ATTACHMENT TO

JOINT WORK STATEMENT FOR THE ANNEX TO THE PNC-DOE AGREEMENT: DEVELOPMENT OF FUNDAMENTAL THERMODYNAMIC AND ADSORPTION DATA

For research to be conducted at Pacific Northwest Laboratory
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FY 1996 SCOPE OF WORK

Task I. DEVELOPMENT OF THERMODYNAMIC DATA FOR 25°C

Carbonato Complexes of Tetravalent Actinides

Carbonate can make strong complexes with tetravalent actinides. To determine the complexation constants of Th and U(IV) with carbonate and to determine the solubilities of ThO_2(am) and UO_2(am) in the presence of carbonate, studies of the solubility of ThO_2(am) and UO_2(am) as a function of HCO_3 (ranging in concentrations from 0.001M to 1.0M), CO_3 (ranging in concentrations from 0.001M to 5.0M), and as a function of OH at a fixed CO_3 were completed in the first year of this contract (FY 1993). These studies (Rai et al. 1995a) showed that 1) carbonate makes strong complexes with Th and U(IV), 2) the solubilities of ThO_2(am) and UO_2(am) increase with the increase in HCO_3 and CO_3, and 3) the solubility of ThO_2(am) and UO_2(am) at a fixed CO_3 decrease with the increase in OH. Although the slopes of the log Th and log U versus log HCO_3 or CO_3 are similar, the total U concentrations at any given HCO_3 or log CO_3 are four to six orders of magnitude lower than that of Th. These differences in U and Th concentrations may be due to the differences in the solubility products of ThO_2(am) and UO_2(am) and/or in the values for carbonato complexation constants. Under the second year of the contract studies on the solubility of NpO_2(am) in carbonate media are in progress. The preliminary results indicate that aqueous Np concentrations in equilibrium with NpO_2(am) are similar to those observed for UO_2(am) solubility, indicating stronger aqueous complexes between Np and carbonate than between U

and carbonate. These results indicate that complexation of Pu(IV) with carbonate may be even stronger than between Np(IV) and carbonate. Given these facts and that no reliable data are available to predict PuO_2(am) solubility in carbonate media, studies on the solubility of PuO_2(am) in carbonate media are planned for the third year of the contract. PuO_2(am) solubility studies will be carried out at both PNC and PNL and will result in a joint paper. PNC will emphasize studies in low carbonate media while PNL will emphasize studies in concentrated carbonate solutions.

In addition to these studies, PNL in FY 1997 will provide input and peer review of thermodynamic data to be used in performance assessment calculations by PNC. The emphasis of this activity will be on actinides. For specific milestones see Table 1.

Task 2. DEVELOPMENT OF MECHANISTIC DATA AT HIGHER TEMPERATURES

There is a paucity of reliable thermodynamic data at temperatures higher than ambient. $Nd(OH)_3$(c) solubility and hydrolysis constants of Nd at 25° and 90°C were studied under the first and second year of this contract. Studies on $NdOHCO_3$(c) solubility at high temperatures are being initiated under the second year of the contract. These studies will provide information on the solubility and complexation constants of Nd with carbonate of trivalent actinides, especially Am. These data will be useful in interpreting Am behavior at higher than ambient temperatures. These studies of $NdOHCO_3$ at high temperatures will be completed in FY 1996. In addition to the affect of temperature on aqueous complexation constants and solubility products, temperature may affect the crystallinity of the solids which in turn may significantly affect the predicted solubilities (expected solubilities of crystalline actinide oxides are about 8 orders of magnitude lower than the amorphous hydrous oxides). Experiments on the kinetics of ThO_2(am) crystallization and associated changes in solubilities at temperatures higher than ambient will be initiated in FY 1996. For specific milestones see Table 1.

Task 3. DEVELOPMENT OF MECHANISTIC ADSORPTION CONSTANTS

The emphasis of these studies is on developing comprehensive mechanistic data for reliably predicting Np(V) adsorption. These studies will include the adsorption of Np(V) by montmorillonite and aluminum/iron oxides in the absence and presence of carbonate as a function of pH, ionic strength (maintained by $NaClO_4$), and Np(V) concentrations. We need to point out that in order to interpret these data, reliable values of Np(V) hydroxo and carbonto complexes will be required and have recently become available.
No activities under this task are planned in FY 1996.

Task 4. VALIDATION OF THERMODYNAMIC DATA

Thermodynamic data are being developed with the intention that it will help either set upper limits or accurately predict the aqueous concentrations of important radionuclides that can leach from the wastes disposed of in geologic environments. Therefore the reliability/accuracy/applicability of the thermodynamic data to help make these predictions must be ascertained.

Three types of experiments are required to accomplish this goal. These include 1) verification of the data with specific system, where only available data are for analog system (e.g., information about $PuOHCO_3$ solubility is deduced from $AmOHCO_3$ but data specifically for $PuOHCO_3$ will be required for accurate prediction), 2) checking the reliability of thermodynamic data in mixed electrolytes for application to groundwaters that contain many ions, because most often thermodynamic constants are obtained from single electrolytes, and 3) studying the leachability of wastes to determine if thermodynamic data can be used to explain the observed behavior. These experiments are also necessary to show whether the needed thermodynamic data for important solid and aqueous phase reactions are available. Data for important reactions responsible for leachability are required to develop a mechanistic understanding of waste form dissolution. We previously developed comprehensive thermodynamic data for trivalent rareearths and actinides (Rai et al. 1983,