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June 13, 1986

Dr. D. J. Brooks
Geotechnical Branch
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Safety and Safeguards
U.S. Nuclear Regulatory Commission
Room 623-SS
Washington, D.C. 20555

Dear Dave:

Enclosed are the letter reports referenced in the monthly progress report for May. If you have any questions on the letter reports, please call the authors directly.

Sincerely,

Gary

Gary K. Jacobs
Manager, NRC Waste Program
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GKJ/

Enclosures:

Letter Reports LR-287-42, 43, 44, 46

cc w/o encl:

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LETTER REPORT

Title: Review and Evaluation of Progress Report on the Hydrothermal Interaction of Defense Waste Glasses with Basalt and Groundwater at 150°C, SD-BWI-TI-312, Jan., 1986, by D. L. Lane, C. C. Allen, and R. R. Adee.

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 data that DOE/Hanford has obtained on the hydrothermal stabilities of two slightly different radionuclide-doped SRL-165 borosilicate glasses: a U-, Pu-, ²⁴³Am-, Np-, and Tc-doped SRL-165 glass labeled ATM-9 glass; and a U-, Pu-, ²⁴¹Am-, Np-, Tc-, and Sm-doped SRL-165 glass labeled ATM-11 glass. Three hydrothermal experiments--designated runs D6-23, D6-30, and D5-9--have been completed to date, and two additional experiments--runs D10-1 and D11-1--are currently in progress. The starting materials for the experiments were: runs D6-23 and D6-30--ATM-9 glass + basalt + GR-3 groundwater; run D5-9--ATM-11 glass + basalt + GR-3 groundwater; run D10-1--ATM-11 glass + GR-3 groundwater; and run D11-1--ATM-11 glass + GR-4 groundwater. All of these experiments have been (are being) performed at 10 MPa, 150°C.

Central goals of the experimentation were to obtain data on: (1) the nature and extent of hydrothermal alteration of radionuclide-bearing SRL-165 glass, (2) the effects of basalt on groundwater pH and the hydrothermal stability of SRL-165 glass, (3) the geochemical behavior of radionuclides liberated from SRL-165 glass, (4) the effects of filtration on the concentrations of groundwater-borne radionuclides, and (5) the degree to which radionuclides are precipitated and/or sorbed during hydrothermal experimentation.

Starting Materials

Solid Starting Materials

Two types of solid starting materials were employed in the experiments: SRL-165 glass and Umtanum basalt. SRL-165 glass is a simulated defense high-level waste (DHLW) glass that is intended to be representative of vitrified waste from the Defense Waste Processing Facility (DWPF) at the Savannah River Plant (SRL) in Aiken, South Carolina. SRL-165 glass is a borosilicate glass that contains approximately 29 wt. % waste (in the form of oxides) and 71% SRL-165 "black frit" (Baxter, 1983). At the behest of DOE/Hanford, two varieties of this glass waste form--i.e., two slightly different radionuclide-doped SRL-165 glasses designated ATM-9 and ATM-11--were fabricated by the Materials Characterization Center (MCC) of the Pacific Northwest Laboratory (PNL). All glass constituents (elements) with nominal concentrations greater than 1×10^{-5} gram per gram of glass (e.g., Ni, Rb, Sr, Y, Zr, Mo, Ru, Pd, and Cs) were simulated with non-radioactive elements. The concentrations of the rare earth elements, with the exception of samarium, were summed and represented compositionally by neodymium. Radionuclide dopants in ATM-9 glass were: depleted uranium; weapons-grade plutonium ($\sim 94\%$ ^{239}Pu , $\sim 6\%$ ^{240}Pu); ^{243}Am ; ^{237}Np ; and ^{99}Tc . Radionuclide dopants in ATM-11 glass were: depleted uranium; weapons-grade plutonium ($\sim 94\%$ ^{239}Pu , $\sim 6\%$ ^{240}Pu); ^{241}Am ; ^{237}Np ; ^{99}Tc ; and ^{151}Sm . The concentrations of

radionuclides in the glasses were selected to simulate the radioisotopic inventory of a 300-year-old SRL-165 glass.

The ingredients of the two SRL-165 glasses were melted in a nitrogen-atmosphere glove box at PNL. To more accurately simulate SRL fabrication of a vitrified waste form, 0.7 wt. % graphite was added as a reducing agent. After preparation, the two glasses were crushed and sieved by PNL, and the -120/+230 mesh fraction was provided to DOE/Hanford for use in experimentation.

Lane et al. examined the powdered ATM-9 and ATM-11 glasses with a scanning electron microscope (SEM). It was observed that particles of ATM-9 glass display angular, fractured outlines and possess adhering fines, both of these features being attributable to crushing. However, ATM-9 glass was also observed to contain "original" cracks and vesicles. To further investigate the nature of ATM-9 glass, several grains of the glass were examined via SEM back-scattered electron (BSE) imagery. This analytical technique is capable of detecting micron-scale concentrations of heavy elements. No concentrations of heavy elements were detected in the ATM-9 glass particles.

SEM examination of ATM-11 glass revealed that, like crushed ATM-9 glass, crushed ATM-11 glass consisted of sharp-edged particles. Furthermore, imaging by SEM/BSE to detect inhomogeneities revealed numerous scattered (<1 vol. %) "bright spots" that were invariably $\leq 1\mu$ in diameter. Analysis of several of these spots by SEM/EDS indicated that some spots were rich in ruthenium, whereas others were rich in molybdenum. Evidently, these spots are tiny crystals of refractory phases that failed to melt during the preparation of ATM-11 glass.

