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subject: Estimates of Dissolved Concentrations for +III, +IV, +V, and +VI Actinides in a Salado and a Castile Brine under Anticipated Repository Conditions

This memorandum documents best estimates for dissolved +III, +IV, +V, and +VI actinide concentrations for input to the WIPP Compliance Certification Application. The +III, +IV, and +V estimates are calculated using the thermodynamic models developed for the WIPP. The +VI estimates are based on examination of empirical solubility experiments in brine compositions relevant to the anticipated chemical conditions in the WIPP disposal rooms. The dissolved concentrations, in Molar units, symbol M, moles per liter of solution, are summarized in the following table. Concentrations are given in molal units, symbol m, moles per kilogram of water, in all other locations.

Initial Brine brine as modified by waste/backfill interactions	ERDA6 (Castile) brine saturated with Halite and Anhydrite		SPC (Salado) brine saturated with Halite and Anhydrite	
	at Brucite and Magnesite saturation	at Portlandite and Calcite saturation	at Brucite and Magnesite saturation	at Portlandite and Calcite saturation
+III actinides†	2.9×10 ⁻⁷ to 2.9×10 ⁻⁵ M	3.1×10 ⁻¹¹ to 3.1×10 ⁻⁹ M	4.5×10 ⁻⁷ to 4.5×10 ⁻⁵ M	1.1×10 ⁻¹⁰ to 1.1×10 ⁻⁸ M
+IV actinides†	5.7×10 ⁻¹⁰ to 5.7×10 ⁻⁸ M	1.1×10 ⁻¹⁰ to 1.1×10 ⁻⁸ M	4.4×10 ⁻⁷ to 4.4×10 ⁻⁵ M	1.0×10 ⁻¹⁰ to 1.0×10 ⁻⁸ M
+V actinides†	7.4×10 ⁻⁶ to 7.4×10 ⁻⁴ M	1.3×10 ⁻⁶ to 1.3×10 ⁻⁴ M	7.6×10 ⁻⁷ to 7.6×10 ⁻⁵ M	7.1×10 ⁻⁷ to 7.1×10 ⁻⁵ M
+VI actinides*	7.0×10 ⁻⁶ to 7.0×10 ⁻⁴ M	1.4×10 ⁻⁶ to 1.4×10 ⁻⁴ M	1.0×10 ⁻⁶ to 1.0×10 ⁻⁴ M	8.7×10 ⁻⁷ to 8.7×10 ⁻⁵ M

† from calculations with thermodynamic models
* from empirical data and chemical arguments

Calculation of Concentrations for Dissolved +III, +IV, and +V Actinides under Anticipated WIPP Disposal Room Conditions

Estimates of the dissolved concentrations of +III, +IV, and +V actinides were made in a series of equilibrium calculations. Reported or standard WIPP brine compositions were brought into equilibrium with preponderant WIPP salts and actinides were added. Brine compositions were altered in two steps to reflect interactions among the brines, waste, and backfill: first by consideration of the dominant inorganic chemical reactions, followed by consideration of the dominant organic chemical reactions. The names and brief descriptions of the brine alteration process at each step are summarized in Table 1. Calculated brine compositions, in total molality per element, are given in Table 2. Calculated species compositions are given in Table 3. Table 4 lists the computer files used to run or generated by the equilibrium calculations. The process of the calculations is summarized below.

The chemical compositions of brines relevant to the disposal rooms at the WIPP Site are effectively characterized by the sources of the brines: the Salado Formation and the Castile Formation. The chemical composition of a standard Salado WIPP brine called "Brine A" or "SPC Brine" is given in Table 2.2 of Brush (1990). The chemical composition of brine taken from the Castile Formation through well ERDA6 is given in Table 2.3 of Brush (1990). These brine formulations are taken to represent the compositions of brines that may be present in the WIPP disposal rooms after closure of the repository.

The minerals halite, $\text{NaCl}(s)$, and anhydrite, $\text{CaSO}_4(s)$, are ubiquitous in the Salado and Castile Formations in the vicinity of the WIPP Site. The Salado is a bedded halite formation containing anhydrite interbeds, and the Castile is a bedded anhydrite formation containing halite. For this reason, it is likely that all brines that may be present in the WIPP disposal rooms will be at saturation with halite and anhydrite. The formulations of SPC and ERDA6 Brines in equilibrium with halite and anhydrite are called SPC_HA and ERDA6_HA Brines for the purposes of this memorandum. The suffix "_HA" indicates that saturation with halite and anhydrite is maintained regardless of any other chemical alterations that may affect the brines.

The actinides Am(III), Th(IV), and Np(V) serve as the prototypes for the thermodynamic model and data base for estimating the dissolved concentrations of actinides in the +III, +IV, and +V oxidation states, respectively. The thermodynamic data are documented in Novak (1996). The actinides Am(III), Th(IV), and Np(V) were added to SPC_HA and ERDA6_HA Brines until an actinide-bearing solid phase precipitated for each. The compositions of SPC_HA and ERDA6_HA Brines as modified to include Am(III), Th(IV), and Np(V) and an actinide-bearing solid phase for each (the "solubility-controlling solid") are called SPC_HA_An and ERDA6_HA_An for the purposes of this memorandum. The suffix "_An" indicates that saturation with a solubility-controlling solid for each actinide is maintained regardless of any other chemical alterations that may affect the brines, although the particular solubility-controlling solid for each actinide may change as the composition of the brines change.

