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 1994 SCOPE OF WORK

Task 1. 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 will be completed in FY 1993. These studies are showing 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. Based on these observations and the fact that the solubility products of tetravalent actinides decrease with the increase in the atomic number (Rai et al. 1987), the solubilities of tetravalent actinides in the presence of carbonate is expected

to decrease in the following order: Th> U> Np> Pu. Studies with Np(IV) and Pu(IV) in the carbonate system are also required to determine the magnitude of these decreases and to obtain reliable values of carbonato complexes. Therefore, in FY 1994 we will initiate studies to determine the carbonato complexes of Np(IV) and Pu(IV) and the solubilities of NpO_2(am) and PuO_2(am) in the carbonate media. In addition to these studies, two journal articles, one on Th and the other on U, dealing with carbonato complexes and the solubility of hydrous oxides in the presence of carbonate will be prepared under this Task.

Task 2. DEVELOPMENT OF MECHANISTIC DATA AT HIGHER TEMPERATURES

In FY 1993 studies were initiated to determine the hydroxo complexes of Nd^{3+} at 90°C from solubility measurements of crystalline $Nd(OH)_3$(c). Crystalline $Nd(OH)_3$ was prepared by precipitation in high NaOH concentrations. The solubility of $Nd(OH)_3$(c) at 90°C and 25°C as a function of pH will be completed. Special equipment to conduct these studies was built/acquired so that the temperature of the samples can be maintained during all phases of the study including equilibration, filtration, and measurement of pH.

In FY 1994, high temperature studies will be extended to the study of carbonato complexes of Nd/Am. We plan to obtain these data through the solubility of $NdOHCO_3$(c) as a function of pH and pCO_2(g) at 70°C to 90°C. Also in FY 1994, we plan to write a journal article on the hydroxo complexes and solubility product of $Nd(OH)_3$(c) at 90°C.

Task 3. DEVELOPMENT OF MECHANISTIC ADSORPTION CONSTANTS

The emphasis of these studies is on developing a comprehensive mechanistic data for reliably predicting Np(V) adsorption by geologic materials in any given groundwater. 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. In FY 1993, we began a review of the available literature, including some that are currently unpublished, on these complexes. We also obtained and initiated the characterization of important adsorbent materials such as montmorillonite. Accurate characterization of surface areas, site densities, and impurity content is important in obtaining accurate mechanistic data. PNC has been characterizing minerals for absorption studies and will provide PNL with well characterized materials for use in mechanistic studies. PNL will continue studies of Np(V) absorption in FY 1994.

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.

Two types of experiments are required to accomplish this goal. One set of experiments consists of 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.

The other set of experiments consist of 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 mechanistic understanding of the waste form dissolution. We previously developed comprehensive thermodynamic data for trivalent rareearths and actinides (Rai et al. 1983, 1992a, 1992b, 1994; Felmy et al. 1989, 1990; 1992), primarily under PNC funding, and have shown (Rai et al. 1992) that reliable predictions of the leaching behavior of Nd/Am from borosilicate glasses can be made using these data.

We have recently developed (with PNC and DOE funding) an extensive amount of thermodynamic data for Th interactions with Cl, SO_4, F, CO_3, OH (Ryan and Rai 1987; Felmy et al. 1991, 1992, 1993). Therefore, we are now in a position to test whether an adequate amount of data exist to reliably predict the leachability of Th from Th doped borosilicate glasses. We will start a joint experimental effort to be carried out at PNC and at PNL. In this effort, PNC will prepare Th doped glass of the composition slated for use in waste disposal. PNL will use the glasses prepared earlier for Nd studies (Rai et al. 1992).

Preliminary studies with doped glasses at PNL indicated that Th is much more insoluble than the ThO_2(am). Because reliable values of the complexation constants of Th with important groundwater ligands will be available, the emphasis of studies with Th-doped glasses will be on validating the thermodynamic data for their applicability to waste form leaching and identification of solubility controlling solid phase of Th. Powdered doped glass will be used in the studies to enhance the kinetics of dissolution. The leachability of Th will be studied as a function of different variables including pH, carbonate, and potentially Cl and SO_4. The results of the studies from PNC and PNL will be combined into a comprehensive joint manuscript.

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