In DOE/Hanford hydrothermal experimentation, the crushed samples of ATM-9 and ATM-11 glass received from PNL were utilized as-received, i.e., unwashed.

The basalt used in the hydrothermal experiments was obtained from the Umtanum flow of the Grande Ronde Basalt formation. The basalt was collected from a reference surface exposure in the entablature zone of the flow. The major crystalline phases in Umtanum basalt are plagioclase, pyroxene, and titaniferous magnetite. A siliceous glassy mesostasis, containing iron-rich blebs, comprises approximately half of the volume of this basalt. Umtanum basalt also contains small quantities of secondary minerals, the most abundant being smectite clay. The mineralogy and geochemistry of the Umtanum basalt used in DOE/Hanford hydrothermal experiments have been discussed in detail by Allen and Strope (1985) and Allen et al. (1985a).

Prior to experimentation, the Umtanum basalt was crushed and sieved to isolate the -120/+230 mesh size fraction. This crushed basalt was then washed ultrasonically in deionized water in an attempt to remove very fine adhering particles. Values for the specific surface area of the crushed and washed basalt--obtained from nitrogen B.E.T. measurements--were typically $2.7 \text{ m}^2/\text{g}$.

Fluid Starting Materials

GR-3 synthetic groundwater (Jones, 1982) was the starting fluid in four of the five experiments described in this report. The remaining experiment--run D11-1--is being conducted with GR-4 groundwater.

Experimental Conditions

All five hydrothermal experiments were (are being) performed in Dickson-type rocking autoclaves (Seyfried et al., 1979). Experimental conditions for the tests were (are): (1) P = 10 MPa; (2) T = 150°C; (3) (in basalt-present experiments) a 1:1 mass ratio of glass to basalt, (4) a 10:1 initial solution-to-solids mass ratio (this ratio decreased slightly during experimentation owing to periodic extraction of fluid samples); and (5) run duration, between 834 and 4387 hrs.

Experimental Methods

The key activities of the experimentation were: (1) analyzing aliquots of the hydrothermal fluids that were withdrawn periodically from the Dickson autoclaves; (2) analyzing the solid materials captured by filtration; and (3) after quenching, examining and analyzing the solid experimental products.

Analysis of Fluid Samples

The types of fluid samples acquired during experimentation varied from experiment to experiment. The discussion below describes: (1) a typical sampling protocol, and (2) the various methods employed to analyze experimental fluids.

The first step in fluid sampling was to extract approximately 1 mL of solution from the pressure vessel to flush out stagnant fluid in the sampling tube and valve. Immediately thereafter, a fluid sample was collected using a plastic or gas-tight syringe. Various aliquots of the fluid sample were then prepared for chemical/radiochemical analysis. Typically, an undiluted and unfiltered aliquot was used to measure the room-temperature pH of the fluid sample, while another undiluted and unfiltered aliquot was submitted for radiochemical analysis. Next, the remaining fluid was filtered through a 4000 Å filter (to remove particulate matter). This fluid was subsequently divided into aliquots for the following purposes: (1) Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) analysis (after 10-to-200x dilution), (2) ion chromatography (IC) (after 5x dilution), (3) total carbon/total organic carbon (TC/TOC) analysis (no dilution), (4) ICP analysis (no dilution), (5) radiochemical analysis (no dilution); and (6) filtration through a 30 Å filter (to remove colloids). The fluid obtained from (6) was subsequently divided into two additional aliquots, one of which was used to prepare a 10-to-200x diluted sample for ICP, while the other was

sent off (undiluted) for radiochemical analysis. In the foregoing analytical activities, ICP was used to measure the aqueous concentrations of Na, K, Ca, Mg, Fe, Al, Si, B, Mo, Ba, Li, Nd, Ni, P, and Zr. Measured quantities of these elements are believed to be accurate to ± 10 to 15% of the amount present.

Several different techniques were employed to determine the aqueous concentrations of radionuclides. Concentrations of aqueous Pu were measured by liquid scintillation counting. Am and Np were analyzed directly and simultaneously by gamma energy analysis (GEA). Concentrations of aqueous U were determined using a Scintrex UA-3 uranium analyzer. To date, no data on ^{151}Sm have been obtained.

Concentrations of the principal anionic species present in the aliquots of hydrothermal fluid--viz., F^- , Cl^- , and SO_4^{2-} --were measured by IC. TC/TOC analyses were performed with a Dohrmann Model DC-80 total carbon analyzer.

Analysis of Solid Reaction Products

Lane et al. analyzed two types of solid reaction products: solids captured by 4000 Å filtration of fluid aliquots, and solids collected from the Dickson autoclaves at the conclusion of experimentation. To date, the bulk of the analytical work on solid reaction products has been performed with the SEM. The microscope used by Lane et al. is equipped with secondary electron (SE) and backscattered electron (BSE) detectors, an energy dispersive x-ray spectrometer (EDS) and a four-crystal wavelength dispersive spectrometer (WDS). Additionally, selected solid reaction products obtained from 4000 Å filtration have been examined by standard x-ray diffraction (XRD) techniques.

Results

Runs D6-23 and D6-30 (ATM-9 glass + basalt + GR-3 groundwater)

The paragraphs below describe the following features of runs D6-23 and D6-30: the reactivity of SRL-165 waste glass (as indicated by the quantity of boron liberated to GR-3 groundwater), the geochemical behavior of various radionuclides, and the solid reaction products of experimentation. These two runs represent replicate experiments, but run D6-30 was carried out for a longer period of time. Similar results were obtained from the two runs; therefore, unless indicated otherwise, the commentary below applies to both runs.

