ATTACHMENT

FY 1993 SCOPE OF WORK

Task 1. DEVELOPMENT OF THERMODYNAMIC DATA FOR 25 C

Carbonato Complexes of Tetravalent Actinides

Oxides and hydrous oxides of tetravalent actinides have very low solubility and reliable solubility products for these compounds are available (Rai 1984; Rai et al. 1987, 1990; Ryan and Rai 1987). These data suggest that reasonably low upper limits can be set on the concentrations of these elements in repository leachates, provided it can be shown that aqueous complexation due to the presence of CO3 , Cl-, SO4 , F-, and PO4 in the groundwater/glass-leachates do not significantly increase their solubility. Therefore, accurate thermodynamic data for actinide complexes/ion-interactions with groundwater anions are required to determine their influence on the solubility of tetravalent actinide compounds.

Only limited experimental data are available for the An(IV) complexes with carbonate (Moskvin and Gelman 1958; Moskvin 1971; Kim et al. 1983; Moriyama et al. 1989). These data form the basis for values reported in many past reviews of actinide thermodynamic data (Lemire and Tremaine 1980; Phillips 1982; Keller 1971). The reported values (k1=10. to 10.)indicate that carbonate makes very strong complexes. If these values were correct, they would make the An(IV) Oxides extremely soluble. However, recent results show that such high carbonate constant values are at least 20 orders of magnitude too high (Rai and Ryan 1985). We surmise that the reasons for such high values in previous studies include experimental difficulties (such as maintaining a proper oxidation state or effectively separating solids from solution) and difficulties in interpreting the data as a result of very high salt concentrations, inadequate characterization of the equilibrium solid phase/s, and the lack of reliable thermodynamic data for the equilibrium solid and the appropriate hydrolysis species. We are now in a position to overcome many of these difficulties. We propose to obtain the values of carbonato complexes from solubility measurements of tetravalent actinide hydrous oxides, the chemical potentials for which were previously determined, in the presence of varying amounts of carbonates and as a function of pH, where appropriate. We will monitor/control the redox potential and throughly characterize the solid and the aqueous phases. Our proposed studies will involve hydrous oxides of Th, which has only one oxidation state, and we will initiate studies of U and Np, where tetravalent oxidation states can be maintained by using redox agents. Carbonato complexes of Th through Th(OH)-(am) solubility in carbonate media and initiate studies with Np(IV)/U(IV) carbonate complexes (include progress to date) will be included in the report of FY 1993 Work.

Task 2. DEVELOPMENT OF MECHANISTIC DATA AT HIGHER TEMPERATURES

In FY 1993, we will initiate studies to develop thermochemical data at higher temperatures. Few reliable thermochemical data exist for the actinides at higher temperatures. This lack of necessary data includes even the fundamental hydrolysis reactions that must be understood before any of the other strong complexation reactions can be evaluated.

Therefore, in FY 1993 we propose to study the hydrolysis reactions of Nd(III)/Am(III) at higher temperature. These studies will involve the solubility of neodymium hydroxide/oxide over a range of pH values. These data will allow us to design the necessary experiments to evaluate the effects of other strong complexants such as carbonate and sulfate. Nd/Am was selected because of its importance in performance assessment modeling and because of our extensive experimental experience with these elements. Hydrolysis constants of Nd/Am(III) at higher temperature will be included in the report.

Task 3. DEVELOPMENT OF MECHANISTIC ADSORPTION CONSTANTS

The geochemical behavior of those elements and oxidation states that do not form insoluble solid phases can be controlled by the adsorption process. The pentavalent and hexavalent actinides, with a few posible exceptions, do not generally form insoluble solid phases. This is particularly true of Np(V) and pertains to a slightly lesser extent to U(VI) Therefore, to predict the geochemical behavior of these species, the values of mechanistic adsorption constants for these oxidation states are required. Such a mechanistic understanding of the develop reliable and scientifically defensible performance assessment models for both the near and far field.

In the mechanistic adsorption approach, intrinsic stability constants are developed for the adsorption of specific actinide and groundwater species onto discrete adsorption sites or onto functional groups present on the adsorbents/geologic materials. For example, the mechanistic approach may require quantitative data for the adsorption of actinide species onto aluminum oxide or silicon oxide functional groups that are present in the bentonite, or onto iron oxide functional groups that may be present as coatings on bentonite or may form from the corroding overpack material. These quantitative adsorption data for functional groups are then used to interpret the adsorption in complex geologic materials. These quantitative adsorption data for functional groups are then used to interpret the adsorption in complex geologic materials. Therefore, this approach will require data for pure phase adsorbents, such as iron and aluminum oxides and controlled experiments with more complex materials (e.g., bentonite) over a range of pH values, actinide species concentrations, and, if appropriate, competing ion concentrations. Consequently, the adsorbents that must be considered for near-field analyses include iron oxides, montmorillonite/beidellite, aluminum oxide, amorphous aluminosilicates, bentonite, and other repository materials.

Among the pentavalent and hexavalent actinides, U(VI) and Np(V) are most ideally suited for experimental adsorption studies. To unequivocally interpret the adsorption experimental data for the species, however, values of thermodynamic equilibrium constants are also required for the actinide species with the ligands that are expected in the repository environment. Uranium (VI) hydrolyzes very readily, yet reliable values for hydrolysis constants are not available. Neptunium (V) does not readily hydrolyze and does not form strong complexes with many anions such as Cl - and SO . . . Because reliable data for U(VI) hydrolysis is unavailable, we will therefore initiate adsorption studies with Np(V).

Some data for Np(V) adsorption by iron oxides developed at BNW (Girvin et al. 1991) and elsewhere (Nakayama and Sakamoto 1989) are available. Therefore, our initial Np(V) adsorption studies will concentrate on acquiring new data on other important adsorbents, such as aluminum

oxide/hydroxide, which could be present in the repository environment. The adsorption of Np(V) on the selected adsorbents will be studied as a function of pH, Np(V) voncentration, adsorbent quantity, and concentration of major groundwater ions that could compete with Np(V) for adsorption sites and thus possibly displace Np(V) from the selected adsorbent. Limited experimental validation of Np(V) adsorption on Fe/Al oxides will be included in the report.