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Dr. D. J. Brooks
Geotechnical Branch
Office of Nuclear Material
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 April. If you have any questions on the letter reports, please call the authors directly.

Sincerely,



Gary K. Jacobs
Manager, NRC Waste Program
Environmental Sciences Division
1505, MS-3 (FTS: 626-0567)

GKJ:nja

Enclosure:

Letter Reports LR-287-39, -40, -41

cc w/o enclosure:

Office of the Director, NMSS (Attn: Program Support Branch)
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3046

LETTER REPORT

TITLE: Review of "Solubility Limits on Radionuclide
Dissolution at a Yucca Mountain Repository", by
Jerry F. Kerrisk, LA-9995-MS, May, 1984.

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

Mathematical models which calculate the transport of radionuclides in water moving through a nuclear waste repository and the surrounding geologic environment require as input the detailed mechanisms that control the rates of release of radionuclides or control the concentrations of radionuclides near the waste. The range of solubilities of waste elements is quite large and depends in a complex way upon the chemistry of each element, water temperature, and water composition (important for speciation). This report is concerned with two simple solubility-limited dissolution models that can be used to estimate the release rates of radionuclides from solid waste in contact with water. Such models are useful for guiding future experimental work. For example, if solubilities of particular elements are not known accurately but are shown to be important, then an experimental effort to measure them may be justified. On the other hand, if solubilities can be shown to be unimportant to determinations of release rates, then model estimates may be sufficient.

This analysis employed two dissolution models: (1) A saturation-limited dissolution model, in which water flowing through the repository area is assumed to be saturated with each element, (2) a diffusion-limited dissolution model, in which element saturation is assumed at the waste/water interface and dissolution is limited by diffusion of the element into water flowing past the waste. (Chambre et al., 1982).

The first model may be very conservative if the values chosen for the saturation concentrations and water flow rates are defensible, because it is highly unlikely that adequate contact would be obtained between the water and waste to saturate all the water. The second model represents an attempt to employ a more mechanistic approach which may lead to slightly more realistic -- and perhaps more favorable -- estimates of repository performance. However, the second model requires

assumptions about the design of waste containers, water flow characteristics and velocity, and element diffusivities. As a result, the results of this model are presently subject to considerable uncertainty. Neither of the models makes use of the beneficial effects of the engineered barrier system or of components such as spent fuel cladding in limiting waste-element dissolution. These constraints make the estimates of dissolution rates even more conservative.

It is obviously unrealistic to assume solubility-limited dissolution rates for highly-soluble elements such as cesium. The dissolution rates of such elements will be limited by the dissolution rate of the bulk waste form (congruent dissolution). In the models used in this report, if an element's solubility-limited fractional dissolution rate (fraction of remaining element dissolved per unit of time) is greater than the bulk fractional dissolution rate, then the bulk fractional dissolution rate is used for that element. This procedure is compatible with the assumption of congruent dissolution for elements which are not solubility-limited. The author mentions that, under some circumstances, congruent dissolution may not occur as expected. One example is the migration of iodine and cesium into the gap between a fuel element cladding and the fuel, so that in storage of spent fuel these elements could be released at rates faster than the bulk waste-form fractional dissolution rate.

Solubilities used in the calculations were estimated for a number of waste elements in water from well J-13, the principal reference water for the NNWSI effort. The report presents analytical data on water from well J-13. The pH was taken as 7, and oxidizing conditions ($E_h = 700$ mV) were assumed, because present indications suggest that water may be oxidizing in the unsaturated zone and in the upper portions of the saturated zone at Yucca Mountain. This assumption is generally conservative, in that it leads to higher solubilities than under reducing conditions.

The NNWSI program is using the EQ3/6 chemical equilibrium computer program for solubility calculations. However, only a few of the important waste elements are in the thermodynamic data base. Solubility calculations were carried out using EQ3/6 for americium, plutonium, uranium, and strontium. The solubility limits for cesium, technetium, and carbon were assumed to be so large that their dissolution rates would always be limited by bulk waste-form dissolution. Solubilities for radium, tin, and neptunium were estimated from data given in the literature. These ten waste elements account for ~99% of spent fuel activity, 1000 years after discharge from the reactor.

