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July 12, 1986

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Dear Dave:

Please find enclosed the letter reports referenced in the progress report
for the month of June. 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
Building 1505, MS-3

Enclosures:

Letter Reports: LR-287-45,-48,-49,-50

cc w/o encl:

       Office of the Director, NMSS (Attn: Program Support Branch)
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       Branch Chief, Waste Management Branch, RES
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LETTER REPORT

TITLE: Review of "Plutonium Speciation in Selected Basalt, Granite, Shale, and Tuff Groundwaters," by J. M. Cleveland, T. F. Rees, and K. L. Nash (1983). Nuclear Technology 62, 298-310.

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

This is the second of two papers by the same authors on the behavior of actinide elements in natural groundwaters. The first paper by Cleveland, et al. (1983) concerned the behavior of neptunium and americium and was reviewed by O'Kelley (1986), while the present paper is concerned with the much more complicated chemical behavior of plutonium. Letter reports on these two papers have been prepared because this work has been cited frequently in the literature of waste chemistry without much evaluation in light of current research.

The authors describe their experiments as a study of the chemical speciation of plutonium in actual groundwaters. The four waters were the same as in Cleveland, et al. (1983): (a) granite groundwater from the Climax mine at the Nevada Test Site (NTS); (b) basalt groundwater from well DC-15, which penetrates into Grande Ronde basalt at the Hanford, Washington site; (c) tuff groundwater from well J-13 at the NTS; and (d) a shale groundwater from a rural well near Rapid City, South Dakota, known to penetrate into Pierre shale. For comparison, a deionized water of unspecified properties was also included. All groundwaters contained about 6 mg/L of dissolved oxygen at the time of the experiments, although no other data on redox conditions were given. The alkalinities of the various groundwaters differed greatly; the shale water was most strongly buffered, while the basalt, granite, and tuff groundwaters were only slightly buffered. The value of pH varied widely among the four groundwaters, with the value for the tuff water being lowest, at pH 7.8, and the basalt water the highest, at pH 9.3.

Plutonium stock solutions containing primarily Pu(III) and Pu(IV) or Pu(V) and Pu(VI) were prepared by electrolysis. The oxidation states of plutonium present in the groundwaters and the deionized water were determined after adding small aliquots of the stock solutions and

allowing the solutions ($\sim 10^{-9}$ M in Pu) to stand for periods of 1-30 days. The concentrations of Pu(III) and Pu(IV) were determined by conventional radioanalytical techniques, and the concentrations reported for Pu(V + VI) were determined by difference. The effect of temperature was investigated by running separate sets of experiments at 20-27°C and at 90-95°C. In one case the oxidation state of insoluble plutonium was studied. Some auxiliary experiments on a few selected cases were carried out to determine the scope of effects due to sorption on particles, pH, ionic strength, carbonate ions, sulfate ions, fluoride ions, and alkaline earth ions.

Results were presented as a series of bar graphs showing distributions between soluble and insoluble Pu, Pu(III), Pu(IV), and Pu(V + VI) as a function of time for the five waters employed. Each water system was very different, and so it is difficult to separate the variables involved. However, the authors did summarize the principal conclusions, which they felt were justified:

Over the limited time frame of this investigation, their study of dissolved oxygen showed little effect on speciation. High percentages of insoluble plutonium, noted particularly in the shale groundwater, was apparently sorbed onto container walls and not onto particles already in the water. Differences in the distribution between oxidation states in the basalt and shale groundwaters was not a pH effect. Limited adjustments of carbonate concentration and ionic strength had little effect. The authors attributed a profound effect on solubilization due to fluoride; on the other hand, sulfate was found to decrease solubility. However, for cases where high concentrations of fluoride and sulfate both were present, the results were ambiguous. This result again points to the difficulty of deducing the behavior of such complex systems without detailed knowledge of the effects of each component of the system. The authors conclude, surprisingly, that their results show the inadvisability of basing conclusions on laboratory studies of systems using pure water or synthetic groundwaters. Finally, they conclude that maximum immobilization of plutonium occurred in waters low in free fluoride ions and high in sulfate ions.

EVALUATION

This paper and another by the same authors have both been widely discussed in the literature of nuclear waste chemistry. Thus, it is of interest to discuss the experimental results and interpretations in the light of current knowledge in the field.

