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Dear Dave:

Please find enclosed the letter reports referenced in the March monthly progress report.

Sincerely,

*Gary*

Gary K. Jacobs  
Manager, NRC Waste Program

GKJ/

Enclosure:

LR-287-32,36,37,38

cc w/o enclosures:

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LETTER REPORT

TITLE: Review of "Solubility Experiments for the Nevada Nuclear Waste Storage Investigations Project," by Jerry F. Kerrisk, LA-10560-MS, November, 1985.

AUTHOR: G. D. O'Kelley

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
NRC #50 19 03 01

REVIEW

The objective of this report, as stated by the author, was to define a group of experiments for providing the solubilities of important waste elements under conditions characteristic of the Yucca Mountain site, which would also satisfy the requirements of the U.S. Nuclear Regulatory Commission technical position on solubility (NRC, 1984). The stated intent of the approach was to determine those solubility values that would represent upper limits on waste-element concentrations, i.e., conservative values. The subject matter presented in the report does not parallel the order of the draft position on solubility, so in the discussion below, the appropriate issue in Section 3.0 of NRC (1984) will be indicated in brackets.

Two natural waters are suggested as representing limiting conditions in the unsaturated zone near the repository [Sec. 3.0, (1)]. Water from well UE25p#1 has about ten times the ionic strength of the water from well J-13 [Sec. 3.0, (1),(2)]. The author proposes that solubility experiments will employ these waters, as well as a dilute, noncomplexing medium such as sodium perchlorate in pure water. Measurements will be made over the nominal range of pH 5.5-10. Because the Eh of all natural waters at and near Yucca Mountain is oxidizing, all solubilities will be measured under oxygen-saturated conditions. Attempts will be made to determine values of Eh for these solutions.

Compositional changes in the water induced by the reaction with the host rock, the waste package, and the engineered barrier will be investigated at temperatures up to the maximum repository temperature. These experiments will be confined to reactions with J-13 well water. A related aspect of the solubility measurements will be a study of the stability of the water as a function of time.

Solubility measurements will be made over a range of temperatures chosen to represent conditions at the repository and along flow paths to the environment. For J-13 well water, which has been selected, but not

proven, as characteristic of vadose water in the host rock, solubility measurements are planned for temperatures of 25, 60, and 90°C. For water from well UE25p#1 and the noncomplexing electrolyte, the temperatures will be 25 and 60°C, which are considered to be temperatures characteristic of the saturated zone under the repository [Sec. 3.0, (1)].

In carrying out solubility measurements, the author proposes to approach steady-state concentrations of solute from undersaturation and oversaturation [Sec. 3.0, (3)]. Experiments approaching steady-state concentrations from oversaturation will be done first, so the solids which form can be characterized. If possible, the solids identified will then be prepared and used to approach the steady state from undersaturation. Ideally, the steady-state concentration should be the same for both kinds of experiments. Although the author briefly acknowledges some of the difficulties inherent in this method, the only one discussed in much detail is the practical problem of phase separation [Sec. 3.0, (4)].

In another document, Kerrisk (1985) has explored some of the parameters which might be used to identify and rank the priorities of elements to be used in solubility measurements. Kelmers (1986) has evaluated this report and found that, because so many conclusions were dependent on data not yet known (such as solubility, sorption, speciation), the recommendations were generally only qualitative. Nevertheless, on the basis of the analysis in Kerrisk (1985), the author proposes the following groups of elements as candidates for solubility measurements:

1. Pu, Am, and Np,
2. U and Th,
3. Ra, Ni, and Zr, and
4. other waste elements.

The category of other waste elements was not specified, but at present it is not thought that it will include C, Tc, Cs, Sr, or I.