To implement the saturation-limited dissolution model it is necessary to assume that each element is at its solubility limit at the calculated flow rate, or is limited by dissolution of the bulk waste form, whichever gives the lower dissolution rate. To obtain the flow rate of the water, the author used a value of the decay heat of 1135 W/MTHM (watts per metric ton of heavy metal) for PWR fuel at 10 years after discharge, combined with a maximum thermal loading of 10 W/m² and an assumed water recharge rate of 8 mm/year. These assumptions led to a

water flow rate of 910 L/year through the horizontal area of 114 m^2 associated with each MTHM of PWR waste. This flow rate was used as the nominal parameter both for spent-fuel and high-level waste, since PWR fuel exhibited a slightly higher decay heat/MTHM than did PWR high-level waste.

The diffusion-limited dissolution model assumes saturation at the interface between the waste and the water flowing past. Dissolution, then, is limited by diffusion of waste elements into the water. It is not clear whether flow paths away from the solid waste interface are continuous or discontinuous. Continuous flow was assumed to be conservative, in that this flow overestimates the importance of diffusion. The author assumed that the porosity of the rock surrounding the waste form was 10%. The velocity of water flowing by the waste was taken as the recharge rate (8 mm/year) divided by the porosity of the rock (0.10), or $8 \times 10^{-2} \text{ m/year}$. It was also necessary for this model to assign dimensions for PWR spent fuel elements and for PWR high-level waste containers. An estimate of flow through the waste forms increased fractional dissolution rates only by about 15%.

Calculations were carried out for PWR spent fuel and PWR high-level waste, at decay times of 10^2 , 10^3 , 10^4 , and 10^5 years after discharge from the reactor. In addition, parameters such as bulk fractional dissolution rate, solubilities, and water discharge rates were varied from the nominal values to assess the influence of these quantities on calculated dissolution and radioactivity release rates. Summaries of the significant results are included with the discussion in the text, and complete computer outputs are included in an Appendix for all calculations using nominal values for the parameters.

Some of the elements did not exhibit solubility-limited dissolution because of the relationship between solubility, concentration, and water flow rate. Such elements were assumed to dissolve congruently. In the calculations using the diffusion-limited model, most of the radioactivity released at early times comes from elements that do not exhibit solubility-limited dissolution, such as cesium and strontium. However, the waste package should remain intact long enough for these elements to decay to insignificant levels. Thus, the release of these elements at 100 years is unlikely, especially since high temperatures during this early period may not permit liquid water to exist near the waste. At 1000 years and longer, technetium and neptunium are found to contribute most of the radioactivity release. Transport of neptunium away from the repository area should be very limited, because the tuff shows excellent sorption capacity for neptunium. However, technetium presents a unique problem, because neither solubility nor sorption appears to limit its transport. Tin and americium showed solubility limits on their dissolution rates for all cases examined, and uranium and plutonium showed solubility limits under most conditions. Radium has a low solubility, but showed solubility-limited dissolution in only one set of circumstances because it is expected to be present in very low concentrations.

EVALUATION

This report uses two simple models to predict the dissolution of nuclear waste in saturated tuff. The first model assumes that water flowing through the repository is saturated with each element, while the other model assumes saturation at the waste/water interface and limitation on the dissolution of waste by diffusion of the particular elements into the water. The dissolution rates of highly-soluble elements was taken to be the dissolution rates of the bulk waste form (congruent dissolution). This multifaceted approach is a useful first step toward the development of a nonbounding model which could yield a performance more favorable to the licensee than a bounding, saturation model. The present approach is more valid than the first-order model used in the Draft Environmental Assessment for the NNWSI, which has been criticized (Pigford and Pigford, 1985) on the grounds that the water flow rate calculations were not appropriate and that simple congruent release of all radioelements was assumed.

