen). In their experiments, Keiling and Marx found a significant impact of the organic ligands on the actinide solubility. In the aforementioned experiments, the competing metals which will compete for the complexation sites are essentially absent (i.e., only small quantities of



calcium are present). At the PSI, the influence of the organic ligands EDTA, NTA, citrate, and oxalate on the speciation of Cs, Sr, Ra, Ag, Mn, Ni, Pd, Tc, Sn, Zr, Th, U, Np, Pu, Am, and Cm in cement pore waters was studied. In this study, it was found that EDTA complexes predominate only in the cases of Mn, Ni, and Pb, and that "in all other cases calcium-organic or metal-hydroxo complexes successfully prevent any significant influence of EDTA, NTA, citrate, or oxalate on the speciation of radionuclides." The introduction of the competing metals completely rendered the organic ligands inconsequential on the actinide solubility. These data constitute direct experimental confirmation of the combination of theory, calculations, and experimental measurements which appropriately allowed the dismissal of the influence of organic ligands on the speciation of radionuclides in the WIPP.

#### References for DOE's response to EEG comment #3:

28. Bynum, Vann, Bob Moore, FSU, and Jim Nowak: The Role of Organic Ligands in the WIPP. Presentation by Vann Bynum at the  $K_d$  Meeting with EEG, July 30, 1997, Albuquerque, NM.

29. Katz, J. J. and G. T. Seaborg: *The Chemistry of the Actinide Elements*, p. 300, John Wiley and Sons, Inc., New York (1957).

30. Rocky Flats Materials Hazard Manual

31. Hummel, W.: Organic Complexation of Radionuclides in Cement Pore Water: A Case Study. Paul Scherrer Institut, report number TM-41-93-03, January 25, 1993.

32. Keiling, Ch., and G. Marx: Investigations into the Influence of Organic Complexing Agents on the Leaching Behaviour and Mobility of Radionuclides Solidified in ILW Forms. Radiochim. Acta 52/53, 287 (1991).



#### EEG Comment #4: Solubility - Nesquehonite Effects

#### Text of EEG Comment:

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

#### **DOE Response:**

The EEG questions the use of hydromagnesite, rather than nesquehonite, as the equilibriumconstraining mineral phase in actinide-solubility calculations. The EEG refers to experiments conducted by SNL in early 1997 in support of their argument. It is imperative to note that those experiments were conducted to investigate long-term reactivity of MgO with  $CO_2$ , to address concerns of the Conceptual Model Peer Review Panel (Papenguth et al., 1997). Those experiments were <u>not</u> designed to define the mineral assemblage used in actinide-solubility calculations.

The choice of magnesium-carbonate mineral phase to constrain equilibrium calculations is clearly shown in the MgO-CO<sub>2</sub>-H<sub>2</sub>O phase diagram published in Dr. Friedrich Lippmann's definitive treatise on carbonate mineralogy (1973). As illustrated in Lippmann's figure, the <u>only</u> thermodynamically stable magnesium carbonate mineral in the MgO-CO<sub>2</sub>-H<sub>2</sub>O system is magnesite (Figure 1). Because of strongly held waters-of-hydration, water tends to be incorporated along with the magnesium carbonate minerals formed at temperatures near 25°C tend to be hydrated forms. At earth-surface temperatures, maturation of hydrated magnesium carbonate minerals to the anydrous form, magnesite, is slow. For actinide solubility calculations, we have elected to use a <u>metastable</u> hydrated magnesium carbonate mineral as the equilibriumconstraining MgCO<sub>3</sub> phase.

Generation of  $CO_2$  in the WIPP repository requires the presence of water to support microbial degradation of carbon substrates. If water is available for microbial activity, it will also be available for reaction (hydration) with MgO to form brucite  $[Mg(OH)_2]$ , a relatively fast reaction.



As CO<sub>2</sub> is generated, the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) will begin to increase. On the phase diagram (Figure 1), the reaction path, therefore, begins at 25°C at the left, and moves isothermally to the right. Brucite is present in the system. The pCO<sub>2</sub> continues to increase until the hydromagnesite-brucite join is met, at approximately  $10^{-4.2}$  atm pCO<sub>2</sub> (Figure 1). That point on the phase diagram <u>is</u> the invariant point. Because the moles of emplaced MgO exceeds the maximum possible amount of CO<sub>2</sub> generated by a factor of nearly four, the phase diagram shows that nesquehonite will <u>never</u> be produced in the WIPP.

The experiments conducted to address concerns of the Conceptual Model Peer Review Panel were designed to investigate long-term reactivity of MgO with  $CO_2$ . To achieve that objective, the DOE used one atmosphere pCO<sub>2</sub> to obtain measurable CO<sub>2</sub> uptake results in the time frame of months rather than decades. In terms of the MgO-CO<sub>2</sub>-H<sub>2</sub>O phase diagram, the initial reaction path began 25°C at log pCO<sub>2</sub> of 0, clearly in the nesquehonite "metastability" field. After extended periods of reaction, the crust that formed above the MgO pellets essentially reduced the delivery rate of CO<sub>2</sub> so that the hydromagnesite "metastability" field was encountered (reaction path moves isothermally to the left). Indeed, proto-hydromagnesite was identified in some of the long-term experiments (Papenguth et al., 1997; Davies and Bubela, 1973).

Lippmann's MgO-CO<sub>2</sub>-H<sub>2</sub>O phase diagram also demonstrates that an actinide solubility calculation constrained by the nesquehonite-brucite invariant point is not realistic. Such a calculation requires suppressing the precipitation of hydromagnesite, as well as magnesite. There is no evidence in the scientific literature that the precipitation of hydromagnesite is kinetically inhibited under moderately low  $pCO_2$  conditions. An equilibrium calculation constrained by the nesquehonite-brucite system is an unrealistic modeling construct (i.e., not consistent with the phase diagram) that produces a conservative modeling prediction.

In conclusion, the DOE strongly believes that the appropriate actinide solubility calculation for the WIPP should be constrained by the hydromagnesite-brucite system.

Figure 1.-Tentative phase diagram of the system MgO-CO<sub>2</sub>-H<sub>2</sub>O, modified from Langmuir (1965). Metastable fields are delimited by dashed lines and marked by the names of the metastable phases in italics. Triangles refer to direct experimental data, circles to thermodynamic data. (Figure and caption from Lippmann, 1973).







#### **References for DOE Response to EEG Comment #4:**

Davies, P.J., and B. Bubela. 1973. "The Transformation of Nesquehonite into Hydromagnesite," *Chemical Geology*. Vol. 12, no. 4, 289-300.

Langmuir, D. 1965. "Stability of carbonates in system MgO-CO<sub>2</sub>-H<sub>2</sub>O," Journal of Geology. Vol. 73, 730-754.

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

Papenguth, H.W., J.L. Krumhansl, R.V. Bynum, E.J. Nowak, Y. Wang, J.W. Kelly, N.J. Linarez-Royce. 1997. "Chemical Conditions Model: Results of the MgO Backfill Efficacy Investigation. Prepared for the WIPP Conceptual Models Peer Review Panel, April 23, 1997. WPO#44536.

# EEG Comment # 5: Recommendation of EEG for use of alternative solubility data and compliance impact of Nesquehonite-controlled solubility or no-MgO backfill solubilities.



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

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

#### **DOE Response:**

On the basis of the overall experimental and modeling justification for the solubility values used in the CCA, and the responses provided to EEG issues 1 through 4 in this document, DOE believes: (1) that the solubility-related concerns raised by the EEG have been discussed forthrightly; (2) that the information provided allows a reasonable scientific reviewer to consider the issues resolved; and (3) that additional justification for the CCA solubility values is not necessary.

The EEG has steadfastly claimed that MgO backfill cannot be simultaneously claimed for compliance with assurance requirements and containment requirements, despite clear and straightforward language in 40 CFR 194 that obligates the DOE to account for the solubility effects of MgO in the calculations performed to address containment requirements. The EEG has conducted and documented an analysis of disposal system performance without MgO (EEG 12/31/97 Letter, Attachment 1, page 2), as has the DOE, which has been provided to the EPA (documented in WPO# 43220). Both of these analyses demonstrate compliance with containment requirements without MgO backfill. There is no rational scientific or regulatory basis for the EEG's assertions that the MgO backfill emplacement plan and its treatment in the CCA models does not satisfy both the original intent and the letter of the assurance requirement regulations.



#### EEG Comment #6: 2D/3D BRAGFLO Calculations



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

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

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

- Since the discrepancy occurs above the fracture initiation pressure, the simulations should be limited to parameter vectors that result in pressures above 12.7 MPa at some time during the 10,000 year time frame.
- Direct brine release calculations should be sensitive to increased brine saturations above the waste residual brine saturation. Vectors that had either large brine saturations or a mobile brine component (saturations above the residual saturation) are more likely to be sensitive to increased brine inflow. Figure 5.1.5 of the preliminary sensitivity analysis report (Helton, 1996) indicates one vector with a 10,000 year pressure above 14 MPa and a brine saturation above 0.4. This is a likely candidate.
- The potential for brine consumption by corrosion should be assessed. Vectors with both slow and fast corrosion rates that also meet the above two criteria should be run.
- If the first simulations indicate a large change in saturation, then assess whether the 3D BRAGFLO simulations indicate a much larger number of significant direct brine releases than those calculated in the CCA. Simulations using brine saturations on the order of 0. 1 and 0.3 should be performed.



#### **DOE Response:**

The DOE previously responded to this issue with a memorandum submitted to the EPA docket on January 26, 1998 (Vaughn and Schreiber, 1998). That memo is reproduced as Attachment 1 for convenience.

Additionally, more complex supplementary 3D calculations were performed in concert with EEG's recommendations made during discussions with EEG at a January 17, 1998 meeting (Vaughn, Bean, Schreiber and Dotson, 1998). These results collectively show that the 2D geometry used by BRAGFLO in the 1996 CCA performance assessment calculations is appropriate and does not result in an underestimate of direct release during human intrusion. In all cases investigated (10 simulations using 9 CCA realizations) the 2D simulations consistently predict either the same or larger repository pressure and brine saturation than their 3D counterparts. Both larger pressure and brine saturation in the repository at the time of intrusion would lead to larger releases. Thus, the 2D geometry results in a conservative estimate of the releases when compared to results from a 3D representation. These calculations are also reproduced in Attachment 1.





#### **EEG Comment #7: Spalling**





#### **EEG Comment Text:**

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

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

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

The temporal and spatial discretization of the EPA investigation is far too coarse to investigate the potential for evacuation up the borehole of spall material created in the first few hundred seconds. For example, in the case of a two foot penetration with 0.25 m<sup>3</sup> spall cavity, the first element of the EPA analysis is 0.39 m thick. In the *Hansen et al.* model, the first element is 0.01 m thick. In the EPA investigation the first time step is 86 seconds compared to 0.001 seconds in the *Hansen et al.* model. These differences in both temporal and spatial discretization are an indication that the EPA modeling cannot predict gas velocities from local depressurization reliably. Hence, the EPA model cannot be used to judge the conservatism of the spall model described by *Hansen et al.*, nor the extension of the *Hansen et al.* model to potential spa from air drilling.

Hansen et al. also considered the issue of maximum particle size that could be transported up the borehole. Their results indicate that particles as large as 10,000 microns may be transported to the surface after the mud column has been expelled from the borehole, about 250 seconds after intrusion, and that transport of such large particles could occur for much more than 200 seconds. Two-hundred and fifty seconds is still very early in the EPA investigation (3 time steps). The discretization of the EPA model is too coarse to accurately calculate the flow rates this early in the 11-day period. In conclusion, the calculations of *Hansen et al.* indicate that transport of spall material up the borehole will not limit the release of spall material to the surface. DOE's Response to EEG Comments of 12/31/97 29 02/23/98

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



#### **DOE Response:**

As the EEG's comment addresses the analysis and treatment of the EPA rather than the DOE, the DOE declines to provide a specific response. For extensive discussion of the spalling issue, the EEG is directed to the DOE 1/26/98 submittal to the EPA docket.



### EEG Comment #8: Spallings - stuck pipe and gas erosion





The CCA (Chapter 6. p. 6-100) states that permeability of the waste compacted under a lithostatic load was found to be in the range of 10<sup>-12</sup> to 10<sup>-16</sup> m<sup>2</sup>, but assigns a constant value of  $1.7 \times 10^{-13}$  m<sup>2</sup>. which is much greater than the assumed threshold of  $10^{-16}$  m<sup>2</sup> for the "stuck pipe" scenario.

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

The EEG continues to believe that the "stuck pipe" is a plausible scenario because the threshold of  $1 \times 10^{-16}$  m<sup>2</sup> for stuck pipe and gas erosion may be faulty. This value resulted from the CCA Spallings model (as part of CUTTINGS S), which was found to be conceptually flawed.

Berglund (1994) states that, for model simplicity, a value of  $1 \times 10^{-16}$  m<sup>2</sup> will be used for a cutoff for blowout. The new spallings model, GASOUT (Hansen et al., 1997), shows that blowout will cease when permeability is between  $10^{-14}$  and  $10^{-15}$  m<sup>2</sup>. Berglund (et al., 1994) has shown that when blowout stops, the stuck pipe and gas erosion mechanisms of spall take over because the failed waste will be introduced into the borehole cavity and will not be blown out. Thus, the permeability threshold for the stuck pipe and the gas erosion scenarios appears to be  $10^{-14} - 10^{-15}$ . rather than 10<sup>-16</sup>. In any case, because of the stuck pipe and the gas erosion scenarios coming DOE's Response to EEG Comments of 12/31/97 02/23/98

into play when the blowout ceases, release to the surface will occur even when the conditions for blowout of the mud column cease. We therefore recommend that it should be assumed that all of the calculated spall material will reach the surface.



#### **DOE Response:**

The DOE notes that this issue has been previously addressed in the 1/26/98 DOE submittal to the EPA docket, in a memorandum by Knowles, Hansen, and Thompson (1998). For convenience, this memorandum is included in this document as Attachment 2.



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#### EEG Comment #9. Sensitivity of containment requirement compliance to spall releases

#### **EEG Comment Text:**



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

#### **DOE Response:**

The EEG is conveniently imprecise in its calculational method and claims about the sensitivity of compliance with the containment requirements to the magnitude of spalling release. First, the EEG ignores the probability aspect of releases - it has not attempted to determine the likelihood of a stuck pipe or gas erosion occurrence (note that the DOE believes stuck pipe and gas erosion are properly excluded from the calculations because they are not relevant to the future state of the waste). By omitting consideration of probabilities, the EEG has ignored an essential component for the construction of the CCDF (see section 6.1 of the CCA for a discussion of CCDF construction). Its treatment of the probability of the occurrence of stuck pipe/gas erosion is not discussed and is without basis. Without assessing the likelihood of stuck pipe occurring, the EEG's CCDF and sensitivity analysis are essentially meaningless. Second, in its sensitivity analysis the EEG multiplies releases used for the EPA-mandated PAVT. There is no physical basis to support this scaling of releases.

In summary, the EEG's sensitivity analysis is not reasonable nor even based on speculative worst-case conditions. It is simply without basis, and its only intent is to show failure of the WIPP to comply with the containment requirements.

#### EEG Comment #10: Direct Brine Release During Air Drilling

#### **EEG Comment Text:**



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

#### **DOE Response:**

The DOE responded to this issue in its 1/26/98 submittal to the EPA docket in a memorandum by Vaughn and O'Brien (1998). For convenience, this memorandum is attached to this document as Attachment 3.

#### EEG Comment #11: Fluid Injection - Hartmann Scenario



#### **EEG Comment Text:**

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

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

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


#### **DOE Response:**

In summary, the EEG assumes that the legal resolution of the Hartman v. Texaco case provides scientific evidence that a particular event occurred; i.e., the flow of significant quantities of water through a single zone in the Salado. Furthermore, the EEG assumes that there is enough injection data and geologic data to constrain the problem sufficiently for a meaningful verification of the DOE codes to be performed. In addressing this comment, the DOE notes that EEG did not mention hydrofracture of the Salado as a necessary component of the movement of such quantities of water over long distances in the Salado. However, as it is unlikely that the flows observed at Bates #2 occurred from intact evaporite rock, it is assumed that the EEG's statement "what is believed to have happened at the Bates Lease" is an oblique reference to the hypothesis of Bredehoeft (1997), in which a two mile or longer hydrofracture is postulated to have occurred from the Texaco Rhodes-Yates waterflood injection wells to the Bates Lease.

The stratigraphy and well-completion practices are different in the WIPP region than the Rhodes-Yates area. In its original analysis of the possible effects of fluid injection on the WIPP, the DOE investigated the effects of these differences (Stoelzel and O'Brien, 1996). This analysis found that the stratigraphic differences do matter, and that the well completion practices used at Rhodes-Yates would be expected to present greater hazard to the evaporite section. The original conclusion remains valid today: whatever its cause, the brine flow at the Bates #2 well is not relevant to the conditions at WIPP.

However, the DOE desires to address the EEG verification concern directly. Recently, the EEG courteously provided the DOE with copies of the documents in their possession relevant to the Hartman vs. Texaco case (and DOE provided the EEG with copies of relevant documents in possession of Sandia National Laboratories). Presumably, the EEG has concluded that these documents contain scientific evidence (1) demonstrating that a 2-mile hydrofracture actually occurred in the manner alleged by Bredehoeft and the EEG, and (2) that makes the Hartman situation a meaningful verification case for the BRAGFLO model of hydrofracture. Therefore, the DOE has conducted a review of these documents in an attempt to establish whether they contain such information. It is DOE's understanding that the majority of the court documents in EEG's possession were selectively copied for relevance to the hydrofracture issue from the case records of the legal counsel for Doyle Hartman. Thus, it seems reasonable to presume that the best evidence available for the presence of a long hydrofacture and water flows exists within these documents.

First, the finding by the jury in favor of Hartman, and the subsequent upholding of this verdict on appeal, has no bearing on either the quantity or quality of the scientific evidence in this matter, regardless of the technical qualifications of the witnesses. A legal proceeding is not analogous to a scientific proceeding. It can be assumed that the litigants on both sides of the case presented evidence perceived to be consistent with their aims in court. No assumptions regarding the quality of evidence presented seems tenable. In the case of Doyle Hartman and his expert witness, Van Kirk, it is clear that their motivation was to gain as much monetary compensation from Texaco as possible. In doing so, their testimony and exhibits presented only information they felt served their goal. Similarly, the testimony and exhibits introduced by Texaco were DOE's Response to 02/23/98 EEG Comments of 12/31/97 36



chosen in the best interest of Texaco according to a strategy that is only known to Texaco. From the pre-trial motions and proceedings, it is clear that neither party was interested in engaging in discussion during the trial exploring all of the potentially relevant issues. The finding of the jury is irrelevant as far as the use of data from the Bates lease and Rhodes-Yates field for scientific purposes is concerned. Therefore, the documents provided by the EEG were reviewed for their information content rather than the scientifically irrelevant proceedings, motions, and findings of the court.

The EEG challenges the DOE to verify its BRAGFLO model using data from the Hartman scenario. This is a curious situation, not commonly encountered when the reasonableness of a code is demonstrated in a quality assurance program. The EEG does not explicitly claim that the Hartman scenario is valid. Rather, the EEG states a belief about what happened. Thus, the DOE is challenged to verify its codes against a conceptual model that might not be valid. Therefore, two items must be addressed in this response: (1) is there adequate information to demonstrate validity of the Hartman scenario, and (2) is there adequate information provided by the Hartman case to provide a meaningful verification?

For a responsible scientific reviewer, a demonstration of validity of the Hartman scenario would include the following:

1. Evidence from the blowout zone of the intersection of a fracture.

2. Evidence from the injection zone of the formation of a fracture.

3. Evidence of the propagation of a fracture between the injection zone and the blowout zone, with significant flows through it, and

4. Evidence that alternative hypotheses are clearly not plausible.

If the Hartman scenario were found to be valid on the basis of the above criteria, then to perform a meaningful verification of BRAGFLO codes, quantitative information - hard data - would be necessary. Without adequate constraining data, too many variables and parameters in the verification would remain speculative, destroying the purpose of a verification attempt.

The following sections summarize the information available for the indicated topics.

# 1. The nature of the blowout zone.

It is known from records that the rate of drilling for the Bates #2 well accelerated as the blowout zone was approached (Hartman report, page 1 of 4 pages, undated, included in this document as Attachment 4).

The quantity of brine removed from the well, and the rates of its removal, are known to some extent, as is a shut-in pressure for the well after it was controlled (Attachment 4, p.2). This information was previously discussed in Bredehoeft (1997). The pressure gradient from the surface to the injection zone is also known approximately, as 0.966 psi/ft.





The geologic structure of the blowout zone is known. In his court testimony (page 689) Van Kirk states that the Bates #2 is located in "this little anticline, a – a place where fluids could accumulate." On page 5 of his report to Hartman, Van Kirk states, "Hartman's choice for the Bates #2 location was based upon two important factors: (a) the location was near the top of a structural high and (b) the Bates #1 well had been prematurely abandoned before producing its recoverable reserves from the Yates gas zone."

Although at least one sample of the fluid produced from the blowout zone appears to have been collected by a field worker, it was later discarded. There are no known elemental or isotopic analyses of the brine encountered at Bates #2.

Hartman plugged the blowout zone using large quantities of cement injected into the cavity that was intersected (Hartman report, page 4 of 4, Attachment 4; Van Kirk, 1994, Swift et al., 1997a). During the injection of this cement, pressure breakdowns occurred, indicating insufficient cement injection to fill the cavity. Hartman reports that a good squeeze was accomplished in accordance with NMOCD regulations.

#### **Discussion:**

Bredehoeft (1997) estimated the permeability of the production zone from the flow and pressure data presented, and his estimate was the subject of comment by Swift et al. (1997a and 1997b), who conclude that his estimate is of limited utility, at best, because he made assumptions that cannot be verified due to the absence of constraining data, and because his estimate ignored transient effects.

The minimum size of the cavity intersected by the Bates #2 well can be bounded by Hartman's description of the quantity of cement injected into the cavity to plug the hole. Hartman's description does not provide adequate description of the final injection sequence for assurance that the entire cavity was filled (although, even if the cavity was not completely filled, an effective plug may have been created).

Van Kirk (1994) discounts the possibility of the Bates #2 blowout occurring due to an encounter of a natural brine accumulation. His discussion is circumstantial, however, and does not consider the fact that natural brine reservoirs in Permian Basin evaporites have very high pressures, approaching lithostatic pressure in some cases. (For example, Van Kirk [1994] states on page 10 that natural water sources have pressure gradients of approximately 0.465 psi/ft, a hydrostatic gradient). His statements that brine reservoirs have not been encountered in the Bates lease township previously is not evidence of absence of brine reservoirs there.

Hartman located the Bates #2 on the crest of what he believed was an anticline. In the WIPP region, high-pressure natural brine flows from the evaporite section are associated with deformation or anticlinal structures (CCA, Appendix MASS). The conceptual model for brine accumulations in these structures, supported by observations at WIPP-12, is that a fracture network dominated by high-angle fractures contain brine. When one of the dominant high-angle fractures is intersected, rapid flows of brine can occur; over time, these larger fractures can be DOE's Response to EEG Comments of 12/31/97



replenished by flow from smaller fractures in the network. Natural flows may be observed in one well and not observed in a nearby well (CCA, Appendix MASS), suggesting that the dominant fractures in the network are spaced far enough apart that a borehole may pass through rock containing a reservoir without experiencing significant flows during the duration of drilling and casing.

In summary, there are few quantitative data regarding the nature of the blowout zone itself, other than observations of flows and pressures taken at the surface. The rates of production and decline suggests that it is valid to assume a very conductive feature was encountered, probably a fracture or fracture network, containing a fairly large quantity of brine. An interpretation of the permeability and thickness of the blowout zone (Bredehoeft, 1997) is regarded as having limited utility, at best (Swift et al., 1997b). There is no evidence whatsoever regarding the source of the fluids encountered. The hypothesis that the brine flows are due to encounter of a natural brine reservior is entirely consistent with the available facts, such as they are, as is the hypothesis that a feature origin for the Hartman scenario does not exist at the Bates #2 location. If such evidence exists, it needs to be found elsewhere.

#### 2. The nature of the injection field

Injection in the Rhodes-Yates field has occurred since about 1973. A total of approximately 41 million barrels had been injected by 1991. This represents an injection/withdrawal ratio of about 2.0. From 1977 to 1991, the cumulative injection/withdrawal ratio was ~1.9 or greater each year. From 1977 until 1991, an average of about 1.9 million barrels of water were injected per year, which is approximately 0.95 million barrels greater than fluids extracted (court exhibit prepared by plaintiff). The production rate of oil and gas declined dramatically in the late 1980's and early 1990's.

The Rhodes-Yates field, operated by Texaco, has the highest injection pressures of three injection fields in the Bates area, and is the furthest of the three from the Bates Lease (Van Kirk, 1994). Citing Texaco documents, Van Kirk states the reservoir pressure in November 1992 was about 2,200 psi in the Yates, an increase of approximately 650 psi from a 1927 pressure measurement of 1550 psi. (The top of the Yates is approximately 2700' deep; bottom ~ 3200' deep.) Hydrofracture stimulation of this formation in 1993 showed fracture closure pressures of 2600 to 2700 psi (Van Kirk, court testimony, p. 699). Van Kirk found that since ~ 1977 three of the injection wells operated by Texaco in the Rhodes-Yates field have operated fairly continuously with surface injection pressures greater than fracture pressures measured during step-rate tests (Van Kirk, 1994), and a fourth was operated from ~ 1977 to ~ 1983 with surface injection pressures in excess of fracture pressure. According to Van Kirk's map (1994, Figure 1), Texaco uses up to 34 injectors at its Rhodes-Yates waterflood unit.

Since 1979, Texaco has inferred casing leaks and Salado waterflows from well-logging tests in some injectors in the evaporite section, and has worked over the detected leaks to repair casing. For example, squeeze jobs were performed on Texaco No. 4 Rhodes "B" Federal NCT-1 at depths of 1190', 1650', and 2450' in October 1979 to repair leaking casing (Van Kirk, 1994). DOE 's Response to EEG Comments of 12/31/97 39 02/23/98

Water-bearing zones in the Salado within the injection field are documented or inferred by Van Kirk from Texaco data in three wells within its injection field: in the "B Number 1" well at 1635' and 2500' (sonant log; court testimony p. 683); in the "RYU 15" well at 2600' (temperature survey, court testimony p. 683); and the previously mentioned Texaco No. 4 Rhodes "B" Federal NCT-1 (Van Kirk, 1994).

#### **Discussion:**

Because water-bearing zones are observed in the Rhodes-Yates Unit in the evaporite section, leaky casing on some injectors there is plausible. The net quantity of fluid injected into the Yates is known, and presumably the quantity of fluid injected by each of the 34 injectors is also known. The physical properties of the Yates Formation are not well known (except, perhaps to Texaco), and the actual state of the wellbores is not known (again, except perhaps to Texaco). Although casing leaks into the evaporites is a plausible conclusion, it is impossible to determine how much fluid might have been lost to the Salado due to casing leaks. Conservative assumptions could be made, but to do that would defeat the purpose of a model verification. A verification study is conducted to demonstrate model realism and accuracy with respect to the known behavior of a well-understood system.

#### 3. The nature of the rock between the Rhodes-Yates waterflood and Bates #2.

Van Kirk, both in his 1994 report and court testimony, does not discuss flow between wells. He discusses similarity in pressure gradients calculated from well head pressures, and mentions similarity in the stratigraphic horizon for observed water flows in four wells. The mechanism of how these pressure gradients and waterflow elevations came to be similar is not explicitly stated, but rather seems left to the reader. He states that "Injection water has escaped from the interval being waterflooded due to the extremely high injection pressures utilized in past and in current operations" (1994, p. 2), and "The Texaco RYW has injected 20 million barrels more water than the amount of produced fluids. This unaccounted for volume of excess injected water is a highly suspect source for the water flows encountered within the RYW and at the Bates Lease." In the documents reviewed, the DOE has not found text in which Van Kirk states a belief that brine has flowed from the Rhodes-Yates waterflood to the Bates #2 location, or that hydrofractures extend from the Rhodes-Yates waterflood to the Bates lease, through any stratigraphic horizon.

Similarity in stratigraphic horizon among observed water-bearing zones in the Salado is circumstantial evidence for a long fracture with fluid flowing through it. This will remain the case unless or until the fluid observed in this stratigraphic horizon can be demonstrated to have originated in a Texaco injector well. In the WIPP region, brine reservoirs in the Castile are observed at similar stratigraphic intervals when geologic structure is present.

The EEG and Bredehoeft (1997) and Bredehoeft and Gerstle (1997) extend the hypothesis that a leaky casing on one of the injectors allowed enough liquid to escape into the Salado, at sufficient pressure, that a horizontal fracture formed within 12 years extending at least 2 miles. (The fracture would have to have formed in less than 12 years if Texaco had been conducting required Bradenhead tests every five years and annulus shut-in tests annually, and repairing casings if DOE's Response to EEG Comments of 12/31/97 40



necessary) Could this happen? An analysis of this hypothesis (Warpinski and Hansen, 1998, section 9, included as Attachment 5)) suggests that casing leaks with a rate of fluid release suggested by Bredehoeft and Gerstle (1997) would produce vertical hydrofractures with a lateral extent no greater than several hundred meters. The formation of hydrofractures with properties suggested by the EEG, Bredehoeft, and Gerstle, in the time frames required by their hypothesis, is not reasonable.

# 4. Summary and Conclusions

The analysis of Hartman documents and related information has revealed the following:

- At the location of the Bates #2 well, there is insufficient evidence to distinguish between an anthropogenic source of brine and a natural source of brine on the basis of available observations either concept is viable because neither can be disproven;
- Van Kirk, Hartman's expert witness, does not state the mechanism of pressure gradient equalization between the Rhodes-Yates waterflood and the Bates #2 blowout zone; and
- Fracturing and flow across 2 miles due to a leaking injection well is not credible on the basis of analysis with industry-standard models.

