Ionic Diffusion Coefficients for Transport Modeling in GoldSim

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Recent discussions about the diffusion coefficients currently used in contaminant transport models in GoldSim have centered on exploring ion-specific D_m values, as opposed to the single value of 4.3×10^{-5} cm^2/s for transuranics (TRU) as used in the Performance Assessment (PA) for the Greater Confinement Disposal (GCD) boreholes at the NTS (Cochran, et al. 2001). The GCD PA justifies the use of this value thus: "The molecular diffusion coefficient is not radionuclide -specific ... because the radionuclides themselves are of similar size." While that may hold true for the TRU waste in the GCD boreholes, it most definitely is not true for the wide variety of radionuclides found in low-level radioactive wastes disposed in other facilities.

I investigated approaches for incorporating individual D_m values for the chemical elements in the model, a long list spanning most of the periodic table with extreme ranges of ion sizes. Thus it would seem prudent to derive D_m values for each element used in the model. However, after investigating this issue I will provide two arguments for using a range of D_m values, rather than attempting to provide individual values.

D_m derivation: Ionic and molecular diffusion coefficients are derived in theory from the Stokes-Einstein equation:

$$D_{AB} = RT/6\pi\,\eta_B\,r_A,$$

where

- R = universal gas constant,
- T = temperature,
- η_B = absolute viscosity of the solvent (water), and
- r_A = radius of the "spherical" solute.

A variety of empirical equations have been derived based on the Stokes-Einstein equation for different scenarios. For a dilute solution of a single salt the diffusion coefficient can be derived from the Nernst-Haskell equation (Reid et al., 1987). This equation includes the valence of the cation and anions as well as ionic conductances. Specific ionic conductances are required for each cation and anion species. When two or more chemical species are present at different concentrations, interdiffusion (counterdiffusion) must be included to satisfy electroneutrality (Lerman 1979). For a geochemical system as large as that found in LW disposal facilities this quickly becomes too complex to model, even if ionic conductivities are available for each species.

The second difficulty in deriving diffusion coefficients lies in the large number of potential ions. The number of LLW elements typically modeled may be 30 to 40, and for each element in this list one can expect multiple forms. For example, U has 4 redox states, and many soluble species for each of these. Assuming oxic conditions U will be primarily found as $UO_2(CO_3)_3^{-4}$, $UO_2(CO_3)_2^{-2}$, and $UO_2CO_3^{0}$, however there are at least 8

additional forms of U(+6) that may be found. Thus the potential number of ions that would need to be included in the model would easily be in the hundreds. Obtaining the parameters for each species that would be required to model the ionic diffusion would be difficult.

Solution: I propose a D_m range be incorporated. This range can be derived from Table 3.1 in Lerman (1979). For conditions near 25°C, the range of D_m for the elements of interest is 4×10^{-6} to 2×10^{-5} cm^2/s. For cooler temperatures, which would be expected in the deeper subsurface, the values are somewhat lower. The values for 25°C are reproduced in the following table:

Cation	D_m (10^{-6} cm^2/s)	Anion	D_m (10^{-6} cm^2/s)
K^+	19.6	Cl^-	20.3
Cs^+	20.7	I^-	20.0
Sr^{2+}	7.94	IO_3^-	10.6
Ba^{2+}	8.48		
Ra^{2+}	8.89		
Co^{2+}	6.99		
Ni^{2+}	6.79		
Cd^{2+}	7.17		
Pb^{2+}	9.45		
UO_2^{2+}	4.26		
Al^{3+}	5.59		

from Table 3.1 in Lerman (1979)

Based on this discussion, the value chosen for the GoldSim element \Materials\Water_Properties\Dm is a uniform stochastic, varying from 3×10^{-6} to 2×10^{-5} cm^2/s.

References

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