As pointed out in a letter report on the authors' study of neptunium and americium (O'Kelley, 1986), the authors have consistently used the term "speciation" in the sense of defining the oxidation states present, although most chemists use the term to mean the precise chemical species

present, such as PuO_2^+, PuO_2^{2+}, etc. No information is presented in this paper which would permit the reader to deduce the amounts present of plutonium oxo-ions, hydrolytic species or complexes. Although it is of some use in setting the scope of plutonium waste chemistry to know the oxidation states of plutonium in groundwaters, the promise of the title is unfulfilled.

This study used groundwaters of complex composition, which makes the results difficult to interpret, since the effect of a single component cannot be deduced unambiguously. The values of pH for the four ground-waters, for example, ranged from 7.8 to 9.3 and did not relate simply to the alkalinity, expressed as $CaCO_3$ concentration. Thus, other complex equilibria and compositional dependences were involved. From this it should be clear that any conclusions drawn from quantitative comparisons of the results should be viewed with extreme caution.

There is no indication that the experiments were carefully monitored and controlled. Although initial values of pH were given for each ground-water and for the deionized water, there is no indication that values of pH were either followed or controlled over the course of the investiga-tions. Similarly, there were no attempts made to monitor and control either the atmospheres over the groundwaters or the redox conditions. The authors persisted in their apparent belief that the only purpose in controlling the atmosphere was to control the amount of dissolved oxy-gen. In fact, control of the partial pressure of CO_2 is important to control the CO_2-HCO_3^--CO_3^{2-} equilibrium, which can play an important role in actinide complexation; in turn, complexation may be important in determining the redox potential of a chemical system. The failure to characterize adequately the redox environment may have made it more dif-ficult to assess the role of complexation.

The authors made numerous observations concerning the results of their various experiments. However, because conditions were not well controlled and because all of the groundwaters had complex compositions, each different from the others, it is difficult to draw quantitative conclusions from the data. Most of the summary of results takes the form of a list of observations for which detailed explanations are lacking. For example, the observation that fluoride ion greatly increased plutonium mobility is quite reasonable, since it is known that Pu(IV) can be stabilized as the fluoride complex. On the other hand, the presence of sulfate ion seemed to increase the formation of insol-uble plutonium species; however, the insoluble species were not iden-tified, and so only speculations could be invoked to explain this effect.

One consideration not stressed in the interpretations of the data is that of kinetic effects. It is a well-known aspect of plutonium chem-istry that certain oxidation-reduction reactions, hydrolysis reactions, and the related formation of colloids, all are governed by intricate kinetic relationships, only a few of which are understood. It can be

suspected that, in a number of experiments for which parameters were varied, kinetic effects may have additionally complicated, even dominated, the results to an unknown degree.

It seems surprising that the authors concluded that their results showed the superiority of their experimental approach over laboratory experiments on simpler solutions or synthetic groundwater solutions. On the contrary, it seems to this reviewer that the results reported in this paper demonstrate the need to carry out systematic investigations on less complex systems, for which the various parameters can be controlled and the results quantified, before advancing to studies of multicomponent systems. The authors chose to begin with research on a series of intricate and different groundwater solutions, with the result that their observations are only qualitative and offer little which might be applied more generally to chemical problems of nuclear waste repositories.

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Letter Report

TITLE:	Review of: The organic chemistry of ground waters from the Palo Duro Basin, Texas: implications for radionuclide complexation, ground-water origin, and petroleum exploration, BMI/ONWI-578, May 1985, 78 p., by J. L. Means and N. J. Hubbard.
AUTHOR:	K. L. Von Damm
PROJECT TITLE:	Technical Assistance in Geochemistry
PROGRAM 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 composition of organic matter found in deep brines from the Palo Duro Basin, Texas, and addresses two major concerns with respect to radioactive waste disposal. The first concern addressed is the amount of radionuclide mobility in the presence of aliphatic acid anions and the second is the usefulness of these organic compounds as indicators of petroleum producing potential. Eleven water samples were obtained from wells throughout the Palo Duro Basin and were analyzed for the aliphatic acid anions. Of the total organic carbon (TOC) present in the sample, 100% of it appeared to be aliphatic acid anions in eight of the eleven samples, and an average of 90% of this was acetate.

The authors present a complete literature review as well as very detailed documentation of their sample collection and methods analysis. They have documented the loss of acetate in samples which are stored without a bacteriacide and the interference of chloride in some of the analytical procedures. The analyses reported herein were, for the most part, from poisoned samples and steps were taken to overcome the chloride interference problems. The method of standard additions verified that there were no interferences. The data presented in this report should therefore be excellent, and the authors state that it supercedes their earlier reports in which some of these problems were not recognized. The authors have obviously put much effort into verifying their analytical results.