The chemical conditions in the repository are expected to be strongly influenced by waste-brine interactions. The WIPP Gas Generation Program has suggested that brine compositions in the WIPP disposal rooms will be constrained to be in chemical equilibrium with brucite, $Mg(OH)_2(s)$, and magnesite, $MgCO_3(s)$, or with portlandite, $Ca(OH)_2(s)$, and calcite, $CaCO_3(s)$ (Wang, 1996). Accordingly, the compositions of SPC_HA_An and ERDA6_HA_An brines were modified by addition of brucite and magnesite, or portlandite and calcite, until saturation with the added minerals was achieved. These brines are called SPC_HA_An_Mg and SPC_HA_An_Ca for the SPC_HA_An brine brought into saturation with the magnesium minerals brucite and magnesite, or the calcium minerals portlandite and calcite, respectively. Similarly, the ERDA6_HA_An brine brought into saturation with brucite and magnesite, or with portlandite and calcite, are called ERDA6_HA_An_Mg and ERDA6_HA_An_Ca, respectively. The suffix "_Mg" indicates that saturation with brucite and magnesite is maintained regardless of any other chemical alterations that may affect the brines; the suffix "_Ca" indicates that saturation with portlandite and calcite is maintained regardless of any other chemical alterations that may affect the brines.

In the final modification, the organic ligands acetate, citrate, EDTA, and oxalate are added to the brines. The total maximum concentrations of these ligands were taken from the work of Weiner (1996), converted to molal units using

the largest m/M ratio, 1.154, observed in these brines (see Table 2).

	Acetate	Citrate	EDTA	Oxalate
M (from Weiner, 1996)	1.062×10^{-3}	4.65×10^{-4}	4.18×10^{-6}	7.404×10^{-3}
m, with m/M=1.154	1.2×10^{-3}	5.4×10^{-4}	4.8×10^{-6}	8.5×10^{-3}

The brines modified to contain organic ligands at the above specified concentrations are called SPC_HA_An_Mg_OL, SPC_HA_An_Ca_OL, ERDA6_HA_An_Mg_OL, and ERDA6_HA_An_Ca_OL. The suffix "_OL" indicates that the total dissolved concentration of organic ligands are maintained at the above specified concentrations¹ regardless of any other chemical alterations that may affect the brines.

In addition to element concentrations and solid phases, Table 2 gives the calculated Total Dissolved Solids (TDS) of the solution, the approximate solution density based on a correlation between the density of NaCl solutions and the TDS of those NaCl solutions, and the resulting conversion factor between molar and Molal units. Inspection of the rows labeled "m/M, kg H₂O/liter" in Table 2 shows that molal concentrations in these brines are about 15% higher than Molal concentrations.

The ratio of dissolved actinide concentrations in the brines in the presence and absence of organic ligands are presented in Table 5, as calculated from information in Table 2. The total dissolved concentrations of Am(III), Th(IV), and Np(V) in ERDA6 brine at brucite+magnesite saturation are calculated to be increased by factors of 8.0, 0.96, and 33, respectively, with the addition of organic ligands, i.e., from run ERDA6_HA_An_Mg to ERDA6_HA_An_Mg_OL. The addition of the organic ligands thus increases the calculated solubilities of Am(III) and Np(V) under these conditions, while causing an insignificant decrease in Th(IV) concentrations.² It is under the chemical conditions in ERDA6 brine that the organic ligands are expected to have the largest influence

¹ The total dissolved concentration of oxalate can be decreased below this level if the solubility of one of the oxalate solids included in the data base is exceeded, which is the case for run ERDA6_HA_An_Ca_OL.

² The calculated Th(IV) concentrations under these conditions are very low, on the order of 10^{-9} m. Calculations at such small concentrations are sensitive to the small changes in speciation caused by the addition of the organic ligands.

on actinide concentrations. Magnesium, with a concentration of 0.04m, is calculated to tie up 27% of total acetate, 56% of total citrate, 41% of total EDTA, and 90% of total oxalate.

In ERDA6 at portlandite+calcite saturation, the calculated solubility of Am(III) is much lower than at brucite+magnesite saturation, that of Th(IV) is slightly lower, and that of Np(V) is slightly higher, the last because of the increased importance of the first and second hydrolysis products, $\text{NpO}_2\text{OH}(\text{aq})$ and $\text{NpO}_2(\text{OH})_2^-$. The increase in dissolved actinide concentrations caused by the organic ligands is small, a factor of 1.6 or less, because of increased competition with OH^- , which is present at about 1000 times larger concentration than in the analogous Mg case. In addition, the model calculates that $\text{Na}_2\text{Ox}(\text{s})$ will precipitate under these conditions, reducing the total dissolved oxalate concentration to about 54% of its original value. Magnesium, with a concentration of $2 \times 10^{-8}\text{m}$, does not complex with the organic ligands to any significant extent. However, the Ca^{2+} concentration in these brines is 0.02m, i.e., about the same as Mg^{2+} in the ERDA6_HA_An_Mg cases, and could reasonably be expected to complex with the organic ligands to approximately the same extent as Mg^{2+} does. Therefore, the contribution of the organic ligands to an increase in actinide solubilities in the ERDA6_HA_An_Ca_OL case is probably overestimated here.

