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1. PURPOSE

The objective of this calculation is to estimate the quantity of fissile material that could accumulate in fractures in the rock beneath plutonium-ceramic (Pu-ceramic) and Mixed-Oxide (MOX) waste packages (WPs) as they degrade in the potential monitored geologic repository at Yucca Mountain. This calculation is to feed another calculation (Ref. 31) computing the probability of criticality in the systems described in Section 6 and then ultimately to a more general report on the impact of plutonium on the performance of the proposed repository (Ref. 32), both developed concurrently to this work. This calculation is done in accordance with the development plan TDP-DDC-MD-000001 (Ref. 9), item 5. The original document described in item 5 has been split into two documents: this calculation and Ref. 4.

The scope of the calculation is limited to only very low flow rates because they lead to the most conservative cases for Pu accumulation and more generally are consistent with the way the effluent from the WP (called source term in this calculation) was calculated (Ref. 4). Ref. 4 ("*In-Drift Accumulation of Fissile Material from WPs Containing Plutonium Disposition Waste Forms*") details the evolution through time (breach time is initial time) of the chemical composition of the solution inside the WP as degradation of the fuel and other materials proceed. It is the chemical solution used as a source term in this calculation. Ref. 4 takes that same source term and reacts it with the invert; this calculation reacts it with the rock. In addition to reactions with the rock minerals (that release Si and Ca), the basic mechanisms for actinide precipitation are dilution and mixing with resident water as explained in Section 2.1.4. No other potential mechanism such as flow through a reducing zone is investigated in this calculation. No attempt was made to use the effluent water from the bottom of the invert instead of using directly the effluent water from the WP.

This calculation supports disposal criticality analysis and has been prepared in accordance with *AP-3.12Q, Calculations* (Ref. 49). This calculation uses results from Ref. 4 on actinide accumulation in the invert and more generally does reference heavily the cited calculation. In addition to the information provided in this calculation, the reader is referred to the cited calculation for a more thorough treatment of items applying to both the invert and fracture system such as the choice of the thermodynamic database, the composition of J-13 well water, tuff composition, dissolution rate laws, $Pu(OH)_4$ solubility and also for details on the source term composition. The flow conditions (seepage rate, water velocity in fractures) in the drift and the fracture system beneath initially referred to the TSPA-VA because this work was prepared before the release of the work feeding the TSPA-SR. Some new information feeding the TSPA-SR has since been included. Similarly, the soon-to-be-qualified thermodynamic database data0.ymp has not been released yet.

2. METHOD

The method outlined in this section is in accordance with the development plan TDP-DDC-MD-000001 (Ref. 9). Since the development plan does not address the control of electronic management of data, the evaluation was done according to *AP-SV.1Q, Control of the Electronic Management of Information* (Ref. 50). Source terms and thermodynamic databases were sent by email attachment from the computer where they were obtained as Technical Product Outputs to the computer where they were used.

The calculation proceeds first by setting up the different source terms including decay or no decay of the plutonium into uranium to bracket the breach times (early in the history of the proposed repository plutonium would not have had time to decay to uranium as it would at later times). The calculation then progresses by doing PHREEQC runs to compute actinide accumulation for different parameter values. The main parameter is surface area. Each of its values corresponds to several different pairs of saturation states of the fracture system and average fracture aperture. The calculation finishes with the application of the correction for worst-case criticality described in Section 2.4.

This Method section examines first the general mechanisms for actinide precipitation, then the details of the translation of the simulation results to the final results. Finally, two simplifying and timesaving corrections are described. It should be noted that PHREEQC is a one-dimensional code and that runs are independent of the chosen mechanism. The results need to be scaled to the appropriate model. Sections 2.1.1 and 2.1.2 are intended to show that dilution and mixing are plausible mechanisms at the scale of interest but not to give accurate results about the spatial distribution of their effects. Both mechanisms are illustrated by analytical solutions developed for porous media. For this reason, they are not applicable in their details to fracture systems. Actinide accumulation occurs in volumes of size smaller than the size of the porous media equivalent to the fracture system should be. More accurate results could be provided by fully coupled geochemical and flow models. Section 6 will only give bounding results.

With regard to the development of this calculation, the control of electronic management of data was evaluated in accordance with AP-SV.1Q, *Control of the Electronic Management of Information* (Ref. 50). The evaluation (Ref. 45) determined that current work processes and procedures are adequate for the control of electronic management of data for this activity.

2.1 DILUTION OF THE EFFLUENT

The purpose of this section is to show that dilution is a credible mechanism for precipitation of actinide minerals. Dilution leads to a shift in equilibrium leading to possible precipitation of actinides. This dilution mechanism is combined with the fracture wall mineral dissolution (Section 5.1.5). Dilution of the effluent from the WP could occur through two mechanisms: (1) local dilution due to re-mixing with water flowing around the drift (this mechanism is applicable to unsaturated cases) and (2) classical dispersion resulting from the dispersion of effluent over a complex network of fractures underneath the drift applicable to both unsaturated and saturated cases.

2.1.1 Local Dilution

When the successive engineered barriers divert the percolation flux, a "dry shadow" builds up underneath the drift (Ref. 2). As the flow proceeds downwards, water progressively invades this volume. This section does not attempt to accurately model the "dry shadow" underneath the drift but to establish that local dilution is a plausible dilution mechanism within a limited distance underneath the drift. As a corollary of this model with local dilution alone, the area where precipitation occurs is limited to the vertical "shadow" of the drift and the envelope of U mineralization is box-like.

The Total System Performance Assessment-Viability Assessment (TSPA-VA) seepage model indicates that a very low seep flow rate of 1.5 liter/year (see Section 5.1.3) can be attained with a small percolation rate of about 3 mm/year (Ref. 1, Fig. 2-112). ***Percolation rate*** is defined as the water flow rate through the unsaturated pile of volcanic rocks overlying the potential repository while the ***seepage rate*** is defined as the actual flow rate of water entering the drift. The ***drip rate*** is the amount of water dripping into and out of the WP. Because all the seepage is assumed to flow through the WP, seepage rate and drip rate are numerically equal. For such a low percolation rate (3 mm/year), the percentage of water actually seeping into the drift made available by percolation (seepage percentage) is about 1%. The seepage percentage is calculated, as described in Ref. 1 (p. 2-111), by dividing the seep flow rate by the percolation rate, dividing by the area of 75 m^2, and multiplying by 100. The same conclusions can be drawn from the new data released for the TSPA-SR (see Assumption 3.17). Such a low seepage percentage suggests that dilution is large under such a mechanism.

The process of local dilution is roughly consistent with a simplified analytical solution by Philip et al. (Ref. 2) that describes the saturated perturbation introduced by a cylindrical cavity in a uniform unsaturated flow field. Philip et al. determined that the length d of the down-gradient zone beyond which the flow field is back in some sense (Ref. 2, p. 26 and see below) to its undisturbed condition is given, with Ref. 2 notations, by (Ref. 2, Eq. 87c):

$$r_*(\pi) \approx l(18 + 5.5\alpha l) \qquad \text{(Ref. 2, Eq. 87c)}$$

where l is the radius of the cavity (top of their Section 4.1) and α is the coefficient of the exponential form of the relative permeability. With this calculation notation, their Eq. 87c becomes:

$$d \approx \frac{D}{2}\left(17 + 5.5\alpha\frac{D}{2}\right) = 46.75 + 41.60\alpha \quad \text{(m)} \qquad (2.1)$$

where the equation has been modified to shift the origin to the bottom of the cylindrical cavity (i.e., subtracting l from their Eq. 87c), D is the diameter of the cylindrical cavity, α (in length^{-1} units) is the coefficient of the exponential form of the relative permeability k_r, and the drift diameter, 5.5 m, has been substituted for D in the second part of the equation. The relative permeability is given by:

$$k_r = \exp(-\alpha\Psi) \tag{2.2}$$

where Ψ(m) is the absolute value of the capillary pressure (function of saturation). The parameter α typically varies from less than 1 m^{-1} for fine texture material to more than 5 m^{-1} for coarse material. A fracture system can be approximated by very coarse material, i.e., the parameter α is likely to be high.

Eq. 2.1 is applicable when some measure of the flow field is almost back to its original value. That measure turns out to be the relative permeability (function of saturation). The initial measure given in Ref. 2 is the ratio ϑ (their Eq. 14) of the final to the original Kirchhoff potential Θ defined by (their Eq. 4):

$$\Theta = \int_{-\infty}^{\Psi} K d\Psi = K_0 \int_{-\infty}^{\Psi} k_r d\Psi = K_0 \int_{-\infty}^{\Psi} \exp(-\alpha\Psi) d\Psi = -\frac{K_0}{\alpha}\left[\exp(-\alpha\Psi)\right]_{-\infty}^{\Psi} \tag{2.3}$$

Hence

$$\vartheta = \frac{\Theta}{\Theta_0} = \frac{\left[\exp(-\alpha\Psi)\right]_{-\infty}^{\Psi}}{\left[\exp(-\alpha\Psi)\right]_{-\infty}^{\Psi_0}} = \frac{k_r}{k_{r0}} \tag{2.4}$$

Eq. 2.1 was derived by assuming that the limit of the region of influence is given by $|\vartheta - 1| = \varepsilon$ (beginning of their Section 5.7) with ε=0.01 (beginning of their Section 7.6), i.e., when the relative permeabilities (initial and at some point down-gradient of the drift) differ by only 1%. Eq. 2.1 can be scaled to other values of ε by observing that in their Eq. 78, their dimensionless distance r is proportional to $\varepsilon^{-2/3}$:

$$d \approx \left(\frac{0.01}{\varepsilon}\right)^{2/3} (46.75 + 41.60\alpha) \quad \text{(m)} \tag{2.5}$$

The correction coefficient is equal to 0.215 for $\varepsilon = 0.1$.

Table 2-1. Zone of Influence of Local Dilution as a Function of α_{VG} (see file **expo-VG.xls** in electronic media - Attachment VIII)

Van Genuchten α_{VG} (Pa^{-1})	Exponential α (m^{-1})	Zone of Influence at 99% (ε=0.01) *d* (m)	Zone of Influence at 90% (ε=0.1) *d* (m)	Zone of Influence at 50% (ε=0.5)[a] *d* (m)
2×10^{-4}	4.84	248	53	18
4×10^{-4}	9.61	>300	96	33
9×10^{-4}	21.78	>300	205	70
3×10^{-3}	72.76	>300	>300	226

NOTE: [a] Results for ε=0.5 are only indicative as the derivation assumed small ε.

To approximate the length of the zone of influence by Eq. 2.1, it is necessary to estimate α for the fracture system surrounding the drift. Least-square fitting α (see file **expo-VG.xls**) to the Van Genuchten expressions of relative fracture permeability and capillary pressure (see Eq. 2-12 and 2-13 of Ref. 1) with m=0.492 (Ref. 36) and α_{VG} approximated as a range between 2×10^{-4} and 3×10^{-3} Pa^{-1} (Tables T2-19 and T2-21 of Ref. 1 for formation Tsw34 to Tsw36), yields a value of α between approximately 5 and 70 m^{-1}. Table 2-1 gives the length of the zone of influence for a range of α and three values of ε. A similar table with m=0.633 would display slightly larger values (see file **expo-VG.xls** - worksheet Exponential alpha m= 0.633).

The ratio of the permeability varies faster than the ratio of the saturation because permeability varies by several orders of magnitude. This is especially true at the low saturations considered in this calculation. An example read from Figure 2-1 (left lowermost diamond) shows that, even if the permeability is only 50% of what it is above the drift, the saturation is already at 85% of its value of 0.05 above the drift. Another example with an initial saturation of 0.3 shows that the saturation is already back to about 97.5% of its value although the relative permeability is only at 90% of its original value. The conclusion from the inspection of Figure 2-1 is that the saturation (i.e., ultimately the volume of water per unit surface area) is almost back to their original values with the measure ϑ at only 0.5. Figure 2-1 also shows that there is more than 85% recovery at 18 meters from the bottom of the drift (with exponential α = 4.84) or at 226 meters with exponential α = 72.76 (see file **expo-VG.xls** - worksheet Dilution factors). If we assume that 1% of the total flow actually goes through the drift and the WP, this means that the WP water is diluted by a factor of 85 in 18 or 226 meters.

Despite its rigorous derivation, Eq. 2.1 presents only an order of magnitude of the zone of influence. It was derived for homogeneous porous media. The Van Genuchten α values are also subject to caution. They were derived assuming average fracture intensity. In this calculation, only higher fracture intensity is of interest, as only it can generate substantial accumulation. The direction that the Van Genuchten α values take for higher intensities is unclear. Full dilution, i.e., saturations back to original conditions, is clearly more conservative over short distances as it maximizes the accumulation density of the fissile material. This section suggests that that short

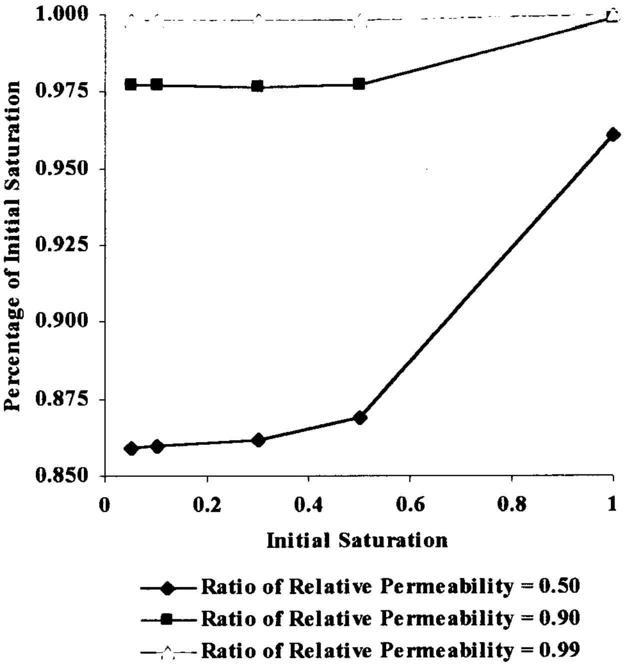


Figure 2-1. Percentage of the Initial Saturation Recovered as a Function of the Initial Saturation and Recovery Criteria

distance can be as small as 10 meters. Although no hard values from Section 2.1.1 are used, this section was intended to prove that dilution and mixing could occur on short distances.

2.1.2 Dispersion

With dispersion, dilution increases with distance from the source and, for example, a dilution factor of 10% for a cell corresponds to a "loss" through dispersion in the course of the cell length of 10% of the moles initially present. The mineralization region is relatively more spread out with dispersion than it is with local dilution. The shape of the U mineralization envelope resembles a more or less hollow cone of increasing diameter for a point source and a pair of diverging planes for a line source. Because the solution near the source and toward the center of the envelope may be too concentrated in total dissolved species to allow precipitation of actinides (see Section 2.1.4), a region free of mineralization may remain in the center of the envelope at some distance from the source as time progresses. However, far from the source, the solution toward the center of the envelope becomes dilute enough to allow precipitation, so that a horizontal bridge of mineralization fills in the mineralization envelope, leaving a region free of mineralization near the source and toward the center of the envelope. The shape of the mineralization also changes through time. At time 0 after breach time, the sharp concentration gradient between the resident water and the WP water produces a thin mineralization zone at the front of the infiltration area. As time proceeds, the mineralized zone moves forward with the water flow in the same way as a redox roll front would do (but the main parameter in this case is dilution and decrease in pH- see Section 2.1.4). The mineralized zone also moves sideways due to transverse dispersion and will eventually deplete the front of material to precipitate. It should be noted that this is a bounding calculation, the ionic strength of the WP water will actually decrease progressively mitigating this process. The most favorable time for accumulation is at early time after breach time when the mineralization is as compact as possible.

Dispersion can be conceptualized by comparing the dilution factors to the following formula (Ref. 3, Eq. 10.6.39, p. 634 where his D' is D_L and his D'' is D_T and where the Darcian velocity q has been replaced by the pore water velocity $q/n=v_x$) representing the steady-state concentration distribution of a point source in a uniform two-dimensional flow field (i.e., a line source in a three-dimensional representation) (see file **dispersion_linesource.xls** in electronic media - Attachment VIII).

$$\frac{C}{C_0}=\frac{Q}{2\pi\sqrt{D_L D_T}}\exp\left(\frac{xv_x}{2D_L}\right)K_0\left(\left(\frac{v_x^2}{4D_L}\left(\frac{x^2}{D_L}+\frac{y^2}{D_T}\right)\right)^{0.5}\right) \tag{2.6a}$$

where C_0 is the injection concentration taken as 1, Q is the seepage rate per meter of line source, D_L and D_T are the longitudinal and transverse dispersion respectively, v_x is the field velocity assumed uniform and x and y are the coordinates spanning the two-dimensional space beneath the proposed repository where the source term has for coordinates (0,0). K_0 is the modified Bessel function of second kind and zero order. For a three-dimensional model with a point source (see file **dispersion_pointsource.xls** in electronic media - Attachment VIII), the following formula can be derived (see Attachment I):

$$\frac{C}{C_0}=\frac{Q}{2\pi\sqrt{D_L D_T D_T}}\left(\frac{x^2}{D_L}+\frac{y_1^2}{D_T}+\frac{y_2^2}{D_T}\right)^{-0.5}\exp\left(\frac{xv_x}{2D_L}\right)\exp\left(-\left(\frac{v_x^2}{4D_L}\left(\frac{x^2}{D_L}+\frac{y_1^2}{D_T}+\frac{y_2^2}{D_T}\right)\right)^{0.5}\right) \tag{2.6b}$$

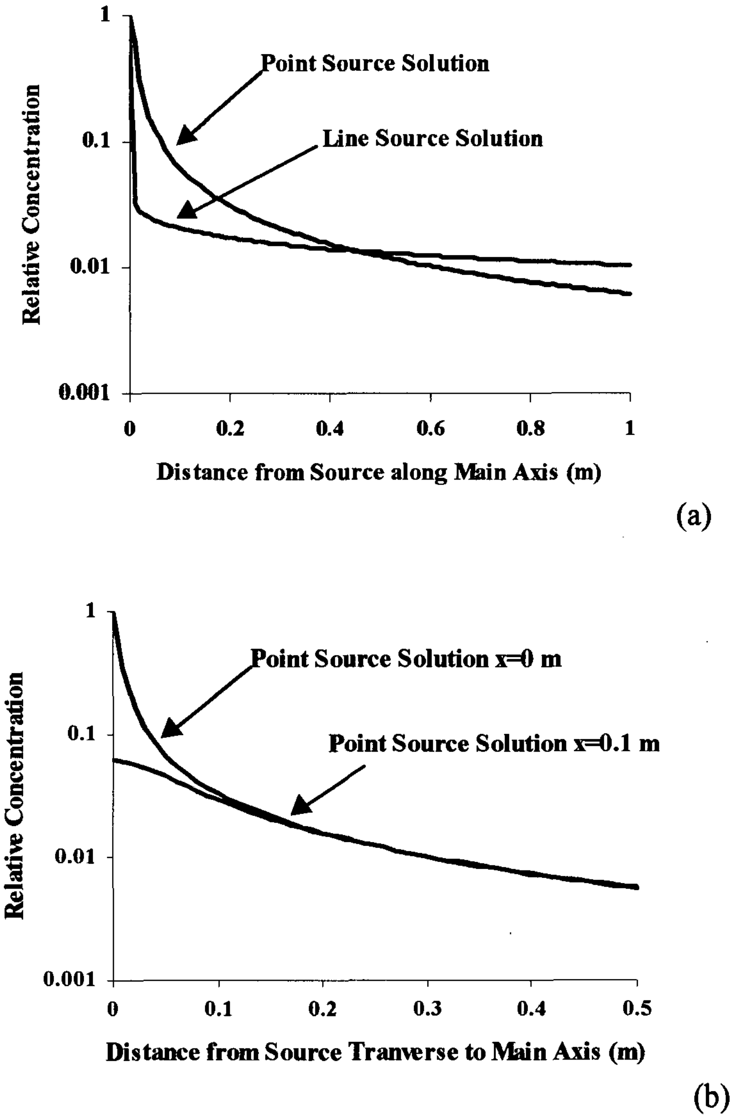
where y_1 and y_2 are the coordinates of a horizontal plane perpendicular to the main direction of flow and where Q is the seepage rate in m^3/s. Whether a point or a line source is appropriate depends on the geometry of the repository. If a single WP is considered, the point-source representation is more suitable. The base case of the present calculation (dilution of 10%) shows mineral precipitation for dilution factors ranging from 1 to 40. Thus, the three-dimensional space where precipitation can occur is such that x, y_1 and y_2 satisfy

$$(0.9)^{40}=0.015<\frac{C}{C_0}<0.9=(0.9)^1 \tag{2.7}$$

NOTE: 40 and 1 are true exponents.

Choice of transverse and longitudinal dispersions has some effect on the results. They are usually expressed as a linear function of the velocity. The proportionality coefficient, or dispersivity, is usually taken as 10% of the characteristic length of the system in a saturated system for longitudinal dispersivity and 1% for transverse dispersivity (Assumption 12). In unsaturated systems, the dispersivity is higher, up to the characteristic length of the system.

Figure 2-2 suggests that dispersion is applicable to distances one order of magnitude smaller than mixing and that the mineralization front is on the order of one meter across. However, the source term Q moves downward with the front. The maximum potential for actinide accumulation occurs along the symmetry axis/plane. Classical dispersion does not have any scale restriction and is also applicable instead of local dilution in the immediate vicinity of the drift in the case of saturated fractures because the source term has to spread out to be diluted by the ambient water. The possible accumulation can grow outside of the initial footprint.



NOTE: From file **dispersion_pointsource_plot.xls**.

Figure 2-2. Relative Concentration for Point and Line Source Solutions as a Function of Distance (a) Longitudinal Direction (b) Transverse Direction

2.1.3 Implementation of Dilution: the MIX Keyword

Local dilution is clearly a mixing process but classical dispersion is as well. The geochemical code PHREEQC (Section 4) does have a built-in keyword to handle dispersion and diffusion. However, it was felt more appropriate for this work to directly use the MIX keyword (that is also used by the code to handle directly dispersion and diffusion). The relationship between mixing and dispersion is given by Eq. 110 of the PHREEQC manual (Ref. 22, p.85):

$$Mixing\ Factor = \frac{D_L \Delta t}{n(\Delta x)^2} \tag{2.8}$$

where n is a numerical parameter used in PHREEQC and is different from 1 only in cases where the mixing factor is larger than 1/3. This calculation uses dilution factors up to 0.2, thus legitimating the use of $n=1$. Eq. 2.8 can be modified by using the definition of the hydrodynamic dispersion D_L:

$$\frac{D_L \Delta t}{(\Delta x)^2} = \frac{\alpha_L (\Delta x / \Delta t)\Delta t}{(\Delta x)^2} = \frac{\alpha_L}{\Delta x} \tag{2.9}$$

where α_L is the longitudinal dispersivity and Δx is the cell length. We are also interested in transverse dispersivity because of the trail left by the front as it moves downwards:

$$Mixing\ Factor = \frac{\alpha_T}{\Delta x} \tag{2.10}$$

where α_T is the transverse dispersivity equals to 1% of the characteristic length of the system (Assumption 12). This characteristic length, defined as the length with significant actinide deposition, must be iterated with the results (See Section 6.1.3.1 about sensitivity of the mixing factors). Uranium or plutonium have significant accumulation for approximately 10 to 20 cells, that is $\alpha_T = 0.01 * (10\, or\, 20) * \Delta x$, consistent with the mixing factor of 10% used in the PHREEQC simulations.

Figure 2-3a represents classical dispersion and assumes that any mass leaving the central axis of the system is lost for the simulation. This assumption is acceptable as the relative concentration outside of that central axis is low (that is lower than the 0.015 mentioned in Eq. 2-7). The model represented by Figure 2-3a gives an upper bound of the density of mineralization because the actual source is not a point but of finite area. The point-source approximation is strictly valid only if the source area is small compared to the distance considered during the simulations. This is clearly not the case because the vertical extent of the actinide mineralization is at most of the same order of magnitude as the area of infiltration. The actual mineralization lies between the mixing cases described in the next sections and no mixing at all (this is likely to be the case in the central part of the infiltration area). The approach taken is thus conservative. Figure 2-3b displays a case with local dispersion and assumes that the 1% seepage fraction is progressively diluted in 100 cells to reach the 100% percolation rate existing above the drift. The PHREEQC simulation is still done in successive cells of one kilogram each but the run results have to be multiplied by the number of cells (equivalent in this case to the cell number) to obtain the final results.

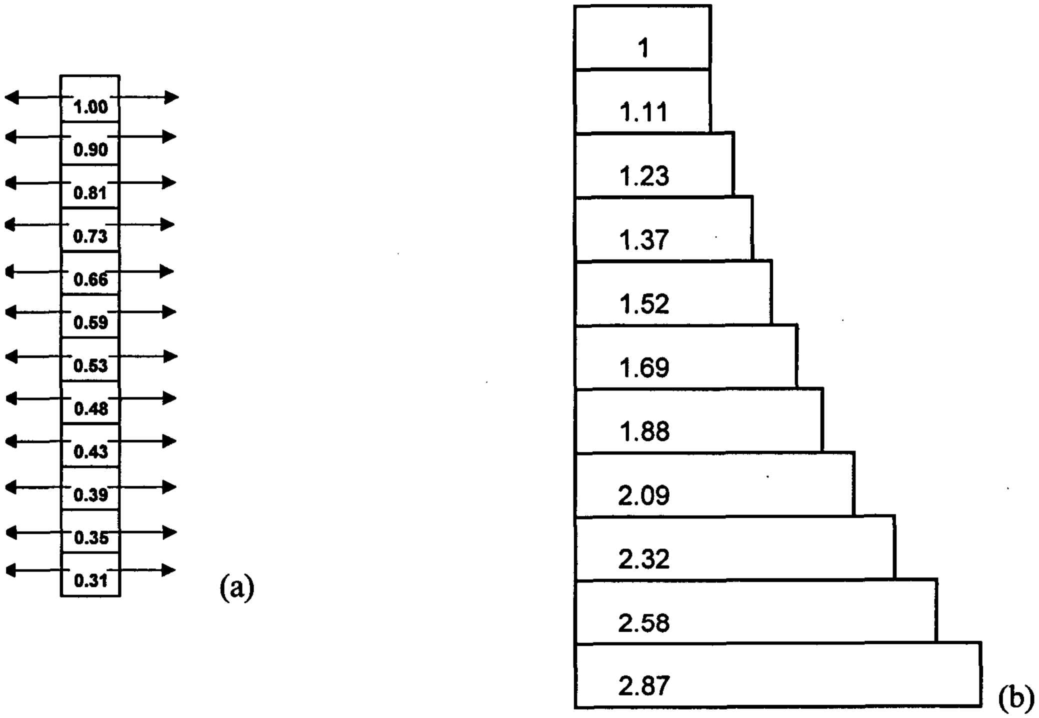


Figure 2-3. Implementation of the MIX keyword: a) Classical Dispersion, Numbers Show Reduction in Concentration in Successive Cells b) Local Dilution, Numbers Show Increase in Volume in Successive Cells

2.1.4 Why Dilution Initiates Actinide Precipitation

The purpose of this section is to describe the dilution-triggered precipitation mechanisms, and to illustrate these mechanisms by examples. Both mechanisms are driven by the dilution of the WP effluent by the J-13 well water (Assumption 3.2 and Section 5.1.1),, which has two effects:

- It brings the pH down from about 8.8 in the WP effluent of the pe0a1231 case (see Section 5.1.2.1) or higher (about 10 in the PW2a1231 case - see Section 5.1.2.1) to 8.1 in the J-13 well water (Table 5-2). It should be noted that the pH of 8.1 is somewhat above the value nominally assumed in connection with J-13 well water. This is because the unsaturated zone is expected to be in equilibrium with a higher carbon dioxide concentration, as is explained in connection with the water compositions given in Table 5-1 of Ref. 7
- It brings the ionic strength down from 2 and above (see Section 5.1.2.1) too much lower values.

In systems open to the atmosphere and at high pHs, Pu and U are complexed by carbonate ions yielding aqueous species such as the tri-plutonyl carbonate [$(PuO_2)_3(CO_3)_6^{6-}$] or plutonyl carbonate [$PuO_2(CO_3)_3^{4-}$] and uranyl carbonates [$UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$] (these are the most common Pu and U aqueous species in the different runs of this work). When the pH goes down, availability of the carbonate ion is less, forcing the actinides out of solution (see also Ref. 5 - Figures C-2 and C-3), down to a pH of 7 (which is well above the minimum of 8.1 used here). Another important aspect of the Pu and U complexes is their large size and charge. Charge is an important parameter when it comes to estimating equilibrium concentrations because equilibrium concentrations are written in terms of activity, product of the molal concentration and of the activity coefficient. Activity coefficients are functions of both the charge of the species and the ionic strength of the solution (see Attachment 5 - Eq. V-1b). At high ionic strength, activity coefficients of highly charged species are small, making their apparent concentration or activity small and thus "hiding", in effect, the actinide complexes within the solution. When the ionic strength decreases (e.g., by dilution), the activity coefficient increases by orders of magnitude. The activity coefficient increases faster than the concentration decreases, thus the activity as a whole increases leading to precipitation of minerals.

To illustrate these two mechanisms, a simplified pe0a1231 case was set (see Attachment III - Section III-1) and a few sensitivity analysis runs were done. The Saturation Index (SI), log of the ratio of the ion activity product to the reaction constant, gives a measure of how much actinide could precipitate. If SI is negative, the mineral cannot precipitate. On the other hand, the more positive SI is, the more abundant the precipitation of that mineral species is (ignoring kinetics considerations). To keep the pH at the same level while varying the ionic strength, the fictitious species pH_fixH and pH_fixOH were introduced. They maintain the pH at a given level by adding HCl or KOH respectively to the solution. To keep the ionic strength at the same level while varying the pH, the compound KCl was added in an amount sufficient to reach the target ionic strength. This was done to keep the actinide concentration identical (at 1%) in the same set of runs. The runs were done at two levels of actinide concentrations by mixing 99% of WP effluent with 1% of J-13 well water and by mixing 1% of WP effluent to 99% of J-13 well water. Table 2-2 illustrates that decreasing either pH or ionic strength increases the SI of actinide minerals typically expected to precipitate in the fracture system. Rows 1 and 2 of Table 2-2 show that when pH decreases by less than one pH unit, the SIs increase by several orders of magnitude. Rows 3 to 5 indicate that at constant pH (around 8.0 to 8.1), the SIs decrease with increasing ionic strength. Rows 10 and 11 at low ionic strength and constant pH indicate that the ionic strength effect is not an artifact of reaching the validity limit of the B-dot formulation at high ionic strength but is a true effect.

Table 2-2. Influence in Variations in pH and Ionic Strength for Actinide Precipitation (varying parameter in italics)

	Saturation Index (SI) of:						
Row #	**Soddyite**	**Haiweeite**	**$Pu(OH)_4$**	**pH**	**Pe**	**I.S.** [b]	**Comments**
Variable pH at High Ionic Strength with High Actinide Concentration							
1	5.30	4.01	1.72	*8.0*	12.606	1.898	File: **ST1_pH=8.0.** [a] Correction for pH
2	-1.26	-2.89	0.01	*8.84*	11.765	1.963	File: **ST1.** [a] No pH or I.S. Corrections
Constant pH and Variable Ionic Strength with Low Actinide Concentrations							
3	5.75	10.41	2.34	8.115	12.48	*0.996*	File: **ST99_0.1K.** [a] Correction for I.S. by adding 0.1 moles of KCl.
4	3.11	7.70	1.12	8.023	12.589	*1.487*	File: **ST99_1.5K.** [a] Correction for I.S. by adding 1.5 moles of KCl
5	2.71	7.48	0.94	8.036	12.58	*1.969*	File: **ST99_2K.** [a] Correction for I.S. by adding 2 moles of KCl
Variable pH at High Ionic Strength with Low Actinide Concentration							
6 4[c]	3.11	7.70	1.12	*8.023*	12.589	1.487	File: **ST99_1.5K.** [a] Correction for I.S. by adding 1.5 moles of KCl
7	-3.31	2.56	-0.59	*8.818*	11.795	1.505	File: **ST99_1.5K_pH=8.8.** [a] Correction for pH and for I.S. by adding 1.5 moles of KCl
Variable pH at low Ionic Strength							
8	6.27	11.40	2.75	*8.263*	12.338	0.0213	File: **ST99.** [a] No pH or I.S. Corrections
9	1.80	7.67	1.51	*8.795*	11.806	0.0342	File: **ST99_pH=8.8.** [a] Correction for pH
Constant pH and Variable Ionic Strength at Low Ionic Strength							
10	3.66	8.33	0.92	8.52	12.081	*0.3795*	File: **ST75_NoNa_pH=8.52.** [a] Correction for pH and for I.S. by deleting Na
11	3.13	7.30	1.21	8.524	12.079	*0.4995*	File: **ST75.** [a] No pH or I.S. Corrections

NOTE: [a] .dat for input file and .out for output file.
[b] I.S. = Ionic Strength.
[c] Both cases describe the same run.

2.2 SCALING BY THE VOLUME OF WATER

The fracture system is modeled by a series of 100 cells ("solution 1 to 100"), each of vertical length l_c. The first cell receives the constant composition solution dripping from the WP ("solution 0"). At each time step TS, the water is moved from one cell to the next and a fresh solution is moved into the first cell. The incoming water augmented of the products of the wall dissolution reacts with the solids already present in the cell and produces a solution of possibly different composition ready to move to the next cell. Dilution is handled by mixing, in given proportions, resident water ("solution 999" - see Section 5.1.1) and the current cell water.

The two main interacting parameters are the rock surface area accessible for mineral dissolution and the amount of water contacting that surface area. The surface area is a simple function of the geometry of the system. Because the PHREEQC runs are normalized to one kilogram of water (~one liter of water), the surface area needs to be scaled by the volume of water in a cell. If the fracture intensity is I m/m^2 over a cross-sectional area of infiltration (or footprint) A m^2, the total surface area is: $SA=2*I*A*l_c$ where l_c is the vertical cell length and the factor 2 accounts for the 2 walls of a fracture (Figure 2-4). The volume of water contained in the fractured rock is: $V=I*A*l_c*(2B)*S$, where S is the average water saturation in the fracture and $2B$ is the fracture width.

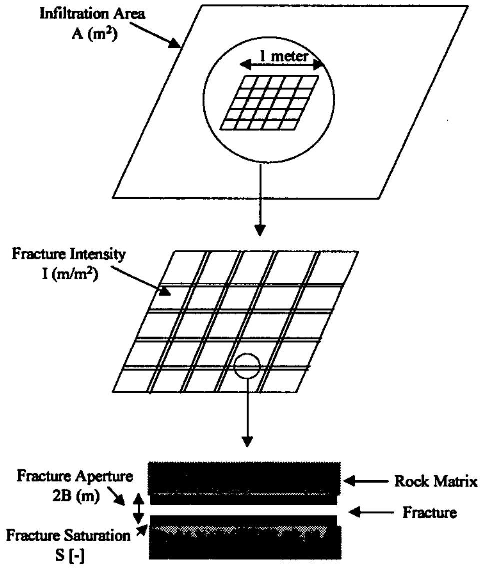


Figure 2-4. Conceptual Model of the Fractured Rock

Hence, the surface area per liter of water SA_{SC1} is expressed by:

$$SA_{SC1} = \frac{2*I*A*lc}{I*A*lc*(2B)*S}(\mathrm{m}^2/\mathrm{m}^3) = \frac{20}{(2B)*S}(\mathrm{cm}^2/\mathrm{L}) \qquad (2.11)$$

Thus, for a fully saturated fracture system 1 mm in width, SA_{SC1} is equal to 20,000 cm^2/L. For a 10% saturated fracture system 1 mm in width, SA_{SC1} is equal to 200,000 cm^2/L. This formulation does not take into account neither plugging of the matrix pores nor other means of limiting the exchange between the rock minerals and the fracture water. It is possible to increase the surface area to account for micro-porosity within grains (called the B.E.T. formulation in this calculation). It is also assumed that the surface areas stay constant as the tuff dissolves (Assumption 3.14). Note that the factor $(2B)*S$ is less variable than $2B$ because large fractures will have smaller degrees of saturation for the same flow rate than narrower ones. If the simulation time step TS is larger than the residence time RT (=1/DR where DR is the drip rate) the surface area is scaled further to SA_{SC2}.

$$SA_{SC2} = \frac{20}{(2B)*S}\frac{RT}{TS}(\mathrm{cm}^2/\mathrm{L}) \quad . \tag{2.12}$$

Despite the final scaling (Eq. 2.21), this formulation is only approximate and as the time step varies further from the residence time, the quality of the approximation deteriorates.

The saturation fraction S is a function of four parameters: the flow rate DR out of the WP (which is assumed identical to the seepage rate into the WP), the footprint A, the fracture aperture $2B$, and the fracture intensity I. The saturation fraction will adjust to achieve a steady state between the cross-sectional area open to flow and the flow rate (Assumption 3.16). The mathematical expression of the saturation fraction S is given by the Van Genuchten formulation (Ref. 1 - Eq. 2-12 and 2-13) and by the assumption that water saturation is the saturation sustaining the infiltration rate FU scaled to a unit area. Numerically, the infiltration rate and the conductivity are identical (vertical flow with a unit gradient – Assumption 3.3):

$$\mathrm{FU}=\mathrm{DR}/A=K*k_r \tag{2.13}$$

K is the saturated hydraulic conductivity and k_r is the relative permeability. The conductivity k is given by the cubic law (Ref. 13, Eq. 3.38, pp. 86-87 where N is used for fracture intensity instead of I in this calculation) and lowered by a roughness coefficient computed from the field data scaling:

$$\frac{K}{I} = r\frac{\rho g(2B)^3}{12\mu} \tag{2.14}$$

where ρ, g and μ are the water density, the gravitational constant and the water viscosity respectively. The roughness coefficient r, which is assumed identical for all fractures (Assumptions 3.8 and 3.9), is obtained through field results:

$$\frac{K_{field}}{I_{field}} = r\frac{\rho g(2B_{field})^3}{12\mu} \tag{2.15}$$

where K_{field}, I_{field} and $2B_{field}$ are obtained from field data.