The aliphatic acid anion content, principally acetate, found in oil field brines, to which these Palo Duro Basin brines can be compared, reflects the rates of two major processes. The first of these is the production of aliphatic acid anions from the degradation of kerogen and the second is their destruction as a

result of thermal decarboxylation, and microbial activity. Hence the total aliphatic acid anion content of a solution does not necessarily bear a simple relationship to the petroleum bearing potential of an area. Time and temperature also affect the acetate content. The authors have therefore examined a total of 6 source rock indicators and 3 (including acetate) groundwater indicators, all of which indicate that Swisher county has a higher potential for petroleum production than does Deaf Smith county.

A second major concern is if these anions are potentially important in complexing radionuclides and increasing their mobility. Under the brine conditions found in the Palo Duro Basin, this does not appear to be a problem. The authors calculate that any actinide-acetate complexes will be negligible compared to the actinide -chloride, -sulfate, and -fluoride complexes because of the high concentrations of these species in the fluids. They suggest acetate would have to be from 30 to 100 times more concentrated to be an important complexing agent. These calculations are rather qualitative and are done for 25° C. It is difficult to evaluate quantitatively if acetate would become a better complexing agent at higher temperatures, but its rate of decomposition should increase, decreasing the amount available in solution.

In summary this is a well-done study, encompassing the known literature, well-verified analytical methods, and a complete and well-done discussion of the important aspects relating to organic matter contents in the deep brines of the Palo Duro Basin. The authors also use their organic data to make several other inferences about the origin of the dissolved constituents of these brines, including that the iodine and bromine must also be derived from a marine organic matter source (kerogen). Their data suggest that Deaf Smith county is a better site for a repository than Swisher county as the lower organic carbon content of the groundwaters infers a lower potential for both petroleum occurence, and organic complexing and transport of radionuclides.

LETTER REPORT

Title: Review and Evaluation of <u>Reactions in the System</u>
           <u>Basalt/Simulated Spent Fuel/Water</u>, Mat. Res. Soc.
           Proc., V. 26, 1984, by D. E. Grandstaff, G. L.
           McKeon, E. L. Moore, and G. C. Ulmer.

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 paper describes data obtained from Umtanum basalt + Umtanum
groundwater ± simulated spent fuel experiments performed at 30 MPa, 100,
200, and 300°C. The principal goals of the experimentation were to:
(1) elucidate the geochemical characteristics (composition, pH, and
redox conditions) of the groundwaters; (2) identify the types of
secondary minerals that crystallized during experimentation, and (3)
determine the quantities and ultimate fates of radionuclide-analog
elements released from simulated spent fuel in the
basalt/fuel/groundwater experiments.

Starting Materials

Solid Starting Materials

Two types of solid starting materials were employed in the experiments:
Umtanum basalt and simulated spent fuel (Woodley et al., 1981). These
solid starting materials were identical to those employed in earlier
experiments performed by Apted and Myers (1982) and Myers et al. (1983).

Fluid Starting Materials

In all experiments, the starting fluid was a synthetic groundwater with
a composition similar to the groundwater flowing through the Umtanum
basalt at a depth of -1 km beneath the Hanford Reservation (Smith,
1981).

Experimental Conditions

Grandstaff et al. performed their experiments in Dickson-type rocking
autoclaves (Seyfried et al., 1979). The experiments were conducted at
30 MPa, 100, 200, and 300°C for periods up to 7,000 hrs. In basalt +
groundwater experiments, water/rock mass ratios ranged from 5/1 to 50/1.
In basalt + simulated spent fuel + groundwater experiments, the
water/basalt/fuel mass ratio was 20/1/1.

Experimental Methods

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

Analysis of Fluid Samples

Concentrations of major cations and anions were determined using the same analytical techniques employed by Apted and Myers (1982) and Myers et al. (1983). The concentrations of trace elements were measured by neutron activation analysis. Measured concentrations of aqueous elements are believed to be accurate to ±1-6% of the amount present. Measured room-temperature pHs are believed to be accurate to ±0.05 pH units. Estimates of pH at hydrothermal conditions were obtained from a computer code that calculates the equilibrium distribution of aqueous species in rock/water systems at elevated pressures and temperatures (Reed, 1982; Moore, 1983).

Analysis of Solid Reaction Products

Solid reaction products were examined by x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive x-ray (EDX) spectrometry.