The total dissolved concentrations of Am(III), Th(IV), and Np(V) in SPC Brine at brucite+magnesite saturation are calculated to be increased by factors of 1.2, 1.0, and 3.3, respectively, with the addition of organic ligands, i.e., from run SPC_HA_An_Mg to SPC_HA_An_Mg_OL. The addition of the organic ligands causes only a minor increase because of the complexation of the organic ligands by Mg^{2+} . Magnesium, with a concentration of 0.5m, is calculated to tie up 74% of total acetate, 65% of total citrate, 88% of total EDTA, and 98% of total oxalate. The increase in dissolved Np(V) concentrations is caused by the formation of NpO_2Ox^- .

In SPC at portlandite+calcite saturation, the calculated solubilities of Am(III) and Th(IV) are much lower than at brucite+magnesite saturation, and that of Np(V) is the same to slightly higher. The Am(III) concentration decreases because the concentrations of the cationic hydrolysis products are much reduced by the high OH^- concentration. The Th(IV) concentration decreases because the

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carbonate concentration is no longer sufficient to stabilize thorium as the $\text{Th}(\text{CO}_3)_5^{6-}$ ion. For Np(V), the concentrations of the hydrolysis products increase while the neptunyl ion concentration decreases, resulting in a small net change in total Np(V) dissolved concentrations. Under these conditions, the addition of organic ligands does not increase the dissolved concentrations of Am(III) or Th(IV). The dissolved concentration of Np(V) increases by a factor of 1.6 from the formation of NpO_2Ox^- . As for the ERDA6 case at portlandite+calcite saturation, the low concentration of Mg^{2+} , $2 \times 10^{-6}\text{m}$, does not significantly complex with the organic ligands. However, the Ca^{2+} concentration in these brines is 1m, about 3 times greater than the Mg^{2+} in the SPC_HA_An_Mg cases, and thus could reasonably be expected to complex with the organic ligands to approximately three times the extent that Mg^{2+} does. Therefore, the contribution of the organic ligands to an increase in actinide solubilities in the SPC_HA_An_Ca_OL case is probably overestimated here.

The actinide dissolved concentration models were targeted to be accurate within one order of magnitude for solubility predictions. The models have been shown to be more accurate than this when compared with solubility data in complex synthetic brines in the absence of organic ligands. However, confirmatory studies of the accuracy of predictions in the presence of organic ligands are not yet completed. Therefore, we adopt the order of magnitude targeted accuracy for providing the best estimates of dissolved +III, +IV, and +V actinides under anticipated WIPP disposal room conditions. The final values for input to Performance Assessment incorporate an order of magnitude uncertainty in the total dissolved actinide concentrations calculated in runs ERDA6_HA_An_Mg_OL, ERDA6_HA_An_Ca_OL, SPC_HA_An_Mg_OL, and SPC_HA_An_Ca_OL, as given in Table 2. Total dissolved concentration values were converted from molal to Molar units using the m/M ratio for each brine. For example, Table 2b lists the Th(IV) concentration in run SPC_HA_An_Mg_OL as $5.03 \times 10^{-6}\text{m}$, and $\text{m/M}=1.146$. The final concentration is thus $4.4 \times 10^{-6}\text{M}$ with an order of magnitude uncertainty, i.e., within the range $4.4 \times 10^{-7}\text{M}$ to $4.4 \times 10^{-5}\text{M}$. These final recommended values are set forth in the table on the first page of this memorandum.

Estimation of Concentrations for Dissolved +VI Actinides under Anticipated WIPP Disposal Room Conditions

The dissolved concentrations of +VI actinides under anticipated WIPP conditions but in the absence of organic ligands were estimated to be 10^{-5} m, with an order of magnitude uncertainty in the values, i.e., the concentration would be in the range from 10^{-6} to 10^{-4} m (Hobart, 1996). Thermodynamic constants for complexation of UO_2^{2+} with the organic ligands acetate, citrate, EDTA, and oxalate are available. However, in the absence of an inorganic model for U(VI) there is no reliable way to calculate the free UO_2^{2+} concentration, and thus such a method cannot now be used to calculate the extent of potential increase in U(VI) concentrations due to complexation with organic ligands.

An engineering approximation of the potential increase in U(VI) concentrations caused by complexation with organic ligands can be made by considering the apparent stability constant values for the actinides with each organic ligand. The apparent stability constants, $\log\beta^{\text{app}}$, taken from Moore (1996a; 1996b) over a range of NaCl concentrations can be summarized as

	$\log\beta^{\text{app}}$ with acetate	$\log\beta^{\text{app}}$ with citrate	$\log\beta^{\text{app}}$ with EDTA	$\log\beta^{\text{app}}$ with oxalate
Th^{4+}	4 ± 0.5	9.8 ± 0.5	16 ± 1	7.2 ± 0.2
UO_2^{2+}	2.5 ± 0.5	6 ± 1	12 ± 0.5	6.3 ± 0.5
Am^{3+}	1.5 ± 0.5	5.5 ± 0.5	14 ± 0.5	4.4 ± 0.2
NpO_2^+		2.4 ± 0.2	6.2 ± 0.7	4.2 ± 0.4

These data show that the uranyl ion, with an effective charge of +3.2, exhibits complexation behavior intermediate between that of Th^{4+} and Am^{3+} . Therefore, it is reasonable to propose that the increase in U(VI) dissolved concentrations caused by the presence of the organic ligands would be between the increases estimated for Th(IV) and Am(III). The ratios by which total dissolved actinide concentrations are increased in the presence of organic ligands are given in Table 5. Total Am(III) concentrations are more strongly influenced by the organic ligands than total Th(IV) concentrations. The Am(III) ratios were chosen to be applied to total U(VI) concentrations in the absence of organic ligands to estimate total U(VI) concentrations in the presence of organic ligands. Because U(VI) hydrolyzes much more extensively than Am(III), the activity of free UO_2^{2+} is likely

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to be less than the activity of Am^{3+} in comparable systems, suggesting that this approximation will overpredict the effect of organic ligand complexation on total U(VI) dissolved concentrations. The factors by which the solubility of Am(III) was increased due to the organic ligands, given in Table 5 as 7.99, 1.59, 1.17, and 1.00 from Table 5, combined with the m/M values for the appropriate brines from Table 2, with the order of magnitude uncertainty on total dissolved concentrations, provide the estimates for total dissolved U(VI) concentrations as given on the first page of this memorandum.