It is proposed that radiation-induced effects on solubility will arise through changes in the composition of the water or changes in the crystallinity of solids that form. Both gamma and alpha radiation exhibit similar effects in the water, namely, a reduction in pH and a trend toward more oxidizing conditions. Gamma radiation will be most important early in the life of the waste and will affect only the water near the waste. Because alpha particles generally have a very short range in matter compared to beta or gamma rays, solids containing high concentrations of alpha emitters are expected to undergo self-irradiation damage, so that actinide oxides or hydroxides are expected to precipitate as amorphous solids. The author states that, although no solubility measurements are contemplated in artificial gamma radiation fields, the effects of alpha radiation on solubility will be investigated. The ranges of water composition contemplated for the solubility studies is expected to include the composition ranges induced by radiation effects.

As recommended in NRC (1985), an experimental matrix has been devised for the solubility measurements [Sec. 3.0, (1)]. This matrix includes the range of water compositions discussed above, a range of values of pH from about 5.5 to 10, temperatures of 25° to 90°C, and the range of elements mentioned earlier. In addition, some measurements will be carried out with mixtures of isotopes to test the effects of alpha activity on solubility, at various specific activities of Pu and Am.

A thermodynamic modeling effort will be associated with the solubility studies [Sec. 3.0, (5)]. At present, the author proposes that the EQ3/6 chemical equilibrium code will continue to be used to model waste-element solubilities as a method for testing thermodynamic modeling of the solubility process. It is anticipated that comparison between calculated and measured quantities will be useful in the design of experiments to measure quantities which are poorly known. Thus, as recommended in NRC (1985) [Sec. 3.0, (5)], the planned thrust of the modeling program will be to interpret experimental results and to plan new experiments.

### EVALUATION

This document outlines an approach to the experimental determination of solubility information for the Yucca Mountain site. However, there are few specifics discussed regarding the experimental methods to be employed in acquiring the necessary data. For example, it is not clear that the conventional methods of chemical analysis will lead to an adequate characterization of the species present in dilute solutions in equilibrium with sparingly-soluble solids. Measurements at relatively high concentrations cannot be related with confidence to the speciation characteristic of extremely dilute solutions. Knowledge of such speciation is essential to an understanding of transport and retardation processes. Although slow kinetic behavior is mentioned as a problem in some systems, the report does not discuss how this problem might be handled.

The choice of oxidizing conditions for the tests should lead to conservative values for solubilities. It is also helpful that the program will emphasize results that will aid in understanding and modeling solubility even if it is not yet clear how this will be done.

The selection of waste elements to be studied is incomplete. As discussed by Kelmers (1986), the recommendations in Kerrisk (1985) appear to be somewhat speculative, and the conclusions suggest much additional work on solubility and sorption before final choices can be made. In the current report the reader gains the impression that the selection of waste elements is likely to be a cyclic process, in which new data on solubility and sorption will make possible a continuous refinement of the list of elements and priorities for the program.

This report addresses most of the requirements in the technical position on solubility, NRC (1985). The principal weakness is a failure to discuss in detail the complex question of evaluating uncertainties [NRC, 1985; Sec. 3.0, (4)]. Uncertainties in measured values of solubilities

due to radiation damage and incomplete phase separation were mentioned, but only in qualitative terms.

It is not sufficient to restrict the choice of aqueous media to J-13 and UEp#1 well waters and one composition of a noncomplexing electrolyte such as  $\text{NaClO}_4$  (mentioned in the report as a "neutral electrolyte"). To make meaningful comparisons between the complexing and noncomplexing media, it would be advisable to carry out experiments using noncomplexing media with several values of ionic strength in the range delimited by the two well waters. Also, to make the comparisons complete, solubility tests in the noncomplexing solutions should be carried out over the full temperature range of  $25^\circ - 90^\circ\text{C}$ , and not just  $25^\circ - 60^\circ\text{C}$ .