It is important to note that the models used do not attempt to account for effects of other parts of the engineered barrier system or of components such as spent-fuel cladding in limiting waste-element dissolution, which add further conservatism to the results.

The author's estimate of volumetric water flow/MTM appears to be conservative, compared with earlier estimates which used only the waste dimensions and ignored the spread in the plume of contaminated groundwater described by Pigford and Chambre (1985) and references therein. Although the saturation-limited dissolution model generally gave smaller release rates than simple congruent dissolution for the same elements, the diffusion model tended to yield even lower release rates. At 10^3 to 10^5 years after discharge the diffusion model produced somewhat lower rates of release of elements from PWR high-level waste than congruent dissolution, while the release rates of elements from PWR spent fuel were factors of 5 to 50 less than for congruent dissolution. The nature and extent of release rates calculated by the diffusion model depends sensitively upon the quality of the input data. For this reason the report develops a need for better data on necessary physical data, such as dimensions of waste containers, water flow characteristics and velocity, element diffusivity, etc. A limitation in the model as reported is the use of a simple, one-dimensional treatment; however, the results obtained are sufficiently useful to demonstrate the applicability of the general approach and the need for further refinements.

As mentioned earlier, it is known that, in some cases, the dissolution rates of highly soluble species will not be controlled by bulk dissolution rates. More work is needed to be certain that all such exceptions have been identified. These exceptional cases seem more likely to occur in spent fuel elements.

The author's objective was to predict waste-element dissolution rates and to assess the importance of solubility in limiting dissolution. The results and conclusions are presently strong functions of the assumptions made about solubilities and model parameters. Even though the simple models used here may be considered only a first step toward a comprehensive, validated model for estimating source terms for nuclear repository performance assessments, this report demonstrates the importance of solubility-limited dissolution and the need for further measurements in several experimental areas.

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Pigford, R. L., and Pigford, T. H. (1985). "Letter Report to Dr. John Plodinec, Savannah River Laboratories, E. I. duPont de Menours and Co."

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05/02/86

LETTER REPORT

Title: Review and Evaluation of A Final Report on Hydrothermal Testing of ⁹⁹Tc-Doped Glass Waste Form and Waste Package Components, SD-BWI-TI-229, July, 1984, by J. A. Schramke, L. E. Thomas, S. G. McKinley, S. A. Simonson, and D. G. Coles.

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 summarizes the data that DOE/Hanford has obtained from its first four hydrothermal experiments with a ⁹⁹Tc-doped borosilicate-glass waste form. These experiments have been designated runs B-48-01, B-48-02, B-48-05, and B-48-06. The starting materials for the experiments were: run B-48-01--glass + groundwater; run B-48-02--glass + basalt + groundwater; run B-48-05--glass + steel + groundwater; and run B-48-06--glass + basalt + steel + groundwater. Central goals of the experimentation were to: (1) identify the effects of basalt and steel on the behavior of ⁹⁹Tc released from the glass waste form, and (2) determine the kinds and quantities of secondary minerals that formed during experimentation. The report presents detailed information on the

starting materials and the reaction products of the experiments.

Starting Materials

Solid Starting Materials

The ^{99}Tc -doped glass used in the experiments was a crushed and blended mixture of: (1) ^{99}Tc -doped PNL 76-68 borosilicate glass (Bradley et al., 1979); and (2) undoped MCC 76-68 glass with a composition similar to ^{99}Tc -doped PNL 76-68 glass. Autoradiographic studies of the PNL 76-68 glass by Bradley et al. showed that all of the ^{99}Tc occurs in a soluble Na(?) - Cs - Tc phase within vesicles in the glass. Additionally, Bradley et al. determined that PNL 76-68 glass contains minor amounts of an Fe-Cr-Zn spinel, small spherical "ingots" of Pd containing ~5% Te, rounded particles of Ru metal, and minor RuO_2 . The basalt used in the experiments, designated RUE-2 basalt, was collected from an outcrop of the entablature section of the Umtanum flow. The steel filings used in the experiments were obtained from a bar of ASTM A27 Grade 60-30 cast mild steel.