References

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Table 1. Summary of brines used in calculating dissolved concentrations of +III, +IV, and +V actinides (see prose for details).

Source or modification	Brine Name		Brine Name	
from Brush (1990)	SPC*		ERDA6	
saturation with halite and anhydrite	SPC_HA		ERDA6_HA	
equilibrium with Am(III), Th(IV), and Np(V) solubility controlling solids	SPC_HA_An		ERDA6_HA_An	
saturation with brucite and magnesite	SPC_HA_An _Mg		ERDA6_HA_ An_Mg	
saturation with portlandite and calcite		SPC_HA_An _Ca	-	ERDA6_HA_ An_Ca
addition of organic ligands to specified totals	SPC_HA_An _Mg_OL	SPC_HA_An _Ca_OL	ERDA6_HA_ An_Mg_ OL	ERDA6_HA_ An_Ca_ OL

* SPC Brine was called Brine A by Brush (1990)

Table 2a. Calculated element concentrations, in molal units, and the associated equilibrium solid phases for a Castile Formation brine.

Element	ERDA6	ERDA6_ HA	ERDA6_ HA_An	ERDA6_ HA_An_ Mg	ERDA6_ HA_An_ Mg_OL	ERDA6_ HA_An_ Ca	ERDA6_ HA_An_ Ca_OL
Hydrogen	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02
Oxygen	5.65E+01	5.65E+01	5.65E+01	5.65E+01	5.65E+01	5.64E+01	5.63E+01
Sodium	5.63E+00	6.20E+00	6.22E+00	6.20E+00	6.20E+00	6.23E+00	6.22E+00
Potassium	1.09E-01	1.09E-01	1.09E-01	1.09E-01	1.09E-01	1.10E-01	1.10E-01
Magnesium	2.14E-02	2.14E-02	2.14E-02	4.43E-02	5.41E-02	3.01E-07	4.54E-07
Calcium	1.26E-02	1.05E-02	1.12E-02	1.33E-02	1.33E-02	2.00E-02	2.14E-02
Chlorine	5.40E+00	5.97E+00	5.98E+00	5.97E+00	5.97E+00	6.00E+00	6.00E+00
Sulfur	1.91E-01	1.89E-01	1.89E-01	1.91E-01	1.91E-01	1.33E-01	1.24E-01
Carbon	1.71E-02	1.73E-02	1.86E-02	3.15E-05	3.10E-05	1.43E-05	1.38E-05
Oxalate	0	0	0	0	8.50E-03	0	4.61E-03
Boron	7.09E-02	7.09E-02	7.09E-02	7.08E-02	7.08E-02	7.08E-02	7.08E-02
Bromine	1.24E-02	1.24E-02	1.24E-02	1.24E-02	1.24E-02	1.24E-02	1.24E-02
Acetate	0	0	0	0	1.20E-03	0	1.20E-03
Th(IV)	0	0	3.88E-03	6.78E-09	6.50E-09	1.29E-09	1.29E-09
Am(III)	0	0	4.49E-04	4.12E-07	3.29E-06	2.23E-10	3.54E-10
Np(V)	0	0	1.74E-04	2.53E-06	8.40E-05	1.30E-05	1.52E-05
EDTA	0	0	0	0	4.80E-06	0	4.80E-06
Citrate	0	0	0	0	5.40E-04	0	5.40E-04
Charge	5.38E-16	2.77E-16	1.80E-15	-1.97E-15	-2.17E-17	-1.43E-14	-1.71E-14
pH	6.178	6.158	5.1899	9.240	9.233	12.402	12.388
pmH	6.740	6.810	5.843	9.893	9.886	13.057	13.042
density*, g/liter	1200	1217	1218	1217	1218	1215	1215
TDS*, g/kg H ₂ O	350.9	384.0	385.9	384.7	385.3	380.8	380.2
m/M*, liter/ kg H ₂ O)	1.125	1.137	1.138	1.137	1.138	1.136	1.136
		halite anhydrite	halite anhydrite	halite anhydrite brucite magnesite glauberite	halite anhydrite brucite magnesite glauberite	halite anhydrite brucite portlandite calcite	halite anhydrite brucite portlandite calcite sodium oxalate
	calcite	calcite	AmOHCO ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ 2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ 2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ 2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) NpO ₂ OH (aged)	Am(OH) ₃ (s) ThO ₂ (am) NpO ₂ OH (aged)

* Density is calculated based on a correlation between the TDS (total dissolved solids) and the density of NaCl solutions. Both quantities are used to calculate the molal/Molar ratio.

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Table 2b. Calculated element concentrations, in molal units, and equilibrium solid phases for a Salado Formation brine simulant.