The Hartman scenario cannot be considered valid to the exclusion of other conceptual models on the basis of available data. Furthermore, even if it were considered valid for the sake of argument, there is insufficient constraining evidence of the rates of fluid loss through leaky casing and the properties of the blowout zone to meaningfully constrain a verification.

There is an alternative route to building confidence in the reasonableness of the BRAGFLO predictions. The petroleum industry stakes millions of dollars routinely on its ability to design and execute hydrofracture jobs. Warpinski and Hansen (1998) (Attachment 5) compare and contrast the Bredehoeft and Gerstle (1997) fracture model and the BRAGFLO fracture model to industry standard models and documented field experience. The principal conclusions of this comparison are:

- The Bredehoeft and Gerstle (1997) model of fracturing excludes the three essential features of any hydrofracture analysis, and instead focuses on a secondary effect;
- The BRAGFLO model treats all of the essential features of hydrofracture physics in an acceptable manner;
- LEFM-based fracture models routinely overpredict the extent of fracture length, and industry practitioners deliberately alter the formulation of LEFM governing equations to reduce predicted fracture lengths;
- The hypothesis of Bredehoeft and Gerstle (1997) regarding the events at the Bates #2 well cannot be confirmed using the standard practices of the petroleum industry.

As discussed in Attachment 5, the physical representation of the fracturing process by BRAGFLO is sound. If the model conditions are right for the creation of long fractures due to

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high fluid pressure, long fractures will form. This is demonstrated in the CCA. The conditions necessary for long fractures are

- low leak-off from the fracture,
- constrained fracture geometry, and
- high rates of fluid injection.



In the case of gas-generated fractures from the WIPP, the anhydrite and halite permeabilities are very low, creating a low leak-off condition. The fractures are constrained to the interbeds. The rates of fluid injection (i.e., gas production) are calculated by BRAGFLO probabilistically to evaluate the range of uncertainty in future repository conditions. In replicate 1 of the CCA calculations, two of 100 vectors created gas at a high enough rate to drive fractures 1900 meters away from the repository (less in the down dip direction). Getting back to the EEG concern directly, does the BRAGFLO model calculate long fractures with dip effects? Yes, but only if the conditions are such that long fractures would be expected. In the case of waterfloods, differences in the stratigraphy and well-completion practice indicate by modeling analysis that fluid injection effects in the vicinity of the WIPP site are of low consequence to WIPP performance.

In summary, the Hartmann Scenario is neither demonstrably valid nor meaningful for verification of BRAGFLO performance. Confidence in the reasonableness of the BRAGFLO formulation is available by other means, for example comparison with industry-standard oil-field simulators. The Bredehoeft and Gerstle LEFM formulation does not incorporate appropriate physics and is not verifiable.

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#### EEG Comment #12: Fluid Injection - CO<sub>2</sub> Floods

#### **EEG Comment Text:**

"The EPA does not anticipate the CO<sub>2</sub> injection for oil recovery will be a widespread practice in the future near WIPP (EPA CARD-23, p. 131). However, EPA's reasons do not have supporting references and appear to be at odds with the published literature. The EPA technical support document (III-B-22) states "at this time, the only examples of CO<sub>2</sub> injection enhanced recovery techniques are some distance from the WIPP site and under much different geologic conditions (Magruder 1990; Trash 1979)". But an examination of the current and relevant literature strongly suggests that the Delaware Mountain Group sands are excellent prospects for future  $CO_2$ flooding. First, CO<sub>2</sub> flooding has been demonstrated to be quite successful in mature fields in the Delaware Basin such as the Twofreds (Silva, 1996, pp. 142-145). Second, the DOE continues to sponsor university research on Delaware Basin oilfields, such as the Geraldine Ford and the West Ford, aimed at optimizing infill drilling and CO<sub>2</sub> flooding throughout the Delaware Basin. Third, oil and gas companies continue to purchase mature fields, such as the El Mar in the Delaware Basin, specifically for carbon dioxide flooding. Fourth, the recently drilled reservoirs surrounding the WIPP such as Cabin Lake, Livingston Ridge, Los Medanos, and Lost Tank have oil and reservoir characteristics that easily qualify them as potential candidates for future CO<sub>2</sub> flooding using the enhanced oil recovery (EOR) screening criteria."

#### **DOE Response:**

The EEG states that the EPA's conclusion that CO2 injection will not be a widespread practice near WIPP in the future is in error and in conflict with available literature. The EEG attempts to support this by characterizing the Twofreds flood as "quite successful." The EEG also infers that because the DOE is currently subsidizing CO2 flood research, that the technology's use near WIPP is eminent. The EEG also states that reservoirs near WIPP have oil and reservoir characteristics which "easily qualify them as potential candidates for future CO2 flooding."

Clarification is warranted on the reported "success" of the limited number of Delaware Canyon CO2 floods in the Delaware Basin of Texas. Of 60 fields that have been flooded in the Permian Basin, only four have been in the Delaware Basin. These are within the Ford-Geraldine, Twofreds, East Ford, and El Mar Fields of Loving, Ward, and Reeves Counties, Texas.

All four of these floods have been implemented within the upper Delaware Mountain Group and specifically within the Bell Canyon Series and, even more specifically, within the upper sandstone interval called the Uppermost Bell Canyon Sand or Ramsey Sand lying just beneath the Lamar (Delaware) Limestone. The Ramsey sand is considered the best of the Delaware Canyon Group Sands with permeabilities ranging up to 400 millidarcies in the channel facies. The Ford-Geraldine Field has two sands, the upper about 30 net and 50 gross feet thick and a second sand about 12 feet in thickness (Dutton et al. 1997; Thomas 1980; and Twofreds Engineering Sub-Committee 1961). The permeabilities of the productive sands average 35-40 millidarcies with porosities of 20% (Dutton et al. 1997; Thomas 1980). At the Twofreds field, the Ramsey Sand averages 25 feet in net thickness, 20% porosity, and 40 millidarcies DOE's Response to EEG Comments of 12/31/97 02/23/98





permeability (Twofreds Engineering Sub-Committee 1961; and Wilson 1980). The El Mar Field also produces from the uppermost Delaware Sand where the average thickness of the reservoir is 50 gross feet, the porosity averaging 21%, and the permeability averaging 24 millidarcies (Thomason 1980; and OGJ 1996). The East Ford Field averages 23% porosity and 64 millidarcies permeability (OGJ 1996). As of 1992, the average reservoir thickness for active CO2 floods in the Permian Basin was 97 feet (OGJ 1992).

Production from the upper Delaware Mountain group (Bell Canyon) section in the vicinity of WIPP has not been established. The New Mexico Bureau of Mines and Mineral Resources (NMBMMR 1995) notes that "at present, reservoir quality sandstones in the Bell Canyon are used for disposal of produced oil-field brines in the vicinity of WIPP." The nearest Bell Canyon production is the Triste Draw field over seven miles from the WIPP boundary. The Delaware production in the WIPP vicinity has been limited to the Cherry and Brushy Canyon formations which are poorer quality than the coarser, more permeable Ramsey Sand. The Nash Draw Project (NDP) has "porosity values ranging from 11 to 18 percent and permeability values ranging from .5 to 4 millidarcies." Clearly, both the porosity and the permeability for the reservoirs near WIPP at the NDP are less than the CO2 flooded reservoirs in Texas. There is no CO2 flood analogue for the Cherry or Brushy Canyon. Clearly, the models for CO2 flooding in the Delaware Basin are the uppermost and best of the Delaware Sands which are better quality sands and which are not productive in the vicinity of WIPP. There are marked differences between the characteristics of these four Texas fields and those near WIPP; trying to create a meaningful analogous relationship between the two is misleading and inappropriate.

The EEG statement that the U.S. Department of Energy continues to support work on Delaware Basin oilfields is true. How to recover more oil from the Ramsey Sand oilfields is indeed a challenge and worthy of government co-funded research. However, to draw the analogy of the Ramsey Sand projects in Texas to the WIPP-area Delaware Sands is both misleading and inconsistent when the specific properties of the reservoirs at both locations are considered.

The EEG states that WIPP-area reservoirs exhibit characteristics which easily qualify them as CO2 flood candidates. Recent data have become available regarding the Nash Draw Project, a cost-sharing endeavor by the DOE and Murphy Oil. This project's objective was to demonstrate the feasibility of waterflooding Delaware Sand reservoirs. Strata (1997) states that:

"the initial geologic interpretation suggested that the Brushy Canyon sands at the [Nash Draw Project] NDP appear to be blanket type sands. However, data and analyses obtained in the DOE class III project suggest the sands at the NDP are laterally discontinuous and complex in nature."

Early project results show that the permeability of the sandstones/siltstones is sufficiently poor to have caused Murphy to abandon plans for a waterflood. Each of the CO2 projects above have substantially better reservoirs than at Nash Draw and have attempted waterfloods, albeit with only limited success. The preliminary conclusions at the Nash Draw Project underscore the differences in reservoir characteristics between the Ramsey Sand reservoirs of Texas, and the WIPP-area reservoirs.



Finally, a point needs to be made regarding the relative merits of CO2 flooding within the best of the Delaware Sands (such as the Ramsey) versus those of the typical Permian Basin reservoirs (carbonates). The typical carbonate field of the Permian Basin produces about 10-15% of its oil in place via primary production. The waterflood phases adds another 20-25% or more than doubles the recovery during the primary phase. A good CO2 flood will add another 10-15%. The total recovery for a carbonate reservoir is thus around 40-55% of the OOIP. The few Delaware Sand floods have shown relatively poor performance. Dutton et al. points out that "thirteen years of primary production and 28 years of secondary (waterflood) and tertiary (CO2 flood) development in the Ford-Geraldine Unit have resulted in a recovery efficiency of only 28%." The lower permeability and porosity of the WIPP-area sandstone reservoirs would likely yield even lower recovery efficiency. Since the Delaware fields are small when compared to the carbonate fields, and because CO2 flooding is expensive, it is not likely that the recent growth of CO2 flooding in the Permian Basin will move into the upper Delaware Basin with its poorer quality reservoirs.

The DOE has commissioned a comprehensive independent assessment on CO2 flooding in the Permian Basin and an assessment of the potential for CO2 flooding near the WIPP site in both Lea and Eddy counties. This report (developed by Steve Melzer of the University of Texas of the Permian Basin) is provided in Attachment 6.

In the technical support documents to its proposed certification rule, EPA provides its assessment of the potential for fluid injection operations to adversely affect repository performance. This argument is made by assigning a probability of occurrence to each element of a scenario leading to an impact on the performance of the repository. The EPA's calculation resulted in a 1 in 667 million probability that fluid injection would affect repository performance. On the basis of EPA's calculations, and with the information from the report in Attachment 6, a meaningful comparison can be made contrasting the probability of EPA's fluid injection scenario elements with estimated CO2 injection scenario element analogs. This analogous probability argument leads DOE to estimate a 1 in 2 billion chance that CO2 injection could affect repository performance. DOE continues to believe that CO2 flood activities will not compromise the WIPP's compliance with EPA standards.

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#### EEG Comment #13: Fluid Injection - Natural Gas Storage

#### **EEG Comment:**

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

#### **DOE Response:**



The EEG has taken the EPA's statement out of context. Discussions and analyses of human activities with regard to resource extraction are implicitly limited to the Delaware Basin. The EPA states in CARD 32, p. 16, "Hydrocarbon storage takes place in the Delaware Basin but involves reinjection of gas into pre-existing boreholes into depleted reservoirs." This is a correct statement, and it is clear that the EPA considers the Delaware Basin as the appropriate region of interest, and that gas storage activities outside the basin are excluded from consideration. This is reasonable and appropriate due to geologic variations and differences elsewhere in New Mexico and Texas.

In addition, the EEG's statement and map which display three natural gas storage facilities in the Salado are incorrect. The facilities identified by the EEG are not natural gas storage facilities, but liquified petroleum gas (LPG) storage facilities. Also, as identified in the following map, there are five such LPG storage facilities, not three. Nonetheless, these facilities in the Salado are located outside of the Delaware Basin.





Underground Gas Storage Units Near the WIPP Site

# EEG Comment #14: Fluid Injection - Solution Mining

# **EEG Comment:**

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

#### **DOE Response:**

The DOE thoroughly addressed this issue in its May 14, 1997 response to the EPA's March 19, 1997 request for additional information. That response provides information on the DOE's screening decision and its basis, and is reproduced here for convenience:

#### Statement of Issue

The 40 CFR Part 194 criteria require that performance assessments for the Waste Isolation Pilot Plant (WIPP) Compliance Certification Application (CCA) include an analysis of the effects on the disposal system of any activities that occur in the vicinity of the disposal system prior to disposal or are reasonably expected to occur in the vicinity of the disposal system soon after disposal.

40 CFR Part 194 also states that performance assessments should assume future drilling practices and technology will remain consistent with practices in the Delaware Basin<sup>1</sup> at the time a compliance application is prepared. A survey of activities in the Delaware Basin has shown that there are a number of boreholes used for the solution mining of halite, to recover brine for use in drilling oil and gas boreholes.

Solution mining involves the injection of freshwater and the recovery of brine, which results in the formation of cavities at depth. If these cavities become sufficiently large, subsidence may take place in overlying strata. Losses from leaking boreholes could affect the hydrogeology of units overlying the halite and could change the geochemical environment in these units. Subsidence, changes in hydrogeology, and changes in the geochemical environment could all have an effect on the performance of the disposal system if solution mining occurs in the vicinity of the WIPP.



<sup>&</sup>lt;sup>1</sup> In 40 CFR Part 194, the Delaware Basin means those surface and subsurface features which lie inside the boundary formed to the north, east and west of the disposal system by the innermost edge of the Capitan Reef, and formed, to the south, by a straight line drawn from the southeastern point of the Davis Mountains to the most southwestern point of the Glass Mountains.

Hicks (1997) discussed solution mining and presented screening arguments for eliminating it from performance assessment calculations. The screening arguments were based on the solution mining operations in the New Mexico portion of the Delaware Basin. The DOE has recently reviewed solution mining operations in the remainder of the Delaware Basin, and additional material has been added to the following screening argument.

#### **Summary of Screening Decision**

Historical and current solution mining has been eliminated from performance assessment calculations on the basis of low consequence to the performance of the disposal system. Near-future solution mining has been eliminated from performance assessment calculations on the basis of low probability. Future solution mining has been eliminated from performance assessment calculations on regulatory grounds.

#### **Basis for Screening Decision**

#### Solution Mining in the Delaware Basin

#### Purpose

Oil and gas reserves in the Delaware Basin are located in structures within the Delaware Mountain Group and lower stratigraphic units. Boreholes drilled to reach these horizons pass through the Salado and Castile Formations which comprise thick halite and other evaporite units. In order to avoid dissolution of the halite units during drilling and prior to casing of the borehole, the fluid used for lubrication, rotating the drilling-bit cutters, and transporting cuttings (drilling mud) must be saturated with respect to halite. Most oil- and gas-field drilling operations in the Delaware Basin therefore use saturated brine (10 to 10.5 pounds per gallon) as a drilling fluid until reaching the Bell Canyon Formation, where intermediate casing is set.

One method of providing saturated brine for drilling operations is solution mining, whereby fresh water is pumped into the Salado Formation, allowed to reach saturation with respect to halite and then recovered. This operation may be performed in the vicinity of the drilling operation or remotely. In the latter case, the brine is transported by tanker or pipeline to the drilling site.

# Techniques

Two principal techniques are used for solution mining; single-borehole operations, and doublet or two-borehole operations.

In single-borehole operations, a borehole is drilled into the upper part of the halite unit. After casing and cementing this portion of the borehole, the borehole is extended, uncased into the halite formation. An inner pipe is installed from the surface to the base of this uncased portion of the borehole. During operation, fresh water is pumped down the annulus







of the borehole. This dissolves halite over the uncased portion of the borehole, and saturated brine is forced up the inner tube to the surface.

In doublet operations, a pair of boreholes are drilled, cased and cemented into the upper part of the halite unit. The base of the production well is set some feet below the base of the injection well. In the absence of natural fractures or other connections between the boreholes, hydrofracturing is used to induce fractures around the injection well. During operation, fresh water is pumped down the injection well. This initially dissolves halite from the walls of the fractures and is then pumped from the production well. After a period of operation a cavity develops between the boreholes as the halite between fractures is removed. Because of its lower density, fresh water injected into this cavity will rise to the top and dissolve halite from the roof of the cavity. As the brine density increases it sinks within the cavern and saturated brine is extracted from the production well.

#### Distribution

The DOE has conducted a survey of boreholes drilled within the Delaware Basin. This survey has identified eleven operating solution mining operations (Table 1). The distribution of these operations in New Mexico and Texas are shown on the accompanying map (Figure 1). Three active wells were identified within 4 miles (6.4 kilometers ) of Carlsbad. These are all more than 20 miles (32 kilometers) from the WIPP site. In addition, there is one inactive, temporarily abandoned well near Carlsbad, and a permit has been filed to drill a brine well in Lea County (Section 32, Township 23 South, Range 33 East), about 14 miles (22 kilometers) southeast of the WIPP site. However, no drilling has yet taken place at this latter site. The permit is only valid until January 12, 1999, and the operator has indicated that the well will likely not be drilled. There are no pending applications for brine solution wells in Eddy or Lea County.



# Table 1

ACTIVE BRINE WELLS IN THE DELAWARE BASIN			
Facility	Operator	County/Location Description	BR Number
Carlsbad	I & W	Eddy, 22S, 27E, Sec 24	BR 006
Carlsbad	Rowland Trucking	Eddy, 22S, 26E, Sec 36	BR 019
Carlsbad	Scurlock Permian Corp.	Eddy, 22S, 27E, Sec 23	BR 027
Orla	West Texas Water System	Loving/Blk 56, Twp 1, Sec. 30	BR 50030
Mentone	Herricks & Son	Loving/Blk 1	BR 50046
Barstow	Permian Brine Sales	Ward/Blk 34, NE of Barstow	BR 50022
Coyanosa	Permian Brine Sales	Reeves/Blk 7, Section 21	BR 50023
N. Pecos	Permian Brine Sales	Reeves/Blk 4	BR 50028
Peyote	Permian Brine Sales	Ward/Blk 16, Section 29	BR 50032
E. Mentone	Permian Brine Sales	Loving	BR 50062
N. Mentone	Permian Brine Sales	Loving	BR 50063

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#### Constraints

There are several constraints on the development of a solution mining operation:



(I) Availability of halite in sufficient amounts for economic extraction.

(ii) Availability of fresh water or dilute brine of appropriate quality and in sufficient quantities.

(iii) Convenient location with respect to drilling operations requiring brine, and to a suitable distribution network.

(iv) Absence of more valuable resources that would be damaged or otherwise lowered in value by solution mining.

The first of these constraints is satisfied throughout much of the Delaware Basin, where there are thick Permian evaporite deposits. In the region of the WIPP, the Salado and Castile Formations are both potential sources of halite.

The accompanying map of solution mining operations shows the importance of the second constraint. The majority of operations are situated along the Pecos River valley where shallow aquifers yield sufficient quantities of fresh water.

Oil and gas drilling operations in the Delaware Basin that are close to a suitable water supply are assumed to use locally-derived brine. Drilling operations remote from a suitable water source have two possible approaches to obtaining brine:

- Transport fresh water by tanker or pipeline to the site for solution mining.
- Transport brine by tanker or pipeline to the site for use in drilling muds.

The topography of the Delaware Basin is such that there are no major natural obstacles to transport either by road, rail, or pipeline. The decision on whether to transport fresh water or brine will depend on the relative economics of these approaches. Transport costs for fresh water and for brine are comparable on a mile by mile basis, so that the principal difference will be in the costs of solution mining. A specialized operation that can supply a large number of drilling operations will, in general, be more economic than a localized operation developed to service only a small group of wells. The majority of oil- and gas-drilling operations in the Delaware Basin obtain brine from specialized suppliers. Such specialized solution mining companies site their operations near suitable water supplies in order to reduce their transport, storage and development costs.

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Surface drainage in the region of the WIPP is intermittent, and is expected to remain so even under conditions of increased precipitation. The nearest perennial stream is the Pecos River, 12 miles (19 kilometers) southwest of the WIPP site boundary. Shallow aquifers along the Pecos River valley provide sources of abundant fresh water for solution mining, and no changes in the distribution of these aquifers is expected. Specialized solution mining operations are therefore unlikely to be sited close to the WIPP site.

With respect to the constraint imposed by other resources, there are several places in the Delaware Basin where potash resources are found within formations that might otherwise be used for solution mining. Because of the value of these resources<sup>2</sup>, there are restrictions on the type of drilling activities that may be conducted within the potash enclaves. These restrictions apply to oil- and gas-drilling that is targeted at deeper formations. Solution mining in support of oil and gas drilling could remove or render unminable large volumes of potash above or alongside a solution cavity and would also be restricted while potash reserves remain.

# **Consequences of Solution Mining**

# Subsidence

Regardless of whether the single-borehole or two-borehole technique is used for solution mining, the result is a sub-surface cavity which could collapse and lead to subsidence of overlying strata. Gray (1991) quoted earlier analyses that show cavity stability is relatively high if the cavity has at least 50 feet of overburden per million cubic feet of cavity volume (26.9 meters per fifty thousand cubic meters). There are two studies - discussed below - of the size of solution mining cavities in the Carlsbad region. These studies concern the Carlsbad Eugenie Brine Wells and the Carlsbad Brine Well and show that neither of these cavities are currently close to this critical ratio, but that subsidence in the future, given continued brine extraction, is a possibility.

Hickerson (1991) considered the potential for subsidence resulting from operation of the Carlsbad Eugenie Brine wells, where fresh water is injected into a salt section at a depth of 583 feet (178 meters) and brine is recovered through a borehole at a depth of 587 feet (179 meters). The boreholes are 327 feet (100 meters) apart. Hickerson noted that the fresh water, being less dense than brine, tends to move upwards, causing the dissolution cavern to grow preferentially upwards. Thus, the dissolution cavern at the Carlsbad Eugenie Brine wells is approximately triangular in cross-section, being bounded by the top of the salt section and larger near the injection well. Hickerson estimated that brine production from 1979 until 1991 had created a cavern of about  $3.4 \times 10^6$  cubic feet (9.6 x  $10^4$  cubic meters). The size of this cavern was estimated as 350 feet (107 meters) by 153 feet (47 meters) at the upper surface of the cavern with a depth of 127 feet (39 meters).



<sup>&</sup>lt;sup>2</sup> Potash mining in Eddy and Lea Counties, New Mexico produced 83 percent of the nation's domestic potash in 1992

Gray (1991) investigated the potential for collapse and subsidence at the Carlsbad Brine Well. Based on estimated production rates between 1976 and 1991, approximately  $3.4 \times 10^6$  cubic feet (9.6 x  $10^4$  cubic meters) of salt has been dissolved at this site. The well depth is 710 feet (216 meters) and thus there are about 210 feet of overburden per million cubic feet of capacity (112 meters of overburden per fifty thousand cubic meters of capacity).

Gray (1991) also estimated the time required for the cavity at the Carlsbad Brine Well to reach the critical ratio. At an average cavity growth rate of  $2.25 \times 10^5$  cubic feet per year (6.4 x 10<sup>3</sup> cubic meters per year), a further 50 years of operation would be required before cavity stability was reduced to levels of concern. A similar calculation for the Carlsbad Eugenie Brine well, based on an overburden of 460 feet (140 meters) and an estimated average cavity growth rate of  $2.8 \times 10^5$  cubic feet per year (7.9 x  $10^3$  cubic meters per year), shows that a further 15 years of operation is required before the cavity reaches the critical ratio.

# Hydrogeological effects

In regions where solution mining takes place, the hydrogeology could be affected in a number ways:

• Subsidence above a large dissolution cavity could change the vertical and lateral hydraulic conductivity of overlying units.

- Extraction of fresh water from aquifers for solution mining could cause local changes in pressure gradients.
- Loss of injected fresh water or extracted brine to overlying units could cause local changes in pressure gradients.

The potential for subsidence to take place above solution mining operations in the region of Carlsbad is discussed above. Some subsidence could occur in the future if brine operations continue at existing wells. Resulting fracturing may change permeabilities locally in overlying formations. However, because of the restricted scale of the solution mining at a particular site, and the distances between such wells, such fracturing will have no significant effect on hydrogeology near the WIPP.

Solution mining operations in the Delaware Basin extract water from shallow aquifers so that, even if large drawdowns are permitted, the effects on the hydrogeology will be limited to a relatively small area around the operation. Since all the active operations are more than 20 miles from the WIPP, there will be no significant effects on the hydrogeology near the WIPP.

Discharge plans for solution mining operations typically include provision for annual





mechanical integrity tests at one and one-half the normal operating pressure for four hours (OCD, 1994). Thus, the potential for loss of integrity and consequent leakage of freshwater or brine to overlying formations is low. If, despite these annual tests, large water losses did take place, from either injection or production wells, the result would be low brine yields and remedial actions would most likely be taken by the operators.

#### Geochemical effects

Solution mining operations could affect the geochemistry of surface or sub-surface water near the operation if there were brine leakage from storage tanks or production wells. Discharge plans for solution mining operations specify the measures to be taken to prevent leakage and to mitigate the effects of any that do take place. These measures include berms around tanks and annual mechanical integrity testing of wells (OCD, 1994). The potential for changes in geochemistry is therefore low, and any brine losses that did take place would be limited by remedial actions taken by the operator. In the event of leakage from a production well, the effect on geochemistry of overlying formation waters would be localized and, given the distance of such wells from the WIPP site, such leakage would have no significant effect on geochemistry near the WIPP.

#### Screening Analysis

# Low probability

Brine production through solution mining has not taken place near the WIPP site, and there are no plans for wells in this area in the near future<sup>3</sup>. The constraints upon the location of solution mining operations imposed by the availability of water indicate that there is a low probability of brine production through solution mining near the WIPP site in the near future.

Brine production through solution mining near the WIPP site can be eliminated from performance assessment calculations on the basis of low probability of occurrence in the vicinity of the disposal system.

#### Low consequence

Brine production\_through solution mining takes place in the Delaware Basin, and the DOE assumes it will continue in the near future.

Despite oil and gas exploration and production taking place in the vicinity of the WIPP site, the nearest operating solution mine is more than 20 miles from the WIPP site. The nearest

<sup>3</sup> Near-future human activities are those activities that may be expected to occur based on existing plans and leases. The DOE assumes that all such activities will occur and will continue until their completion, potentially at some time after disposal.





permitted site is 14 miles from the WIPP site, but the operator has indicated that there are no plans to proceed with drilling at this site. These locations are too far from the WIPP site for any changes in hydrogeology or geochemistry, from subsidence or fresh water or brine leakage, to affect the performance of the disposal system. Thus, the effects of historical, current, and near-future solution mining in the Delaware Basin can be eliminated from performance assessment calculations on the basis of low consequence to the performance of the disposal system.

Consistent with 40 CFR §194.33(d) performance assessments need not analyze the effects of techniques used for resource recovery subsequent to the drilling of a borehole in the future<sup>4</sup>. Therefore, future brine production from within and outside the controlled area has been eliminated from performance assessment calculations on regulatory grounds.

#### **References for DOE Response to Comment #14**

Gray, J.L., 1991. "Carlsbad Brine Well Collapse and Subsidence Investigation, Simon Environmental Services Project No. 502-939-01". Letter from J.L. Gray (Simon Environmental Services, Norman, Oklahoma) to W. Price (Unichem International Inc., Hobbs, New Mexico).

Hickerson, A.L., 1991. Letter from A.L. Hickerson (Odessa, Texas) to V. Pierce (B&E Inc., Carlsbad, New Mexico), April 12, 1991.

Hicks, T.W., 1997. "Solution Mining for Brine". Memo from T.W. Hicks (Galson Sciences Ltd., Oakham, UK) to P.N. Swift (Sandia National Laboratories, Albuquerque, New Mexico), March 7, 1997.

OCD, 1994 "Attachment to Discharge Plan BW-26 Approval Salado Brine Sales No. 3 Brine Facility Discharge Plan Requirements". Attachment to letter from W.J. LeMay, (Oil Conservation Division, Santa Fe, New Mexico) to W.H. Brininstool (Salado Brine Sales, Jal, New Mexico), January 12, 1994.

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<sup>&</sup>lt;sup>4</sup> Future human activities are those that occur within or outside the controlled area subsequent to repository closure, for which there are no existing plans and leases.

#### EEG Comment #15: Fluid Injection - Culebra water level rises

#### **EEG Comment:**

"There are other fluid injection issues that have either not been fully addressed or in which there appears to be a misunderstanding of the issue including, for example, the yet to be explained water level rises in the Culebra aquifer......"

#### **DOE Response:**



The EEG has not considered the effects of Culebra water level rises in the context of their potential impact on the performance of the WIPP. Because the EEG did not address the question of whether Culebra water level rises matter to WIPP performance, it has once again raised the issue of Culebra water level rises without considering or even mentioning the complete record of the DOE's technical basis for its treatment of water level rises in the CCA. The DOE is candid that the water level rises observed at H-9 are unexplained (CCA Chapter 2). However, the specific water level rise at H-9 is but one of many possible water level fluctuations that might occur in the near future. DOE recognizes that prediction of future water level changes in the Culebra while resources are continuing to be extracted is impossible. To evaluate the effects of water level fluctuations in the Culebra in general, as part of its FEP screening, the DOE conducted a bounding analysis of the possible effects of water level rises in the Culebra are of low consequence to the performance of the disposal system. There is no compelling WIPP safety or compliance issue associated with determination of the cause(s) of water level rises in the vicinity of H-9.