Fluid Starting Materials

In each of the four experiments, the starting groundwater was GR-3 synthetic groundwater (Jones, 1982). The pH of this groundwater was adjusted to 9.74 prior to experimentation.

Experimental Conditions

All four hydrothermal experiments were performed in Dickson-type rocking pressure vessels. Experimental conditions for the tests were: (1) P = 30 MPa; (2) T = 200°C; (3) a 10:1 (by weight) initial solution-to-solids ratio (this ratio decreased slightly during experimentation owing to

periodic extraction of fluid samples); and (4) run duration, -3 months.

Experimental Methods

The key activities of the experimentation were: (1) analyzing the fluid samples that were withdrawn periodically from the Dickson autoclaves; and (2) after quenching, examining and analyzing the solid reaction products.

Analysis of Fluid Samples

Upon extracting a sample of fluid, the first step was to measure its pH. Subsequently, aliquots of each fluid sample were filtered through a 4000 Å filter (to remove particulate matter), or a 18 Å filter (to remove both particulate matter and colloids). The resulting aliquots of unfiltered and filtered groundwater were then analyzed chemically using a variety of techniques. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) was used to obtain the aqueous concentrations of Na, K, Ca, Mg, Fe, Al, Si, B, Mo, and Zn. Concentrations of the anionic species F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , and NO_3^- were obtained by Ion Chromatography (IC). Concentrations of aqueous ^{99}Tc were determined by radiochemical analysis of unfiltered solutions. Finally, the internal consistencies of solution analyses were checked by calculating charge balance. In general, calculated charge balances fluctuated around neutral. This observation implies an absence of systematic errors in the ICP and IC analyses.

Analysis of Solid Reaction Products

After an experiment was terminated, the gold bag in the Dickson autoclave was opened and its contents photographed. Next, samples of solid material were collected for mineralogic and chemical analysis. Samples were selected on the basis of texture, color, and location in

the gold bag. The solids thus obtained were analyzed by scanning electron microscopy (SEM), x-ray diffractometry (XRD), selected-area electron diffraction (SAD) in a transmission/scanning-transmission electron microscope (TEM/STEM), and energy-dispersive x-ray spectrometry (EDXS) (both in the SEM and the TEM/STEM).

Results

In runs B-48-01, B-48-05, and B-48-06, pH rose from an initial value of 9.74 to 10.1-10.3 during the early stages of experimentation. Thereafter, pH remained steady until experimentation was concluded. In run B-48-02, however, pH initially dropped to 9.34, then rose to approximately the same pH as in the other three experiments (10.1-10.3). This aberrant behavior of pH in run B-48-02 remains unexplained at the present time.

ICP analyses of fluid samples revealed measurable quantities of Na, Si, B, Mo, K, and Tc. By contrast, the elements Fe, Al, Ca, and Mg were present only in amounts at or below the detection limits of ICP. Concentrations of F^- , Cl^- , and SO_4^{2-} remained unchanged during experimentation.

The concentrations of aqueous boron were used to monitor the degree of glass dissolution. In runs B-48-01 (glass + groundwater) and B-48-05 (glass + steel + groundwater): (1) steady-state concentrations of aqueous boron were attained within the first several hundred hours of experimentation, indicating little or no glass dissolution in the later stages of these experiments; and (2) judging from the concentrations of aqueous boron in these experiments, equal amounts of glass were dissolved. By contrast, in runs B-48-02 and B-48-06, the concentrations of aqueous boron appeared to be increasing at the close of experimentation, thus indicating that glass dissolution was continuing. Data on aqueous boron in the four experimental samples further indicate

that less 76-68 glass was dissolved in the basalt-present experiments (runs B-48-02 and B-48-06) than in the basalt-absent experiments (runs B-48-01 and B-48-05). Also, evidently, the least amount of glass was dissolved in run B-48-02 (glass + basalt + groundwater).