Element	SPC	SPC_HA	SPC_HA_An	SPC_HA_An_Mg	SPC_HA_An_Mg_OL	SPC_HA_An_Ca	SPC_HA_An_Ca_OL
Hydrogen	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02
Oxygen	5.58E+01	5.58E+01	5.58E+01	5.59E+01	5.59E+01	5.56E+01	5.56E+01
Sodium	2.06E+00	2.90E+00	2.90E+00	4.69E+00	4.69E+00	3.50E+00	3.48E+00
Potassium	8.65E-01	8.65E-01	8.65E-01	1.05E+00	1.05E+00	1.06E+00	1.06E+00
Magnesium	1.62E+00	1.62E+00	1.62E+00	5.09E-01	5.20E-01	5.98E-06	6.71E-06
Calcium	2.25E-02	3.00E-02	3.05E-02	3.31E-02	3.31E-02	1.31E+00	1.32E+00
Chlorine	6.10E+00	6.95E+00	6.95E+00	6.67E+00	6.66E+00	7.12E+00	7.11E+00
Sulfur	4.49E-02	5.25E-02	5.29E-02	6.02E-02	6.03E-02	1.97E-03	1.97E-03
Carbon	1.12E-02	1.12E-02	1.15E-02	4.08E-05	4.11E-05	5.87E-06	5.88E-06
Oxalate	0	0	0	0	8.50E-03	0	8.49E-03
Boron	2.25E-02	2.25E-02	2.25E-02	2.72E-02	2.72E-02	2.44E-02	2.43E-02
Bromine	1.12E-02	1.12E-02	1.12E-02	1.36E-02	1.36E-02	1.22E-02	1.22E-02
Acetate	0	0	0	0	1.20E-03	0	1.20E-03
Th(IV)	0	0	4.37E-04	4.98E-06	5.03E-06	1.16E-09	1.16E-09
Am(III)	0	0	2.57E-04	4.39E-06	5.15E-06	1.25E-09	1.25E-09
Np(V)	0	0	1.78E-05	2.64E-06	8.75E-06	4.85E-06	8.20E-06
EDTA	0	0	0	0	4.80E-06	0	4.79E-06
Citrate	0	0	0	0	5.40E-04	0	5.39E-04
Charge	1.78E-15	-8.14E-16	-1.66E-15	-8.17E-16	-5.88E-15	-5.68E-15	-7.91E-15
pH	3.591	3.481	4.971	8.690	8.690	11.466	11.468
pmH	4.114	4.140	5.630	9.366	9.365	12.124	12.122
density*, g/liter	1197	1222	1223	1229	1229	1239	1240
TDS*, g/kg H ₂ O	344.6	395.2	395.5	407.8	408.4	429.8	430.0
m/M*, liter/kg H ₂ O)	1.123	1.141	1.141	1.146	1.146	1.154	1.154
		halite anhydrite	halite anhydrite	halite anhydrite brucite magnesite magnesium oxychloride	halite anhydrite brucite magnesite magnesium oxychloride	halite anhydrite brucite portlandite calcite calcium oxy- chloride A	halite anhydrite brucite portlandite calcite calcium oxy- chloride A
			Am(OH)CO ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ 2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ 2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) KNpO ₂ CO ₃ 2H ₂ O(s)	Am(OH) ₃ (s) ThO ₂ (am) NpO ₂ OH (aged)	Am(OH) ₃ (s) ThO ₂ (am) NpO ₂ OH (aged)

* Density is calculated based on a correlation between the TDS (total dissolved solids) and the density of NaCl solutions. Both quantities are used to calculate the molal/Molar ratio.

Table 3a. Calculated aqueous species concentrations for a Castile Formation brine, in molal units.