Because there is so little detailed information in the report, a meeting on solubility might be useful, if it were to emphasize experimental methods, problems, and uncertainties. Many of the possible topics would be just the subjects addressed in the current report. Some suggested agenda items are listed below:

1. NNSWI water compositions
  - a. Effects of waste emplacement
  - b. Reactions between water and host rock, waste package, and engineered barrier
  - c. Water stability with time
  - d. Temperature effects on water compositions
2. Speciation, including colloid formation, in solutions equilibrated with solid phases
3. Experimental methods for determination of solubilities
4. Temperature effects on solubility
5. Radiation effects
6. Selection of waste elements for solubility studies
7. Experimental matrix for a solubility program
8. Role of modeling in solubility studies

## REFERENCES

Kelmers, A. D. (1986). "Review of An Assessment of the Important Radionuclides in Nuclear Waste", letter report LR-287-30, February 18, 1986.

Kerrisk, J. F. (1985). "An Assessment of the Important Radionuclides in Nuclear Waste", Los Alamos National Laboratory report LA-10414-MS.

U.S. Nuclear Regulatory Commission (1984). "Determination of Radionuclide Solubility in Groundwater for Assessment of High-Level Waste Isolation", Technical Position.

LETTER REPORT

Title: Review and Evaluation of FY-1984 Annual Report:  
Spent Fuel and UO<sub>2</sub> Source Term Evaluation Results,  
PNL-5650, DOE/CH-19, UC-70, Feb., 1986, by W. J.  
Gray and G. L. McVay.

AUTHOR: J. G. Blencoe

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
NRC #50 19 03 01

REVIEW

This report describes the results of various "leach" tests of unclad, real spent fuel and simulated spent fuel (sintered UO<sub>2</sub> pellets). The tests were conducted with two different fluid starting materials: a synthetic, salt-saturated brine; and distilled water. In addition to spent fuel, the solid starting materials for some of the experiments included small pieces ("coupons") of: (1) ductile iron, which was used to simulate canister metal; and (2) zircaloy-4 cladding material.

The leach tests were performed with two principal objectives in mind. First, Gray and McVay wanted to determine the quantities of U, Pu, Tc, and Cs that would be released from real spent fuel, and the quantity of U that would be released from simulated spent fuel. Second, it was considered important to determine the fate of radionuclides after release from the real or simulated spent fuel. To achieve the latter goal, measurements were made of the quantities of radionuclides that were: (1) in true aqueous solution, (2) in aqueous suspension (as particulates and/or colloids), and (3) sorbed onto solid materials [i.e., the quantities of radionuclides that had "plated out" on the walls of the sample container, on the iron coupon (if present), and/or on the zircaloy coupon (if present)].

Experimental Methods

Recent Leach Tests with Real Spent Fuel

Specimens of real spent fuel were leach tested in Permian Basin brine No. 1 (PBB1) at 30 and 90°C for periods ranging from 28 to 180 days. The spent fuel used in these tests was obtained from a fuel bundle discharged from the H. B. Robinson II reactor on June 6, 1974. PBB1 brine simulates the saturated solution obtained by dissolving Permian Basin Cycle 4 salt in deionized water. The purpose of the tests was to obtain data that would complement and supplement data obtained from earlier, similar leach tests of real spent fuel (Barner et al., 1985). In particular, Gray and McVay sought to determine whether the results of leach tests with real spent fuel would be affected significantly by

extending the durations of the tests from 28 days to as long as 180 days. Furthermore, it was decided that some of the new leach tests should elucidate the effects of adding additional candidate waste package materials to experimental samples. Accordingly, in fourteen of the new tests, solid starting materials included a ductile iron coupon, while in four other new tests, the solid starting materials included both a ductile iron coupon and a short piece of zircaloy-4 cladding.

The leach sample in each test consisted of three fragments of spent fuel with predetermined  $^{137}\text{Cs}$  activities. The individual fragments were assembled into groups of three in a manner which ensured that the total  $^{137}\text{Cs}$  activity of each three-fragment specimen was the same within  $\pm 5\%$ . This procedure guaranteed that the radioactivity of each spent-fuel specimen was representative of the total mass of spent fuel being tested. Total surface areas of the three-fragment spent-fuel specimens ranged from 2.6 to 4.1  $\text{cm}^2$ . In all tests, the ratio of spent-fuel surface area to leachant volume was  $10 \text{ m}^{-1}$ . Also, by design, the surface areas of iron and zircaloy coupons were identical to the average spent-fuel specimen (approximately 3.3  $\text{cm}^2$ ).