After 50 days, the concentration of dissolved boron was approximately 50 mg/L. This concentration indicates that a minimum of 4-5% of the ATM-9 glass was altered after 50 days.

Radionuclide data were obtained from solutions filtered through 4000 Å and 30 Å filters. The data suggest that aqueous concentrations of ^{99}Tc increased at first, and then gradually decreased with increasing run duration. Filtration through 30 Å filters had little effect on the aqueous concentrations of ^{99}Tc .

After initial release, the concentrations of aqueous ^{239}Pu remained essentially constant with time. Furthermore, like the concentrations of aqueous ^{99}Tc , the concentrations of aqueous ^{239}Pu were little affected by 30 Å filtration.

In contrast to the aqueous concentrations of other radionuclides, the aqueous concentrations of ^{243}Am were affected markedly by 30 Å filtration. Changes of approximately an order of magnitude were evident upon filtration through a 30 Å filter. This is strong evidence that ^{243}Am was associated with colloidal material. Concentrations of ^{243}Am versus time revealed no clear trend.

After initial release, the aqueous concentration of U did not change significantly with time. Also, filtration appears to have had little effect of the concentration of U.

Concentrations of ^{237}Np were always below the limits of detection.

By comparing the concentrations of groundwater-borne radionuclides with the quantities of radionuclides originally present in the waste glass, it was possible to calculate values of "% inventory in solution" (Schramke et al., 1984). Although the concentrations of dissolved B imply that 4-5% of the ATM-9 glass was altered, the data for radionuclides indicate that only approximately 0.01% of the Tc, Pu, and Am inventories, and only approximately 0.5% of the U inventory, were taken up in solution. Therefore, it is evident that most of the Tc, Pu, Am, and U released to groundwater was subsequently sorbed or precipitated.

The major effect of experimentation on particles of basalt was partial dissolution of the glassy mesostasis. Crystals of plagioclase, pyroxene, and magnetite were apparently unaffected by hydrothermal activity.

Examination of grains of ATM-9 glass from run D6-23 showed that the rough edges of the particles had been rounded by dissolution. Reaction rinds around the grains were not visible in light-optical microscopic examinations, but SEM analyses revealed that significant quantities of Na had been leached from the surfaces of the grains. Furthermore, the glass grains were observed to be sparsely coated with tiny ($\leq 5\mu$ in diameter), platy, subhedral crystals of a secondary solid phase. SEM/EDS analyses suggest that this phase possesses a high Si/Al ratio and contains significant quantities of Na and K. This mineral is believed to be a zeolite, but further characterization is needed to confirm this.

The 4000 Å filter used to strain part of the fluid sample obtained after 163 hrs was observed to be partially coated with solid reaction products. SEM analysis revealed that this material contained numerous micron-scale grains of partially-reacted waste glass. XRD analysis of this material has not yet been performed, so it is not known at present whether the filter sample contains any microcrystals of secondary solid phases.

Experiment D6-30 was identical to experiment D6-23 except that it ran longer. Compared to grains of glass from run D6-23, grains of glass from run D6-30 were more rounded and the concentrations of boron were lower. Examination with a light-optical microscope revealed alteration rinds a few microns thick surrounding each glass grain. These rinds are significantly depleted in Na. Also, the glass grains were sparsely to completely coated with crystals of a secondary solid phase. These crystals are similar in size, shape, and composition to the crystals observed coating grains of glass reacted in run D6-23.

Like the 4000 Å filter used to strain part of the fluid sample obtained from run D6-23 after 163 hrs, the 4000 Å filters used to strain aliquots of the fluid samples obtained from run D6-30 after 40 and 1192 hrs were observed to be partially coated with solid reaction products. The filter sample obtained after 40 hrs contained numerous micron-scale shards of glass, the majority of which had chemical compositions similar to that of the SRL-165 starting glass. However, XRD analysis of this material revealed the presence of a significant amount of smectite clay. This clay is believed to have sloughed off the altered surfaces of glass grains. The filter sample obtained after 1192 hrs contained numerous micron-scale grains of partially-reacted SRL-165 glass. Additionally, this filter sample contained small clumps of the "zeolite" observed coating the grains of glass reacted in this experiment.

Run D5-9 (ATM-11 glass + basalt + GR-3 groundwater)

The paragraphs below describe the following features of run D5-9: the reactivity of SRL-165 waste glass (as indicated by the quantity of boron liberated to GR-3 groundwater), the geochemical behavior of various radionuclides, and the solid reaction products of experimentation.

After 4386 hours, the concentration of dissolved B approached 100 mg/L. However, the concentration of B did not appear to be at a steady-state. This concentration of B indicates that approximately 7% of the inventory of B was solubilized. Concentrations of other elements in solution at a given time, including radionuclides, were approximately the same as in runs D6-23 and D6-30. Thus, it is evident that ATM-9 and ATM-11 glass behave similarly in hydrothermal experiments.

Fluid samples from run D5-9 yielded abundant data on the geochemical behavior of radionuclides during experimentation. Concentrations of ^{99}Tc increased to 5×10^{-3} mg/L within the first 10 days of experimentation, but decreased by approximately an order of magnitude in the next 69 days. Between 79 and 183 days, the aqueous concentration of ^{99}Tc was essentially constant.

The aqueous concentration of ^{239}Pu was essentially constant between 10 and 79 days, but increased by more than an order of magnitude between 79 and 183 days. This unexpected behavior cannot be explained at present.

The aqueous concentrations of U increased to approximately 3 mg/L after 10 days, and then decreased by approximately an order of magnitude during the remaining time of the test.

