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A CONCEPTUAL PERFORMANCE ASSESSMENT MODEL OF THE
DISSOLVED ACTINIDE SOURCE TERM FOR THE WIPP

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ABSTRACT

This paper presents a performance assessment model of dissolved actinide concentrations for the Waste Isolation Pilot Plant (WIPP). The model (1) assesses the concentration of each actinide oxidation state and (2) combines these concentrations with an oxidation state distribution. The chemical behavior of actinides in the same oxidation state is presumed to be very similar for almost all situations, but exceptions arising from experimental evidence are accommodated. The code BRAGFLO [1] calculates the gas pressure, brine mass, gas volume, and mass of remaining Fe and cellulose for each time step and computational cell. The total CO_2 in the repository and dissolved $\text{Ca}(\text{OH})_2$ is estimated. EQ3/6[2] is used to construct lookup tables for pmH^+ and $f(\text{CO}_2)$ as a function of brine type and volume, moles of CO_2 , and $\text{Ca}(\text{OH})_2$. Amounts of five soluble complexants are considered. A model based on the formulation of Harvie et al. [3] produces tables of solubilities for each actinide oxidation state (+III, +IV, +V, +VI) as a function of pmH , $f(\text{CO}_2)$, brine composition, and complexant.

Experimental data yield lookup tables of fractions of Th, U, Np, Pu, and Am in each oxidation state as a function of $f(\text{CO}_2)$ and complexant. The tables are then used to provide a concentration of a particular actinide at particular values of pmH and $f(\text{CO}_2)$. Under steady-state conditions, the oxidation state of each actinide that is most stable in the particular chemical environment controls the concentration of that actinide in solution. In the absence of steady-state conditions, the oxidation state distribution of interest is that of the dissolved actinide, and the oxidation states may be treated as if they were separate compounds. In addition, the amount of an actinide dissolved cannot exceed the inventory of that actinide: the total amount of the actinide present in the emplaced waste.

THE WIPP DISSOLVED ACTINIDE SOURCE TERM

It is anticipated that, if there is human intrusion into the WIPP repository (as, for example, drilling for petroleum resources), the repository may be inundated with brine. The source of the brine could be the geological formation in which the repository is located--the Salado Formation, geological units overlying the Salado Formation, or a brine pocket in the Castile Formation under the Salado Formation. The relationship of the repository to its geological environment is shown

* pmH is the negative \log_{10} of the hydrogen ion molality (moles of hydrogen ion per kg of brine) and is a more appropriate parameter for concentrated, high ionic strength solutions than pH.

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in Figure 1 [taken from Reference 1, Vol. 4, p. 2-13]. The brine is either Salado brine, which contains a high concentration of $MgCl_2$, or Castile brine, which is primarily $NaCl$. Composition of these brines is given in Table 1 [4]. A relatively small amount of dilute brine from the Culebra Member of the Rustler Formation may also enter the repository from above the Salado through the intrusion borehole. However, as this dilute brine dissolves the $NaCl$ in the host rock, it may acquire a composition essentially the same as Castile brine.

The chemical composition of this brine can be affected by a number of constituents: dissolved CO_2 that is a product of microbial metabolism, crushed or dissolved iron and other metals alloyed in steel, nitrate salts, water-soluble complexing agents, calcium salts from cemented waste, or magnesium oxide used as backfill. As a consequence, a range of chemical conditions, pmH and CO_2 values in particular, can exist in the inundated repository. This range is illustrated by Figures 2 and 3.

Actinides in the TRU waste can be mobilized by dissolution in brine, and moved by the brine to the accessible environment, but the extent of that dissolution is very uncertain because of the uncertainty of conditions in the repository throughout the 10,000-year regulatory period. It is therefore necessary to estimate actinide solubility with a model that is applicable over a wide range of redox conditions, salt concentration, and pmH . That model--the actinide source term for the repository--must then be coupled to the other performance assessment models. In particular, the actinide source term is the link between the performance assessment BRAGFLO and PANEL or NUTS (Figure 4).