Following Assumption 3.4 that all the fractures are conductive to water and Assumptions 3.5 and 3.6 that the fractures are all identical and of constant aperture, the local saturated hydraulic conductivity is given by:

$$K = K_{field} \frac{I}{I_{field}} \frac{(2B)^3}{(2B_{field})^3} \tag{2.16}$$

The relative permeability coefficient k_r is given by the Van Genuchten (Assumption 3.11) expression (Eq. 2-13 of Ref. 1):

$$k_r = S_e^{1/2}[1-(1-S_e^{1/m})^m]^2 \tag{2.17}$$

where m is the Van Genuchten coefficient and S_e is the reduced saturation with a residual water saturation of 0.01. Hence,

$$FU = K_{field} \frac{I}{I_{field}} \frac{(2B)^3}{(2B_{field})^3} S_e^{1/2}[1-(1-S_e^{1/m})^m]^2 \tag{2.18}$$

Eq. 2.18 is solved iteratively for S_e for given FU, I, and $2B$ (see file **sat_calc.xls** in electronic media - Attachment VIII) according to the following formula:

$$\left[\frac{FU/K}{[1-(1-S_e^{1/m})^m]^2}\right]^2 = S_e \tag{2.19}$$

Among the seven parameters cited (DR, $2B$, I, A, l_c, S and TS), five need to be provided by the user: generally DR, $2B$, I, A, and, in addition, the saturation S that is computed from the four previous parameters. The volume of water in the fractured rock within the vertical distance l_c of a cell length is $V = I * A * l_c * (2B) * S$. At steady state, mass balance considerations require that $V = \text{DR} * \text{TS}$. Hence l_c and TS can be chosen so that:

$$\text{V} = \text{DR}*\text{TS} = I*A*l_c*(2B)*S \ . \tag{2.20}$$

Because, in PHREEQC, one kilogram of water is moved to the next cell every time step, the true mass of solid precipitated in a time step can be scaled to the true amount of water in the system considered:

$$TRUE\,results = PHC\,results * V = PHC\,results * DR * TS \tag{2.21}$$

where *TRUEresults* represent the final results and *PHCresults* are the direct results from a PHREEQC run.

2.3 CORRECTING FOR EARLY TERMINATION

To avoid unproductive use of computer resources and time, most of the runs were not allowed to run to completion, but were stopped after a few hundred simulated years. Early termination is justified because the system quickly reaches steady-state conditions as all the inputs are constant (concentrations, flow rates, surface area). As illustrated in Section 6.1.1 and Figure 6-3, the masses of most species within a given cell are approximately linear functions of simulated time and, therefore, simple multiplicative factors can be applied. However, some species in some cells do not show a constant rate of increase, but show a nearly constant value. In such cases, no correction for early termination is necessary. Similarly, when a variable concentration source term was used, no early termination correction was applied because in this case the rate of increase in the mineral accumulation is not constant.

2.4 CORRECTING FOR WORST-CASE CRITICALITY

The footprint of a WP (parameter A from Section 2.2) is about 8 m^2 (WP Length x WP Diameter = 5.165 m x 1.564 m = 8.1 m^2 - Ref. 33, Table 5). However, the area considered for accumulation may exceed this value by more than one order of magnitude and then be scaled back to a smaller area according to the correction for worst-case criticality. The reasoning behind this correction is twofold. It is conceivable that the water will keep flowing along the drift grade past many fractures depending on the geometric details of the fracture intersection with the drift floor and thus the infiltration area may occupy an area larger than a typical WP footprint. Secondly and more importantly, a cubic shape is more conservative for criticality than a rectangle for the same mass of fissile material because closest to a spherical shape, the most reactive shape everything else being equal. Consequently, all accumulations elongated in the vertical direction can be made more conservative and can integrate at the same time uncertainties about the water velocity by recalculating their dimensions to obtain a cube according to the following equation:

$$\mathrm{DR}*\mathrm{TS}=I*(n*l_c * n*l_c)*l_c *(2B)*S \qquad (2.22)$$

Eq. 2.22 is derived from Eq. 2.20 by posing that $A=(n*l_c)^2$ where n is the number of cells with significant actinide accumulation. Eq. 2.22 is then solved for l_c. This scaling does not affect the density of the mineralization (i.e., total mass and volume stay the same), which is the true driver of criticality.

3. ASSUMPTIONS

The following assumptions are used in the course of this calculation.

3.1 *It is assumed that the effluent from the WP is not chemically affected by its contact with the invert.* The rationale of this assumption is that it is conservative for fracture precipitation because no fissile material is lost in the invert and all of the fissile material is available to be precipitated in the fractures underneath the drift. In this case, there is no accumulation in the invert. No processes in the invert could change the chemistry of the solution in such a way to reduce the potential for fissile deposition in the rock below the invert. This includes Eh and pH as well as loss of fissile materials in the invert. This assumption was made to maximize the mass of actinides available for deposition and to take into account a possible invert shortcut. This assumption is used in Section 5.1.

3.2 *It is assumed that the ambient water in the fracture system has the same composition as the J-13 well water.* The rationale for this assumption is that the groundwater composition is controlled largely by transport through the host rock, over pathways of hundreds of meters. The actual water composition is given in Table 5-4 of Ref. 7, and the explanation for the modification in pH is given in connection with that table, and in Section 2.1.4 of this document. J-13 well water is most appropriate for the groundwater composition because it was collected from the same stratigraphic unit that the repository will occupy, although the repository location is above the water table. The host rock composition is similar in both the unsaturated and the saturated areas of this unit and is not expected to change substantially over time. The travel time along the fracture system is very large in most instances (Fig. 2-116 of Ref. 1) so that the water has time to equilibrate with the host-rock before it reaches the water table. Hence the water present in the fracture system in the vicinity of the drift and the saturated zone water as represented by the J-13 well water have likely a similar composition. This assumption is used in Section 5.1.

3.3 *It is assumed that advective transport occurs in the vertical direction.* The rationale of this assumption is that most of the fractures are vertical (Ref. 6, Appendix 2 and 3 Tables). This assumption is used in Section 2.2. A corollary of this assumption is that vertical permeabilities are used.

3.4 *It is assumed that all the fractures within the footprint area beneath the WP are conductive to water.* The rationale of this assumption is that connectivity of fractures is high (Ref. 10 p. 7-26; Ref. 11, p. 64; and Section 5.1.7.3) and that it is conservative for mineralization. This assumption is used throughout Section 2.2.

3.5 *It is assumed that all of the fractures have the same average aperture.* The rationale of this assumption is the following: if it were not the case, the largest fracture(s) would take most of the flow according to the cubic law (Ref. 13, pp. 86-87). This assumption is then conservative because it leads to a more compact mineralization shape. Aperture variability would favor the widest fractures and would lead to a more elongated mineralization less conservative for criticality. This assumption is used in Section 2.2.

3.6 *It is assumed that the fracture aperture is constant within a single fracture.* The rationale of this assumption is that it is conservative. In reality, apertures vary within the same fracture. However, this assumption is conservative because it leads to a more compact mineralization shape. Aperture variability would favor the widest section of the fractures and lead to a more elongated mineralization less conservative for criticality. This assumption is used in Section 2.2.

3.7 *It is assumed that there is no channeling in the fracture planes.* No part of the fracture is restricted from flow and from the accompanying precipitation and dissolution. The rationale for this assumption is that it is conservative because it increases the surface area available for tuff dissolution and because it leads to a more compact mineralization shape. This assumption is used in Section 6.1.

3.8 *It is assumed that the fracture surface area is independent of fracture aperture.* The fracture surface area is calculated as the surface area of parallel plates; the distance between them has no effect on the surface area. The rationale of this assumption is that the increase in surface area resulting from a different model would be difficult to ascertain and can be addressed by sensitivity studies. This assumption is used in Section 2.2.

3.9 *It is assumed that the fracture roughness as defined by Eq. 2.15 is the same for all apertures.* The rationale of this assumption is that it is consistent with the fracture plate model used in this calculation. This assumption is used in Section 2.2.

3.10 *Three mutually exclusive alternative assumptions are made about the time the WP is breached. The assumptions yield three alternative scenarios in which (a) a negligible amount of the Pu has decayed to U by the time the WP is breached, (b) half of the Pu has decayed to U by the time the WP is breached, and (c) virtually all of the Pu has decayed to U by the time the WP is breached.* ^{239}Pu decays to ^{235}U with a half-life of about 24,000 years, so the three scenarios represent breach times of approximately (a) a thousand years or less, (b) 24,000 years, and (c) 120,000 years or more. The rationale of the assumptions is that the resulting set of decay scenarios bounds the possible WP breach times (cases a and c) and provides a reasonable intermediate case (case b). These assumptions are used in Section 5.

3.11 *It is assumed that the relationship between fracture saturation and relative permeability follows the Van Genuchten formulation with* $m = 0.492$ (Ref. 38). The rationale of this assumption is that it is reliable except at very low water saturation; and at very low water saturation, whether or not the assumption holds is unimportant because low water saturation systems are less prone to critical mineral deposition. This assumption is used in Section 2.2.

3.12 *It is assumed that longitudinal dispersivity is about 10% of the characteristic length of the system for a fractured saturated medium with good connectivity and the same as the system characteristic length for fractured, unsaturated medium.* The rationale of the first part of this assumption is engineering practice and is illustrated in Fig. 2.17, p. 72 and Fig. 2.18, p. 73 of Ref. 14. The second part of the assumption states that the dispersivity in an unsaturated medium can be one order of magnitude higher than in a saturated medium. Attachment II details the rationale of this assumption. This assumption is used in Section 2.2. *It is further assumed that transverse dispersivity is approximately 10% of the longitudinal dispersivity.* The rationale of this assumption is engineering practice and is further justified in Attachment II. This assumption is used in Section 2.2.

3.13 *It is assumed that solutes do not diffuse into the rock matrix.* The rationale for this assumption is that deposits are likely to plug small pores responsible for matrix diffusion practical. This will happen at early times preventing a significant amount of radionuclides to diffusing in the matrix. This assumption is used in Section 6.1.

3.14 *It is assumed that the surface area and volume of fractures do not change as the tuff dissolves.* The rationale of the first part of this assumption is that it is conservative because it maximizes the amount of chemical elements, such as Si, needed for actinide precipitation. The only direction that the tuff surface area can go is towards a decrease because of the precipitation of alteration or new minerals. The second part of the assumption is conservative as well because it allows a larger surface area per liter of water, which is favorable to precipitation (Figure 6-17). This assumption is used in Sections 2.2 and 6.1.

3.15 *It is assumed that the partial pressures of CO_2 and O_2 are the same in the fractures and in the drift.* The rationale of this assumption is that the fractures are unsaturated and atmospheric pumping will equilibrate fracture and drift pressures. The case of saturated fractures with reducing conditions is not treated in this calculation. This assumption is used in Section 5.1.

3.16 *It is assumed that the average fracture water saturation is the saturation that would sustain the infiltration rate FU* (numerically, the infiltration rate and the conductivity are identical, because of Assumption 3.3). The rationale of this assumption is conservation of mass at steady state. This assumption is used in Section 2.2.

3.17 *It is assumed that the average velocity in the fracture system is 0.03 m/year.* The rationale for this assumption is the following. A seepage rate of 1.5 liter/year translates into a percolation flux of 3 mm/year, which gives a seepage fraction of about 1% (Ref. 1, Fig. 2-112). This percolation flux needs now to be translated into a flow velocity into the system. Fig. 2-116 of Ref. 1 shows that the 50th percentile transport time between the repository and the water table located 250 meters below is 2,000 years for the present-day climate (percolation rate of 8 mm/year). This translates into an average velocity of 0.125

meter/year. Interpolating linearly Fig. 2-116 between present day infiltration rate at 8 mm/year and one fifth of present day infiltration to obtain average velocity at 3 mm/year yields a 50th percentile transport time of 8,000 years. This number is assumed to be representative of the average velocity that can be computed at 250 m / 8000 years = 0.03 meter/year to be consistent with the seepage rate of 1.5 liter/year. This assumption is used in Section 6.1. Note: since these calculations were performed, new data are available for the seepage rate (Ref. 37). A seepage rate of 1.5 liter/year translates into an average infiltration rate of 4.15 mm/year [(1.5 L/year - 0 L/year)/(3.21 L/year -0 L/year)x(5 mm/year -3.4 mm/year) + 3.4 mm/year]. This value is very similar to the 8 mm/year used previously, especially if the standard deviation of the seepage rate (about 1.5 L/year) is taken into account.

3.18 *It is assumed that the velocity of 0.03 meter/year is also applicable in the few meters underneath the repository in saturated conditions.* The rationale of this assumption is that the velocity of 0.03 meter/year is a rough approximation that can be changed to produce more conservative results (in the criticality sense) but still realistic and consistent with the original input. *In unsaturated conditions, the velocity of 0.03 meter/year is a lower bound of the velocity in the few meters underneath the disposal drifts.*). The rationale of this part of the assumption is the following. The dry shadow area footprint A stays constant but the area open to flow increases with the saturation S. At the same time the flow Q becomes progressively larger as mixing progresses. Conservation of mass, that should always be verified, tells that $Q=vAnS$ where n is the porosity and v the pore velocity. The saturation is in general smaller underneath the disposal drifts than away from them because of the "dry-shadow" effect (Section 2). If the saturation S increases slower than the steady-state flow rate Q increases, v has to increase to satisfy the conservation of mass equation. This is indeed the case as shown in worksheet "convex" of the spreadsheet **sat_calc.xls** (Attachment VIII). This assumption is used in Section 6.1.

3.19 *The composition of the effluent solution is assumed constant for the duration of the simulation.* The rationale of this assumption is that it is conservative because it maximizes the mass of uranium released. The duration of the simulation is chosen so that this assumption is realistic. This assumption is used in Section 5.1. This assumption will be relaxed in sensitivity analyses.

3.20 *It is assumed that adsorption on clays and Fe hydroxides is lumped with precipitation.* The rationale of this assumption is that even high partition coefficients (Kd) generates smaller accumulations than true precipitation. This assumption is used in Section 6.1.1.

3.21 *It is assumed that all solids that are deposited remain in place*; no solids are entrained or otherwise re-mobilized, except possibly by dissolving later. The rationale for this assumption is that it is conservative because it precludes the loss of fissile material from the mineralization region as suspended solids. This assumption is used in Section 6.1.

3.22 *It is assumed that PuO_2 does not precipitate and that the log10 of the solubility product for $Pu(OH)_4$ can be reduced by 4 orders of magnitude: The reaction $Pu(OH)_4 + 4.\ H^{+1} = Pu^{+4} + 4.$* H_2O was given a $\log_{10}$ of the solubility product of –3.75 instead of the value of 0.75 as in the data0.nuc.R8a EQ6 database. The rationale for this assumption is that there are indications (see Ref. 26, Ref. 34, and Ref. 4 - Section 5.1.3) that the solubility of $Pu(OH)_4$ is lower than that indicated by the EQ3/6 thermodynamic data library and that it is consistent with the source term. The assumption is conservative for external criticality considerations since it favors precipitation of Pu. This assumption is used in Section 5.1.

3.23 *It is assumed that 25°C thermodynamic data can be used for the calculations.* The rationale of this assumption is two-fold. First, the initial breach and filling of a WP is unlikely to occur before 10^4 years (Ref. 24, Figure C-12), when the WP contents have cooled to <50°C (Ref. 25, Figure 3-22). Second, the assumption is conservative, with respect to loss of many actinides; most studies (Ref. 26, Table 3; Ref. 27, Table 2) show that actinide solubility decreases slightly as temperature increases, apparently due to the increase in crystallinity and precipitation rates at higher temperatures. This assumption is used in Section 5.1.

3.24 *It is assumed that the concentrations of the minor constituents of J-13 well water can be adequately represented by values for Li, B, and PO_4 taken from Reference 35, Table 4.2; values for Al, Fe, and Mn in equilibrium with diaspore, pyrolusite, and goethite, respectively; and the values for the trace elements, Cr and Mo, set to a molality of 10^{-16}.* The rationale for this assumption is that even if the chemistry of the infiltrating water varies substantially, the effects of such variations will likely be insignificant for WPs that undergo significant degradation. An evaluation of the effects of varying the chemistry of the water dripping into a WP is given in Section 5.3.2 of Ref. 7. This assumption is used in Section 5.1.

4. USE OF COMPUTER SOFTWARE AND MODELS

This calculation uses the baselined software package PHREEQC and one software routine: transl.c.

4.1 SOFTWARE

4.1.1 PHREEQC Software Package

The PHREEQC Version 2.0.38(beta) [shortened to Version 2.0(beta)] software has been qualified under the *AP-SI.1Q* procedure under the Software Tracking Number 10068-2.0-00 and the Software Activity Number LV-1999-002. Ref. 30 gives the Validation Test Report information. PHREEQC runs were performed on a Duke Engineering & Services Dell Pentium II computer (CPU#DES52134, Room 204, DE&S, 9111 Research Boulevard, Austin, TX). The software was obtained through Configuration Management. Input and output files are listed in Attachment IV and are accessible from the electronic media (Attachment VIII). All input parameters used in the input files are described in Section 5 of this calculation and output files are processed in Section 6. The software is appropriate for use in this calculation and has been used within the range of parameters for which the software has been verified.

4.1.2 PHREEQC Description

The PHREEQC family of software products originated in the late 1970's and was developed by the U.S. Geological Survey. However, PHREEQC is a totally new, integrated version rewritten in the C language (Ref. 22). PHREEQC Version 2.0(beta) contains capabilities such as speciation-solubility and kinetically controlled reaction pathway features, which are found in many geochemical software packages, but also includes surface complexation, ion exchange, absorption and solid solutions, and a very versatile treatment of rate laws. In addition, PHREEQC has transport features with handling of dispersion and diffusion in a double-porosity medium. It also has inverse modeling capabilities. However, unlike EQ6, which is a similar geochemical modeling program, PHREEQC supports only the use of the Davies or B-dot equations for the activity coefficients. The thermodynamic database used by PHREEQC in this work is a direct transcription of the EQ6 database (data0.nuc.R8a), translated into a PHREEQC-readable format using the software routine *transl.c* as described in Attachments V and VI.

PHREEQC models the consequences of reacting an aqueous solution with a set of reactants according to thermodynamic laws. It can also include very complex kinetics laws through a BASIC interpreter coupled to the program. PHREEQC handles advective transport by moving aqueous solutions from one cell to the next, allowing the contents of each cell to reach equilibrium (or not) with the solids and surface features present in the cell (Ref. 22). Diffusion and dispersion are handled by mixing the contents of cells in proportion to the diffusion (or dispersion) parameters. PHREEQC uses a finite-difference scheme and is therefore subject to numerical dispersion. Inclusion of dispersion-diffusion increases several-fold the run time of a particular set of parameters. PHREEQC uses a hybrid Newton-Raphson technique to solve the set of equations at each time step. It is restricted to a constant time step, unlike the dynamic time stepping of EQ6.

4.2 SOFTWARE ROUTINES

4.2.1 C Program "transl.c" Version1.0s

PHREEQC is distributed with a limited thermodynamic library, making the use of the more extensive EQ6 thermodynamic data library desirable. Using the EQ6 library also adds consistency and accuracy to the PHREEQC outputs and comparability and compatibility with calculations made using EQ6 as well. Because the two programs require different input formats, a C programming language routine named "transl.c" Version 1.0s was written to handle the translation ("s" stands for "short" as opposed to the long version where temperature variations are included - temperature variations are not required in this calculation). The code "transl.c" is included as Attachment VI and its user's manual is included as Attachment V). The resulting thermodynamic database, called phreeqc.nuc_xx-xx or phreeqc.nuc_xx, is valid for a range of temperatures or at a constant temperature, as specified by the user of "transl.c". This calculation uses the thermodynamic database phreeqc.nuc_25, which was translated from the EQ6 thermodynamic database "data0.nucR8a". Files related to the database translation are in the directory Database_files on electronic media (Attachment VIII).

4.2.2 Microsoft Excel Spreadsheets

Spreadsheet analyses were performed with Microsoft Excel 97 SR-2, installed on a PC. The specific spreadsheets used for results reported in this document are in the included electronic media (Attachment VIII). The spreadsheets are sufficiently labeled to allow an independent reviewer to redo the calculations. The spreadsheet functions have been summarized in Attachment VII. The spreadsheets have been verified and documented according to the procedure *AP-SI.1Q, Software Management* (Ref. 51). Formulas used are listed in the spreadsheets and have been checked where used and found to be identical. The macro "goalseek_saturation" V.1.0 developed in the spreadsheet **sat_calc.xls** is also listed in Attachment VII along with the method and results of verification.

4.2.3 Surfer Plotting Software

When a 2-D (two-dimensional) representation as given by plots on spreadsheets is not adequate, the 3-D (three-dimensional) surfer32 plotting software was used. All the information needed to build the Surfer input files was developed on excel spreadsheets.

4.3 MODELS

None used.

5. CALCULATION

5.1 INPUTS

5.1.1 J-13 Well Water Composition

The J-13 well water has been widely used as a surrogate for the fracture water of the unsaturated zone (Assumption 3.2). Original analyses of the J-13 well water (Table 5-1) were provided by Harrar et al. (Ref. 35, Table 4.1 [DTN: MO0006J13WTRCM.000, Ref. 44] and Table 4.2).

Table 5-1. J-13 Well Water Composition

PH	7.41[a]
Element/Ion	**Concentration (mg/l)**
Na+	45.8
Si	28.5
Ca	13
K	5.04
Mg	2.01
Alkalinity	143[a]
F-	2.18
Cl-	7.14
NO3-	8.78
SO4--	18.4
Li+[b]	4.80E-02
B[b]	1.34E-01
PO4-[b]-	1.20E-01

DTN: MO0006J13WTRCM.000

NOTES: [a] Initial values. Recalculated assuming equilibrium CO_2 and O_2
[b] Minor constituents not covered by DTN (Assumption 3.24).

In addition, Al, Fe, and Mn are assumed to be in equilibrium with diaspore, pyrolusite, and goethite, respectively, and trace elements (Cr, Mo) are set to a molality of 10^{-16} (Assumption 3.24). With these assumptions, the J-13 well water composition, as given in Table 5-1, changes to the composition given in Table 5-2 (see files **J13ww.dat** and **J13ww.out** for PHREEQC run and file **J13ww.xls** for comparison in directory j13ww in electronic media - Attachment VIII).

J-13 well water is used as resident water in the cells before the breakthrough of the WP water ("solution 1 to 100" of PHREEQC input file of Attachment III - Section III-2) and as mixing water ("solution 999" of PHREEQC input file of Attachment III - Section III-2) (Assumption 3.2). For consistency, the retained J-13 well water is the one used in Ref. 4 and copied from the EQ6 pickup files. Table 5-2 gives its composition. CO_2 and O_2 are also assumed to be in equilibrium with their atmospheric concentrations (Assumption 3.15).

Table 5-2. Elemental Molar Composition for J-13 Well Water

PH	8.1	Element	Mole/kg
Pe	12.5	P	1.26E-06
Element	Mole/kg	K	1.29E-04
Al	2.55E-08	Li[a]	6.92E-06
B	1.24E-05	Mg	8.27E-05
Ca	3.24E-04	Mn[a]	3.05E-16
Cl	2.01E-04	Mo[a]	1.00E-16
Cr[a]	1.00E-16	N	1.42E-04
F	1.15E-04	Na	1.99E-03
Fe	3.60E-12	S	1.90E-04
C	2.09E-03	Si	1.01E-03
LogPO2	-0.7	logPCO2	-3.0

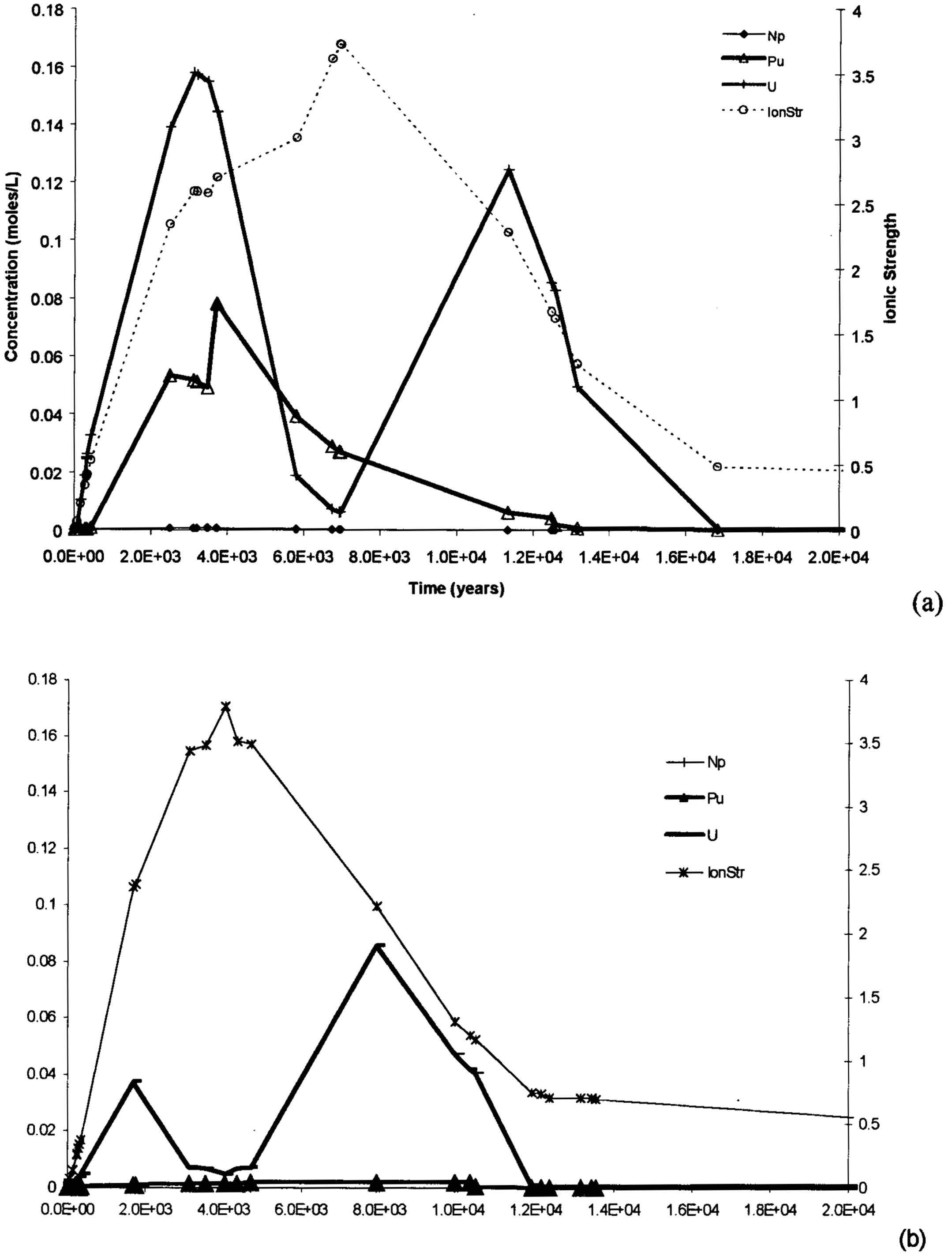
SOURCE: files **J13ww.out** and **J13ww.xls** (Attachment VIII)
NOTE: [a] Concentration set to zero for the simulations.

5.1.2 WP Source Terms

The source terms have WP effluent water composition, i.e., either the invert is shortcut or its chemical effects are ignored (Assumption 3.1). It is a conservative position as the mechanisms described in this calculation (dilution, mixing with J-13 well water and reaction with the tuff) also occur in the invert. The chemistry of the solution is then no more altered than it will be by reacting in the fracture system. Precipitation of fissionable elements may also occur if solutions encounter reducing conditions (related to the presence of steel in the invert) before they enter the fracture system. Ignoring this effect is conservative, as it permits the maximum amount of fissionable elements to enter the fracture system.

5.1.2.1 Pu-Ceramic Source Terms

The Pu-ceramic source terms for all of the breach-time scenarios are taken "as is" or in modified form (to account for the decay of Pu), from Ref. 4 (Section 5.2), EQ6 run pe0a1231 at time 2,500 years (Figure 5-1a, Table 5-3a, and files **pe0a1231.elem_aqu.txt** and **pe0a1231.elem_aqu.xls** in electronic media - Attachment VIII) and from EQ6 run pw2a1231 at times 4,050 and 7,940 years (Figure 5-1b, Table 5-4 and Table 5-5, and files **pw2a1231.elem_aqu.txt** and **pw2a1231.elem_aqu.xls** in electronic media - Attachment VIII). Ref. 4 (Section 5.3) gives details about the differences between the two source terms. In short, pw2a1231 has smaller degradation rates, thought to be more realistic, leading to smaller Pu and U concentrations. It is otherwise assumed that the source terms are not affected by the invert (Assumption 3.1). Because the Pu concentration in the WP effluent is approximately constant (within one order of magnitude) between 2,000 and 4,000 years after breach time for pe0a1231 and because the U concentration is at its peak, it is assumed that the source term stays constant during 2,500 years (Assumption 3.19). For case pw2a1231, although the Pu concentration is reasonably constant for about 7,000 years, the U concentration varies by one order of magnitude. Consequently, two time intervals of constant source terms have been retained: one at the lowest U concentration (time=4,050 years) and one at the U peak (time=7,940 years). The first constant source term (at 4,050 years) is applicable for 3,000 years, from 3,000 years after breach time to 6,000 years after breach time while the second constant source term (at 7,940 years) is applicable for 4,000 years, from 6,000 years after breach time to 10,000 years after breach time. The total accumulation is the sum of the accumulations during both time intervals. It should be noted that the high ionic strength makes the calculation approximate in the first cells before concentration reaches lower levels by dilution in the further downstream cells.



SOURCE: Data from Ref. 4.
NOTE: Both source terms are plotted on the same scale.

Figure 5-1. Uranium, Pu, and Np Molar Concentrations and Ionic Strengths from Time of WP Breach for Source Terms (a) pe0a1231 and (b) PW2a1231

Table 5-3. Elemental Molar Composition for Non-Decayed Source Term at Time=2,500 Years (source term pe0a1231 from EQ6 output file **pe0a1231.elem_aqu.txt**)

Characteristic	**Value**
PH	8.78E+00
Eh	7.00E-01
Pe	1.18E+01
Element	**Concentration (mole/L)**
Na	9.76E-01
C	5.52E-01
U	1.39E-01
Cr	1.32E-01
B	9.79E-02
K	6.64E-02
Pu	5.32E-02
S	1.41E-02
F	4.03E-03
N	2.71E-03
Np	5.37E-04
Cl	2.01E-04
Si	1.00E-04
Ca	6.63E-05
Mg	4.26E-05
Li	6.92E-06
Gd	2.64E-07
P	1.62E-07
Ni	3.15E-08
Al	6.94E-09
Ba	1.03E-09
Zr	6.18E-10
Ti	2.06E-10
Fe	1.29E-12
Mn [a]	4.32E-16
Cu [a]	1.00E-16
Mo [a]	1.00E-16
Pb [a]	1.00E-16
Tc [a]	1.00E-16

SOURCE: Ref. 4.
NOTE: [a] Concentration set to zero for the simulations.

Table 5-4. Elemental Molar Composition for Non-Decayed Source Term at Time=7,940 Years (source term PW2a1231 from EQ6 output file **PW2a1231.elem_aqu.txt**)

Characteristic	**Value**
PH	9.66E+00
Eh	6.48E-01
Pe	1.09E+01
Element	**Concentration (mole/L)**
Na	1.39E+00
C	6.16E-01
Cr	2.18E-01
B	1.51E-01
K	8.92E-02
U	8.56E-02
S	1.21E-02
N	4.41E-03
F	4.33E-03
Pu	1.81E-03
Si	6.74E-04
Cl	2.01E-04
P	3.79E-05
Np	2.05E-05
Ca	5.68E-06
Mg	4.99E-06
Gd	5.49E-07
Al	5.11E-09
Zr	6.02E-10
Ni	5.70E-10
Ti	2.01E-10
Ba	3.78E-11
Fe	2.78E-12
Mn[a]	3.06E-15

SOURCE: Ref. 4.

NOTE: [a] Concentration set to zero for the simulations.

Table 5-5. Elemental Molar Composition for Non-Decayed Source Term at Time=4,050 Years (source term PW2a1231 from EQ6 output file **PW2a1231.elem_aqu.txt**)

Characteristic	**Value**
pH	10.00E+00
Eh	6.29E-01
pe	1.06E+01
Element	**Concentration (mole/L)**
Na	3.27E+00
C	1.69E+00
K	2.11E-01
B	2.06E-01
Cr	1.73E-01
S	4.23E-02
F	1.44E-02
U	4.69E-03
N	3.52E-03
Si	2.97E-03
Pu	1.61E-03
P	3.65E-04
Cl	2.01E-04
Np	1.62E-05
Ca	3.06E-06
Mg	2.92E-06
Gd	8.36E-07
Al	1.34E-09
Zr	4.46E-10
Ti	1.49E-10
Ni	1.05E-10
Ba	1.99E-11
Fe	3.53E-12
Mn[a]	6.79E-15

SOURCE: Ref. 4.
NOTE: [a] Concentration set to zero for the simulations.

5.1.2.1a Early Breach Time (negligible decay of Pu)

The source term for the scenario in which the WP is breached before a substantial fraction of the Pu has decayed to U is taken directly from Ref. 4 (Section 5.2). That is EQ6 run pe0a1231 at time 2,500 years after breach or EQ6 run pw2a1231 at times 4,050 and 7,940 years after breach.

5.1.2.1b Medium Breach Time (50% decay of Pu)

The source term for the scenario in which the WP is breached after one half-life of ^{239}Pu is adapted from Ref. 4 (Section 5.2). That is EQ6 run pe0a1231 at time 2,500 years after breach (Table 5-3) and EQ6 run pw2a1231 at times 4,050 and 7,940 years after breach (Table 5-4 and Table 5-5) with the U and Pu concentrations adjusted as shown in Table 5-6, Table 5-7, and Table 5-8. However, because changing the composition of a solution alters its equilibrium, uranium and plutonium minerals were allowed to equilibrate before entering the first cell (practically, this is equivalent to precipitation of Pu(OH)4 and Soddyite and Haiweeite within the WP). Those runs have a "_mod" ending - see Attachment VI). Alternatively, in some early runs, this correction of the source term was not done but the Pu and U minerals in the first cell were disregarded as precipitation that should have happened in the WP.

Table 5-6. Elemental U and Pu Concentrations for the Three Breach Time Scenarios (pe0a1231 case)

	Elemental Concentration (mole/L)		
Breach Time Scenario	**U**	**Pu**	**Sum**
Early (no Pu decay)	1.39E-01	5.32E-02	1.92E-01
Medium (50% Pu decay)	1.66E-01	2.66E-02	1.92E-01
Late (100% Pu decay)	1.92E-01	0.00E+00	1.92E-01

Table 5-7. Elemental U and Pu Concentrations for the Three Breach Time Scenarios (pw2a1231 case at 4,050 years after breach)

	Elemental Concentration (mole/L)		
Breach Time Scenario	**U**	**Pu**	**Sum**
Early (no Pu decay)	4.69E-03	1.61E-03	6.30E-03
Medium (50% Pu decay)	5.50E-03	0.80E-03	6.30E-03
Late (100% Pu decay)	6.30E-03	0.00E+00	6.30E-03

Table 5-8. Elemental U and Pu Concentrations for the Three Breach Time Scenarios (pw2a1231 case at 7,940 years after breach)

	Elemental Concentration (mole/L)		
Breach Time Scenario	**U**	**Pu**	**Sum**
Early (no Pu decay)	8.56E-02	0.181E-02	8.74E-02
Medium (50% Pu decay)	8.65E-02	0.090E-02	8.74E-02
Late (100% Pu decay)	8.74E-02	0.00E+00	8.74E-02

5.1.2.1c Late Breach Time (complete decay of Pu)

The source term for the scenario in which the WP is breached after five or more half-lives of ^{239}Pu is adapted from Ref. 4 (Section 5.2). That is EQ6 run pe0a1231 at time 2,500 years after breach (Table 5-3) and EQ6 run pw2a1231 at times 4,050 and 7,940 years after breach (Table 5-4 and Table 5-5) with the U and Pu concentrations adjusted as shown in Table 5-7 and Table 5-8.

5.1.2.2 MOX Source Term

The MOX source terms for all of the breach-time scenarios are taken, "as is" or in modified form (to account for the decay of Pu), from Ref. 8, EQ6 run mox03ap2 at time 13,880 years (Figure 5-2, Table 5-9 and files **mox3ap2_elem_aqu.txt** and **mox3ap2_elem_aqu.xls** in electronic media - Attachment VIII). The source term modification for decay of Pu was handled as described in Section 5.1.2.1.