Visual inspection of the glass particles in the run products of the four experiments indicates that ^{99}Tc was released from the glass as glass dissolution/alteration reached the vesicles that contained the soluble ^{99}Tc -bearing solid phase (Bradley et al., 1979). No ^{99}Tc was detected in the altered surface layers of glass particles, and examination of crushed samples of the run products revealed that the soluble ^{99}Tc -bearing solid phase was still present in the unaltered interiors of the glass particles.

In experiments without basalt, the predominant reaction product was a gel-like material that was green in color in the glass-only experiment (run B-48-01) and dark green in the glass + steel experiment (run B-48-05). This material was found to contain smectite clay and a small amount of amorphous (quench?) material. In contrast, clinoptilolite was the only secondary mineral that crystallized in the basalt-present experiments (runs B-48-02 and B-48-06).

The paragraphs below present additional information on the behavior of aqueous ^{99}Tc in the four hydrothermal experiments and the nature of secondary solid phases that formed during these experiments.

Run B-48-01 (^{99}Tc -doped glass + GR-3 groundwater)

Aqueous ^{99}Tc rapidly reached a steady-state concentration of ~ 60 mg/l. This concentration of aqueous ^{99}Tc indicates that approximately 32% of the total inventory of ^{99}Tc was released to the groundwater within the first 1000 hrs of experimentation. The concentration of aqueous ^{99}Tc was not affected by filtration through 4000 and 18 Å filters. The

amount of glass that dissolved in this experiment was approximately 15%, as indicated by the amount of boron present in the groundwater.

Material from the top of the gold bag consisted of: (1) U- and Cs-bearing smectite clay; and (2) small particles of crystalline material--mostly spinel, Ru, and Pd--released from the glass waste form. Material from the bottom of the gold bag consisted mainly of slightly rounded glass particles with altered surface layers 10-15 μm thick. The soluble Na(?) -Cs-Tc solid phase was still present in vesicles within the unaltered interiors of the glass particles, but was absent in altered surface layers.

Run B-48-02 (^{99}Tc -doped glass + RUE-2 basalt + GR-3 groundwater)

During the first 500 hrs of experimentation, the concentration of aqueous ^{99}Tc was -5 mg/l. This concentration of aqueous ^{99}Tc represents -3-4% of the total ^{99}Tc inventory. In comparison, 1-2% of the glass waste form was dissolved, based on the amount of boron present in the groundwater.

The reduced concentration of aqueous ^{99}Tc during the early stages of run B-48-02 relative to the steady-state concentration of aqueous ^{99}Tc in run B-48-01 (-60 mg/l) is mainly attributable to the smaller quantity of glass that was dissolved during run B-48-02. However, it is also evident that the concentration of aqueous ^{99}Tc in run B-48-02 was further reduced by precipitation and/or sorption of ^{99}Tc . This conclusion is supported by the following experimental observation. After approximately 700 hrs, it was observed that the concentration of ^{99}Tc declined sharply from its initial steady-state concentration (-5 mg/l), subsequently achieving a new apparent steady-state concentration of -0.001 mg/l. This behavior implies a sudden change in the rate of ^{99}Tc release from the glass vis-a-vis the rate of ^{99}Tc removal from solution by precipitation and/or sorption. This suggestion is supported

by the observation that, after approximately 700 hrs, the concentration of aqueous boron stabilized, indicating that the rate of glass dissolution had slowed to nearly zero. This observation coincides with the abrupt drop in the concentration of aqueous ^{99}Tc . It is therefore possible that, as the rate of ^{99}Tc release to the groundwater slowed, the reaction(s) that removed ^{99}Tc from solution continued unabated, thereby reducing the concentrations of aqueous ^{99}Tc to its detection limits. In any event, throughout this experiment it was observed that most of the ^{99}Tc was in true solution, but toward the end of the experiment, some ^{99}Tc was found to be associated with particulate matter.