Species	ERDA6	ERDA6_HA	ERDA6_HA_An	ERDA6_HA_An_Mg	ERDA6_HA_An_Mg_OL	ERDA6_HA_An_Ca	ERDA6_HA_An_Ca_OL
H2O	5.55E+01	5.55E+01	5.55E+01	5.55E+01	5.55E+01	5.55E+01	5.55E+01
Na+	5.63E+00	6.20E+00	6.22E+00	6.20E+00	6.20E+00	6.23E+00	6.22E+00
K+	1.09E-01	1.09E-01	1.09E-01	1.09E-01	1.09E-01	1.10E-01	1.10E-01
Ca++	1.26E-02	1.04E-02	1.12E-02	1.09E-02	1.09E-02	1.57E-02	1.67E-02
Mg++	2.13E-02	2.13E-02	2.14E-02	3.86E-02	4.00E-02	1.83E-08	1.97E-08
MgOH+	1.38E-07	1.93E-07	2.09E-08	4.19E-04	4.26E-04	2.79E-07	2.88E-07
H+	1.82E-07	1.55E-07	1.44E-06	1.28E-10	1.30E-10	8.78E-14	9.08E-14
Cl-	5.40E+00	5.97E+00	5.98E+00	5.97E+00	5.97E+00	6.00E+00	6.00E+00
SO4=	1.91E-01	1.89E-01	1.87E-01	1.91E-01	1.91E-01	1.33E-01	1.24E-01
HSO4-	4.38E-07	4.39E-07	4.00E-06	3.55E-10	3.60E-10	1.70E-13	1.65E-13
OH-	2.18E-08	1.98E-08	2.20E-09	2.40E-05	2.36E-05	3.42E-02	3.31E-02
HCO3-	1.40E-02	1.44E-02	8.07E-04	7.08E-06	6.97E-06	5.50E-09	5.32E-09
CO3=	1.40E-05	1.31E-05	8.04E-08	7.97E-06	7.74E-06	8.70E-06	8.18E-06
CO2(aq)	3.05E-03	2.87E-03	1.45E-03	1.17E-09	1.17E-09	6.44E-16	6.45E-16
CaCO3(aq)	5.56E-06	5.56E-06	3.43E-08	3.34E-06	3.24E-06	5.56E-06	5.56E-06
MgCO3(aq)	9.37E-06	1.17E-05	6.85E-08	1.24E-05	1.24E-05	6.73E-12	6.73E-12
B(OH)3(aq)	6.99E-02	6.99E-02	7.07E-02	7.70E-03	7.79E-03	6.79E-06	6.99E-06
B(OH)4-	3.89E-04	4.00E-04	4.50E-05	5.32E-02	5.30E-02	6.65E-02	6.62E-02
B3O3(OH)4-	1.68E-04	1.92E-04	2.20E-05	3.01E-04	3.06E-04	2.89E-10	3.04E-10
B4O6(OH)4-	1.56E-06	1.58E-06	1.97E-08	3.42E-04	3.46E-04	4.06E-10	4.25E-10
CaB(OH)4+	2.03E-05	1.79E-05	2.05E-06	2.42E-03	2.41E-03	4.36E-03	4.63E-03
MgB(OH)4+	2.08E-05	2.20E-05	2.38E-06	5.23E-03	5.37E-03	3.06E-09	3.25E-09
Br-	1.24E-02	1.24E-02	1.24E-02	1.24E-02	1.24E-02	1.24E-02	1.24E-02
NpO2+	0	0	1.74E-04	1.70E-06	1.75E-06	8.60E-09	8.88E-09
NpO2OH(aq)	0	0	1.92E-09	2.08E-07	2.11E-07	1.58E-06	1.58E-06
NpO2(OH)2-	0	0	8.79E-16	1.04E-09	1.04E-09	1.14E-05	1.10E-05
NpO2CO3-	0	0	6.56E-07	6.27E-07	6.28E-07	3.66E-09	3.56E-09
NpO2(CO3)2-	0	0	1.89E-11	1.94E-09	1.88E-09	1.20E-11	1.10E-11
NpO2(CO3)3=	0	0	1.48E-16	2.05E-12	1.97E-12	1.07E-14	9.44E-15
Am+++	0	0	3.40E-04	7.76E-11	8.18E-11	3.02E-20	3.44E-20
AmCO3+	0	0	3.15E-06	7.19E-11	7.31E-11	2.65E-20	2.74E-20
Am(CO3)2-	0	0	3.32E-10	7.48E-13	7.36E-13	3.14E-22	3.04E-22
Am(CO3)3=	0	0	3.71E-12	8.70E-13	8.34E-13	0	0
Am(OH)2+	0	0	5.03E-09	1.42E-07	1.45E-07	9.71E-11	1.00E-10
Am(OH)3(aq)	0	0	3.98E-16	1.26E-10	1.26E-10	1.26E-10	1.26E-10
Th++++	0	0	1.95E-10	0	0	0	0
Th(SO4)2(aq)	0	0	1.35E-05	9.33E-22	9.95E-22	0	0
Th(SO4)3=	0	0	5.91E-04	4.11E-20	4.38E-20	0	0
Th(OH)3(CO3)-	0	0	2.03E-07	1.79E-09	1.76E-09	1.39E-12	1.35E-12
Th(CO3)5=	0	0	3.27E-03	3.71E-09	3.45E-09	0	0
Th(OH)4(aq)	0	0	1.29E-09	1.29E-09	1.29E-09	1.29E-09	1.29E-09
H2Ox(aq)	0	0	0	0	2.03E-18	0	6.10E-24
HOx-	0	0	0	0	1.30E-09	0	5.51E-12
Ox=	0	0	0	0	7.82E-04	0	4.61E-03
ThOx++	0	0	0	0	1.27E-16	0	0
HAc(aq)	0	0	0	0	2.37E-08	0	2.33E-11
Ac-	0	0	0	0	8.76E-04	0	1.20E-03
NpO2Ac(aq)	0	0	0	0	7.02E-08	0	5.10E-10
H3Citrate(aq)	0	0	0	0	8.26E-21	0	0
H2Citrate-	0	0	0	0	4.66E-14	0	5.67E-20
HCitrate=	0	0	0	0	1.04E-08	0	1.74E-11
Citrate=-	0	0	0	0	2.37E-04	0	5.40E-04

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H4EDTA(aq)	0	0	0	0	0	0	0
H3EDTA-	0	0	0	0	8.82E-22	0	0
H2EDTA=	0	0	0	0	3.08E-14	0	1.87E-15
HEDTA--	0	0	0	0	1.70E-11	0	1.32E-09
EDTA===	0	0	0	0	4.35E-11	0	4.66E-06
AmAc++	0	0	0	0	6.15E-11	0	2.73E-20
AmCit(aq)	0	0	0	0	7.30E-09	0	6.45E-18
AmEDTA-	0	0	0	0	2.84E-06	0	1.28E-10
AmOx+	0	0	0	0	2.66E-08	0	5.65E-17
NpO2Cit-	0	0	0	0	2.85E-08	0	3.77E-10
NpO2EDTA-	0	0	0	0	3.77E-11	0	2.17E-08
NpO2Ox-	0	0	0	0	8.13E-05	0	2.58E-06
AmOH++	0	0	1.07E-04	2.69E-07	2.78E-07	1.26E-13	1.34E-13
ThAc+++	0	0	0	0	0	0	0
ThCit+	0	0	0	0	2.19E-14	0	0
ThEDTA(aq)	0	0	0	0	5.91E-14	0	1.97E-21
MgAc+	0	0	0	0	3.23E-04	0	2.17E-10
MgOx(aq)	0	0	0	0	7.63E-03	0	2.29E-08
MgCit-	0	0	0	0	3.03E-04	0	3.67E-10
MgEDTA=	0	0	0	0	1.96E-06	0	1.20E-07

Table 3b. Calculated aqueous species concentrations for a Salado Formation brine simulant, in molal units.