BRAGFLO (version 6.62Z0; BRine And Gas FLOW) calculates the volume of brine entering the repository under various scenarios, and the volume of (hydrogen) gas generated by corrosion of iron in the repository and of (carbon dioxide) gas generated by microbial action. NUTS (version 1.02Z0; NUclide Transport System) and PANEL (version 3.60) calculate decay and growth in the actinides and transport them through the repository. The purpose of constructing a link between BRAGFLO and PANEL/NUTS is to deliver to transport codes a concentration of actinides consistent with the brine input and with the pmH developed by CO_2 dissolved in the brine.

Modeling Actinide Solubility

The following description of the WIPP actinide source term is intended to provide a general context for the performance assessment interface.

The regulation 40 CFR Part 191 [5] details the release limits for the WIPP for certain actinides. Many of the radionuclides are present in the waste in such small quantities that release is limited by the total emplaced amount -- the inventory. For americium ($Am-241$) and plutonium ($Pu-238$, $Pu-239$, $Pu-240$), however, release depends on solubility rather than inventory. Neptunium ($Np-237$), curium ($Cm-245$), and several isotopes of uranium ($U-233$ and $U-234$) are solubility-dependent also. Direct measurement of solubility under WIPP conditions was essentially impossible, so that a model of solubility as a function of pmH (actually pmH) was constructed according to the Pitzer formalism [6] that describes activity coefficients of electrolytes in very high

ionic strength solutions. This model and the associated calculation code FMT version 2.0 are described elsewhere [7]. Figure 5 shows a typical result from the model.

Parameters for building the model are not available for all of the actinides for which a model is needed. Therefore, one actinide in each of the oxidation states +III, +IV, and +V is modeled, and an oxidation state analogy is invoked. That is, actinides in the same oxidation or valence state are assumed to exhibit sufficiently similar chemical behavior that one actinide can serve as a model for each oxidation state. Thus the modeled actinide for the +III state is americium; for the +IV state, thorium; for the +V state, neptunium. The model parameter data available for the +VI state is inadequate, so an estimate of solubility of U(+VI) was made from published values and some preliminary experimental measurements [8].

All of these four oxidation states are not equally stable in brine solution for all of the actinides under simulated WIPP conditions. Thorium exists only as Th(+IV). Under WIPP conditions, americium and curium are most stable as Am(+III) and Cm(+III). Uranium can exist as U(+IV) and U(+VI), and neptunium as Np(+IV) and Np(+V). Plutonium can exist under similar conditions in all four most likely oxidation states (+III, +IV, +V, +VI), although recent experimental work suggests that neither Pu(+V) nor Pu(+VI) are expected to be stable under WIPP conditions [9]. Because the inundated WIPP system is expected to be exceedingly dilute in actinides, radiolytically mediated redox reactions and redox reactions between actinides, while possible at isolated locations in the repository, can be neglected on the average over the entire repository.

Experimental Results

The two radionuclides whose solubility is most critical are plutonium and americium. A number of studies of americium [10, 11] indicate that Am(+III) will be the only stable oxidation state of americium under WIPP conditions. However, as indicated above, identification of the oxidation states of plutonium under WIPP conditions is critical. In synthetic WIPP brine, brought carefully to about pH 8, Pu(+III), Pu(+IV), and Pu(+V) precipitate noticeably and rapidly but Pu(+VI)--PuO₂²⁺--forms polychloro complexes and is stable in solution at approximately millimolar concentrations. Experiments with reductants, notably iron, iron powder, and Fe²⁺, indicate that in the reducing and basic environment of the WIPP, Pu(+VI) will be reduced to lower, less soluble oxidation states [9].

The possible oxidation states, in WIPP brine solution, of the important actinides in the WIPP are shown in Table 2.

THE ACTINIDE SOURCE TERM/ PERFORMANCE ASSESSMENT INTERFACE

The interface that was designed takes the modeling results (illustrated by Figure 5) and combines them with the oxidation state distribution shown in Table 2. The interface is diagramed in Figure 6. It should be noted that since this interface was proposed, the project has elected to use a backfill (MgO) that is expected to buffer at about pmH 9.4 in Salado brine and about pmH 10 in Castile brine, and to maintain $f(\text{CO}_2)$ at about 10^{-7} atm, so that there is a single most likely

solubility for each oxidation state and brine type instead of a range of pmH-dependent solubilities.