# EEG Comment #16: Waste Issues - Waste Inventory Uncertainty



# **EEG Comment:**

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

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

# **DOE Response:**

First of all, the DOE does not assert that there is no uncertainty in the waste inventory. Rather, DOE has acknowledged all those uncertainties and developed appropriate approaches to obtain the best estimates of waste inventory (DOE/CAO, TWBIR,1996). The PA calculations are based on the values documented in Transuranic Waste Baseline Inventory Report (DOE/CAO, 1996), which is the best source so far available for waste inventory. The waste inventory and waste form may change in the future, but those changes will be taken into account in WIPP every-five-years re-certifications.

In addition, the repository performance is very robust. For example, the PA calculations show that brine release for most radionuclides will be solubility-limited; therefore, an increase in the radionuclide inventory will not significantly increase releases of radionuclides in brine. Furthermore, the quantity of MgO emplaced in the repository is enough to control repository chemistry, even if all waste drums are fully filled with cellulosics, plastics, and rubbers. Due to the robustness of WIPP repository, there is no perceivable changes (or uncertainty) in waste inventory or waste form that can degrade the performance of WIPP repository.

# EEG Comment #17: Waste Issues - Cellulosics, Rubbers, and Plastics



# **EEG Comment Text:**

DOE has concluded that a maximum repository of  $2x10^7$  kg of cellulosics, rubber, and plastics (CRP) should be set in order to prevent production of more CO<sub>2</sub> than can be controlled by the MgO backfill. EPA has concurred in this recommendation. The expected amount of CRP is  $2.1x10^7$  kg.

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

#### **DOE Response:**

It has been demonstrated in the memorandum by Wang (1998) included as Attachment 7 that, even if all waste drums are fully filled with CRP, the amount of MgO emplaced in the repository will still be enough to control repository chemistry. Consequently, there is no need for imposing a upper limit on CRP inventory and therefore for accurately quantifying the uncertainty in determining weight parameters of those materials.

# EPA Comment #18: Waste Issues - Repository Limits



# **EPA Comment Text:**

DOE has concluded that all repository limits need to be controlled only for full repository. EPA has concurred in this recommendation and concluded that DOE's WIPP Waste Information System (WWIS) is capable of controlling repository limits. There are two concerns that do not appear to have been addressed:

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

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

# DOE Response:

Note that MgO will be emplaced in the inter-drum space and over the layer of three stacks of waste drums so that each drum will be surrounded by about equal amounts of MgO. The amount of MgO emplaced in the WIPP is sufficient to control repository chemistry even if all drums are fully filled with CRP (see memo by Wang, Attachment 7). Thus, the configuration of MgO emplacement will ensure that the chemistry in each drum will be effectively controlled by the surrounding MgO regardless of the variation of CRP concentration among individual waste drums. Therefore, there is no need to control CRP limits either on a full repository or a per-panel basis.

# Reference for DOE Response to EEG Comment #18:

DOE/CAO (1996) Transuranic Waste Baseline Inventory Report (Revision 3). DOE/CAO-95-1121.

# EEG Comments #19 - #24: Culebra Retardation Coefficient

#### **EEG Comment:**

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

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

The August 29, 1997 letter and the attachments (docket # II-D-17) contained the EEG position on this issue based on the July 30, 1997 meeting in Albuquerque, which was organized by the EEG. Copies of this letter with the attachments were mailed to several EPA officials and the EPA WIPP docket. The DOE also sent a copy of their impressions of the July 30 meeting (Dials to Neill 8/25/97 letter with attachments, docket #II-D-15) to the EPA on August 25, 1997, four days before the EEG letter.

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

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

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

# **DOE Response:**

Each of the six specific recommendations made by EEG in the next to last paragraph of their comment above is addressed individually in the following responses:





# EEG Comment #19: Culebra Retardation Coefficient - Actinides in Column Tests

# **EEG Comment:**

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..... EEG has recommended conducting both batch and column tests for at least the actinides Pu(III), Pu(IV), and Am(III) in the Culebra brine; .....

# **DOE Response:**

The WIPP Project carried out numerous batch and column sorption experiments with Am(III) and Culebra brines for the performance-assessment (PA) calculations to support the WIPP Compliance Certification Application (CCA). Triay and her group at Los Alamos National Laboratory (LANL) carried out many empirical (batch) sorption experiments with Am(III) in two fluids representative of those in the Culebra Dolomite member of the Rustler Formation, AISinR and H-17 (see Brush, 1996). D. A. Lucero and his colleagues at Sandia National Laboratories (SNL) carried out one experiment each with Am(III) in each of three cores (C-3, D-3, and E-2) from the Culebra in the AIS, using a Culebra fluid (Brush, 1996).

Plutonium exhibits behaviors quite unique among all of the elements. Of these unique behaviors, the ability to exist simultaneously in multiple oxidation states causes significant complications in performing plutonium experimental work. Under certain conditions, plutonium can effectively be maintained in a single oxidation state. For example,  $Pu^{+4}$  can reliably be maintained in concentrated nitric acid solutions, Pu<sup>+3</sup> can be maintained in concentrated hydrochloric acid solutions, and Pu<sup>+5</sup> has been reported to be the stable oxidation state in seawater. Outside of these specific conditions, plutonium typically exists as a mixture of two or more oxidation states.  $Pu^{+4}$  is perhaps the most difficult to maintain in a pure oxidation state due to its propensity to undergo disproportionation and the tendency to form polymeric species in all but highly acidic media. Experimentally, plutonium work is most easily accomplished at either extreme of its oxidation state possibilities (i.e. +3 or +6) where very strong reductants or very strong oxidants (redox controllers) may be utilized to maintain the oxidation state purity. Even under these circumstances the experiments are less than ideal in that one must segregate the effects associated with the plutonium from those that may arise from the redox controller being utilized. Therefor, using oxidation state analogs, which have previously been shown to be an appropriate approximation, are the best solution for obtaining reliable data on Pu<sup>+4</sup> behavior.

# Reference for DOE Response to Comment #19:

Brush, L.H. 1996. "Ranges and Probability Distributions of K<sub>d</sub>s for Dissolved Pu, Am, U, Th, and Np in the Culebra for the PA Calculations to Support the CCA." Unpublished memorandum to M.S. Tierney, June 10, 1996,. Albuquerque, NM: Sandia National Laboratories. WPO #38801. Contained in the CCA as Attachment 15-3 to Appendix MASS.



# EEG Comment #20: Retardation Coefficient - Uranium Uncertainty



#### **EEG Comment Text:**

..... EEG has recommended ..... setting the lower end of  $K_d$  for U(VI) to be zero;.....

#### **DOE Response:**

There is no credible scientific basis for setting the lower end of the range of  $K_{ds}$  for U(VI) to 0. The methods used by Brush (1996) to establish the ranges and probability distributions of  $K_{ds}$  for the CCA PA calculations included several conservative approaches and assumptions. For example, he established *separate* ranges and distributions for deep (Castile and Salado) and Culebra brines for each actinide element or elemental oxidation state and selected the range and distribution that resulted in *less retardation (greater transport)* of that element or oxidation state. In the case of U(VI), Brush (1996) established a range of 0.03 to 30 ml/g for the deep brines Brine A and ERDA-6 and 0 to 70 ml/g for the Culebra brines AISinR and H-17, specified a uniform probability distribution for both ranges, and selected the range established for the deep brines for the CCA PA calculations.

There is absolutely no scientific basis for setting the lower end of the range for the deep brines to 0. In fact, Brush (1996) probably should have increased the lower end of this range from 0.03 ml/g (a value obtained from Lucero's column-transport study) to 4 ml/g (obtained from Triay's batch sorption study)! Use of data from the column transport study to set the lower limit of this range (and the lower limits of the ranges for Np) was inappropriate. Consideration of the multi-rate diffusion model (Holt, 1997) for the column-transport study indicates that results from the column-transport study are quite conservative, because a relatively small fraction of the porosity of the intact cores was accessed on the temporal and spatial scales of the these experiments. By similar arguments (presented at several meetings with the EEG), results obtained from the batch study are more appropriate than those obtained from the column-transport study. However, use of a lower limit of 0.03 ml/g did introduce additional conservatism to the U transport calculations.

# References for DOE Response to Comment #20:

Brush, L.H. 1996. "Ranges and Probability Distributions of  $K_ds$  for Dissolved Pu, Am, U, Th, and Np in the Culebra for the PA Calculations to Support the CCA." Unpublished memorandum to M.S. Tierney, June 10, 1996,. Albuquerque, NM: Sandia National Laboratories. WPO #38801. Contained in the CCA as Attachment 15-3 to Appendix MASS.

Holt, R.M. 1997. Conceptual Model for Transport Processes in the Culebra Dolomite Member, Rustler Formation. SAND97-0194. Albuquerque, NM: Sandia National Laboratories.



# EEG Comment #21: Retardation Coefficient - Organic Ligands Effects

#### **EEG Comment Text:**

.....EEG has recommended ..... conducting sensitivity analysis for potential impact of organic ligands; .....

#### **DOE Response:**



Despite the fact that there is no credible scientific evidence that organic ligands will affect actinide  $K_{ds}$  in the Culebra, the WIPP Project carried out a sensitivity study of the effects of actinide  $K_{ds}$  on the overall performance of the repository and presented the results to the EEG on July 30, 1997. Although this study does not constitute evidence that organic ligands would actually affect actinide  $K_{ds}$ , the results can be used to assess the potential impact of organics.

# **References for DOE Response to Comment #21:**

Hrncir, D.C, J.F. Bresson, P.J. Robinson, and E.J. Bonano. 1996. *Waste Isolation Pilot Plant Waste Characterization Analysis Supplementary Peer Review Report*. Carlsbad, NM: U.S. Department of Energy Carlsbad Area Office. WPO #43151.

US Department of Energy. 1996. "The Role of Organic Ligands," *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Appendix SOTERM*. Carlsbad, New Mexico: US Department of Energy Carlsbad Area Office, SOTERM-36 - SOTERM-41.

# EEG Comment #22: Retardation Coefficient - Effects beyond 10,000 Years



#### **EEG Comment Text:**

..... EEG has recommended ..... extending performance assessment calculations beyond 10,000 years to see how long the chemical retardation delays the releases to the environment: .....

# **DOE Response:**

While feasible, extending PA calculations beyond 10,000 years is not necessary to demonstrate compliance with Federal regulations 40 CFR part 191 and 40 CFR part 194, which is the purpose of the CCA.



# EEG Comment #23: Retardation Coefficient - Sorption Isotherms

# **EEG Comment Text:**

..... EEG has recommended ..... investigating the potential impact of nonlinear sorption on radionuclide transport; .....

# **DOE Response:**

Inclusion of nonlinear sorption in the CCA PA would have resulted in less transport (greater retardation) of Am(III) in the Culebra. The ranges of nonlinear Am(III) K<sub>d</sub>s obtained by Triay during her batch sorption study are 70 to 2,000 ml/g for the deep brines and 80 to 900 ml/g for the Culebra brines (see Brush, 1996). Both of these ranges of nonlinear Am(III) K<sub>d</sub>s predict less transport than the range of linear K<sub>d</sub>s for Pu(V) used by Brush (1996) to establish the range for Am(III) (and Pu(III)) used in the CCA PA, 20 to 500 ml/g.

The nonlinear Am(III)  $K_ds$  discussed above probably resulted from precipitation and/or coprecipitation of Am(III), mechanisms that were conservatively excluded from the CCA PA. (The SECO-TP model used to predict radionuclide transport in the Culebra included only linear reversible sorption, it did not include potential retardation mechanisms such as precipitation and co-precipitation of radionuclides.) Therefore, inclusion of nonlinear  $K_ds$  and retardation mechanisms such as precipitation and co-precipitation would have resulted in less transport.

Nowak (1997, included as Attachment 9) also discussed this issue in considerable detail. His Viewgraph #7, for example, concluded that,  $Pu(V) K_ds$  are "conservative lower bounds" for Am(III) K<sub>d</sub>s because "Am(III) K<sub>d</sub>s are larger than  $Pu(V) K_ds$  in a preponderance of empirical results from many sources." This statement applies to linear, reversible Am(III) and  $Pu(V) K_ds$  obtained from studies carried out for applications other than the WIPP Project. Therefore, use of linear or nonlinear Am(III) K<sub>d</sub>s in the CCA PA would have resulted in predictions of less transport than did use of the linear  $Pu(V) K_ds$  submitted by Brush (1996).

# References for DOE Response to Comment #23:

Brush, L.H. 1996. "Ranges and Probability Distributions of  $K_ds$  for Dissolved Pu, Am, U, Th, and Np in the Culebra for the PA Calculations to Support the CCA." Unpublished memorandum to M.S. Tierney, June 10, 1996,. Albuquerque, NM: Sandia National Laboratories. WPO #38801. Contained in the CCA as Attachment 15-3 to Appendix MASS.

# EEG Comment #24: Retardation Coefficient - Pu and Am Phase



# **EEG Comment Text:**

..... EEG has recommended ..... checking the validity of the  $K_d$  values derived from the column tests by examining the cores to identify whether the Pu and Am are present in adsorbed or crystalline solid phase.

# **DOE Response:**

The WIPP Project carried out extensive posttest analysis of cores from Lucero's columntransport study, including an investigation of the mechanism(s) responsible for the immobilization of Pu and Am, and presented the results to the EEG. Perkins and Lucero (1997, included as Attachment 10) presented the results of detailed, destructive, post-test analysis of E Core from Lucero's column transport study to the EEG. The objective of this analysis was to identify the mechanism responsible for the immobilization of Pu and Am in this core. (Lucero never observed any breakthrough of Pu, Am, nor Th. Therefore, he was only able to calculate minimum values of the retardation factor R and K<sub>d</sub> for Pu, Am, and Th prior to these posttest analyses.) Perkins (1997, Viewgraphs 12 and 13) analyzed the profiles of 241Pu and 241Am in the upper 1 to 3 mm of E Core and concluded that, "Nearly all the recovered 241Am was in the top 1 mm of rock (probably precipitated)," but that, "The recovered 241Pu profile exhibits some structure more indicative of sorption."

As pointed out above (see Investigate the Potential Impact of Nonlinear Sorption on Radionuclide Transport), the WIPP Project conservatively omitted precipitation and/or co-precipitation of Am(III) (and other actinides) from the Culebra-transport calculations carried out for the CCA PA.

# **References for DOE Response to Comment #24:**

Brush, L.H. 1996. "Ranges and Probability Distributions of  $K_ds$  for Dissolved Pu, Am, U, Th, and Np in the Culebra for the PA Calculations to Support the CCA." Unpublished memorandum to M.S. Tierney, June 10, 1996,. Albuquerque, NM: Sandia National Laboratories. WPO #38801. Contained in the CCA as Attachment 15-3 to Appendix MASS.

Bynum, Vann, Bob Moore, FSU, and Jim Nowak. 1997. "The Role of Organic Ligands in the WIPP." Unpublished presentation to the EEG, July 30, 1997, Albuquerque, NM. Albuquerque, NM: Sandia National Laboratories. Included as Attachment 7.

Holt, R.M. 1997. Conceptual Model for Transport Processes in the Culebra Dolomite Member, Rustler Formation. SAND97-0194. Albuquerque, NM: Sandia National Laboratories.

Hrncir, D.C, J.F. Bresson, P.J. Robinson, and E.J. Bonano. 1996. Waste Isolation Pilot Plant Waste Characterization Analysis Supplementary Peer Review Report. Carlsbad, NM: U.S. Department of Energy Carlsbad Area Office. WPO #43151.

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Nowak, E.J. 1997. "Experimental Results and  $K_d$  Value Ranges in the CCA." Unpublished presentation to the Environmental Evaluation Group, January 30, 1997, Albuquerque, NM. Albuquerque, NM: Sandia National Laboratories. Included as Attachment 8.



Perkins, W.G, and Dan Lucero. 1997. "Intact-Core Column Results." Unpublished presentation to the Environmental Evaluation Group, January 30, 1997, Albuquerque, NM. Albuquerque, NM: Sandia National Laboratories. Included as Attachment 9.

US Department of Energy. 1996. "The Role of Organic Ligands," *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Appendix SOTERM.* Carlsbad, New Mexico: US Department of Energy Carlsbad Area Office, SOTERM-36 - SOTERM-41.

#### EEG Comment #25. Brine reservoir probability

#### **EEG Comment:**

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

#### **DOE Response:**

This EEG comment addresses the EPA treatment of the brine reservoir in the PAVT. Without commenting on the PAVT, the DOE states its belief on this issue that examination of results of both the CCA and the PAVT indicates that the penetration of a brine reservoir by an intrusion borehole has very little impact on compliance with the containment requirements. Credible sensitivity analyses from the CCA and PAVT, conducted using different assumptions about the characteristics and probability of penetration of a brine reservoir, indicate that the possible presence of a brine reservoir below the waste panels does not significantly alter the predicted performance of the WIPP. More succinctly, the possible presence of brine reservoirs beneath the waste panels does not affect the safety of WIPP.
## EEG Comment #26. Assurance Requirements/Engineered Barriers



#### **EEG Comment:**

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

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

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

• According to the September 1997 WIPP Final Supplemental Impact Statement (DOE/ES-0026-S-2), 27,000 m<sup>3</sup> of alpha emitting low level waste at INEEL will be processed to convert it to TRU waste.

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

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

In summary, of the existing 104,400 m<sup>3</sup> of CH-TRU waste, DOE plans to treat or repackage 88,900 m<sup>3</sup> or 85%. Of 15,500 m<sup>3</sup> not being processed, 3,000 m<sup>3</sup> is intended for shipment to meet scheduled commitments between DOE and the State of Idaho. EPA should recognize DOE's efforts in stabilizing the waste & encourage DOE to also fix the yet-to-be generated waste.

#### **DOE Response:**

The EEG has steadfastly claimed that MgO backfill cannot be simultaneously claimed for compliance with assurance requirements and for compliance with 40 CFR 191.13, despite clear and straightforward language in 40 CFR 194 that obligates the DOE to account for the solubility effects of MgO in the compliance calculations. The EEG has conducted and documented an analysis of disposal system performance without MgO (attachment 1, page 2), as has the DOE, which has been provided to the EPA. Both of these analyses demonstrate compliance with containment requirements without MgO backfill. There is no rational scientific or regulatory basis for the EEG's assertions that the MgO backfill emplacement plan and its treatment in the CCA models does not satisfy both the intent and the letter of the assurance requirement regulations. Thus, the MgO issue is not relevant to the EEG's desire for the DOE to process all waste that will be shipped to WIPP.

Initially, the waste brought to WIPP will not be treated in any fashion. This is entirely in conformity with the PA accomplished in the CCA. The CCA conservatively did not employ any credit in the performance assessment using knowledge of the many waste streams that DOE intends to treat prior to shipment to WIPP. It is presumed that the EPA's pending certification of the WIPP will allow only waste types discussed in the CCA to be emplaced until a recertification application is prepared and submitted that includes the effects of emplacement of alternative forms of waste. If necessary, concerns at WIPP raised by proposals to dispose of alternative forms of waste will be addressed systematically in future recertification applications and in revised operating procedures at the WIPP.

M



#### Attachment 1

January 15, 1998 memorandum from Vaughn and Schreiber to Marietta, "Response to EEG Issue Concerning Impact on Direct Release Due to 2D Repository Fluid Flow Modeling" (previously provided as part of January 26, 1998 DOE submittal to the EPA docket.)

and



February 25, 1998 memorandum from Vaughn, Bean, Schreiber and Dotson to Memo to Record, "Addendum to FEP Screening Analysis (S1: Verification of 2D-Radial Flaring Using 3D Geometry) : Response to EEG Issue Concerning Impact on Direct Release Due to 2D Repository Fluid Flow Modeling".



Operated for the U.S. Department of

Energy by

Sandia Corporation

Albuquerque, New Mexico 87185-1328

date: January 15, 1998

to: Melvin Marietta, 6821, MS 1395

trom: Palmer Vaughn, 6848, MS 1328, Jim Schreiber, 6849, MS 1328

subject: Response to EEG Issue Concerning Impact on Direct Release Due To 2D Repository Fluid Flow Modeling, In Letter from R. H. Neill, EEG to F. Marcinowski, EPA, 12/31/97

EEG has expressed some concern regarding results presented in FEP Screening Analysis S1: Verification of 2D-Radial Flaring Using 3D Geometry. At issue is Figure 15 of FEP S1 which shows "Cumulative Net Brine In and Outflow at Repository – Doubled Gas Generation Rate," comparing results for 2D and 3D BRAGFLO runs. In this plot, the net inflow of brine into the repository after 1000 years is nearly  $6 \times 10^6$  kg (about 5000 m<sup>3</sup>) for the 3D run, but zero for the 2D run. Thereafter, the 2D and 3D runs show similar behavior. EEG is concerned that this implies that 2D BRAGFLO runs, as used in the CCA calculations, may under-predict the actual inflow of brine into the repository. And more importantly, EEG speculates that the primary effect of higher brine inflows would be to increase releases associated with direct brine releases significantly above those considered during the CCA (Compliance Certification Application) calculations.

We feel that this concern is unwarranted for the following reasons. The FEP analysis results in question are from a run in which the gas generation rate was fixed at 3200 mol/(drum yr), which is twice the expected rate of 1600 mol/(drum yr) that was current when the calculations were carried out (May 1995). Furthurmore, the gas generation rate was not dependent on brine saturation nor on iron or cellulose inventory, and brine was not consumed during the gas generation reaction of corrosion. All of these assumptions are contrary to the modeling assumptions used in the CCA calculations and result in an overestimation of gas generation rates, total gas production, and brine availability in the repository. These assumptions were used in order to allow comparisons with another multiphase flow code, TOUGH28W, which had limited capabilities compared to BRAGFLO for WIPP-related simulations. Thus, extrapolation of these results to CCA calculations can be misleading when the details of the assumptions used are not taken into consideration.

Brine inflow prior to 1000 years in the 3D run occurs only after fracturing has occurred. In this run, anhydrite layer fracturing occurs after about 700 years as a result of very rapid





pressure buildup owing to the unrealistically high gas generation rate imposed and described above. In only one realization of 100 in the CCA undisturbed scenario (R1S1) did fracturing occur before 1000 years, so fracturing in this time period is not typical behavior. (In Replicate 2, fracturing occurred in three realizations prior to 1000 years, and in Replicate 3, it occurred in one realization.) In the CCA calculations, not only is the fully inundated gas generation rate much less than in the "doubled gas generation rate" 3D run, but the CCA gas generation rate is dependent on brine availability. In no case during the CCA calculations was all of the ferrous metal inventory consumed. The limited brine availability in the CCA calculations causes the gas generation rate and the consequent pressure buildup to be much slower than in the 3D run.

A more realistic comparison of 2D and 3D behavior can be seen in the results using the base case gas generation rate. In this case, pressures were not high enough during the first 1000 years to cause fracturing. (Since this was a human intrusion scenario, pressures dropped rapidly at the time of intrusion, 1000 years, and stayed low for the remaining 9000 years.) In this case, brine inflow during the first 1000 years was actually slightly lower in the 3D simulation than in the 2D run. Following the intrusion, cumulative net brine inflow in the 3D run was only slightly higher than in the 2D run, with the difference peaking at about 8000 years at about 10%. By 10,000 years, the brine inflow was nearly identical in the two runs, with the 3D inflow less than 1% higher than the 2D inflow. This result should be more typical of the 88% of the CCA realizations in which fracturing never occurred. In those few realizations where fracturing did occur in the CCA runs, the gas generation rate while fractures were open are closer to the base case rate than to the double rate, so the amount of brine inflow would be expected to be similarly low.

The impact of not accounting for the consumption of brine during the 3D simulation is sufficient to remove the concern raised by EEG. Analysis of the BRAGFLO results from the undisturbed scenario, Replicate 1, of the CCA calculations indicates that if all of the ferrous metals had been corroded (as was the case in the 3D simulation in question) approximately 56,000 m<sup>3</sup> of brine would have been consumed. In the 3D simulation the corrosion process is assumed to be completed in 1050 years. Thus had brine been consumed, it would have been so within the first 1050 years. Thus the amount of brine to be expected in the repository is better represented by reducing the volume of brine indicated from the 3D simulation by the amount consumed during corrosion of ferrous metals. When one accounts for this, the brine saturation is reduced by 63% of the pore volume. Since the 3D simulation predicts a maximum brine saturation of only 50% of pore volume (and this at 10,000 years), the conclusion is that there is insufficient brine inflow to consume all of the metal. Two further implications are that had brine consumption been considered in the 3D runs: 1) the repository would have become dry early on (i.e., prior to 1000 years), and 2) had gas generation been dependent on brine availability, much less gas would have been generated and its rate of generation would have been much slower.

Consideration of brine consumption during corrosion results in more realistic repository conditions. These more realistic repository conditions suggest little impact DOE's Response to 02/23/98 EEG Comments of 12/31/97 76



on Direct release. By referring to figure 4 of the above subject letter (also from Helton , "Preliminary Summary of Uncertainty and Sensitivity Analysis Results Obtained in Support of the 1996 Compliance Certification Application for the Waste Isolation Pilot Plant, Memo, Sandia National Laboratories, December, 1996.) it can be seen that the repository conditions that result when brine consumption is considered in the 3D simulation are within the uncertainty established and considered in the CCA calculations.

The conclusion of our evaluation is that the two-dimensional geometry used to model fluid flow by BRAGFLO does not result in repository conditions which cause an under-prediction of direct brine release or spallings release.

Please contact us if there is additional information you require for addressing this issue.



Operated for the U.S. Department of Energy by Sandia Corporation

Albuquerque, New Mexico 87185-1328

date: February 25, 1998

Memo to Record to: Palmillerghon for Jim Bear Vaughn, 6849, MS 1328, Jim Bean, 6848 Geocenters, James Schreiber, 6849, MS 132 from: Lori Dotson 6822, MS 1328 Palm Varyton for for Portson

subject: Addendum to FEP Screening Analysis (S1: Verification of 2D-Radial Flaring Using 3D Geometry) : Response to EEG Issue Concerning Impact on Direct Release Due To 2D Repository Fluid Flow Modeling.

## SUMMARY of ANALYSIS :

Our analysis concludes that the 2-D geometry used by BRAGFLO in the 1996 CCA performance assessment calculations is appropriate and does not result in an underestimate of direct release during human intrusion. In all cases investigated (10 simulations using 9 CCA realizations) the 2-D simulations consistently predict either the same or larger repository pressure and brine saturation than their 3-D counterparts. Both larger pressure and brine saturation in the repository at the time of intrusion would tend toward larger releases during drilling should the repository be breached. Thus, the 2-D geometry results in a conservative estimate of release during a drilling event when compared to results from 3-D representations. The 9 realizations selected for evaluation where selected based on their greater sensitivity to geometric and dimensional differences and are consistent with EEG's recommendations as defined during discussion with EEG at a 1/17/98 meeting with SNL.

## DESCRIPTION of the ISSUE :

EEG has expressed some concern regarding results presented in FEP Screening Analysis S1: Verification of 2D-Radial Flaring Using 3D Geometry. FEP S1 involved the use of some idealized and simplified processes so that verification could be made with Tough28w which had limited capabilities in the generation of gas and consumption of brine. The FEP S1 simulations differ from those of the CCA .With respect to gas generation FEP S1 represents an unrealistically large gas generation rate and total gas generated.

At issue is Figure 15 of FEP S1 which shows "Cumulative Net Brine In and Outflow at Repository – Doubled Gas Generation Rate," comparing results for 2D and 3D BRAGFLO runs. In this plot, the net inflow of brine into the repository after 1000 years is nearly  $6 \times 10^6$  kg (about 5000 m<sup>3</sup>) for the 3D run, but zero for the 2D run. Thereafter, the 2D and 3D runs show similar behavior after the intrusion at 1000 years. EEG is concerned that this implies that 2D BRAGFLO runs, as used in the CCA calculations, may under-predict the actual inflow of brine into the repository. And more importantly, EEG speculates that the primary effect of higher brine inflows would be to increase releases associated with direct brine release significantly above those considered during the CCA (Compliance Certification

Application) calculations. The EEG agrees with one of the conclusion of FEP S-1 that the increased brine inflow to the repository in the 3-d simulation did not increase release to the accessible environment through the marker beds. However, they also believe that the FEP S-1 did not demonstrate that the increased brine inflow predicted using the 3-D geometry will not lead to increased release during human intrusion. They speculate that the results of the 3-D modeling indicate that there is a potential for a combination of both high pressure and high brine saturation in the repository at the time of intrusion. These two conditions, they argue, did not occur simultaneously in the CCA calculations and this occurrence could lead to larger direct releases during intrusion if they did occur simultaneously.

#### **RESOLUTION APPROACH:**

To resolve this issue, the EEG recommends that an additional (and if possible, several) 3-D BRAGFLO simulations of the repository should be performed using parameter values from vectors used in the CCA performance assessment and not the idealized case used in FEP S1. EEG agrees that the potential for brine consumption by corrosion should be included in the 2D/3D calculations as it was in the CCA calculations. In selecting the particular vector/vectors from the CCA performance assessment calculations EEG suggest that consideration be given to the **undisturbed scenario** and vectors having higher pressures, larger degree of fracturing, higher DBR release, and larger repository brine saturation. Primary focus should be given to conditions leading to **higher repository pressure and interbed fracturing**.