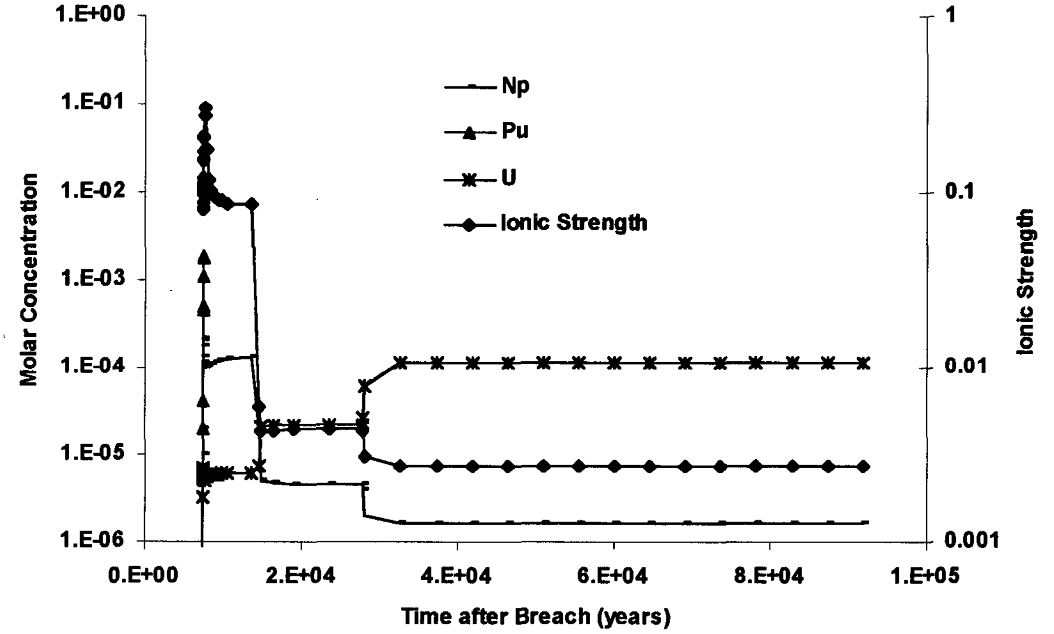


Figure 5-2. Uranium, Pu, and Np Molar Concentrations and Ionic Strengths from Time of WP Breach for Source Term mox03ap2

Table 5-9. Elemental Molar Composition for Non-Decayed Source Term at Time=13,880 Years (source term mox03ap2 from EQ6 output file **mox03ap2.elem_aqu.txt**)

Characteristic	**Value**
PH	5.99
Eh	0.86
Pe	14.61
Element	**Concentration (mole/L)**
Mo	0.0504
Cs	0.0206
Ni	0.0144
Tc	0.0111
B	0.00825
Pd	0.00598
Ca	0.00411
Y	0.00390
Rb	0.00345
Sr	0.00310
Na	0.00286
Mg	0.00277
Sm	0.00253
Ag	0.00252
Pr	0.00178
La	0.00100
Gd	0.000866
K	0.000653
N	0.000639
Eu	0.000588
Nd	0.000389

Element	**Concentration (mole/L)**
Ba	0.000221
Am	0.000147
C	0.000126
F	0.000118
Np	9.35E-05
S	1.28E-05
Cr	1.10E-05
Li	6.92E-06
U	4.91E-06
Cl	3.87E-07
Pu	8.80E-08
Sn	2.15E-08
Al	3.44E-09
Zr	5.39E-10
Si	4.23E-10
Ti	1.80E-10
Mn[a]	6.94E-12
Fe	3.83E-12
P[a]	1.40E-12
Ru[a]	2.31E-13
Cu[a]	1.05E-16
Zn[a]	1.00E-16
Pb[a]	1.00E-16
Ce[a]	4.12E-17
Rh[a]	2.81E-19

SOURCE: Ref. 8.
NOTE: [a] Concentration set to zero for the simulations.

5.1.3 Drip Rates

The drip rate is taken from a correlation between percolation rate and drip rate (Ref. 1, Fig. 2-112). Specifically, percolation rates of 40 mm/year and 8 mm/year correlate with drip rates onto the WP of 0.15 m^3/year and 0.015 m^3/year, respectively. The choice of these particular percolation and drip rates is discussed in detail in Ref. 7. For the present study, the drip rate was restricted to a value of 1.5 L/year consistent with the input conditions of the source term. It should be noted that the MOX case has a flow rate of 15 L/year but eventually it is not relevant because very little actinide is precipitated (Section 6.4).

5.1.4 Thermodynamic Database

The EQ6 thermodynamic database data0.nuc.R8a (consistent with Ref. 4) is used. The EQ6 thermodynamic database data0.nuc.R8a is a composite thermodynamic database derived from the data0.skb and other databases provided by Lawrence Livermore National Laboratory tailored for WP degradation studies. The detailed history of the database is provided in the heading of the file **data0.nuc.R8a** in directory **database_files** (Attachment VIII - electronic media). The most significant modification is that the precipitation of Pu is enhanced by 4 orders of magnitude (Assumption 3.22). The more recent database data0.nuc.R8s (Ref. 4 - Section 5.1), modified from data0.nuc.R8a in the course of Ref. 4 calculation by using information from Ref. 42, is also used as part of the sensitivity analysis. All calculations are done at 25°C (Assumption 3.23).

5.1.5 Fracture Wall Dissolution

The walls are made of tuff whose normalized composition is computed in spreadsheet **Tuff_compostion.xls** (Attachment VIII) and reproduced in Table 5-10. The initial rock makeup comes from Ref. 36. Because the different species making up the tuff have approximately the same density, molar and relative surface compositions are numerically identical.

Table 5-10. Normalized Molar Composition of Tuff

Component	Relative Surface Area
Annite	0.020
Phlogopite	0.009
Anorthite	0.028
Albite	0.306
Microcline	0.276
Cristobalite	0.361
Sum	1.000

The rate laws follow the transition-state theory (TST) formalism (Ref. 4, Section 5.3.2):

$$\frac{\Delta Moles}{\Delta t} = SA * SA_{rel} * \left(a + b\left[OH^-\right]^{0.3}\right) * (1 - SR) \tag{5.1}$$

for cristobalite, microcline, albite, and anorthite and of the form:

$$\frac{\Delta Moles}{\Delta t} = SA * SA_{rel} * \left(a\left[H^+\right]^{0.37} + b + c\left[H^+\right]^{-0.22}\right) * (1 - SR) \tag{5.2}$$

for annite and phlogopite where SA is the surface area and SR is the saturation ratio. The coefficients *a*, *b*, and *c* are fitted to experimental results. Details about the choice of the numerical values of these coefficients are given in Ref. 4 (Section 5.3.2). The original sources for that information are Ref. 39, 40 and 41 for quartz, feldspars and micas respectively. It should be noted that if the same minerals become supersaturated, they do not precipitate back in the rock, but stay in a supersaturated solution because re-precipitation under the same mineralogical form is very slow.

5.1.6 Precipitation of Minerals

Unlike the EQ6 code that senses the phases that should be precipitated, PHREEQC requires the user to specify them. This can be a challenging task in an unknown complex system. This is the reason why the potential minerals for precipitation are chosen with the help of EQ6 runs in similar systems (that is in the invert). They are given in the "EQUILIBRIUM_PHASES" field of the PHREEQC input file (Attachment III - Section III-2). Table 5-11 displays the list of minerals that appeared in EQ6 invert runs (Ref. 4) and that were used in the PHREEQC runs. In addition quartz was not used because it is less soluble than cristobalite, which is the most common silica phase in the rock. Instead, chalcedony was chosen as the $Si0_2$ species (Ref. 4 - Section 6.2). Dolomite was also suppressed because of slow kinetics deposition at 25°C. A sensitivity run was done with dolomite with no effect on the actinide accumulation (see electronic media ***_withDol.xls** - Attachment VIII). In the couple goethite/hematite, only one of these two species is allowed to precipitate in the same run. All runs were done with goethite. One sensitivity run was done with hematite with no effect on the actinide accumulation (see electronic media ***_withHem.xls** - Attachment VIII). The different species of nontronite and saponite represent an approximation of the smectite solid solution.

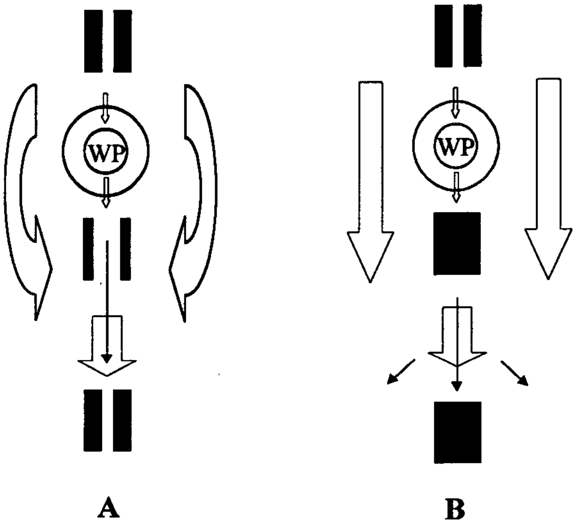
Table 5-11. List of Minerals Allowed to Precipitate in All PHREEQC Runs

GdOHCO3	Saponite-Na
GdPO4:H2O	Nontronite-Ca
Haiweeite	Nontronite-K
Calcite	Nontronite-Mg
Magnesite	Nontronite-Na
Chalcedony	Boehmite
Diaspore	Pu(OH)4
Goethite / Hematite	Ni2SiO4
Clinoptilolite-Ca	Soddyite
Clinoptilolite-K	Schoepite
Clinoptilolite-Na	UO2CO3
Saponite-Ca	UO2(OH)2(beta)
Saponite-H	Na2U2O7
Saponite-K	CaUO4
Saponite-Mg	

5.1.7 Fracture System Effects on Actinide Precipitation

The fracture system is described in the following sections and subsections. The initial geometry of the system as described below is not a function of the source term although after correction for worst-criticality (Section 2.4), the footprint A and cell length l_c are indeed functions of the source term.

Two ideal systems, bounding cases of the general system, will be considered. In one system, Case A, the fracture system underneath the repository is unsaturated. In Case A, local dilution will be the main mechanism and the vertical column where minerals can precipitate is the region directly underneath the footprint of the WP (Figure 5-3). The other system, Case B, results from assuming saturated flow (i.e., $S=1$). Local saturation could occur because of local plugging or constrictions or because there are only very few active fractures. In Case B, dilution can happen only by transverse dispersion laterally and longitudinal dispersion at the front; the cross section of the cone-like region affected by the mineral deposition can be much larger than the footprint of the WP. It is, nevertheless, conservatively assumed that the mineralization is contiguous and convex (Section 2.1).



NOTE: Large arrows represent water flow, simple arrows represent transport.
Size of black rectangles represent the water saturation in the fracture system.

Figure 5-3. Conceptual Model of Cases A and B

Table 5-12 displays the parameters for Cases A and B. For Case A, the surface area per unit fluid volume should decrease with mixing, because the saturation increases, reflecting an increased water volume. However, it is conservative to assume a constant surface area, because an increase in surface area produces either an increase in the mineral deposition (Figure 6-15) or at least no decrease (Figure 6-16). The only difference between cases B1 and B2 is the fracture aperture, 1 mm and 0.2 mm, respectively. The only difference between cases B2 and B3 is the change in surface area due to the B.E.T. formulation.

The initial cell length can be very roughly approximated by considering field data (base case of Chapter 2 of TSPA-VA - Ref. 1) (Assumption 3.17) and can be modified according to the method described in Section 2.4. At the given drip rate of 1.5 liter/year and assuming a constant source term with no Pu decay, the system releases a total of 521 moles (~124 kg) of uranium and 200 moles (~48 kg) of Pu in 2,500 years (pe0a1231 source term). Similarly, in the pw2a231 case, the system releases a total of 21+513=534 moles (~5+122=127 kg) of uranium and 7.2+10.9=18.1 moles (~1.8+2.6=4.4 kg) of Pu in 7,000 years.

Table 5-12. Input Parameters for Cases A and B

Parameter	Case A	Cases B1, B2, and B3
Fracture Aperture 2B (mm)	0.75	1, 0.2, 02
Fracture Intensity I (m/m^2)	10	10
Initial Cross-Sectional A (m^2)[a]	150	3.3, 16.67, 16,67
Drip Rate DR (L/year)	1.5	1.5
Time-step TS (year)	0.67	0.67
Water Velocity (m/year)	0.03	0.03
Saturation Fraction	0.03	1
Surface Area SA (cm^2/L)	1,000,000	20,000 - 100,000 – 1,000,000
Initial Cell Length l_c (m)[a]	0.03	0.03

NOTE: [a] These two parameters are called "initial" because they will be scaled towards conservatism according to Section 2.4.

Details about the geometry of the fractured system (parameters *I* and *2B*) near the repository are given in the following subsections.

5.1.7.1 Fracture Intensity I

Fracture intensity can be studied on surface outcrops, along survey lines in the ESF and in boreholes. The drawback of borehole studies is the inability to tell long fracture trace lengths from short fractures. The fracture intensity I can be expressed in several ways: in #/m (=I1 or fracture frequency), in m/m^2 (=I2) or in m^2/m^3 (=I3). Because most of the fractures are vertical (Ref. 6 Appendix 2 and 3 Tables), I2 and I3 are equivalent. The fracture frequency or I1 is reported from ESF studies as 1.880, 1.810 and 2.10 fracture/meter in TSw34, TSw35, and TSw36 respectively for fractures having a trace length larger than 1m (Ref. 36). About 50% of the fractures are less than 1m long (Ref. 10, Table 7.17) in TSw34. The fracture frequency is corroborated by Fig 7.5, p7-24 of Ref. 10, which shows 4 fractures/m along survey line in TSw34 (for fractures>0.3 in length). Some areas of the ESF are more densely fractured because fracture frequency as high as 1/0.23=4.35 fracture/m for fracture > 1m are sustained for several meters of drift in TSw34 (Ref. 6, Table 13) and can even reach 8 fracture/m (Ref. 6, Fig.4b) in the IFZ (Intensely Fractured Zone) along at least 10 meters of drift.

Fracture frequency (or I1) is only part of the picture as the average trace length needs to be incorporated into the characterization process. Both fracture frequency and average trace length and to a lesser degree fracture orientations come together to compose fracture intensity (or I2). Fracture intensity is more relevant to flow in the system because it describes the fracture porosity in the formation and then gives the permeability from the cubic law. Although fracture intensity can be derived from the parameters mentioned above either analytically or through numerical simulation, direct outcrop or ESF measurements are more accurate. Outcrop measurements are representative of the subsurface as shown by the fracture intensity measurements in the TSw34 formation (Ref. 6, Appendix 2 Tables) and give a fracture intensity of 1.7 m/m^2 for fractures

>1.5m (Ref. 6, p102). Ref. 12 (Table 3 for FSU3 unit equivalent to the TWs34 and Tws35 horizons) mentions I1=1.82 fracture/m and I2=1.22 m/m^2 from ESF studies for fractures greater than 1.5 meters in length. This work uses a conservative fracture intensity of 10 m/m^2 consistent with the highest fracture frequency for fracture > 1m found within the current underground works. The highest fracture density is the most conservative because it increases the porosity available for accumulation of materials per given volume of rock.

5.1.7.2 Fracture Aperture 2B

In the ideal world of parallel plate fractures, the aperture is constant (Assumption 3.6) but real fractures always show aperture variations. For this reason fracture aperture is difficult to measure directly and one measurement may not be representative of the entire fracture. As for all spatially variable properties, they can be characterized by three parameters: an average value, a measure of the range generally through the standard deviation, and a measure of how fast these variations take place, optionally including anisotropy. Chemical transport properties are more sensitive to the last two parameters (see section on dispersivity) than flow. Because of this difficulty, one has to introduce both concepts of hydraulic and solute or tracer aperture. The later is always larger than the former (Ref. 43). Flow tends to be impeded by constrictions (that are measured as hydraulic aperture) while transport is more function of the largest openings where the solute has to diffuse (or disperse).

In the project, borehole pneumatic tests executed on small volumes isolated with packers yield the fracture permeabilities that can be directly translated to hydraulic aperture by application of the cubic law. Ref. 10, Chap.7 provides details and references. Ref. 10 (Table7.12) presents an average hydraulic aperture of 140 μm in Tsw34, 182 μm in Tsw35 and 190 μm in TSw36 whereas Ref. 1 (Chap. 2, p2-40) and Ref. 10 (Chap. 7 p7-18) mention an average hydraulic aperture of 81 μm for TSw34. In this work, the average aperture is assumed to vary in the range 100-1000 μm to take into account the solute transport effect. The highest fracture aperture is the most conservative because it allows the maximum accumulation of materials per given volume of rock for a given fracture intensity.

5.1.7.3 Fracture Network Connectivity

Several arguments suggest that the connectivity of the fracture network is good even at the meter scale (Ref. 10, p7-26). Numerical simulations by Anna and data from two boreholes (Ref. 12, Table 4) suggest that only 30% to 35% of the fractures >1.5m are not connected to the network. Using geometric arguments, Sonnenthal et al. (Ref. 10, p7-25) claim that the network is well above its percolation threshold and likely to form a well-connected network geometrically. More generally, Sweetkind and Williams-Stroud (Ref. 11, p64) establish that the connectivity is high in welded units such as TSw34 to TSw36. On the other hand, computer simulations suggest that only, 18% to 27% (Ref. 23) of these connected fractures are active under ambient conditions. As such, it is legitimate to assume that at the beginning of the flow domain (bottom of the drift) all the fractures contacted by dripping water are active. This is the physical basis for Assumption 3.4, that all the modeled fractures in a WP footprint are conductive to water.

5.1.7.4 Fracture Orientation (dip and directions)

Visual inspection of Fig. 11 in Ref. 12 indicates two main nearly vertical sets of fractures oriented N30E and N115E (that are crossing at an angle of approximately 90°). The fracture cutoff was 1.5 m and only fractures with a length above 1.5 m were studied. The fractures can be modeled as 2 perpendicular sets of vertical fractures. The N30E set is more abundant that the other set.

5.1.8 Molar Volumes

Molar volumes are directly extracted from the EQ6 database data0.nuc.R8a and approximated as explained in the notes to Table 5-13 when data are missing.

Table 5-13. Molar Volumes of Relevant Minerals

Mineral	Molar Volume (cm^3/mole)
Calcite	36.934
Chalcedony	22.688
Clinoptilolite	700[a]
Diaspore	17.76
Haiweeite	322.00
Nontronite	135.00[b]
Pu(OH)4	36[c]
Saponite	140[b]
Soddyite	131.27

NOTES: [a] Calculated from dehydrated mineral=544.7 cm^3/mole and information from data0.
[b] Maximum value for all species.
[c] Calculated from Pu=12 cm^3/mole and PuO2 =23.83 ~24 cm^3/mole.

5.2 EXAMPLES

The constant source terms are taken to be the effluent from the WP (Ref. 4, Section 5.2, EQ6 runs pe0al231 at 2,500 years and pw2al231 at 4.050 and 7,940 years after WP breach, respectively, and Ref. 8 EQ6 run mox03ap2). The source solution flows first through the invert, which is assumed inert for this calculation (Assumption 3.1), and then through the fractured rock, where it reacts with the fracture walls. As it moves along, the effluent water is diluted by the surrounding water, represented in the calculation by the J-13 well water composition (Assumption 3.2). Results of the simulations are presented in a normalized fashion (moles of minerals precipitated per liter of water); they are then scaled according to the geometry of the system as described in Section 2.2 (Eq. 2.21).

Because the PHREEQC results need to be scaled to provide useful information, the same run can be used along with different scalings to produce different realistic cases. The three source terms: pe0al231, pw2al231, and mox03ap2 are treated in a similar way. The "run matrix" is determined by 2 main factors: the amount of Pu decayed (none, half or all) and the surface area of fracture wall per liter of water (from 0 to 1,000,000 cm^2 but mainly 20,000 and 1,000,000 cm^2). The latter is a surrogate for the mass of Si and Ca injected in the solution and needed to form the U minerals typical of this type of environment. Most runs admit a mixing factor of 10% but some use 5%, 20%, or no dilution. A given value of the surface area, i.e., of the product (2B)*S [aperture * saturation], can be interpreted as the surface area of a fully saturated fracture system with a small aperture or as the surface area of a larger unsaturated fracture aperture. When the PHREEQC results are translated to a 3-D system, the cross-sectional area and volume on which to apply the results can vary (Section 2.2). A fully saturated fracture can transport much more water than the very small flux assumed in this study and thus can provide a more compact mineralization than unsaturated fractures. The relative probability of each case still needs to be determined.

6. RESULTS

Three cases are presented for the pe0a1231 source term (Section 6.1): unsaturated fractures with a surface area of 1,000,000 cm^2/liter of water (Case A of Table 5-12) used as a base case and, saturated fractures with surface areas of 20,000, 100,000, and 1,000,000 cm^2/liter of water (Cases B1, B2 and B3 of Table 5-12). The base case is also treated for variable amounts of Pu decay according to Section 5.1.2 (Section 6.2). The pw2a1231 and mox03ap2 source terms are presented as part of the sensitivity analysis in Sections 6.3 and 6.4. All the results presented in this section are extracted from files stored on electronic media (Attachment VIII).

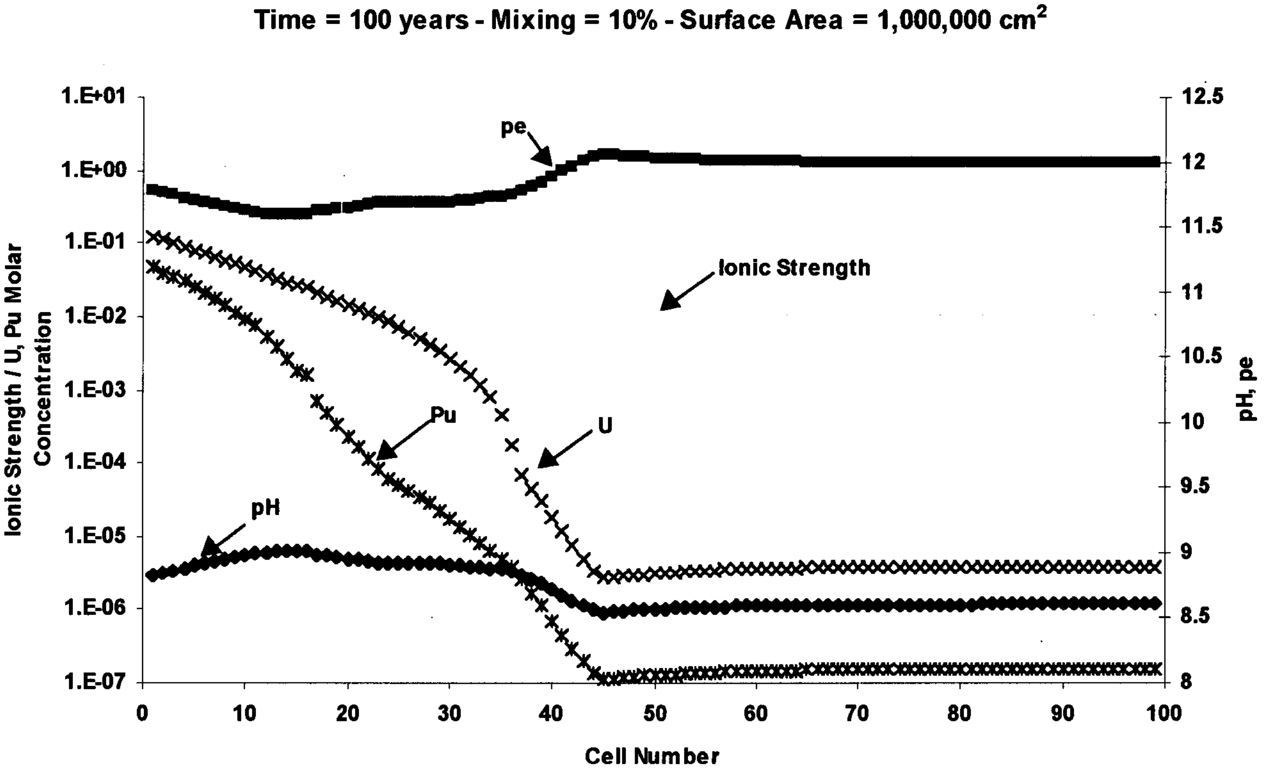
Three major components of the calculation are planned to be updated in the near future: the thermodynamic database, the fracture system geometry, and the percolation/seepage results.

This document may be affected by technical product input information that requires confirmation. Any changes to the document that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System (DIRS) database.

6.1 RESULTS FOR THE EARLY BREACH TIME SCENARIO (PE0A1231 CASE)

6.1.1 Uranium and Plutonium Mineral Precipitation

The results show that dilution is an efficient means to precipitate minerals. A comprehensive analysis is also presented for the base case, Case A, with dilution = 10% and surface area = 1,000,000 cm^2/liter of water. Figure 6-1 and Figure 6-2 display solution parameters and elemental concentrations. The chemical parameters pH and pe show little change, varying from 9 to 8.5 and 11.5 to 12, respectively. The ionic strength ranges from more than 2 orders of magnitude greater than 1 down to approximately 0.01. Figure 6-3 illustrates the linear increase through time of the mass precipitated in a given cell (case B2). This observation justifies the method for correcting for early termination that is described in Section 2.3.



NOTE: The base case is defined by mixing = 10% and surface area = 1,000,000 cm^2. The plateaus of U and Pu concentrations correspond to redissolution of soddyite and Pu(OH)4 after an initial precipitation.

Figure 6-1. Spatial Variation in Chemical Parameters for the Base Case A at 100 Years after Breach Time

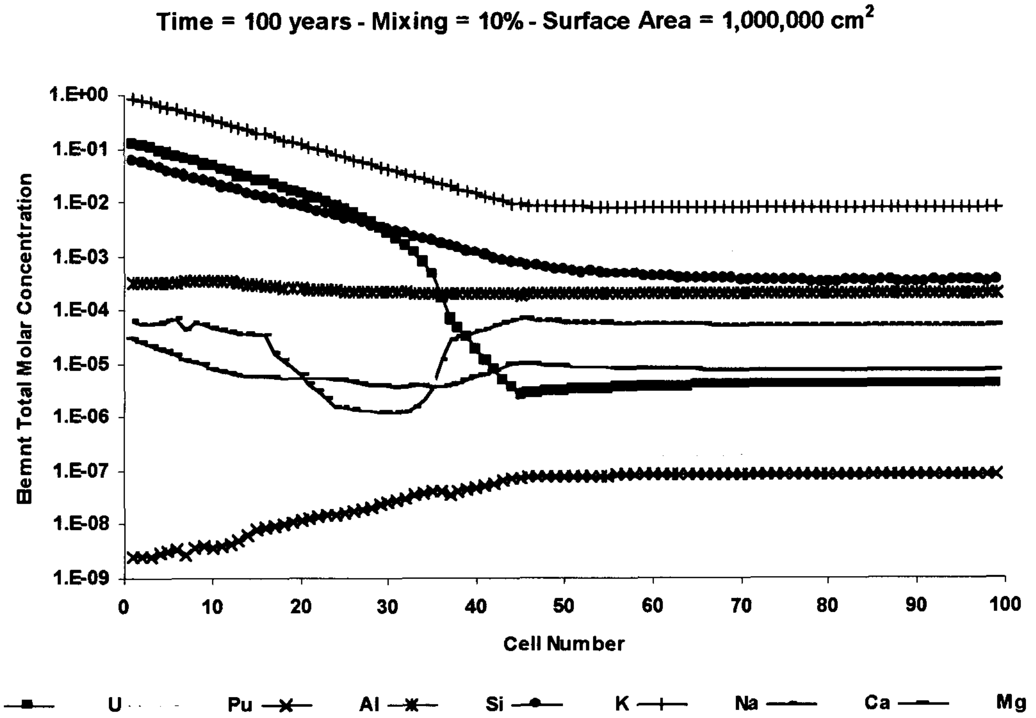


Figure 6-2. Spatial Variation in Aqueous Molar Concentrations for the Base Case A at 100 Years after Breach Time

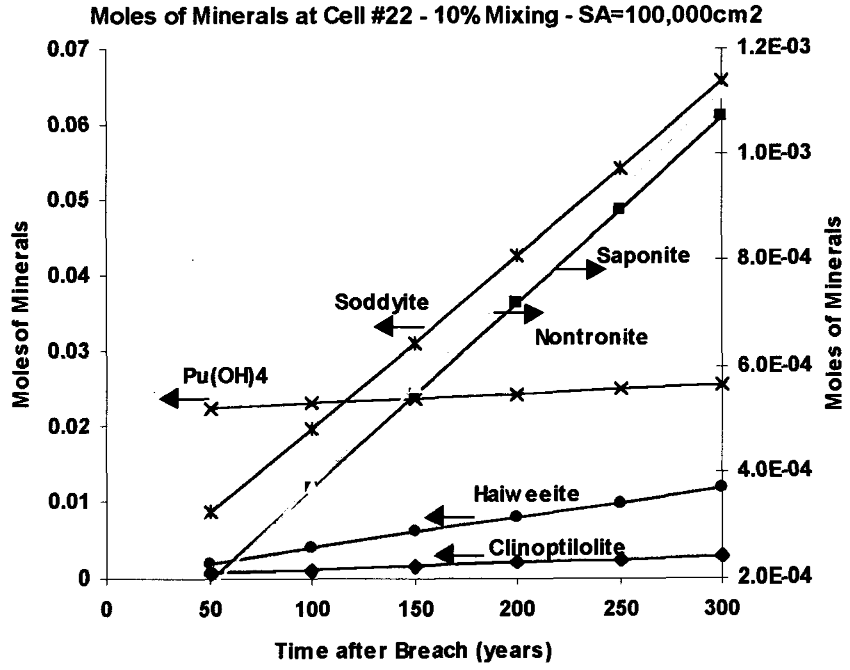


Figure 6-3. Precipitation of Minerals in Cell 22 over Time (SA=100,000 cm^2) for Base Case B2

All the cases use 100 cells. If the assumption (Assumption 3.18) is made that the velocity of 0.03 meter/year is also applicable in the few meters underneath the disposal drifts, then the 100 cells used in the simulation represent 3 meters (they will be scaled later according to Section 2.4). The different cases assume that mineralization is uniformly distributed over all the fractures (Assumption 3.7), that none precipitates in the matrix (Assumption 3.13), that adsorption is lumped into precipitation (Assumption 3.20) and, that there is no remobilization of precipitated minerals (Assumption 3.21).

6.1.1.1 Case A

This case corresponds to unsaturated fractures. The total number of moles precipitated in 2,500 years is extrapolated from the incremental precipitation in 50 years because the precipitation rates are fairly constant through time and thus can be scaled to any duration. The spatial distribution of the actinide mineralization is plotted on Figure 6-4.

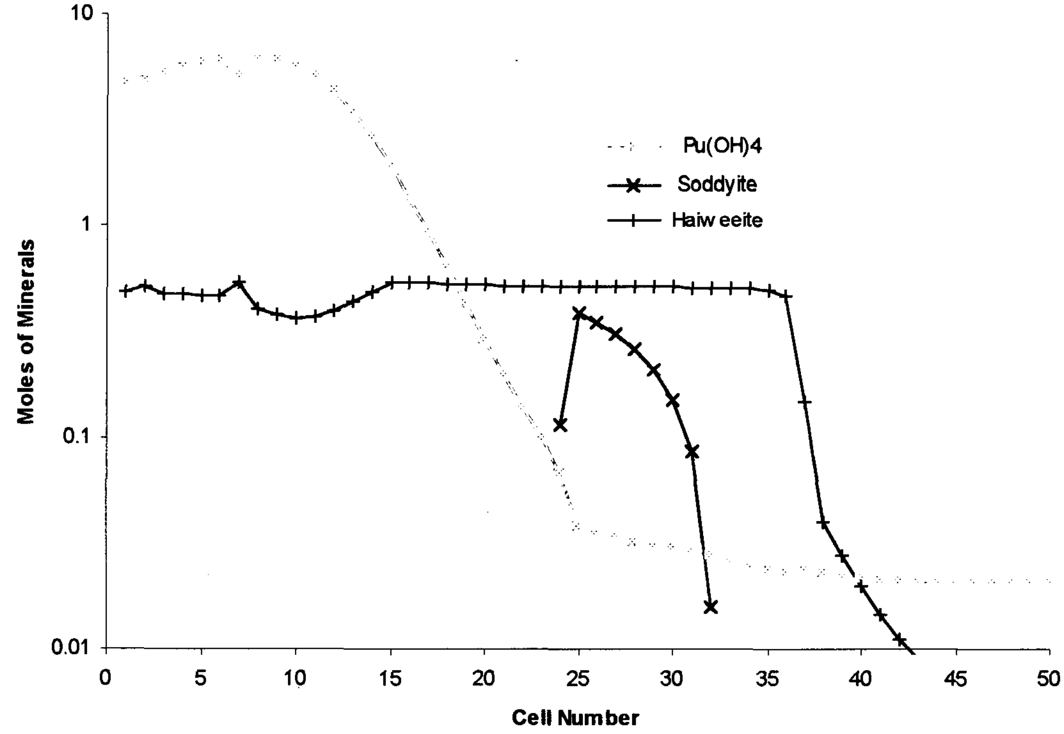


Figure 6-4. Spatial Distribution of Actinide Minerals after 2,500 Years of Precipitation (case A- SA=1,000,000 cm^2)

As mentioned in Section 2.4, if a water velocity of 0.03 m/year is assumed, the cross-sectional area over which infiltration takes place is fairly large (150 m^2), on the other hand, if the true WP footprint (~8 m^2) is used, the mineralization is elongated in the vertical direction. The criticality worst-case corresponds to a cube of dimensions given by Eq. 2.22 with *n* = *40*. This is approximate because the saturation fraction S changes slightly and non-linearly with the footprint A. However, the saturation increases with decreasing footprint, therefore decreasing the surface area per liter of water and the scaling is consequently conservative.

Figure 6-5 displays all the other significant minerals accompanying the actinide deposits. They mainly consist of clays and zeolites. Under conditions where U silicates do not precipitate, chalcedony takes over, similarly calcite and soddyite are exclusive.

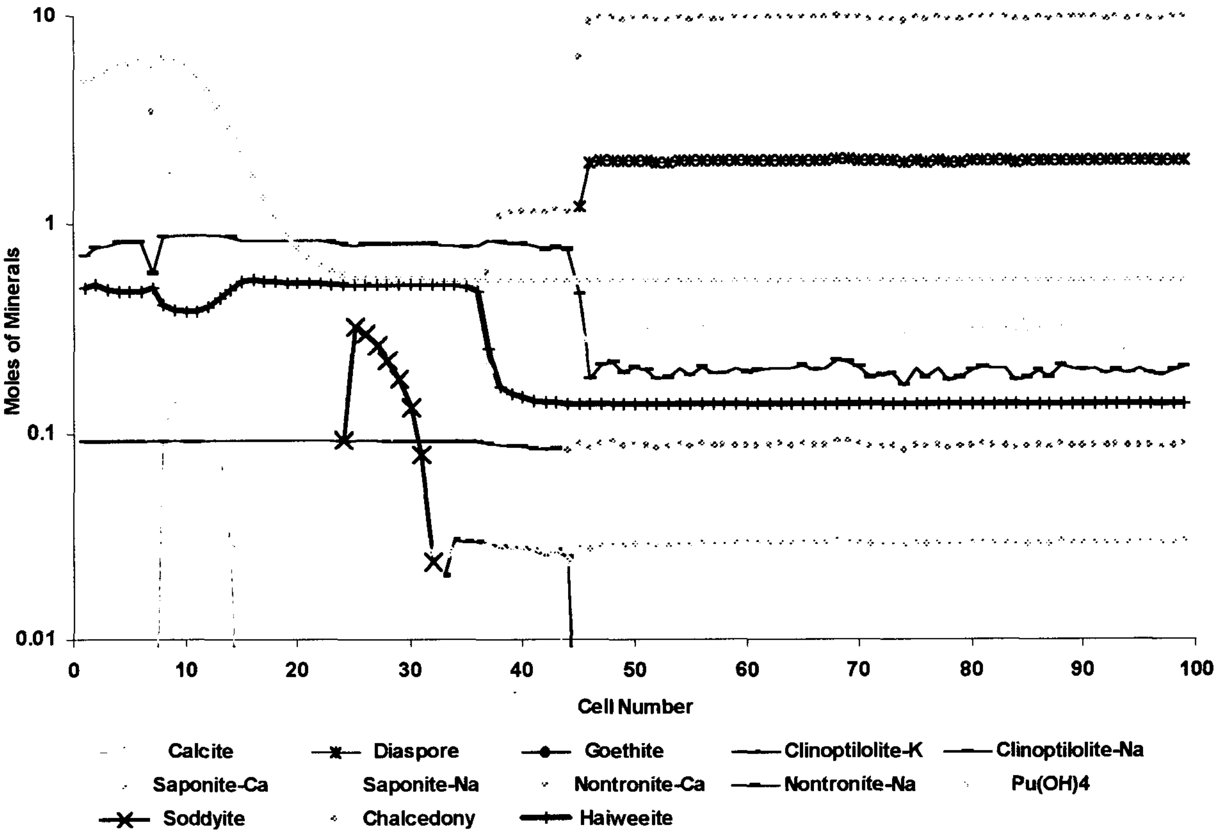


Figure 6-5. Spatial Variations in Mineral Deposits for Case A (SA=1,000,000 cm^2 after 2,500 years)

6.1.1.2 Cases B1 and B2

Case B1 assumes classical dispersion in accordance with the ranges of applicability of the dilution mechanisms provided in Table 2-1. In this case, the treatment can only be qualitative because PHREEQC is fundamentally a one-dimensional model. Figure 6-6 displays the amounts of uranium minerals present in a cell at a given time step for the base case. Haiweeite precipitates initially in cells 60 and beyond but then very slowly dissolves away. Haiweeite mass is smaller than that of soddyite in Case B1 because the surface area available to dissolution is much less, therefore reducing the availability of Ca (from anorthite). Case B2 has plots of similar shapes.