The interface is constructed as follows:

1. The code BRAGFLO calculates brine and gas volumes entering the repository under various scenarios. Scenarios both with and without microbes are considered. For scenarios without microbes, there will be no CO_2 , and the pmH of the brine will depend only on the brine type and the amount of cementitious material in the waste.
2. Using the code EQ3/6, pmH and CO_2 fugacity are calculated as a function of $\text{Ca}(\text{OH})_2$ dissolution, total CO_2 generated, and brine volume. Calculations are performed for the two different brine types: one a Salado brine and the other a Castile brine.
3. The code FMT [7], using the Pitzer formalism [6] calculates the concentration of actinides in solution as a function of pmH and CO_2 fugacity. The oxidation state analogy is invoked here, so that the FMT calculations provide eight lookup tables: two types of brine and four oxidation states for each brine type.
4. The waste contains some water-soluble complexing agents, primarily acetate, citrate, oxalate, and EDTA. The concentrations of actinides in solution containing these four complexing agents can also be calculated using the FMT code, for a total of 16 lookup tables: one set of eight with complexing agents and one set without. Although this capability exists in the modeling system, it is expected that non-ferrous metals present in the TRU waste, and Mg^{2+} present in the backfill of the repository, will bind the complexing agents so that they will not be available to bind to actinides.
5. The experimental determination of oxidation state speciation, as reflected in Table 2, is combined with the appropriate solubility according to the equation

$$C_{\text{An}} = \sum_{i=1}^4 k_i S_i$$

where C_{An} is the concentration of the particular actinide, S_i is the solubility of the particular oxidation state as calculated by the FMT code, and k_i is either 1 or 0, depending on whether the oxidation state is expected to be stable under WIPP conditions or not. For example, for neptunium, at a particular pmH and CO_2 fugacity,

$$C_{\text{Np}} = S_4 + S_5$$

where S_4 and S_5 are the solubilities of the +IV and +V oxidation states, respectively, at the particular pmH and $f(\text{CO}_2)$. This concentration is then decayed and transported by NUTS or PANEL.

In addition, the inventory of the particular actinide is used to deplete the actinide--a step that is important for neptunium and curium, but is less important in considering dissolved concentrations of the other actinides, because they are projected to be present in considerable abundance in the WIPP. For some actinides, like Am-241, the inventory is not large enough to support solubility-limited concentrations throughout the 10,000-year regulatory period, and the concentration is limited by the total amount of Am-241 remaining after radioactive decay, rather than by the solubility of americium. More abundant and very long-lived isotopes, like Pu-239, can support solubility limits throughout the regulatory period.

This scheme includes some simplifying assumptions that result in conservatism (overprediction of releases). The most notable of these is the treatment of each oxidation state of an actinide as a separate compound. The result of this treatment is that, unless the solubilities of the oxidation states are of about the same order of magnitude, the greater solubility will dominate.

CONCLUSION

The scheme presented provides a way to integrate an actinide source term into the WIPP performance assessment, if conditions in the repository, pmH in particular, can be predicted only within a range covering several orders of magnitude. Since this scheme was proposed, the project has elected to use a backfill (MgO) that is expected to buffer at about pmH 9.4 in Salado brine and about pmH 10 in Castile brine, and to maintain $f(\text{CO}_2)$ at about 10^{-7} atm, so that there is a single most likely solubility for each oxidation state and brine type instead of a range of pmH-dependent solubilities. Moreover, complexing agents present in the waste are expected to have no impact on actinide solubility, as has been discussed.