The leach tests were conducted in fused silica containers that were cleaned in accordance with MCC-1 requirements. The spent fuel, iron, and zircaloy specimens were placed in separate compartments of perforated fused silica baskets to minimize contact between the specimens and the container, and to maximize the surface areas of the specimens exposed to the leachant. After experimentation, the containers were cooled to ambient hot-cell temperature and weighed to determine if any leachate had been lost. Shortly thereafter, the leachate pH was measured, and two aliquots of leachate were taken for chemical analysis (one of these aliquots was passed through a 1.8 nm filter prior to chemical analysis).

Next, the leach container and specimen basket were exposed to a volume of 5.0M  $\text{HNO}_3$ -0.05M HF solution slightly greater than the original leachant volume. The leach container and specimen basket remained submerged in the acid solution for at least 2 hrs at ambient temperature to dissolve any material that had plated out on the container walls and on the basket. Material plated out on the iron and zircaloy coupons was removed by soaking each coupon successively in three fresh solutions of 6M HCl for ten minute periods. Thereafter, the solutions were combined and diluted to a known volume. Each of the acid solutions obtained from the foregoing procedures was analyzed for uranium, plutonium, cesium, and technetium.

#### Recent Leach Tests with Simulated Spent Fuel

Gray and McVay also conducted new leach tests with simulated spent fuel. In each of these tests, the simulated spent fuel consisted of sintered  $\text{UO}_2$  pellets. Fluid starting materials for the experiments were either PBB1 brine or deionized water. Furthermore, in half of the experiments, the  $\text{UO}_2$  pellets possessed "highly oxidized" surfaces. Both surface-oxidized and "as-prepared" (completely reduced)  $\text{UO}_2$  pellets were leached in this series of experiments because previous experimentation indicated the desirability of testing the hypothesis that a more highly

oxidized--and therefore (presumably) more soluble--surface layer on  $UO_2$  pellets dissolves quickly during experimentation, thereby establishing a uranium solubility different from that observed for completely reduced  $UO_2$  pellets. The thought behind this experimental strategy was that, if the "oxidized" surfaces of real spent fuel contain one or more uranium-bearing solid phases that are more soluble than the unexposed  $UO_2$  matrix of the spent fuel, then this would help to explain why uranium release from real spent fuel is so much higher than from completely reduced  $UO_2$  pellets (a result obtained from earlier tests performed by Gray, McVay, and co-workers).

$UO_2$  pellets were prepared by cold-pressing  $^{235}U$ -depleted  $UO_2$  powder and sintering the compacted material at  $1700^\circ C$  in a 50%  $H_2$ -50% Ar atmosphere for 4 hrs. After these steps, the  $UO_2$  was compacted to 96% of theoretical density. The average pellet produced by this procedure was 9.1 mm in diameter, 8.2 mm long, and (therefore) possessed a surface area of approximately  $3.6\text{ cm}^2$ . Next, the pellets were centerless ground, cleaned with ethanol and dried, and fired again at  $1045^\circ C$  in a 50%  $H_2$ -50% Ar atmosphere for 4 hrs to ensure that any surface material that might have been oxidized during centerless grinding was again reduced to  $UO_2$ . Thereafter, 16 of the pellets were heated at  $215^\circ C$  in air for 10 days to generate a thin  $U_3O_7$  layer on the surfaces of the pellets. Weight gains for these pellets averaged 2.0 mg. This average increase in weight is equivalent to  $5.5 \times 10^{-4}\text{ g/cm}^2$ , and because the density of  $U_3O_7$  is  $11.05\text{ g/cm}^3$  vis-a-vis  $10.75\text{ g/cm}^3$  for  $UO_2$ , a  $5.5 \times 10^{-4}\text{ g/cm}^2$  gain in weight is equivalent theoretically to a  $U_3O_7$  surface layer 18  $\mu m$  thick.