Species	SPC	SPC_HA	SPC_HA_ An	SPC_HA_ An_Mg	SPC_HA_ An_Mg_ OL	SPC_HA_ An_Ca	SPC_HA_ An_Ca_ OL
H2O	5.55E+01	5.55E+01	5.55E+01	5.55E+01	5.55E+01	5.55E+01	5.55E+01
Na+	2.06E+00	2.90E+00	2.90E+00	4.69E+00	4.69E+00	3.50E+00	3.48E+00
K+	8.65E-01	8.65E-01	8.65E-01	1.05E+00	1.05E+00	1.06E+00	1.06E+00
Ca++	2.25E-02	3.00E-02	3.05E-02	3.18E-02	3.18E-02	1.29E+00	1.30E+00
Mg++	1.62E+00	1.62E+00	1.62E+00	4.96E-01	4.97E-01	1.55E-06	1.56E-06
MgOH+	2.69E-08	3.68E-08	1.14E-06	1.73E-03	1.74E-03	4.42E-06	4.45E-06
H+	7.70E-05	7.24E-05	2.34E-06	4.31E-10	4.31E-10	7.52E-13	7.55E-13
Cl-	6.10E+00	6.95E+00	6.95E+00	6.67E+00	6.66E+00	7.12E+00	7.11E+00
SO4=	4.49E-02	5.24E-02	5.16E-02	6.02E-02	6.03E-02	1.97E-03	1.97E-03
HSO4-	1.76E-05	2.47E-05	7.88E-07	3.05E-10	3.05E-10	1.13E-14	1.12E-14
OH-	1.09E-10	7.63E-11	2.36E-09	7.74E-06	7.74E-06	1.31E-02	1.33E-02
HCO3-	9.22E-05	9.49E-05	2.39E-03	1.78E-06	1.78E-06	1.37E-10	1.36E-10
CO3=	1.30E-09	8.15E-10	6.35E-07	8.34E-07	8.34E-07	3.14E-07	3.17E-07
CO2(aq)	1.11E-02	1.11E-02	9.10E-03	1.21E-09	1.21E-09	6.24E-16	6.23E-16
CaCO3(aq)	1.41E-10	1.94E-10	1.54E-07	7.48E-07	7.47E-07	5.56E-06	5.56E-06
MgCO3(aq)	1.17E-08	1.31E-08	1.02E-05	1.24E-05	1.24E-05	6.73E-12	6.73E-12
B(OH)3(aq)	2.25E-02	2.25E-02	2.24E-02	4.71E-03	4.70E-03	2.36E-06	2.35E-06
B(OH)4-	5.20E-07	4.45E-07	1.37E-05	9.74E-03	9.73E-03	4.07E-03	4.06E-03
B3O3(OH)4-	2.32E-08	2.34E-08	7.16E-07	1.85E-05	1.84E-05	2.11E-12	2.08E-12
B4O5(OH)4=	9.69E-13	7.11E-13	6.70E-10	5.61E-06	5.60E-06	4.37E-13	4.33E-13
CaB(OH)4+	3.68E-08	4.54E-08	1.42E-06	1.25E-03	1.25E-03	2.03E-02	2.03E-02
MgB(OH)4+	1.75E-06	1.65E-06	5.08E-05	1.14E-02	1.14E-02	1.30E-08	1.30E-08
Br-	1.12E-02	1.12E-02	1.12E-02	1.36E-02	1.36E-02	1.22E-02	1.22E-02
NpO2+	0	0	1.74E-05	2.40E-06	2.40E-06	7.30E-08	7.33E-08
NpO2OH(aq)	0	0	1.54E-10	1.17E-07	1.17E-07	2.42E-06	2.41E-06
NpO2(OH)2-	0	0	4.64E-17	1.77E-10	1.77E-10	2.35E-06	2.35E-06
NpO2CO3-	0	0	4.20E-07	1.21E-07	1.22E-07	1.16E-09	1.17E-09
NpO2(CO3)2=	0	0	3.43E-09	1.47E-10	1.48E-10	2.48E-12	2.55E-12
NpO2(CO3)3=	0	0	0	5.30E-12	5.40E-12	0	0
Am+++	0	0	1.94E-04	3.22E-09	3.23E-09	1.42E-17	1.46E-17
AmCO3+	0	0	7.26E-06	2.88E-10	2.88E-10	3.04E-19	3.04E-19
Am(CO3)2-	0	0	1.29E-09	2.11E-13	2.11E-13	0	3.81E-23
Am(CO3)3=	0	0	1.21E-10	3.73E-14	3.73E-14	0	0
Am(OH)2+	0	0	1.78E-09	5.69E-07	5.69E-07	1.11E-09	1.11E-09
Am(OH)3(aq)	0	0	6.11E-17	1.26E-10	1.26E-10	1.26E-10	1.26E-10
Th+++	0	0	1.45E-09	0	0	0	0
Th(SO4)2(aq)	0	0	1.42E-05	1.18E-20	1.18E-20	0	0
Th(SO4)3=	0	0	4.22E-04	8.47E-20	8.51E-20	0	0
Th(OH)3(CO3)-	0	0	6.88E-07	4.78E-10	4.78E-10	1.52E-13	1.52E-13
Th(CO3)5=	0	0	0	4.98E-06	5.03E-06	0	0
Th(OH)4(aq)	0	0	1.12E-09	1.22E-09	1.22E-09	1.16E-09	1.16E-09
H2Ox(aq)	0	0	0	0	1.99E-18	0	1.49E-22
HOx-	0	0	0	0	3.58E-10	0	1.62E-11
Ox=	0	0	0	0	1.50E-04	0	8.48E-03
ThOx++	0	0	0	0	2.41E-15	0	0
HAc(aq)	0	0	0	0	2.05E-08	0	7.58E-11
Ac-	0	0	0	0	3.10E-04	0	1.20E-03
NpO2Ac(aq)	0	0	0	0	2.65E-08	0	1.75E-09
H3Citrate(aq)	0	0	0	0	1.54E-20	0	0
H2Citrate-	0	0	0	0	2.48E-14	0	2.07E-20
HCitrate=	0	0	0	0	3.71E-09	0	3.69E-12
Citrate=-	0	0	0	0	1.88E-04	0	5.39E-04