Results

Grandstaff et al. do not offer detailed accountings of their experiments; rather, they summarize key results and present their interpretations. Basalt/groundwater and basalt/fuel/groundwater interactions were most extensive in experiments performed at 300°C; therefore, the discussions provided by Grandstaff et al. tend to focus on information obtained from experiments performed at this temperature.

Basalt + Groundwater Experiments

In experiments performed at 300°C, concentrations of aqueous Si, K, and Al increased sharply at the beginning of experimentation due principally to partial dissolution of the glassy mesostasis of basalt particles.

However, the concentrations of most aqueous elements peaked after approximately 10-50 hrs of experimentation, and thereafter remained steady or decreased slightly. According to Grandstaff et al., the gradual changes in the concentrations of several important aqueous elements (e.g., Si and K) that were observed after 50 hrs of experimentation are attributable to the growth and maturation of secondary solid phases.

Grandstaff et al. also observed that groundwater composition was still evolving slowly at the end of each of their experiments. This observation indicates that complete steady-state conditions were not achieved during experimentation. However, in experiments performed at 200 and 300°C, groundwater composition and pH had largely stabilized by the time experimentation was terminated; therefore, at these temperatures, final measured concentrations of aqueous elements probably closely approximate true steady-state values.

Final average pHs achieved during experimentation--calculated from a computer code developed by Moore (1983)--were 7.2 at 100°C, 7.5 at 200°C, and 7.6 at 300°C. These calculated pHs are quite alkaline; for example, at 300°C, a pH of 7.6 is nearly two pH units above neutrality. Grandstaff et al. believe that pH is stabilized in basalt/groundwater experiments when a balance is achieved between hydrogen-ion-generating reactions, such as reactions that attend precipitation of some phyllosilicates and/or sulfate reduction, and hydrogen-consuming reactions, such as dissolution reactions.

Grandstaff et al. observed that sulfide formed in their 300°C experiments. They attribute this observation to slow reduction of aqueous sulfate during experimentation. Using calculated values of f_{O_2} and f_{S_2}, and a phase diagram for the system Fe-S_2-O_2 at 30 MPa, 300°C, Grandstaff et al. estimate that Eh was approximately -0.7 V in these experiments. However, sulfide concentrations were still rising and sulfate concentrations were still decreasing at the end of each 300°C

experiment; therefore, it is evident that complete steady-state redox conditions were not achieved in 300°C experiments.

No measurable amounts of sulfide were produced in experiments performed at 100 and 200°C. Grandstaff et al. attribute this observation to sluggish rates of sulfate-to-sulfide reduction at these temperatures.

SEM photographs of reacted basalt particles revealed very little pitting or etching of the grains. Plagioclase, and pyroxene appeared to be present in almost original amounts. This observation indicates that the glassy mesostasis of basalt grains was the principal source of the substantial quantities of Si, K, and Al that were incorporated into groundwater during the early stages of each basalt/groundwater experiment. Grandstaff et al. also observed secondary minerals coating the surfaces of reacted basalt grains. These minerals included smectite, chlorite, a zeolite (heulandite? wairakite?), illite, one or more silica minerals, and K-feldspar.

Basalt + Simulated Spent Fuel + Groundwater Experiments

In many respects, results obtained from basalt/fuel/groundwater experiments were similar to results obtained from basalt/groundwater experiments. For example, it was observed that the concentrations of aqueous Si, Na, K, and Al at a given point in time during basalt/fuel/groundwater experiments performed at 30 MPa, 300°C were similar to the concentrations of these elements at the same point in time during basalt/groundwater experiments performed at 30 MPa, 300°C. This observation implies that the concentrations of most major aqueous elements were controlled by basalt/groundwater reactions.

In experiments performed at 100°C, comparatively large quantities of I, Mo, and Cs were released to groundwater via dissolution of simulated spent fuel. Moreover, the aqueous concentrations of these elements remained high throughout experimentation. For example, almost the

entire inventory of I in the simulated spent fuel was liberated to, and retained within, the groundwater. In comparison, aqueous concentrations of Mo and Cs were approximately 40 and 60% of the inventories of these elements, respectively. The concentrations of Sr, Pd, and Te reached a peak after approximately 1 hr of experimentation, and then steadily decreased thereafter. This behavior results from rapid dissolution of the primary phases containing these elements, and subsequent incorporation of the liberated elements into secondary phases. Concentrations of Rh, Th, and Ce remained below the limits of detection throughout experimentation. Concentrations of aqueous U were also very low, approximately 0.5 mg/L; this concentration represents less than 0.003% of the inventory of U in the simulated spent fuel.