Data obtained from fluid samples indicate that 30 Å filtration had little or no effect on the aqueous concentrations of Tc, Pu, and U. By contrast, aqueous concentrations of ^{241}Am were decreased significantly by 30 Å filtration. This observation suggests that ^{241}Am was colloidal

or associated with colloidal material.

While data obtained from fluid samples indicate that approximately 7% of the inventory of B was in solution at the end of run D5-9, the maximum values of % inventory in solution for radionuclides were as follows: ^{99}Tc , -0.1%; ^{239}Pu , -2%; ^{241}Am , -0.06%; U, -0.4%; and ^{237}Np , -0.05%.

Grains of glass from this run were extensively rounded, but not greatly reduced in size compared to the grains of starting glass. Some of the grains of glass were observed to possess thin alteration rinds. Also, a majority of the glass particles were sparsely coated with crystals of a secondary solid phase. This solid phase appears to be the same "zeolite" mineral that crystallized in runs D6-23 and D6-30.

SEM examination of grains of basalt revealed dissolution of mesostasis glass, but little or no dissolution of mineral phases.

Filter samples were obtained from aliquots of fluid samples taken after 233, 1891, and 4386 hrs. The filter sample obtained after 233 hrs was coated with a layer of poorly crystalline material similar in chemical composition to the SRL-165 starting glass. This material also contained significant quantities of smectite clay similar to the smectite clay observed in filter samples from run D6-30. The filter sample obtained after 4386 hrs appeared to contain small quantities of smectite clay and small clumps of the "zeolite" mineral.

Run D10-1 (ATM-11 glass + GR-3 groundwater)

Unlike run D5-9, run D10-1 contained no basalt. The absence of basalt in this run is noteworthy, because the results of experimentation differ markedly from the results obtained from run D5-9. The different results appear to be correlative with elevated levels of pH. After 163 hrs, measured room-temperature pH was 11, which is only slightly higher than at a comparable time in run D5-9. However, by 984 hrs, pH had increased

to approximately 12. Measured room-temperature pH was also approximately 12 after 2000 hrs of experimentation. These high pHs are correlative with elevated aqueous concentrations of Si, Na, B, Li, and Mo. The increase in pH from 163 to 984 hrs was accompanied by four- to five-fold increases in the concentrations of Si, Na, and Li, while the concentration of B increased 14-fold. After 2000 hrs of experimentation, the concentration of B reached ~2200 mg/L; this concentration represents approximately 80% of the inventory of B.

Concentrations of ^{99}Tc reached $\sim 10^{-3}$ mg/L during the first few hundred hours of experimentation, and appeared to remain constant for the next 1000 hrs. Concentrations of ^{99}Tc were not affected significantly by filtration.

After approximately 240 hrs, aqueous concentrations of ^{239}Pu were two orders of magnitude higher than at a comparable time in run D5-9. Unfortunately, the measured concentration of ^{239}Pu in the fluid sample obtained after 1000 hrs is spurious, apparently due to co-precipitation of ^{239}Pu and silica gel from this sample. Therefore, additional data will be needed to clarify the behavior of ^{239}Pu in this run.

Data for ^{241}Am indicate that filtration decreased ^{241}Am concentrations by orders of magnitude. Also, the concentrations of ^{241}Am apparently decreased with time and were lower than those in run D5-9 by as much as an order of magnitude.

Concentrations of U were roughly comparable to those in the fluid samples from run D5-9. However, results obtained at 163 hrs indicate that, with filtration through a 4000 Å filter, concentrations of U decreased by approximately 40-50%, and decreased by approximately another 60% with subsequent filtration through a 30 Å filter.

Preliminary data also suggest that the aqueous concentrations of ^{237}Np were reduced by filtration. However, little else can be said about the

behavior of ^{237}Np at this time, because the aqueous concentrations of this radionuclide were usually below the limits of detection.

Calculated values of % inventory in solution for ^{241}Am and ^{237}Np in unfiltered solutions were: ^{241}Am , 0.05 to 0.3%; and ^{237}Np , $\leq 0.07\%$.

Calculated values of % inventory in solution for ^{99}Tc , ^{241}Am , and U from 4000 Å filtered solutions were: ^{99}Tc , $< 0.02\%$; ^{241}Am , 3×10^{-3} to $8 \times 10^{-4}\%$; and U, $\sim 0.1\%$.

Because run D10-1 is currently in progress, data on solid reaction products originate entirely from filter samples. A filter sample obtained after 984 hrs revealed numerous 1-10 micron particles, some of which contained significant quantities of uranium. Further characterization of this filter sample is scheduled.

Run D11-1 (ATM-11 glass + GR-4 groundwater)

Geochemical conditions for this ongoing experiment are identical to those for run D10-1, except that GR-4 groundwater was used as the starting fluid. All data obtained to date indicate that the results of this experiment are essentially identical to the results obtained from run D10-1.

Because run D11-1 is currently in progress, data on solid reaction products originate entirely from filter samples. XRD analysis of the material coating a filter sample obtained after 188 hrs indicates the presence of small quantities of smectite clay. This clay appears to be very similar to the clay discovered in the filter samples obtained from run D6-30. However, the volume of clay in the filter sample from run D11-1 is much smaller than the volumes of clay observed in the filter samples from run D6-30.

Major Conclusions

Near the end of the subject report, Lane et al. present a list of conclusions that they developed from the results of their hydrothermal experimentation. Three of these conclusions are reiterated below.