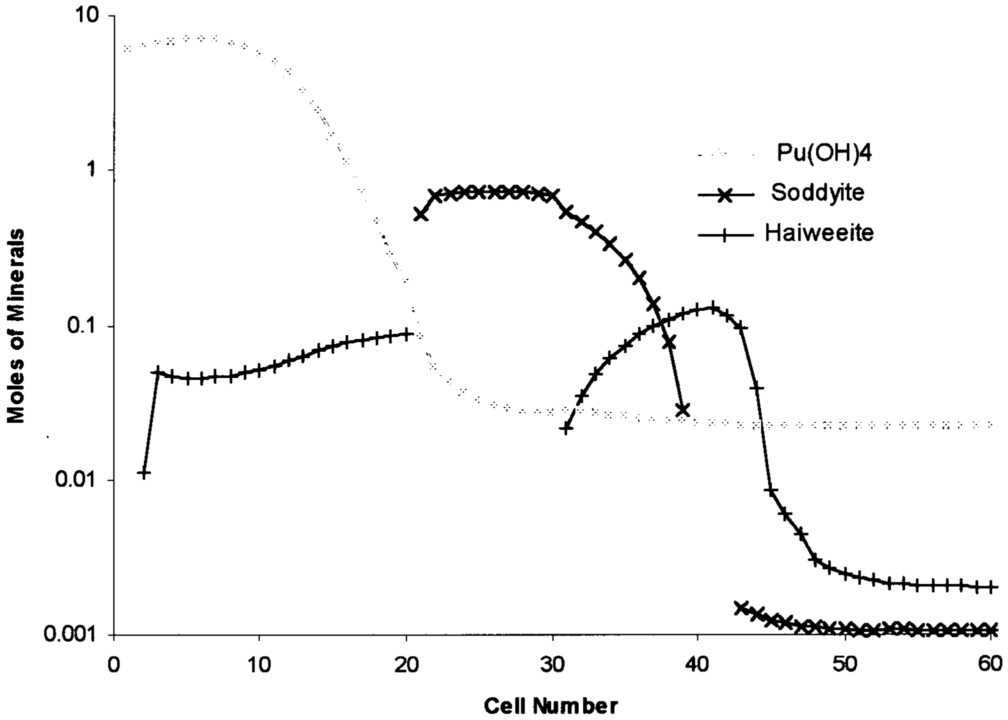


Figure 6-6. Moles of Pu and U Minerals Precipitated as a Function of Cell Number (case B1 - SA=20,000 cm^2 for 2,500 years)

6.1.1.3 Summary of Cases

Table 6-1 summarizes the results.

Table 6-1. Summary of Results (pe0a1231) (accumulation for 2,500 years)

Case A (Unsaturated) SA=1,000,000 cm^2/L	**Case B1 (Saturated) SA=20,000 cm^2/L**	**Case B2 (Saturated) SA=100,000 cm^2/L**	**Case B3 (Saturated + B.E.T.) SA=1,000,000 cm^2/L**
177.9 moles Pu 474.4 moles U # of cells = 40	85.3 moles Pu 23.2 moles U # of cells = 40	84.6 moles Pu 25.3 moles U # of cells = 40	78.5 moles Pu 39.7 moles U # of cells = 40
A= 5.85 x 5.85 m^2 l_c= 0.146m	A= 1.6 x 1.6 m^2 l_c = 0.04 m	A= 2.72 x 2.72 m^2 l_c = 0.068 m	A= 2.72 x 2.72 m^2 l_c = 0.068 m
Average Density: 0.9 moles/m^3 Pu 2.3 moles/m^3 U	Average Density: 20.8 moles/m^3 Pu 5.7 moles/m^3 U	Average Density: 4.2 moles/m^3 Pu 1.3 moles/m^3 U	Average Density: 3.9 moles/m^3 Pu 2.0 moles/m^3 U

The higher total number of moles in the unsaturated case (case A) is the consequence of the choice of considering the mineralization front being in contact with the drift. As the front moves downwards, the trail it leaves on the sides will increase the mass of mineralization. Both mechanisms will end up precipitating most of the actinides present in the WP water.

If the results for the saturated results are plotted on the same graph and the uranium density in moles/m^3 is used (Figure 6-7), it appears that the actinide density is smaller for higher surface areas.

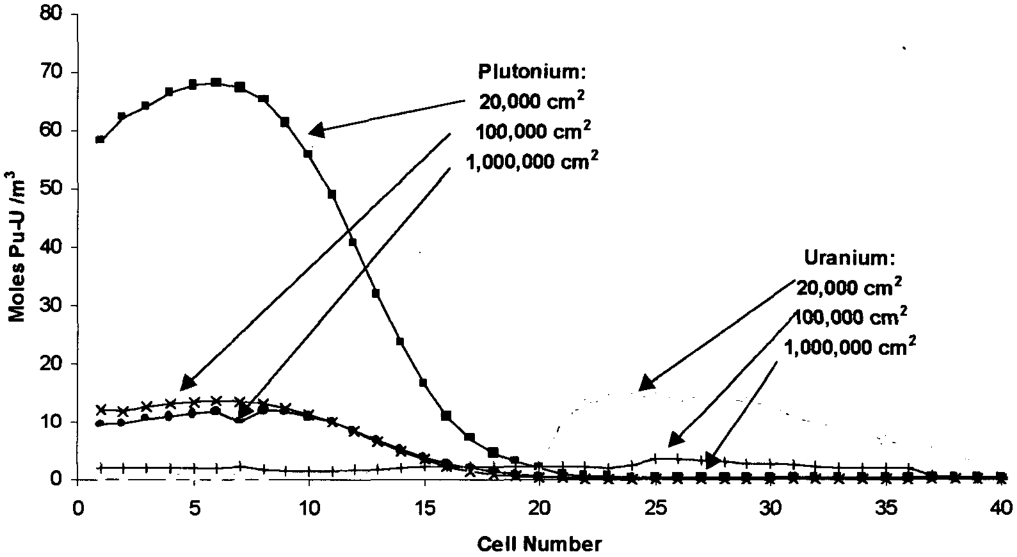


Figure 6-7. Spatial Variation in Actinide Density for the Different Saturated Cases (B1, B2, and B3)

If the actinide accumulation is further scaled according to Sections 2.1.3 and 2.4 to yield their true spatial accumulation (Figure 6-8 and Figure 6-9) so that unsaturated and saturated cases can be compared, case A comes out with a much higher density. It should be noted again that saturated cases represent early stages of the front when the mineralization is still largely in contact with the bottom of the drift.

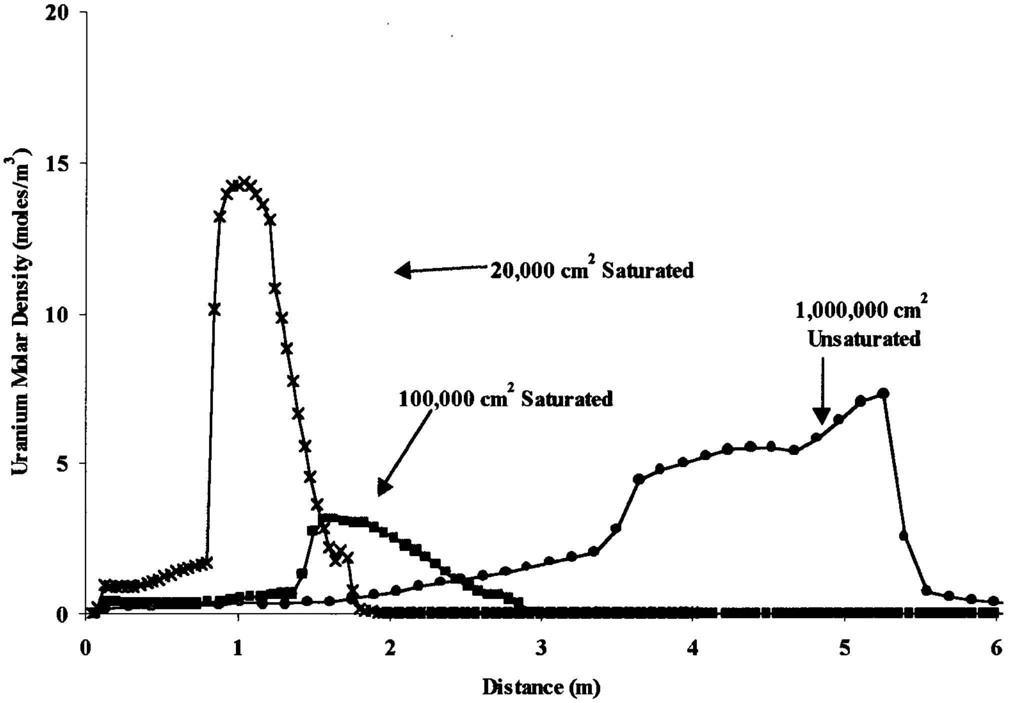


Figure 6-8. Uranium Accumulation Molar Density

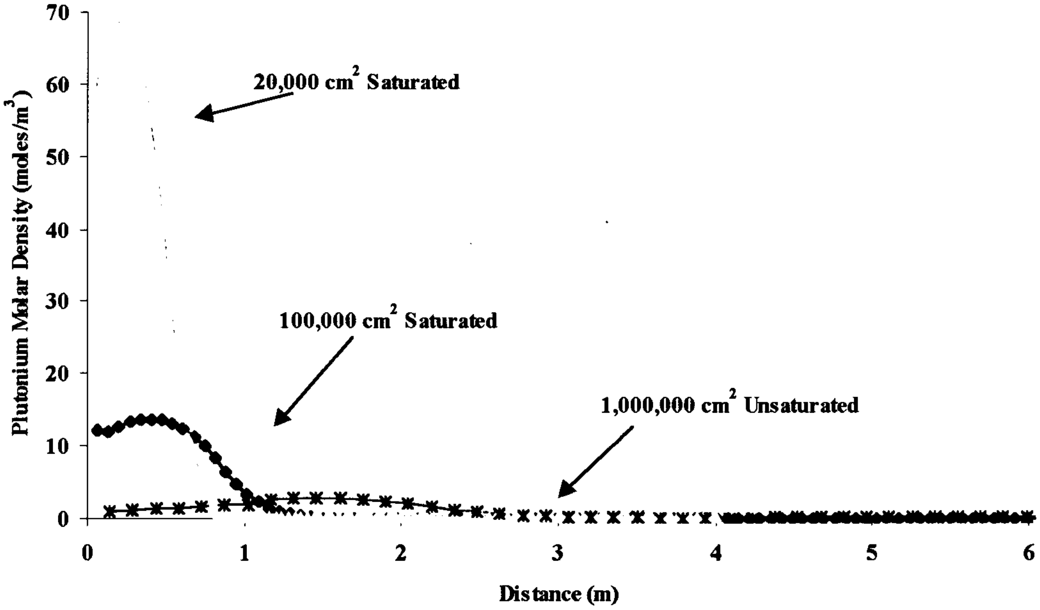


Figure 6-9. Plutonium Accumulation Molar Density

6.1.2 Precipitation of Other Minerals

Figure 6-10 and Figure 6-11 show that the history of mineral deposition is complex. Deposition only occurs over limited ranges of dilution. Because other minerals also take space in the fracture opening, it is important to check that all minerals occupy a volume smaller than the available fracture space. Figure 6-10 can be misleading because although mineral deposits occupy almost 100% of the water space, the water itself occupies only a very small fraction of the fracture space (low saturations) leaving plenty of space for additional precipitation.

Using molar volumes from Table 5-13, the maximum volume occupied by the precipitated minerals is less than 200 cm^3 /liter of water (Figure 6-12), i.e., less than 20% of the fracture space is occupied by the new minerals in the saturated case. The two other curves represent unsaturated cases whose saturation is 10% at most (see file **sat_calc.xls** - Attachment VIII), i.e., a maximum of ~1000 cm^3 /liter of water x 0.1liter of water / liter of fracture volume = ~100 cm3 / liter of fracture volume = ~10% of fracture volume at most. Similarly in the 500,000 cm^2 case, only about 6% of the fracture volume is occupied by minerals. In addition, the increase in fracture volume by mineral dissolution is not taken into account.

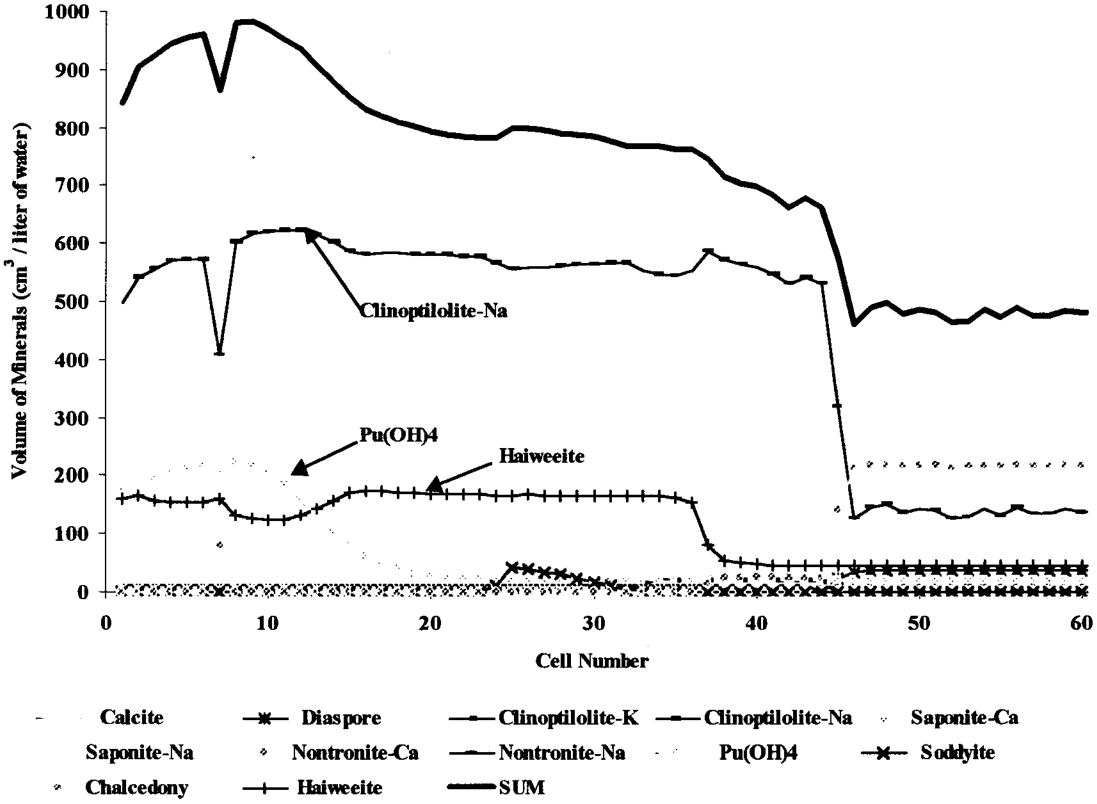


Figure 6-10. Volumes of Minerals as a Function of Cell Number for Case A (SA=1,000,000 cm^2)

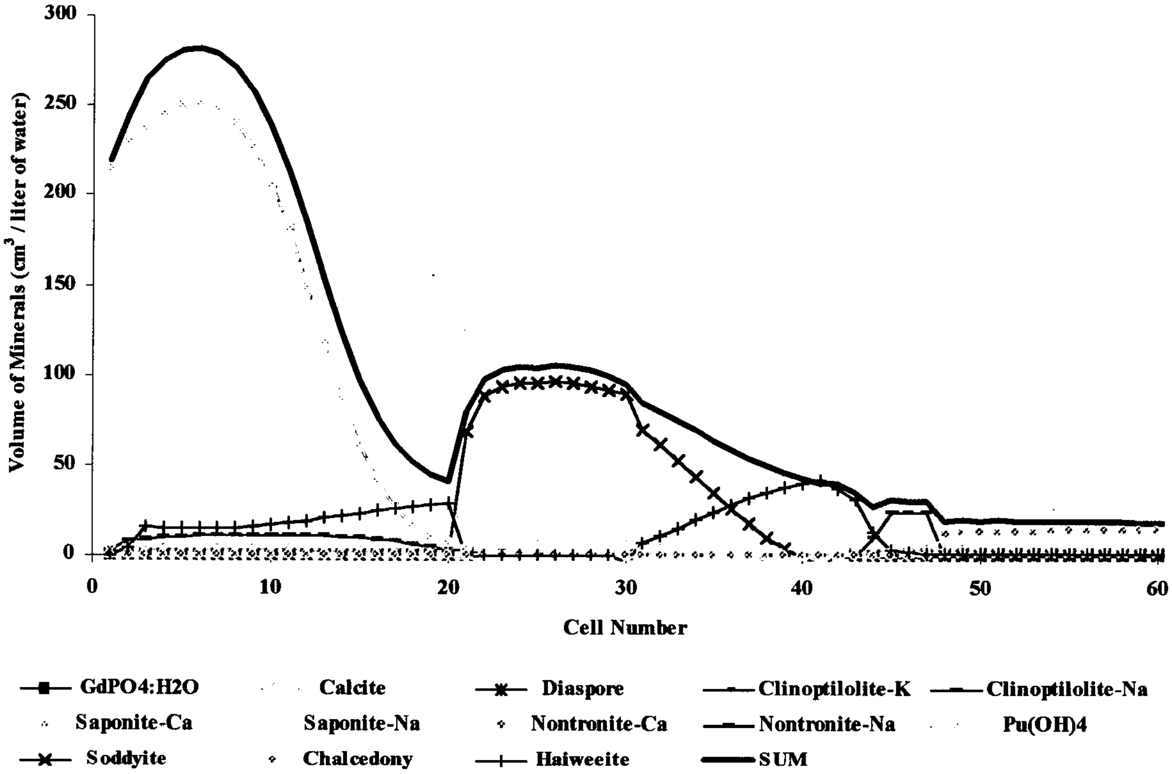


Figure 6-11. Volumes of Minerals as a Function of Cell Number for Case B1 (SA=20,000 cm^2)

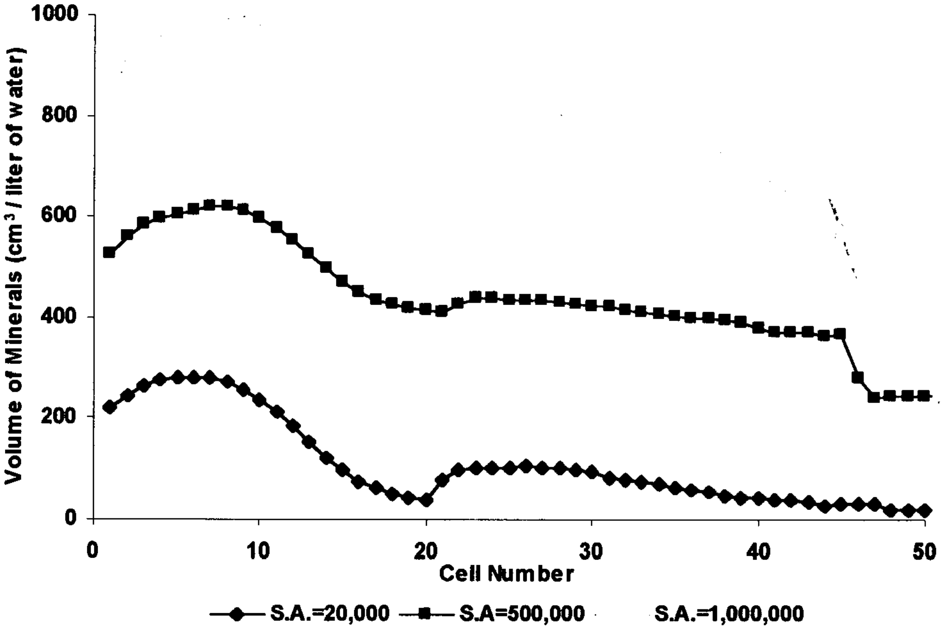


Figure 6-12. Comparison of Volume of Minerals Produced as a Function of the Wall Surface Area / Liter of Water

6.1.3 Sensitivity Evaluations

Sensitivity analyses were done on the base case B1 (SA=20,000 cm2, source term = p0a1231) by varying the dilution factors (5, 10 and 20%), the rock surface areas (from 0 to 1,000,000 cm^2 /liter of water), the thermodynamic database, and by using variable mixing and multiple source terms. It is concluded that the total actinide accumulation is not very sensitive to any of the aforementioned factors except sharp decrease with low or no dilution.

6.1.3.1 Dilution Factors

Figure 6-13 and Figure 6-14 show that even if the total amount of precipitation is similar for different levels of dilution, the actinide density increases with dilution.

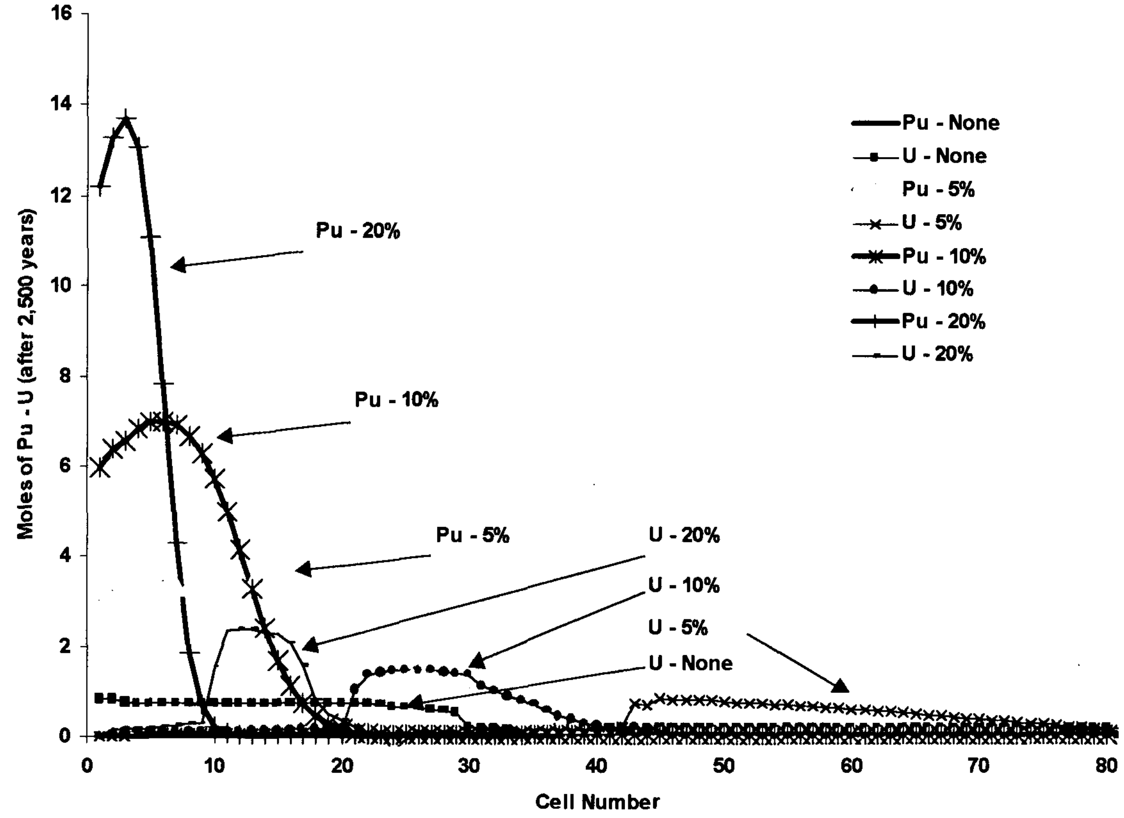


Figure 6-13. Sensitivity Analysis for Dilution Factors (SA=20,000 cm^2)

Figure 6-14 also illustrates that with no dilution, little plutonium and uranium is precipitated. A dilution factor between 5 and 10% is the most conservative. For practical reasons (number of runs done), the value of 10% was picked as representative and conservative.

Figure 6-15 shows that uranium accumulation increases with surface area mainly because of the increased availability of Si and Ca present in the U minerals. Such high surface area without dilution is only possible with very high B.E.T. surface area. These high B.E.T. surface areas, even if present at the early stages of precipitation, are unlikely to stay high because of the accumulation itself that would plug the small pores initially responsible for them.

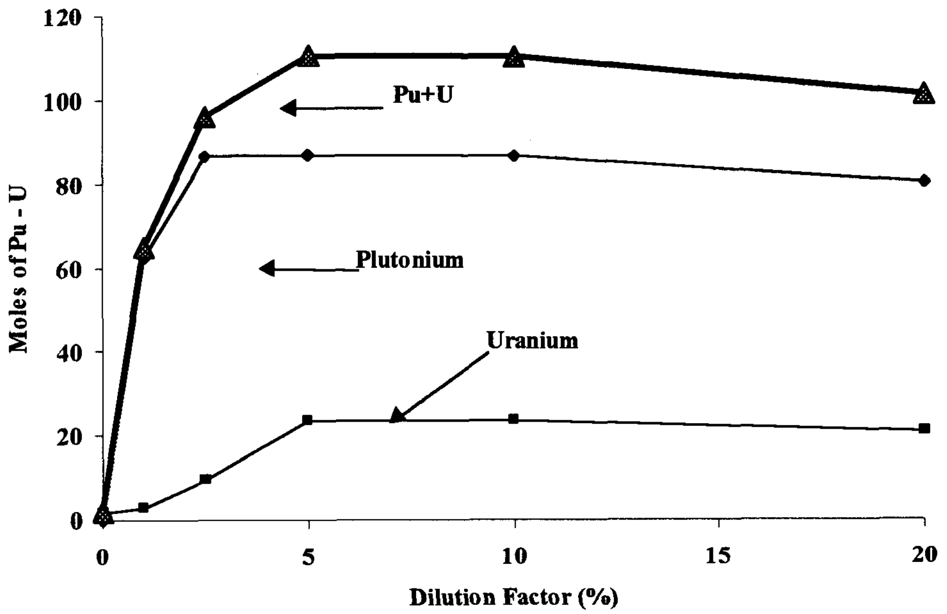


Figure 6-14. Total Number of Moles of Actinide Precipitated as a Function of Dilution (SA=20,000 cm^2)

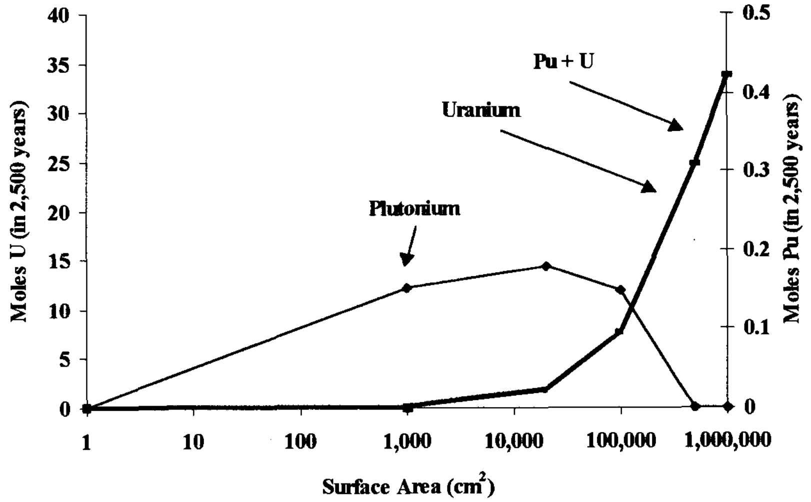


Figure 6-15. Total Number of Moles of Actinide Precipitated as a Function of Surface Area (NO dilution)

6.1.3.2 Surface Areas

Surface areas have little influence on the total amount deposited except for high values where the U accumulation increases (Figure 6-16 and Figure 6-17). However, the latter case has the lowest density (Figure 6-7).

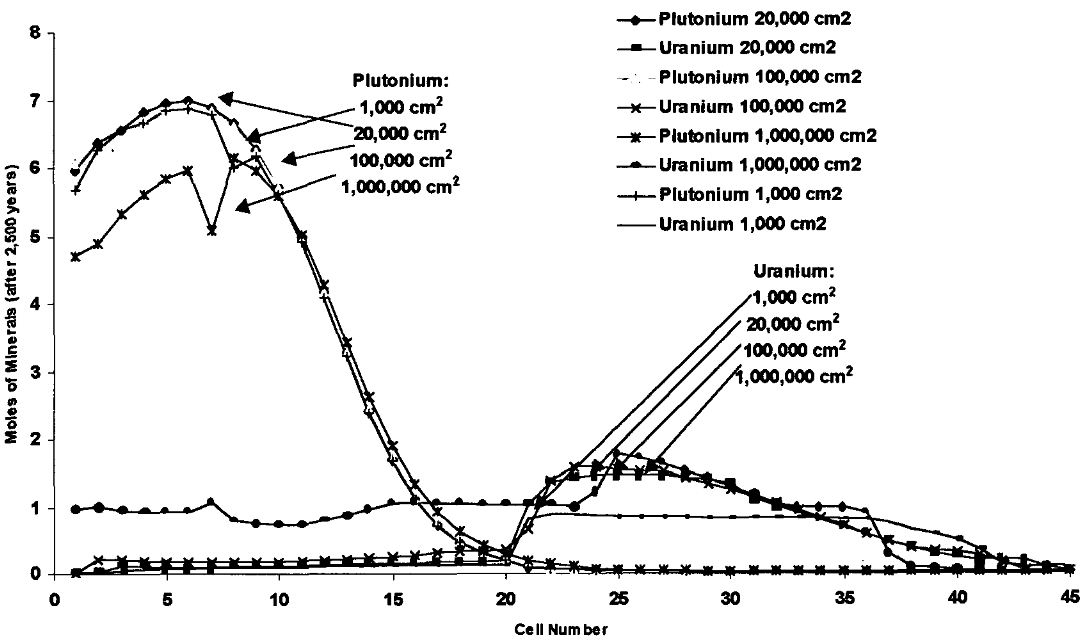


Figure 6-16. Sensitivity Analysis for Surface Areas (dilution factor of 10%)

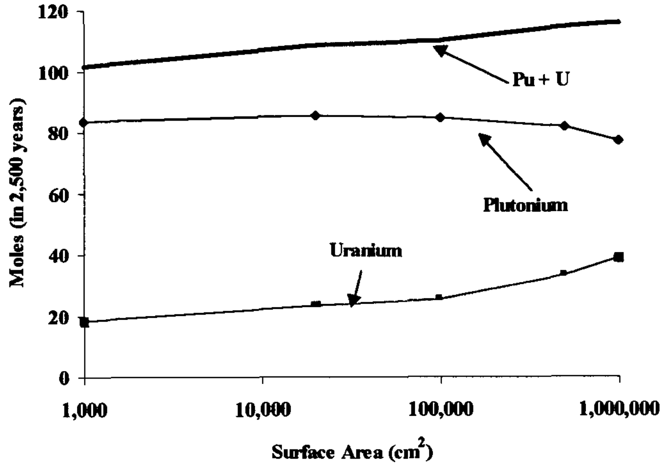
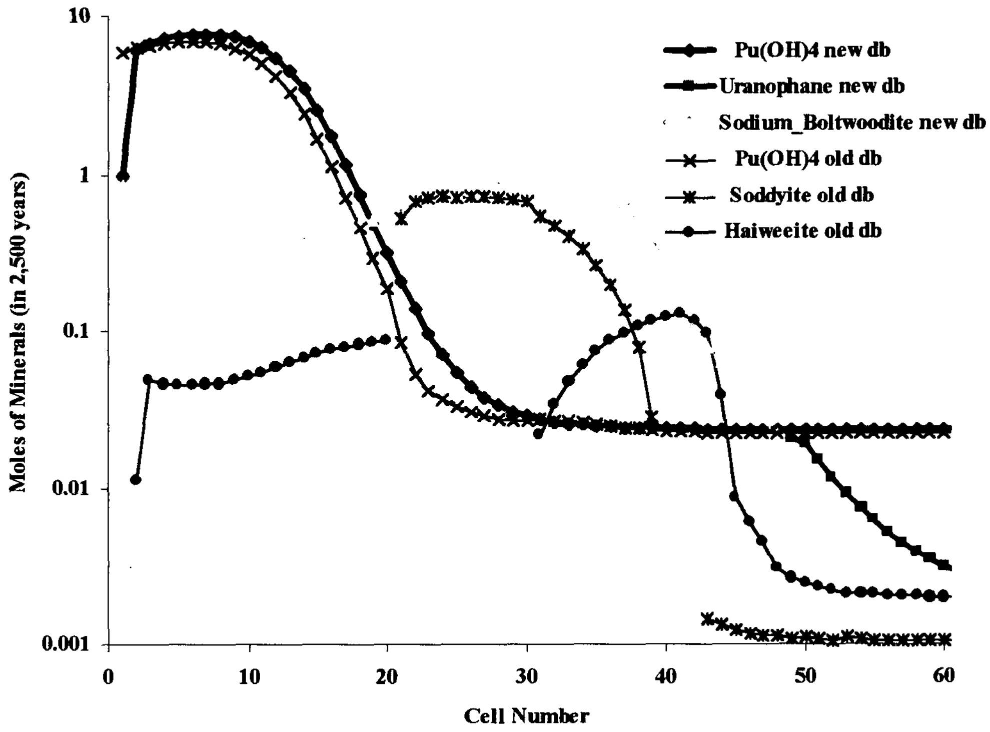


Figure 6-17. Total Number of Moles of Actinide Precipitated as a Function of Surface Area (dilution factor of 10%)

6.1.3.3 Databases

Changes to the thermodynamic database (see Section 5.1.4 for details) may have a big impact on the final results. To test the sensitivity of the results presented in this report (that use the data0.nuc.R8a database), a few cases were executed with a preliminary version (data0.nuc.R8s) of the database that will ultimately be used (data0.ymp).

The results differ in the details (Figure 6-18 and Figure 6-19); in particular, uranium minerals are more consistently high, but they agree with each other (Table 6-2). Soddyite $[(UO_2)_2SiO_4{:}2H_20]$ and haiweeite $[Ca(UO_2)_2(Si_2O_3)_3{:}5H_20]$ are substituted by uranophane $[Ca(UO_2)(SiO_3)(OH)_2{:}5H_20]$ and Na-boltwoodite $[NaUO_2SiO_4H_30{:}H20]$. The "new" database predicts a slightly higher accumulation for Pu and about twice as much U. It should be noted that the source term used in these runs was also obtained by running EQ6 with that same "new" database.



NOTE: db stands for database.

Figure 6-18. Pu - U Minerals Accumulation for the Old (data0.nuc.R8a) and New (data0.nuc.R8s) Databases (SA=20,000 cm^2)

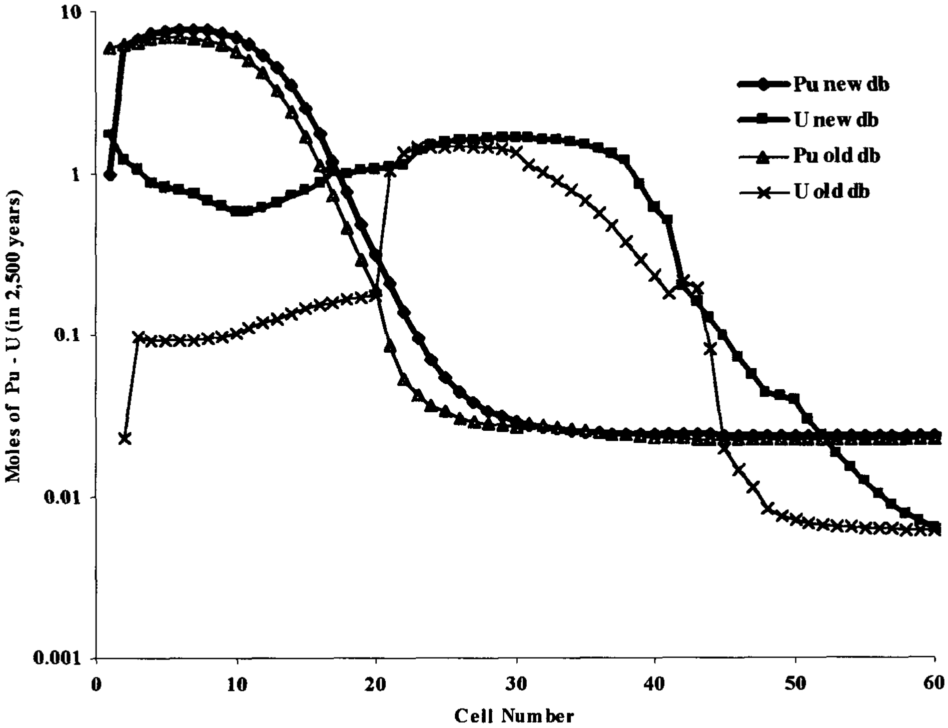


Figure 6-19. Actinide Accumulation for the Old (data0.nuc.R8a) and New (data0.nuc.R8s) Databases (SA=20,000 cm^2)

Table 6-2. Summary of Results for Different Databases (accumulation starts 2,500 years after breach time for 2,500 years)

SA=20,000 cm^2/L Data0.nuc.R8s ("New" database)	**SA=20,000 cm^2/L Data0.nuc.R8a ("Old" database)**
94.6 moles Pu 46.8 moles U # of cells = 40	85.3 moles Pu 23.2 moles U # of cells = 40
A= 1.6 x 1.6 m^2 l_c= 0.04 m	A= 1.6 x 1.6 m^2 l_c= 0.04 m
Average Density: 23.1 moles/m^3 Pu 11.4 moles/m^3 U	Average Density: 20.8 moles/m^3 Pu 5.7 moles/m^3 U

6.1.3.5 Multiple Source Terms

One run was done using a variable source term mimicking the time-varying EQ6 source terms. The variable source terms were approximated by a step function. Each step starts midway between the current and previous EQ6 times and ends similarly midway between the current and next EQ6 times as displayed on the hypothetical case of Figure 6-20.

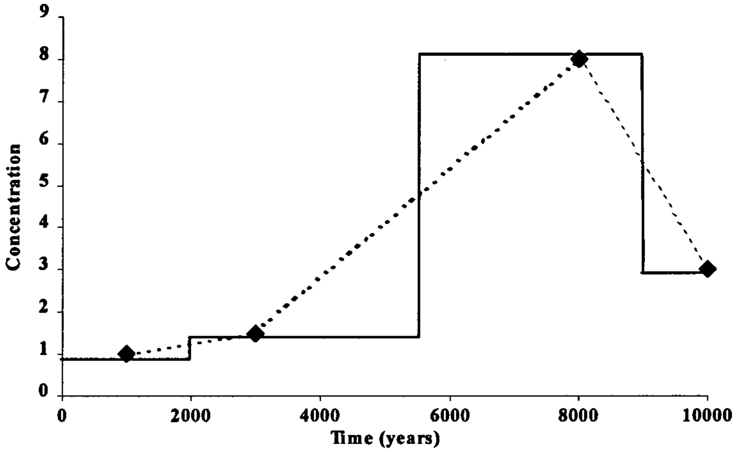


Figure 6-20. Hypothetical EQ6 Source Terms and Corresponding PHREEQC Step Function

Because the time step used (20 years) is different from the residence time (0.67 years), the extra scaling described in Section 2.2 was used. Distortions are introduced because of this scaling and results should only be considered informative. The surface area used in this case is 900,000 cm^2 comparable to the 1,000,000-cm^2 case. Figure 6-21 shows that accumulations at ~4,000 years after breach time follow the same pattern. The plateaus of the Pu(OH)4_Multi curve beyond cell 25 and of the Haiweeite_Multi curve beyond cell 40 are likely due to PHREEQC artifacts and should be disregarded.