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Scenario Consequence Estimation

CUTTINGS
(Release of Cuttings to Accessible Environment)

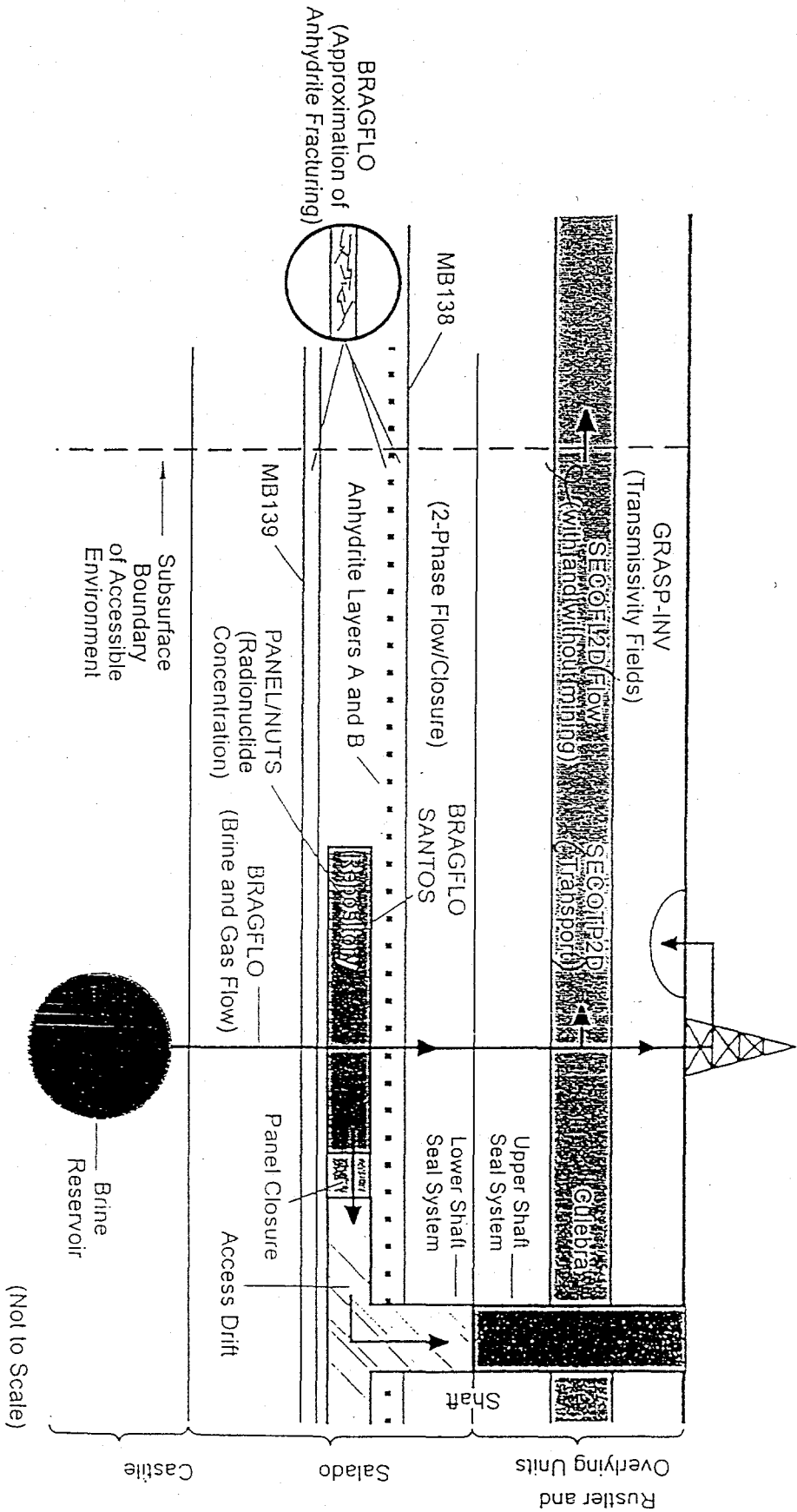


Figure 1. Schematic view of the WIPP disposal system showing WIPP performance assessment codes with the component of the system each code simulates.

Table 1. Some Measured Chemical Components of WIPP Brines.