Solid material sampled from the upper part of the gold bag was a thin gel-like mass containing black granular material. Some of this material may have been deposited during quenching of the experiment. Material that sloughed off the sides of the gold bag after experimentation proved to be a mixture of microcrystalline clinoptilolite and small particles of basalt.

Material from the bottom of the gold bag consisted mainly of granular basalt and rounded glass particles. Visual inspection of the basalt revealed that a significant fraction of the glassy mesostasis in the basalt particles had dissolved during experimentation (crystals of plagioclase, pyroxene, and titaniferous magnetite were seen protruding from partially dissolved masses of mesostasis). Surprisingly, however, no altered surface layers were observed on the reacted glass particles from this run. Also, it was observed that the soluble Na(?) - Cs - Tc solid phase was still present in vesicles within the unaltered interiors of the glass particles.

Finally, no smectite clays or ^{99}Tc -bearing solid phases were detected in the solid reaction products of this experiment.

Run B-48-05 (⁹⁹Tc-doped glass + steel filings + GR-3 groundwater)

Concentrations of ⁹⁹Tc in the 4000 Å and 18 Å filtered solutions decreased steadily during this experiment. Initial ⁹⁹Tc concentrations were -0.05 mg/l, but these concentrations eventually decreased to -0.001 mg/l. 4000 Å filtration greatly reduced the concentration of ⁹⁹Tc, thus indicating that a significant fraction of aqueous ⁹⁹Tc was associated with filterable particulate matter. Filtration through 18 Å filters caused little or no change in the concentration of aqueous ⁹⁹Tc.

The foregoing results are significant in light of the fact that as much glass dissolved in this run as in run B-48-01. This observation indicates that, in run B-48-05, considerably greater quantities of ⁹⁹Tc either: (1) were precipitated as a discrete, ⁹⁹Tc-bearing solid phase(s); or (2) were sorbed onto the solid reaction products of the experiment. In any event, it is apparent that ⁹⁹Tc was removed from solution shortly after being released from the glass.

The principal solid reaction product of this experiment was a dark reddish-brown to black U-, Cs-, and Tc-bearing smectite clay similar in texture and quantity to the clay material formed in run B-48-01. The material collected from the bottom of the gold bag consisted of rounded glass particles and slightly corroded (iron-oxide coated) steel filings. The glass particles were found to possess alteration layers 10 to 15 μm thick. XRD analyses indicated that the secondary iron-oxide phase coating the surfaces of steel filings was either magnetite or maghemite.

Run B-48-06 (⁹⁹Tc-doped glass + RUE-2 basalt + steel filings + GR-3 groundwater)

The concentration of ⁹⁹Tc in the 18 Å filtered solutions quickly attained a steady-state concentration of -0.0005 mg/l. Decreases in ⁹⁹Tc concentration after 18 Å filtration suggest that ⁹⁹Tc-bearing

colloids were present in the early stages of this experiment. However, "colloidal" Tc was not detected after 1000 hrs.

At the conclusion of experimentation, a small amount of gelatinous material was found near the top of the gold bag. This material consisted mainly of microcrystalline clinoptilolite and small particles of basalt. The associated gel-like material may have formed during quenching.

Material from the bottom of the gold bag consisted of rounded glass particles, slightly altered particles of basalt, and slightly corroded steel filings. The glass particles exhibited poorly defined surface alteration layers $\sim 5 \mu\text{m}$ in thickness. The glassy mesostasis of basalt particles showed evidence of chemical attack, but this attack was apparently much less extensive than in run B-48-02. As in run B-48-05, the surfaces of steel filings were coated with magnetite/maghemite. No smectite clay was detected in the solid run products of this experiment.