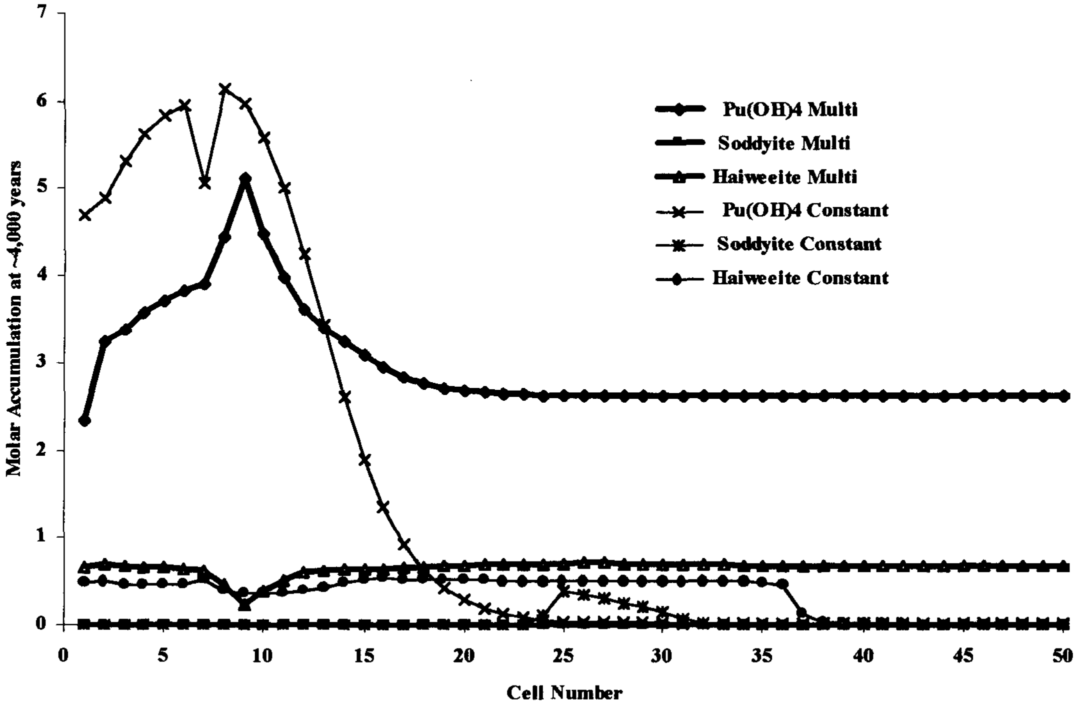


Figure 6-21. Result Comparison of Time-Varying and Constant Source Term (at ~4,000 years)

However, as displayed in Figure 6-22, accumulation keeps increasing to about 6,000 years. However, the sum of the first 31 cells yields a total Pu accumulation of 48.5 moles and the sum of the first 51 cells yields a total U accumulation of 11.5 moles compared to the 78.5 and 39.7 moles of Pu and U, respectively, for the constant source term case (Table 6-1). Figure 6-23 and Figure 6-24 display actinide mineral accumulation through space and time (Note the difference in the vertical scale). The sharp peak of $Pu(OH)_4$ of Figure 6-23 corresponds to the peak on Figure 6-22. However, the plateaus in higher cell numbers in all the three figures should be disregarded.

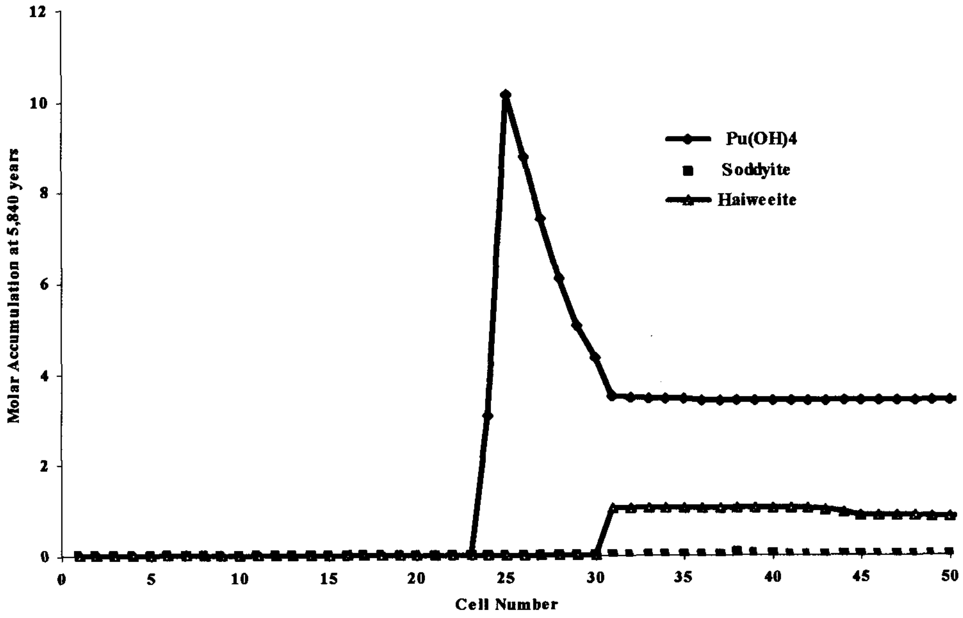


Figure 6-22. Maximum Actinide Accumulation with Variable Source Term (at time 5,840 years)

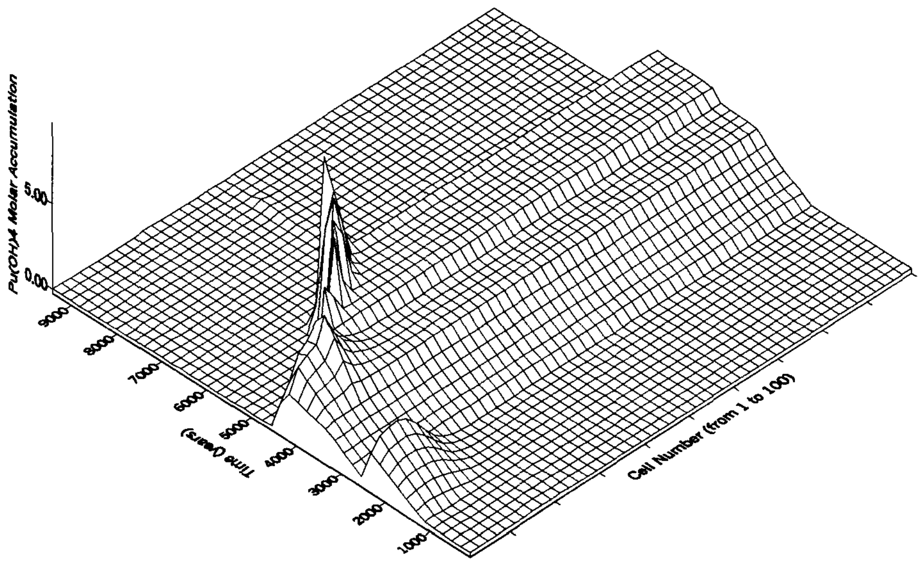


Figure 6-23. Accumulation of $Pu(OH)_4$ Through Time (left axis) and Space (bottom axis) for the Variable Source Term

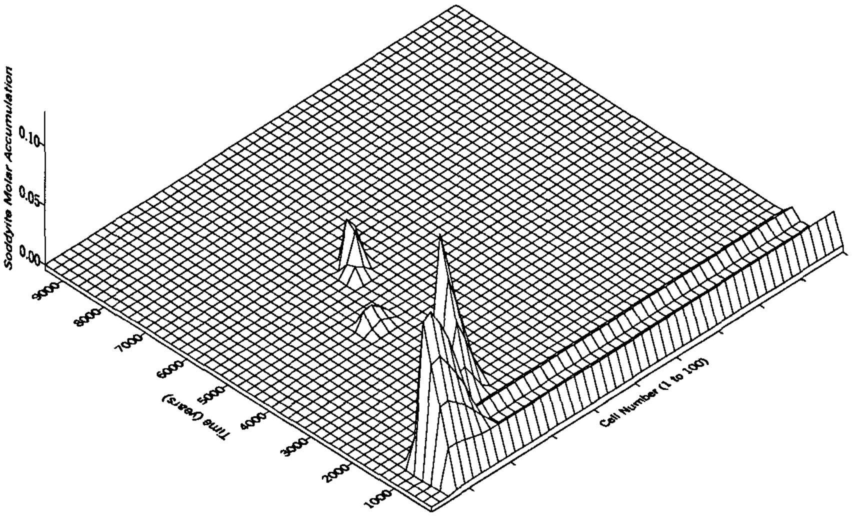


Figure 6-24. Accumulation of Soddyite Through Time (left axis) and Space (bottom axis) for the Variable Source Term

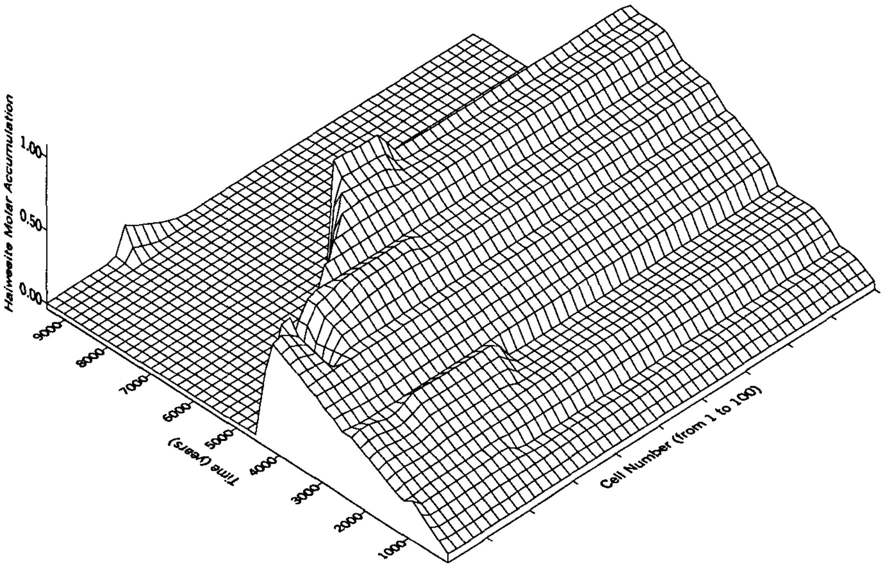


Figure 6-25. Accumulation of Haiweeite Through Time (left axis) and Space (bottom axis) for the Variable Source Term

6.2 RESULTS FOR THE MEDIUM BREACH AND LATE BREACH TIME SCENARIOS

Results for medium and late breach times are summarized in Table 6-3 and Table 6-4 for 20,000 and 1,000,000 cm^2 respectively. Figure 6-26 and Figure 6-27 plot the results as a function of the cell numbers for the case 1,000.000 cm^2. Figure 6-28 and Figure 6-29 compare the results for different Pu decays. The surface area has little effect on the Pu precipitation (42.8% for 20,000 cm^2 vs 30.3% for 1,000,000 cm^2) but has a larger effect on the U precipitation (4.5% vs 7.5%) because of the extra Si released into the system, needed to precipitate uranyl silicates, the main form of U precipitation.

Table 6-3. Summary of Results for Case pe0a1231 for Different Pu Decay (SA=20,000 cm^2)

	Pu all Pu	U all Pu	Pu half Pu	U half Pu	U no Pu
Total Accumulation in the first 50 cells (moles)	85.3	23.2	30.2	36.4	57.4
Percentage of Total Actinide mass going through the system	42.8	4.5	30.3	5.9	8.0
Total Actinide in the first 50 cells (moles)	108.6		66.6		57.4

Table 6-4. Summary of Results for Case pe0a1231 for Different Pu Decay (SA=1,000,000 cm^2 - saturated)

	Pu all Pu	U all Pu	Pu half Pu	U half Pu	U no Pu
Total Accumulation in the first 50 cells (moles)	77.0	39.0	26.8	51.2	124.5
Percentage of Total Actinide mass going through the system	38.6	7.5	26.9	8.4	17.3
Total Actinide in the first 50 cells (moles)	116.1		79.0		124.5

Table 6-5. Summary of Results for Case pe0a1231 for Different Pu Decay (SA=1,000,000 cm^2 - unsaturated)

	Pu all Pu	U all Pu	Pu half Pu	U half Pu	U no Pu
Total Accumulation in the first 50 cells (moles)	177.9	474.4	56.4	575.9	630.4
Percentage of Total Actinide mass going through the system	89.3	91.6	56.6	92.7	87.5
Total Actinide in the first 50 cells (moles)	652.3		632.2		630.4

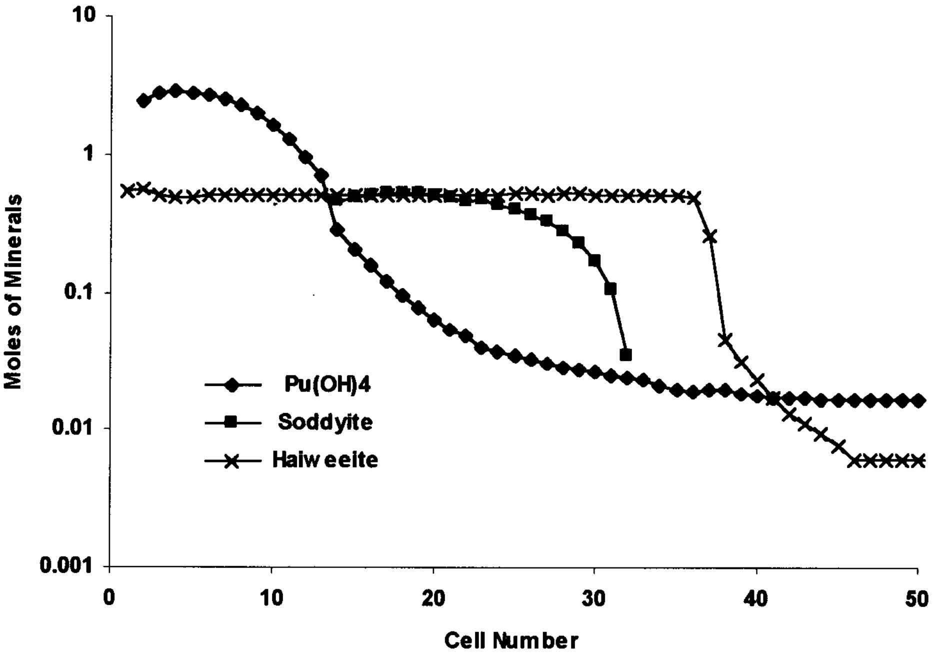


Figure 6-26. Actinide Mineral Precipitation after 2,500 Years (SA=1,000,000 cm^2- half Pu decayed)

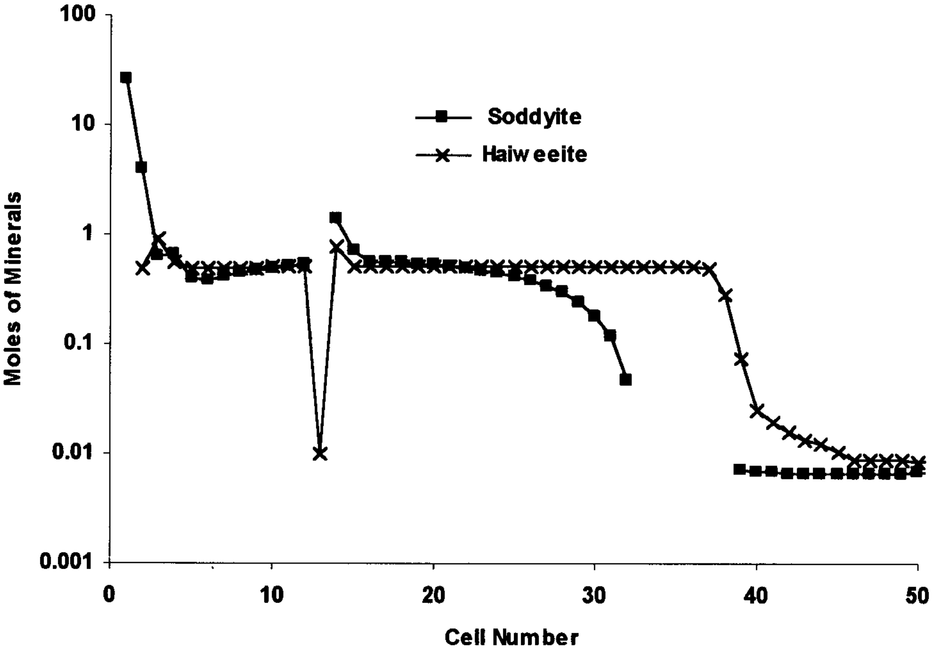


Figure 6-27. Actinide Mineral Precipitation after 2,500 Years (SA=1,000,000 cm^2- all Pu decayed)

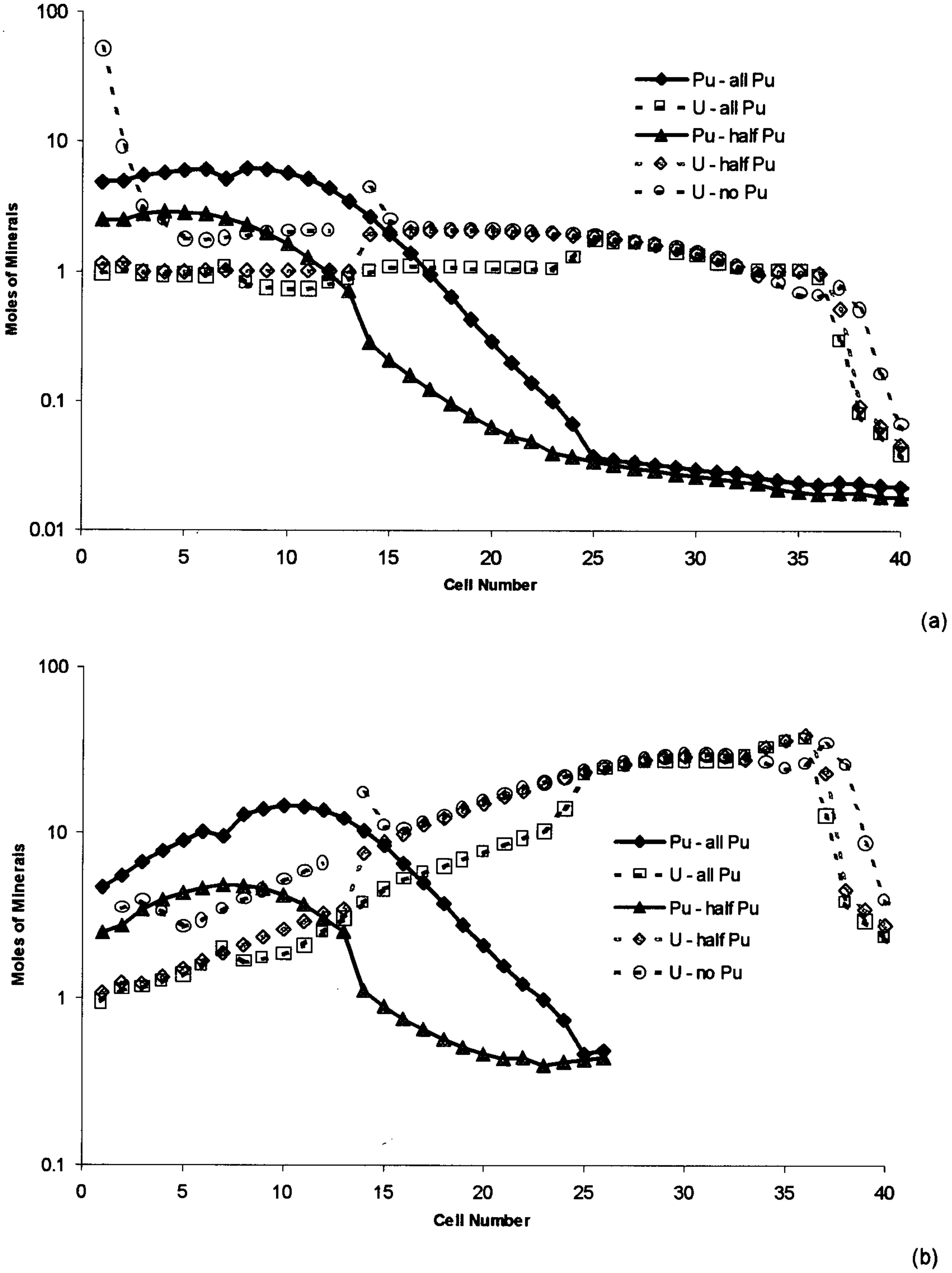


Figure 6-28. Actinide Precipitation as a Function of the Cell Number and Pu Decay (after 2,500 years of deposition - case pe0a1231): (a) 1,000,000 cm^2 Saturated (b) 1,000,000 cm^2 Unsaturated

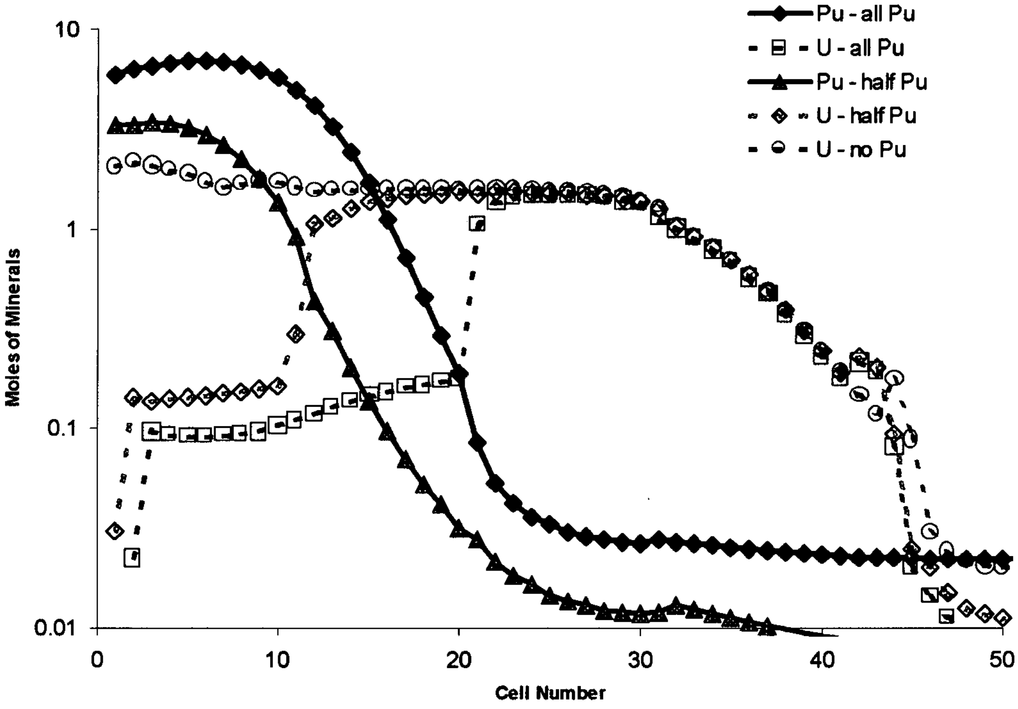


Figure 6-29. Actinide Precipitation as a Function of the Cell Number and Pu Decay (after 2,500 years of deposition - case pe0a1231 - 20,000 cm^2)

General results mimic results from Section 6.1.

6.3 RESULTS FOR PW2A1231 SCENARIOS

An analysis similar to the ones in Sections 6.1 and 6.2 was also performed with the source term pw2a1231. The saturated cases with surface area of 20,000 cm^2 are likely to be closer to criticality than the unsaturated case with surface area of 1,000,000 cm^2 because they are less spread out. The different cases are briefly presented in Table 6-6 and Table 6-7.

Table 6-6. Summary of Results for Case pw2a1231 for Different Pu Decay (SA=20,000 cm^2)

	Pu all Pu	U all Pu	Pu half Pu	U half Pu	U no Pu
Total Accumulation in the first 50 cells (moles)	0.32	8.07	0.12	8.20	8.32
Percentage of Total Actinide mass going through the system	1.8	1.6	1.3	1.6	1.6
Total Actinide in the first 50 cells (moles)	8.39		8.32		8.32

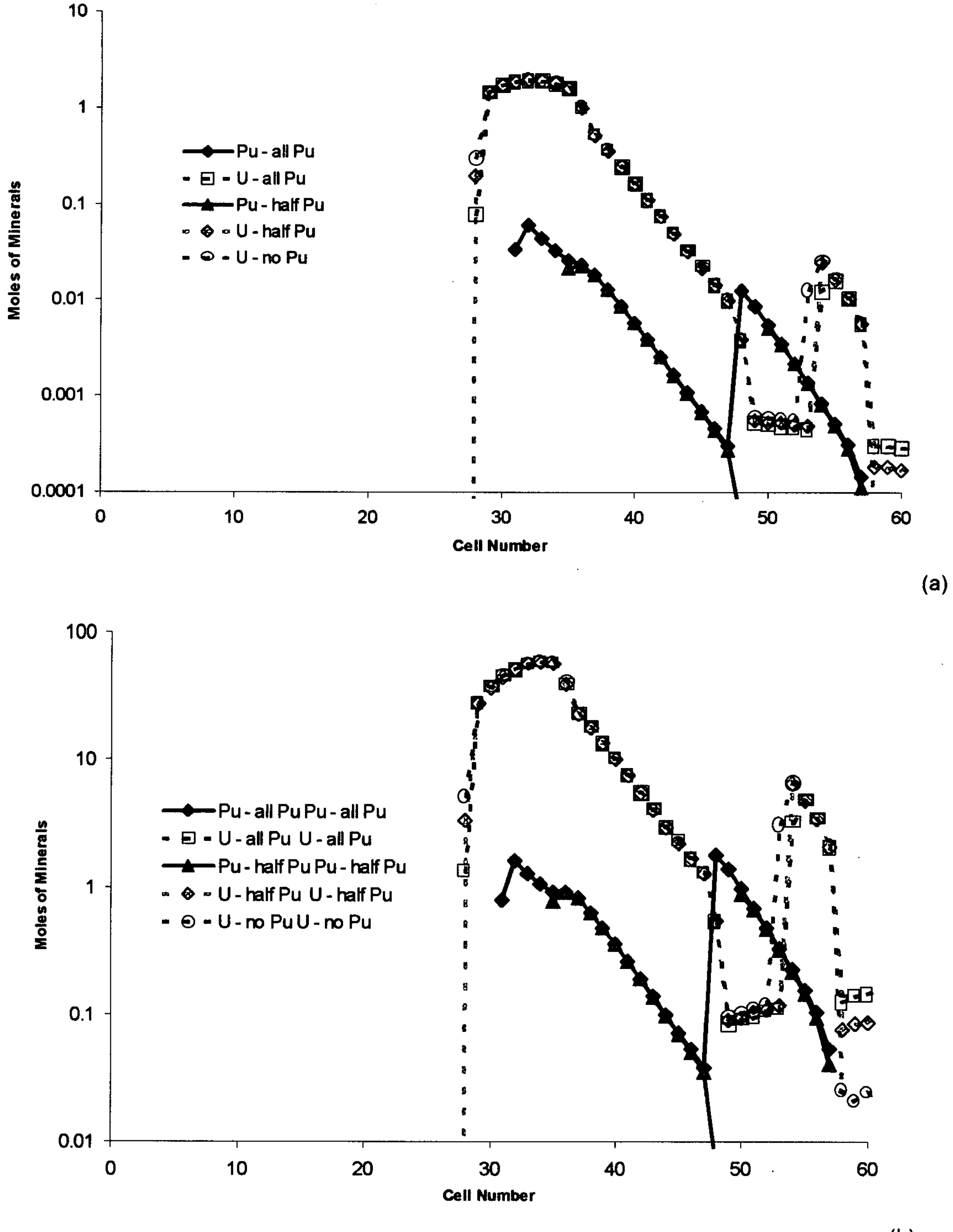
Table 6-7. Summary of Results for Case pw2a1231 for Different Pu Decay (SA=1,000,000 cm^2 - saturated)

	Pu all Pu	U all Pu	Pu half Pu	U half Pu	U no Pu
Total Accumulation in the first 50 cells (moles)	0.3	15.0	0.1	15.2	15.4
Percentage of Total Actinide mass going through the system	1.7	2.9	1.3	2.5	2.9
Total Actinide in the first 60 cells (moles)	15.3		15.3		15.4

Table 6-8. Summary of Results for Case pw2a1231 for Different Pu Decay (SA=1,000,000 cm^2 - unsaturated)

	Pu all Pu	U all Pu	Pu half Pu	U half Pu	U no Pu
Total Accumulation in the first 50 cells (moles)	15.8	474.4	7.5	482.5	490.6
Percentage of Total Actinide mass going through the system	87.2	92.0	83.5	92.0	91.9
Total Actinide in the first 60 cells (moles)	490.2		490.1		490.6

The results are to be compared to Table 6-3 and Table 6-4 and are one order of magnitude lower for the saturated cases. In the unsaturated case, the actinide density is similar in both source terms. The pw2a1231 case has less mass but also less cells with significant accumulation, i.e., 490.2 moles of actinide over 30 cells (16.3 moles/cell) compared to 652.3/50 = 13.0 moles/cell for the pe0a1231 case (Table 6-5). However, the Pu accumulation is significantly higher in the pe0a1231 case (89.3 moles against 15.8) because of the higher Pu source term concentration (see Section 5.1.7).



NOTE: The double peaks correspond to the combination of the two source terms at 4,050 and 7,940 years.

Figure 6-30. Actinide Precipitation as a Function of Cell Number and Decay (after 7,000 years of deposition - case pw2a1231): (a) 1,000,000 cm^2 - Saturated (b) 1,000,000 cm^2 - Unsaturated

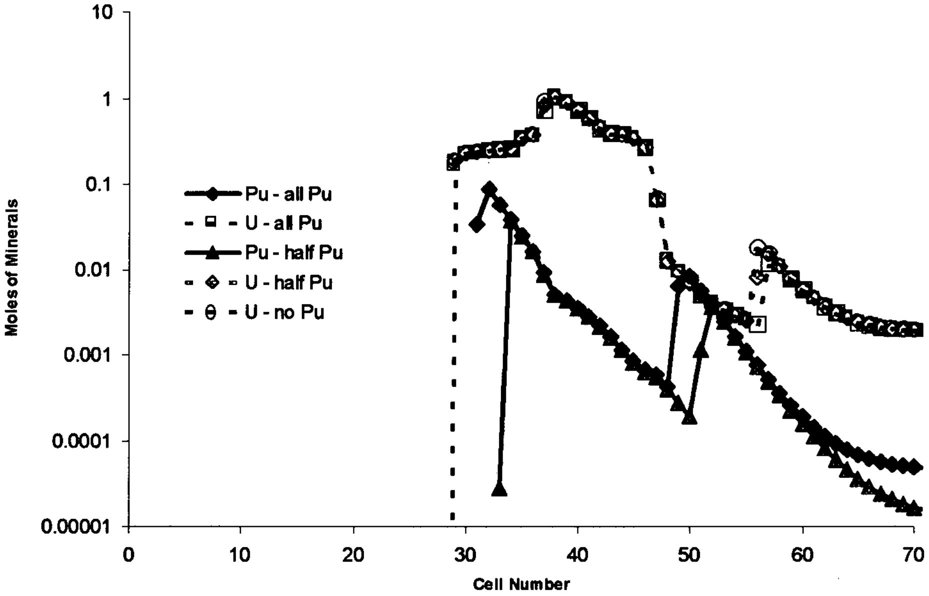


Figure 6-31. Actinide Precipitation as a Function of the Cell Number and Pu Decay (after 7,000 years of deposition - case pw2a1231 - 20,000 cm^2)

6.4 RESULTS FOR THE MOX03AP2 SCENARIOS

Results show that actinide accumulation is not possible under a MOX WP. The source term shows only a very short-lived Pu spike, not likely to generate Pu accumulation, and U mineralization is only possible, if any, in the first two cells in moderate quantities (Figure 6-32).

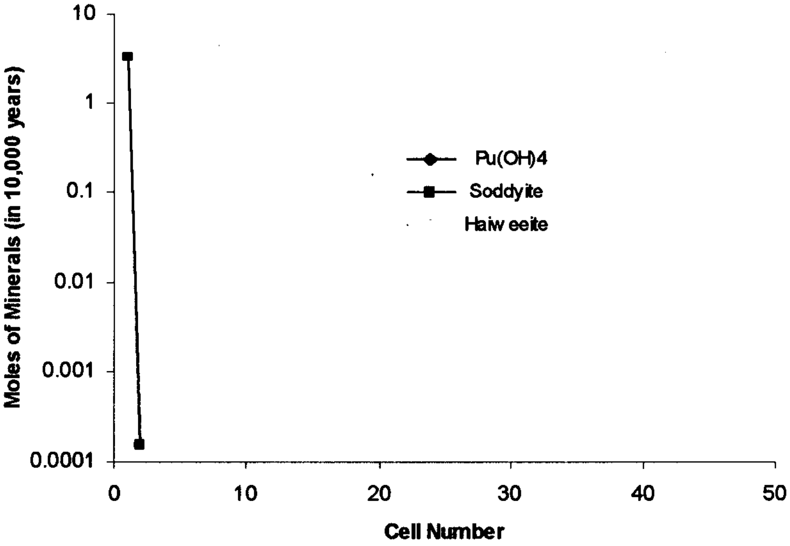


Figure 6-32. Accumulation of Actinides in the mox03ap2 Case (SA=20,000 cm^2)

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8. ATTACHMENTS

A list of attachments to this calculation is provided below.

Attachment	Title
I	Derivation of the 3-D Point Source Concentration Distribution (2 pages)
II	Dispersivity in Unsaturated Fractured Porous Media (2 pages)
III	Example Input File (7 pages)
IV	Files on Electronic Media Compact Disk-Read Only Memory (CD-ROM) (6 pages)
V	User's Manual for transl.c (9 pages)
VI	C Language Code for transl.c (24 pages)
VII	Software Routines (3 pages)
VIII	Electronic Media (CD-ROM)

ATTACHMENT I

Derivation of the 3-D Point Source Concentration Distribution

Bear (Ref. 3, p. 634, Eq. 10.6.37) states that the effect of an instantaneous slug of mass $dM=C_oQdt$ is:

$$dC(x,y,t)=\frac{dM}{2\pi\sqrt{2D_xt}\sqrt{2D_yt}}\exp\left\{-\frac{(x-vt)^2}{4D_xt}-\frac{y^2}{4D_yt}\right\} \tag{I-1}$$

where q/n has been changed to v and D' and D'' have been changed to D_x and D_y following notations of Section 2.1. Eq. 2.6b of Section 2.1 is obtained by integrating Eq. I-1 through time to obtain a continuous source term. The purpose of this attachment is to integrate the corresponding 3-D equation written as follows:

$$dC(x,y_1,y_2,t)=\frac{dM}{\sqrt{4\pi D_xt}\sqrt{4\pi D_yt}\sqrt{4\pi D_yt}}\exp\left\{-\frac{(x-vt)^2}{4D_xt}-\frac{y_1^2}{4D_yt}-\frac{y_2^2}{4D_yt}\right\} \tag{I-2}$$

Eq. I-2 can be integrated following the same scheme that is displayed in Eq. 10.6.38 of Ref. 3 to yield:

$$C(x,y_1,y_2,t)=\int_{\theta=0}^{\theta=t}\frac{C_0Q}{\sqrt{4\pi D_x(t-\theta)}\sqrt{4\pi D_y(t-\theta)}\sqrt{4\pi D_y(t-\theta)}}\exp\left\{-\frac{(x-v(t-\theta))^2}{4D_x(t-\theta)}-\frac{y_1^2}{4D_y(t-\theta)}-\frac{y_2^2}{4D_y(t-\theta)}\right\}d\theta \tag{I-3}$$

and after rearranging:

$$C(x,y_1,y_2,t)=\frac{C_0Q}{(4\pi)^{3/2}\sqrt{2D_xD_yD_y}}\exp\left(\frac{xv}{2D_x}\right)\int_{\theta=0}^{\theta=t}\frac{1}{(t-\theta)^{3/2}}\exp\left\{-\left(\frac{y_1^2}{4D_y}+\frac{y_1^2}{4D_y}+\frac{y_2^2}{4D_y}\right)\frac{1}{(t-\theta)}-\frac{v^2(t-\theta)}{4D_x}\right\}d\theta \tag{I-4}$$

A table of integrals (Ref. 28, p. 342, Eq. 3.478 - item 4) yields for t=∞ (that is for steady concentrations):

$$\int_0^\infty x^{\upsilon-1}\exp\left(-\beta x^p-\gamma x^{-p}\right)dx=\frac{2}{p}\left(\frac{\gamma}{\beta}\right)^{\frac{\nu}{2p}}K_{\frac{\nu}{p}}\left(2\sqrt{\beta\gamma}\right) \tag{I-5}$$

where $K_{\nu/p}$ is the modified Bessel function of the second kind and ν/p order. Comparing Eq. I-4 and I-5, we have:

$$\nu\text{-}1=\text{-}3/2 \text{ that is } \nu=\text{-}1/2,\ p=1 \text{ that is } \nu/p=\text{-}1/2,\ \beta=\left(\frac{y_1^2}{4D_y}+\frac{y_1^2}{4D_y}+\frac{y_2^2}{4D_y}\right) \text{ and } \gamma=\frac{v^2}{4D_x} \tag{I-6}$$

By noting that (Ref. 29, Eq. 10.2.17):

$$K_{0.5}(x) = K_{-0.5}(x) = \sqrt{\frac{\pi}{2x}}\exp(-x) \tag{I-7}$$

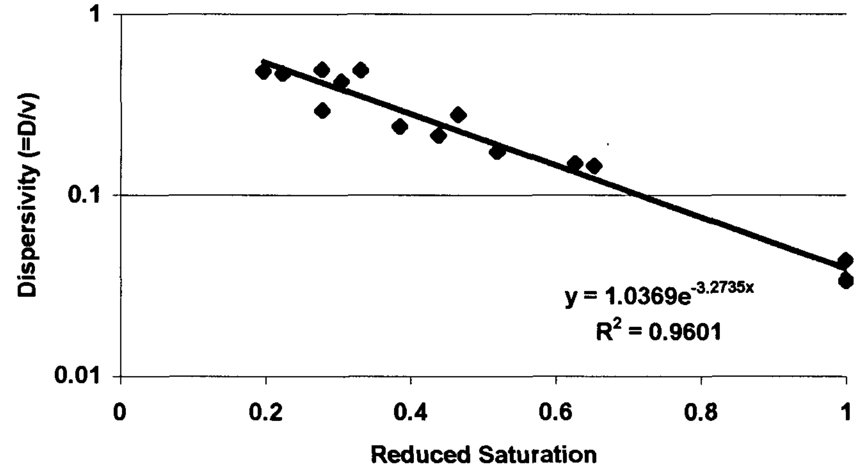
Eq. 2.6b is obtained.