Ion or Chemical Property	Brine A (Salado)	ERDA-6 (Castile)
Alkalinity (HCO ₃ ⁻ equivalent, mM)	--	43
B ³⁺ (mM)	20	63
Br ⁻ (mM)	10	11
Ca ²⁺ (mM)	20	12
Cl ⁻ (mM)	5,350	4,800
K ⁺ (mM)	770	97
Mg ²⁺ (mM)	1,440	19
Na ⁺ (mM)	1,830	4,870
pH	6.5	6.17
SO ₄ ²⁻ (mM)	40	170
TDS (mg/liter)	306,000	330,000

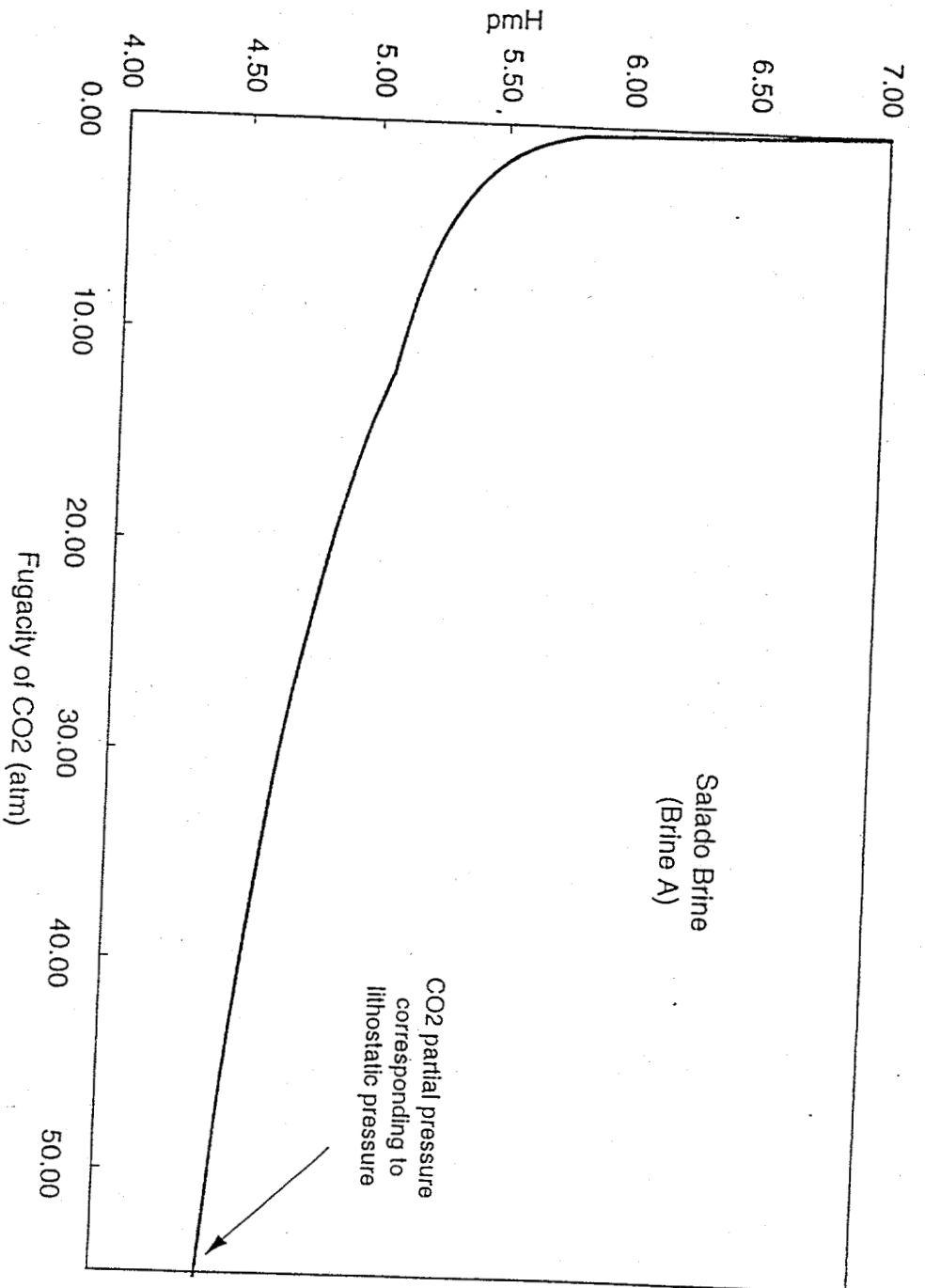


Figure 2. Plot of pmH v. CO₂ fugacity for Salado brine.