We accept and go beyond EEG's suggestion and have analyzed 10 3-D calculations using 9 vectors from the undisturbed scenario across the 3 replicates. In our first and primary simulation for comparison, the two differences between the 2-D and 3-D counterpart are 1) the geometry modeled and 2) a simplified shaft seal system is used in the 3-D representation. to reduce the size of the 3-D mesh. Since the shaft seal system design is effective in isolating the repository as evidenced in the CCA PA, the shaft simplification does not impact the results of the 3-D calculations. Outside of the geometric differences, all parameter values and all processes are as they were during the running of the particular 2-D CCA BRAGFLO simulation. In order to evaluate the adequacy or conservatism of the 2-D geometry used in the CCA BRAGFLO calculations over a broader range of CCA conditions, 9 additional simulations are made for secondary comparisons. In these simulations 3 differences exist between the 2-D CCA simulations and their 3-D counterparts. First, the geometry is different as in our primary simulation. Second, the same shaft simplification is used, as describe above. Third, the fracturing of the interbeds in the 3-D representations is confined to the horizontal directions (lateral fracturing in the x -y plane). In the 2-D CCA simulations, the potential for fracturing in the vertical as well as the lateral direction was permitted. Since the anhydrite layers are bounded vertically by low permeability halite, the simulations produce the same results whether vertical fracturing is permitted or not. The reason for disabling vertical fracturing in the 3-D simulations is to achieve faster run times. This permits the adequacy of the 2-D geometry to be investigated over more realizations and CCA conditions. An explanation of why results are the same with and without vertical fracturing and a justification in the form of a direct comparison is presented in Attachment 1.





# SELECTION of VECTORS for CONSIDERATION :

The nine 2-D BRAGFLO CCA vectors (realizations) chosen for comparison in this analysis and the basis for their selection is given below

- Large brine inflow into the repositoryLarge brine inflow to repository
- from marker beds
- High repository pressure
- Long fractures
- High repository saturation and pressure
- Large direct brine release (DBR)

R1S1V023, R1S1V094, R2S1V028 R1S1V023

R2S1V081, R3S1V045 R1S1V014, R2S1V081, R3S1V029 R3S1V022 R2S1V024

Vector R2S1V081 is selected for the primary 2-D/3-D comparison. This vector is distinguished by having repository pressure in excess of lihostatic for one of the longest periods of time. This vector is also re-run with vertical fracturing ' disabled' to justify the disabling of this feature for other secondary comparisons (see attachment 1). The remaining vectors selected are run with vertical fracturing disabled.

# SELECTION of METRICS for EVALUATION of COMPARISONS :

Since pressure and saturation are the two primary dependent variables that BRAGFLO solves for, it is reasonable to use these as a basis for evaluation of the comparison. Further more since the focus of the EEG's concern is the impact on releases during a possible drilling event, parameters that most influence this type of release should be compared. The two BRAGFLO output variables that impact releases during drilling are the pressure and brine saturation in the repository. These two output variables are selected for the purpose of evaluating the 2D/3D comparisons and impact on drilling intrusion releases.

#### SOFTWARE USED :

BRAGFLO version BRAGFLO v.4.10 was used for generating the results of the 2-D CCA simulations. BRAGFLO version BF2\_FEPS1\_CG.for was used for generating the results of the 3-D simulations. Both versions were executed on the DEC ALPHA platform under OPEN VMS AXP version 6.1. All input files and executables are stored and available in the Configuration Management System (CMS) on the Alpha network.

## DESCRIPTION of CALCULATION : Repository

Use volume as modeled in the CCA =  $436 \ 144.4 \ m^{3}$ .

Use design N-S length = 2064 ft = 629.1072 m; round off to 630 m.

This length is from Fig. 10-1 of "WIPP Design Validation Final Report," Bechtel National, Inc., San Francisco, CA, October, 1986, p. 10-6.

Use height as modeled in the CCA = 3(1.3208 m) = 3.9624 m (= 13 ft). Then total width is:

 $\frac{436144.4 \text{ m}^3}{(630 \text{ m})(3.9624 \text{ m})} = 174.72 \text{ m}$ 

In 3D, we model half of the repository width = 174.72 m/2 = 87.36 m. Actual repository volume as now modeled =  $(2)(87.36)(630)(3.9624) = 436 155.63 \text{ m}^3$ .

#### **Operations** Region

Use volume as modeled in the CCA, including the 80-m-long seal at the north end of repository: =  $(80 \text{ m} + 283 \text{ m} + 50 \text{ m})(3.9624 \text{ m}) = 30929.3 \text{ m}^3$ .

Use design length from Fig. 10-1 of Bechtel, from repository to center of waste handling shaft = 1200 ft = 365.76 m; round off to 366 m.

Use height as modeled in the CCA = 3.9624 m. Then total width is:

 $\frac{30929.3 \text{ m}^3}{(366 \text{ m})(3.9624 \text{ m})} = 21.33 \text{ m}$ 

In 3D model, we use half of this width = 10.66 m. Actual volume as now modeled = (2)(10.66)(3.9624) = 30919.1 m<sup>3</sup>.

#### Shaft

Use shaft dimensions as modeled in the CCA:  $\Delta x = 10 \text{ m}$ ,  $\Delta y = 10 \text{ m}$ . In 3D model, we use half of this width = 5 m =  $\Delta y$ .

#### Experimental Region

Use volume as modeled in the CCA = [(500 m)(53.1 m) + (60 m)(20.5 m)](3.9624 m)= (26550 + 1230)(3.9624) = (27780)(3.9624)=  $110 075.472 \text{ m}^3$ 

Design length (N-S) from Fig. 10-1 of Bechtel, from center of waste shaft to north wall of northernmost E-W drift is 1100 ft + 400 ft + 340 ft = 1840 ft = 560.832 m; use 560 m, as in the CCA. Note that this length does not include a couple of short N-S drifts that extend north another 98 ft from this northernmost wall.

Use height as modeled in the CCA = 3.9624 m. Then total width is:



 $\frac{110075.472 \text{ m}^3}{(560 \text{ m})(3.9624 \text{ m})} = 49.61 \text{ m}$ In 3D, we model half of this width = 49.61 m/2 = 24.8 m. Actual volume as now modeled = (2)(24.8)(560)(3.9624) = 110 059.6 m<sup>3</sup>.



<u>Operations Region  $\Delta y$ 's</u>  $\Delta y_1 = 5 \text{ m}$  (dictated by shaft width)  $\Delta y_2 = 10.66 \text{ m} - 5 \text{ m} = 5.66 \text{ m}$ 

Experimental Region  $\Delta y$  $\Delta y_3 = 24.8 \text{ m} - 10.66 \text{ m} = 14.14 \text{ m}$ 

<u>Repository  $\Delta y$ </u>  $\Delta y_4 = 87.36 \text{ m} - 24.8 \text{ m} = 62.56 \text{ m}$ 





Figure 2: 3-D geometry; vertical cross-sectional view.

#### **RESULTS and DISCUSION :**



In figures 3 and 4 the repository pressure and the brine saturation, respectively, are compared between the 2-D CCA simulation and its 3-D counterpart for realization 081 of the undisturbed scenario, replicate 2. This realization is characterized by high pressure and long fractures. Vertical fracturing is enabled in both simulations. Both the pressure and brine saturation in the 2-D version are either nearly the same or slightly larger than its 3-D counterpart. Since larger pressure and higher brine saturation result in larger releases during drilling , everything else being equal, the 2-D geometry used by BRAGFLO for the CCA calculations leads to a conservative (larger) estimate of release than the 3-D representation.

In figures 5 through 10 the repository pressure and the brine saturation resulting from an additional 8 simulations are compared between the 2-D CCA simulation and their 3-D counterparts. The characteristics leading to the selection of these additional realizations are outlined in an earlier section. Vertical fracturing is disabled in the 3-D simulations as justified in Attachment 1. Both the pressure and brine saturation in the 2-D version are either nearly the same or slightly larger than their 3-D counterparts. Since larger pressure and higher brine saturation result in larger releases during drilling , everything else being equal, the 2-D geometry used by BRAGFLO for the CCA calculations leads to a conservative (larger) estimate of release than the 3-D representation.



Figure 3: Replicate 2- 2D/3D Comparison of Repository Pressure with vertical fracturing











Figure 6: Replicate 1- 2D/3D Comparison of Repository Saturation

February 25, 1998

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Figure 8: Replicate 2- 2D/3D Comparison of Repository Saturation





Figure 10: Replicate 3- 2D/3D Comparison of Repository Saturation

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#### **CONCLUSION** :

The conclusion of our evaluation is that the two-dimensional geometry used to model fluid flow by BRAGFLO during the CCA calculations does not result in repository conditions which cause an under-prediction of direct brine release or spallings release.

Distribution: Melvin Marietta. MS1395 Margaret S. Y. Chu, MS 1335 Kurt W. Larson, MS1335 D. Richard Anderson, MS 1328 Hong-Nian Jow, MS 1328 James Nowak, MS 1320 Roger A. Nelson, CAO SWCF-A:1.2.07.3:PA:QA:TSK:S1:Responce to EEG 12/31/97 EPA letter



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Attachment 1 : Justification for disabling vertical direction fracturing.

In BRAGFLO. as in many other multi-phase flow simulators, flow between adjacent numerical grid blocks is proportional to an average permeability of the neighboring blocks. A commonly used averaging technique and the one used in BRAGFLO is based on the harmonic average. This averaging results from mass conservation considerations. The harmonic average is defined as twice the product divided by the sum of the differing permeabilities. For widely different permeabilities, the harmonic average weights heavily the lower permeability value. This makes intuitive sense, since it is the lower permeability that restricts flow to or from one location to another.

When applied to vertical flow between an anhydrite layer and the adjacent halite in the WIPP stratigraphy, there is virtually no difference in the resulting permeability average regardless of whether the interbed is vertically fractured or not (see table 1 below). This is because both the intact and fractured permeability of the anhydrite are large (in excess of 2-3 orders of magnitude) compared to that of the halite. This does not mean that there is no leakage to or recharge or from the halite, only that this leakage or recharge is the same irrespective of vertical fracturing.

Table 1: Comparison of harmonic average permeability (m<sup>2</sup>)

Harmonic Average	Anhydrite Permeability	Halite Perme	eability
1.9998 x 10 <sup>-23</sup>	1.0 x 10 -19	$1.0 \times 10^{-23}$	Intact anhydrite
2.0 x 10 <sup>-23</sup>	1.0 x 10 <sup>-9</sup>	1.0 x 10 <sup>-23</sup>	Fully fractured anhydrite

In order to verify this result, the 3-D simulation of realization 081, of the undisturbed scenario, replicate 2 ,used for comparison in the main text, was rerun with the vertical fracturing disabled. In figures 1 and 2 of this attachment the repository pressure and brine saturation, respectively, are compared for this 3-D simulation with and without vertical fracturing. The results are, as expected, visually identical. We are, therefore, justified in making additional 2-D/3-D comparisons with vertical fracturing disabled.



Figure 1: Comparison of repository pressure in 3D models with and without vertical fracturing



Figure 2: Comparison of repository saturation in 3D models with and without vertical fracturing

# Attachment 2



January 20, 1998 memorandum from Knowles, Hansen, and Thompson to Memo of Record on waste permeability clarification, "*Clarification of Waste Properties*" (previously provided as part of January 26, 1998 DOE submittal to EPA Docket).



#### To: Memo of Record



From: M.K. Knowles, F.D. Hansen, MS 1395; T.W. Thompson, CTAC

Date: February 23, 1998

Re: Clarification on Waste Properties

Waste properties have been measured and discussed as part of several experimental programs, as noted in the attached list of references. These programs were conducted over a period of years by several different investigators. As a result, a coherent view of the waste character can be difficult to derive from a cursory review of the referenced documents. This memorandum draws information from each of these resources to provide the basis for the SNL position on the expected character and form of the disposed waste at the time of a hypothetical drilling intrusion. This position was presented to the Conceptual Models Peer Review Panel during April, 1997, and is summarized in references [3] and [5]. The SNL position is that the disposed waste should be characterized as a heterogeneous material, with varying degrees of cementation, saturation, degradation and compaction. Mechanical strength parameters discussed in reference [3] are conservative estimates of the weakest materials possible in the underground. Bulk permeability and porosity used in the system performance assessment for disturbed and undisturbed scenarios are appropriate for the CCA calculations.

Early experimental programs on geomechanical aspects of WIPP focused on large scale mechanical compaction processes and results. Mechanical and fluid flow properties derived from these experiments did not include salt encapsulation, cementation, and chemical degradation scenarios. Experiments conducted in support of the Compliance Certification Application (CCA) model for spallings assumed that sand comprised an appropriate analog for simulation of waste behavior. Absent from experiments conducted prior to 1996 was a rigorous analysis of the coupled mechanical and geochemical processes which are most likely to occur in the WIPP underground. Appendix A of reference [3] provides a perspective on these processes, and the rationale used in the development of waste surrogates for testing in 1997:

"It is important to note that the surrogate waste being specified does not represent the expected average waste condition, but rather the extremes in waste conditions."

As noted in Chapter 2 of reference [3]:

"The expected state of the waste at times when spall is most likely to occur comprises compacted drums of waste, encrusted along contact boundaries with minor degradation products."

The processes which occur within a specific waste region will be dependent upon the exact inventory in that room as well as the geomechanical history and hydrological properties of the incipient host rock. Many of these processes will result in chemical alteration and cementation of the waste forms, as noted in reference [6]. The conceptual model of the waste developed in reference [3] is of a heterogeneous, blocky medium with pockets of degraded material. This model applies for all conditions expected in the underground throughout the regulatory period. Computationally, it is quite difficult to characterize this type of waste product. Consistent with the conservative approach used in



the CCA, bounding conditions are assumed to develop materials for waste strength testing. As noted in Chapter 2 of reference [3]:

"Testing is being conducted to capture the "low end" of possible mechanical strength created as a result of extensive degradation."

Specimens were developed for the sole purpose of estimating the strength of the weakest waste forms expected to exist in the underground. Additional testing on waste permeability reference [3] and porosity reference [7] was conducted to provide a complete description of the waste surrogates. Recommended parameters for waste permeability and porosity used in performance calculations remain unchanged from those presented in the CCA. As noted in the preceding paragraphs, the conceptual model for the waste presented to the Conceptual Models Peer Review Panel was of a heterogeneous medium. The large porosity predicted in the CCA for conditions necessary to produce spall also necessitates a high permeability. These two models are mutually consistent; there is no need to modify the CCA value for permeability as a result of testing conducted for waste strength estimation.

A reasoned argument for the effects of spatially-variable waste permeability can be easily deduced. The existence of low permeability pockets in the underground will alter the flow paths in the repository during a drilling intrusion. Gas flowing to a wellbore may encounter these pockets, and will subsequently flow around them. Channeling is not expected due to diffusion processes. Channeling was investigated and described in Chapter 4 of reference [3], as well as analysis of the likely consequences of layering within the waste. These calculations support the position that the homogeneous models used to calculate spall releases (Chapter 3 of reference [3]) would provide conservative results.

Parameters, models, and calculations presented to the Conceptual Models Peer Review Panel represented a systems analysis approach to the issue of spallings releases. Experiments and analyses were conducted to address the specific concerns of the Panel, and to demonstrate that spallings releases presented in the CCA are reasonable.

The strong coupling of parameters and processes is recognized by the Panel and the investigators, and will easily be recognized by a diligent scientific peer. It is necessary to retain contextual correctness in the use of this (and any other) experimental data. Taken out of context, the specimen permeability in reference [3] would seem to imply that the bulk waste permeability used in the CCA is too high. However, when these data is implemented in the applicable conceptual model, no discrepancy arises. The SNL position is that the disposed waste should be characterized as a heterogeneous material, with varying degrees of cementation, saturation, degradation and compaction. Mechanical strength parameters discussed in reference [3] are conservative estimates of the weakest materials possible in the underground. Bulk permeability and porosity used in the system performance assessment for disturbed and undisturbed scenarios are appropriate for the CCA calculations.



DOE's Response to EEG Comments of 12/31/97



#### References

[1] Berglund, J.W. 1994. Memo to Record on August 31, 1994, Subject: The Direct Removal of Waste Caused by Drilling Intrusion into a WIPP Panel; -- A Position Paper. Sandia WIPP Central Files, Sandia National Laboratories, Albuquerque, NM. WPO#9882

[2] Butcher, B.M. 1989. "Waste Isolation Pilot Plant Simulated Waste Compositions and Mechanical Properties," SAND89-0372. Sandia National Laboratories, Albuquerque, NM.

[3] Hansen, F.D., M.K. Knowles, T.W. Thompson, M. Gross, J.D. McLennan, J.F. Schatz; 1997. Description and Evaluation of a Mechanistically Based Conceptual Model for Spall. SAND97-1369. Sandia National Laboratories, Albuquerque, NM.

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[5] Wilson, C.D., D. Porter, J. Gibbons, R. Oswald, G. Sjoblom, 1997. Waste Isolation Pilot Plant Conceptual Models Peer Review: Third Supplementary Report.

[6] Expert Elicitation on WIPP Waste Particle Diameter Size Distribution(s) During the 10,000 Year Regulatory Post-Closure Period.

[7] RE/SPEC Miscellaneous Tasks: Progress Reports for Contract AG-4911. Sandia WIPP Central Files, Sandia National Laboratories, Albuquerque, NM, WPO#47983.

CC:

MS 1320	H.W. Papenguth
MS 1328	H-N. Jow
MS 1328	P. Vaughn
MS 1335	K.W. Larson
MS 1335	D.S. Coffey
MS 1335	M.S.Y. Chu
MS 1395	L.E. Shephard
MS 1395	M.G. Marietta
MS 1395	MKK Day File/Spallings
SWCF-A:WBS 1.1	.01.2.7:QA:TD:Waste properties



# Attachment 3

January 15, 1998 memorandum from Vaughn and O'Brien to Marietta on Response to Direct Brine Release During Air Drilling (previously provided as part of January 26, 1998 DOE submittal to EPA Docket).





date: January 15, 1998

to: Melvin Marietta, 6821, MS 1395

- from: Palmer Vaughn, 6848, MS 1328, Darien G. O'Brien, Solutions Engineering and Teklu Hadgu, Applied Physics
- subject: Response to Air Drilling Letter from R. H. Neill, EEG to F. Marcinowski, EPA, 12/31/97

We have reviewed the subject letter from EEG's work concerning air drilling and have found little basis for their conclusions. Here are our comments and analysis for your consideration. Their conclusions result from four major areas of oversight which we address below. They are: 1) inappropriate and incorrect specification of fluid properties, 2) inappropriate extension of Poettmann and Carpenter correlation, and 3) unreasonable specification of boundary conditions in the S3 scenario. We believe that had the EEG estimates been based on proper application of BRAGFLO\_DBR and proper input specification for treating air - drilling, that no noticeable impact on the CCA (Compliance Certification Application) CCDF's (Complimentary Cummulative Distribution Function) would be observed. The following text summarizes our salient points. The page numbers correspond with those from Enclosure 4 to the 12/31/97 Letter from R. H. Neill, EEG to F. Marcinowski, EPA:



1) Page 1: The change which the EEG employed for modeling air was to reduce the fluid density by 3 orders of magnitude from 1215 kg/m^3 to 1.161 kg/m^3 . In addition, EEG changed the fluid viscosity by three orders of magnitude from 2.1E-03 Pa-sec to 18.6E-06 Pa-sec. This change is reflected on page 10 of the ALGEBRA input file. By altering the ALGEBRA file in this fashion, EEG has assigned the fluid properties of air to both the drilling fluid and the liquid phase fluid in the repository and surroundings. By changing the density and viscosity in this section of the ALGEBRA file, EEG has essentially **artificially increased** the mobility of the brine in the repository to that of air . This greatly increases the transmissivity in the repository and inflates brine release predictions (flow is directly proportional to fluid mobility). This inflation results in the large releases that the EEG reports at the surface.

2) Page 1: The threshold hydrostatic mud column assumed for releases is 8 MPa in the CCA calculations versus 2 MPa proposed by EEG for an air column. These

Doyle Hartman C. T. BATES NO. 2 1980' FSL and 760' FwL (L) Section 10, T-26-5, R-37-E Lea County, New Mexico Rhodes (Y-7R) Gas Elev: 2978.7 GR Proposed TD: 380C' Cactus Rig No. 53 API No. 30-025-311167



01-14-91 Moved in and RU Cactus Rig No. 53. Spudded well at 9:00 PM CST 1-13-91. Drilled a 12-1/4" hole to a total depth of 459' RKB. Circulated hole for 1/2 hour, and pulled out of hole with drill string. Ran 9-5/8" OD, J-55, 36 #/ft, LT&C surface casing as follows and landed at 457' RKB:

1	•	Halliburton 9-5/8" OD Texas Pattern Notched Shoe	0.51
1	-	Jt. 9-5/8" OD, J-55, 36 #/ft, LT&C casing	44.70'
1	-	Halliburton 9-5/8" OD Superseal Float Shoe	1.30'
9	-	Jts. 9-5/8" OD. J-55, 36 =/ft. LT&C casing	391.27'
		Total	437.77
		KB	17.00'
		Below Ground Level	1.83'
		Setting Depth (RKB)	456.60'

Cemented casing with 350 sx of API Class-C cement containing 2% CaCl2 at a cementing rate of 10 BPM. Wooden plug down at 7:15 AM CST 1-14-91. Pressured casing to 1800 psi and pressure held okay. Released pressure and float held okay. Circulated 8 sx of excess cement to pit.

Bit No. 1 was a 12-1/4 inch HP12J with 3 - 13's. Pump pressure - 800 psi and RPM - 125. Total footage was 459 feet in 5 hrs. Bottom hole assembly was a  $12-1/4^{-7}$  bit, bit sub, 6 - 7" OD drill collar, and 8 - 6-1/4" drill collars. Hook load - 50,000 lbs and pump arrangement - 5-1/2 X 16 X 64.

Mud properties are: WT = 8.5, VIS = 32. Daily time breakdown: 1 hr idle, 4 hrs rigging down, 10 hrs moving in and rigging up, 5 hrs drilling 1-1/4 hrs TOTCO, 1/2 hr circulating, 3-1/2 hrs running casing and cementing (Total = 25-1/4 hrs). Deviation surveys were:  $1/4^{\circ}$  @ 250' and  $1/2^{\circ}$ @ 459 feet. After waiting on cement 18 hrs, plan to drill out below surface casing at 1:15 AM CST 1-15-91.

Presently drilling 8-3/4 inch hole in Red Beds at a total 01-15-91 depth of 973 feet. Progress previous 24 hours was 514 feet. Mud properties are: WT - 10.0, VIS - 29, WL - NC, Chlorides - 182,000, PH - 9.5. Deviation survey was 1/2° @ 796'. Daily time breakdown was 1 hr to finish running 9-5/8" OD surface casing, 1/2 hr cementing, (PD @ 7:15 AM CST 1-144-91), 6 hrs WOC, 4-3/44 hrs nippling up BOP, 1/4 hr testing blind rams, 1 hr trip in hole with drill string, 1/4 hr testing pipe rams and casing to 1500 psi, 5-1/2 hrs WOC, 1/4 hr drilling wooden plug, cement, and shoe, 4-1/4 hrs drilling new hole, and 1/4 hr TOTCO. Bit No. 2 is a Reed 8-3/4 inch HP-53 with 2 - 12's and 1 - 10. Pump pressure -1000 psi, bit weight = 40,000 lbs, RPM = 100. Bottom-hole assembly is an 8-3/44 inch bit, bit sub, 2 - 7" OD drill collars, stabilizer, 7" OD drill collar, stabilizer, 3 - 7" OD drill collars and 17 - 5-1/4" OD drill collars. Hook load - 68,000 lbs. Pump arrangement - 5-1/2 X 16 X 62. During last 24 hours added 2 sacks of caustic, 5 sacks of paper, and 40 gal of ASP-725.

01-16-91

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1:45 AM - Drilling in Salt Section at approximate depth of 2270'. Experienced drilling break of 86' in 11 minutes from 2244-2280'. Well flowing salt water and some gas to reserve pit through 4" choke valve with pressure of 800 psig.



changes are reflected in the highlighted sections of the ALGEBRA file for Air Drilling Scenario on pages 11, 12 and 13. These changes have been properly made by EEG to the ALGEBRA input file for the purpose of comparing the 8 MPa with the 2 MPa hydrostatic pressure. The way that the ALGEBRA file works is that a vector is allowed to "blowout" only when the repository pressure exceeds the threshold. So, reducing the threshold from 8 MPa to 2 MPa allows more vectors to be potential candidates for "blowout" consideration. However, the consequences of these additional candidates are greatly inflated by EEG in light of item one above and two additional assumption violations :

A) To determine the releases, the Poettmann and Carpenter correlation is used to obtain the FBHP (Flowing Bottom Hole Pressure) and was developed assuming initial panel pressures between 8 MPa and 16 MPa. Using the Poettmann and Carpenter correlation table created for BRAGFLO\_DBR outside of the 8 to 16 MPa range is not valid because the table has not been defined outside this range.

B) An important assumption was made in the application of the Poettman and Carpenter correlation in BRAGFLO DBR. That is, the FBHP predicted by the correlation at the time that the repository is breached is assumed to be constant through-out the DBR release period of time (11 days). This assumption , while valid when drilling mud is used, becomes invalid and unreasonably conservative for the case of air - drilling. In the case of air - drilling, once the repository is breached, the air in the borehole is quickly evacuated to the surface and replaced with brine from the repository. This process is highly transient and happens very quickly relative to the release time associated with DBR. Once the brine has replaced most of the gas in the air - drilled borehole. (say 60 the 80 % by volume) the FBHP will have changed from the 2 MPa (held fixed in the EEG calculation) to the 8 MPa value representative of brine hydrostatic levels used in the CCA calculations. Thus, the minimum repository pressure necessary to drive brine toward and up the borehole is more representative of the 8 MPa used in the CCA calculations and the use of 2 MPa greatly over predicts the release of brine. Even though there would be more realizations resulting in repository pressure in excess of the EEG 2 MPa air - drilling' threshold, the releases from these situations would be nearly 0 if the transient nature of FBHP was accounted for.

3) The EEG reports S3 scenario releases which are for an intrusion after 1200 years, following an initial intrusion at 1000 years. The S3 releases assume that cement has degraded in the borehole between the waste panel and the Castile formation (brine pocket) through an open borehole. On page 13 of the R. H. Neill letter in the ALGEBRA section "Set Up Boundary Conditions for Previous Intrusions Here", note that the panel pressure (BHP\_OPEN) is determined by taking the Castile pressure and reducing it by the hydrostatic column of brine in the open borehole between the Castile and the panel (which when the density is correctly specified as brine on page 10 causes a 2-3 MPa difference in panel pressures). Specifying air density in the ALGEBRA input file on page 10, however, causes the panel pressure to be essentially at Castile brine pressure conditions. This specification will also cause additional



releases by placing an "injector" at essentially Castile brine pressure adjacent to the intruded borehole.

We note that EEG has had to specify a frequency for air - drilling in their analysis. CAO (Carlsbad Area Office, Department of Energy) has delegated WID (Waste Isolation Division of Westinghouse) the ongoing responsibility for monitoring current practice in the Deleware Basin. It is our understanding that WID is preparing a statement on the use of air - drilling in current practice and its frequency. Therefore, we do not explicitly comment on this portion of the EEG analysis except to state our belief that the EEG's air - drilling frequency is incorrect because it is too large.

In summary, our analysis concludes that the consequences of air - drilling are similar in magnitude to those predicted by BRAGFLO\_DBR in the CCA and that the likelihood of an air-drill release is significantly less than the likelihood of drilling assumed in the CCA calculations. This results in no impact on the predicted CCA CCDF's.

Please contact us if there is additional information you require for addressing this issue.



# Attachment 4



# Four pages from Hartman's records of the Bates # 2 blowout

DOE's Response to EEG Comments of 12/31/97 C. I. Bates No. 2 Page 2

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01-17-91/ Well flowing salt vater and some gas at a rate of approxiamately 600 to 1200 bbls of water per hour. Unable to shut well in so as to minimize crossflow into fresh water zones above the Rustler formation and in order to prevent cratering the well. All excess water flowing to reserve pit. Estimated water hauling costs equal \$16,000.00 per day. Analyzing options to bring well under control in accordance with NMOCD regulations.

01-20-91 Well continued as follows to flow out of control as defined 01-21-91 by the New Mexico Oil Conservation Division.

Date	Time	Drill Pipe FV (osia)	Drill Pipe BW (csig)	Annulus gu (osia)	Est. Blowout Rate (SVPH)	Remarks	M
	<u></u>		1-2:11	100/04	100000		
1-19-91	8:00	AN .	355	329			
	9:00		135	50 			
	10:00		130	75			
	10:10		560	330			
	. 11:00		130	05			
	12:00	<b>6</b> 14	133	70			
	1.00	<b>r</b> n	175	80			
	2.00		135	80			
	2.10		355				
	3:00		135	75			
	4:00	212		90		Puttoed 6	0 bbls of fresh water
	4:10	425		305			
	5:00					Started	pumping fresh water
	5:20					Finished	pumping fresh water
	5:30	510		310		Shut-in	
	5:37	250		10	16	7-min. t	est
	5:40	510		310		Shut•in	
	5:45	512		310			
	5:50	278		40			
	5:53	260		15			
	6:00	250		10			
	6:10	51Z		310			
	7:00	240		15			
	8:00	240		10			
	8:10	515		310		/	
	9:00	237	40	20			
	10:00		40	20		11	
	10:10	512	315	300			
	11:00	237	40	20			diment of the second
1.70.01	12:00		23	20		N N	
1-20-91	12:10	AN 309	312	10			
	2.00		25	10			
	2.00		265	280			
	3:00		25	10			
	4:00		25	8			
	4:10		260	275			
	5:00		20	10			
	6:00		20	10			
	6:10		300	290			
	7:38		15 .	8		Pumped f	resh vater
	7:50	450		270			
	7:52	210		5			
	7:54	205		5		Red beds	heaving
	8:00	220		5	8.5		
	8:28					Shut-in	
	8:28	310		175			
	8:30	430		225			
	8:35	475		290			
	8:40	485		300			
	8:43	490		300			

Pumped fresh water down drill pipe at the ate of 6 BPM at 1100 psi. Pumped 30 bbls of 17.3 PPG mud, broke off Kelly and Kelly sub and then installed lower Kelly valve. Nippled up drill string for running string shot. Rigged up Apollo Wireline Services. Pumped 40 bbls of fresh water down drill C. T. Bates No. 2 Page 3



pipe at 6 BPM at 1100 psi to clear any mud from drill string. Ran into hole with string shot and landed string shot in bid sub. Pumped down drill string at 3-1/2 BPM at 600 psi. Shot string shot and then pumped down drill string at 3-1/2 BPM at 250 psi. Pulled out of hole with wireline. Pumped down drill string at 6 BPM at 600 psi.