Ductile iron coupons with surface areas of  $3.6\text{ cm}^2$  (same as the  $UO_2$  pellets) were used in half of the  $UO_2$ -pellet leach tests. The ratio of total- $UO_2$ -pellet surface area to leachant volume was  $10\text{ m}^{-1}$  in all tests. The leach tests were conducted with Teflon leach containers and specimen baskets, both of which were cleaned in accordance with MCC-1 requirements. The baskets prevented contact between the  $UO_2$  pellets and juxtaposed coupons (if present), and minimized contact of the pellets and coupons with the walls of the leach container.

After experimentation, each leach container was cooled to ambient laboratory temperature and weighed. In each case, weight loss (loss of water) was found to be negligible. Next, the leachate pH was measured, and various analytical solutions were prepared using techniques similar to those employed for the leach tests conducted with real spent fuel. The amounts of dissolved, suspended, and sorbed uranium were then determined using the same analytical methods employed to measure the concentrations of uranium in solutions obtained from leach tests with real spent fuel.

## Results

Gray and McVay present their various data on radionuclide release from real and simulated spent fuel in terms of normalized mass loss, which is the mass of an element released from the spent fuel divided by: (1) the mass fraction of the element in the unleached spent-fuel specimen, and (2) the surface area of the specimen. This practice facilitates

comparisons of leach data for spent-fuel specimens of different size and composition. Gray and McVay also identify the "locations" of released radionuclides. Specifically, the total mass of a released radionuclide is differentiated into the mass of the radionuclide that was found to be dissolved and/or suspended in the leachate (the leachate concentration), the mass of the radionuclide that plated out on the container, and the mass of the radionuclide that plated out on the iron and/or zircaloy coupons (if present during experimentation). The mass of "dissolved" radionuclide (the filtrate concentration) is defined as the mass of a radionuclide that passed through a 1.8 nm filter. Therefore, the difference between the leachate concentration and the filtrate concentration represents the mass of suspended radionuclide-bearing material.

Integrating the information obtained from their most recent leach tests with information obtained from previous, similar tests, Gray and McVay reach the following conclusions concerning the leach behavior of real spent fuel and simulated spent fuel (sintered  $UO_2$  pellets) in spent fuel + brine or distilled water  $\pm$  iron  $\pm$  zircaloy experiments.

1. Essentially all of the uranium leached from both real and simulated spent fuel is released during the "first few days" of experimentation. To Gray and McVay, this observation suggests that uranium release is controlled either by the solubility of the  $UO_2$  matrix of the spent fuel, or by the solubility of a surface phase that is more soluble than  $UO_2$ .
2. Regardless of the presence or absence of iron and/or zircaloy, U, Pu, Tc, and Cs are rapidly released from real spent fuel into PBB1 brine or distilled water.
3. In spent fuel + PBB1 brine  $\pm$  iron  $\pm$  zircaloy experiments performed over the range 25-75°C, the amount of uranium leached from real spent fuel is more than 100 times greater than the amount leached from simulated spent fuel.
4. Considerably more uranium is leached from simulated spent fuel in tests with distilled water than in corresponding tests with PBB1 brine. At 25°C and in the absence of iron, the quantities of uranium released to deionized water and brine differ by a factor of five. At 75°C and in the absence of iron, this difference increases to a factor of about 20. At 150°C and in the absence of iron, the difference increases to a factor of about 50. However, at 25 and 75°C and with iron present, similar results are obtained with deionized water and brine, and at 150°C, the amount of uranium released to distilled water is only 3 to 4 times that released to brine.
5. The amounts of uranium leached from real and simulated spent fuel in PBB1 brine are essentially independent of temperature over the range 25-150°C. By contrast, leaching of simulated spent fuel in deionized water is strongly dependent on temperature. For example, in the absence of iron, uranium-release values in deionized water are 50 to

300% higher at 150°C than at 75°C, and 300 to 500% higher at 75°C than at 25°C.