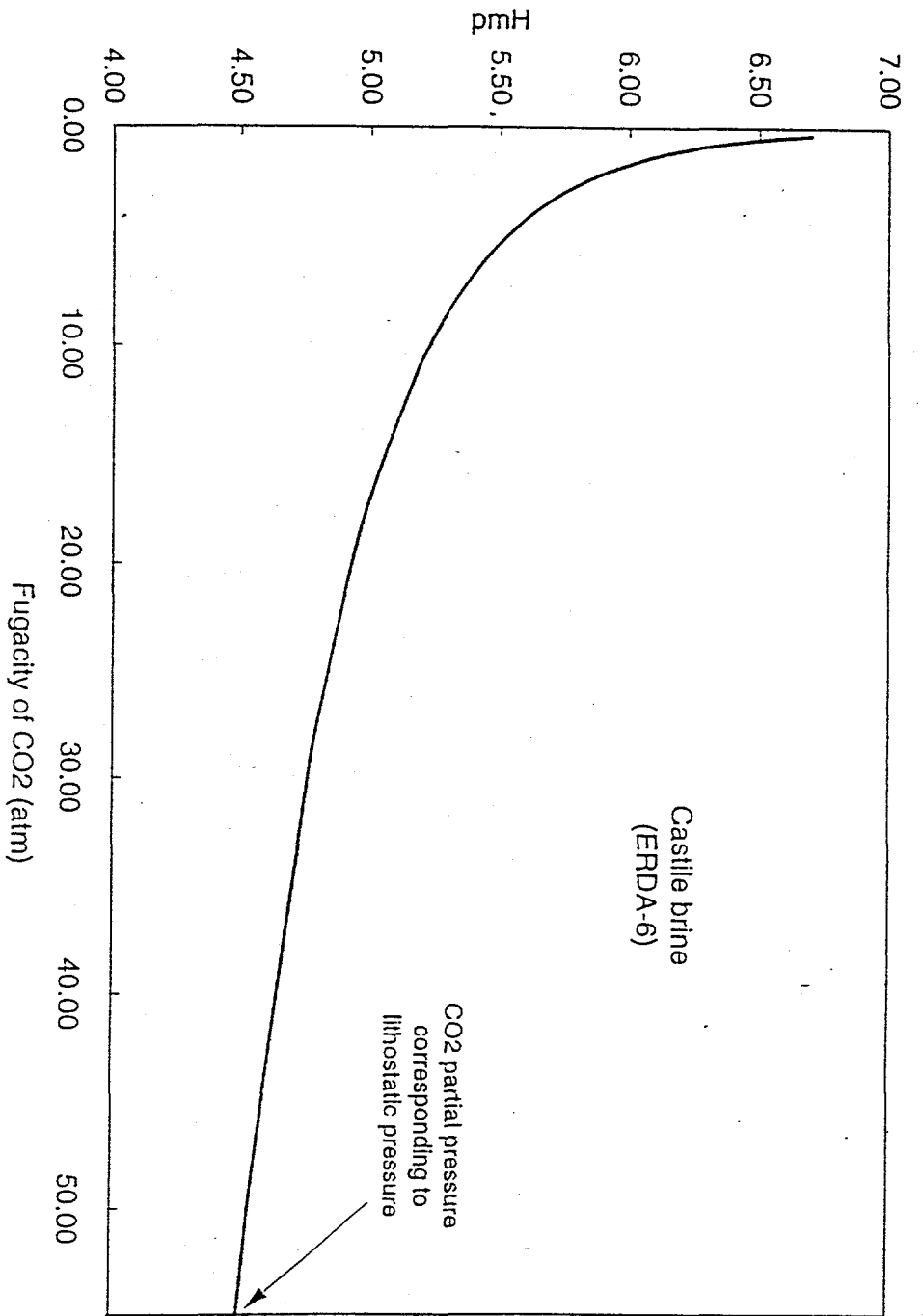


Figure 3. Plot of pH v. CO₂ fugacity for Castile brine.



Figure 4. Code configuration for a scenario in which the WIPP repository is intruded upon by two intrusions: one that penetrates a reservoir of Castile brine and one that penetrates the disposal area.. This figure is provided only to illustrate the relationships among modeling codes.