Rigged up Halliburton to well. Pumped fresh water down drill string at 6 BPM at 700 psi. At 2:48 PM, started mixing and pumping cement in order to bring water blowout under control in compliance with NMOCD requirements. Mixed and pumped thixotropic cement down 9-5/8" casing X 4-1/2 DP ennulus at an average rate of 32.5 BPM. Maximum pump rate for thixotropic cement was 35 BPM. Initial surface pump pressure for thixotropic cement was 1100 psig and final pump pressure for thixotropic cement was 1800 psig. After a total of 2300 sx of thixotropic cement had been pumped at the surface, started getting returns of cement back to surface through the drill pipe. By the time 2600 sx had been pumped at the surface, the returns were excellent quality cement and then after 3000 sx had been pumped, the returns again became water cut.

With a total of 4400 sx of thixotropic cement pumped, switched from pumping thixotropic cement to pumping a 50-50 blend of API Class-H cement and calseal. Pumped a total of 750 sx of calseal at an initial rate of 26 BPM and a final rate of 12 BPM. Pump pressure for the calseal cement was 2200 psi.

Although returns of thixotropic cement occurred after 2300 sx had been pumped, Jerry Sexton (District Supervisor of NMOCD District No. 1), so that quality of annular cement job could be ascertained, would not allow cement to be pumped down drill pipe as well as down annulus. Once returns back up drill pipe occurred, approximately 10 BPM out of 32.5 BPM being pumped into ground returned through the drill pipe. consequently, well annulus and blowout zone was cemented with a total of 4260 sx of thixotropic and calseal cement and approximately 877 sx of thixotropic cement was circulated back to surface. Finished cementing down 9-5/8" casing X 4-1/2"" DP annulus at 4:25 PM CST 1-20-91.

After shutting down pumping of calseal cement and before surface lines could be cleared, surface lines set up indicating calseal cement had a setting time of approximately 4 minutes.

In accordance with NMOCD instructions, continued to flow saturated brine back through drill string while cement in 9-5/8" casing X 4-1/2" DP annulus thoroughly set and reacted. Tested water flow through drill pipe at the rate of 8.3 BPM and a surface flowing pressure of 85 psi.

Also in accordance with NMOCD requirements, waited on cement for six hours to run into hole with temperature log to determine the net annular interval effectively cemented. Rigged up Apollo Wireline Services and attempted to go into hole with temperature tool, but did not have enough weight to get into hole. Checked shut-in pressure on drill pipe. Shut-in pressure was 900 psig which confirms that much of annulus is not cemented off and also proving that it might have been a catastrophe to have shut in well for any prolonged period of time before  $9-5/8^{\circ}$  casing X  $4-1/2^{\circ}$  DP annulus was thoroughly cemented. Now attempting to changeout Halliburton changeover swage so that a larger sinker bar can be run on temperature tool in order to get tool to bottom of well.

01-22-91

91 Finished running temperature survey as specified by the NMOCD. Could not run cement bond log because of outside diameter of the bond log tool. Logged well with temperature log from total depth back to the surface. Found bottom of the drill nine at 2224' RKB and found bottom of the cement



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C. T. Bates No. 2 Page 4

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that well had been effectively cemented in the  $9-5/8^{\circ}$  csg X  $4-1/2^{\circ}$  DP annulus in accordance with NMOCD requirements. Ran GRN correlation log from TD to surface. Prior to shutting well in to run temperature log, well was flowing water through drill pipe at the rate of 8.5 BPM (12,240 BWPD) with a flowing surface pressure of 85 psig.

Rigged up Halliburton to finish cementing well so as to bring well under control in accordance with procedures defined by NMOCD. Prior to pumping into well, recorded a shut-in wellhead pressure of 1000 psi which corresponds to a blowout pressure gradient of 0.966 psi/ft {((2240' X .52 psi/ft) + 1000 psi/ft)/2240' - 0.966 psi/ft]. A pressure gradient of 0.966 psi/ft closely corresponds to the water injection gradients in Texaco's Rhodes "B" Federal, Rhodes "A" Federal and Rhodes Yates Unit waterflood projects situated more than two miles south of the Bates No. 2 blowout well. A blowout gradient of 0.966 psi/ft is in excess of the anticipated fracture gradient for the area.

Started the squeeze cement procedure as defined by the NMOCD at 6:00 PM 1-21-91. Initially started pumping thixotropic cement into well at a rate of 6 BPM and a 2000 psi surface pressure. After pressure broke back to 1600 psi, increased rate to 9.5 BPM. By the time 500 sx of thixotropic cement had been pumped, pressure had increased to 2350 psi. After 600 sx of cement had been pumped, then pumping pressure broke back and thereafter fluctuated between 1950 psi and 2100 psi until the end of the cement job. Pumped a total of 1500 sx of thixotropic cement down drill pipe followed by 250 sx of a 50-50 blend of API Class-H cement and calseal. Finished cement job at 7:10 PM CST 1-21-91. After ceasing to pump, pressure held at 1250 psi indicating a good squaeze had been accomplished and that the well was finally under control in accordance with NMOCD prescribed procedures. After waiting on cement for six hours, removed BOP and backed off top joint of drill pipe. BOP's were sent to shop for repairs. Released rig at 5:00 AM 1-22-91. Will not be able to move rig for approximately three days so as to allow roads to dry out.

01-23-91

Starting to assess cost of salt water blowout and preparing to formulate plans for drilling a replacement well for the Bates No. 2 well.



Attachment 5

# February 10, 1998 memorandum from Warpinski and Hansen to Marietta, critique of Bredehoeft and Gerstle 1997, LEFM model



Operated for the U.S. Department of Energy by Sandia Corporation Albuquerque, New Mexico 87185-1395

date: February 10, 1998

to: Melvin Marietta, 6821, MS 1395

N. R. Warpinski, 6114, MS 0705 and F. D. Hansen, 6801, MS 1395

from:

subject: Hydraulic Fracturing Analyses Applied to WIPP

The report entitled "Linear Elastic Model for Hydrofracture at WIPP and Comparison with BRAGFLO Results" by W. Gerstle and J. Bredehoeft raises a number of speculative issues relative to hydraulic fracturing at the WIPP site. Most extensions of their LEFM calculations to the WIPP setting are inconsistent with extensive experience and known material responses. Because statements in the subject publication stand contradictory to an overwhelming body of knowledge and experience, this memo is an issue by issue repudiation of their contentions.

The primary contentions declared by Gerstle and Bredehoeft include:

- 1. "LEFM" (linear elastic fracture mechanics), as they apply it, is the "most reasonable" model for predicting hydrofracture in salt or anhydrite.
- 2. "LEFM", as they apply it, is widely used by the gas and oil industry for predicting hydraulic fracture behavior.
- 3. BRAGFLO does not correctly account for the mechanics of fracture.
- 4. Gas-driven cracks will extend thousands of meters from the repository.
- 5. The "LEFM" results are consistent with hydraulic fracturing models while BRAGFLO is not.
- 6. A gas-driven hydrofracture will develop over seconds, thus leaving little time for leakoff.
- 7. Wawersik's stress test experiments validate their "LEFM" model.
- 8. It is impossible to have permeability and porosity increase at pressure levels less than lithostatic.
- 9. The observed behavior in the Hartman case supports their "LEFM" results and shows that waterflooding or brine injection operations could result in fracturing into the WIPP site.

#### **Linear Elastic Fracture Mechanics**

Before refuting the primary contentions of Gerstle and Bredehoeft, it might be helpful to review Linear Elastic Fracture Mechanics (LEFM) and what it is really about. This will help show the differences between it and other fracture/flow models.

Linear Elastic Fracture Mechanics is a branch of solid mechanics that deals with the fracture of brittle materials.<sup>1</sup> Analytically, the development of LEFM is derived from an examination of the near-tip stress field around a crack, which has been found to be

$$\begin{cases} \sigma_{11} \\ \sigma_{12} \\ \sigma_{22} \end{cases} = \frac{K_I}{\sqrt{2\pi r}} \cos\left(\frac{\theta}{2}\right) \begin{cases} 1 - \sin(\theta/2)\sin(3\theta/2) \\ \sin(\theta/2)\cos(3\theta/2) \\ 1 + \sin(\theta/2)\sin(3\theta/2) \end{cases},$$
(1)

where the  $\sigma_{ij}$  are the stresses, r is the distance from the tip,  $\theta$  is the direction, and  $K_I$  is the strength of the crack tip singularity. It is important to also know that this is a failure criterion only and gives no information about the mechanical deformation of the material.<sup>1</sup> Fracture toughness, or the critical stress intensity factor, comes into play with the **hypothesis** that the  $K_I$  at failure is a material property, called  $K_{Ic}$ . This hypothesis works for very brittle materials and can be applied to reasonably sized flaws or fractures (e.g., certainly less than a meter). The extension of this hypothesis to large cracks (e.g., tens or hundreds of meters) has never been demonstrated by any laboratory or field evidence. Furthermore, we know that it does not work for ductile materials, which use a reformulation (J integral is an example) to handle ductility.

To apply this fracture criterion analytically, the approach is usually to find solutions of appropriate stress fields and compare resulting equations to get the strength of the singularity,  $K_I$ . For example, a penny-shaped or radial crack results in

$$K_I = \frac{2}{\sqrt{\pi a}} \int_{-a}^{a} rP(r) \sqrt{\frac{a+r}{a-r}} dr \quad , \tag{2}$$

where a is the crack radius. It is by applying Equation 2 for a constant internal pressure that Gerstle and Bredehoeft obtained their failure criterion. To do this they set  $K_I = K_{Ic}$ . Reviewing the assumptions for the use of this equation: small cracks; brittle material; constant internal pressure;  $K_{Ic}$  is a material property.

# 1. "LEFM" (linear elastic fracture mechanics), as Gerstle and Bredehoeft apply it, is the "most reasonable" model for predicting hydrofracture in salt or anhydrite.

To show the error in this assertion, it is necessary to start by examining hydraulic fracture models as used by industry. All industry models, and there are many, have three principal components, as given by Nordgren:<sup>2</sup>

1. width equation --- defines the opening of the crack for conductivity and storage

2. flow equation --- defines the pressure drop due to fluid flowing down the fracture

3. leakoff equation --- defines the fluid loss to the formation.

These equations are coupled and hence must be jointly solved to determine the correct fracture behavior. Vertical fractures will have a fourth relation for fracture height, but since Gerstle and Bredehoeft are using a radial fracture model, this can be ignored for now.

In attempting to refine models using second-order effects, some commercial models have also added a "tip equation" to determine when growth occurs. However, all commercial models will give essentially the same results whether a fracture toughness (critical  $K_{Ie}$ ) is zero or whether a typical lab value is employed. This result occurs because the width equation and the flow equation are the dominant effects. LEFM applied to length extension of a hydraulic fracture yields only small corrections and this correction will <u>reduce</u> length.

If we now examine the Gerstle-Bredehoeft model, it can be seen that they have only one mechanism, the tip equation. There is no flow equation, the width is not coupled to the flow, and there is no leakoff. Thus they have ignored the three dominant mechanisms associated with a hydraulic fracture and instead concentrated on a secondary effect.


However, the one physical aspect they did consider is of questionable validity here, as the application of the LEFM model to material such as anhydrite or salt for conditions lasting centuries is impossible to substantiate, as it violates all of the assumptions needed for LEFM. It furthermore brings into question the application of LEFM to fractures that are orders of magnitude larger than the scale over which it has been verified. No part of their "LEFM" model can be substantiated with any laboratory or field evidence.

Additionally, all models of fractures initiating from wellbores account for the wellbore and its effect on the fracture, including both the stress concentrations around the wellbore and the scale of the flaws available to start fractures. For fractures emanating from the WIPP, the Gerstle and Bredehoeft model ignores a 600-m wide repository in their calculations. The size, shape and characteristics of the repository will have a dominant effect on initial crack growth and its presence cannot be ignored in any realistic simulation.

Considering the absence of all important physics in the Gerstle and Bredehoeft model and the dubious application of LEFM to large fractures in materials such as salt and anhydrite, their contention that the "LEFM" model is the "most reasonable" model for predicting hydrofracture behavior at WIPP is demonstrably wrong.

## 2. "LEFM", as they apply it, is widely used by the gas and oil industry for predicting hydraulic fracture behavior.

As explained in the previous section, the Gerstle and Bredehoeft model has no resemblance whatsoever to hydraulic fracture models used by industry. Their model would predict fractures so long that well spacing rules would need to be extended to several square miles, whereas the industry trend is reduction of spacing because fractures are found to be much shorter than expected. The clearest way to show this result is to compare their model with commercial fracture models. In 1994 a model comparison study was published<sup>5</sup> that gave the fracture dimensions predicted by several different available simulators. This test case had the following parameters:

Sandstone thickness	51.8 m
Injected volume (V)	1600 m <sup>3</sup>
K <sub>Ic</sub>	2.2 MPa√m
Young's modulus (E)	58,606 MPa
Poisson's ratio (v)	0.21
Stress in reservoir	39.3 MPa
Stress in shales	49.3 - 50.7 MPa

The model study resulted in fracture wing lengths (each side) ranging from 275 -1143 m, pressure ranging from 1.95 - 9.9 MPa, and heights from 89 - 275 m. Much of the discrepancy in results had to do with some models using enhanced tip effects to minimize fracture length and increase the pressure while others avoided the use of such effects.

We can apply the same "LEFM" approach as Gerstle and Bredehoeft used, with the exception that the radial model cannot be used because of the high stresses in the surrounding shales. Appendix A gives the derivations of the exactly equivalent equations for a 2-D "LEFM" approach, where

While the fracture height, *H*, is not known *a priori*, we will find that the pressure is so low that the fracture will be confined to the sandstone giving a height equal to the sandstone thickness. Putting in the numbers, the "LEFM" approach predicts a wing length of 6,150 m, a pressure of 0.016 MPa, and a height of 51.8 m. The LEFM model predicts fracture lengths an order of magnitude greater and average pressures two orders of magnitude less than predicted by conventional fracturing models. If the "LEFM" lengths were achieved, well spacing in such reservoirs would need to be considerably greater than twice the wing length (e.g., about 15 km) to avoid draining neighboring resources. Of course, the state is aware that such wing lengths are **not** achieved and their own spacing regulations are consistent with fracture lengths of a few hundred meters (e.g., 160 acre spacing = 800 m between wells). No oil company would seriously consider a model which predicts lengths of several thousand meters.

(3)

#### 3. BRAGFLO does not correctly account for the mechanics of fracture.

To respond to this argument, it is necessary to compare the physics in the BRAGFLO model with the physics in a commercial hydraulic-fracture simulator (e.g., the three primary elements described in 1). In the BRAGFLO model, there is a smeared zone of increased porosity and permeability associated with pressures elevated above the fracturing pressure. This mechanisms is fully comparable to the width equation of a commercial hydraulic-fracture model, as the increased porosity and permeability account for conductivity of the crack and the storage within the crack.. The flow equation is obviously handled, as BRAGFLO is a flow model. The leakoff equation is also handled by flow into the elements. Thus, it can be seen that BRAGFLO has all three of the elements that every commercial hydraulic fracture simulator must have. It does not have a tip equation because commercial simulators have shown that the tip equation has little effect on fracture behavior. In fact, by not having a tip equation the BRAGFLO model gives a conservative estimate because the tip effect would only serve to reduce fracture lengths (in this case, the lengths of the increased porosity and permeability zones).

It must be noted here that the fracturing model employed in BRAGFLO has been reviewed by independent technical peers as required by DOE and EPA. Results of extensive review conclude the BRAGFLO model to be technically acceptable.

#### 4. Gas-driven cracks will extend thousands of meters from the repository.

The discussion in Section 1 has already shown that the Gerstle/Bredehoeft model has avoided most of the pertinent physics and achieves spectacular results by the application of one questionable mechanism to the exclusion of all others. Nevertheless, to illustrate just how problematic the Gerstle-Bredehoeft model is, it is instructive to check on the flow through a fracture using their parameters. If their fracture is a reasonable size, the flow through it needs to be consistent with volumes generated in the repository.

The flow in a radial fracture for laminar conditions (usually the case considered in hydraulic fractures) is given by<sup>5</sup>

 $Q = \frac{\pi w^3 \Delta P}{6\mu \ln \left[\frac{R}{r_w}\right]}$ 

For the Gerstle-Bredehoeft worst case scenario of an extra-long fracture, the parameters are approximately:

 $\Delta P = 0.0017$  MPa fracturing pressure (above the in situ stress)

 $\mu = 1 \times 10^{-5} \text{ N-sec/m}^2$  for hydrogen

R = 4000 m fracture radius

 $r_w = 600 \text{ m}$  repository radius

w = 0.005 m fracture average width, using about one-half the max value

Putting in these numbers, we get  $5.86 \text{ m}^3$ /sec which translates into  $1.85 \times 10^7 \text{ m}^3$ /year at lithostatic pressure. Thus, if we calculate the flow needed to support their fracture at its maximum extent, it would require orders of magnitude more gas in one year than calculated as the maximum repository production over its entire lifetime. Because they neglected the flow mechanism, they end up with a fracture that cannot be supported by the gas available. Assumptions that we made in this flow calculation include: (1) the average width is about half the maximum width (this is a very conservative assumption as the average width is more like 2/3 of the maximum width, depending on the pressure distribution); (2) the pressure drop is from the maximum pressure at the repository to the in situ stress level at the tip; and (3) hydrogen is the only component flowing in the fracture.

It is also instructive to check volumes, i.e., conservation of mass. For a radial symmetric crack opened by constant internal pressure, the average width is 2/3 of the maximum crack width.<sup>6</sup> Then the volume in the crack is

$$V = \frac{2\pi \, w_{\max} R^2}{3} \,, \tag{5}$$

where the repository volume is small compared to the total and is ignored. Putting in the Gerstle and Bredehoeft numbers for R = 4000 m and  $w_{max} = 0.01$  m, I get 335,000 m<sup>3</sup>. Their calculation shows a fracture volume of slightly under 200,000 m<sup>3</sup> for this fracture length. It looks like they may have made a mistake in their volumetrics. If true, their resultant fracture lengths would be considerably smaller.

Furthermore, the neglect of a pressure drop down the fracture results in fractures much longer than would be obtained with a physically realistic pressure behavior. For example, by using a more-realistic pressure distribution in Equation 2, such as a linear pressure drop down the length of the frcture, the critical pressure would be 4.66 times greater, yielding a crack that is much shorter and wider. Since their equations show that the fracture radius is proportional to the inverse of  $4.66^{2/5}$ , the crack lengths under this more-realistic pressure loading would be about 54% of Gerstle and Bredehoeft's value. Their maximum length of 4000 m would be reduced to 2200 m

Compounding the pressure-loading problem, the idea that LEFM can be extrapolated to large crack sizes is undergoing considerable scrutiny by the oil industry at this time. Most diagnostic data from commercial fracturing shows that pressures are higher and cracks are shorter than predicted by the models.<sup>3,4</sup> To achieve the measured results, crack modelers are adding enhanced tip-effect mechanisms to minimize length extension. These tip effects are the equivalent of having fracture toughnesses that are 2-4 orders of magnitude greater than those measured in the



(4)

lab. Thus, one of the current theories is that there is a scale dependence to cracks in the earth which results in a dilatant zone around the crack tip or some other effect which hinders length growth. This is the opposite direction that the Gerstle-Bredehoeft model leads. If one follows oil-industry reasoning and uses fracture toughnesses that are an order of magnitude greater than the lab values, the fracture lengths are reduced by a factor of  $10^{2/5} = 2.5$ , e.g., from 4000 m to 1600 m. For two orders of magnitude, the lengths are reduced to 630 m.

When one attempts to put all of the physics into the problem and to apply the knowledge gained from oil-industry hydraulic fracture research, it is clear that such "LEFM" fractures would have lengths reduced by 1-2 orders of magnitude.

## 5. The "LEFM" results are consistent with hydraulic fracturing models while BRAGFLO is not.

The easiest way to check the Gerstle-Bredehoeft numbers, as well as the BRAGFLO results is to use an elegant analytic solution from Geertsma and de Klerk<sup>5</sup> for a long-time/ low-leakoff asymptotic solution. These are exactly the repository conditions, with fluid leaking into a possible fracture over many hundreds of years. The Geertsma/de Klerk solution is

$$R = \frac{1}{\pi} \sqrt[4]{\frac{Q^2 t}{C^2}},$$
 (6)

where Q is the flow rate, t is the time, and C is the leakoff coefficient. The flow rate can be estimated by taking all of the possible gas generated (200,000 m<sup>3</sup> at fracturing pressures) and injecting it over some reasonable time period. I use 1000 years. The only question is the leakoff coefficient, C. The most conservative approximation is that the leakoff is compressibility dominated (viscosity dominated leakoff is always greater), so that C is given by

$$C = \Delta P \sqrt{\frac{k\phi c}{\mu}} , \qquad (7)$$

where k is the permeability,  $\phi$  is the porosity, c is the compressibility of the gas, and  $\mu$  is the viscosity. Using permeabilities of 10<sup>-18</sup> m<sup>2</sup> for the anyhdrite,  $\phi = 0.015$ , a hydrogen viscosity of 1 x 10<sup>-5</sup> N-sec/m<sup>2</sup>, a net fracturing pressure (above the smallest stress) of 1 MPa, and assuming the compressibility is that of the water in the pore space (0.00048 MPa<sup>-1</sup>), the leakoff coefficient is about 0.00000085 m/vsec. The fracture length can finally be calculated and yields 366 m. A check using the Geertsma and de Klerk full solution also resulted in a length of 366 m, showing that the asymptotic solution is a valid approximation here. This number is an order of magnitude smaller than that given by Gerstle and Bredehoeft and consistent with the BRAGFLO results for the zone of modified permeability and porosity.

6. A gas-driven hydrofracture will develop over seconds, thus leaving little time for leakoff. Gerstle and Bredehoeft contend that "the hydrofracture could develop rapidly (over a matter of seconds), thus leaving little time for fluid to leak off into the anhydrite and halite continuuum...". Of course it is easy to have the process occur in a few seconds if you ignore fluid flow. In fact, it will occur instantaneously if you ignore fluid flow as their model does. In reality, gas dynamics calculations would show that gas flow out of the repository would be very slow and the crack would quickly stabilize.

Furthermore, their scenario presumes that the gas would build up until reaching its ultimate pressure, and it would then rupture the repository. However, all geologic materials contain an



assortment of flaws and fractures of varying sizes, and the WIPP site is surrounded by a heterogeneous array of fractures within MB 139, drift corners, slabbed faces, and other readily available sites for fracture growth upon exposure to internal pressure. It is inconceivable that excess pressure would not immediately initiate fracturing from the repository. Following this argument, it is common that slabs, fractures and other failure planes around underground structures will be on the order of the size of the openings, e.g., tens of meters. Available fracture initiation sites may be even larger if the anhydrite zones contain fracture discontinuities that are longer. Such fracture initiation sites will begin to propagate at very low excess pressures (pressures above the stress level), eliminating any possibility of a high-pressure breakdown of the site. Thus, the fracturing process would be a continuous one over long time periods.

#### 7. Wawersik's stress test experiments validate their "LEFM" model.

Gerstle and Bredehoeft note that the fractures in the Wawersik stress-test experiments had residual apertures of 0.2 mm and likely had open apertures of 0.3 mm. Since this is about the aperture that they predict for a 100 m fracture, they contend that these results support their model. This statement is an inappropriate extension of Wawersik's work, seeing as how the stress test pump had a few liters of water injected in a few minute time period, compared to the continuous repository outflow of a low viscosity gas that would occur for years. Furthermore, the stress tests resulted in multiple fractures radiating from the borehole, rather than a single radial crack. There is nothing about these two fracture cases that is even distantly related.

## 8. It is impossible to have permeability and porosity increase at pressure levels less than lithostatic

Gerstle and Bredehoeft question the possibility of permeability and porosity increasing significantly at pressures less than lithostatic, which is the vertical stress due to the weight of the overburden. However, industry hydraulic fractures most generally occur at pressures below the lithostatic value. Fractures are created when the stress exceeds the minimum in situ stress, which is usually much less than the lithostatic stress. If the horizontal stress in the anhydrite is less than lithostatic, fractures will form when pressures exceed that lower stress value. Furthermore, porosity and permeability changes can occur even below the minimum in situ stress level. Many laboratory fracture experiments have shown that natural fractures and other weakness planes (such as those that exist in the anhydrite) are highly stress sensitive with permeabilities often changing by an order of magnitude for the first few MPa of loading. The oil industry now understands this behavior and has begun conducting step-pressure tests to examine the stress sensitivity of reservoirs at pressures below fracturing pressure.

# 9. The observed behavior in the Hartman case supports their "LEFM" results and shows that waterflooding or brine injection operations could result in fracturing into the WIPP site.

Their contention that "the LEFM model is supported by the observed behavior in the Hartman vs. Texaco case" is false, given that (1) their model ignores all of the important element of fracturing and (2) the Hartman case proved nothing scientifically. However, we can examine the mechanics of a brine-injection or waterflood leak using commercial oil-industry models to determine what might occur.

Gerstle and Bredehoeft suggest that leaks as great as 0.1 or 0.2 m<sup>3</sup>/min may occur in nearbly wells and result in fractures that extend kilometers into the repository. The worst case scenario is a leak into a thin anhydrite layer and the formation of a vertical fracture that stays contained within the anhydrite. If such a fracture could be created, it could conceivably extend large distances. The important question to consider is if such a fracture can be created.





Figure 1. Height-pressure relationship for anhydrite fracture.

Figure 1 shows that a fracture will stay well contained in the anhydrite as long as the net pressure stays below about 2.2 MPa (or the total pressure stays below 14.8 MPa). However, fractures initiated at the kind of rates suggested by Gerstle and Bredehoeft would quickly exceed that pressure level and the fractures would grow radially. By the time the fractures extended 1000 m laterally, they would also extend 1000 m vertically and breach the surface or eject fluid into some higher permeability or lower stress surface layers. If the stress in the anhydrite is greater than 12.6 MPa, which is highly likely, then the radial fracturing will occur sooner and for lower injection rates.

Using a conventional fracture simulator, parameters used in Gerstle and Bredehoeft's report, and best-practices modeling, several simulations were performed to determine when the fracture would become radial (essentially minimizing any significant additional lateral growth in the anhydrite). The results are shown in Figure 2.



Figure 2. Maximum length at which radial fracturing begins vs rate.

As noted earlier, if leakage rates are large, the fracture will quickly become radial due to the high pressures developed. If the flow rates are very low, then the fracture could stay contained in the anhydrite, but in this situation the injection rates are sufficiently low that leakoff into the formation can accommodate much of the fluid and fractures extend very slowly. A thirty year cutoff is put in this calculation because it is not expected that any given well will have continuous injection for 30 years without being abandoned or having a new liner installed. The maximum fracture length under the worst case scenario at just the ideal leakage rate is 2000 m.

These calculations, which ignore all of the enhanced tip effects commonly used by the oil industry and also ignore changes in permeability and porosity (increased leakoff as the pressure increases) are extremely conservative and still show that injection-induced fracture lengths cannot get excessively large under any realistic conditions.

#### Summary

We have provided a point-by-point repudiation of the primary contentions made by Gerstle and Bredehoeft. Their results are erroneous due to the absence of most of the important physics of the problem. Using standard oil-field hydraulic-fracture simulation techniques and theory, it has been shown that their calculations overestimate both gas-driven and fluid driven fracture lengths by one to two orders of magnitude. These calculations also show again that the BRAGFLO model produces an accurate simulation of flow and fracturing in this medium.

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#### Appendix A: 2-D "LEFM" Derivation

For a 2-D "LEFM" approach, the most conservative model (predicting the shortest fracture lengths) would have the geometry shown in Figure A-1, with a constant height width fracture over the entire height. More likely, the fracture is elliptic in shape, but then questions arise about the exact geometry around the tip of the crack. Making this assumption, we get the shortest-crack-length 2-D "LEFM" model possible.



Figure A-1. Geometry for 2-D "LEFM" crack.

The important relationships here are

$$K_{lc} = (P - \sigma_o)\sqrt{\pi L} \quad , \tag{A-1}$$

$$w = \frac{4(1 - v^2)(p - \sigma_o)L}{E} , \qquad (A-2)$$

$$V = \frac{\pi}{4} L H w . \tag{A-3}$$

These three relations have three unknowns, the width, pressure and length. While the height is initially an unknown, we will quickly find that the pressure is so low that the fracture cannot propagate into the higher stress bounding shales (e.g.,  $\sigma_0$  of the shales is much greater than  $\sigma_0$  in the sandstone). Solving, the appropriate relationships are

$$L = \left[\frac{VE}{\sqrt{\pi}\left(1 - v^2\right)HK_{Ic}}\right]^{2/3}$$
(A-4)

and

$$(p - \sigma_o) = \frac{VE}{\pi (1 - v^2) HL^2}$$
 (A-5)

As is shown in the text, these relationships overpredict length by an order of magnitude and underpredict pressure by two orders of magnitude.