6. Iron has no effect on the total uranium released in spent fuel + PBB1 brine + iron experiments, but it apparently causes a substantial reduction in solution concentration of uranium in these experiments--probably because it lowers the oxidation state of the uranium (and, hence, uranium solubility) in the brine. The latter suggestion is supported by the observation that iron acts as a sorbent; that is, after experimentation it is consistently observed that uranium has plated out on the iron coupon. Furthermore, in all experiments with iron present: (1) there were comparatively large quantities of uranium deposited on the walls of sample containers, and (2) substantial quantities of filterable uranium-bearing particles were present in the reacted PBB1 brine. Iron has similar effects on the release characteristics and apparent solubilities of Pu and Tc in leach tests with real spent fuel. As expected, however, the presence of iron had no significant effects on the release behavior and apparent solubility of Cs.
7. At a given temperature, approximately the same quantities of uranium are leached from "as-prepared" (completely reduced)  $UO_2$  pellets and surface-oxidized pellets in simulated spent fuel + brine  $\pm$  iron  $\pm$  zircaloy experiments. Therefore, there is no evidence that the leach characteristics of real spent fuel are affected significantly by surface oxidation.
8. Oxidized zircaloy coupons have negligible effects on the leach characteristics of real and simulated spent fuel in spent fuel + PBB1 brine  $\pm$  iron + zircaloy experiments.

## REFERENCES

Barner, J. O., W. J. Gray, G. L. McVay, and J. W. Shade. 1985. Interactive Leach Tests of UO<sub>2</sub> and Spent Fuel with Waste Package Components in Salt Brine. PNL-4898, Pacific Northwest Laboratory, Richland, Washington 99352.

## EVALUATION

This report presents a wealth of information on the leach characteristics of real and simulated spent fuel in spent fuel + brine or distilled water  $\pm$  iron  $\pm$  zircaloy experiments performed at 30-90°C for 28-180 days. Some of the salient results obtained by the authors are itemized below. (In the information items below, real spent fuel refers to ~10-year-old spent fuel obtained from the H. B. Robinson II reactor, simulated spent fuel is pelletized and sintered  $UO_2$  powder, and PBB1 brine is a synthetic salt-saturated brine obtained by dissolving Permian Basin Cycle 4 salt in deionized water.)

1. Regardless of the presence or absence of iron and/or zircaloy, uranium is rapidly released from spent fuel (real or simulated) into PBB1 brine or distilled water.
2. Regardless of the presence or absence of iron and/or zircaloy, U, Pu, Tc, and Cs are rapidly released from real spent fuel into PBB1 brine or distilled water.
3. In spent fuel + PBB1 brine  $\pm$  iron  $\pm$  zircaloy experiments performed over the range 25-75°C, the amount of uranium leached from real spent fuel is more than 100 times greater than the amount leached from simulated spent fuel.
4. Considerably more uranium is leached from simulated spent fuel in simulated spent fuel + distilled water experiments than in corresponding experiments with PBB1 brine.
5. Iron has no effect on the total quantities of U, Pu, and Tc released from real spent fuel in spent fuel + PBB1 brine + iron  $\pm$  zircaloy experiments, but it apparently causes substantial reductions in the dissolved concentrations of these radionuclide. This observation suggests that iron lowers the oxidation states (and, hence, the apparent solubilities) of these radionuclides.

For the most part, the experimental data obtained by Gray and McVay are consistent with the conclusions listed above. However, it is also true that the experimental results obtained to date leave the following questions unresolved.

1. What is the uranium-bearing solid phase(s) that controls the "solubility" of uranium in spent fuel + PBB1 brine + iron  $\pm$  zircaloy experiments?

Evidently, this phase has a much lower solubility than  $UO_2$ .

2. Why are the total amounts of U, Pu, and Tc released to brine approximately the same regardless of the presence or absence of iron?