1. Room-temperature pHs of fluids sampled from basalt-absent hydrothermal experiments with SRL-165 glass are systematically higher than the room-temperature pHs of fluids sampled from corresponding basalt-present experiments. This observation, coupled with evidence obtained from hydrothermal experiments with SRL-131 glass (Allen et al., 1985b), indicates that basalt tends to buffer pH at levels that are low enough to significantly decrease the rate of alteration of SRL-165 glass.
2. In analyzing fluids sampled from hydrothermal experiments with SRL-165 glass, it was observed consistently that the aqueous concentrations of Am were decreased significantly by filtration through 4000 Å and 30 Å filters. These effects of filtration were observed in both basalt-present and basalt-absent experiments. With only a few exceptions, corresponding data for Tc, Pu, U, and Np indicate little or no effect of filtration.
3. In both basalt-present and basalt-absent hydrothermal experiments with SRL-165 glass, the calculated value of "% inventory in solution" for individual radionuclides is invariably significantly smaller than the corresponding value for boron. This observation indicates that a large fraction of the mass of an individual radionuclide released from SRL-165 glass was eventually either precipitated or sorbed.

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EVALUATION

This report summarizes data obtained on the hydrothermal stabilities of two radionuclide-doped SRL-165 waste glasses (glasses ATM-10 and ATM-11) in five hydrothermal experiments that were designed to simulate geochemical conditions in the near field of a basalt-hosted HLW repository during the early post-containment period. The experiments have provided valuable information on the hydrothermal reactivity of SRL-165 glass and the geochemical behavior of Tc, Pu, Am, U, and Np released from this glass during experimentation. Also, it is noteworthy that both smectite clay and a "zeolite" mineral crystallized during the experiments.

Notwithstanding the abundant useful data obtained from the hydrothermal experiments described in this report, several noteworthy deficiencies are evident in the work that has been completed to date. These apparent deficiencies are summarized in the discussion items below.

1. Lane et al. make the tacit assumption that room-temperature pHs of fluid samples directly reflect the pHs of hydrothermal fluids at elevated (experimental) pressure-temperature conditions. This assumption may or may not be valid.
2. In one of the basalt-present experiments performed by Lane et al. (run D5-9), the aqueous concentration of boron was still changing after 4386 hrs of experimentation. Therefore, it is evident that steady-state conditions were not achieved in this experiment.
3. The subject report contains very little useful information about the secondary solid phases that formed during experimentation (smectite clay and a "zeolite" mineral). At the very least, these phases should be subjected to thorough x-ray diffraction analysis. Also, if feasible, it would be valuable to have electron microprobe data

on the phases.

4. Lane et al. note the presence of smectite clay in the Umtanum basalt that was used as a solid starting material in basalt-present experiments, but they do not speculate on the fate of this clay during hydrothermal experimentation. Could the basalt be the source of some (or most) of the clay in the solid reaction products of these runs, or did most of the clay form during experimentation via hydrothermal alteration of SRL-165 glass?
5. To date, it has not been possible to determine the fate of Tc, Pu, Am, U, and Np released from SRL-165 glass during hydrothermal experimentation. Small fractions of the total inventories of these radionuclides are retained in solution, but most of the released radionuclides are either precipitated or sorbed. Therefore, additional effort should be expended to identify the location(s) of radionuclides in the solid run products of hydrothermal experiments with SRL-165 glass.
6. Lane et al. do not mention that the results that they obtained from basalt-present experiments contrast with comparable results obtained by Schramke et al. (1984). Lane et al. observed that smectite and a "zeolite" crystallized in their basalt-present experiments, whereas in the basalt-present experiments performed by Schramke et al., clinoptilolite was the single secondary solid phase that crystallized during experimentation. These disparate results may be attributable to the fact that the simulated waste glasses used in the two sets of experiments have significantly different compositions.
7. DOE/Hanford continues to use freshly crushed basalt as a solid starting material in hydrothermal experiments. This practice would seem to be ill-advised because the crushed basalt in the packing material of basalt-hosted waste packages will almost certainly be

partly to mostly altered to secondary minerals by the end of the containment period. Therefore, hydrothermally altered basalt, not freshly ground "unreacted" basalt, should be used in these experiments.

LETTER REPORT

TITLE: Review of: Uranium-series dating of secondary carbonate and silica precipitates relating to fault movements in the Nevada Test Site region and of caliche and travertine samples from the Amargosa desert, U.S.G.S. Open-File Report 85-47, 12p., 1985, by B.J. Szabo and P.A. O'Malley, and Uranium, thorium analyses and uranium-series ages of calcite and opal, and stable isotopic compositions of calcite from drill cores UE25a#1, USW G-2 and USW G-3/GU-3, Yucca Mountain, Nevada, U.S.G.S. Open-File Report 85-224, 25p., 1985, by B.J. Szabo and T.K.Kyser.

AUTHOR: K. L. Von Damm

PROJECT TITLE: Short Term Technical Assistance in Geochemistry, Task Order No. 34

PROJECT MANAGER: G. K. Jacobs

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

The two subject reports document attempts to date carbonate materials at the Yucca Mountain site by uranium-series methods as well as an attempt to determine the source of the carbonate through stable isotopic measurements. The methods reported by the authors are standard ones. While the documented procedures are relatively straight forward, their interpretation is not, and is based on a series of underlying assumptions. The first part of this letter report will address questions relating to the uranium-series results reported, which will be followed by a discussion of the stable isotopic data.

