APPENDIX B: GLASS DISSOLUTION SOLUTION
by Greg Pohll

White (1983) gives the following linear mass transfer equation for glass dissolution, normalized by area

$$\zeta = \zeta_0 + k_l t \tag{B1}$$

where ζ is the cumulative mass dissolved per unit area (moles/cm^2), ζ_0 is the initial dissolved mass per unit area (moles/cm^2), k_l is the linear rate constant (moles/cm^{2}s), and t is the time (s).

Taking the first derivative of Eq. B1 with respect to time determines the normalized rate of change (with respect to area) of the glass. Note also that the sign must be changed to account for a *loss* of mass from the glass, rather than a gain as was written in Eq. B1

$$\frac{d}{dt} = - k_l \tag{B2}$$

To calculate the actual mass dissolution rate in gm/s, we must multiply Eq. B2 by the specific surface area, gram formula weight and the available mass of glass

$$\frac{dM}{dt} = - k_l M A_{sp} G_{fw} \tag{B3}$$

where M is the mass of glass at any time t (gm), A_{sp} is the specific surface area of the glass (gm/cm^2), and G_{fw} is the gram formula weight (gm/mole).

Note that the units of dM/dt are now gm/s. One could also remove the gram formula weight, which would produce moles/s. Now separate variables to solve for M

$$\frac{dM}{M} = - k_l A_{sp} G_{fw} dt \tag{B4}$$

Integrating both sides gives

$$ln(M) = - k_l A_{sp} G_{fw} t + C' \tag{B5}$$

where C' is the integration constant. For simplicity, lets define a new variable k_g, which will be defined as

$$k_g = k_l A_{sp} G_{fw} \tag{B6}$$

which then simplifies Eq. B5 to

$$ln(M) = - k_g t + C' \tag{B7}$$

Taking the exponents of both sides of Eq. B7 yields

$$M = C' \, e^{-k_g t} \tag{B8}$$

The integration constant is simply the initial mass of the glass (at $t = 0$), so Eq. B8 can be written as

$$M = M_0 \, e^{-k_g t} \tag{B9}$$

where M_0 is the initial glass mass (gm).

Therefore, Eq. B9 defines the mass at any time t for the glass structure. For modeling purposes, we are more interested in the amount of glass that is in solution, which can be described as

$$M_{soln} = (M_0 - \zeta_0 A_{sp} G_{fw})(1 - e^{-k_g t}) + \zeta_0 A_{sp} G_{fw} \tag{B10}$$

Eq. B10 also includes the small amount of mass that is lost instantaneously as defined in Eq. B1 by White (1983). This term was not included in Eq. B9, but can be easily added, by redefining (more correctly) the integration constant to include the mass lost at $t = 0$

$$M_{solid} = (M_0 - \zeta_0 A_{sp} G_{fw}) \, e^{-k_g t} \tag{B11}$$

For modeling purposes, the amount of glass lost to solution between any two time steps is important so the numbers of particles that should be released can be obtained. The algorithm is as follows:

1. Assume that p is the percentage of mass released hydraulically, and thus $1-p$ represents the mass in the glass.

2. Next, one must address how much mass is lost due to the instantaneous dissolution ($\zeta_0 A_{sp} G_{fw}$). A problem is that this term is in real mass units, which makes it difficult to use a unit mass within the transport model. Rather than relying on classified data, which will remove much of the analysis from public review, the instantaneous dissolution term is ignored here. This is justified for two reasons. First, the mass involved in this term is very small relative to the total mass dissolved. The inclusion of this term is important for short-term experimental work but not for the long-term, total dissolution process considered here. Second, the process leading to this instantaneous dissolution is considered to be due to surface ion exchange, which is handled through the partioning of the radionuclides into both glass and surface deposits. The portion assigned to surface deposits (conservatively assumed to be 5% of the refractory nuclides, despite evidence that the actual percentage is closer to 1 or 2%) is assumed instantaneously dissolved in groundwater, accounting for this term.

3. By ignoring the instantaneous dissolution term, then one can simply use Eq. 3.1 in the body of the main report. Note that Eq. 3.1 simplifies to k_g as defined by Eq. B6 above, using the gram formula weight of SiO_2