Major Conclusions

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

1. The ^{99}Tc in the PNL 76-68 synthetic glass waste form was released from the glass as surface dissolution/alteration reached vesicles containing a soluble Na(?) - Cs - Tc solid phase.
2. The candidate waste-package components basalt and steel, both singly and together, operate to reduce the quantities of aqueous ^{99}Tc . The net effect of the presence of basalt and/or steel in experimental samples is postulated to be reduction of aqueous $^{99}\text{Tc(VII)}$ to a lower oxidation state, perhaps $^{99}\text{Tc(IV)}$, followed by precipitation

or sorption.

3. In addition to reduced quantities of aqueous ^{99}Tc , two other experimental results from runs B-48-05 and B-48-06 strongly suggest that steel promotes reducing conditions in waste/barrier/groundwater experiments. These results are: (1) the absence of iron-silicate colloids in the fluid samples collected during these experiments, and (2) the lack of any apparent effect of steel on glass dissolution in the glass + steel + groundwater experiment (run B-48-05).

4. From examinations of the run products of basalt-present and basalt-absent experiments, it is evident that the presence of basalt promotes the crystallization of clinoptilolite. Smectite clay was not observed in the run products of basalt-present experiments, despite the fact that smectite clay is a common secondary mineral formed during the alteration of basalt. Evidently, these observations are attributable to the fact that dissolution of the glassy mesostasis in basalt particles provides the aluminum that is prerequisite for the crystallization of clinoptilolite. In the absence of basalt, smectite clay was the single secondary mineral that formed during experimentation.

REFERENCES

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Jones, T. E. 1982. Reference Material Chemistry, Synthetic Groundwater Formulation. RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Washington.

EVALUATION

This report contains a wealth of information on the geochemical behavior of ^{99}Tc and the crystallization of secondary minerals in four hydrothermal experiments that were designed to simulate various possible local geochemical environments in the near field of a basalt-hosted HLW repository during the early post-containment period. By systematically testing the effects of the presence of two key candidate waste-package components--basalt and steel--it was discovered that: (1) the apparent solubility of ^{99}Tc in GR-3 groundwater is greatly reduced when either basalt or steel is present in experimental samples, and (2) the kind(s) of secondary minerals that form during waste/barrier/groundwater experiments depend on whether basalt is present or absent (specifically, it was observed that clinoptilolite crystallized in basalt-present experiments, whereas smectite clay crystallized in basalt-absent experiments).

Notwithstanding the impressive amount of 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. For some unexplained reason, the GR-3 groundwater used in the experiments described in this report contained 15% more NaCl than the original GR-3 "recipe." Hopefully, this "excess NaCl" had no significant effect on experimental results.
2. In the basalt-present experiments performed by Schramke et al., the aqueous concentrations of various elements were still changing after three months of experimentation. Consequently, additional basalt-present experiments with ^{99}Tc -doped glass should be performed for

durations in excess of three months to see if it is possible to achieve steady-state conditions.

3. To date, it has not been possible to determine the fate of most of the ^{99}Tc released from PNL 76-68 glass during hydrothermal experimentation. Some of the ^{99}Tc is retained in solution, but most of it is either precipitated or sorbed. Therefore, additional effort should be expended to identify the location(s) of ^{99}Tc in the solid run products of hydrothermal experiments with PNL 76-68 glass.
4. To date, all hydrothermal experiments with ^{99}Tc -doped PNL 76-68 glass have been performed at 200°C. Therefore, it is not known whether similar or significantly different results would be obtained at lower temperatures. For this reason, additional experiments should be performed at one or more appropriate temperatures in the range 90-150°C.
5. DOE/Hanford continues to use freshly crushed basalt as a solid starting material in many of its 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.
6. To date, ^{99}Tc -doped PNL 76-68 glass is the only glass waste form that DOE/Hanford has used in their hydrothermal experiments. Consequently, it is not known whether changing the composition of the glass waste form would have a significant effect on experimental results. For this reason, it may be wise for DOE/Hanford to investigate the hydrothermal stability of a significantly different synthetic glass waste form.