This finding is extraordinary and begs explanation. Obviously, additional experimentation and analytical work should be performed to

clarify the behavior of U, Pu, and Tc in leach tests performed with real spent fuel.

3. Are values of normalized radionuclide mass loss for different specimens of real spent fuel really comparable as Gray and McVay claim?

The concept of normalized radionuclide mass loss hinges on minimal penetration of fluid into the specimens of spent fuel, but Gray and McVay do not mention that this phenomenon has been investigated. Perhaps the surfaces of fragments of real spent fuel are highly microfractured and thus relatively permeable to aqueous fluids. If so, then the physical property of greatest pertinence to the reactivity of spent-fuel fragments would not be surface area, but instead reactive surficial mass. Furthermore, if the spent fuel is microfractured in an irregular manner, the latter quantity might be very difficult to quantify.

4. Why are the amounts of uranium leached from real spent fuel in spent fuel + PBB1 brine  $\pm$  iron  $\pm$  zircaloy tests so much greater than the amounts leached from similar tests with simulated spent fuel?

Gray and McVay state that the amounts of uranium leached from these two types of spent fuel can differ by two orders of magnitude. Such large disparities in uranium release are difficult to rationalize solely on thermodynamic grounds. It seems unreasonable to suppose that the different amounts of uranium release are entirely attributable to differences between the physical states of the  $UO_2$  in the two different types of spent fuel. (Specifically, that the greater releases from real spent fuel are attributable to a higher free energy resulting from greater numbers of microfractures and/or radiation damage.) A possible explanation is that, in the tests with real spent fuel, uranium release is (in one fashion or another) promoted by radiolytic reactions in the brine.

5. How would the results of the leach tests be affected by fine-grinding of the spent-fuel starting materials?

Gray and McVay imply that metastable equilibrium is achieved in the leach tests with fragments of real spent fuel and  $UO_2$  pellets. If so, then the same results would be achieved if the spent fuel was comminuted prior to experimentation. It is evident that at least a small amount of additional experimentation should be conducted to investigate the effects of using ground-up spent fuel in spent fuel + PBB1 brine or distilled water  $\pm$  iron  $\pm$  zircaloy experiments.

LETTER REPORT

TITLE: Review of: "Leaching Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment," in Scientific Basis for Nuclear Waste Management VIII, Mat. Res. Soc. Symp. Vol. 44, 247-256, 1985, by N.E. Bibler, G.G. Wicks and V. M. Oversby.

AUTHOR: K. L. Von Damm

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
NRC #50 19 03 01

The subject report documents the effects of gamma irradiation, and the presence and absence of both tuff and 304L stainless steel on the dissolution and release of Cs-137, Sr-90, and Pu-238 from an actual (radioactive) and a simulated (non-radioactive) glass. The series of experiments were done at 90°C, a surface area to volume ratio of 100 m<sup>-1</sup>, and in the radioactive case, a dose rate of approximately 1000 rad/hr. In these experiments wafers of glass were supported inside cups made from tuff from an outcrop at NTS and contained J-13 water. The tuff cups were then placed inside teflon vessels and the space inbetween filled with J-13 water. In this design, the glass and water come in contact with only those materials expected to be present in the repository. The duration of the experiments was from 14 to 180 days. The purpose of the experiments was to simulate the case of glass dissolution in a saturated tuff environment, which is considered to be an improbable case.

The authors present four major conclusions from this study.

1. The glass containing radionuclides leaches at the same rate as that which does not.
2. The presence of the tuff buffers the pH at a higher value.
3. The presence of the tuff decreases the concentrations of Cs-137, Sr-90 and Pu-238 in solution.
4. The presence of the 304L stainless steel does not affect the leaching process.