Significantly, Grandstaff et al. observed that the aqueous concentrations of radionuclide-analog elements were generally greatest at 100°C and progressively lower at successively higher temperatures (200 and 300°C). For example, measured steady-state concentrations of Sr were 0.75 mg/L at 100°C, 0.3 mg/L at 200°C, and 0.2 mg/L at 300°C. For another example, measured steady-state concentrations of U were 0.5 mg/L at 100°C, 0.09 mg/L at 200°C, and 0.12 mg/L at 300°C. Grandstaff et al. speculate that higher aqueous concentrations of radionuclide-analog elements at 100°C can be ascribed to slower rates of growth of secondary solid phases.

Measured (25°C) and calculated (300°C) pHs for the system Umtanum basalt + simulated spent fuel + Umtanum groundwater at 300°C indicate that the addition of simulated spent fuel to the assemblage Umtanum basalt + Umtanum groundwater did not significantly alter calculated steady-state pHs. This conclusion also applies to basalt/fuel/groundwater experiments performed at 100 and 200°C. Final average calculated pHs in basalt/fuel/groundwater experiments were 7.6 at 100°C, 7.2 at 200°C, and 7.7 at 300°C.

As noted previously, Grandstaff et al. found that aqueous concentrations of sulfide increased steadily and aqueous concentrations of sulfate decreased steadily in Umtanum basalt + Umtanum groundwater experiments performed at 300°C. However, in corresponding Umtanum basalt + simulated spent fuel + Umtanum groundwater experiments performed at 300°C, no measurable amounts of sulfide were produced, and concentrations of sulfate did not decrease significantly. Although sulfide may have been removed from solution by precipitation of sulfides such as PdS, Grandstaff et al. suggest that the absence of aqueous sulfide can be attributed to elevated redox conditions induced by the presence of simulated spent fuel.

Examination of solid reaction products after experimentation revealed that the UO_2 component of the simulated spent fuel had not been strongly attacked during experimentation. In contrast, most of the other constituents of the simulated spent fuel--SrO, MoO_2, Pd and Mo metal, and Cs-bearing phases--were almost completely dissolved.

The secondary silicate minerals that formed in basalt/fuel/groundwater experiments included all of the secondary silicate minerals observed in the solid reaction products of basalt/groundwater experiments. However, owing to the presence of simulated spent fuel, some additional secondary solid phases were found to be present. For example, it was observed that the surfaces of grains of simulated spent fuel were covered by: (1) blocky crystals of a K-U-Si phase, probably weeksite or boltwoodite; and (2) acicular to tabular crystals of a U-Si phase, probably coffinite. Also, EDX examination of solid reaction products revealed that Cs was incorporated into phyllosilicates, whereas Mo and Pd were housed in powellite/scheelite and PdS, respectively.

Major Conclusions

At the end of the subject paper, Grandstaff et al. present four conclusions that they developed from the results of their hydrothermal experimentation. These conclusions are summarized below.

1. According to computer calculations performed by Grandstaff et al., final (steady-state) pHs in Umtanum basalt + Umtanum groundwater experiments were as follows: ~7.2 at 100°C, ~7.5 at 200°C, and ~7.6 at 300°C. These pHs are very alkaline. Similar pHs were calculated for Umtanum basalt + simulated spent fuel + Umtanum groundwater experiments performed at 100, 200, and 300°C.

2. From computer calculations of equilibria among sulfur-bearing aqueous species, Grandstaff et al. estimate that Eh was approximately -0.7 V in the basalt/groundwater experiments that they performed at 300°C. Corresponding calculations for the system Umtanum basalt + simulated spent fuel + Umtanum groundwater at 300°C indicate that redox conditions were slightly more oxidizing (i.e., Eh was less negative than -0.7 V in this system).

3. In the system Umtanum basalt + simulated spent fuel + Umtanum groundwater, hydrothermal reactions generate a wide variety of secondary minerals that incorporate radionuclide-analog elements into their crystal structures. These secondary minerals include smectite, chlorite, one or more zeolites, illite, weeksite/boltwoodite, and coffinite.

4. The UO_2 component of simulated spent fuel was highly resistant to chemical attack during hydrothermal experimentation. Also, the elements held in crystalline solution in UO_2 remained essentially inert. By contrast, substantial amounts of I, Mo, Cs, Sr, Pd, and Te were released from the simulated spent fuel to coexisting groundwater. Essentially all of the released Sr, Pd, and Te were

subsequently incorporated into secondary solid phases. In contrast, large quantities of I, Mo, and Cs remained in solution.