Uranium-Series

The assumptions related to use of the uranium series for dating are quite important and are not stated explicitly in either of these reports. The assumptions are included in an earlier report (Szabo et al., 1981) which is essential to critiquing the data in the subject reports. Ivanovich and Harmon (1982) provide a series of papers in which the validity of the assumptions under specific cases is very well presented. Szabo and co-authors assume a closed system for the dated carbonates which requires, according to Ivanovich and Harmon (1982):

1. The samples should be impermeable to groundwaters because the flow of water through the system may cause alteration in the U or Th content.
2. There should be no evidence of weathering in the sample.

3. Samples partially replaced by secondary materials should not be dated.
4. In the case of carbonate samples, there should be little (or no) HNO_3 -insoluble residue.
5. In the case of terrestrial carbonate, there should be no (or little) ^{232}Th present in the sample as this nuclide is usually indicative of the presence of detrital material in the sample.
6. Apparent radiometric ages must be in agreement with stratigraphic sequence.
7. Agreement should be obtained for ages determined by several independent methods such as $^{230}\text{Th}/^{234}\text{U}$, $^{231}\text{Pa}/^{235}\text{U}$, $^{231}\text{Pa}/^{230}\text{Th}$, He/U , and ^{14}C .

The authors point out, and it is evident in the age data, that not all of the samples meet criteria #1. Travertines and the harder calcites, such as those found in veins, appear to satisfy this better than the other, more porous, types of carbonate. The authors have examined the samples for compliance with criteria #2 and #3. Unfortunately many of the samples do not meet criteria #4 very well. The authors use a mathematical method to correct for the presence of ^{232}Th and implied presence of ^{230}Th which has previously yielded good results, to comply with criteria #5. Criteria #6 is met for those samples which can be tested by K-Ar dating on adjacent basaltic flows. Criteria #7 is not addressed by the authors. In general, the dates appear to be reasonable based on other available evidence, including geomorphology. The authors use the $^{230}\text{Th}/^{234}\text{U}$ method. For dates less than ~150,000 years, use of the $^{231}\text{Pa}/^{235}\text{U}$ method would provide an independent check on the date. Also for very young samples, those less than ~35,000 years, ^{14}C might provide an additional independent check.

The authors also attempt to use uranium-series dating on opal in some of the fracture fillings. Although they cite a reference for this application, it has not been, in general, a standard procedure as is true for carbonates. It appears to give reasonable results, when compared to the carbonate dates. The authors discuss possible loss of uranium from the opal as it is recrystallized, and state that this may cause an increase in uranium in coexisting calcites. Although they do not point it out, their calcite sample 348.8-B from drill hole USW-G-2, which is intermixed with opal, shows a uranium increase with respect to another calcite (348.8-A) from that depth, which may infer a gain of uranium lost from the opal. This is evidenced by that calcite having a much higher uranium content than the other calcite and a younger age than either the opal or the other calcite.

Carbon and Oxygen Isotopes

Carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopic data are presented in only the second (OFR 85-224) of the two subject reports. The authors suggest that the observed variation in isotopic values with depth is due to precipitation of calcite in equilibrium with an elevated geothermal gradient. The authors suggest that the oxygen isotopic value decreases, and that the carbon isotopic value increases, systematically with depth. Both of these correlations are weak and it could be argued, in

both cases, that no depth trend exists. They conclude on the absence of any correlation between oxygen isotopic composition and dates that the composition of the fluids has remained constant in time and that they have not undergone any systematic diagenesis. They do not discuss the equally viable explanation that the calcites may all have re-equilibrated, in what they would consider a "non-systematic" way, possibly, with modern meteoric fluids. Some of their observed variation for both carbon and oxygen could be due to progressive precipitation of calcite from the fluids with increasing depth leading to isotopic fractionation in the fluids, and resulting in a systematic change in the isotopic composition of the calcites. Hydration of the rock could also lead to some of their observed changes. In general the interpretation of the isotopic data is not very well constrained, due in part to no isotopic data being reported on the host rocks. Water/rock reactions may be important in altering the fluid chemistry, but it appears that isotopic data for the rock both near to and far from the fractures (which could indicate previous water/rock interactions) is not available. The correlation of the isotopic data with a geothermal gradient is more convincing than the correlation of either isotope with depth. It is a reasonable explanation based on the available data, but may not be the only explanation. There is probably no other independent approach to determine the source of the carbonate, however the system needs to be better constrained by isotopic analysis of the coexisting host rocks.

In summary, the uranium-series dates have their limitations, which are important to be aware of. In general the uranium-series method appears to provide reasonable ages for Yucca Mountain carbonates. If it is important to better define the most recent date of tectonism, $^{231}\text{Pa}/^{235}\text{U}$ should be applied to some of the younger samples as an independent check on the $^{230}\text{Th}/^{234}\text{U}$ method. The carbon and oxygen isotopic systematics need additional work. Primarily, the isotopic composition of the host rocks needs to be examined to better evaluate the possible importance of water/rock interactions. A correlation of the isotopic values with a reasonable geothermal gradient does exist, however, the argument is not that strong. The additional isotopic work suggested above would aid in refining this argument.

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LETTER REPORT

TITLE: Review of "Neptunium and Americium Speciation in Selected Basalt, Granite, Shale, and Tuff Groundwaters," by J. M. Cleveland, T. F. Rees, and K. L. Nash (1983). Science 221, 271-273.

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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 paper has been cited frequently in the literature on geologic storage of nuclear waste. For this reason, it seemed appropriate to review the work and, more importantly, to evaluate the results and conclusions in the light of current research in the field.