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H4EDTA(aq)	0	0	0	0	0	0	0
H3EDTA-	0	0	0	0	2.52E-22	0	0
H2EDTA=	0	0	0	0	5.86E-15	0	8.46E-19
HEDTA=-	0	0	0	0	1.93E-11	0	1.72E-11
EDTA==	0	0	0	0	5.60E-10	0	4.79E-06
AmAc++	0	0	0	0	8.88E-10	0	1.43E-17
AmCit(aq)	0	0	0	0	2.16E-08	0	4.02E-17
AmEDTA-	0	0	0	0	5.63E-07	0	5.25E-14
AmOx+	0	0	0	0	1.78E-07	0	3.76E-14
NpO2Cit=	0	0	0	0	3.10E-09	0	4.64E-11
NpO2EDTA=-	0	0	0	0	3.32E-11	0	8.45E-10
NpO2Ox-	0	0	0	0	6.08E-06	0	3.36E-06
AmOH++	0	0	5.60E-05	3.81E-06	3.82E-06	1.19E-11	1.18E-11
ThAc+++	0	0	0	0	2.45E-23	0	0
ThCit+	0	0	0	0	3.90E-13	0	0
ThEDTA(aq)	0	0	0	0	2.48E-13	0	1.30E-22
MgAc+	0	0	0	0	8.89E-04	0	5.68E-09
MgOx(aq)	0	0	0	0	8.34E-03	0	6.80E-07
MgCit-	0	0	0	0	3.52E-04	0	5.56E-10
MgEDTA=	0	0	0	0	4.23E-06	0	4.48E-09

Table 4. Computer files used to run or generated by the equilibrium calculations.

Name in this memorandum	Specific File Name on WIPP DEC Alphas* ‡
SPC	SPC
SPC_HA	SPC_WS
SPC_HA_An	SPC_WS_AN
SPC_HA_An_Mg	SPC_WS_AN_BF
SPC_HA_An_Mg_OL	SPC_BF_OR2
SPC_HA_An_Ca	SPC_WS_AN_CM
SPC_HA_An_Ca_OL	SPC_CM_OR2
ERDA6	ERDA6
ERDA6_HA	ERDA6_WS
ERDA6_HA_An	ERDA6_WS_AN
ERDA6_HA_An_Mg	ERDA6_WS_AN_BF
ERDA6_HA_An_Mg_OL	ERDA6_BF_OR2
ERDA6_HA_An_Ca	ERDA6_WS_AN_CM
ERDA6_HA_An_Ca_OL	ERDA6_CM_OR2

- * Each FMT run requires the problem-specific input files <fln>.in and <fln>.inguess, where <fln> is the specific FiLe Name. Each FMT run generates the problem-specific output files <fln>.out and <fln>.for088, where <fln> is the specific FiLe Name.
- ‡ All FMT runs documented in this memorandum require one of the following sets of data base files (the data within these files that are used in this memorandum are identical):
- HMW_3456_960318.CHEMDAT and HMW_3456_960318.RHOMIN
- or
- HMW_345_960325.CHEMDAT and HMW_345_960325.RHOMIN

Table 5. Model-predicted influence of organic ligands on total dissolved concentrations of Am(III), Th(IV), and Np(V).

<u>with organic ligands</u> <u>without organic ligands</u>	Am(III)	Th(IV)	Np(V)
<u>ERDA6_HA_An_Mg_OL</u> <u>ERDA6_HA_An_Mg</u>	7.99	0.959	33.2
<u>ERDA6_HA_An_Ca_OL</u> <u>ERDA6_HA_An_Ca</u>	1.59	1.00	1.17
<u>SPC_HA_An_Mg_OL</u> <u>SPC_HA_An_Mg</u>	1.17	1.01	3.31
<u>SPC_HA_An_Ca_OL</u> <u>SPC_HA_An_Ca</u>	1.00	1.00	1.69