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MODELING URANIUM SOLUBILITY IN AGED VAULT DISPOSAL (U)

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Using Version 3.0 of the ESP software from OLI Systems containing thermo dynamic data for uranium in the expanded data base, I have modeled the uranium solubility with the highest degree of accuracy available considering the limitations of the model. Uranium solubility in most oxic environments is taken to be complete, i.e. all the uranium present is present as soluble uranyl salts at low concentrations. However, in modeling the chemistry of aged waste disposed in TRU vaults it is assumed that the organic components have been converted by aerobic and biological decay to an anoxic slurry and the steel waste containers have oxidized in part to a ferrous/ferric hydroxide slurry. The solubility modeling is valid only in anoxic regions where the redox potential is controlled by the ferrous/ferric couple. The redox behavior of the organics and biological activity are not addressed, but would only decrease the solubility further at pH < 8 where some uranyl species contribute to the overall solubility. By contrast, the calculated solubility due to carbonate complexes at pH < 7 could be low since the available carbonate in solution is not controlled by the solubility of CaCO₃ until pH 7 is attained.

Table 1 contains concentration data for the major species of U(IV) and U(VI) determined by the ESP data base and equilibrium calculations at pH 4 - 8. In each case there were initially equal amounts (1.00E-6 Molar) of U(IV) and U(VI) and equal amounts (1.00E-4 Molar) Fe(II) and Fe(III).

The following redox equation was used to describe these two redox couples:

In acid medium ferrous ion is incapable of reducing uranyl salts, but at higher pHs the low solubility of Fe(III) and U(IV) combine to form a product sink which drives the reaction to near completion by pH 8. Above pH 8 the solubility is controlled almost entirely by U(IV) (OH)₄aq in equilibrium with UO₂xtal. These effects are clearly indicated graphically in Figures 1 and 2 which present the total solubility and speciation of this solubility as a function of pH.

TABLE I

U Speciation as a Function of pH

Species/pH	4.0	5.0	6.0	7.0	8.0
UO ₂ solids	0	0	1.977E-6	1.999E-6	2.000E-6
U(IV) ion	0	0	0	0	0
U(OH) ₁ ion	0	0	0	0	0
U(OH) ₂ ion	0	0	0	0	0
U(OH) ₃ ion	1.12E-20	0	0	0	0
U(OH) ₄ ion	8.39E-18	3.38E-12	3.04E-10	3.04E-10	3.04E-10
U(OH) ₅ ion	0	2.11E-17	1.89E-14	1.83E-13	3.68E-17
SU(IV) sol.	8.40E-18	3.38E-12	3.04E-10	3.04E-10	3.04E-10
U(VI)O ₂ ion	1.91E-6	7.68E-7	7.64E-11	3.43E-16	3.39E-21
U(VI)O ₂ OH ion	6.96E-8	2.81E-7	2.79E-10	1.36E-14	1.62E-18
U(VI)O ₂ CO ₃	2.31E-8	9.19E-7	8.24E-9	1.32E-12	6.01E-17
U(VI)O ₂ (CO ₃) ₂ ion	1.42E-9	1.73E-8	1.39E-8	6.37E-11	7.86E-15
SU(VI) sol.	2.00E-6	1.98E-6	2.24E-8	6.50E-11	7.93E-15
Total U sol.	2.00E-6	1.98E-6	2.27E-8	3.69E-10	3.04E-10

The speciation presented in table I results from calculations based upon thermodynamic data compiled at Lawrence Berkeley Laboratory by Phillips et al. and published as "Thermodynamic Tables for Nuclear Waste Isolation, Aqueous Solution Database" NUREG/CR-4864, 1988 page 138.

URANIUM SPECIATION

Figure 1 Solubility of 2 micromolar uranium as a function of pH.

Figure 2 Speciation of soluble uranium as a function of pH.

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