

426.1/B0290/JWB/84/09/26/0

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SEP 27 1984

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Dear Susan:

Subject: Contract B-0290, "Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques and Procedures"

I have reviewed the August, 1984 Monthly Progress Report for the subject contract dated September 7, 1984. Based on my review, progress to date is satisfactory.

Pertaining to the neptunium sorption experiments, I am pleased to hear that rate studies have been initiated. In the experiments designed to determine the effects of surface area/volume ratios on neptunium sorption, what range of these ratios do you plan to study and how does this compare with anticipated SA/V ratios in a nuclear repository? How is this parameter going to be varied inasmuch as it is a function of both grain size and water/rock mass ratio?

For the chromatographic studies, the difference between your results and BWIP's results using batch (?) experiments needs further explanation. Comparison is difficult without details of the experiments. Is it that they measured apparent solubility limits (vertical portion of a sorption isotherm) or is it that physicochemical conditions were different for the two sets of experiments? Have you made predictions as to the americium speciation in your tests?

Do you observe peak broadening and skewing in these experiments as you do in experiments involving neptunium? In the Draft Quarterly Report, April-June

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1984, the statement is made that peak broadening and skewing, which results from sorption/desorption disequilibria, increases with increasing temperature. This makes no sense to me. Some other factors must be producing this phenomenon.

One justification given for performing chromatographic sorption experiments is that multiple speciation can produce nonconservative radionuclide concentrations in the liquid in batch experiments. This statement has appeared in the Letter Report (L-290-3), the Quarterly (April-June, 1984), and your letter to me dated September 7, 1984. I would appreciate it if you would consider the following analysis.

The statement has been made that when multiple species are present in solution "the sorption isotherm measured represents a weighted average of the sum of the curves for the individual species and will be conservative for more strongly adsorbed species and nonconservative for less strongly adsorbed species". Figure 1 is a sorption isotherm modified after Figure 4 of the Letter Report.

From the discussion, point X is the measured concentration (or bulk composition) of radionuclide in solution. The discussion and diagram imply that the "lever rule" can be used to describe concentrations of species in solution. Thus, $X = bC_B/(a+b) + aC_A/(a+b)$, where a is the quantity of solution containing A at concentration C_A and b is the quantity of solution containing B at concentration C_B . However, the lever rule is normally used to explain the relationship between quantities and compositions of two phases. Here, the lever rule is being applied to one phase, the liquid. Furthermore, in Figure 1, the chemical conditions (Eh, pH, ligands, etc.) necessary to produce the isotherm involving pure B in the liquid are different from those necessary to produce the isotherm involving pure A. These conditions are, in turn,

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different from those in the sorption experiments involving both A and B. Thus, the three isotherms represent three separate sets of experiments and comparison to evaluate conservatism is invalid. (In addition, the apparent solubility limit could be different for the different set of conditions, e.g. U as a function of pH.)

Figure 2, an idealized sorption isotherm, is produced from a set of batch sorption experiments in which all physicochemical parameters (T, P, X_j) are held constant and only the radionuclide concentration (X_1) is allowed to vary. For comparison of Figures 1 and 2, the measured isotherm (solid line) in Figure 2 can vary between the extreme isotherms (dashed lines) in Figure 1 in response to changes in the physicochemical conditions of the experiments. The total concentration (C_T) of radionuclide in solution is $C_A + C_B$. Under these conditions, C_T is always greater than or equal to C_A or C_B . Thus, when considering multiple speciation, batch experiments should yield conservative results for a given set of physicochemical conditions.

By no means is this analysis meant to reduce the importance of chromatographic studies. As pointed out in your letter, chromatographic studies have several advantages over batch tests in that the effects of multiple speciation, multiple radionuclides, and sorption/desorption disequilibria can be determined.

A package of information and forms for acquiring Yucca Mountain samples will be sent to DOE shortly. This package includes the Letter Report L-290-6 requesting the samples, the SOW, and Work Plans for B0290, and the QA Programs for Oak Ridge.

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I am in the process of reviewing the Quarterly Progress Report, April-June, 1984. This review should be completed by next week if the "brush fires" are kept to a minimum.

Please note, my telephone number is FTS 427-4055. I see on the NRC Form 426A that it was listed as 427-4571. That is no longer my number.

The action taken by this letter is considered to be within the scope of the current contract FIN B-0290. No change to cost or delivery of contract products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contract products.