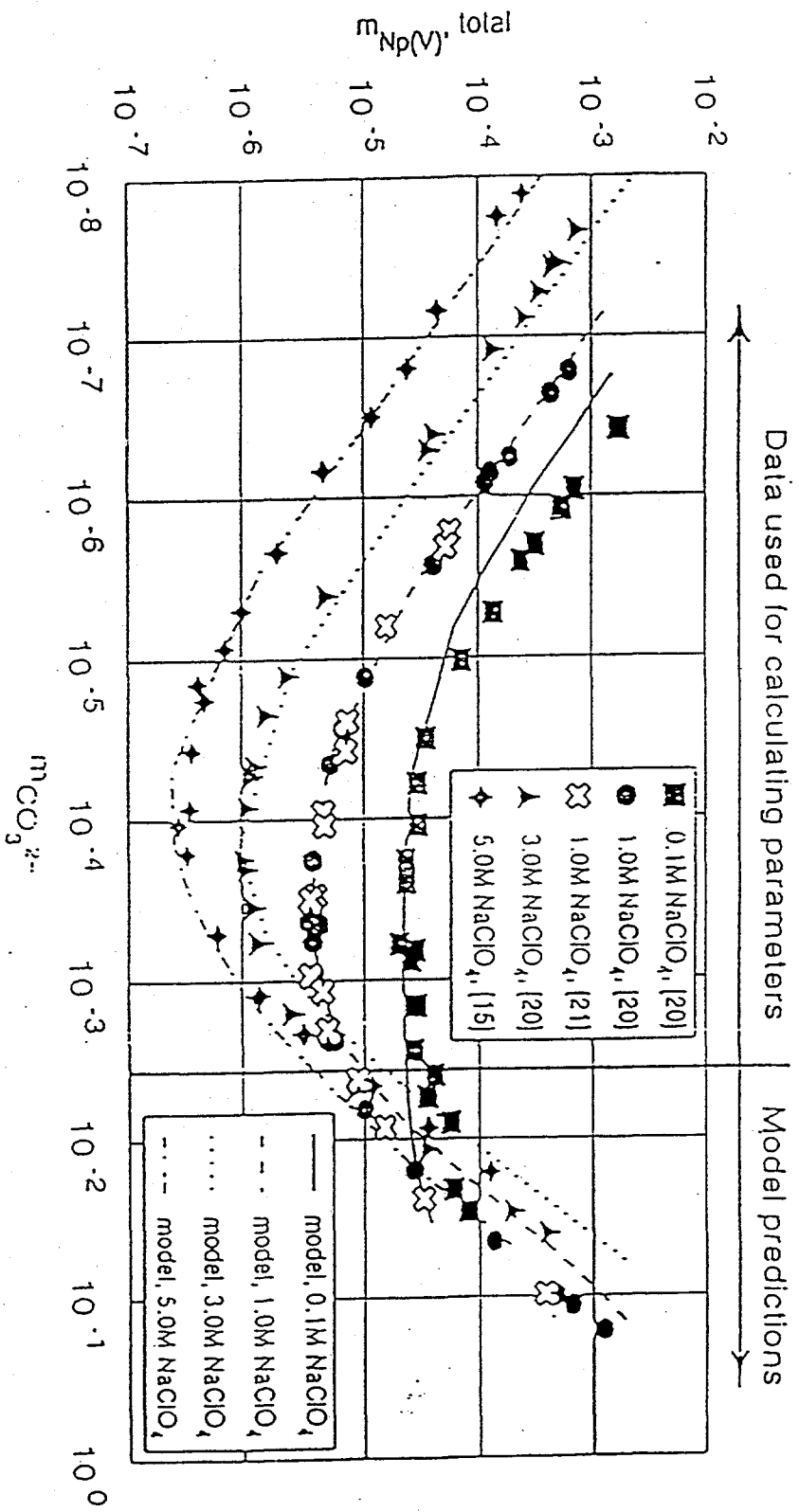


Figure 5. FMT modeling results for neptunium (from Reference 7).

Table 2. Oxidation States of the Actinides Expected to be Present in the WIPP.