ATTACHMENT II

Dispersivity in Unsaturated Fractured Porous Media

Dispersivity is a measure of the heterogeneity of a porous medium (Ref. 19, Chapter 5). Dispersivity is linearly proportional to the variance of the permeability and to the correlation length of the permeability field. Dispersivity in saturated porous media has been described in numerous books and papers (e.g., Refs. 3, 14, 15). The introduction of fractures and unsaturated conditions presents complications that affect the dispersivity in ways that are not as well understood. Heterogeneity increases with decreasing water saturation, because, for example, details of the arrangement of grains do not matter when the medium is saturated, but do matter when the saturation is low. Therefore, dispersivity increases with decreasing water saturation (Ref. 15,). The introduction of fractures also causes an increase in dispersivity because the representative volume is increased relative to that of an unfractured porous medium.

A few recent publications (Refs. 16, 17, and 18) illustrate the increase in dispersivity due to decreasing water content in porous media. Haga et al. (Ref. 17, Fig. 8) show a factor of ten decrease in the Peclet Number, which is inversely related to dispersivity (Ref. 17, Eq. 4), from a fully saturated medium to a medium at minimal saturation. Data extracted from Padilla et al. (Ref. 16, Tables 1 and 2) displays the same behavior: about a factor of ten change in dispersivity between fully saturated and minimal saturation (Fig. II-1).



NOTE: Data from Ref. 16.

Figure II-1. Dispersivity vs Saturation

Ref. 18 deals with a field experiment and does not provide a clear relationship between saturation and dispersivity; however, the trend is the same (Ref. 18, Section 5). Other publications (Refs. 20 and 21) present results for saturated, fractured rock. Haldeman et al., discussing results from a laboratory experiment, suggest that the longitudinal dispersivity is equal to the characteristic length of the system for saturated, fractured rock (Ref. 20, p. 63).

Very little information exists relative to the transverse dispersivity in a unsaturated/fractured medium. The general rule of thumb for uniform saturated medium is 10% of the longitudinal dispersivity (Ref. 14, Top of p. 66 cites a range of 1/6 to 1/20 that is ~17% to 5%). Ref. 18 (Section 5) cites from a field experiment in unsaturated medium a transverse dispersivity as high as 25 to 50% of the longitudinal dispersivity.

ATTACHMENT III

Example Input Files

III -1 Base Case PHREEQC Input File

Simplified Input file to illustrate precipitation mechanisms (file **ST99_1.K_pH=8.8.dat)**

```
TITLE

SOLUTION 0  Waste Package Water
        pH  8.7794
        pe 11.825
      temp  25.
     -units mol/kgw
Na        9.7614E-01
C         5.5165E-01
U         1.3905E-01
K         6.6410E-02
Pu        5.3155E-02
S         1.4148E-02
N         2.7142E-03
Cl        2.0140E-04
Si        1.0042E-04
Ca        6.6338E-05
Mg        4.2609E-05
Al        6.9361E-09
Fe        1.2873E-12

SOLUTION 1  J13 WATER
        pH   8.1
      pe 12.0    O2(g)  -0.7
            temp  25.0
     -units mol/kgw
Al        2.55E-08
Si        1.01E-03
Cl        1.500201 #2.01E-04
Fe        3.60E-12
C         2.09E-03
K         1.500129  #1.29e-04
Na        1.99E-03
S         1.9e-4
Ca        3.244e-4
Mg        8.27e-5
F         1.15e-4
N         1.42e-4

PHASES
Pu(OH)4
Pu(OH)4 + 4. H+1 =  Pu+4 + 4. H2O
#lowered 4 orders of magnitude
       log_k          -3.2422

pH_fixH
# to fix pH<8.1
 H+1 =  H+1
       log_k          0.0

pH_fixOH
# to fix pH>8.1
O H-1 =  OH-1
```

```
        log_k         0.0

EQUILIBRIUM_PHASES 0-1
CO2(g)               -3.0       9.9
O2(g)                -0.7       9.9
#pH_fixH              -8.0  HCl
pH_fixOH             -5.2 KOH     # (5.2+8.8=14)

MIX 1
0 0.01
1  0.99
INCREMENTAL_REACTIONS  false

EQUILIBRIUM_PHASES 1
Haiweeite            0.0        0.0
Calcite              0.0        0.0
Magnesite 0.0        0.0
Chalcedony           0.0        0.0
Diaspore             0.0        0.0
Goethite             0.0        0.0
Boehmite             0.0        0.0
Pu(OH)4              0.0        0.0
Soddyite             0.0        0.0
Schoepite            0.0        0.0
END
```

III -2 Base Case PHREEQC Input File

Input file for Base Case (Case A)

```
TITLE  concentrations at time 2,500 years pe0al231 - old database

SOLUTION 0  Waste Package Water
        pH  8.7794
        pe 11.825
       temp  25.
     -units mol/kgw
Na        9.7614E-01
C         5.5165E-01
U         1.3905E-01
Cr        1.3167E-01
B         9.7868E-02
K         6.6410E-02
Pu        5.3155E-02
S         1.4148E-02
F         4.0338E-03
N         2.7142E-03
Np        5.3664E-04
Cl        2.0140E-04
Si        1.0042E-04
Ca        6.6338E-05
Mg        4.2609E-05
Li        6.9154E-06
Gd        2.6408E-07
P         1.6192E-07
Ni        3.1497E-08
Al        6.9361E-09
Ba        1.0341E-09
Zr        6.1769E-10
Ti        2.0614E-10
Fe        1.2873E-12
#Mn       4.3219E-16
#Cu       1.0000E-16
```

```
#Mo      1.0000E-16
#Pb      1.0000E-16
#Tc      1.0000E-16
SOLUTION 1-100  J13 WATER
      pH   8.1
     pe 12.0    O2(g)  -0.7
         temp  25.0
    -units mol/kgw
Al       2.55E-08
Si       1.01E-03
Cl       2.01E-04
Fe       3.60E-12
C        2.09E-03
K        1.29e-04
Na       1.99E-03
S        1.9e-4
P        1.26e-6
B        1.24e-5
Ca       3.244e-4
Mg       8.27e-5
F        1.15e-4
N        1.42e-4
#Cr      1.e-16
#U       1.E-16
#Ni      1.e-16
#Gd      1.e-16
#Pu      1.e-16
#Ba      1.e-16
#Ag      1.e-16
#Sm      1.e-16
#Cu      1.e-16
#Li      1.e-16
#Np      1.e-16

SOLUTION_SPECIES
H2O + 0.01e- = H2O-0.01
         log_k       -9.0

PHASES
Pu(OH)4
Pu(OH)4 + 4. H+1 =  Pu+4 + 4. H2O
#lowered 4 orders of magnitude
     log_k          -3.2422

EQUILIBRIUM_PHASES  0-100
CO2(g)                 -3.0        9.9
O2(g)                  -0.7        9.9
PRINT
         -saturation_indices     false
         -species    false
SAVE SOLUTION 0-100
END

SOLUTION 999  J13 WATER
      pH   8.1
     pe 12.0    O2(g)  -0.7
         temp  25.0
    -units mol/kgw
Al       2.55E-08
Si       1.01E-03
Cl       2.01E-04
Fe       3.60E-12
C        2.09E-03
K        1.29e-04
Na       1.99E-03
S        1.9e-4
```

```
P        1.26e-6
B        1.24e-5
Ca       3.244e-4
Mg       8.27e-5
F        1.15e-4
N        1.42e-4
#Cr      1.e-16
#U       1.E-16
#Ni      1.e-16
#Gd      1.e-16
#Pu      1.e-16
#Ba      1.e-16
#Ag      1.e-16
#Sm      1.e-16
#Cu      1.e-16
#Li      1.e-16
#Np      1.e-16
EQUILIBRIUM_PHASES 999
CO2(g)                -3.0      9.9
O2(g)                 -0.7      9.9
SAVE SOLUTION 999
END

USE SOLUTION 0-100
USE SOLUTION 999
EQUILIBRIUM_PHASES 1-100
#Quartz               0.0       0.0
GdOHCO3               0.0       0.0
GdPO4:H2O             0.0       0.0
Haiweeite             0.0       0.0
Calcite               0.0       0.0
Magnesite 0.0         0.0
Chalcedony            0.0       0.0
#Dolomite             0.0       0.0
Diaspore              0.0       0.0
Goethite              0.0       0.0
Clinoptilolite-Ca     0.0       0.0
Clinoptilolite-K      0.0       0.0
Clinoptilolite-Na     0.0       0.0
Saponite-Ca           0.0       0.0
Saponite-H            0.0       0.0
Saponite-K            0.0       0.0
Saponite-Mg           0.0       0.0
Saponite-Na           0.0       0.0
Nontronite-Ca         0.0       0.0
Nontronite-K          0.0       0.0
Nontronite-Mg         0.0       0.0
Nontronite-Na         0.0       0.0
Boehmite              0.0       0.0
Pu(OH)4               0.0       0.0
Ni2SiO4               0.0       0.0
Soddyite              0.0       0.0
Schoepite             0.0       0.0
#Na4UO2(CO3)3         0.0       0.0
UO2CO3                0.0       0.0
UO2(OH)2(beta)        0.0       0.0
Na2U2O7               0.0       0.0
CaUO4                 0.0       0.0
#Kasolite             0.0       0.0
CO2(g)                -3.0      9.9
O2(g)                 -0.7      9.9

RATES
Cristobalite(alpha)
-start
300  SR_crst = SR("Cristobalite(alpha)")
```

```
310 ko=PARM(1)+(PARM(2)*((ACT("OH-"))^0.3))
320 moles = ko * PARM(3)*PARM(4)*(1 - SR_crst)* TIME
330 IF (moles<0) THEN moles=0
370 SAVE moles
-end

Annite
-start
300 SR_ant = SR("Annite")
310 ko=PARM(1)*((ACT("H+"))^0.37)+PARM(2)+PARM(3)*((ACT("H+"))^-0.22)
320 moles = ko * PARM(4)*PARM(5)*(1 - SR_ant)* TIME
330 IF (moles<0) THEN moles=0
370 SAVE moles
-end

Phlogopite
-start
300 SR_phl = SR("Phlogopite")
310 ko=PARM(1)*((ACT("H+"))^0.37)+PARM(2)+PARM(3)*((ACT("H+"))^-0.22)
320 moles = ko * PARM(4)*PARM(5)*(1 - SR_phl)* TIME
330 IF (moles<0) THEN moles=0
370 SAVE moles
-end

Maximum_Microcline
-start
200 SR_mxm = SR("Maximum_Microcline")
210 ko=PARM(1)+(PARM(2)*((ACT("OH-"))^0.3))
220 moles = ko * PARM(3)*PARM(4)*(1 - SR_mxm)* TIME
230 IF (moles<0) THEN moles=0
270 SAVE moles
-end

Albite_low
-start
200 SR_alb = SR("Albite_low")
210 ko=PARM(1)+(PARM(2)*((ACT("OH-"))^0.3))
220 moles = ko * PARM(3)*PARM(4)*(1 - SR_alb)* TIME
230 IF (moles<0) THEN moles=0
370 SAVE moles
-end

Anorthite
-start
200 SR_anh = SR("Anorthite")
210 ko=PARM(1)+(PARM(2)*((ACT("OH-"))^0.3))
220 moles = ko * PARM(3)*PARM(4)*(1 - SR_anh)* TIME
230 IF (moles<0) THEN moles=0
370 SAVE moles
-end

KINETICS 1-100
# second to last parameter is % volume of the mineral in tuff
#  last parameter is scaled surface area times time (SA_sc*TS)

Cristobalite(alpha)
        -m      100.0
        -parms  3.e-16       7.5e-15                     0.361086097     1000000
Annite
        -m      100.0
        -parms  1.99526e-15  2.51189e-17  1.58489e-19  0.020076447     1000000
Phlogopite
        -m      100.0
        -parms  1.99526e-15  2.51189e-17  1.58489e-19  0.008682137     1000000
Maximum_Microcline
        -m      100.0
```

```
        -parms    1.e-16    2.5e-15                        0.276489793        1000000
Albite_low
        -m         100.0
        -parms    1.e-16    2.5e-15                        0.305706489        1000000
Anorthite
        -m         100.0
        -parms    1.e-16    2.5e-15                        0.027959037        1000000


#TRANSPORT
#  1 year = 3.1536 e7 seconds
#           -cells              10
#           -shifts             10000  #for 7,000 years
#           -time_step2.1024e7
#           -lengths            10*0.1  #length is only used for dispersion
#           -dispersivities     10*0.1
#           -punch_frequency    50
#           -dump               doe_noss5.dmp
#           -dump_frequency     10
ADVECTION
            -cells              100
            -shifts             450
            -time_step2.1024e7  #0.67  years
            -punch_frequency    75
SELECTED_OUTPUT
            -file       pe0a1231.xls
            -totals Al Si Cr U Cl Fe C K Na S P B Ca Mg F N Ni Gd Pu Ba Ag Sm Li Ti Mn Cu Np
            -equilibrium_phases   GdOHCO3  GdPO4:H2O Calcite Dolomite  Diaspore  Goethite Clinoptilolite-Ca  Clinoptilolite-K
Clinoptilolite-Na  Saponite-Ca Saponite-H  Saponite-K Saponite-Mg Saponite-Na  Nontronite-Ca Nontronite-K  Nontronite-Mg Nontronite-Na
Boehmite Pu(OH)4  Ni2SiO4  Soddyite  Schoepite Chalcedony Haiweeite O2(g) CO2(g)  Na4UO2(CO3)3 UO2CO3 UO2(OH)2(beta) Na2U2O7
CaUO4  Kasolite
            -kinetic_reactants  Cristobalite(alpha) Annite Phlogopite Maximum_Microcline Albite_low Anorthite
            -saturation_indices   Pu(OH)4  Soddyite  Schoepite Uraninite Haiweeite Na4UO2(CO3)3 UO2CO3 UO2(OH)2(beta) Na2U2O7
CaUO4  Kasolite Cristobalite(alpha) Chalcedony  Annite Phlogopite Maximum_Microcline Albite_low Anorthite Calcite Magnesite
Rhodochrosite  Siderite Smithsonite Strontianite Dolomite Goethite O2(g) CO2(g) Clinoptilolite-Ca   Clinoptilolite-Cs Clinoptilolite-K
Clinoptilolite-NH4  Clinoptilolite-Na  Clinoptilolite-Sr  Saponite-Ca Saponite-H  Saponite-K Saponite-Mg Saponite-Na Beidellite-Ca
Beidellite-K  Beidellite-Mg Beidellite-Na  Montmor-Ca  Montmor-K  Montmor-Mg  Montmor-Na Nontronite-Ca Nontronite-K  Nontronite-Mg
Nontronite-Na  LaPO4:H2O CePO4:H2O  NdPO4:H2O GdPO4:H2O SmPO4:H2O
#           -solid_solutions Calcite Magnetite  Rhodochrosite  Siderite Smithsonite Strontianite Clinoptilolite-Ca   Clinoptilolite-Cs
Clinoptilolite-K Clinoptilolite-NH4   Clinoptilolite-Na   Clinoptilolite-Sr  Saponite-Ca Saponite-H  Saponite-K Saponite-Mg Saponite-Na
Beidellite-Ca Beidellite-K  Beidellite-Mg Beidellite-Na  Montmor-Ca  Montmor-K  Montmor-Mg  Montmor-Na Nontronite-Ca Nontronite-K
Nontronite-Mg Nontronite-Na  LaPO4:H2O CePO4:H2O  NdPO4:H2O GdPO4:H2O SmPO4:H2O
            -molalities CO3-2 HCO3-1  (PuO2)3(CO3)6-6 PuO2(CO3)2-2 PuO2(CO3)2-3 PuO2(CO3)3-5 PuO2(CO3)3-4 PuO2CO3
(UO2)3(CO3)6-6 UO2(CO3)2-2 UO2(CO3)3-5 UO2(CO3)3-4  UO2CO3
            -time       true
            -step       true
            -ionic_strength true


PRINT
            -reset                  false
            -selected_output        true
KNOBS
            -logfile                false
            -diagonal_scale         true
MIX 1
1  0.9
999  0.1
MIX 2
2  0.9
999  0.1
........
MIX 99
99  0.9
999  0.1
MIX 100
100  0.9
```

```
999  0.1
INCREMENTAL_REACTIONS  false

END

# This command will write a dummy file into the Phreeqc directory at the end of the run
# thus fixing the ending time of run
SELECTED_OUTPUT
        -file       finish_time
END
```

ATTACHMENT IV—FILES ON ELECTRONIC MEDIA (CD-ROM)

All the input, output, and pre- and post-processing files related to this calculation have been copied to a CD-ROM (Attachment VIII). Details about the organization of the CD-ROM and a list of files follow.

The files are organized into five sections. The general files and the files related to the database translation are presented below. The three remaining sections comprise run files whose nomenclature is detailed in the new paragraph. The files "**dispersion**…" describe particular cases of the equations presented in Section 2.1.2. The file **expo-VG.xls** computes the α of the exponential form of the permeability (Section 2.1.1). The files **PuAccProfile_pe0a1231.xls** and **PuAccProfile_pw2a1231.xls** present summary of the results and contain plots and tables described in the report. The file **sat_calc.xls** computes the fracture saturation for a given flow rate and fracture geometry.

The directory **Database_files** contains the routine transl text (**transl.c**), parameter (**watersys.dat**) and executable (**transl.exe**) files, the EQ6 source thermodynamic databases (**data0.nuc.R8s** and **data0.nuc.R8a**) and the output PHREEQC thermodynamic databases used in this calculation (**phreeqc.nucR8s_25** and **phreeqc.nuc_25**).

The directory **J13ww** contains PHREEQC input, output and post-processing files related to the setup of the J-13 well water.

The directory **Why_ppt** contains PHREEQC input (***.dat**) and output (***.out**) files used to justify the use of dilution in this calculation. Details about the files are given in Section 2.1.4.

File Name	**Size (bytes)**	**Date**	**Time**
dispersion_linesource.xls	7,251,456	09-08-00	1:26 pm
dispersion_pointsource.xls	3,810,816	09-08-00	1:26 pm
dispersion_pointsource_plot.xls	247,808	09-08-00	1:29 pm
expo-VG.xls	55,808	09-08-00	1:35 pm
PuAccProfile_pe0a1231.xls	501,248	09-08-00	1:38 pm
PuAccProfile_pw2a1231.xls	183,296	09-08-00	1:39 pm
sat_calc.xls	130,048	09-08-00	1:45 pm
Tuff_composition.xls	39,936	09-08-00	6:51 pm
Directory: Database_files			
data0.nuc.R8a	2,299,784	11-25-98	9:15 pm
data0.nuc.R8s	2,299,935	11-09-99	7:47 pm
phreeqc.nuc_25	228,515	09-11-99	4:47 pm
phreeqc.nucR8s_25	228,522	11-15-99	6:47 pm
transl.c	45,460	09-11-99	4:37 pm
transl.exe	245,809	09-11-99	4:47 pm
watersys.dat	349	09-11-99	4:21 pm

Directory: J13ww

J13ww.dat	552	06-30-00	12:54 pm
J13ww.out	82,153	06-30-00	12:55 pm
J13ww.xls	19,456	09-22-00	10:05 am

Directory: Why_ppt

ST1.dat	1,161	05-17-00	4:52 pm
ST1.out	139,462	05-17-00	4:52 pm
ST1_pH=8.0.dat	1,436	05-17-00	7:47 pm
ST1_pH=8.0.out	140,045	05-17-00	7:47 pm
ST75.dat	1,161	05-18-00	7:47 pm
ST75.out	139,466	05-18-00	7:47 pm
ST75_NoNa_pH=8.52.dat	1,421	05-18-00	8:37 pm
ST75_NoNa_pH=8.52.out	126,746	05-18-00	8:40 pm
ST99.dat	1,161	05-17-00	5:09 pm
ST99.out	139,466	05-17-00	5:09 pm
ST99_2K.dat	1,182	05-17-00	5:59 pm
ST99_2K.out	139,493	05-17-00	6:00 pm
ST99_0.1K.dat	1,182	05-17-00	5:15 pm
ST99_0.1K.out	139,501	05-17-00	5:16 pm
ST99_1.5K.dat	1,182	05-17-00	5:26 pm
ST99_1.5K.out	139,494	05-17-00	5:27 pm
ST99_1.5K_pH=8.8.dat	1,436	05-17-00	7:33 pm
ST99_1.5K_pH=8.8.out	140,064	05-17-00	7:34 pm
ST99_pH=8.8.dat	1,415	05-17-00	10:53 pm
ST99_pH=8.8.out	141,269	05-17-00	10:54 pm

Run files have the following format:

xxxxx_: first field represents the EQ6 generated source term;

(calcul,)_: second field is optional and applies only to the processed outputs;

SA=x_: third field gives the surface area in 10^3 cm^2;

(all,half,all)_: fourth field refers to the presence and decay of the Pu:
- all: all the Pu is present
- half: half of the Pu is decayed into U
- no: all the Pu is decayed into U
-

(NoDil, dil=20%, dil=5%, varmix, mod, multi, withDol, withHem).: fifth field represents self-explanatory variations from the base case:
- NoDil: no mixing with J13 water'

- dil=20%: dilution is 20%
- dil=5%: dilution is 5%
- varmix: the mixing is variable according to Figure 2-3
- mod: the source term has been modified to the new equilibrium when half or all of the Pu has decayed to U.
- multi: run with multiple source terms
- withDol: dolomite not suppressed
- withHem: hematite used instead of goethite.

(dat,txt,xls): sixth field represents either input (***.dat**), output (***.out**) or processed (***.xls**) file.

File Name	**Size (bytes)**	**Date**	**Time**
Directory: Pu_MOX			
mox03ap2_calcul_SA=20_all.xls	449,536	01-24-00	5:48 am
mox03ap2_calcul_SA=20_all_NoDil.xls	404,480	01-21-00	9:44 pm
mox03ap2_Elem_aqu_all.txt	46,828	01-20-00	5:13 pm
mox03ap2_Elem_aqu_all.xls	442,880	01-21-00	10:00 pm
mox03ap2_SA=1,000_all.dat	10,446	01-21-00	5:48 pm
mox03ap2_SA=1,000_all.xls	471,240	01-23-00	4:06 pm
mox03ap2_SA=1_all.dat	10,427	12-24-99	3:21 am
mox03ap2_SA=1_all.xls	1,413,992	12-26-99	11:08 am
mox03ap2_SA=20_all.dat	10,434	12-24-99	3:21 am
mox03ap2_SA=20_all.xls	1,413,992	12-28-99	2:40 pm
mox03ap2_SA=20_all_NoDil.dat	7,100	12-24-99	3:21 am
mox03ap2_SA=20_all_NoDil.xls	1,413,992	12-26-99	3:44 am
Directory: Pu_pe0a1231			
pe0a1231.elem_aqu.txt	34,416	12-01-99	7:58 pm
pe0a1231.elem_aqu.xls	264,704	01-13-00	11:13 pm
pe0a1231_calcul_multi.xls	2,384,384	02-02-00	9:58 pm
pe0a1231_calcul_SA=0.001_all_NOdil.xls	581,632	05-17-00	7:12 pm
pe0a1231_calcul_SA=0_all.xls	412,672	01-27-00	8:15 pm
pe0a1231_calcul_SA=1,000_all.xls	1,250,304	06-29-00	12:05 pm
pe0a1231_calcul_SA=1,000_all_NOdil.xls	1,256,448	01-14-00	3:13 pm
pe0a1231_calcul_SA=1,000_all_varmix.xls	538,112	01-24-00	5:00 am
pe0a1231_calcul_SA=1,000_half.xls	496,128	01-20-00	4:44 am
pe0a1231_calcul_SA=1,000_no.xls	244,224	01-20-00	4:48 am
pe0a1231_calcul_SA=1,000_NOdil_half.xls	634,368	01-17-00	3:09 pm
pe0a1231_calcul_SA=100_all.xls	901,120	01-18-00	12:11 am
pe0a1231_calcul_SA=100_all_NOdil.xls	584,192	05-18-00	1:31 pm
pe0a1231_calcul_SA=1_all.xls	1,807,872	01-14-00	4:07 pm

pe0a1231_calcul_SA=1_all_NOdil.xls	585,728	05-17-00	8:03 pm
pe0a1231_calcul_SA=20_all.xls	1,190,400	06-29-00	12:08 pm
pe0a1231_calcul_SA=20_all_dil=1%.xls	588,288	05-17-00	2:02 pm
pe0a1231_calcul_SA=20_all_dil=2.5%.xls	588,800	05-17-00	2:16 pm
pe0a1231_calcul_SA=20_all_dil=20%.xls	1,811,968	01-18-00	9:15 pm
pe0a1231_calcul_SA=20_all_dil=5%.xls	582,656	01-18-00	9:23 pm
pe0a1231_calcul_SA=20_all_NOdil.xls	1,217,024	01-24-00	8:39 pm
pe0a1231_calcul_SA=20_all_varmix.xls	202,752	01-24-00	5:01 am
pe0a1231_calcul_SA=20_all_withDol.xls	499,200	02-02-00	2:04 pm
pe0a1231_calcul_SA=20_all_withHem.xls	221,696	02-02-00	9:57 pm
pe0a1231_calcul_SA=20_half.xls	647,168	02-01-00	2:18 pm
pe0a1231_calcul_SA=20_no_mod.xls	641,024	01-22-00	6:00 pm
pe0a1231_calcul_SA=500_all.xls	620,544	01-24-00	1:55 pm
pe0a1231_calcul_SA=500_all_NOdil.xls	584,192	05-18-00	9:15 pm
pe0a1231_multi.dat	228,130	01-15-00	2:07 pm
pe0a1231_multi.xls	22,205,673	01-17-00	2:47 pm
pe0a1231_SA=0.001_all_NOdil.dat	7,019	05-17-00	3:46 pm
pe0a1231_SA=0_all.dat	8,432	01-27-00	1:15 pm
pe0a1231_SA=0_all.xls	474,492	01-27-00	7:08 pm
pe0a1231_SA=1,000_all.dat	10,390	12-22-99	7:25 pm
pe0a1231_SA=1,000_all.xls	471,240	12-23-99	6:01 am
pe0a1231_SA=1,000_all_NOdil.dat	7,055	01-13-00	8:36 pm
pe0a1231_SA=1,000_all_NOdil.xls	1,413,992	01-14-00	5:21 am
pe0a1231_SA=1,000_all_varmix.dat	11,901	01-20-00	7:15 pm
pe0a1231_SA=1,000_all_varmix.xls	471,240	01-22-00	3:00 pm
pe0a1231_SA=1,000_half.dat	10,441	01-09-00	3:22 pm
pe0a1231_SA=1,000_half.xls	708,909	01-11-00	11:30 am
pe0a1231_SA=1,000_half_comp_Mod_NotMod.xls	150,528	01-19-00	2:15 pm
pe0a1231_SA=1,000_half_mod.dat	10,520	01-17-00	4:48 pm
pe0a1231_SA=1,000_half_mod.xls	471,240	01-20-00	3:34 am
pe0a1231_SA=1,000_no.dat	10,429	01-07-00	9:55 pm
pe0a1231_SA=1,000_no.xls	708,909	01-09-00	3:16 pm
pe0a1231_SA=1,000_no_Comp_Mod_NoMod.xls	130,048	01-24-00	2:19 pm
pe0a1231_SA=1,000_no_mod.dat	10,527	01-17-00	6:58 pm
pe0a1231_SA=1,000_no_mod.xls	471,240	01-20-00	5:41 pm
pe0a1231_SA=1,000_NOdil_half.dat	7,077	01-14-00	3:51 pm
pe0a1231_SA=1,000_NOdil_half.xls	471,240	01-17-00	1:09 pm
pe0a1231_SA=100_all.dat	10,384	12-22-99	7:25 pm
pe0a1231_SA=100_all.xls	1,413,992	12-27-99	5:34 pm
pe0a1231_SA=100_all_NOdil.dat	7,049	05-17-00	3:44 pm
pe0a1231_SA=1_all.dat	10,372	12-22-99	7:25 pm
pe0a1231_SA=1_all.xls	1,413,992	12-25-99	10:23 am
pe0a1231_SA=1_all_NOdil.dat	7,037	05-17-00	3:42 pm

pe0a1231_SA=20_all.dat	10,379	12-21-99	6:16 pm
pe0a1231_SA=20_all.xls	708,909	12-22-99	2:09 pm
pe0a1231_SA=20_all_dil=1%.dat	10,578	05-15-00	11:18 pm
pe0a1231_SA=20_all_dil=2.5%.dat	10,774	05-15-00	11:16 pm
pe0a1231_SA=20_all_dil=20%.dat	10,378	12-22-99	7:43 pm
pe0a1231_SA=20_all_dil=20%.xls	1,413,992	12-25-99	10:38 am
pe0a1231_SA=20_all_dil=5%.dat	10,578	12-22-99	7:43 pm
pe0a1231_SA=20_all_dil=5%.xls	1,413,992	12-24-99	6:04 am
pe0a1231_SA=20_all_NOdil.dat	7,043	01-14-00	3:33 pm
pe0a1231_SA=20_all_NOdil.xls	1,413,992	01-15-00	9:32 am
pe0a1231_SA=20_all_varmix.dat	11,888	01-23-00	8:17 pm
pe0a1231_SA=20_all_varmix.xls	474,492	01-24-00	12:04 am
pe0a1231_SA=20_all_withDol.dat	10,377	12-22-99	7:26 pm
pe0a1231_SA=20_all_withDol.xls	1,413,992	12-26-99	2:19 pm
pe0a1231_SA=20_all_withHem.dat	10,415	02-02-00	2:20 pm
pe0a1231_SA=20_all_withHem.xls	482,370	02-02-00	8:29 pm
pe0a1231_SA=20_half.dat	10,508	01-21-00	9:06 pm
pe0a1231_SA=20_no_mod.dat	10,515	01-21-00	9:04 pm
pe0a1231_SA=20_no_mod.xls	1,413,992	01-22-00	2:33 pm
pe0a1231_SA=500_all.dat	10,384	01-23-00	10:52 pm
pe0a1231_SA=500_all.xls	471,240	01-24-00	1:24 pm
pe0a1231_SA=500_all_NOdil.dat	7,049	05-17-00	3:45 pm
pe0s1231.elem_aqu.txt	34,416	12-01-99	8:20 pm
pe0s1231.elem_aqu.xls	119,808	12-22-99	2:56 am
pe0s1231_calcul_SA=20_all_newdb.xls	705,024	05-21-00	1:26 pm
pe0s1231_SA=20_all_newdb.dat	10,535	12-22-99	3:28 am
pe0s1231_SA=20_all_newdb.xls	1,245,184	12-23-99	6:01 am

Directory: Pu_PW2a1231

PW2a1231.elem_aqu.txt	31,736	01-13-00	9:27 pm
PW2a1231.elem_aqu.xls	406,016	01-31-00	5:30 pm
PW2a1231_calcul_SA=1,000_all_4,050.xls	201,216	01-20-00	9:23 pm
PW2a1231_calcul_SA=1,000_all_7,940.xls	546,304	01-20-00	9:33 pm
PW2a1231_calcul_SA=1,000_half_4050.xls	192,512	01-24-00	7:02 pm
pw2a1231_calcul_SA=1,000_half_7,940_mod.xls	248,832	01-20-00	9:33 pm
PW2a1231_calcul_SA=1,000_no_4050.xls	188,928	01-24-00	7:07 pm
PW2a1231_calcul_SA=1,000_no_7940_mod.xls	219,136	02-02-00	1:29 pm
PW2a1231_calcul_SA=20_all_4050.xls	195,584	01-24-00	3:09 am
PW2a1231_calcul_SA=20_all_7,940.xls	201,216	01-24-00	3:02 am
PW2a1231_calcul_SA=20_half_4050.xls	192,000	01-24-00	3:06 am
pw2a1231_calcul_SA=20_half_7940_mod.xls	197,120	01-24-00	2:48 am
PW2a1231_calcul_SA=20_no_4050.xls	189,440	01-24-00	3:09 am
pw2a1231_calcul_SA=20_no_7940_mod.xls	227,840	01-31-00	8:46 pm
PW2a1231_SA=1,000_all_4,050.dat	10,286	01-20-00	2:13 am

PW2a1231_SA=1,000_all_4,050.xls	471,240	01-20-00	1:27 pm
PW2a1231_SA=1,000_all_7,940.dat	10,286	01-18-00	12:34 am
PW2a1231_SA=1,000_all_7,940.xls	471,240	01-19-00	2:35 pm
PW2a1231_SA=1,000_half_4050.dat	10,326	01-20-00	10:00 pm
PW2a1231_SA=1,000_half_4050.xls	474,290	01-24-00	2:19 pm
PW2a1231_SA=1,000_half_7,940_mod.dat	10,428	01-19-00	2:47 pm
pw2a1231_SA=1,000_half_7,940_mod.xls	474,492	01-20-00	7:04 pm
PW2a1231_SA=1,000_no_4050.dat	10,310	01-20-00	9:59 pm
PW2a1231_SA=1,000_no_4050.xls	474,290	01-24-00	2:19 pm
PW2a1231_SA=1,000_no_7940_mod.dat	10,418	02-01-00	1:18 pm
PW2a1231_SA=1,000_no_7940_mod.xls	474,492	02-02-00	5:57 am
PW2a1231_SA=20_all_4050.dat	10,285	01-20-00	10:01 pm
PW2a1231_SA=20_all_4050.xls	474,290	01-22-00	2:17 pm
PW2a1231_SA=20_all_7,940.dat	10,275	01-18-00	7:23 pm
PW2a1231_SA=20_half_4050.dat	10,312	01-20-00	9:59 pm
PW2a1231_SA=20_half_4050.xls	474,290	01-22-00	6:03 am
PW2a1231_SA=20_half_7940_mod.dat	10,428	01-20-00	10:02 pm
pw2a1231_SA=20_half_7940_mod.xls	474,492	01-21-00	11:41 pm
PW2a1231_SA=20_no_4050.dat	10,297	01-20-00	10:00 pm
PW2a1231_SA=20_no_4050.xls	474,290	01-21-00	5:30 pm
PW2a1231_SA=20_no_7940_mod.dat	10,416	01-20-00	10:01 pm
pw2a1231_SA=20_no_7940_mod.xls	474,492	01-24-00	9:28 am
PW2a1231SA=20_all_7,940.xls	471,240	01-20-00	3:22 pm

ATTACHMENT V—USER'S MANUAL FOR TRANSL.C

A USER'S MANUAL FOR: TRANSL

Version 1.0s

A TRANSLATION PROGRAM
FROM THE EQ3/6 TO THE PHREEQC
THERMODYNAMIC DATABASE FORMATS.

Jean-Philippe Nicot
Duke Engineering & Services, Austin, TX

August 1999

The program ***transl*** translates an EQ3/6 thermodynamic database in the "com" data01.f format into a PHREEQC compatible format. The translation program is only valid for "com" archetype data1f files (activity coefficients calculated with Davies or B-dot equations) and is not valid for "hmw" archetype data1f files (activity coefficients calculated with the Pitzer formulation). This manual first briefly overviews the key differences between PHREEQC and EQ3/6, then details the main aspects of the translation. Version 1.0s does not include temperature variations and produces a thermodynamic database only valid for a user-supplied constant temperature.

DIFFERENCES BETWEEN THE PHREEQC AND EQ3/6 FORMATS

Differences between the PHREEQC and EQ3/6 thermodynamic database formats are detailed below:

1- PHREEQC requires a list of all the primary master species (roughly equivalent to the strict basis species of EQ3/6) and secondary master species (roughly equivalent to the auxiliary basis species of EQ3/6) at the beginning of the input file because the order a) strict basic; b) auxiliary basic and; c) non-basic is not enforced in PHREEQC. This implies scanning for the PHREEQC secondary species in the reaction section of the aqueous field of the EQ3/6 thermodynamic database.

2- PHREEQC expresses redox reactions in terms of O_2(aq) (because all master species must be aqueous); EQ3/6 does it with O_2(g) as an exception to the rule that all basic species are aqueous. This implies recomputing all the log_k constants involving O_2.

3- EQ3/6 displays O_2 thermodynamic data in the aqueous field. Because of point 2, PHREEQC displays these O_2 data in the PHASES field.

4- PHREEQC requires aqueous species of interest to be the first species on the right-hand side of the reaction. EQ3/6 writes it on the left-hand side. This implies writing the reaction the other way around for the aqueous species and also using the negative of all log_k analytical coefficients as read in EQ3/6. However, species are written the same way in the PHREEQC "PHASES" field and in the EQ3/6 thermodynamic database.