Sincerely,

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John W. Bradbury
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosures:
As Stated

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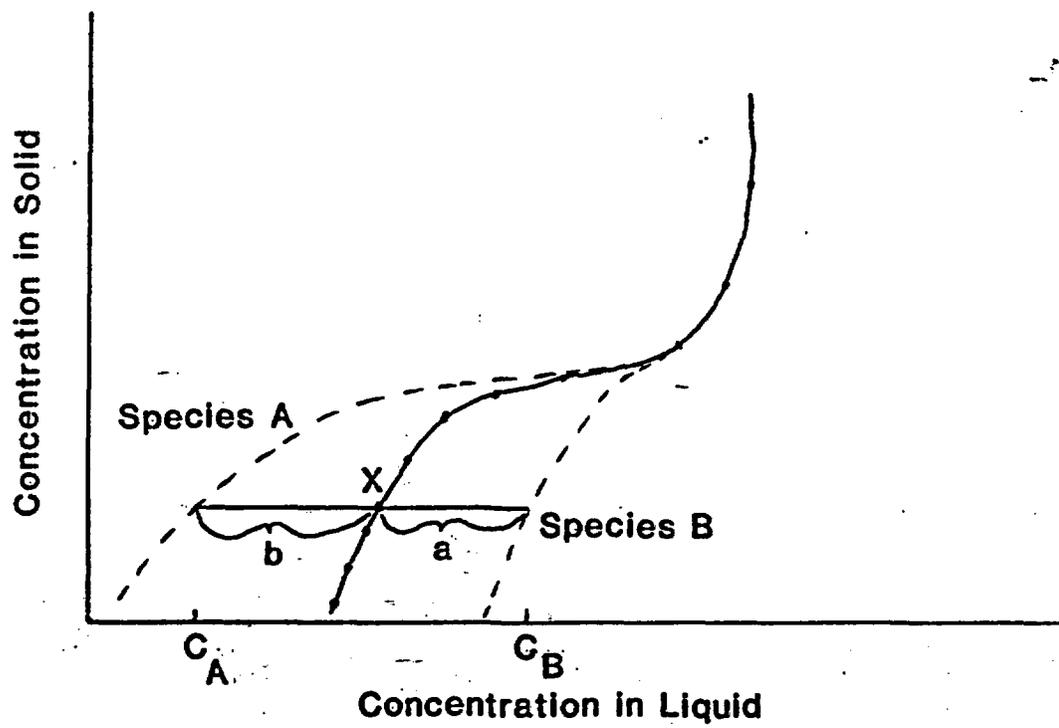


Figure 1

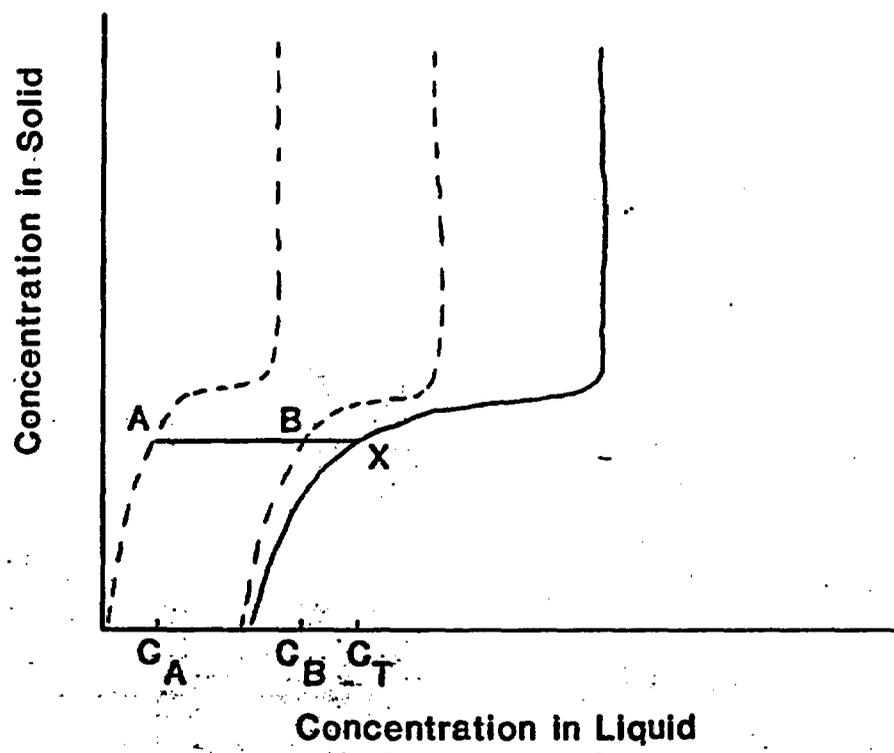


Figure 2