ACTINIDE ELEMENT	OXIDATION STATES			
thorium		IV		
uranium		IV		VI
neptunium		IV	V	
plutonium	III	IV		
americium	III			
curium	III			

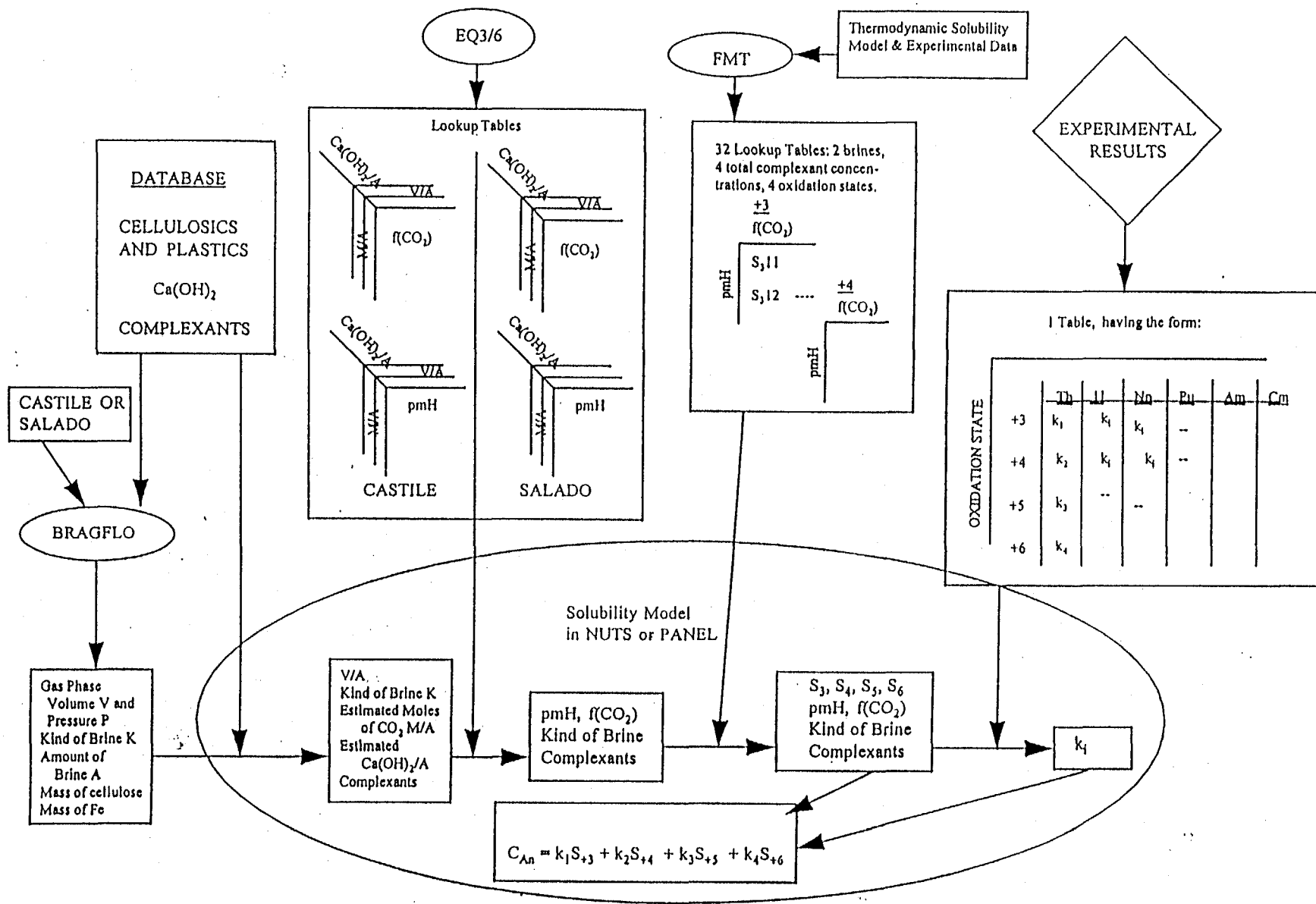


Figure 6. The actinide source term/performance assessment interface.