The stated objective of the work was to study the chemical speciation of neptunium and americium in groundwaters associated with rock types proposed as possible hosts for nuclear waste repositories. The sources of the four waters investigated were (a) well DC-15, which penetrates into Grande Ronde basalt at the Hanford, Washington site; (b) seepage from granite in the Climax mine at the Nevada Test Site (NTS); (c) well J-13, in saturated tuff near Yucca Mountain at NTS, and currently a source of reference water for the NMWSI program; and (d) a rural well near Rapid City, South Dakota, known to penetrate into Pierre (cretaceous) shale. For comparison, the study also included a deionized water of unspecified characteristics.

Small additions of ^{237}Np or ^{241}Am in 0.5-1.0 M HClO_4 were made to the groundwater solutions so that final concentrations of about 10^{-8} M neptunium and about 10^{-11} M americium were achieved. Only the deionized water samples required adjustment of the pH after this procedure, presumably because of the high buffering capacity of the groundwaters. After equilibration periods of 1-30 days at either 25°C or 90°C, replicate samples were analyzed by conventional radiochemical methods for Np(V), for Np(III) and (IV) together, and for Am(III). To assess the effect of initial oxidation state, separate sets of experiments were carried out using starting solutions of Np(IV) and Np(V). No attempt was made to control the atmosphere above the groundwater samples. It must be assumed that pH was not monitored during the equilibrations, since none of the data reported include any information about variations

in pH. The paper contains relatively little experimental detail for such a complex study.

The results were presented in terms of percentages of the original concentrations of neptunium and americium remaining in solution after various periods of time. For neptunium, the oxidation states were reported either as Np(IV) or as Np(V). For groundwaters containing added Np(V), almost all of the Np remained in solution as Np(V), except for the shale groundwater at 90°C, in which the Np(V) slowly reduced and precipitated as Np(IV).

When neptunium was added as Np(IV), solubilities were generally lower. Again, solubility in the shale groundwater was very low and had decreased to about half of its original value in 30 days, although in the other waters >75% of the neptunium remained in solution over the same time period. At 90°C, only the basalt groundwater and the deionized water were able to maintain most of the neptunium in solution for 30 days. In a related paper, Cleveland, et al. (1983) asserted that plutonium insolubility in shale groundwater was the result of a high concentration of sulfate ions. In the case of neptunium, low solubilities also were observed in shale groundwater, but the explanation for this behavior is not apparent from the results of this or the plutonium study. By contrast, the authors attributed the high solubility of plutonium in basalt groundwater to fluoride complexing. Although Np(V) appeared to be consistently soluble in basalt groundwater, it is known to form only weak fluoro complexes. Moreover, the authors state that Np(V) is relatively soluble as an uncomplexed ion, which they felt was supported by the observation that Np(V) was found to be equally soluble in deionized water containing no fluoride ion.

Am(III) is the only oxidation state of americium expected in natural waters. Percentages of Am(III) remaining in solution appeared to be substantially independent of temperature. Americium exhibited a high solubility only in the granite groundwater, and half or less of it was soluble in the basalt, tuff, and deionized waters. The solubility of Am(III) in deionized water was about the same as that in basalt groundwater, which suggests that the relatively high concentration of fluoride ion in the basalt water, 52 mg/L, is relatively ineffective in retaining Am(III) in solution by complexation. All of the actinides studied by the authors were least soluble after prolonged exposure to the basalt groundwater.

EVALUATION

Because this paper has been widely quoted in the literature of nuclear waste chemistry, its results and interpretations need to be examined carefully.

The title leads the reader to expect that the "speciation" of neptunium and americium are to be reported. The authors use the term "speciation" in the sense of defining the oxidation states of certain elements present. However, to most chemists the term "speciation" implies the process of assembling a list of all soluble species in a chemical system [O'Kelley and Meyer (1984)]. This paper made no attempt to determine speciation within the conventional meaning of the term, although in some solutions the relative concentrations of Np(IV) and Np(V) were reported. No information was presented which would allow the reader to deduce, for example, the amounts present of Np(V) species such as NpO_2^+ , NpO_2OH , $\text{NpO}_2\text{CO}_3^-$, etc.

The paper is so lacking in experimental detail that it is difficult to evaluate some of the experiments. With diligence, the reader can fill in some of the missing information by referring to a companion paper on plutonium by Cleveland, et al. (1983). For example, although the present paper on neptunium and americium does not give the initial values of pH for the various groundwaters used, this information can be found in the authors' paper on plutonium. Moreover, there is no indication that values of pH were followed or controlled over the course of the experiments. The variations in initial values of pH for the groundwaters make any quantitative comparisons of results risky at best. Some of the data on "solubility" are probably related to the proclivity of elements such as Am(III) to sorb onto the walls of containers, when present at tracer concentrations in near-neutral solutions. Because of the generally qualitative nature of the results, it does not seem feasible to make general application of the reported data to other systems.

No attempts were made to monitor and control either the atmospheres over the groundwaters or the redox conditions. The authors appeared to believe that the only purpose in controlling the atmosphere was to control the amount of dissolved oxygen, when, in fact, the $\text{CO}_2\text{-HCO}_3^-\text{-CO}_3^{2-}$ equilibrium is very important to actinide speciation. The failure to characterize the redox environment of the experiments may also have led to increased uncertainty, since complexing agents play a well-known role in controlling the redox potentials of chemical systems.

The authors made a number of observations which were interpreted on the basis of little data. One example is that a number of unexpected phenomena seemed to be associated with the shale groundwater, although the data obtained were insufficient to interpret the observations. In the shale groundwater, Np(V) was reduced to Np(IV) at 90°C. Another characteristic of the shale groundwater system was that the solubility of Np(V) and Pu(V,VI) was low and was believed to be due to a high concentration of sulfate in the groundwater. However, the authors admitted that they were unable to advance a satisfactory mechanism by which sulfate could limit the solubility of these elements. This paper is seriously deficient in the kind of detailed characterization needed to explain the results. Lacking such a characterization, the paper merely

takes the form of a series of random observations with little chance for understanding.