The authors use the concentration of lithium and boron to monitor the dissolution of the glass. As the rock used for the cups is from outcrop it contains caliche-type material which contains some boron, complicating the interpretation for this element. The results for the radionuclides compared to the lithium show that their concentration in the solution is not controlled by simple dissolution of the rock, but is lowered by sorption or another process. The lithium concentration itself is lower in solution when tuff is present, compared to glass

alone, again demonstrating the importance of the presence of tuff to the overall reactions occurring. At the termination of the experiments, the tuff cups were found to be radioactive, suggesting that the Cs, Sr and Pu have reacted with the tuff. In the experiments longer than 28 days Sr-90 was found to have migrated through the tuff to the solution between the tuff and the teflon. Work is currently underway to determine a diffusion coefficient for Sr based on this result.

The experimental conditions simulate the case where a glass waste form is in contact with 50 liters of water which has accumulated in the borehole. Since a flux of 1 liter per year past the canister is expected, the test conditions are much more unfavorable. Upon extrapolation of these results the authors conclude that the annual fractional release of the three radionuclides will be much less than  $10^{-5}$ .

This experiment is complimentary to that reported by Bates and Oversby (1985), (the subject of LR-287-34), which investigated the dissolution of glass in an saturated environment with an excess of air present. They found that radiolysis lowered the pH by producing  $\text{HNO}_3$  through reaction with air, which increased the dissolution of the glass. In most cases the presence of tuff buffered the pH to a higher level, retarding dissolution. The results from the subject document imply that radiolysis will not be important if there is sufficient tuff available to buffer any change in pH due to radiolysis reactions.

LETTER REPORT

**TITLE:** Review of: "Parametric Testing of a DWPB Borosilicate Glass," in Scientific Basis for Nuclear Waste Management VIII, Mat. Res. Soc. Symp. Vol. 44, 303-310, 1985, by F. Bazan and J. Rego.

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**PROJECT TITLE:** Technical Assistance in Geochemistry

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**ACTIVITY NUMBER:** ORNL #41 88 54 92 4 (FIN No. B0287)  
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The subject report is a very brief description of a series of leaching experiments on a DWPB borosilicate glass, presented with very little interpretation of the data. A series of leaching tests were done with this glass (non-radioactive) at 90°C, a range of surface area to volume ratios of from 0.1 to 1.0 cm<sup>-1</sup>, and a duration of from 1 to 182 days. The test cases are as follows.

1. Glass monoliths and crushed glass were reacted with deionized water.
2. Glass monoliths were reacted with J-13 water.
3. Glass monoliths were reacted with J-13 water and crushed tuff.
4. Glass monoliths were reacted with J-13 water, crushed tuff and stainless steel.

The tuff used was from an outcrop of the Topopah Spring formation which had been pretreated to remove the caliche material. Chemical results for lithium, boron, sodium and silica are reported. However, only lithium reached concentrations significantly higher than what was observed in the blanks.

The results show that lithium is leached from the glass at a much higher rate in deionized water compared to J-13 water. The presence or absence of 304L stainless steel appears to have no effect on the leach rate. This agrees with the results of Bibler et al. (1985) (subject of LR-287-37) for the same steel. Unlike the results of Bibler et al. (1985) which clearly showed that the presence of tuff decreased the amount of lithium present in solution, the experiments in the subject report show no clear trend for the effect of tuff on lithium in solution. The two sets of experiments were done at the same temperature, hence the possible differences may be due to differences in the tuff, the amount of tuff present, or the surface area/volume ratios. Bibler et al. (1985) did not pretreat their tuff to remove caliche, while Bazan and Rego have, including a heating to 90°C with J-13. Presumably the tuff cups in which the experiments of Bibler et al. (1985) were done provided a greater surface area of available tuff

than the experiments in the subject report. This report did not examine any radionuclides; the difference in the behavior of lithium in the presence of tuff raises a question as to whether the radionuclides would also have shown a behavior different. This report thus raises two points which need to be addressed. 1.) The deionized water was a stronger leaching agent than J-13. How important is the solution composition for determining the leach rate, as in many ways J-13 is a relatively dilute water? 2.) What affect does tuff really have on leaching and what factors may cause the magnitude of this affect to vary?