Distribution: D. R. Anderson, MS 1328 Peter J. Chen, MS 1328 Margaret S. Y. Chu, MS 1335 F. D. Hansen, MS 1395 Hong-Nian Jow, MS 1328 M. Kathy Knowles, MS 1395 Kurt W. Larson, MS 1335 L. E. Shephard, MS 1395 Peter N. Swift, MS 1341 Palmer Vaughn, MS 1328 SWCF-C:WBS 2.0.1.5.3.1:DPRP1:QA:Anhydrite Fracture:LEFM:





#### Attachment 6

Background on CO<sub>2</sub> Flooding in the Permian Basin and an Assessment of the Potential for CO<sub>2</sub> Flooding Near the Waste Isolation Pilot Plant, Eddy and Lea Counties, New Mexico

An Independent Report by Steve Melzer, University of Texas of the Permian Basin

DOE's Response to

EEG Comments of 12/31/97





## BACKGROUND ON CO<sub>2</sub> FLOODING IN THE PERMIAN BASIN AND AN ASSESSMENT OF THE POTENTIAL FOR CO<sub>2</sub> FLOODING NEAR THE WASTE ISOLATION PILOT PLANT

### L. Stephen Melzer

February 23, 1998



#### About the Author:



Mr. L. Stephen Melzer holds a Bachelor of Science Degree from Texas A&M University in Geological Engineering (1968), and a Master's of Science Degree from Purdue University in Civil Engineering/Rock Mechanics (1969). Mr. Melzer is a Registered Professional Engineer in the State of Texas (#46859).

Mr. Melzer combines his technical academic background with both research and oil and gas operational experience. For the past twenty years, he has worked in the headquarters of the Permian Basin, Midland, Texas where 70% of the world's carbon dioxide floods (CO<sub>2</sub>) are underway. Especially noteworthy projects during the last ten years include developing (in conjunction with Shell and Mobil Oil) a series of six short courses on CO<sub>2</sub> miscible flooding; developing the concept and directing an annual three-day CO<sub>2</sub> miscible flooding conference; planning and directing a Department of Energy Workshop on Carbonate Reservoirs, and Pioneer Natural Resources Spraberry Symposium; planning and directing a shallow off-shore drilling, logging, and seismic project at the Enewetak carbonate atoll in the Marshall Islands of the Pacific Ocean; conducting a detailed hydrologic modeling study of a carbonate aquifer in Kentucky for the U.S. Army Waterways Experiment Station; oil and gas field reserve estimations; and waterflood unitization and flood design. Recent sponsors of his work include the University of Texas, major and independent oil and gas companies, the U.S. Army and Air Force, Defense Advanced Research Projects Agency, and the U.S. Bureau of Mines. He has authored numerous recent papers on the subject of CO<sub>2</sub> flooding.

Mr. Melzer is a past director of the Petroleum Industry Alliance, a part of the University of Texas System, located at the Center for Energy and Economic Diversification between Midland and Odessa, Texas. In this position he was responsible for directing research and technology transfer activities for the University in the Permian Basin area. Prior to accepting the position as director of the Petroleum Industry Alliance, Mr. Melzer was a Department Manager and Senior Geotechnical Engineer for Science Applications International Corporation (SAIC). He headed the Midland, Texas office for SAIC from 1978 until October 1992.

Mr. Melzer has been actively engaged in oil and gas exploration and development through a family owned business, Melzer Exploration Company. The partnership, formed with his father in 1978, has invested in over 75 successful oil and gas wells, supervised drilling operations in over twenty wells of which twelve are currently producing, and has operated numerous wells. The blend of oil industry production experience coupled with the government contracting and research experience provides a particularly unusual and broad background.

#### BACKGROUND ON CO<sub>2</sub> FLOODING IN THE PERMIAN BASIN AND AN ASSESSMENT OF THE POTENTIAL FOR CO<sub>2</sub> FLOODING NEAR THE WASTE ISOLATION PILOT PLANT

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#### 1.0 BACKGROUND ON PERMIAN BASIN CARBON DIOXIDE FLOODING



#### 1.1 COMMON RECOVERY TECHNIQUES

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The first discoveries of oil and gas in what has become known as the Permian Basin of West Texas and southeastern New Mexico occurred in Eddy County New Mexico in the early 1920's and in Mitchell and Reagan Counties of Texas in the late 1920's. The 1930's saw numerous field discoveries and tremendous development activity and the delineation of several of the "giant" fields in West Texas and southeast New Mexico. These fields were produced through the 1950's on primary production, i.e., the pressure and energy within the reservoir were the "drive" mechanisms by which oil and gas moved from the rock matrix to the wellbore of the producing wells.

During the 1950's and into the 1960's, many fields could no longer maintain economic viability with primary production alone. These fields advanced to a secondary production phase using a process called "waterflooding." In this process, water is injected into the reservoir via selected wells within the field to repressure the pore space within the rock and to build a "flood front" which sweeps additional oil toward the producing wells.

Production observations have shown that a typical Permian Basin reservoir will produce about 15% of the original oil in place (OOIP) during its primary production phase. Secondary recovery, (waterflooding) has shown that another 20-25% is producible (French et al. 1991; Hickman 1994; and Hadlow 1992). This combination totals 35-40% of the OOIP in the reservoir, leaving slightly more than half of the oil behind after completion of the primary and secondary production phases.

In the 1970's, some oil companies began investigating methods to get the additional oil from the reservoirs. Various techniques were tried such as in-situ combustion, steam injection, and polymer injection. A technique which was identified in this time-frame that seemed to have some promise based on laboratory and small-scale field pilots was a solvent injection technique using carbon dioxide  $(CO_2)$  as the injectant.

The first full-scale  $CO_2$  flooding techniques were tested in the Permian Basin of West Texas. Two such projects consisted of the SACROC flood in Scurry County, Texas, implemented in January 1972, and the North Crossett flood in Crane and Upton Counties initiated in April 1972. These two  $CO_2$  flood projects were encouraged by regulatory relief offered by the Texas Railroad Commission and special tax treatment of oil income generated by these experimental procedures. Over the next five to ten years, the petroleum industry observed that incremental oil could indeed be produced by the injection of  $CO_2$ . The numbers of  $CO_2$  flood projects began to grow shortly thereafter. Figure 1 illustrates the growth of new projects and production from 1984 to the present.









The  $CO_2$  used as the injectant for the first projects was separated from produced natural gas which came from the south region of the Permian Basin. Later, some oil companies began to develop source fields containing  $CO_2$  that could offer larger quantities of  $CO_2$  and in nearly pure form. Three source fields were developed: Sheep Mountain in south central Colorado (Roth 1983), Bravo Dome in northeastern New Mexico (Johnson 1983), and McElmo Dome in southwestern Colorado (Gerling 1983). Pipelines were constructed in the early 1980's to connect these  $CO_2$  source fields with the Permian Basin fields (Figure 2). The new supply of  $CO_2$  led to a growth of  $CO_2$ flood projects in the Permian Basin through the early 1980's until the "bust of 1986," whereupon the price of oil dropped approximately 50% and available capital for such endeavors became scarce.

#### 1.2 CURRENT CO<sub>2</sub> FLOODING ACTIVITIES

Recent years have once again seen a flourish of new  $CO_2$  floods in the Permian Basin. Today, 44  $CO_2$  floods are active in the Permian Basin of which 18 have been implemented in the last four years. For the first time since the three source field pipelines were constructed in the early 80's, drilling of new wells at the  $CO_2$  source fields has proven necessary and  $CO_2$  deliverabilities are being pushed to the limits of the pipeline throughput capacity. Clearly,  $CO_2$  flooding is now recognized as a viable tertiary recovery method for a select group of large, mature oilfields.

The Permian Basin of Texas and Southeastern New Mexico accounts for 1.1 million barrels per day (bpd) or approximately 12% of the daily U.S. oil production. Today,  $CO_2$ flooding is responsible for 140,000 bpd and is expected to continue growing to 153,000 bpd by the end of 1997 year and to 170,000 bpd by 2002 (Melzer 1996).  $CO_2$ deliverability can reach approximately 1.75 billion cubic feet (bcf) per day (some time during 1998) whereupon no more growth will be realized until new sources of  $CO_2$ become available. Flat deliverabilities of  $CO_2$  will lead to flattening of  $CO_2$ -derived oil production sometime after the turn of the century (Melzer 1997).

Nearly all of the oil produced by  $CO_2$  flood operations comes from the "giant" fields of the Permian Basin. Smaller fields generally pose unacceptable economic risks because of the huge investments which must be made in pipelines and surface treating facilities which are required to implement an economically viable and profitable  $CO_2$  project. For example, a recent press release announcement in North Dakota and Canada estimates the cost of the  $CO_2$  project there at \$1.1 billion (PanCanadian News Release 1997). Not considering the time value of money, this investment will require that more than 75 million barrels of recoverable oil (at \$15/bbl net to investors) be produced to show a profit. Since  $CO_2$  flooding can only reasonably expect to get 10% of the OQIP in a given reservoir, this target field must have at least 750 million barrels of OOIP.







FIGURE 2: Permian Basin CO<sub>2</sub> Pipelines - Adapted from McCollough et al (1987) and Melzer, et al (1995a)

#### 1.3 LONG TERM NATURE OF THE PROCESS

Because of the huge investment in purchased  $CO_2$  and pipeline and compression infrastructure coupled with the delayed returns of the oil production,  $CO_2$  flooding requires a long-term commitment on the part of the oil company. Both of the first two floods (SACROC and Crossett) remain in operation and are currently producing nearly 10,000 bpd. After 25 years of operation, these floods are still injecting  $CO_2$  (OGJ 1996).

Recent estimates have indicated that more than three billion barrels of oil will be produced from  $CO_2$  floods in the Permian Basin (Marino 1996). This oil will be produced from existing reservoirs and should ultimately represent about 10% of the OOIP within the reservoirs.

Figure 3 illustrates a forecast of  $CO_2$  enhanced production into the next century. An assumption of this study is a continuing and available  $CO_2$  supply for future projects. A condition of this forecast was availability of 1.5-1.75 bcf per day of new (non-recycled)  $CO_2$  for injection. For a reference point, the current injection rates are approximately 1.35 bcf per day. The forecast illustrates that the number of active projects will peak just below 60 and remain constant at that point as old projects terminate and new projects are initiated.

 $CO_2$  floods are often measured in terms of their effectiveness in "utilizing" a thousand cubic feet (mcf) of  $CO_2$  to produce a barrel of oil. Considering only the new  $CO_2$  injected (not recycled and reinjected), an acceptable ratio would be 6-10 mcf of  $CO_2$  per barrel of oil produced. If, as pointed out above, three billion barrels of oil are to be produced from  $CO_2$  floods in the Permian Basin, there must be 18-30 trillion cubic feet (tcf) of  $CO_2$  delivered to the basin.

At a constant daily deliverable rate of 1.75 bcf per day, it will take 30-40 years to deliver the quantity of  $CO_2$  necessary to produce those three billion barrels of oil. The reserves available to the Permian Basin are within this range as the supply sources of  $CO_2$  for the Permian Basin are thought to contain 26 tcf (Roth 1983; Johnson 1983; and Gerling 1983).

#### 1.4 PROJECT PLANNING UNDERWAY WITHIN THE PERMIAN BASIN

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Several Permian Basin companies are currently planning new CO<sub>2</sub> fields. For example, the "backlog" of projects at Altura Energy Company (the merged Permian Basin companies of Shell and Amoco) is reported to be ten new or expanded floods. Three new floods in the Scurry and Borden County area are also being planned. Numerous other floods have been discussed and are under consideration in Crane, Dawson, Ector, Gaines, Seminole, and Yoakum Counties. Texaco publicly announced in August 1997 the start of their Central Vacuum project in Lea County, NM (Texaco News Release 1997).





FIGURE 3: Forecast of Cumulative Oil Barrels produced via CO<sub>2</sub> flooding in the Permian Basin (Melzer 1997a)

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Much of the impetus for planning new  $CO_2$  floods results from a combination of three factors. First, the maturity of the waterfloods in the Permian Basin leaves little time before the fields will be faced with abandonment. Second, there is now an established awareness of the demonstrated technical success of tertiary  $CO_2$  flooding. Lastly, new tools and procedures for characterizing and operating reservoirs are being developed. These technological advancements include such things as three-dimensional seismic techniques which now enable the industry to identify heretofore unknown features of the target reservoir. The ability to more effectively characterize and model the reservoir allow the strategic use of new simulation tools to more accurately predict the effects of  $CO_2$  injection. A related aspect has to do with accelerated technology transfer activity which is playing a critical role in flood implementation.

In addition, the DOE's co-funded oil research is clearly providing a leadership role in both advancing current technology and disseminating information about new technology.

The  $CO_2$  flooding activity in the Permian Basin has been focused on large fields with large oil in place targets. It is only the larger fields that can justify the incremental costs of obtaining a detailed understanding of the reservoir and amortize the costs of the pipeline construction needed to implement the flood. The list of recently implemented floods (Melzer 1996) and future projects (Melzer 1995a) appear to continue to be concentrated in the largest fields.

To date, the development of  $CO_2$  flooding has clearly favored the Permian Basin. In addition to nearby source fields, the Permian Basin has a large number of large and mature fields which have been proven amenable to  $CO_2$  injection, and has a well-developed pipeline infrastructure which can be used for implementing new floods (Figure 5).

#### 1.5 NEW U.S. DEVELOPMENTS OUTSIDE OF THE PERMIAN BASIN



While the Permian Basin clearly dominates the  $CO_2$  development picture today, it is important to note that the necessary infrastructure is now forming in other regions. Transpetco Transportation Company recently constructed a 120-mile long pipeline from Bravo Dome in northeastern New Mexico to the panhandle of Oklahoma, a new pipeline has just been completed in Michigan to deliver  $CO_2$  from a plant to a nearby oilfield, and Pan Canadian Petroleum and Dakota Gasification Company have just announced a joint venture to deliver byproduct  $CO_2$  from a coal gasification "synfuels" plant in North Dakota to the Weyburn Field in southern Saskatchewan, Canada. Some consideration is also being given to strategically locate new fertilizer and ethanol plants to establish them as originating points for pipelines to distribute  $CO_2$  to flood projects. However, small plant sources of  $CO_2$  have not provided the consistency of delivery or expansion opportunity which is so critical to the economics of a project as expensive as a  $CO_2$  flood.







FIGURE 4: Permian Basin Pipeline Infrastructure (adapted from Oil and Gas Investor Magazine 1996)



Development of new  $CO_2$  source fields is not out of the question. A new  $CO_2$  source field is currently being drilled in eastern Arizona by Arizona Ridgeway Corporation (Heylmun 1997). Early drilling suggests reserves as large as 6-8 tcf and well deliverabilities of 1-2 million cubic feet (mmcf) per day. If continued drilling indicates reserves at or larger than the above amounts and well deliverabilities are sufficient, the field will probably be developed and a pipeline constructed to transport the  $CO_2$  to oilfields to the west or east. Ridgeway appears intent on finding ways to get the  $CO_2$  to the oilfields of California where numerous fields in the San Joaquin Valley and Ventura areas appear amenable to  $CO_2$  flooding (Riggs 1997).

#### 2.0 CO<sub>2</sub> FLOOD REQUISITES

#### 2.1 FACTORS AFFECTING CO<sub>2</sub> FLOOD SUCCESS

Based on the large incremental expenses of initiating and continuing a successful  $CO_2$  flood, operators must carefully select their reservoirs for  $CO_2$  flooding. The first step of reservoir screening is to test against some simple rules of thumb. These are as follows:

- reservoir depth greater than 2500' and/or reservoir pressure at 1,200-1,500 psi or greater
- 2) sufficiently large oil in place target to justify the cost of a pipeline from the  $CO_2$  source point to the field
- 3) injectivity rates in wells exceeding 1.5-2 mmcf per day
- 4) oil viscosities less than 10 centipoise and API gravities 25° or greater, and
- 5) spatial distributions of reservoir permeability allowing development of planar or cylindrical expanding flood fronts (Melzer et al. 1995b; Taber et al. 1996).

#### 2.1.1 Minimum Miscibility Conditions

The ability of a solvent to mix with and move oil is the fundamental goal of a solvent injection process such as  $CO_2$  flooding. Since water and oil do not mix, considerable "moveable" oil is left behind in the waterflood process. Some of this reservoir oil will not be recoverable even with a tertiary process but, as already stated, approximately 10-15% of the original oil in place may be directly attributable to a successful tertiary  $CO_2$  flood (Melzer 1995a).

The minimum miscibility conditions for oil and CO<sub>2</sub> are dependent on

- 1) the pressure at which the mixing is to occur
- 2) the properties of the oil, and
- 3) the impurities present in the  $CO_2$ .

Several extensive treatments of minimum miscibility conditions are available in the literature. Hadlow (1992) and Taber et al. (1996) provide a good overview.



The oil reservoirs of the WIPP area will likely meet the minimum miscibility test. The range of depths of reservoirs is in excess of 2,500' and the reservoir pressures are in excess of 1,500 psi.



#### 2.1.2 Oil in Place Targets

Previous discussion has mentioned that large fields have been the primary targets for current properties under  $CO_2$  flooding, primarily because the high costs of constructing a pipeline to the field normally preclude fields containing less than 10 million barrels of oil. This is an attribute not present in the Delaware Basin oil fields. More will be presented on this later.

#### 2.1.3 Well Injectivity Rates

The nature of a  $CO_2$  flood is such that the time from initial capital expenditures for pipelines and related equipment to the onset of the oil revenue is generally greater than three to four years. Reservoirs that cannot introduce and move the injectant through the formation efficiently are at a tremendous economic disadvantage. This requires permeabilities which allow the  $CO_2$  to be injected at high enough rates to contact and activate the oil such that the time from injection to oil response is less than two years. Experience has shown that permeabilities in the range of 5 millidarcies or less will seriously affect economics of a project. Otherwise stated, the key to successful  $CO_2$  flooding is to "process" the  $CO_2$  quickly.

#### 2.1.4 Oil Viscosity and Gravity

A widely accepted criterion for screening a potential  $CO_2$  flood is that of oil viscosity and gravity. A successful  $CO_2$  flood requires that the reservoir oil gravity value be above 25 degrees API (not a heavy or thick crude) and that the viscosity be less than 10 centipoise. The gravity and viscosities of the Delaware Basin oil reservoirs have been well established from existing production and, in general, the gravities exceed 35 degrees API and the viscosities are generally less than 2 centipoise. Both of these values are well within the screening test limits for a viable  $CO_2$  flood candidate.

#### 2.1.5 CO<sub>2</sub> Containment and Adequate Flood Front Development

The loss of  $CO_2$  containment can be defined as the movement of  $CO_2$  into a zone or area not intended to be flooded. This loss of containment can result in inadequate flood front development and is often caused by accelerated movement of  $CO_2$  along a high permeability channel or fracture. It can also be caused by movement of  $CO_2$  upward or downward into zones not intended for the flood. The net result in all cases is the lack of development of the intended cylindrical or planar flood front which contacts the large volumes of oil necessary for oil mobilization, thereby reducing production.  $CO_2$  breakthrough (Melzer et al. 1995b) occurs when unmixed  $CO_2$  quickly appears in a nearby producing well(s) and indicates the lack of adequate flood front development. Various mitigating techniques are tried including cement squeezing and other conformance control measures in attempts to reestablish flood fronts and to clog breakthrough channels.

The most common cause for  $CO_2$  flood failures in the Permian Basin has been loss of  $CO_2$  containment and lack of flood front development (Melzer 1996b). The nearby Conoco Maljamar flood (Pittaway 1997), the west side of the Denver Unit (Fox 1995), and the El Mar Delaware Basin  $CO_2$  flood (Burlington Resources 1997) have either battled this problem or abandoned the floods entirely because of this problem.

The attributes of the Delaware Sand reservoirs suggest that vertical confinement is generally quite good and has not been a problem on the four Delaware Basin  $CO_2$  floods to date, but that channelization of  $CO_2$  and premature  $CO_2$  breakthrough is a distinct possibility due to the nature of the sand deposition (Dutton 1997). The established presence of higher permeability channels along trend are challenges for flood operators in any of the Delaware Mountain Group reservoirs. More will be presented later on the characteristics and nature of the Delaware Sand reservoirs.

#### 2.2 FACTORS IN CO<sub>2</sub> FLOOD FAILURES

Operating experience over the last 25 years has identified reservoir properties which are generally considered poor attributes for a candidate  $CO_2$  flood. For example, the presence of permeable natural fractures can be detrimental especially if their orientation cannot be predicted with confidence. And, even if their orientation is known, multiple orientations (trends) can lead to accelerated and unpredictable movement of  $CO_2$ . Another concern is when vertical permeabilities significantly exceed horizontal permeabilities. Although this issue may be worked around, it can lead to "override" or "underrunning" of the  $CO_2$  depending on the relative densities of the  $CO_2$  and oil at reservoir pressure (Melzer 1997b).

Since the cost of  $CO_2$  is significant, it is imperative that the injectant is effective at contacting oil in the reservoir. Loss of  $CO_2$  to gas caps or water zones below the oil/water contact can be detrimental to the economic success of a flood. The loss of  $CO_2$  can be due to natural permeability, or it can be due to hydrofracturing that occurred at the time of completion of the well.

#### 2.3 ATTRIBUTES OF SUCCESSFUL CO<sub>2</sub> FLOODS

A good method to analyze the desirable attributes of a prospective  $CO_2$  flood target is to examine some of the attributes of the successful  $CO_2$  floods. Figure 5 displays the lithologies of the formations under flood in the Permian Basin. The vast majority of floods







in the Permian Basin occur in carbonate reservoirs; only a handful of sandstone reservoir floods have been attempted. As will be discussed later, the oil reservoirs in the vicinity of the WIPP site consist of fine-grained sandstones and/or siltstones.

Figure 5 also depicts, in frequency format, the depth of the reservoirs under flood in the Permian Basin. Note that only two  $CO_2$  floods are at depths less than 2,500' and only two are at depths greater than 8,000'. The shallower the reservoir, the more unlikely that the  $CO_2$  and oil will be miscible and form an effective flood front. If the two are immiscible, they will behave much like oil and water, with little or no incremental benefit expected from the use  $CO_2$  over that of a water (waterflood). The deeper the reservoir, the higher the original bottom hole pressure, and the higher the surface injection pressure must be to achieve miscibility. This adds to the cost of pumping (compressing) the  $CO_2$  to inject into the reservoir, and adds to the economic risk of the project.

Another parameter of significance relates to the success of the waterflood. Hickman (1995) and French et al. (1991) present an assessment of waterflood performance of Permian Basin reservoirs. Figure 6 shows a composite analysis of the information they provided which illustrates the ratio of waterflood produced oil to primary produced oil. In successful waterfloods, the waterflood production is always greater than the primary production, i.e. the ratios are always in excess of one. These reservoirs can be shown to be quite profitable under waterflooding due to the high recoveries of oil. Reservoir sweep likewise could be presumed to be quite effective. Later sections will compare what is known, and what is forecasted related to the WIPP area reservoirs.

#### 2.4 ECONOMIC AND ORGANIZATIONAL ISSUES RELATING TO $CO_2$ FLOODING

The costs to implement a  $CO_2$  flood are very high; a  $CO_2$  flood is labor intensive and technically complex with regard to the necessary up-front planning and evaluations.  $CO_2$  floods also carry a very intensive operating burden. The degree of commitment is high and requires that great care be taken to monitor all aspects of an operating  $CO_2$  flood. Those companies which typically undertake such a venture have a very capable group of employees experienced in all phases of oil recovery. Also, the company typically has large amounts of available capital to invest in the large pre-flood costs. As mentioned earlier,  $CO_2$  flood ventures require a company which can withstand long payout lag times. Rates of return, which are usually in the 10 to 20 percent range, will deter many companies, well capitalized or not.

Operators involved in  $CO_2$  floods must have the understanding and authority to make decisions and adjustments to the injection process at the field reservoir site. The day-to-day operations are data intensive and important decisions must be made quickly and responsibly. Although it may be possible for a company to manage such a flood from a distance, the operations will likely be far less than optimal. Capable and qualified on-site









FIGURE 6: Secondary (WF) to Primary Ratio Comparisons, Permian Basin Reservoirs

personnel are extremely important. The availability (or lack thereof) of qualified personnel may reduce the list of candidate organizations capable of operating a successful  $CO_2$  flood. Table 1 is a list of the floods implemented in the Permian Basin since 1993 and the companies operating the floods. Only ten companies are on that list, and each is of substantial size, or is a subsidiary of a larger petroleum corporation. A total of twenty-two companies are operating the 44 current  $CO_2$  floods in the Permian Basin today.

**TABLE 1:** Recently Implemented<sup>1</sup>  $CO_2$  floods in the Permian Basin (OGJ 1996) and (Melzer and Stiles 1996)



1)	Altura Energy <sup>2</sup>	Anton Irish (Clearfork)
2)	Altura Energy <sup>2</sup>	Bennett Ranch (SA)
3)	Altura Energy <sup>2</sup>	Cedar Lake (San Andres)
4)	Altura Energy <sup>2</sup>	Midcross (Devonian)
5)	Altura Energy <sup>2</sup>	No. Cowden (SA)
6)	Burlington	El Mar (Del SS)
7)	Conoco	E. Huntley (SA)
8)	Conoco	So. Huntley (SA)
9)	' Fina	Penwell (SA)
10)	Fina	W. Brahaney (SA)
11)	Mobil	Salt Creek (Penn Reef)
12)	Orla Petco	E. Ford (Del SS)
13)	OXY	So. Welch (SA)
14)	Phillips	Emmons (SA)
15)	Phillips	So. Cowden (SA)
16)	Texaco	C. Vacuum (Glorietta)
17)	Texaco	Slaughter Sundown (SA)
18)	Unocal	Dollarhide (Clearfork)

Hale, Lubbock Cos. Yoakum Co. Dawson Co Crane Co. Ector Co. Lovina Co. Garza Co. Garza Co. Ector Co. Yoakum Co. Kent Co. Reeves Co. Dawson Co. Ector Co. Ector Lea Co., NM Hockley Co. Andrews Co.



<sup>1</sup> Implemented between 1/1/93 and 8/16/97

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<sup>2</sup> Altura Energy was formed through a merger of the Permian Basin oil companies of Shell and Amoco.

#### 3.0 CHARACTERISTICS OF PETROLEUM RESERVOIRS IN THE VICINITY OF THE WIPP SITE

Figure 7 is a map of the immediate area near the WIPP site showing the location of oil and gas fields. Drilling in the nine-township area surrounding the WIPP site is continuing. A recent independent review of oil and gas resource estimates was performed for the DOE by the New Mexico Bureau of Mines & Mineral Resources (NMBMMR 1995). The information in that report is treated as the current status of oil production for the purposes of this report. The NMBMMR study did not assess the potential or viability of tertiary recovery techniques. However, by using reservoir characteristics as reported in the NMBMMR evaluation, an assessment of the potential for future  $CO_2$  flooding of the area reservoirs can be conducted (see Section 4.0). This section briefly reviews the geologic setting and describes the results of the survey of production.



FIGURE 7: Oil and Gas Fields Near the WIPP Site

#### 3.1 PRODUCING RESERVOIRS NEAR THE WIPP

The WIPP site lies at the northern end of the Delaware Basin which is part of the oil and gas province referred to as the Permian Basin (Hill 1996). Producing formations in the area are generally typical of those throughout the basinal (non-slope) areas of the Delaware Basin. In the nine-township area surrounding the WIPP site, production has been established from numerous separate formations (NMBMMR, 1995). Figure 8 illustrates a stratigraphic column of the area. Past activity has determined that the formations with commercial oil production are of the Pennsylvanian or Permian Age. The shallowest of these are the Bell Canyon, Cherry Canyon, and Brushy Canyon Formations of the Delaware Mountain Group, and the deepest is the Morrow Formation.

#### 3.1.1 The Bell Canyon Formation

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The Delaware Sands of the Bell Canyon Formation consist of several sand/siltstone intervals separated by silty shales. Normally the Delaware Sands are referred to as blanket and channel sands and are generally quite correlatable between wells and fields. The typical depth of the Delaware Sand interval is 3,800-5,500'. Considerable drilling activity for the Delaware Sands occurred prior to the 1970's and is continuing to the present day and accounts for a large portion of the oil production near the WIPP.

The better oil production from the Delaware Sands is believed to be concentrated in channels composed of sandstones/siltstones with lesser percentages of silt sized particles and clay. Once outside of the cleaner sand/silt channels, permeability is lower and commercial production is unlikely. The axis of the channels can be determined by mapping of oil production and has been the subject of several recent DOE cosponsored studies (Dutton, et a, 1997 and Strata Production, 1997). Figure 9 illustrates the nature of the channels at the Ford-Geraldine Field, an Upper Bell Canyon Field which has been  $CO_2$  flooded in the past. Note that the channels are roughly one-third of a mile wide (two locations on the field developed well spacing of 40-acres).

The presence of the channels defines some imposing conditions on future  $CO_2$  flooding. As discussed previously, establishing cylindrical or planar flood front development within the reservoir is required for success of the solvent process. Effective sweep of the reservoir can lead to recovery of 10-15% of the oil in place (Holm el al. 1986). Zones of higher permeability <u>c</u>an lead to channeling from injector to producer (breakthrough) which will short-circuit the process, and lead to a potential economic failure of the flood.

The Uppermost member of the Delaware Bell Canyon is often referred to as the Ramsey Sand and produces oil in many Texas fields. The four  $CO_2$  floods in the Delaware Basin have all flooded this member. The Ramsey sand is considered the very best of the Delaware Canyon Group Sands with permeabilities ranging up to 400 millidarcies in the channel facies (Dutton et al. 1997).





FIGURE 8: Stratigraphic Column for WIPP



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At the Geraldine-Ford Field (Dutton et al. 1997; Thomas 1980) the Ramsey has two sands, the upper, about 30 net and 50 gross feet thick, and the lower, about 12 feet in thickness. The permeabilities of the productive sands average 35-40 millidarcies with porosities of 20%. At the Twofreds field, the Ramsey Sand averages 25 feet in net thickness, 20% porosity, and 40 millidarcies permeability (Twofreds Engineering Subcommittee Report 1961; Wilson 1980). The El Mar Field also produces from the uppermost Delaware Sand where the average thickness of the reservoir is 50 gross feet, the porosity averages 21%, and the permeability averages 24 millidarcies (Thomason 1980; OGJ 1996). The East Ford Field averages 23% porosity and 64 millidarcies permeability (OGJ Worldwide EOR Survey, 1996). The uppermost member of the Bell Canyon does not produce in the vicinity of the WIPP site (NMBMMR 1995).