LETTER REPORT

TITLE: Review of: "Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of seawater and the origin of saline formation waters," in Geochim. Cosmochim. Acta Vol. 50, 419-433, 1986, by L. P. Knauth and M. A. Beeunas.

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)
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The subject report documents the oxygen and deuterium isotopic contents of fluid inclusions from Permian halites, in an attempt to determine the origin of these fluids. Inclusions in Swisher, Deaf Smith, Randall, Oldham, and Donley counties from the Palo Duro halite as well as inclusions from Death Valley, California, Verdi Valley, Arizona, Lyons, Kansas and the WIPP Site are included in the study.

The authors have tested several reported methods for removing and analyzing water from the fluid inclusions and have demonstrated that a vacuum crushing method which does not involve heating does not provide results in agreement with the other methods. For small inclusions a vacuum method in which the samples are heated to at least 800°C appears to be necessary in order to insure that the water is quantitatively collected and not left behind in a hydrous phase, which in turn would cause an isotopic fractionation. Heating was initially avoided in order to assure no material from any organic matter or other hydrous phases was incorporated. As it is not possible to avoid heating under these conditions it becomes very important to insure that the sample contains almost no organic matter or minerals other than salt.

The measured $\delta^{18}O$ and δD data from the fluid inclusions have a range in values and a unique source or history for the fluid cannot be determined. The authors propose a number of scenarios which they discuss in detail and are able to limit the range of possible fluid sources. Potential sources for the fluids include: connate marine evaporite brine, evaporation of meteoric water, gypsum dehydration penetration of the salt by subsurface formation water whose isotopic composition is usually dominated by equilibration with calcite, penetration of the salt by younger ground waters, and a mix of Permian meteoric and marine evaporite brines. Their discussion virtually eliminates gypsum dehydration, calcite equilibration, and evaporation of present day meteoric waters as quantitatively important sources. Their preferred explanation is of a mix of evaporated Permian seawater and

evaporated Permian meteoric water, although intrusion of small amounts of more recent fluids cannot be eliminated.

Chevron-type versus other fluid inclusions are thought to be original rather than potentially a result of recrystallization. The chevrons from Deaf Smith county show a variation which can be attributed to deposition from an evaporated seawater, partial dissolution due to an input of meteoric water followed by deposition from a mixed marine-meteoric fluid. The chevrons show an isotopic composition distinct from the other types of inclusions. Chemical data, which are not yet available for these fluid inclusions, in conjunction with the isotopic data, would help to distinguish these two sources from each other. The data also show a variation in the the basin which does not appear to be due to a strict stratigraphic control, i.e. the deeper samples do not show less of a meteoric input, but suggest instead a complicated flow path for the input of meteoric waters.

Two important general conclusions from this study are: the composition of Permian seawater was similar to that of today, and negative $\delta^{18}O$ and δD values can be produced by the simple evaporation of seawater due to its hook-shaped path, and does not require a special mechanism.

This study has several important implications for a salt repository, related primarily to brine abundance, composition, and the general impermeability of the basin. First there is no a priori way to predict the distribution of the brine or variations in its composition. Based on this study one would expect the brine to vary in composition depending on its source and its variability will not be in a strict stratigraphic manner. Seawater usually contains more magnesium than meteoric water, at least before evaporative concentration begins, and high magnesium brines have been shown to be more corrosive under repository conditions. Hence the relative importance of seawater versus a meteoric source for the fluid inclusions may be important in determining the corrosiveness of the fluids under repository conditions. A second and possibly more disturbing point raised by this study is that salt may not be as impervious to post-depositional fluid intrusion as is usually assumed. This study shows that meteoric input is probably important but cannot definitively prove that the meteoric input was solely in the Permian, and has not occurred throughout the basins history. The fluid inclusion data suggest that less than 50% of the fluid is meteoric, but this still allows for a reasonable amount of infiltration and recrystallization of the salt.