5- PHREEQC requires the presence of several species of the H_20 system. They must be added to the thermodynamic database if not present. The species are: H(0),e-,O(0) for the SOLUTION_MASTER_SPECIES field and H20, O2, H2 and OH- for the SOLUTION_SPECIES field.

6- The reaction 2 H2O = O2 + 4 H+ + 4 e- is hard-wired into EQ3/6 but needs to be included in the PHREEQC thermodynamic database. log_k's values for this reaction are provided by the xlkeh EQ3/6 field.

7- PHREEQC does not allow descriptive information like (g) for gas or (aq) for aqueous in brackets at the end of a species. They all have to be removed.

MAIN STEPS OF TRANSLATION

PRACTICAL ASPECTS

The translation program requires two input files: ***data1f.nuc*** and ***watersys.dat***. The former is obtained by running the EQPT (Ref. 46) program with the data0.* EQ6 thermodynamic database. The extrastep of going from data0 to data1f was added to allow for a perfect PHREEQC-EQ3/6 fit of the temperature-dependent variations of log_k and to better constrain the B-dot parameters in the version of the translation program which includes temperature variations (Non QA). The file ***watersys.dat*** contains only one data field: the O_2(g) field cut and pasted from the EQ3/6 thermodynamic database.

The executable file results from the compiling of one file written in the ANSI C language:

transl.c: main and general purpose routine.

The program generates one output file:

phreeqc.nuc: the actual thermodynamic database.

After launching the program, it will ask at what constant temperature the PHREEQC thermodynamic database has to be computed. It will then ask what activity coefficient formulation is desired (Davies or B-dot). The program will then computes log_k's and b-dot parameters strictly identical to the ones computed in EQ6.

MAIN STEPS

The program flow chart is displayed in Figures V-1 to V-3. Because the information is displayed in a different order in both thermodynamic databases, all of the EQ3/6 thermodynamic database must be read first before writing to the PHREEQC thermodynamic database. The code first reads the EQ3/6 element field. It then reads all the information provided on species including elements making up the species and the subscript for that element. This also allows the code to separate primary master species from all secondary species. A key point of PHREEQC is that all the secondary species must be written in terms of primary master species, directly or indirectly. In addition, if an element in a secondary species has a redox number different from the master primary species, a secondary master species with that redox number must be also declared. The code scans all the reactions to detect if redox is involved. If it is, the redox state associated with the element is computed and species, element and redox state are stored in a temporary array.
Meanwhile, minor routines check for the correct writing of the reaction by deleting extra characters, inverting species if needed, rewriting charges, checking for misleading spelling and problematic species and recomputing the value of log_k to accommodate the different expression of O_2 in redox reactions. B-dot parameters are then calculated for the chosen constant temperature. The species included in the alkalinity declaration and in the gram formula weight

(gfw) correspond to the common practice and can be changed either in the code itself or in the thermodynamic database ***phreeqc.nuc***.

The code then starts writing to the ***phreeqc.nuc*** thermodynamic database. It first sorts and writes all the primary master and secondary master species. The code then writes reaction, log_k information, and B-dot information if applicable for aqueous species, minerals and gases. However, mineral and gas subfields must be preceded by the species name.

ACTIVITY COEFFICIENTS

Although EQ6 and PHREEQC have both the option of using either the Davies or B-dot model for the activity coefficients, there are small differences detailed below. The general expression for charged species for the Davies (Eq. V-1a) and B-dot (Eq. V-1b) models are:

$$\log_{10}\gamma = -Az^2\left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - c\mu\right) \tag{V-1a}$$

where c=0.2 in EQ6 and c=0.3 in PHREEQC

$$\log_{10}\gamma = -\frac{Az^2\sqrt{\mu}}{1+Ba^o\sqrt{\mu}} + b\mu \tag{V-1b}$$

In these equations, γ is the activity coefficient, z is the species charge, μ is the ionic strength, A and B are constant at a given temperature, a^o is the hardcore diameter of the species and b is the B-dot parameter. EQ6 provides coefficients for the analytical expressions of A, B and b as a function of temperature and a list of the hardcore diameters a^o. PHREEQC requires the parameters a^o and b; A and B are computed internally. The parameter a^o is constant for a given species and not function of temperature and can be written with no change from EQ6 to PHREEQC.

Activity of neutral species in PHREEQC and EQ6 are handled differently as shown on the following table:

	EQ6	PHREEQC
Charged Species	Davies or B-dot Model (Temperature varying B-dot)	Davies or B-dot Model (constant B-dot)
Neutral Species (Not strongly polar)	$\log_{10}\gamma = \log_{10}\gamma_{CO2}$ (Temperature varying)	$\gamma=0.1\mu$
Neutral Species (Strongly polar)	$\gamma=1$	$\gamma=0.1\mu$

Where γ_{CO2} is the activity of CO_2 expressed in an analytical form.

OTHER COMMENTS

This code has been tested on Unix DEC and HP workstations using standard C compilers and on Pentium PCs using the Microsoft Visual C++ compiler.

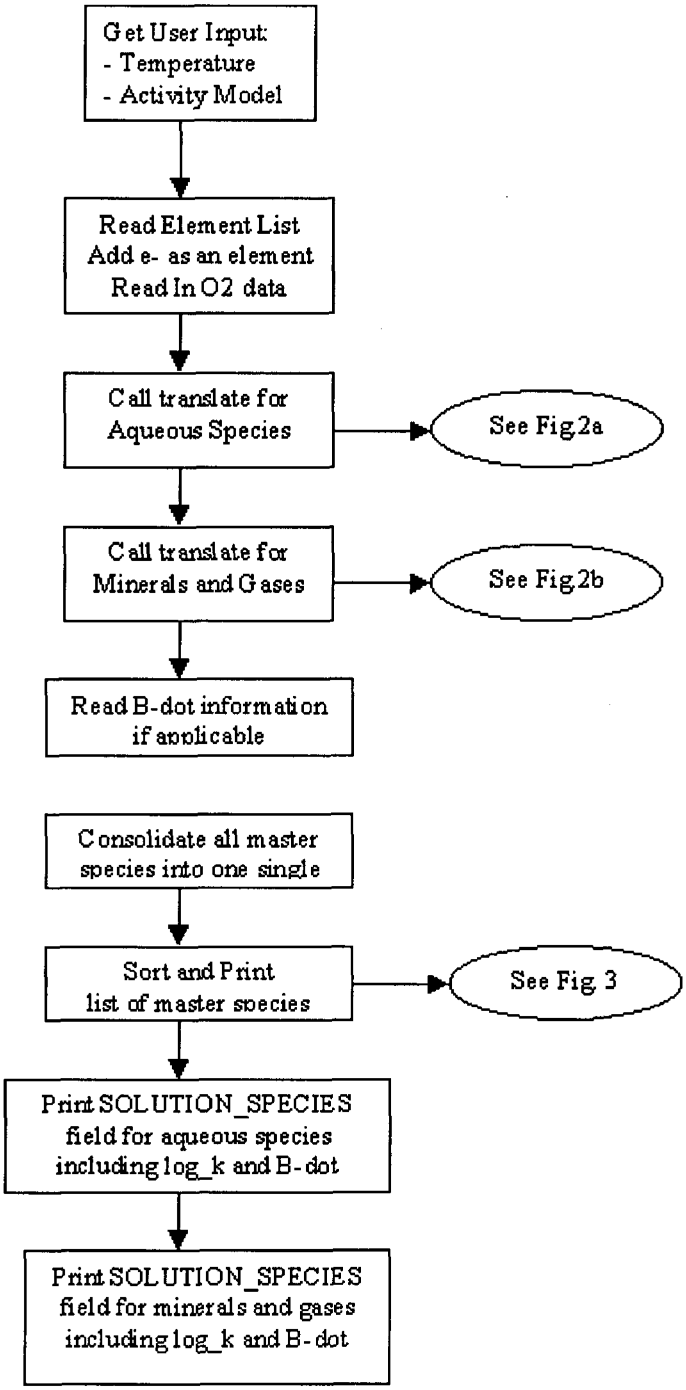


Figure V-1. "Main" Flow Chart

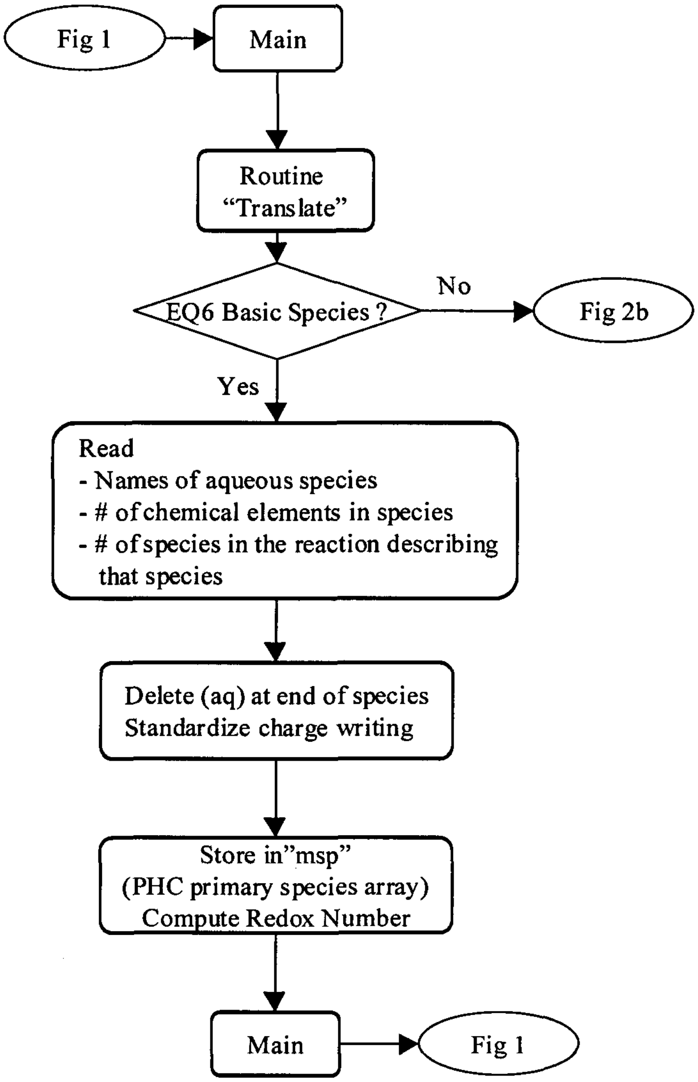


Figure V-2a: Routine "Translate" Flow Chart (first part)

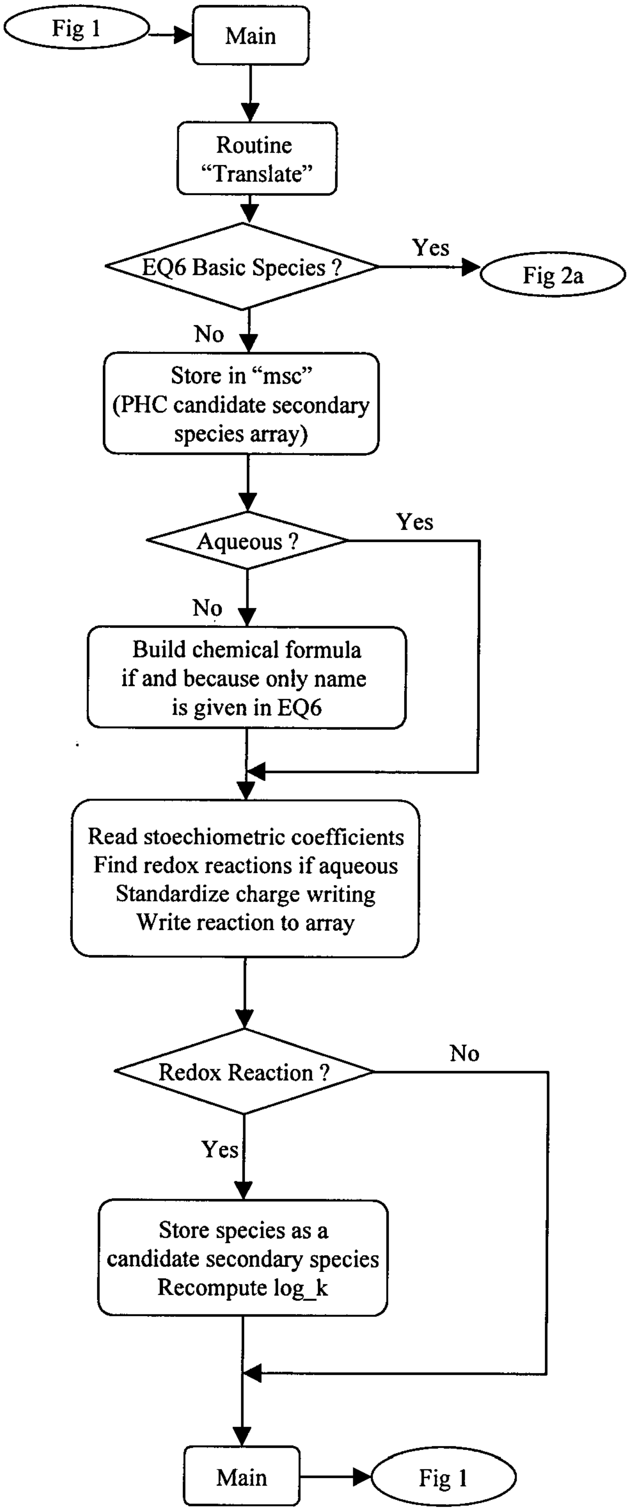


Figure V-2b. Routine "Translate" Flow Chart (second part)