By contrast, Broadhead (1993) characterizes the Bell Canyon reservoirs in the vicinity of the WIPP site with porosities in the range of 20-24%, and with permeabilities from 7-24 millidarcies. The range of porosity compares favorably to the Ramsey sand reservoirs in Texas but the permeabilities of 7-24 millidarcies are significantly lower. Additionally, oil or gas production from the upper Delaware Mountain group (Bell Canyon) section in the vicinity of WIPP has not been established (NMBMMR 1995). This last reference notes that "at present, reservoir quality sandstones in the Bell Canyon are used for disposal of produced oil-field brines in the vicinity of WIPP." The nearest Bell Canyon production is the Triste Draw field over seven miles from the WIPP boundary.

#### 3.1.2 The Cherry and Brushy Canyon Formations

The Cherry Canyon Formation (~5,000-6,000' depths) is very similar in lithology to the Bell Canyon above and the Brushy Canyon below. Only minimal quantities of Cherry Canyon oil are currently being produced within the nine-township area surrounding the WIPP (NMBMMR 1995).

The deeper Brushy Canyon Formation (~6,000-7,700' depths) is also very similar in lithology to the other formations in the Delaware Mountain Group. Commercial discoveries of oil in the late 1980's and 90's have generated considerable excitement making the Brushy Canyon interval and the deeper Bone Springs Formation a target for new exploratory drilling (Kerans and Fitchen 1997) and (Hill 1996). The WIPP site is within this area of production interest.

A DOE cosponsored project is underway at the Nash Draw Fields west of the WIPP Site. The project is two years into their reservoir characterization work and the Brushy Canyon reservoir is characterized by a 14% porosity and 1 millidarcy permeability. The project is attempting to assess the feasibility of advanced recovery (waterflooding or tertiary) and early results show little hope for success.





#### 3.1.3 The Bone Springs, Wolfcamp and Morrow Formations

The Bone Springs Formation is the fourth interval of production and, with the recent drilling, has become the second-most produced formation in the area (behind the Delaware Sands). The interval lies at a depth of 7,700-11,000' and is noted for interbedded sandstones and carbonates with some intervals of organic shales (Thomerson and Catalano 1997).

The deeper Wolfcamp interval has also been a target for drilling but is a relatively minor player in the 9-township area. The deeper Strawn and Atoka intervals (13,000-14,000' in depth) have scattered wells, some of which are quite prolific, but predominantly produce gas.

Finally, the deepest drilled horizon in the area is the Morrow Formation which does not produce appreciable quantities of oil in the area of the site. The zone is primarily gas and is found between 14,000 and 15,000 feet in depth.

In summary, the three primary zones classified as oil intervals (Delaware Sands, Brushy Canyon, and Bone Springs) have been drilled to an extent which allow an evaluation of their  $CO_2$  flooding potential based on reasonably well known characteristics. The next section of this report provides a summary of this evaluation.

#### 3.2 FIELDS IN THE WIPP SITE AREA

The fields in the WIPP Site area have multiple producing zones and should not be viewed as single-interval fields. Most wells are drilled with multiple zone objectives since, individually, the formations are, with a few exceptions, not sufficiently prolific to justify the risk of poorly or undeveloped reservoirs at the well site. Compounding target formation objectives is a technique used to make the economics of a drilling venture acceptable. The established single zone oil recoveries do not generally justify the expense of drilling when considering the risk of finding non-commercial production.

The list of fields in the immediate area of the WIPP site are:

Bilbrey Bootleg, NW Cabin Lake Cherry Creek Cruz Diamondtail E. Livingston Ridge Forty-Niner Ridge Livingston Ridge NE Livingston Ridge SE Los Medaños Lost Tank Nash Draw Quahada Ridge Quahada Ridge SE Red Tank S Red Tank W Triste Draw Triste Draw W Sand Dunes E Sand Dunes W



Since the cost of installation of a pipeline to transport  $CO_2$  to an area is significant, a flood candidate must have a minimum number of wells to be considered viable (see Section 2). Only the largest of fields even rate a "quick-look" evaluation. Since Livingston Ridge, Cabin Lake, and Los Medaños have several wells producing oil from a common source of supply, these fields were chosen as appropriate for evaluation.

#### 4.0 WIPP AREA CO<sub>2</sub> FLOOD ASSESSMENT

A significant difference between a  $CO_2$  flood and a waterflood lies in the cost of the injectant. When an operator is paying \$0.65-\$1.00 per mcf for  $CO_2$  and is expecting to have to inject 5-10 mcf for every barrel of oil recovered, the incremental costs per produced barrel for the  $CO_2$  alone are \$3.25-\$10.00. If the gross price received is \$18 (assumed) a barrel, after payment of royalties and taxes of 25%, the net per barrel price drops to only \$13.50. The capital required to implement a new flood (including the  $CO_2$  pipeline) and operating expenses of the producing and injection wells must be paid from the remaining \$3.50 - 10.25 per barrel. What is left is the operator's potential return on investment.

With such a narrow margin for profit, the operators take great care to limit the technical risks as much as possible, and must be certain that the  $CO_2$  is contacting oil. One of the more important risks is containment of the  $CO_2$  within the patterns of the flood. Loss of  $CO_2$  containment will quickly lead to economic failure of the flood. Therefore, the operators of  $CO_2$  floods have opted to use more sophisticated surveillance programs to assure the flood is operating as designed. The surveillance checks are performed at least daily. In some cases, wells are monitored remotely so that real-time data are provided to field engineers.

As discussed in Section 2.3, the performance of the waterflood is often considered the best measure of the success potential of a given tertiary  $CO_2$  project. In a successful waterflood, the reservoir sweep efficiency has been validated and will be relied upon to optimize the efficient use of  $CO_2$ . If the waterflood production met or exceeded the production from the primary  $CO_2$  is the production from the primary  $CO_2$  is the performance of the waterflood production from the primary  $CO_2$  is the performance of the waterflood production from the primary  $CO_2$  is the performance of the waterflood production from the primary  $CO_2$  is the performance of the waterflood production from the primary  $CO_2$  is the performance of the waterflood production from the primary  $CO_2$  is the performance of the performance of the performance of the production from the primary  $CO_2$  is the performance of the performan


phase, the sweep efficiency can be considered good to excellent. Figure 6 in Section 3.1 provided a graphical look at typical waterflood/primary recoveries for classes of Permian Basin reservoirs. These same data are now displayed in logarithmic format in Figure 10. Data from the NMBMMR (1995, Chapter XI) using projections for waterflood recoveries at Indian Draw (Delaware) and Paduca (Delaware) Fields are shown in comparison to the data from Hickman (1994) and French et al. (1991). Note that the two Delaware Sandstone Fields compare unfavorably with the Permian Basin San Andres, Clearfork, and Queen Sand reservoirs from regions outside the Delaware Basin. In fact, the only waterfloods with recoveries less than from the primary production phase are the two Delaware Fields.

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A "first-order" rating of the potential of the WIPP-area fields for  $CO_2$  flooding can be accomplished by a comparison of the requisites of a good  $CO_2$  flood as presented in Section 2.0 with the known WIPP-area field attributes. The information needed for such comparison is included in Table 2 below:

 Table 2: Assessment of WIPP-Area Field Against Required Reservoir Characteristics

REQUISITE	<b>ADEQUATE</b>	<b>INADEQUATE</b>	<u>UNKNOWN</u>
Depth	x		
Reservoir Pressure	x		
Target CO <sub>2</sub> Reserves > 7	1 mmbo	<b>x</b> <sup>1</sup>	
High Injectivity Rates			x
Oil Gravity/Viscosity	x		
Lateral Pay Continuity			x
Number of Wells >15		<b>x</b> <sup>2</sup>	<b>x</b> <sup>2</sup>
Proven Reservoir Sweep	)	X	
Pay thickness >40 feet			X <sup>3</sup>

<sup>1</sup> No fields currently report primary resources greater than 10 mmbo leaving 1 mmbo as a target for CO<sub>2</sub> flooding

<sup>2</sup> Most Fields are well below a 15 well count, a few fields possess well counts > 15 but continuity of reservoir is poor

<sup>3</sup> Gross intervals can exceed 40 feet (NMBMMR 1995); however, production appears to be from multiple zones adding concerns regarding vertical and lateral continuity.

Melzer et al. (1995b) and Taber et al. (1996) offer more detailed screening parameters, but the same inadequacies seen above will lead to rejection of any of the WIPP-area reservoirs as viable  $CO_2$  flood candidates. However, it may be appropriate to outline some additional economic parameters which would need to be considered in addition to the reservoir evaluation above.

### 4.1 ECONOMIC CONSIDERATIONS FOR A CO<sub>2</sub> FLOOD NEAR WIPP

With regard to the costs of making  $CO_2$  available to the area, the WIPP site lies between the nearest New Mexico  $CO_2$  projects to the north and the Texas Delaware Sand floods to the south. Burlington Resources' El Mar flood in Loving County is the closest to WIPP, located approximately 25 miles to the south, while Conoco's Maljamar San Andres/Grayburg Dolomite



### PRIMARY ULT REC (PUR) VS. SECONDARY ULT RECOVERY (SUR) FOR PB RESERVIOR TYPES 1000000 CLFRK **SAN ANDRES** QUEEN **2NDRY ULT REC - MBO** ż. DELAWARE 100000 PUR=SUR 10000 1000 1000 10000 1000000 100000 **PRIMARY ULT REC - MBO**

**FIGURE 10:** Comparison of Secondary Ultimate Recovery to Primary Recoveries for Several Reservoir Types Including the Two Delaware Sandstone Waterfloods near the WIPP Site





flood (north) and Orla Petco's E. Ford flood (south-southwest) are both approximately 30 miles away. Texaco's Central Vacuum Unit Glorietta Flood is located approximately 35 miles to the northeast. Neither the Texaco Central Vacuum flood nor the Maljamar flood are in a reservoir similar to any of the reservoirs present in the vicinity of the WIPP site. In fact, only five of the 44  $CO_2$  floods in the Permian Basin are in sandstones. Four of these are in the Delaware Sands in Texas: Conoco's Ford Geraldine Unit, Coastal Management's Twofreds flood, Burlington Resource's El Mar flood, and Orla Petco's E. Ford flood. In discussions with project personnel from the operating companies, both the Twofreds and Ford Geraldine floods were rated as poor economic ventures. The conclusions regarding the two floods is even more significant when viewed in light of the "free"  $CO_2$  which was made available to them by nearby gas plants generating by-product  $CO_2$ . The El Mar and E. Ford projects have not been in operation long enough to evaluate their economic successes.

The nature of a CO<sub>2</sub> flood investment deserves some discussion. The exploration and development of the Delaware projects has been and likely will continue to be controlled by independent operators rather than the major oil companies. Historically, the Delaware Basin oil plays have been controlled by independents. Most independent companies have emphasized exploration rather than production projects. The reason for this is the desired high yields and quick rates of return needed to offset the higher risks present with oil and gas projects. For example, the best Delaware Field in the vicinity of the WIPP site is the Cabin Lake Delaware Field northwest of the WIPP site. It has ten wells producing from the Delaware horizon with average cumulative production of approximately 200,000 barrels per well. At an estimated drilling and completion cost of \$400,000 per well, and an assumed oil price of \$18.00 per barrel, the wells will return about \$2.0 million each over the cost of drilling, completing, royalty, severance/ad valorem taxes, and continued operations. This is a return on investment of 2000/400 or 5/1. The high returns compensate for the high risk nature of the investment type; i.e., adequate compensation for the inevitable dry holes an operator will encounter.

A recovery project, however, is a different sort of investment. Here, the cost of readying the wells and surface locations for injection, the cost of constructing a  $CO_2$  pipeline, the cost of the  $CO_2$ , and increased cost of operations (surveillance), will need to be paid out of the same expected production volumes (since  $CO_2$  reserves for a project need to be roughly equal to primary reserves in these types of reservoirs). If we choose the same example above with ten wells totaling two million produced barrels and include the pipeline costs of \$4 million<sup>1</sup>, the cost of conversion of four wells to injection at \$250,000 per well, and assume the operational costs over ten years are \$5 million, we already have an expense of \$10 million prior to paying for the  $CO_2$ . The  $CO_2$  volume can be estimated by using a 7.5 utilization factor (in mcf/bbl) calculating (7.5 x 2 million barrels =) 15 million mcf. The cost of  $CO_2$  (including pipeline tariffs) can conservatively be estimated at \$0.80 per mcf, giving a total cost for  $CO_2$  of \$12 million. Adding

<sup>&</sup>lt;sup>1</sup> Pipelines have been constructed to transport  $CO_2$  to the Maljamar flood and El Mar projects and either could be the source point for a "trunk" pipeline to the New Mexico Delaware fields in the WIPP area. Pipelines can be emplaced for approximately \$20,000 per inch-mile. Using an 8-inch diameter pipeline, a line to the WIPP site area would cost at least 25x8x\$20,000 or \$4.0 million.

up all costs results in \$22 million with a total expected production revenue of \$36 million. The cost of money on the long term investment will likely consume most of the \$14 million. If there is any significant risk of flood failure, an operator is very likely to choose an exploration investment over a  $CO_2$  flood investment. The economic reality is that a smaller company cannot afford to tie up such a large amount of capital for such a long interval of time.

### 4.2 Flood Surveillance Issues

The high cost of the injectant  $(CO_2)$  creates a dominant need for continuous flood surveillance. As mentioned in Section 2.4,  $CO_2$  flood operators exhibit a high degree of commitment to monitoring the flood. Due to the small margins of profit, any avoidable inefficiencies must be identified and corrected immediately. The enhanced surveillance techniques required for  $CO_2$ floods, driven by cost and oil contact issues, will essentially eliminate concerns over  $CO_2$ escaping the target zone.

As calculated by the EPA (1997), the probability of fluid (brine) injection activities to impact the WIPP is extremely remote at one chance in 667 million. Table 3 below shows estimated changes in the probability of a  $CO_2$  injection well failure compared to the potential fluid injection failures as derived by the EPA. The probability of  $CO_2$  injection to impact the WIPP would be even more remote, due to increased operational surveillance. Operators are very attentive to the conduct and response of a  $CO_2$  flood. Pressure fluctuations, deviations from planned water injection/gas injection cycles, or any other unanticipated occurrence can have a serious impact on the economic success of a  $CO_2$  flood project and are corrected immediately.

### Table 3: Estimated Comparative Probabilities Between Fluid (Brine) Injectionand CO2 Injection Failures Which Impact WIPP(Modified from EPA 1997)



What is the probability of?	Brine Injection <sup>2</sup>	CO <sub>2</sub> Injection <sup>3</sup>
presence of oil industry fluid (brine) or $CO_2$ injection	100%	100%⁴
a neighboring injection well leaking	5%	10% <sup>5</sup>
the leaky well going undetected	5%	2% <sup>6</sup>
undetected leak occurring in annulus	10%	2%6
upward annulus flow reaching interbed 1,900 ft. away	2%	5%'
pressure and flow being sufficient to fracture the interbed at repository level	5%	8%8
interbed permeability being oriented toward and contiguous to the repository	50%	50%
that flow continues for time sufficient to cause interbed pressurization at the repository at 8,800 ft.	2%	1 % <sup>5</sup>
interbed pressurization causing flow into the repository that affects containment by allowing release of radionuclide from the repository	60%	60%
chain of events occurring	1 in 667 million	1 in 2 billion

<sup>2</sup> Values in this column have been taken from EPA's Technical Support Document for Section 194.32: Fluid Injection Analysis, volume 1, Table Q, page 42.

<sup>3</sup>Values in this column are based on the EPA's Technical Support Document for Section 194.32: Fluid Injection Analysis, Volume 1, Table Q, page 42. As described in the footnotes, some values have been adjusted to reflect estimated differences in the behavior of  $CO_2$  compared to brine. The EPA's values are retained without change for those events for which the properties of the fluid phase have little effect on the probability.

 $^{4}$ The probability of this event was conservatively set at 1, although the prospects of a CO<sub>2</sub> flood occurring near the WIPP are unlikely.

<sup>5</sup>The probability of a CO<sub>2</sub> injection well leaking is higher due to the higher pressures within the tubing.

<sup>6</sup>Due to the rigorous monitoring of  $CO_2$  floods, it is very unlikely that a leak would go undetected for a substantial period of time (days to weeks).

<sup>7</sup>Higher tubing pressures (uphole) may result in a higher probability that upward flow reaches the interbed.

<sup>8</sup>At repository depth (2,150'), CO<sub>2</sub> injection pressure would be 10 -15% higher than that of brine.

### 5.0 CONCLUSIONS



Considerable growth in the numbers of  $CO_2$  projects has been observed in the Permian Basin. The trend will likely continue and a higher percentage of the oil produced from the Permian Basin will come from both existing and new  $CO_2$  floods. The question addressed in this summary is whether a similar trend will be observed in the immediate (nine-township) area around the WIPP site.

The reservoirs involved in successful CO<sub>2</sub> flooding are depletion-drive oil reservoirs between depths of 2500 and 10,000'. The subject area has three main reservoirs, the Delaware Sand, the Brushy Canyon Formation, and the Bone Springs Formation, all of which are oil reservoirs within that depth interval. The oil needs to be less than 10 centipoise in viscosity and with a gravity above 25 degrees; both these requisites are met by area reservoirs. However, commercial CO<sub>2</sub> flooding requires large fields with a thick and laterally continuous pay interval. The WIPP-area reservoirs are lacking these two important characteristics. The need for good reservoir sweep is critical and most reservoirs utilize waterfloods to establish sweep patterns as a proving ground for good CO<sub>2</sub> sweep efficiencies. The oil reservoirs of the WIPP-area (in specific) and Delaware Basin oil reservoirs (in general) are not good candidates for waterflooding, hence CO<sub>2</sub> reservoir sweep patterns are suspect. Four Delaware Sand CO<sub>2</sub> floods exist 25-50 miles south of the WIPP site in Texas. None of the four Delaware Sand CO<sub>2</sub> floods are, at least at present, considered to be econorric successes. All four flood the uppermost Delaware Sandstone interval (Ramsey Sand), which demonstrates higher average reservoir permeability than exists within the WIPP site area, that is, the WIPP-area reservoirs possess even worse characteristics than these.

The Delaware Mountain Group production in the WIPP vicinity has been limited to the poorer quality Bell Canyon, Cherry Canyon, Brushy Canyon, and Bone Springs formations for which no  $CO_2$  flood analogue exists. The models for  $CO_2$  flooding in the Delaware Basin are the uppermost and best of the Delaware Sands which are better quality sands and are not productive in the vicinity of WIPP.

In summary, it is extremely unlikely that a field in the vicinity of the WIPP site would be  $CO_2$  flooded in the future. Supporting this statement are the small oil in place targets, the established and sub-marginal reservoir permeability characteristics, and economic factors such as risk, cost, and delayed and minimal or unacceptable returns. However, conditions may change in the future to encourage operators to attempt what we now consider to be very risky and economically marginal. In this unlikely event, the enhanced surveillance and monitoring associated with  $CO_2$  floods driven by cost and oil contact issues, will essentially eliminate concern of  $CO_2$  escaping from the intended flood area.



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February 4, 1998 memorandum from Y. Wang, to M. Chu, "No upper limit needed to be imposed on the inventory of cellulosics, plastics, and rubbers in TRU wastes designated to the WIPP for disposal".



### Sandia National Laboratories

Albuquerque, New Mexico 87185

date: February 4, 1998



to: Margaret S. Y. Chu (Org. 6801)

from: Yifeng Wang (Org. 6821)

subject: No Upper Limit Needed to Be Imposed on the Inventory of Cellulosics, Plastics, and Rubbers in TRU Wastes Designated to the WIPP for Disposal

### **OBJECTIVE**

In this memorandum I want to estimate the increase in organic material inventory in transuranic (TRU) wastes designated to the Waste Isolation Pilot Plant (WIPP) for disposal, assuming that all waste drums will be fully filled with cellulosics, plastics, and rubber, and then I want to check if the WIPP repository chemistry will still be under control by MgO backfill even for this extremely conservative case. If it is, we can then practically remove the upper limit currently imposed on the inventory of those organic materials and thus greatly simplify the requirements for waste characterization.

### CALCULATION

Step 1: For simplicity, we only consider contact-handled (CH) waste, because it accounts for 96% of total waste volume (DOE/CAO, 1996, p. 2-1). CH-TRU waste material parameter disposal inventory is listed in Table 1. With the following bulk density data:

Cellulosics: 135 kg/m<sup>3</sup> (average value from Butcher et al., 1991, p. 15) Plastics: 202 kg/m<sup>3</sup> (average value from Butcher et al., 1991, p. 16) Rubber: 202 kg/m<sup>3</sup> (assumed to be the same as plastics)

the total volume of organic materials as actual waste components (excluding plastic liners) in 1 m3 of CH-TRU waste is estimated to be:

54 (kg/m3)/135 (kg/m3) [cellulosics] + 10 (kg/m3)/202 (kg/m3) [rubber] + 34 (kg/m3)/202 (kg/m3) [plastics] = 0.62 m<sup>3</sup> organic materials/m<sup>3</sup> CH-TRU waste.

According to the conversion factors proposed by Wang and Brush (1996), the amount of equivalent cellulosics in this waste is: 54 (cellulosics) + 10 (rubber) + 1.7 x (34 + 26) (plastics) =  $166 \text{ kg/m}^3$ .

Step 2: Based on the following solid density data:



Steel: 7860 kg/m<sup>3</sup> (Butcher et al., 1991, p. 9) Exceptional Service in the National Interest Margaret S. Y. Chu (Org. 6801)



February 4, 1998

Plastics: 1200 kg/m<sup>3</sup> (Butcher et al., 1991, p. 40)

the bulk volume of actual waste components in 1 m<sup>3</sup> of CH-TRU waste is calculated to be:

- 2 -

1 m<sup>3</sup> [total TRU-CH waste volume]
- 139/7860 [container steel volume]
- 26/1200 [plastic liner volume]
= 0.96 m<sup>3</sup> bulk volume of waste components/m<sup>3</sup> CH-TRU waste

Step 3: Assuming that this bulk volume will be fully filled with organic materials in the same proportion as that given in the current baseline inventory report (DOE/CAO, 1996, p. 2-5), the inventory of organic materials for this extreme case can then be calculated simply by volume scaling:

Cellulosics:  $54 \times 0.96/0.62 = 84 \text{ kg/m}^3$ Rubber:  $10 \times 0.96/0.62 = 15 \text{ kg/m}^3$ Plastics:  $34 \times 0.96/0.62 + 26 \text{ (liners)} = 79 \text{ kg/m}^3$ .

Correspondingly, the total amount of equivalent cellulosics in the waste for this extreme case is:  $84 + 15 + 1.7 \times 79 = 233 \text{ kg/m}^3$ . Therefore, even if all waste drums were fully filled with organic materials, the inventory of total organic carbon would be increased only by a factor of 233/166 = 1.4.

### CONCLUSION

Since the quantity of MgO to be emplaced in the WIPP is at least twice as much as needed to sequester all microbially-generated carbon dioxide estimated from the current waste inventory estimates (DOE, 1996, SOTERM-6), MgO chemical control is thus expected to be still effective, even if all waste drums were fully filled with organic materials. Consequently, there is no need to impose a upper limit on organic materials in waste characterization.

The above conclusion is based on two assumptions (1) that 1 mole organic carbon will produce 1 mole of  $CO_2$  and (2) that all organic materials will be biodegraded. Apparently, the two assumptions are conservative. Under anticipated WIPP conditions, organic materials are expected to be degraded mostly via methanogenesis, in which 1 mole of organic carbon will produce half mole of  $CO_2$  and half mole of  $CH_4$  (Wang and Brush, 1996). If this is the case, the amount of MgO to be emplaced in the WIPP is then about four times as much as needed to sequester all microbially-generated carbon dioxide estimated from the current waste inventory estimates. Furthermore, under WIPP chemical conditions, and due to the nature of organic materials in the waste, a significant fraction of those organic materials is expected to be undegradable. Natural analogue studies, for example, the study of organic carbon burial and



Margaret S. Y. Chu (Org. 6801)

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preservation in sediments, may be conducted in the future to quantify the refractory fraction of organic materials in TRU waste.

Component	Weight parameter
· · · · ·	$(Kg/m^3)$
Iron base metal/alloys	170
Aluminum base metal/alloys	18
Other metal/alloys	67
Other inorganic materials	31
Vitrified	55
Cellulosics	54
Rubber	10
Plastics	34
Solidified inorganic materials	54
Solidified organic materials	5.6
Cement (solidified)	50
Soils	44
Container:	
Steel	139
Plastics	26

### Table 1. WIPP CH-TRU Waste Material Parameter Disposal Inventory<br/>(DOE/CAO, 1996, p.2-5)



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### REFERENCES



- Butcher, B. M., Thompson, T. W., VanBuskirk, R. G., and Patti, N. C. (1991) Mechanical Compaction of Waste Isolation Pilot Plant Simulated Waste. Sandia National Laboratories, Albuquerque, NM. SAND90-1206.
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- DOE/CAO (1996) Transuranic Waste Baseline Inventory Report (Revision 3). DOE/CAO-95-1121.
- Wang, Y., and Brush, L. H. (1996) Estimates of gas-generation parameters for the long-term WIPP performance assessment. Memo to M. S. Tierney, 1/26/1996. WPO#30819.

Distribution:

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### MS 1395 SWCF-C: 1.1.09.1.1:QA:DPRP1:UPPER LIMIT ON INVENTORY, WASTE CHARACTERIZATION

Attachment 8

Bynum, R.V and others. 1997. "The Role of Organic Ligands in the WIPP." Unpublished presentation to the EEG, July 30, 1997, Albuquerque, NM. Albuquerque, NM: Sandia National Laboratories.



## The Role of Organic Ligands in the WIPP

Vann Bynum, Bob Moore, FSU, and Jim Nowak

K<sub>d</sub> Meeting With EEG July 30, 1997







- Which data to use for competition calculations
- (i.e. WIPP specific data with existing literature - data from "disparate and irreconciled sources" data) or data from the article cited by EEG
- Preferential binding of organic ligands
- Validity of BIR organics inventory
- Effect of organic ligands on K<sub>d</sub>



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## Organic Ligands

halo complexes, making an even stronger case that negligible effect on repository performance. The may be enhanced due to the formation of soluble Characterization Analysis Supplementary Peer "The Panel agrees that under the conditions of repository, the availability of transition metals base metals control ligand chemistry"--Waste Panel notes that, even at the basic pH in the MgO backfill, chelating agents will have a Review Report

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### Comparison of Data Sources

### **EEG Cited Article**

- not WIPP specific
- low ionic strength
- NaClO<sub>4</sub> electrolyte
- no pH control
- no description of analytical technique
- no significant recognition of scientists

### WIPP Data

- WIPP specific
- high ionic strength
- NaCl electrolyte
- pH controlled
- state of the art analytical technique
- performed by world recognized expert





### Preferential Binding Does Not Dictate a Direct Effect

- A statement cannot be made regarding preferential binding without respect to the system in which the data are being applied
- To determine an effect, the whole system must be considered
  - concentration of actinide
  - concentration of ligand



– concentration of other metals

## Interaction of Parameters Direct Effect Relies on

## $M^{n+} + L^{m-} \iff ML^{(n+m)}$

# $\beta_{M} = [ML^{(n+m)}]/[M^{n+}][L^{m-}]$



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### **Direct Effect Relies on** Interaction of Parameters (cont.) $\beta_{Fe(II)} = [EDTA-Fe^{2-}] / [EDTA^{4-}] [Fe^{2+}]$ $\beta_{\text{Ni(II)}} = [EDTA-Ni^{2-}] / [EDTA^{4-}] [Ni^{2+}]$ $\beta_{Mg(II)} = [EDTA-Mg^{2-}] / [EDTA^{4-}]$ $Mg^{2+1}$ $\beta_{Th(IV)} = [EDTA-Th] / [EDTA^{4-}] [Th^{4+}]$

 $\beta_{Ca(II)} = [EDTA-Ca^{2-}] / [EDTA^{4-}] [Ca^{2+}]$ 

7

Direct Effect Relies on

Interaction of Parameters (cont.)

[EDTA-Cu<sup>2-</sup>] / [EDTA<sup>4-</sup>] [Cu<sup>2+</sup>] [EDTA-Zn<sup>2-</sup>] / [EDTA<sup>4-</sup>] [Zn<sup>2+</sup>] [EDTA-Cr<sup>2-</sup>] / [EDTA<sup>4-</sup>] [Cr<sup>2+</sup>]  $\beta_{Pb(II)} = [EDTA-Pb^{2-}] / [EDTA^{4-}] [Pb^{2+}]$ and  $\beta c_{r(II)} =$  $\beta c_{u(II)} =$  $\beta_{Zn(II)} =$ 





# Direct Effect Relies on

Interaction of Parameters (cont.)