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EVALUATION

The experimental data and interpretations presented by Grandstaff et al. prompt the following comments.

1. The experimental data obtained by Grandstaff et al. are similar to the experimental data obtained previously by Apted and Myers (1982) and Myers et al. (1983). Therefore, it is evident that Umtanum basalt + Umtanum groundwater and Umtanum basalt + simulated spent fuel + Umtanum groundwater experiments yield reproducible results.

2. The experimental results obtained by Grandstaff et al. indicate that simulated spent fuel has negligible effects on groundwater composition and pH, and only a minor effect on redox conditions. Surprisingly, the latter effect appears to be a slight _increase_ in redox state. This conclusion derives from the observation that extensive reduction of sulfate to sulfide occurred in Umtanum basalt + Umtanum groundwater experiments performed at 300°C, whereas little or no sulfide formed in corresponding Umtanum basalt + simulated spent fuel + Umtanum groundwater experiments performed at 300°C.

3. It is noteworthy that Grandstaff et al. estimate that Eh is approximately -0.7 V in Umtanum basalt + Umtanum groundwater experiments performed at 300°C. It should be borne in mind that this is a _calculated Eh_, not a measured Eh, and, for this reason, it is of questionable reliability. Nevertheless, an Eh as negative (reducing) as -0.7 V is plausible in view of the observation that sulfate was continuously being converted to sulfide during experimentation. For this reason, it may be concluded that the experimental data obtained by Grandstaff et al. are consistent with the suggestion that basalt is an effective reducing agent at 300°C. By the same token, the lack of evidence for reduction of sulfate to sulfide in experiments performed at 100 and 200°C suggests that basalt is a much less effective reducing agent at these

temperatures. However, the (apparent) inability of basalt to convert sulfate to sulfide at 100 and 200°C does not necessarily indicate that basalt is incapable of effecting reduction of radionuclide species at these temperatures. The ability (or inability) of basalt to reduce solubilized radionuclides to lower oxidation states under a given set of geochemical conditions can only be established definitively by: (1) identifying all radionuclide species and coexisting radionuclide-bearing solids, and (2) elucidating the thermochemical behavior of these species and solids under the given set of geochemical conditions.

4. It is significant that Grandstaff et al. observed that, in Umtanum basalt + simulated spent fuel + Umtanum groundwater experiments, the aqueous concentrations of several important radionuclide-analog elements were greater at 100°C than at 300°C. Grandstaff et al. believe that the enhanced concentrations of aqueous radionuclide-analog elements at low temperatures can be attributed to slower rates of growth of secondary solid phases. The validity of this explanation notwithstanding, the point of larger import is that the experimental results obtained by Grandstaff et al. indicate that it is _possible_ for a waste form to exhibit a better radionuclide-isolation performance at high temperatures than at low temperatures. This observation is significant in view of the fact that current NRC regulations require HLW canisters to provide 300 to 1000 years of "substantial" radionuclide containment. This requirement is relevant to the present discussion because, after 300 to 1000 years, it is likely that temperatures in the thermally disturbed zone of a basalt-hosted HLW repository will already have peaked and declined substantially. Specifically, it is likely that temperatures in the disturbed zone during the post-containment period will be no higher than 200°C, and decreasing. For this reason, it is obviously desirable to have a waste form that exhibits an _improved_ isolation performance as temperature declines.

5. This paper emphasizes the high reactivity of the simulated.spent
   fuel that the investigators employed in their experiments. For
   example, Grandstaff et al. note that, during basalt/fuel/groundwater
   experimentation at 100, 200, and 300°C, substantial quantities of I,
   Mo, Cs, and Sr were released to--and retained in--the groundwater.
   However, considering the results obtained recently from
   basalt/fuel/groundwater experiments in which the waste form was <u>real</u>
   <u>spent fuel</u> (Thomas et al., 1985), it is evident that the high
   reactivity of the simulated spent fuel used by Grandstaff et al. is
   largely attributable to the initial physicochemical state of this
   solid material. Specifically, the simulated spent fuel used by
   Grandstaff et al. was unconsolidated (unsintered) and, therefore, it
   was much more reactive than real spent fuel would be under similar
   geochemical conditions. Thus, it would appear that the experimental
   results obtained by Grandstaff et al. are of limited practical use
   in predicting the radionuclide isolation performance of real spent
   fuel in the very-near field of a basalt-hosted HLW repository.