In a discussion of the high solubility of Np(V) in the basalt groundwater of pH about 9.3, the authors appeared to believe that neptunium was soluble, both in this water and in deionized water, as the species NpO_2^+ . The work of Maya (1983) has shown that, in an aqueous system containing Np(V) and at a CO_2 pressure of 0.01 atm, the NpO_2^+ ion is dominant only to about pH 7.2. With high alkalinity due to carbonate, complexes such as $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, and even $\text{NpO}_2(\text{CO}_3)_3^{5-}$ are possible. In cases where high alkalinity is not associated with high carbonate concentrations, hydrolytic species such as NpO_2OH are likely. Hence, the solubility of neptunium at high values of pH can be far more complex than the authors realized. It would be surprising if the deionized water used in the experiments did not exhibit a considerable carbonate concentration, since the authors maintained no atmospheric control. Thus, it is doubtful that uncomplexed NpO_2^+ was the dominant species, even in deionized water.

In one of their summary statements the authors concluded that reducing conditions lowered the mobility of actinides in the groundwaters investigated. Because redox conditions in the groundwater solutions did not seem to have been adequately characterized, the basis for such a conclusion is not clear, especially since Am(III) would not be reduced in natural environments and is more likely to have its mobility controlled by other chemical effects such as complexation, hydrolysis, or polymer formation.

In view of the qualitative nature of the observations and the poor control of experimental parameters, there is little in this paper which could be applied in a general way to the chemistry of nuclear waste repositories.

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LETTER REPORT

TITLE: Review of the paper: J. J. W. Higgs and L. V. C. Rees, "Adsorption of Actinides by Marine Sediments: Effect of the Sediment/Seawater Ratio on the Measured Distribution Coefficient," Environ. Sci. Technol. 20, 483-490 (1986)

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SUMMARY

This paper should be required reading for anyone conducting, interpreting the results of, or modeling release predictions based on, batch contact radionuclide sorption experiments. The authors present both theoretical predictions and experimental results of the effects of the presence of two solution species, and of the test solid/solution ratio, on the distribution coefficient (K_D) values. They suggest that many cases of apparent sorption/desorption disequilibrium can be more readily explained by the presence of a small amount of a poorly sorbed radionuclide form. They suggest that this form often is a microparticulate form of the radionuclide; possibly generated due to the shaking action during the test in some cases. The authors reach a very important conclusion: "... modelers cannot base their assessments on distribution ratios determined at an arbitrarily chosen solid/solution ratio."

1. REVIEW OF THE PAPER

This paper presents an excellent description of the effects of multiple solution species or forms of radionuclides, and the effects of the test solid/solution ratio, on the radionuclide distribution coefficient (K_D) measured in batch contact experiments. The paper begins with a review of the state-of-the-art of approaches to treating multiple solution species in sorption studies. Then, the effect of two stable species on the measured measured K_D value are calculated from theoretical considerations. The calculations are extended to show the interaction of the test solid/solution ratio with the two-species K_D values. A series of plots show that the measured K_D curve may, in some cases, go through a maximum at intermediate solid/solution ratios and decrease at higher or lower ratios.

A series of batch contact experiments with seawater spiked with americium, plutonium, and neptunium were conducted at various solid/solution ratios with several types of ocean sediment. The experimental data were, in some cases, fitted to theoretically generated curves.

The authors then proceed to draw a number of important observations regarding the interpretation of K_D data. Some of the observations are:

- (1) Sorption/desorption experiments often are run by removing the first spiked groundwater after the contact to measure the sorption ratio, and then conducting a second contact with unspiked groundwater to measure the desorption ratio. Typically, the desorption ratio is larger than the sorption ratio and sorption/desorption disequilibrium is assumed to exist. The authors suggest, based on their studies, that the presence of two species, a poorly sorbed species which remains primarily in solution and is removed after the first contact, and a strongly sorbed species which is then measured in the "desorption" contact, is a more likely explanation of the larger desorption coefficient observed in many cases.
- (2) The sorption K_D s for neptunium, americium, and plutonium as a function of solid/solution ratio were different from each other and were different for the several ocean sediment samples. Most of the test results suggested the presence of a minor fraction of poorly sorbed radionuclide.
- (3) Very often, the low K_D species are probably microparticulates containing sorbed radionuclides, although complexes with carbonate or organic constituents may also be formed. The effect of these species on the measured K_D values must be understood in order to utilize the information to assess the suitability of waste repositories.

2. RELEVANCE TO REPOSITORY ASSESSMENT

The authors conclude:

"From the waste disposal point of view it is clear that modelers cannot base their assessments on distribution ratios determined at an arbitrarily chosen solid/solution ratio. Effects such as that observed for plutonium in high-carbonate sediments are probably unusual but if ignored might lead to optimistic predictions. The possibility that the presence of microparticulates or organic complexes have lowered results should always be considered. In general the effect of such material will be to lower the observed R_D values of the main species, and predictions on the basis of such results will be conservative. However, the mobilities of the microparticulates and complexes, themselves, must be considered (assuming that they are not simply generated during shaking). They are likely to be neutral or negatively

charged and could travel a considerable distance before being converted to a more readily sorbable form. The size of such particles could be of critical importance particularly if diffusion is the main transport medium."

I wholeheartedly agree with these conclusions.

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