 $[EDTA-Pb^{2-}] + [EDTA-Cr^{2-}] +$  $EDTA-Fe^{2-}$  +  $[EDTA-Ni^{2-}]$  +  $[EDTA-Mg^{2}] + [EDTA-Th] +$ [EDTA-Cu<sup>2-</sup>] + [EDTA-Zn<sup>2-</sup>] $[EDTA]_{total} = [EDTA^{4-}] +$  $[EDTA-Ca^{2-}] +$ 



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### BIR Is Reasonable Estimation of Organic Ligands in the Repository

- BIR represents only available, researched data base on waste contents
- EDTA inventory at RFETS is an upper bound (later memo recommends 5.9kg)
  - all EDTA in TRU waste
  - no thermal treatment
  - no degradation





### **BIR Is Reasonable Estimation of** Organic Ligands in the Repository (cont.)

- Competition calculations are very conservative
- no hydrolysis of actinides
- no effect from other metals present
- no sorption
- Calculations show no significant effect of

organic ligands





### Relative Impact of Organic Ligands on Actinide Solubility

		Salado	)	Castile				
	no organics	Contribution from BIR % Contribution organics		no brganics crganics crganics		no Janics from BIR % Contribution organics organics	Contribution from BIR organics	% Contribution
+3	6E-7	7E-13	0.01%	7E-8	8E-14	0.01%		
+4	4E-6	3E-10	0.75%	6E-9	5E-13 /	0.83%		
+5	2E-6	1E-20	0.00%	2E-6	1E-20	0.00%		
+6	9E-6	1E-14	0.00%	9E-6	1E-14	0.00%		



7/29/97

### Impact of Organic Ligands

	Salado Concentration	Castile Concentration	EDTA log beta	EDTA beta
Fe2+	1E-4	1E-4	13.3	2.0E+13
Ni2+	4E-4	4E-4	17.4	2.5E+17
Mg2+	5E-1	4E-2	6.7	4.6E+06
Am3+	6E-7	7E-8	14.4	2.7E+14
Th4+	4E-6	6E-9	16.3	1.8E+16
NpO2 +	2E-6	2E-6	6.1	1.2E+06
UO2 2+	9E-6	9E-6	11.5	2.9E+11
Ca2+	3E-2	1E-2	6.7	4.6E+06
Pb2+	1E-6	1E-6	18.0	1.0E+18
Cr2+	1E-6	1E-6	13.6	4.0E+13
Mn2+	1E-6	1E-6	13.9	7.9E+13
V2+	1E-6	1E-6	12.7	5.0E+12
Ga3+	1E-6	1E-6	21.0	1.0E+21
BIR inventory of EDI	ΓA =	5E-6		
scaled inventory of E	DTA=	2E-5		



Salado [EDTA]=	BIR inventory	4E-21	Castile [EDTA]=	BIR inventory	4E-21
[EDTA-Am]= [EDTA-Th]= [EDTA-NpO2 +]= [EDTA-UO2 2+]=		7E-13 3E-10 1E-20 1E-14	[EDTA-Am]= [EDTA-Th]= [EDTA-NpO2 [EDTA-UO2	2 +]= 2+]=	8E-14 5E-13 1E-20 1E-14

### Summary

- Valid and technically defensible data were used in the CCA to dismiss the contribution of organic ligand-actinide interactions.
- When calculations are performed to include system effects, there is insignificant binding between the organic ligands and actinides.
- Based on conservatisms incorporated in the above, there is no justification for revising K<sub>d</sub>s based on organic ligands.

### Attachment 9



Nowak, E.J. 1997. "Experimental Results and K<sub>d</sub> Value Ranges in the CCA." Unpublished presentation to the Environmental Evaluation Group, January 30, 1997, Albuquerque, NM. Albuquerque, NM: Sandia National Laboratories.



Experimental Results and K<sub>d</sub> Value Ranges in the CCA

### E. J. Nowak Sandia National Laboratories

K<sub>d</sub> Meeting with EEG July 30, 1997 Albuquerque, NM





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Laboratories,	Investigators
Principal	Principal

- SNL
- Pat Brady
- Larry Brush
- Vann Bynum (SAIC)
- Chris Crafts
- Dave Hobart (CTAC)
- Dan Lucero
- Bob Moore
- Hans Papenguth
- George Perkins
- Malcolm Siegel

- LANL
- Ines Triay
- FLORIDA STATE UNIVERSITY
- Greg Choppin
- PNL
- Andy Felmy
- Dhanpat Rai





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### In the Context of the CCA, Debates on Values for K<sub>d</sub>s Much Greater than 3 ml/g Are of Little Consequence

- Compliance context sets perspective for discussions about K<sub>d</sub> values:
- Pu and Am are the only two elements that impact the CCDFs significantly.
- Sensitivity studies have shown that K<sub>d</sub> values greater than approximately 3 ml/g limit release and result in compliance.
- Experimental evidence from three experimental approaches supports K<sub>d</sub> greater than 100 ml/g for Pu and Am
  - batch, mechanistic, and core column studies



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sponses to EEG Concerns	ion for K <sub>d</sub> s	ing log-uniform distribution is negligible.	eriments designed to determine range, <u>not</u> distribution	): Pu(V) K <sub>d</sub> Values Conservative Lower Bounds	sis exists for using Pu(V) values as conservative r Pu(III) and Am(III).	(III) sorption data support the chosen ranges.	a Conservative Analog, Providing a Lower Bound	asonable and conservative oxidation state analog for arly Am(III) for Pu(III).	nn flow test results	an 100 ml/g for Am, Pu, and Th.	of organic ligands on K <sub>d</sub> values	nds are complexed with other metals to the extent that	in sorption of actinides is negligible.	ponses to EPA comments give DOEs position on	ntory	
Responses to	Uniform distribution for K <sub>d</sub> s	<ul> <li>Impact of using log-uniform</li> </ul>	<ul> <li>Sorption experiments design</li> </ul>	Pu(III) and Am(III): Pu(V) K <sub>d</sub> Val	<ul> <li>Empirical basis exists for us estimates for Pu(III) and Am(</li> </ul>	<ul> <li>Existing Am(III) sorption data</li> </ul>	Pu(IV): Th(IV) Is a Conservative	<ul> <li>Th(IV) is a reasonable and co Pu(IV); similarly Am(III) for P</li> </ul>	Latest core column flow test re	<ul> <li>K<sub>d</sub> greater than 100 ml/g for</li> </ul>	Negligible effect of organic liga	<ul> <li>Organic ligands are complex</li> </ul>	their effect on sorption of ac	CCA and responses to EPA	organic inventory	



### No Significant Performance Difference between Log-Uniform and Uniform K<sub>d</sub> Distributions

- Results of PA calculations show no impact of distribution type on compliance.
- Sorption experiments were designed to establish K<sub>d</sub> ranges, not distributions.
- distribution; chemical variables were chosen to cover Sorption data should not be plotted to derive a expected ranges, not to represent expected distributions of variables.
- Data should be used only to establish ranges, not distributions.





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<ul> <li>niform distribution for K<sub>a</sub>s</li> <li>Impact of using log-uniform distribution is negligible.</li> <li>Impact of using log-uniform distribution is negligible.</li> <li>Sorption experiments designed to determine range, <u>not</u> distribution <i>u(III) and Am(III)</i>: <i>Pu(V) K<sub>a</sub> Values Conservative Lower Bounds</i></li> <li>Empirical basis exists for using <i>Pu(V) values as conservative estimates for Pu(III) and Am(III)</i>.</li> <li>Existing Am(III) sorption data support the chosen ranges.</li> </ul>	<ul> <li>I(IV): Th(IV) Is a Conservative Analog, Providing a Lower Bound</li> <li>Th(IV) is a reasonable and conservative oxidation state analog for Pu(IV); similarly Am(III) for Pu(III).</li> </ul>	<ul> <li>test core column flow test results</li> <li>K<sub>a</sub> greater than 100 ml/g for Am, Pu, and Th.</li> </ul>	<ul> <li>Organic ligands are complexed with other metals to the extent that their effect on sorption of actinides is negligible.</li> </ul>	<ul> <li>CCA and responses to EPA comments give DOEs position on organic inventory.</li> </ul>
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Pu(III) and Am(III): Pu(V) K<sub>d</sub> Values Are **Conservative Lower Bounds** 

- Am(III)  $K_{A}s$  are larger than Pu(V)  $K_{d}s$  in a preponderance of empirical results from many sources.
- WIPP databases and summaries, SAND reports
- NEA, HMIP, AECL, NAGRA, Swedish Program, sorption databases
- studies of Am(III), Nd(III), and An(V) sorption by carbonates
- Am(III) chemical behavior is quantitatively analogous to Pu(III) chemical behavior - extensive empirical evidence.
- Therefore, Am(III) and Pu(III) are expected to be at least as strongly retarded in the Culebra as is Pu (V).







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Batch K <sub>d</sub> Greater Than 100 Relevant Concentrations; Estimate for Pu(III)	u unnecessary for compliance at brine < 10 <sup>-9</sup> M (based on performance A)	ation on solid to liquid phase with increasing liquid phase	down to concentrations near 1 x 10 <sup>-10</sup> M	or is quantitatively analogous to Pu(III) nsive empirical evidence.	also greater than 100 ml/g down to 10 <sup>-10</sup> M		еес 7/30/97
u(III) and Am(III): I ml/g for Am(III) at Provides E	<ul> <li>Retardation of Am and Pl concentrations below 3 x calculations given in CC/</li> </ul>	<ul> <li>K<sub>d</sub> (ratio of Am concentra concentration) increases concentration</li> </ul>	<ul> <li>K<sub>d</sub> greater than 100 ml/g (10<sup>-9</sup> to 10<sup>-10</sup> M)</li> </ul>	<ul> <li>Am(III) chemical behavio chemical behavior - exter</li> </ul>	<ul> <li>Therefore, K<sub>d</sub> for Pu(III) a concentrations near 1 x</li> </ul>		
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## For Pu(III) and Am(III): Pu(V) K<sub>d</sub> Values **Conservative Lower Bounds**

- Empirical basis exists for using Pu(V) values as conservative estimates for Pu(III) and Am(III).
- Existing Am(III) sorption data support the chosen ranges.



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### **Responses to EEG Concerns**

Uniform distribution for K<sub>d</sub>s

- Impact of using log-uniform distribution is negligible.
- Sorption experiments designed to determine range, not distribution

Pu(III) and Am(III): Pu(V)  $K_d$  Values Conservative Lower Bounds

- Empirical basis exists for using Pu(V) values as conservative estimates for Pu(III) and Am(III).
- Existing Am(III) sorption data support the chosen ranges.

### Pu(IV): Th(IV) Is a Conservative Analog, Providing a Lower Bound

 Th(IV) is a reasonable and conservative oxidation state analog for Pu(IV); similarly Am(III) for Pu(III).

Latest core column flow test results

•  $K_d$  greater than 100 ml/g for Am, Pu, and Th.

Negligible effect of organic ligands on K<sub>d</sub> values

- Organic ligands are complexed with other metals to the extent that their effect on sorption of actinides is negligible.
- CCA and responses to EPA comments give DOEs position on organic inventory



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### Oxidation State Analogs Are Used to Estimate Behavior of Actinides in Same Oxidation State

- Actinides in the same oxidation state exhibit similar trends and behaviors.
- These trends allow the behavior of one actinide in a particular oxidation state to be estimated from the behavior of another actinide in the same oxidation state.





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- Couple with trend of decreasing actinide solubilities across the actinide series.
- Predicted solubility of an "early" actinide series element is used as a bounding estimate for solubility of a "later" actinide series element in the same oxidation state.

# Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw



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### (CU or Th/mol Kg<sup>-1</sup>H<sub>2</sub>O)



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4 m, 7 day 6 m, 8 day

6

Thorium

1 m, 8 day 6 m, 8 day 0.2 m, 104 day 0.03-0.1 m, 40-46 day

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NaCl System

Uranium



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### Pu(IV): Th(IV) Is a Conservative Analog, Providing a Lower Bound

• Th(IV) is a reasonable and conservative oxidation state analog for Pu(IV); similarly Am(III) for Pu(III).





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Uniform distribution for K <sub>a</sub> s
<ul> <li>Impact of using log-uniform distribution is negligible.</li> </ul>
<ul> <li>Sorption experiments designed to determine range, <u>not</u> distribution</li> </ul>
Pu(III) and Am(III): Pu(V) K <sub>d</sub> Values Conservative Lower Bounds
<ul> <li>Empirical basis exists for using Pu(V) values as conservative estimates for Pu(III) and Am(III).</li> </ul>
<ul> <li>Existing Am(III) sorption data support the chosen ranges.</li> </ul>
Pu(IV): Th(IV) Is a Conservative Analog, Providing a Lower Bound
<ul> <li>Th(IV) is a reasonable and conservative oxidation state analog for Pu(IV); similarly Am(III) for Pu(III).</li> </ul>
Latest core column flow test results
<ul> <li>K<sub>d</sub> greater than 100 ml/g for Am, Pu, and Th.</li> </ul>
Negligible effect of organic ligands on K <sub>d</sub> values
<ul> <li>Organic ligands are complexed with other metals to the extent that their</li> </ul>
effect on sorption of actinides is negligible.
<ul> <li>CCA and responses to EPA comments give DOEs position on organic</li> </ul>
inventory
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	$\bigcirc$
<ul> <li>and Pu did not break through core columns C and D</li> <li>conservative minimum K<sub>d</sub>s:</li> <li>190 ml/g for Am</li> <li>175 ml/g for Pu</li> <li>175 ml/g for Pu</li> <li>ast-test destructive analyses of core E support high retardation soth Am and Pu.</li> <li>mographic analyses of core B support high retardation of Th conservative minimum K<sub>d</sub> equal to about 400 ml/g</li> </ul>	greater than 100 m/g for Am, Pu, and Th.
	Am and Pu did not break through core columns C and D - <u>conservative minimum</u> K <sub>d</sub> s: • 190 ml/g for Am • 175 ml/g for Pu Post-test destructive analyses of core E support high retardation of both Am and Pu. Tomographic analyses of core B support high retardation of Th - <u>conservative minimum</u> K <sub>d</sub> equal to about 400 ml/g - <u>st core column flow test results</u> :



### Organic ligands are complexed with other metals to the extent that their effect on sorption of actinides is negligible.

*Negligible effect of organic ligands on K<sub>d</sub> values:* 

- Organic ligands are complexed with other metals to the extent that their effect on sorption of actinides is negligible.
- CCA and responses to EPA comments give DOEs position on organic inventory





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### We Have Shown That:

Sorption experiments were designed to determine ranges, <u>not</u> distributions.

For Pu(III) and Am(III): Pu(V) K<sub>d</sub> values are lower bounds

- Empirical basis exists for using Pu(V) values as conservative estimates for Pu(III) and Am(III).
- Existing Am(III) sorption data support the chosen ranges.

For Pu(IV): Th(IV) is a conservative analog, a lower bound.

 Th(IV) is a reasonable and conservative oxidation state analog for Pu(IV); similarly Am(III) for Pu(III).

Latest core column flow test results show that:

•  $K_d$  is greater than 100 ml/g for Am, Pu , and Th.

**Organic ligands have negligible effect of on K<sub>d</sub> values.** 

- Organic ligands are complexed with other metals to the extent that their effect on sorption of actinides is negligible.
- CCA and responses to EPA comments give DOEs position on organic inventory.

Context: K<sub>d</sub>s greater than 3 ml/g show compliance.

EG 7/30/97





Ranges of Matrix K<sub>d</sub>s (ml/g) Used by PA for the CCA 900 to 20,000 Documentin EEGKd7\_30\_97.ppt 26 200 to d Z 900 to 20,000 ч Н 900 to 20,000 t 0 0.03 0 ന EEG 7/30/91 20 to 500 A B ۱ 900 to 20,000 20 to 500 Ъ С 07/23/97 8:56 AM S ta te × 0 2 > >



**Attachment 10** 



Perkins, W.G. and Lucero 1997. "Intact-Core Column Results." Unpublished presentation to the Environmental Evaluation Group, January 30, 1997, Albuquerque, NM. Albuquerque, NM: Sandia National Laboratories.



### Intact-Core Column **Analysis Results**

## **Presentation to EEG - 30 July 1997**

WIPP Chemical and Disposal Room Processes W. George Perkins & Daniel A. Lucero Sandia National Laboratories Department





### Credits

- Flow studies: Dan Lucero, *et al.* (SNL)
- Non-destructive and destructive analyses of cores: Dan Lucero, *et al.* (SNL)
- Tomography: Glenn Brown, *et al.*, (OSU)
- Analysis and data-fitting program COLUMN: Kent Budge (SNL); Glenn Brown, et al., (OSU)





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Core Column Analyses

## Scope of the Presentation

- Results of core analyses
- B-Core Th-Daughter Tomography
  - E-Core Destructive Analysis
- C-Core non-eluted species (Am/Pu) updates



Core Column Analyses



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### Analyses for Non-Eluted Actinides

- $1^{228}$ Th B-core  $\gamma$ -Ray tomography
- <sup>241</sup>Am and <sup>241</sup>Pu E-core destructive analysis <sup>241</sup>Am and <sup>241</sup>Pu C-Core non-breakthrough



analyses

Core Column Analyses



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### Conclusions from B-Core Tomography of <sup>228</sup>Th Daughters

- Tomography results are consistent with  $R \approx 1 \ge 10^4$
- Using the apparent B-Core porosity (10%) and bulk density of 2.4 g/cm<sup>3</sup>, the apparent  $K_d \approx 400 \text{ mL/g}$ , of the same magnitude as the lower end (900 mL/g) of the range of batch  $K_d$  values



Core Column Analyses



# E-Core Analysis for <sup>241</sup>Am and <sup>241</sup>Pu

- E-Core Dimensions
- ◆ Diameter: 14.5 cm
- Length: 10.2 cm
- Actinide Injection
- ◆ <sup>241</sup>Am
- 1/16/96: 18.5 mL spike at 0.66 μCi/mL (12.2 μCi) 3/22/96: 20 mL spike at 0.67 μCi/mL (13.4 μCi)
- ▶ 241Pu
- 1/16/96: 18.5 mL spike at 0.61 μCi/mL (11.3 μCi)



Core Column Analyses



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### E-Core Analysis for <sup>241</sup>Am and <sup>241</sup>Pu Flow History (AIS Brine)

- 0.1 mL/min from 1/16/96 4/9/96 (83 days)
- Pause from 4/9/96 to 6/4/96
- 0.05 mL/min from 6/4/96 7/15/96 (41 days)
- Brine flow ended and γ-ray spectroscopy posttest analyses began on 7/15/96
- Results of γ-ray spectroscopy analyses were reported earlier



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Core Column Analyses

### **E-Core** Destructive Analysis

- Top brine-distribution plates were acidwashed and the washings were analyzed
- Layers of rock were milled using a drill press tool setup (shown in the next slide)
- Rock powder was captured by vacuum, collected on weighed filter paper, dissolved in 100 mL 0.1 N HCl for each sub-cut
- <sup>241</sup>Pu and <sup>241</sup>Am solutions were analyzed using liquid scintillation counting (LSC)



Core Column Analyses



### POST TEST E CORE



Core Column Analyses

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**E-Core LSC Analysis Results** 

Cut No.	<b>Rock Mass</b>	Am $(\mu Ci)$	$\operatorname{Am}(\%)$	Pu (µCi)	Pu (%)
Dist Plate	0.0	1.8	7.0	0.7	6.2
<b></b> 4	5.5	15.4	60.2	4.5	39.8
2	13.0	0.6	2.5	2.2	19.5
Wall	14.9	0.8	2.9	0.7	6.2
3	20.7	0.1	0.4	0.1	0.9
4	14.4	7.9E-02	0.3	0.1	0.9
2	14.4	5.0E-03	0.0	4.7E-04	4.2E-03
9	14.2	3.1E-03	0.0	2.4E-04	2.2E-03
Totals	97.1	18.8	73.3	8.3	73.5
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Core Column Analyses



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### E-Core Analysis Summary

- Nearly all the recovered <sup>241</sup>Am was in the top 1 mm of rock (probably precipitated)
   The recovered <sup>241</sup>Pu profile exhibits some structure more indicative of sorption
- Approximate retardation parameters for 241 D = 1 = 106. K = ( = 104 mJ/c





### C-Core <sup>241</sup>Am and <sup>241</sup>Pu Elution Conditions



■ C-Core dimensions

Diameter: 14.5 cm

Length: 10.2 cm

Actinide Injection on 7/10/95

◆ <sup>241</sup>Am: 20 mL spike at 0.28 μCi/mL (0.34 μM)

◆ <sup>241</sup>Pu: 20 mL spike at 1.0 μCi/mL (0.04 μM)






### **C-Core Elution Analysis**

### Two separate calculations

- For the non-interrupted flow period (269 d) data cited by Nowak in his earlier presentation
- For the total interrupted flow volume (68.7 L)
- Flow was modeled as though breakthrough had just been observed above the Minimum Detectable Activity (using LSC)
  - ◆ <sup>241</sup>Am: 0.1 nCi/L (1.2 x 10<sup>-13</sup> M)
  - ◆ <sup>241</sup>Pu: 1.5 nCi/L (6.0 x 10<sup>-14</sup> M)



### C-Core Elution Analysis (Continued)



- <sup>241</sup>Pu was modeled at injected concentration
   <sup>241</sup>Am was modeled at injected, saturated, and 0.1-saturated concentrations
- For each <sup>241</sup>Am concentration modeled, the input pulse duration was lengthened to account for reduction in concentration



### Effects of Am Oversaturation

- Saturation concentration: 6.5 x 10<sup>-9</sup> M
   Injection Concentration: 340 x 10<sup>-9</sup> M (oversaturated by a factor of 52.3)
- Calculations for Am were done
  - at saturation concentration (with a 52.3 times longer input pulse)
  - at 0.1 saturation concentration (with a 523 times longer input pulse)



### Large Apparent Retardations Even at 269 Days

- Apparent C-Core Porosity: 3.3%
- Assumed bulk density: 2.4 g/cm<sup>3</sup>
- $R(^{241}Pu) = 12,700; K_d = 175 \text{ mL/g}$
- $R(^{241}Am 0.1 \text{ Sat}) = 13,800; K_d = 190 \text{ mL/g}$
- These <u>MINIMUM</u> K<sub>d</sub> estimates are well above the values required for compliance

# Summary of C-Core Results

- At shortest time of steady elution (269 d) as cited by Nowak earlier •  $R(^{241}Pu) = 12,700; K_d = 175 mL/g$
- $R(^{241}Am 0.1 \text{ Sat}) = 13,800; K_d = 190 \text{ mL/g}$
- For longer elution ( $V_{tot} = 68.7 \text{ L}$ ), pore volume was used as independent variable
- $R(^{241}Pu) = 20,500; K_d = 282 \text{ mL/g}$
- $R(^{241}Am 0.1 \text{ Sat}) = 23,800; K_d = 327 \text{ mL/g}$ •  $R(^{241}Am - Sat) = 25,400; K_d = 349 mL/g$

### Conclusions from Flow Studies



- Tomographic analysis of B-Core implies that  $R = 10^4$  and  $K_d = 400 \text{ mL/g}$
- Destructive analysis of E-Core revealed that <sup>241</sup>Pu and <sup>241</sup>Am remained within the top few millimeters of the core
- Calculated minimum K<sub>d</sub> values for all noneluted species are significantly greater than 100 mL/g, which in turn is significantly greater than 3 mL/g



### Core Column Analyses



### **Elution Experiment Description**

Experimental setup
 Experimental conditions

 Brine-pumping speed
 Input pulse duration and concentration

 Effluent analysis





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Core Column Analyses

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### **Elution Experiment Setup**







### Elution Experiments Brine Flow Rates



Volumetric flux: 0.05, 0.1 mL/min
 Specific discharge: 5.05x10<sup>-6</sup>, 1.01x10<sup>-5</sup> cm/s (averaged over intact-core column 165 cm<sup>2</sup> cross-sectional area)



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Core Column Analyses

### Elution Experiments Radioisotope Input Pulses

Typical duration: 200 min (12,000 s)
Typical volume: 20 mL

	Activity	Concentration
Isotope	(μ <b>Ci/m</b> L)	( <b>pM</b> )
<sup>241</sup> Am	0.28 to 0.66	340 to 800
<sup>241</sup> Pu	0.61 to 1.61	24.6 to 64.8
<sup>228</sup> Th	0.48 to 5.16	2.57 to 27.6

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Core Column Analyses

### **Elution Experiments** Minimum Detectable Activities



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Core Column Analyses

### B-Core Experiments with <sup>228</sup>Th

- B-Core Dimensions
  - ♦ Diameter: 14.5 cm



- Length: 50.9 cm (longest of the cores)
- Equipped with top well for solution injection
- Usage of B-Core
  - ◆ Some actinide breakthrough (mainly <sup>232</sup>U)
  - Mostly <sup>22</sup>Na  $\gamma$ -ray tomography experiments
  - ◆ Focus on tomography of <sup>228</sup>Th daughters
    - + 13.7 mL spike at 2.65 mCi/L (1.4 x 10<sup>-8</sup> M) <sup>228</sup>Th
    - Tomography done at times out to 192 days

### B-Core Analysis for <sup>228</sup>Th



- <sup>228</sup>Th emissions: 5.42 and 5.34 Mev  $\alpha$
- <sup>228</sup>Th daughters: <sup>224</sup>Ra; <sup>220</sup>Rn; <sup>216</sup>Po; <sup>212</sup>Pb; <sup>212</sup>Bi; (<sup>208</sup>Tl, <sup>208</sup>Po)
- Tomography uses <sup>224</sup>Ra and <sup>212</sup>Pb 240-keV γ-rays
- Daughters grow quickly into equilibrium  $t_{1/2} (^{228}\text{Th}) = 1.9 \text{ y}$   $t_{1/2} (^{212}\text{Pb}) = 10.6 \text{ h}$   $t_{1/2} (^{224}\text{Ra}) = 3.7 \text{ d}$



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Core Column Analyses



Core Column Analyses

### B-Core γ-Ray Tomography Results



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Core Column Analyses



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Calculated <sup>228</sup>Th Solution

Concentration



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### Analysis of γ-Ray Tomography Results

Actinide concentration (per unit rock volume)

$$C_{T} = \theta C_{sol} + \rho_{b} S$$

$$C_{T} = \theta C_{sol} + \rho_{b} K_{d} C_{sol}$$

$$C_{T} = \theta C_{sol} [1 + \rho_{b} K_{d} / \theta]$$

$$C_{T} = \theta C_{sol} R$$



### Calculated <sup>228</sup>Th Concentration (per unit rock volume)





Core Column Analyses

### Conclusions from E-Core <sup>241</sup>Am γ-Ray Analysis vs. Depth

Resolution of  $\gamma$ -ray analysis was  $\approx 1 \text{ cm}$ 

Analysis results were consistent with

 $R \approx 1 \times 10^4$ 

Using apparent E-Core advective porosity (10%), apparent <sup>241</sup>Am  $K_d \approx 4 \times 10^2$ 

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Core Column Analyses

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**E-Core Top Surface** 



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Core Column Analyses

### Actinide Activity as f(depth)





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C-Core <sup>241</sup>Am and <sup>241</sup>Pu Elution History (AIS Brine) ■ 0.1 mL/min from 7/10/95 - 4/9/96 (269 d) ■ Pause from 4/9/96 - 6/4/96 (57 d) ■ 0.05 mL/min from 6/4/96 - 7/29/97 (416 d) ■ Total eluted brine volume to date is 68.7 L ■ To date, neither <sup>241</sup>Am nor <sup>241</sup>Pu has been observed above our MDA for LSC ◆ <sup>241</sup>Am: 0.1 nCi/L (1.2 x 10<sup>-13</sup> M)

◆ <sup>241</sup>Pu: 1.5 nCi/L (6.0 x 10<sup>-14</sup> M)

### Large Apparent Retardations <sup>241</sup>Am and <sup>241</sup>Pu: No Breakthrough



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Core Column Analyses

### Calculated Am Elution for 0.1 Saturation (269 d)



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Core Column Analyses

# Summary of C-Core Results

- At shortest time of steady elution (269 d) •  $R(^{241}Pu) = 12,700; K_d = 175 mL/g$ •  $R(^{241}Am - 0.1 \text{ Sat}) = 13,800; K_d = 190 \text{ mL/g}$
- Used pore volumes as independent variable
- for Longer Elution ( $V_{tot} = 68.7 L$ )
- $R(^{241}Pu) = 20,500$ ;  $K_d = 282 \text{ mL/g}$
- $R(^{241}Am Supersat) = 25,500; K_d = 351 mL/g$
- $R(^{241}Am 0.1 \text{ Sat}) = 23,800; K_d = 327 \text{ mL/g}$  $R(^{241}Am - Sat) = 25,400; K_d = 349 mL/g$

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Ms. Mary Kruger WIPP Program Manager Office of Radiation Programs U.S. Environmental Protection Agency 401 M. Street SW Washington, DC 20460

Dear Ms. Kruger:

On December 31, 1997, the Environmental Evaluation Group (EEG) transmitted a letter to the EPA docket that presented an extended list of issues which it had assembled at EPA's request in a meeting between the two organizations held December 10, 1998. The Department of Energy (DOE) has elected to respond to these issues in the belief that they can be resolved by open and frank exposition of the basis for the DOE's position on each issue. The accompanying attachment presents DOE's response.

As you are aware, most of the issues presented in EEG's December 31, 1997, letter have been repeated from earlier comments made on DOE's Compliance Certification Application (CCA). In some cases, the DOE response provided herein simply directs the reader to where and when that information was previously provided, but apparently not considered by EEG. In most of the responses provide herein, DOE has recast its arguments in an attempt to very clearly explain its position, and elucidate the reasoning that should resolve each issue.

The DOE continues to believe that it has met both the spirit and intent of 40CFR194 in its CCA (and supplementary material provided in response to requests by EPA for additional information). We hope that the accompanying material will help EPA resolve the issues. We also hope that it will help EPA's process of issuing the final certification rule in a timely manner. If you have any questions about this information, please contact me at (505) 234-7400.

Sincerely,

George E. Dials Manager

Attachment

cc:

Larry Weinstock (EPA) Frank Marcinowski (EPA) Robert Neill (EEG) Chris Wentz (NMEMNRD)

CAO:ORC:JAM 0333 JAM/SG 02/23/98 ORC:JAM 02/49/98 CAO:MHM 02/27/98 1/1 OOM:GED 02/ /98

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