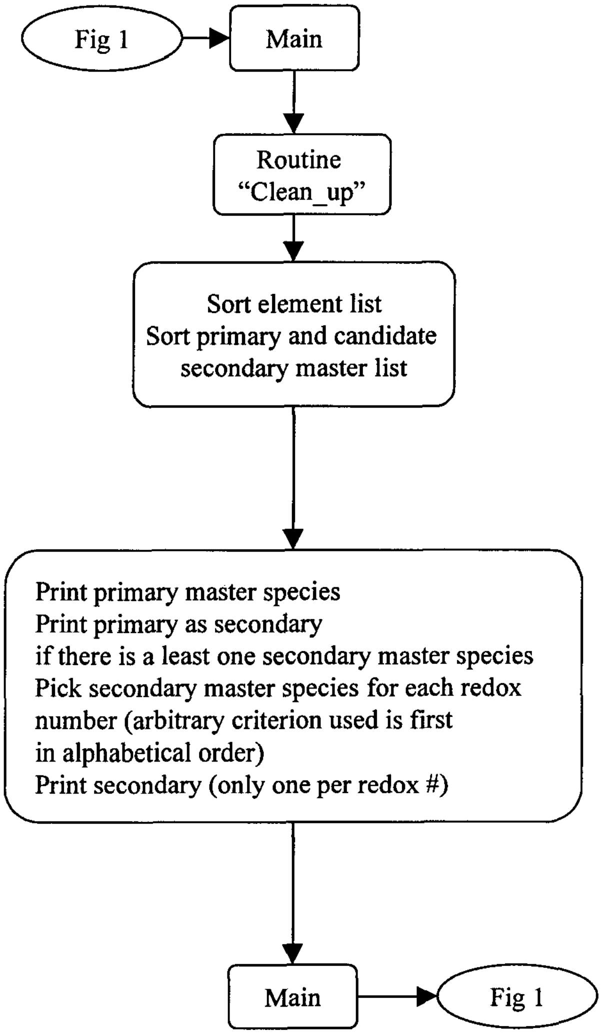


Figure V-3. Routine "clean_up" Flow Chart

ATTACHMENT VI—C LANGUAGE CODE FOR TRANSL.C

```
#include <stdio.h>
#include <string.h>
#include <math.h>
#include <stdlib.h>
#include <errno.h>
#define NBEL  100 /* Maximum number of chemical elements */
#define NRCT 2500 /* Maximum number of reactions */
#define NTUR   10 /* Number of data points for EQ temperature variations of log_k*/
#define MAX1   84 /* Maximum string length for species name */
#define MAX2   90 /* Maximum string length for analytical coefficient string */
#define NTRM   20 /* Maximum number of species in a reaction */
#define MXL   300 /* Maximum string length */
#define MTP     5 /* Maximum string length for temperature input */
void charge_mod(char dummy[],int *l);                                              /* change writing of
charge (e.g., from +++ to +3) */
void react_store(int *flag,char dummy[][MAX1],char nb[][MAX1],int *isp,int *i1);   /* concatenate species
to make reactions */
double calc_log_k(int *flag_redox,double *nbms);                                   /* compute log_k */
int second_species(char ms2[],char msec[],char elms1[][3],double nbms1[],int *iel);/* find the redox number
of secondary species */
void redox_number(char temp[],double *rdnb);                                       /* compare element to
element with a known and fixed redox number */
void translate(int *flag,int *itt0,int *itt1,int *ni0,int *ni1);                   /* read EQ reactions and
write PH reactions */
void shell_sort2(int n, char a[][MAX1],char b[][MAX1]);                            /* sorting routine */
void shell_sort3(int n, char a[][3],char b[][MAX1],char c[][MAX1]);                /* sorting routine */
void clean_up(int *ni0,int *n);                         /* eliminate redundant master species */
double calc_alk(char a[]);                              /* specify alkalinity */
void calc_gfw(char a[],char b[]);                       /* specify gwf */
void del_brak(char a[],int flag_del);                   /* delete brackets at end of string if needed */
void change_USe(char a[]);                              /* Find the string USe (confused with PHREEQC keyword
USE) and replace it with Se#U */
int species_skipped(char a[],int flag_sys);             /* skip H2O system species */
double find_weight(char a[], int *n);                   /* find atomic weight of element */
void find_bdot(void);                                   /* find B-dot parameters */
int part_case(char a[],char b[]);                       /* treat particular cases for redox number calculations
*/
```

```
int test_rmv(char a[]);                           /* compare a species with list of species to be removed
*/
FILE *innuc,*indat,*outp;
char pfile[20];                  /* output file name */
char elm[NBEL][3];               /* element list  (H, K, ...) */
double elw[NBEL];                /* element atomic weight list (1.008, 39.102, ...) */
char msp[NBEL][MAX1];            /* primary master species list (Ca+2, CH4, ...) */
char elmsp[NBEL][3];             /* element of the primary master species (Ca, C, ...) */
char msc[NRCT][MAX1];            /* list of candidates for secondary master species (KNO3, NO3-,NO2-,
...)*/
char elmsc[NRCT][MAX1];          /* element of the candidate for secondary master species (N(+5), N(+5),
N(+3), ....) */
char elmspc[NBEL][MAX1];         /* element of primary master species written as an element of a secondary
species (Ca becomes Ca(+2) */
char nameph[NRCT][MAX1];         /* name of non-aqueous phases (Calcite, O2(g), ...) */
char chemfph[NRCT][MAX1];        /* chemical formula of non-aqueous phases */
char react[NRCT][MXL];           /* list of reactions FeCl2 = Fe+2 + 2Cl-1 */
char allms[NRCT+2*NBEL][MAX1];   /* combined list of primary master and candidate for secondary master
species */
char elallms[NRCT+2*NBEL][MAX1]; /* element of primary master or candidate for secondary master species on
combined list */
char msrmv[NRCT][MAX1];          /* list of species removed from the database */
double anal_EQ[NTUR];            /* coefficient for analytical expression of log_k(T) in EQ  */
double anal_PH[NTUR];            /* coefficient for analytical expression of log_k(T) in PHREEQC */
double log_k[NRCT];              /* log_k for constant temperature runs (in C) */
int flag_davies;                 /* davies(=1) or B-dot(=0) formulation of activity */
int flag_rmv[NRCT];              /* removal(=1) of species if some criteria not met (acceptable thermo.
data) */
int flag_sup100=0;             /* temperature range below (=0), above (=1) or including (=2) 100C */
int flag_o2aq;                   /* flag=1 if redox reaction in terms of O2(aq) rather than O2(g) */
double tc;                       /* constant temperature (C) or midrange if variable*/
static int max1max=0;            /* if max1max>MAX1 a warning message will be displayed and program should
be rerun*/
static int max2max=0;            /* if max1max>MAX2 a warning message will be displayed and program should
be rerun*/
double anal_EQO2[NTUR];          /* read in EQ coefficients for analytical expression of O2 log_k(T) */
double anal_EQH2O[NTUR];         /* coefficients for analytical expression of H2O log_k(T) */
double bdot_EQ[NTUR];            /* read in EQ coefficients for analytical expression of B-dot */
double bb;               /* b-dot parameter */
```

```
char diamspc[NRCT+NBEL][MAX1];   /* read in EQ hard core diameter species */
double diam[NRCT+NBEL];          /* read in hard core diameter */
double gam[NRCT+NBEL][2];        /* ion hydrated parameter and b-dot value optionaly used in PHREEQC */
int neleq;                       /* declared number of elements in EQ database */
int naux;                        /* declared number of auxiliary species in EQ database */
int naqueous;                    /*number of aqueous species (all candidates for secondary species) */
int nbdot;                       /* number of aqueous species with a hard core diameter */
int rmvcount=0;                  /* counter for removed species */
int main()
{     int i,ii,ic,i0,i1,l;       /* loop counters */
      int nel;                   /* number of elements (by counting them)*/
      int ni0;                   /* number of primary master species */
      int ni1;                   /* number of secondary master species */
      int itt0,itt1;             /* loop counters */
      int nallms;                /* number of master species */
      double a,b;                /* dummy variables when reading input files */
      double nbms;               /* temporary element subscript within a species */
      char trsh[MXL];            /* dummy variable */
      char dum[7];               /* dummy variable */
      char answer[2];            /* user answers */
      char tc_str1[MTP],tc_str2[MTP]; /* user input temperature string */
      int flag_molvol;          /* if =0 no molar volume provided => aqueous; if molar volume provided =>
mineral (=1) or gas (=2) */
      innuc=fopen("data1f.nuc","r"); indat=fopen("watersys.dat","r");
/*  USER INPUT */
/*...Temperature inquiry */
lp_temp: printf ("Enter constant temperature in Celsius:  ");
        fgets (trsh,sizeof(trsh),stdin);
        sscanf(trsh,"%s",tc_str1);
        tc=atof(tc_str1);
        strcpy(pfile,"phreeqc.nuc");
        strcat(pfile,"_");
        strcat(pfile,strtok(tc_str1,"."));
        outp=fopen(pfile,"w");
        if (tc>300) {printf("Temperature should be between 0C and 300C\n"); goto lp_temp;}
        if (tc>100) flag_sup100=1;
        printf("Constant temperature is: %fC\n\n",tc);
        fprintf(outp,"# Constant temperature is: %fC\n#\n",tc);
/*...Activity calculation inquiry */
```

```
      printf ("Please, enter the activity model you want to use\n");
lp_dav: printf ("Enter d for Davies or enter b for B-dot  ");
      fgets (answer,sizeof(answer),stdin);
      fgets (dum,7,stdin);
      if (strncmp(answer,"d",1)==0 || strncmp(answer,"D",1)==0)
       {flag_davies=1;
        printf("\nActivity coefficients will be computed according to the Davies model\n\n");
        fprintf(outp,"# Davies model is used for activity\n#\n");}
      else if (strncmp(answer,"b",1)==0 || strncmp(answer,"B",1)==0)
       {flag_davies=0;
        printf("\nActivity coefficients will be computed according to the B-dot model\n\n");
        fprintf(outp,"# B-dot model is used for activity\n#\n");}
      else {printf("%s is not an appropriate answer\n",answer); goto lp_dav;}
/* ADD COMMENTS NEW TO THIS VERSION */
fprintf(outp,"# This program translates an EQ3/6 database in the \".com\" data01.f format\n\
# into a PHREEQC compatible format\n\
#\n\
# Version1.0s\n\
# Author : Jean-Philippe Nicot, DE&S, (512) 425-2000\n\
# Date:  May 1999\n\
#\n\
# This program is only valid for \".com\" archetype data1f files (activity coefficients\n\
# calculated with Davies or B-dot equations) and is not valid for \".hmw\" archetype\n\
# data1f files (activity coefficients calculated with Pitzer formulation).\n\
#\n\
# Main differences between PHREEQC and EQ3/6 database format are:\n\
# 1- PHREEQC requires a list of all the primary master species (roughly equivalent to \n\
#    the strict basis species of EQ3/6 ) and secondary master species (roughly \n\
#    equivalent to the auxiliary basis species of EQ3/6 ) at the beginning of the \n\
#    input file because the order strict basic, auxiliary basic and non-basic is not\n\
#    enforced in PHREEQC. This implies scanning for the PHREEQC secondary species in the\n\
#    reactions of the aqueous field of the EQ3/6 database.\n\
#    In EQ3/6, the strict basic species block must start with H20 and finish with O2(g), not .\n\
#    in PHREEQC.\n\
# 2- PHREEQC expresses redox reactions in terms of O2(aq) (because all master species\n\
#    must be aqueous); EQ3/6 does it with O2(g) as an exception to the rule that all\n\
#    basis species are aqueous.  This implies recomputing all the k constants\n\
#    involving O2. This is also true for any reactions involving gaseous species.\n");
      fprintf(outp,"\
```

```
# 3- EQ3/6 displays O2 thermodynamic data in the aqueous field. Because of \n\
#    point 2, PHREEQC displays these O2 data in the PHASES field.\n\
# 4- PHREEQC expresses temperature variations of k differently from EQ3/6. \n\
#    This implies recomputing all the related analytical coefficients. \n\
# 5- PHREEQC requires aqueous species of interest to be the first species \n\
#    on the right-hand side of the reaction. EQ3/6 writes it on the left-hand side. \n\
#    However, species are written the same way in the PHREEQC \"PHASES\" field and \n\
#    in the EQ3/6 datafile. This implies writing the reaction the other way around\n\
#    for the aqueous species and also using the negative of all log_k analytical\n\
#    coefficients as read in EQ3/6.\n\
# 6- PHREEQC requires the presence of several species of the H20 system.\n\
#    They must be added to the database if not present. The species are:\n\
#    H(0),e-,O(0) for the SOLUTION_MASTER_SPECIES field and \n\
#    H20, O2, H2 and OH- for the SOLUTION_SPECIES field. \n\
# 7- The reaction 2 H2O = O2 + 4 H+ + 4 e- is hard-wired into EQ3/6 but needs to be\n\
#    included in the PHREEQC database. log_k's values for this reaction are provided\n\
#    in the xlkeh EQ3/6 field.\n\
# Other comments:\n\
#  - In this translation:\n\
#    by default, concentrations are given in terms of elements.\n\
#    by default, gwf of E, H(1) and O(-2) are set to zero.\n\
#    by default, gwf of C and C(+4) = HCO3\n\
#    by default, gwf of S and S(+6) = SO4\n\
#    by default, gwf of Si          = SiO2\n\
#  - Alkalinity is computed as: \n\
#    Alk=[OH-1]+2[CO3-2]+[HCO3-1]+[HS-1]+2[PO4-3]-[H+1]-2[Fe+3] \n\
#    Please go to function calc_alk to delete or add species or do it manually on phreeqc.nuc \n\
#\n#\n");
      fprintf(outp,"#\n# TRANSLATION PREPROCESSING:\n\
# The user must execute the following actions:\n\
# - copy the data01.f O2(g) field into the file watersys.dat.\n\
# - provide PHREEQC formatted analytical coefficents for OH- in the reaction:H2O = OH-1 + H+\n\
#   (currently copied from phreeqc.dat database).\n\
# - make sure that the stoichiometric coefficient in front of all species of interest\n\
#   is equal to unity. If not compute new stoichiometric coefficients and new\n\
#   log_k and analytical coefficients accordingly.\n\
#\n#\n");
      fprintf(outp,"#\n# TRANSLATION POSTPROCESSING:\n\
# The user must execute the following actions:\n\
```

```
# - check that the program retained the approppriate secondary master species\n\
#   in BLOCK 16 of phreeqc.out. If not, correct accordingly. \n\
#\n#\n");
/* READ INITIAL INFORMATION */
      fprintf(outp,"# THE FOLLOWING TEXT IS IMPORTED FROM THE EQ DATABASE:\n#\n");
      for (i=0;i<2;i++) {fgets(trsh,MXL,innuc); fprintf(outp,"# %s",trsh);}
      if(strncmp(trsh,"stfipc",6)!=0) {printf("This not a \".com\" archetype file and it cannot be
translated by this code\n"); exit(1);}
      fscanf(innuc,"%d %d\n",&neleq,&naux); fprintf(outp,"#  %d %d\n",neleq,naux);
/* READ AND WRITE INTRODUCTION OF EQ DATA FILE */
      while (strncmp(trsh+10,"-----",5)!=0) {fgets(trsh,MXL,innuc); fprintf(outp,"# %s",trsh);}
      fscanf(innuc,"%lf %lf\n",&a,&b); fprintf(outp,"# %f %f\n",a,b);
      fprintf(outp,"#\n# Even if the original EQ3/6 database had at least partial data for the temperature
range %fC   %fC,\n",a,b);
      fprintf(outp,"#\n# THIS TRANSLATION IS ONLY VALID FOR A CONSTANT TEMPERATURE OF %fC\n#\n",tc);
      if (flag_davies==1) fprintf(outp,"# ACTIVITY COEFFICIENTS WILL BE COMPUTED ACCORDING TO THE DAVIES
MODEL\n");
      if (flag_davies==0)fprintf(outp,"# ACTIVITY COEFFICIENTS WILL BE COMPUTED ACCORDING TO THE B-DOT
MODEL\n");
      fgets(trsh,MXL,innuc); fprintf(outp,"#\n# %s#\n",trsh);
/* READ ELEMENT LIST FROM EQ6 */
      i=0;
      for(;;)
       {fscanf (innuc,"%2s",elm[i]);
        if (strcmp(elm[i],"pr")==0) break; /* Element list stops at "press" */
        fscanf (innuc,"%lf %lf \n",&elw[i],&a);
        i++;}
/* ADD ELECTRON AS AN ELEMENT */
      strcpy(elm[i],"E");
      elw[i]=0.0;
      nel=i+1;
/* READ IN PARAMETER LIST */
      for (i=0;i<10;i++) fgets(trsh,MXL,innuc);
      fscanf(innuc,"%lf %lf %lf %lf %lf\n",&bdot_EQ[0],&bdot_EQ[1],&bdot_EQ[2],&bdot_EQ[3],&bdot_EQ[4]);
      fscanf(innuc,"%lf %lf %lf %lf %lf\n",&bdot_EQ[5],&bdot_EQ[6],&bdot_EQ[7],&bdot_EQ[8],&bdot_EQ[9]);
      if (flag_sup100==1)for (i=0;i<=4;i++) bdot_EQ[i]=bdot_EQ[5+i];
      for (i=0;i<3;i++) fgets(trsh,MXL,innuc);
      fscanf(innuc,"%lf %lf %lf %lf
%lf\n",&anal_EQH2O[0],&anal_EQH2O[1],&anal_EQH2O[2],&anal_EQH2O[3],&anal_EQH2O[4]);
```

```
    fscanf(innuc,"%lf %lf %lf %lf
%lf\n",&anal_EQH2O[5],&anal_EQH2O[6],&anal_EQH2O[7],&anal_EQH2O[8],&anal_EQH2O[9]);
    if (flag_sup100==1) for (i=0;i<=4;i++) anal_EQH2O[i]=anal_EQH2O[5+i];
/* READ IN O2 DATA FROM H20 SYSTEM DATA */
    for (i=0;i<5;i++) fgets(trsh,sizeof(trsh),indat);
    fscanf(indat,"%lf %lf %lf %lf
%lf\n",&anal_EQO2[0],&anal_EQO2[1],&anal_EQO2[2],&anal_EQO2[3],&anal_EQO2[4]);
    fscanf(indat,"%lf %lf %lf %lf
%lf\n",&anal_EQO2[5],&anal_EQO2[6],&anal_EQO2[7],&anal_EQO2[8],&anal_EQO2[9]);
    if (flag_sup100==1) for (i=0;i<=4;i++) anal_EQO2[i]=anal_EQO2[5+i];
/* READ FIRST FIELD ("aqueous") */
     fgets(trsh,MXL,innuc); printf("%s \n",trsh);
     flag_molvol=0;
     itt0=0; itt1=0;
     translate(&flag_molvol,&itt0,&itt1,&ni0,&ni1); /* will read all aqueous species and will extract
needed info */
/* ADD e-, H+ and H20 as primary species */
     strcpy(msp[ni0],"H+1");
     strcpy(msp[ni0+1],"e-");
     strcpy(msp[ni0+2],"H2O");
     strcpy(elmsp[ni0],"H");
     strcpy(elmsp[ni0+1],"E");
     strcpy(elmsp[ni0+2],"O");
     strcpy(elmspc[ni0],"H(+1)");
     strcpy(elmspc[ni0+1],"E(-1)");
     strcpy(elmspc[ni0+2],"O(-2)");
     ni0=ni0+3; naqueous=ni1-1;
/* GO TO NEXT FIELD ("Minerals") */
     fgets(trsh,MXL,innuc); printf("%s \n",trsh);
     flag_molvol=1;
     itt0=ni0; itt1=ni1;
     translate(&flag_molvol,&itt0,&itt1,&ni0,&ni1); /* will read all minerals and will extract needed
info */
/* GO TO NEXT FIELD ("Gases") */
     fgets(trsh,MXL,innuc); printf("%s \n",trsh);
     flag_molvol=2;
     itt0=ni0; itt1=ni1;
     translate(&flag_molvol,&itt0,&itt1,&ni0,&ni1); /* will read all gases and will extract needed info
*/
```

```
       fgets(trsh,MXL,innuc);
/* GO TO NEXT FIELD ("Solid Solutions") */
         while (strncmp(trsh,"endit",5)!=0) {fgets(trsh,MXL,innuc); if (strncmp(trsh,"endit",5)==0) break;}
/* skip solid solutions */
/* GO TO NEXT FIELD (diameter information for B-dot equation) */
      if (flag_davies==0) printf("Ion diameters\n");
      trsh[0]=NULL;
      i=0;
      while (strncmp(trsh,"endit",5)!=0)
       {fgets(trsh,MXL,innuc);
        if (strncmp(trsh,"endit",5)==0) break;
        sscanf (trsh,"%s %lf %f\n",diamspc[i],&diam[i],&a);
        l=strlen(diamspc[i]);
        charge_mod(diamspc[i],&l); /* write charge with PHC format */
        del_brak(diamspc[i],1); /* get rid of (aq) */
        i++;}
      nbdot=i;
/* CONSOLIDATE ALL AQUEOUS MASTER AND SECONDARY MASTER SPECIES IN ONE SINGLE ARRAY */
/* all the info have aready been partially structured in the few calls to routine translate */
       for (i0=0;i0<ni0;++i0)
        {strcpy(allms[i0],msp[i0]);
         strcpy(elallms[i0],elmsp[i0]);}
       ic=ni0;
       for (i0=0;i0<ni0;++i0)
        {strcpy(allms[ic],msp[i0]);
         strcpy(elallms[ic],elmspc[i0]);
         ic++;}
       ic=2*ni0;
      for (i1=0;i1<naqueous;++i1)
         {if (msc[i1][0]!=NULL && elmsc[i1][0]!=NULL)
           {strcpy(allms[ic],msc[i1]);
           strcpy(elallms[ic],elmsc[i1]);
           ic++;}}
       nallms=ic;
/* SORT, CLEAN UP  AND PRINT LIST OF MASTER AND SECONDARY MASTER SPECIES */
       fprintf(outp,"SOLUTION_MASTER_SPECIES \n#\n");
       fprintf(outp,"#element   species  alk  gfw_formula  element_gfw \n#\n");
/*...print Alkalinity species */
```

```
       fprintf(outp,"Alkalinity HCO3-1                    1.0  Ca0.5HCO3      81.05
  \n");
       shell_sort2(nallms,elallms-1,allms-1); /* "-1" because of Numerical Recipes conventions */
       clean_up(&ni0,&nallms); /* list of master species is printed from this routine */
/* FIND B-DOT PARAMETERS */
       bb=bdot_EQ[0]+bdot_EQ[1]*tc+bdot_EQ[2]*tc*tc+bdot_EQ[3]*pow(tc,3)+bdot_EQ[4]*pow(tc,4);
       find_bdot();
/* PRINT LIST OF REACTIONS,LOG_K AND B-DOT PARAMETERS */
/* print SOLUTION_SPECIES field for master species */
      fprintf(outp,"\nSOLUTION_SPECIES \n \n");
      for (i0=0;i0<ni0;i0++)
        {fprintf(outp,"%s = %s \n",msp[i0],msp[i0]);
         i=strlen(msp[i0]);
         if ((flag_davies==0) && ((msp[i0][i-2]=='+')||(msp[i0][i-2]=='-')))  /* write gamma only for
chraged species */
           {fprintf(outp,"       log_k    0.000 \n");
            fprintf(outp,"       -gamma   %5.2f   %6.4f \n \n",gam[i0][0],gam[i0][1]);}
         else fprintf(outp,"       log_k    0.000 \n \n");}
/* print O2 DATA for SOLUTION_SPECIES */
      fprintf(outp,"2 H2O = O2 + 4 H+ + 4 e-\n");
      for (i=0;i<NTUR;i++)  anal_EQ[i]=anal_EQH2O[i];
      nbms=1.0;
      i=1;  /* i.e. flag_redox=1 */
      flag_o2aq=0;
      fprintf(outp,"       log_k  %s   %f \n \n","   ",calc_log_k(&i,&nbms));
/* print SOLUTION_SPECIES field for aqueous species */
       for (i1=0;i1<=naqueous;i1++)
         {if (flag_rmv[i1]==1) continue;
         if (strcmp(react[i1]," O2 =  O2")==0) continue;
         fprintf(outp,"%s \n",react[i1]);
         fprintf(outp,"       log_k  %s   %f \n","   ",log_k[i1]);
         i=strlen(msc[i1]);
         if ((flag_davies==0) && ((msc[i1][i-2]=='+')||(msc[i1][i-2]=='-')))  /* print only if charged
species */
           {fprintf(outp,"       -gamma   %5.2f   %6.4f \n \n",gam[i1][0],gam[i1][1]);}
         else fprintf(outp,"\n");}
/* print SOLUTION_SPECIES field for mineral and gas species */
       fprintf(outp,"PHASES \n \n");
       for (i1=naqueous+1;i1<ni1;i1++)
```

```
         {if (flag_rmv[i1]==1) continue;
         if (strcmp(nameph[i1],"O2(g)")==0) continue;
         fprintf(outp,"%s \n",nameph[i1]);
         fprintf(outp,"%s \n",react[i1]);
         fprintf(outp,"      log_k %s  %f \n \n","   ",log_k[i1]);}
/* print O2(g) for PHASES copied from wartersys.dat */
      fprintf(outp,"O2(g) \n");
      fprintf(outp," O2 = O2 \n");
      nbms=0.0;
      fprintf(outp,"       log_k  %s   %f \n \n","   ",-(anal_EQO2[0]+
anal_EQO2[1]*tc+anal_EQO2[2]*tc*tc+anal_EQO2[3]*pow(tc,3)+anal_EQO2[4]*pow(tc,4)));
      fprintf(outp,"END\n");
   return(0);}   /* End of main */
/* FUNCTION: read EQ reactions and write PH reactions
 * The routine checks if an element has species with different redox numbers
 * In this case, it computes it and all the corresponding secondary species
 * The routine computes log_k's for the constant temperature tc from the EQ6 data
 * and modify it if the reaction is a redox reaction (point 2 from comments) */
void translate(int *flag_molvol,int *itt0,int *itt1,int *ni0,int *ni1)
{     int i,i0,i1,l;            /* counters */
      int iel,iiel;               /* number of elements in a species + counter */
      int isp,iisp;               /* number of species in a reaction + counter */
      int iisp_first_term;        /* !=0 species of interest is not at the right location in reaction */
      int strcount;               /* counter for max1max to check for maximum species length */
      double nbms;                /* temporary double with subscript of an element */
      double nbms3[NTRM];         /* temporary double array with stoichio. coefficient of all species in a
reaction */
      double nbms1[10];           /* temporary double array with subscripts of all elements in a species */
      char snbms[MAX1];           /* temporary string with stoichio. coefficient of a species */
      char snbms3[NTRM][MAX1];    /* temporary string array with stoichio. coefficient of all species in a
reaction*/
      double a,b,c;             /* a is molar weight, b charge and c molar volume */
      char ms2[MAX1];             /* temporary string with species name */
      char elms1[10][3];          /* temporary string array of all elements of a species */
      char elms2[MAX1];           /* temporary string of element */
      char elms3[NTRM][MAX1];     /* temporary string array of all species in a reaction */
      char test_redox[3];         /* temporary string for testing for redox reaction */
      int flag_redox;             /* flag=1 if redox reaction */
      int flag_sys;               /* flag=1 if species belongs toi the water system */
```

```
      char temp[MAX1];
      char msec[MAX1];           /* Transfert from function second_species */
      int lmax1max;              /* counter for max1max to check for maximum species length */
      ms2[0]=NULL;
/* READ MASTER SPECIES AND CANDIDATE SECONDARY MASTER SPECIES LIST FROM EQ6 */
      i0=*itt0; i1=*itt1;
/* read name, number of elements in species and number of species in reaction */
      while (strncmp(ms2,"endit",5)!=0)
        { fscanf (innuc,"%s %d %d",ms2,&iel,&isp);
        if (strncmp(ms2,"endit",5)==0) break;
        del_brak(ms2,1); /* delete (aq) at end of species if any */
        change_USe(ms2); /* change order in USe if needed */
        l=strlen(ms2);
        charge_mod(ms2,&l); /* modify charge writing */
/* READ PRIMARY MASTER SPECIES */
        if (isp==0)  /* no reaction written for that species */
          { strcpy(msp[i0],ms2); /* store species name in species list */
          fscanf(innuc,"%lf %lf \n",&a,&b); /* skip one line */
/* read each indice of element and each element for a given species */
          iiel=0;
          flag_sys=0;
          while (iiel<iel)
            {fscanf(innuc,"%lf %s",&nbms,elms2);
             del_brak(elms2,1); /* delete (aq) at end of element if any */
             nbms1[iiel]=nbms;
             strcpy(elms1[iiel],elms2);
             if ((strcmp(elms2,"H")!=0) && (strcmp(elms2,"O")!=0)) {strncpy(elmsp[i0],elms2,2);
flag_sys=1;}
             iiel++;}
/* handle special case for H+-H2, H2O and O2: skip these primary master species */
          if (species_skipped(ms2,flag_sys)==1) continue;
/* compute primary written as secondary */
          if (second_species(ms2,msec,elms1,nbms1,&iel)==1)
            {printf("FRACTIONAL REDOX NUMBER IN PRIMARY MASTER\n");
            printf("THIS SHOULD NOT BE POSSIBLE\n"); exit(1);}
          strcpy(elmspc[i0],msec);
/* increment primary master species counter */
          i0++;}
/* READ CANDIDATE SECONDARY MASTER SPECIES (INCLUDING GASES AND MINERALS) */
```

```
        else  /* isp>0: there is a reaction written for this species */
          {flag_rmv[i1]=0; /*initialization of flag to remove species if needed */
/* store secondary species name in secondary species list */
          strcpy(nameph[i1],ms2);
          strcpy(msc[i1],ms2);
/* skip one line, read each indice of element and each element for a given species */
          iiel=0; iisp=0;
          if (*flag_molvol==0) /* if aqueous */
            {fscanf(innuc,"%lf %lf \n",&a,&b);
            while (iiel<iel)
              {fscanf(innuc,"%lf %s",&nbms,elms2);
               nbms1[iiel]=nbms;
               strcpy(elms1[iiel],elms2);
               iiel++;}}
          else  /* if mineral or gas; build chemical formula is only name is given */
            { fscanf(innuc,"%lf %lf %lf \n",&a,&b,&c); /* a is molar weight, b charge and c molar volume */
            strcount=0;
            lmax1max=0; /* initialization for length of species string */
            while (iiel<iel)
              {fscanf(innuc,"%lf %s",&nbms,elms2);
               nbms1[iiel]=nbms;
               if (strstr(ms2,elms2)!=NULL) strcount++; /* if element in name, add 1 to strcount */
               strcat(chemfph[i1],elms2);  /* concat elements to make chem. form. */
               lmax1max+=strlen(elms2);
               sprintf(temp,"%8.5f",nbms);
               for (i=7;i>0;i--)                                      /*because temp format has 8
characters */
                 {if (temp[i]!='0') break;                             /* get rid of trailing zeros */
                 else temp[i]=NULL;}
               if (temp[i]=='.')                                      /* if nbms is an integer */
                 {temp[i]=NULL;                                        /* get rid of decimal point */
                 if ((temp[i-1]=='1') &&
                     (temp[i-2]<'1' || temp[i-2]>'9')) temp[i-1]=NULL;}  /* get rid of subscript 1 */
               if (temp[0]==' ') strcpy(temp,temp+1);                /* get rid of initial blank if
appropriate */
               strcat(chemfph[i1],temp);
               lmax1max+=strlen(temp);
               strcpy(elms1[iiel],elms2);
               iiel++;}
```

```
      if (strcount==iel) /* if all elements are in name, name is chemical formula */
        {if (iel>1) strcpy(chemfph[i1],ms2);} /* but only if species is not a pure element */
      if (lmax1max>max1max)
        {max1max=lmax1max;
        if (lmax1max>MAX1) printf("MAX1 must be changed to %d because of %s\n",lmax1max+1,ms2);}}
/* read reaction coefficients and species and find redox reactions */
     flag_redox=0;
     flag_o2aq=0;
     while (iisp<isp)
      {fscanf(innuc,"%s %s",snbms,elms2);
      del_brak(elms2,1); /* delete (aq) at end of species if any for both aqueous species and mineral
and gases */
      del_brak(elms2,3); /* change O2(g) to O2 for both aqueous species and mineral and gases */
/* ...find redox reactions */
      if (strlen(elms2)>1) {test_redox[0]=elms2[0]; test_redox[1]=elms2[1]; test_redox[2]=NULL;}
      else {test_redox[0]=elms2[0]; test_redox[1]=NULL;}
      if (strcmp(test_redox,"O2")==0) flag_redox=1;
/* ...modify charge writing for reaction species */
      l=strlen(elms2);
      charge_mod(elms2,&l);
/* ...save all reaction species in an array */
      strcpy(elms3[iisp],elms2);
      if (strcmp(ms2,elms2)==0) iisp_first_term=iisp;
      strcpy(snbms3[iisp],snbms);
      iisp++; }  /* closure of while (iisp<isp) */
/* ...put formula in first element of array for reaction instead of name */
     if ((*flag_molvol==1) || (*flag_molvol==2))  /* if mineral or gas */
      {strncpy(temp,chemfph[i1],MAX1);
      del_brak(temp,0);  /* delete everything but (aq) and (g) */
      del_brak(temp,1);  /* delete (aq) */
      del_brak(temp,2);  /* delete (g) */
      strncpy(chemfph[i1],temp,MAX1);
      strcpy(elms3[0],chemfph[i1]);}  /*overwrite species in reaction if name is not a chemical
formula */
/* find oxidation number of redox reactions to obtain secondary master species */
     if (flag_redox==1) {if (second_species(ms2,msec,elms1,nbms1,&iel)==0) strcpy(elmsc[i1],msec);
else elmsc[i1][0]=NULL; } /* fractional redox number */
     else  elmsc[i1][0]=NULL;
/* warn if species of interest is not first term of reaction */
```

```
         if ((iisp_first_term!=0) && (isp>2))  printf("%s is not first term of reaction\n",ms2);/* isp>2
because otherwise pick equation like O2 = O2 */
/* read coefficients for EQ analytic expression of log_k=f(T) and store removed species (=no data) in array
*/
          for (i=0;i<NTUR;++i) fscanf(innuc,"%lf",&anal_EQ[i]);
          if (flag_sup100==1) for (i=0;i<=4;i++) anal_EQ[i]=anal_EQ[5+i];
          if (anal_EQ[0]==500.00)
            {flag_rmv[i1]=1;
            if (*flag_molvol==0) /* copy to removed species array if ms2 is an aqueous species, not mineral
or gas */
              {strcpy(msrmv[rmvcount],ms2);
              rmvcount=rmvcount+1;}
            i1++;
            continue;}
          react_store(flag_molvol,elms3,snbms3,&isp,&i1); /* write reactions to array, invert reaction and
take -log_k if needed */
          for(i=0;i<isp;i++) {if (strcmp(elms3[i],"O2")==0) {nbms=atof(snbms3[i]); break;}} /* find O2
stoichiometric coefficient to modify log_k expression */
          log_k[i1]=calc_log_k(&flag_redox,&nbms); /* compute log_k and analytical coefficients if
applicable (correction for O2(aq)-O2(g) inside routines) */
          i1++; }  /* increment candidate secondary master species counter */
        *ni0=i0; *ni1=i1;}  /* save number of primary master species and number of reactions *//* closure
of while (strncmp(ms2.... */
       return;}
/* FUNCTION: find the redox number of secondary species */
int second_species(char ms2[],char msec[],char elms1[][3],double nbms1[],int *iel)
{char temp[3],str[MAX1];
int iiel,count,length;
double rdnb,redox[MAX1];
int nmber,iiel_unkn,rdnbint;
double nmber1; /* nmber is set equal to nmber1, if not we have fractional redox number => skip that species
*/
/* ms2[MAX1]  : IN  species from which one element has a redox number to be computed
 * msec[MAX1]: OUT element with redox number in brackets
 * elms1[][3]: IN  list of elements contained in the species
 * nbms1[]    : IN  list of subscript for element in species
 * *iel       : IN  number of element in species */
/* if ms2 is a single element and is listed in function "redox_number" */
if (*iel==1)
```

```
  {strncpy(temp,elms1[0],2);
  redox_number(temp,&rdnb);
  if (rdnb!=99)
    {strncpy(msec,elms1[0],2);
    if (rdnb>0) strcat(msec,"(+");
    else strcat(msec,"(");
    rdnbint=rdnb;
    sprintf(str,"%d",rdnbint);
    strcat(msec,str);
    strcat(msec,")");
    if (strncmp(ms2,"O2",2)==0) strcpy(msec,"O(0)");
    if (strncmp(ms2,"H2",2)==0) strcpy(msec,"H(0)");
    return(0);}}
/* general case */
count=0;
for (iiel=0;iiel<*iel;iiel++)
  {strncpy(temp,elms1[iiel],2);
  temp[2]=NULL;
  redox_number(temp,&rdnb);
  if (rdnb==99.) count++;
  redox[iiel]=rdnb;}
/* Exit or compute charge of species */
if (count!=1) {msec[0]=NULL; part_case(ms2,msec);}
else
  {length=strlen(ms2);
  if (ms2[length-2]==43) nmber1=atof(&ms2[length-1]);
  if (ms2[length-2]==45) nmber1=-atof(&ms2[length-1]);
  if ((ms2[length-2]!=45) && (ms2[length-2]!=43)) nmber1=0.;
/* compute unknown redox number */
  for (iiel=0;iiel<*iel;iiel++) {if (redox[iiel]!=99.) nmber1=nmber1-nbms1[iiel]*redox[iiel]; else
iiel_unkn=iiel;}
  nmber1=nmber1/nbms1[iiel_unkn];
/* check for fractional redox number */
  nmber=nmber1;
/* conclusion for export */
  strncpy(msec,elms1[iiel_unkn],2);
  msec[2]=NULL;
  if (nmber>0) strcat(msec,"(+");
  else strcat(msec,"(");
```

```
  sprintf(str,"%d",nmber);
  strcat(msec,str);
  strcat(msec,")");
  if ((nmber1-nmber)!=0)
    {if (part_case(ms2,msec)==0) return(0);
    else return(1);}}   /* closure of else for (count!=1) */
return(0);} /* redox number is an integer */
/* FUNCTION: concatenate species to make reactions */
void react_store(int *flag,char dummy[][MAX1],char nb[][MAX1],int *isp,int *i1)
   {char react1[MXL],react2[MXL],reactb[MXL],temp[MXL],nbtemp[MAX1];
   int i,ii,lennb;
   react1[0]=NULL; react2[0]=NULL; reactb[0]=NULL;
   for (i=0;i<*isp;i++)
      {strcpy(nbtemp,nb[i]);
      lennb=strlen(nbtemp);
      ii=lennb-1;
      while (nbtemp[ii]=='0') {nbtemp[ii]=NULL; ii--;}
      if (atof(nbtemp)>0)
        {strcpy(temp,dummy[i]);
        if (nbtemp[0]!=NULL) strcat(react1," + ");
        if (atof(nbtemp)==1.0) strcat(react1,temp);
        else {strcat(react1,nbtemp); strcat(react1," "); strcat(react1,temp);}}
      else
/*...Get rid of minus sign */
        {if (nbtemp[0]!=NULL) {for (ii=0;ii<MAX1-1;ii++) nbtemp[ii]=nbtemp[ii+1]; nbtemp[MAX1-1]=NULL;}
        strcpy(temp,dummy[i]);
        if (nbtemp[0]!=NULL) strcat(react2," + ");
        if (atof(nbtemp)==1.0) strcat(react2,temp);
        else { strcat(react2,nbtemp); strcat(react2," "); strcat(react2,temp);}}}
/*...Clean up terms */
      for (ii=0;ii<MXL-2;ii++) {temp[ii]=react1[ii+2]; react1[ii]=temp[ii];}
      for (ii=0;ii<MXL-2;ii++) {temp[ii]=react2[ii+2]; react2[ii]=temp[ii];}
/*...Write reactions the PHREEQC way: species of interest is first on the right of "=" for aqueous species
*/
      if (*flag==0)  /* flag_molvol=0 */
        {strcat(reactb,react1);
        strcat(reactb," = ");
        strcat(reactb,react2);
        strcpy(react[*i1],reactb);
```

```
        for (i=0;i<NTUR;++i) anal_EQ[i]=-anal_EQ[i]; /* change log_k coefficients */
        temp[0]=NULL;
        for (i=0;i<*isp;i++)  /* change stoichio signs */
          {if (strncmp(nb[i],"-",1)==0) strncpy(nb[i],nb[i]+1,MAX1-1);
          else
            {temp[0]=NULL;
            strncat(temp,"-",1);
            strncat(temp,nb[i],MAX1-1);
            strncpy(nb[i],temp,MAX1);}}}
      else if ((*flag==1) || (*flag==2)) /* flag_molvol=1,2 */
        {strcat(reactb,react2);
        strcat(reactb," = ");
        strcat(reactb,react1);
        strcpy(react[*il],reactb);}}
/* FUNCTION: modify charge writing */
void charge_mod( char dummy[],int *length)
   {int i,count,l,chrcount;
   char temp[MAX1];char chrt[3];
   i=*length-1;
   count=0;
   while (dummy[i]=='+'){count++;i--;}
   while (dummy[i]=='-'){count++;i--;}
/* charge written in the standard way (Al+++, SO4--, ...) */
   if (count>0)
     {l=*length-count;
     for (i=0;i<l;i++) temp[i]=dummy[i];
     temp[l]=dummy[*length-1];
     temp[l+1]=count+48;
     for (i=0;i<=l+1;i++) dummy[i]=temp[i];
     dummy[l+2]=NULL;
     *length=l+1;
     return;}
/* no charge or not standard (Th6(OH)15(9+), U(CO3)5(6-), ...) */
   else
     {if ( (dummy[i]==')') && ((dummy[i-1]=='+') || (dummy[i-1]=='-')) )
       {if (dummy[i-4]=='(')
         {chrt[0]=dummy[i-3];
         chrt[1]=dummy[i-2];
         chrt[2]=NULL;
```

```
         chrcount=2;}
       else if (dummy[i-3]=='(')
         {chrt[0]=dummy[i-2];
         chrt[1]=NULL;
         chrt[2]=NULL;
         chrcount=1;}
       strncpy(temp,dummy,i-2-chrcount);
       temp[i-2-chrcount]=NULL;
       strncat(temp,dummy+i-1,1);
       strcat(temp,chrt);
       strcpy(dummy,temp);}
     return;}}
/* FUNCTION: compute log_k */
double calc_log_k(int *flag_redox,double *nbms)
{ double logk,logkO2;
logk=anal_EQ[0]+anal_EQ[1]*tc+anal_EQ[2]*tc*tc+anal_EQ[3]*pow(tc,3)+anal_EQ[4]*pow(tc,4);
if ((*flag_redox==0)||((*flag_redox==1)&&(flag_o2aq==1))) return(logk);
else if ((*flag_redox==1)&&(flag_o2aq==0))
  {logkO2=anal_EQO2[0]+anal_EQO2[1]*tc+anal_EQO2[2]*tc*tc+anal_EQO2[3]*pow(tc,3)+anal_EQO2[4]*pow(tc,4);
  logk=logk-*nbms*logkO2;
  return(logk);}
else {printf("ERROR IN FUNCTION calc_log_k\n"); exit(1);}}
/* FUNCTION: compare element to element with a known and fixed redox number */
void redox_number(char temp[],double *rdnb)
{int flag=0;
if (strcmp(temp,"O")==0) {*rdnb=-2;flag=1;}
if (strcmp(temp,"H")==0) {*rdnb=+1;flag=1;}
if (strcmp(temp,"F")==0) {*rdnb=-1;flag=1;}
if (flag==0) *rdnb=99;}
/* FUNCTION: sort master species element list a and companion array b */
void shell_sort2(int n,char a[][MAX1],char b[][MAX1])
{int i,j,inc,istr;
char va[MAX1],vb[MAX1],w[MAX1];
for (istr=0;istr<MAX1;istr++)
{inc=1;
do {inc*=3;inc++;} while (inc<=n);
do {inc/=3;
   for (i=inc+1;i<=n;i++)
    {strcpy(va,a[i]);
```

```
    strcpy(vb,b[i]);
    j=i;
    while (a[j-inc][istr] >va[istr] && strncmp(a[j-inc],va,istr)==0)
      {strcpy(w,a[j-inc]);
      strcpy(a[j],w);
      strcpy(w,b[j-inc]);
      strcpy(b[j],w);
      j-=inc;
      if (j<=inc) break;}
    strcpy(a[j],va);
    strcpy(b[j],vb);}}
while (inc>1);}}
/* FUNCTION: sort master species element list a and companion arrays b and c */
void shell_sort3(int n, char a[][3],char b[][MAX1],char c[][MAX1])
{int i,j,inc,istr;
char va[3],vb[MAX1],vc[MAX1],wa[3],w[MAX1];
double vd[NBEL];
for (istr=0;istr<MAX1;istr++)
{inc=1;
do {inc+=3;inc++;} while (inc<=n);
do {inc/=3;
   for (i=inc+1;i<=n;i++)
    {strcpy(va,a[i]);
    strcpy(vb,b[i]);
    strcpy(vc,c[i]);
    j=i;
    while (a[j-inc][istr] >va[istr] && strncmp(a[j-inc],va,istr)==0)
      {strcpy(wa,a[j-inc]);
      strcpy(a[j],wa);
      strcpy(w,b[j-inc]);
      strcpy(b[j],w);
      strcpy(w,c[j-inc]);
      strcpy(c[j],w);
      j-=inc;
      if (j<=inc) break;}
    strcpy(a[j],va);
    strcpy(b[j],vb);
    strcpy(c[j],vc);}}
while (inc>1);}}
```

```
/* FUNCTION: eliminate redundant master species and print list of master species*/
void clean_up(int *ni0,int *n)
/* if there is a secondary master species, the primary master species must also be declared as a secondary
master species
 * and added to the list of master species */
{int icount,i;int iel=1;int i0,ic;int mscount[NBEL]; char temp[3];
/* Sort element list (master species were already sorted in sort2) */
  shell_sort3(*ni0,elmsp-1,msp-1,elmspc-1);
/* count number of master species for each element */
  i=0;
  for (i0=0;i0<*ni0;i0++)
    {mscount[i0]=0;
     for (ic=i;ic<*n;ic++)
       {strncpy(temp,elallms[ic],2); /* copy at most 2 characters to compare with element list */
       temp[2]=NULL;
       if (strncmp(temp+1,"(",1)==0) temp[1]=NULL;
       if (strncmp(temp,elmsp[i0],2)==0) mscount[i0]++; /* compare with element */
       else {i=ic; break; }}}
/* print only selected species */
  i=0;
  icount=0;
  for (i0=0;i0<*ni0;i0++)
    {if (mscount[i0]==2)  /* primary master species has no secondary master species */
       {if (test_rmv(msp[i0])==1)  /* print if not a removed species */
         {calc_gfw(elmsp[i0],temp);
         fprintf(outp,"%-10s %-25s %3.1f    %-10s
%10.4f\n",elmsp[i0],msp[i0],calc_alk(msp[i0]),temp,find_weight(elmsp[i0],ni0));}
       i=i+2;
       icount=icount+2;}
     if (mscount[i0]>2) /* primary master species has at least one secondary master species, the primary
must also be printed as a secondary */
       {if (test_rmv(msp[i0])==1)  /* print if not a removed species */
         {calc_gfw(elmsp[i0],temp);
         fprintf(outp,"%-10s %-25s %3.1f    %-10s
%10.4f\n",elmsp[i0],msp[i0],calc_alk(msp[i0]),temp,find_weight(elmsp[i0],ni0)); /* print primary */
         calc_gfw(elmspc[i0],temp);
         fprintf(outp,"%-10s %-25s %3.1f    %-10s\n",elmspc[i0],msp[i0],calc_alk(msp[i0]),temp);} /* print
primary as a secondary */
       i=i+2;
```

```
       icount=icount+2;
       for (ic=i-1;ic<i+mscount[i0]-2;ic++)
         {if (strcmp(elmspc[i0],elallms[ic])!=0) /* skip primary written as secondary */
           {if (strcmp(elallms[ic-1],elallms[ic])!=0)
             {if (test_rmv(allms[ic])==1)  /* print if not a removed species */
               {calc_gfw(elallms[ic],temp);
               fprintf(outp,"%-10s %-25s %3.1f    %-
10s\n",elallms[ic],allms[ic],calc_alk(allms[ic]),temp);} /* print true secondary */
             icount=icount+1;}
           else icount=icount+1;}}
       i=ic;}}}
/* FUNCTION: specify alkalinity (as it is phreeqc.dat) */
double calc_alk(char a[])
{double alk;alk=0.0;
if (strncmp(a,"H+1",3)==0) alk=-1.;
if (strncmp(a,"Fe+3",4)==0) alk=-2.;
if (strncmp(a,"CO3-2",5)==0) alk=2.;
if (strncmp(a,"HCO3-1",6)==0) alk=1.;
if (strncmp(a,"HS-1",4)==0) alk=1.;
if (strncmp(a,"PO4-3",5)==0) alk=2.;
return(alk);}
/* FUNCTION: specify gram formula weight (as it is phreeqc.dat) */
void calc_gfw(char a[],char b[])
{char temp[MAX1];
/*  Deal with special cases */
if (strcmp(a,"E")==0)      {strcpy(b,"0.0");return;}  /*...electron */
if (strcmp(a,"H(+1)")==0)  {strcpy(b,"0.0");return;}  /*...H(1) */
if (strcmp(a,"O(-2)")==0)  {strcpy(b,"0.0");return;}  /*...O(-2) */
if (strcmp(a,"Si")==0)     {strcpy(b,"SiO2");return;} /*...Si */
if (strcmp(a,"S")==0)      {strcpy(b,"SO4");return;}  /*...S */
if (strcmp(a,"S(+6)")==0)  {strcpy(b,"SO4");return;}  /*...S(+6) */
if (strcmp(a,"C")==0)      {strcpy(b,"HCO3");return;} /*...C */
if (strcmp(a,"C(+4)")==0)  {strcpy(b,"HCO3");return;} /*...C(+4) */
/*  Regular cases: gfw formula is element */
strcpy(temp,a);
strcpy(b,strtok(temp,"("));}
/* FUNCTION: delete brackets at end of string if needed */
void del_brak(char a[],int flag_del)
{int i,lth=strlen(a)-1,flag=0;
```

```
char chrt[1],temp[MAX1];
strcpy(temp,a);
/* delete brackets if they exist if not (aq) or (g) */
if (flag_del==0) /* end is not (aq) or (g) */
  { if (strstr(temp,"(aq)")!=NULL || strstr(temp,"(g)")!=NULL ) return;
  if (strncmp(a+lth,")",1)==0)
    {strncpy(chrt,a+lth,1);
    for (i=lth-1;strncmp(a+i,"(",1)!=0;i--)
      {strncpy(chrt,a+i,1);
      if (chrt[0]<='Z' && chrt[0]>='A') flag=1;}  /* check if it is bracket within chemical formula
(Na(OH)..) */
    if (flag==0) a[i]=NULL;}
  return; }
/* delete (aq) and only (aq)  if it exists */
if (flag_del==1) /* end is (aq) */
  {if (strncmp(a,"O2(aq)",6)==0) flag_o2aq=1; /* check if aqueous species is O2(aq) */
   if (strncmp(a+lth-3,"(aq)",4)==0)
    {strncpy(chrt,a+lth,1);
    for (i=lth-1;strncmp(a+i,"(",1)!=0;i--)
      {strncpy(chrt,a+i,1);
      if (chrt[0]<=90 && chrt[0]>=65) flag=1;}
    if (flag==0) a[i]=NULL;}
  return;}
/* delete (g) and only (g)  if it exists except O2(g) */
if (flag_del==2) /* end is (g) */
  {if (strcmp(a,"O2(g)")==0) return;
  if (strncmp(a+lth-2,"(g)",3)==0)
    {strncpy(chrt,a+lth,1);
    for (i=lth-1;strncmp(a+i,"(",1)!=0;i--)
      {strncpy(chrt,a+i,1);
      if (chrt[0]<=90 && chrt[0]>=65) flag=1;}
    if (flag==0) a[i]=NULL;}
  return;}
/* delete (g) for O2(g) and only for O2(g)  if it exists */
if (flag_del==3) /* end is (aq) */
  {if (strcmp(a,"O2(g)")==0)
    {strncpy(a,"O2",2);
    a[2]=NULL;}
  return;}}
```

```
/* FUNCTION: Find the string USe (confused with PHREEQC keyword USE) and replace it with Se#U */
void change_USe(char a[])
{char temp[MAX1];int i;
strcpy(temp,a);
for (i=0;a+1!=NULL;i++)
  {if (strncmp(a+i,"USe",3)==0)  /* Is the string USe present? */
    {if (a[i+3]>'0' && a[i+3]<='9') /* if of the form USe#, change to Se#U */
      {strncpy(temp+i,"Se",2);
      strncpy(temp+i+2,a+i+3,1);
      strncpy(temp+i+3,"U",1);}
    else  strncpy(temp+i,"SeU",3); }/* if of the form USe, change to USe */
  break;}
strcpy(a,temp);}
/* FUNCTION:  skip H2O system species */
int species_skipped(char a[],int flag_sys)
{int flag_skipped;
flag_skipped=0;
if (strncmp(a,"H+",2)==0 || strncmp(a,"O2",2)==0 || strcmp(a,"H2O")==0 || strcmp(a,"H2")==0)
flag_skipped=1;
else
 {if (flag_sys==0)
/*...catch other HxOx species if H2O system is not set with H+,O2 and H2O */
   {fprintf(stderr,"H2O system not set right \n");
   fprintf(outp,"H2O system not set right \n");}}
return(flag_skipped);}
/* FUNCTION:  find atomic weight of element */
double find_weight(char a[], int *n)
{int i; for (i=0;i<*n;i++) if (strcmp(elm[i],a)==0) return(elw[i]);}
/* FUNCTION:  find B-dot parameters */
void find_bdot(void)
{int i1,i;
for (i1=0;i1<=naqueous;i1++)
  {for (i=0;i<nbdot;i++) {if (strcmp(msc[i1],diamspc[i])==0){gam[i1][0]=diam[i];break;}} /*... hard core
diameter */
  gam[i1][1]=bb;} }  /*... b-dot parameter (constant for all ions at a given temperature */
/* FUNCTION:  treat particular cases for redox number calculations */
int part_case (char a[],char b[])
{if (strncmp(a,"Br3-",4)==0){strcpy(b,"Br(-1)");return(0);}
if (strncmp(a,"CN-",3)==0) {strcpy(b,"N(-5)");return(0);}
```

```
if (strncmp(a,"I3-",3)==0) {strcpy(b,"I(-1)");return(0);}
if (strncmp(a,"N3-",3)==0) {strcpy(b,"N(-1)");return(0);}}
/* FUNCTION:  compare a species with list of species to be removed */
int test_rmv(char a[])
{int i;
for (i=0;i<rmvcount;i++){if (strcmp(a,msrmv[i])==0) return(0);}
return(1);}
```

ATTACHMENT VII

Software Routines

Among all the files cited in Attachment IV, only those files in the main directory, listed below, perform tasks other than plotting or being direct input or output files to PHREEQC runs.

File Name	Comments
dispersion_linesource.xls	Simple implementation of Equation 2.6a. The spreadsheet has been verified by visual inspection and by its reasonable results.
dispersion_pointsource.xls	Simple implementation of Equation 2.6b. The spreadsheet has been verified by visual inspection and by its reasonable results.
dispersion_pointsource_plot.xls	Plot of outputs from the file dispersion_pointsource.xls
expo-VG.xls	Implementation of Equations 2.2 and 2.17. The spreadsheet computes the α coefficient of Equation 2.2 given the α_G of Equation 2.17 using the goalseek function. The spreadsheet has been verified by visual inspection (the curves resulting from both equations coincide).
PuAccProfile_pe0a1231.xls	Summary of results from the different runs (source term pe0a1231). The spreadsheet performs simple operations and plots the results.
PuAccProfile_pw2a1231.xls	Summary of results from the different runs (source term pw2a1231). The spreadsheet performs simple operations and plots the results.
sat_calc.xls	Implementation of Equations 2.11 to 2.19. The spreadsheet computes a water saturation given a flow rate and rock properties. The spreadsheet uses the goalseek_saturation macro described below.
Tuff_composition.xls	Determination of the mineral fraction of the tuff given the normative composition of the tuff.

Description of the Excel Macro goalseek_saturation

The macro goalseek_saturation V.1.0 automatically applies the EXCEL built-in function goalseek to a group of cell. The macro does nothing more and has been verified by hand calculation (reapplying manually the built-in goalseek function on any cell gives the same result)

Listing of the goalseek_saturation V.1.0 macro:

```
Sub goalseek_saturation()
' goalseek_saturation V.1.0 Macro
' Macro recorded 5/19/00 by Jean-Philippe Nicot
    Range("E11").Select
    Range("E11").GoalSeek Goal:=0, ChangingCell:=Range("B11")
    Range("E12").Select
    Range("E12").GoalSeek Goal:=0, ChangingCell:=Range("B12")
    Range("E13").Select
    Range("E13").GoalSeek Goal:=0, ChangingCell:=Range("B13")
    Range("E14").Select
    Range("E14").GoalSeek Goal:=0, ChangingCell:=Range("B14")
    Range("E15").Select
    Range("E15").GoalSeek Goal:=0, ChangingCell:=Range("B15")
    Range("E16").Select
    Range("E16").GoalSeek Goal:=0, ChangingCell:=Range("B16")
    Range("E17").Select
    Range("E17").GoalSeek Goal:=0, ChangingCell:=Range("B17")
```

```
    Range("E18").Select
    Range("E18").GoalSeek Goal:=0, ChangingCell:=Range("B18")
    Range("E19").Select
    Range("E19").GoalSeek Goal:=0, ChangingCell:=Range("B19")
    Range("E20").Select
    Range("E20").GoalSeek Goal:=0, ChangingCell:=Range("B20")
    Range("E21").Select
    Range("E21").GoalSeek Goal:=0, ChangingCell:=Range("B21")
    Range("E22").Select
    Range("E22").GoalSeek Goal:=0, ChangingCell:=Range("B22")
    Range("E23").Select
    Range("E23").GoalSeek Goal:=0, ChangingCell:=Range("B23")
    Range("E24").Select
    Range("E24").GoalSeek Goal:=0, ChangingCell:=Range("B24")
    Range("E25").Select
    Range("E25").GoalSeek Goal:=0, ChangingCell:=Range("B25")
    Range("E26").Select
    Range("E26").GoalSeek Goal:=0, ChangingCell:=Range("B26")
    Range("E28").Select
    Range("E28").GoalSeek Goal:=0, ChangingCell:=Range("B28")
    Range("E29").Select
    Range("E29").GoalSeek Goal:=0, ChangingCell:=Range("B29")
    Range("E30").Select
    Range("E30").GoalSeek Goal:=0, ChangingCell:=Range("B30")
    Range("E31").Select
    Range("E31").GoalSeek Goal:=0, ChangingCell:=Range("B31")
    Range("E32").Select
    Range("E32").GoalSeek Goal:=0, ChangingCell:=Range("B32")
    Range("E33").Select
    Range("E33").GoalSeek Goal:=0, ChangingCell:=Range("B33")
    Range("E34").Select
    Range("E34").GoalSeek Goal:=0, ChangingCell:=Range("B34")
    Range("E35").Select
    Range("E35").GoalSeek Goal:=0, ChangingCell:=Range("B35")
    Range("E36").Select
    Range("E36").GoalSeek Goal:=0, ChangingCell:=Range("B36")
    Range("E37").Select
    Range("E37").GoalSeek Goal:=0, ChangingCell:=Range("B37")
    Range("E38").Select
    Range("E38").GoalSeek Goal:=0, ChangingCell:=Range("B38")
    Range("E39").Select
    Range("E39").GoalSeek Goal:=0, ChangingCell:=Range("B39")
    Range("E40").Select
    Range("E40").GoalSeek Goal:=0, ChangingCell:=Range("B40")
    Range("E41").Select
    Range("E41").GoalSeek Goal:=0, ChangingCell:=Range("B41")
    Range("E42").Select
    Range("E42").GoalSeek Goal:=0, ChangingCell:=Range("B42")
    Range("E43").Select
    Range("E43").GoalSeek Goal:=0, ChangingCell:=Range("B43")
    Range("E45").Select
    Range("E45").GoalSeek Goal:=0, ChangingCell:=Range("B45")
    Range("E46").Select
    Range("E46").GoalSeek Goal:=0, ChangingCell:=Range("B46")
    Range("E47").Select
    Range("E47").GoalSeek Goal:=0, ChangingCell:=Range("B47")
    Range("E48").Select
    Range("E48").GoalSeek Goal:=0, ChangingCell:=Range("B48")
    Range("E49").Select
    Range("E49").GoalSeek Goal:=0, ChangingCell:=Range("B49")
    Range("E50").Select
    Range("E50").GoalSeek Goal:=0, ChangingCell:=Range("B50")
    Range("E51").Select
    Range("E51").GoalSeek Goal:=0, ChangingCell:=Range("B51")
    Range("E52").Select
    Range("E52").GoalSeek Goal:=0, ChangingCell:=Range("B52")
    Range("E53").Select
```

```
    Range("E53").GoalSeek Goal:=0, ChangingCell:=Range("B53")
    Range("E54").Select
    Range("E54").GoalSeek Goal:=0, ChangingCell:=Range("B54")
    Range("E55").Select
    Range("E55").GoalSeek Goal:=0, ChangingCell:=Range("B55")
    Range("E56").Select
    Range("E56").GoalSeek Goal:=0, ChangingCell:=Range("B56")
    Range("E57").Select
    Range("E57").GoalSeek Goal:=0, ChangingCell:=Range("B57")
    Range("E58").Select
    Range("E58").GoalSeek Goal:=0, ChangingCell:=Range("B58")
    Range("E59").Select
    Range("E59").GoalSeek Goal:=0, ChangingCell:=Range("B59")
    Range("E60").Select
    Range("E60").GoalSeek Goal:=0, ChangingCell:=Range("B60")
 End Sub
```