

SC  
OAK RIDGE NATIONAL LABORATORY  
WM DOCKET CENTRAL CENTER  
OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

POST OFFICE BOX X  
OAK RIDGE, TENNESSEE 37831

'86 SEP 18 A10:24

Sept. 8, 1986

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

Dear Dave:

Please find enclosed the letter reports referenced in the August monthly progress report for B0287, "Technical Assistance in Geochemistry."

Sincerely,

*Gary K. Jacobs*

Gary K. Jacobs  
Manager, NRC Waste Programs  
Environmental Sciences Division  
Building 1505, MS-3, FTS/626-0567

GKJ/

Enclosures: Letter Reports LR-287-55, -56, -57, -58

cc w/o enclosures:

Office of the Director, NMSS (Attn: Program Support Branch)  
Division Director, NMSS Division of Waste Management (2)  
Branch Chief, Waste Management Branch, RES  
P. S. Justus, Chief, Geotechnical Branch, NMSS  
K. C. Jackson, Geotechnical Branch, NMSS  
A. P. Malinauskas  
GKJ File

B610240177 B60908  
PDR WMRES EXIORNL  
B-0287 PDR

WM-Res  
WM Record File  
B0287  
ORNL

WM Project 10, 11, 16  
Docket No. \_\_\_\_\_  
PDR ✓  
LPDR B, N, S

Distribution:  
DBrooks  
(Return to WM, 623-SS)

3403

LETTER REPORT

TITLE: Review of "Actinide Solubility in Deep Groundwaters - Estimates for Upper Limits Based on Chemical Equilibrium Calculations", by M. Schweingruber (1983). Eidgenössisches Institut für Reaktorforschung, Würenlingen, Switzerland; EIR Report No. 507.

AUTHOR: G. D. O'Kelley  
Chemistry Division  
Oak Ridge National Laboratory

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

A number of equilibrium calculations have been carried out on the solubilities of nuclear waste elements. However, as pointed out by the author of this report, such calculations often have used actinide databases of rather limited scope and with only a few variations in parameters such as pH, Eh, carbonate concentration, temperature, and ionic strength. The objective of the present report was to determine upper concentration limits for Th, U, Np, Pu, and Am under geochemical conditions of deep groundwaters, including effects of temperature, pH, Eh, ionic strength, inorganic ligands, and the choice of thermodynamic database.

The computer code used appears to be an extension of MINEQL, to include additions for computing temperature dependences of equilibrium constants and a provision for approximating activity coefficients. The model was intended to estimate speciation and maximum solubility of multivalent actinides in aqueous solution, using the following assumptions:

1. Chemical equilibrium is attained among all components of the system.
2. Actinide solubility is limited by pure oxide or hydroxide solids.
3. Mass balance was calculated on the basis of a closed system constrained by fixed pH, Eh, and actinide aquo ion concentration.

4. Temperature effects were estimated by means of a simple van't Hoff isochore approach, which required that standard enthalpies of reaction were constant over the temperature range of interest.
5. Activity coefficients were approximated by a formula due to Davies, said to be valid for a range of ionic strength of 0.0 to 0.5 (Stumm and Morgan, 1970).
6. Pressure effects were neglected.

Once the assumption of chemical equilibrium has been decided, the other assumptions above follow quite naturally. However, a major concern in implementing such models is the quality of the thermodynamic database available. The present report used two databases and compared the results. Database A was derived from compilations by Lemire and Tremaine (1980) for U and Pu, by Langmuir and Herman (1980) for Th, by Phillips (1982) for Am, and data on Np from a variety of sources. Database B used the data of Allard (1983), which was employed in the calculations reported by the KBS project in Sweden (KBS-3, 1983).

In an attempt to determine the most conservative conditions, the author chose a reference water with high values of alkalinity, ligand content and ionic strength. However, the only ligands considered were inorganic, even though it is known that organic ligands can play an important role through increasing the mobility of multivalent cations.

The ionic strength was set either to 0.0 or 0.2. For an ionic strength of 0.2 it was necessary in some cases to include non-reactive components to make up an ionic strength of 0.2 and to satisfy conditions of electroneutrality. Calculations of solubility and speciation were carried out over ranges of Eh and pH of -400 to +700 mV and 5.5 to 10.0, respectively.

Results were presented for Th, U, Np, Pu, and Am. One of the useful features of the report is the extensive display of data in graphical form. For all elements, the results are given graphically for both databases. Plots are shown as a function of pH and Eh for solubility of the limiting phase, concentrations of dominant dissolved species, and total solubility isopleths. Also, plots are included showing solubility and speciation concentration as a function of pH. In most cases curves are given for three selected Eh/pH relationships, which were assumed to bracket the lower and upper redox potentials appropriate for reducing environments and oxygenated waters.

Some of the general results obtained are summarized below. It is not surprising that significant differences are observed between calculations carried out with the two databases, since the stability constants differ greatly for some important dissolved and solid species.

Differences between results obtained with the two databases were small for Th, but large differences were observed for U, Np, Pu, and Am. However, in the case of Np and Am it appears that the differences are of the same order as the uncertainties in the formation constants.

The calculations suggest that tetravalent oxides turn out to be the solubility-limiting phases over much of the Eh-pH region for Th, U, Np, and Pu. Also, the most important inorganic ligands for stabilizing dissolved actinides under the conditions considered are carbonate, fluoride, and phosphate ions.

Sensitivity to model parameters was evaluated by calculating the effects of temperature and ionic strength for selected cases. Solubilities of Th, U, and Pu were calculated at 25° and 75°C, because the appropriate enthalpy data were available for extrapolation to 75°C. Changes in the solubility were about two orders of magnitude for these elements, which is only about the extent of the uncertainties associated with many of the formation constants at 25°C. Ionic strength effects were investigated by calculating uranium solubility and speciation at ionic strengths of 0.0 and 0.2. The model predicted relatively small increases in solubility as the ionic strength increased.

The author felt that, after analyzing all results, the solubilities for U and Th were conservative, but that the values for Am were unrealistically pessimistic. Conservatism of the results for Np and Pu could not be assessed.

## EVALUATION

This report presents a relatively conventional equilibrium treatment of actinide solubility and speciation. The model which was developed appears to be adequate for the task at hand, but not in any way superior to models such as EQ3/EQ6, which take account of activity coefficients more accurately, for example. The principal weakness of all such calculations is the assumption of equilibrium between chemical components of the system. There are few measured quantities on which to base calculations, and so there is always a danger that unknown and unrecognized kinetic behavior of some elements in the groundwater might invalidate the treatment as an equilibrium system. This question poses great difficulties, because geochemical time scales are large.

Even if the assumption of equilibrium turns out to be correct, this report demonstrates that, at present, thermodynamic databases for actinide chemistry are not adequate for calculations at a desirable level of confidence and accuracy. The two databases used in the work reported here sometimes gave widely disparate results. Validation of models presents a formidable problem, since there are few experimental measurements to check the results of calculations. Extrapolation of formation constants from a reference state to another state of different

temperature and ionic strength involves assumptions and approximations which should be checked against experimental data.

The author states that his calculations attempt to derive conservative, upper concentration limits, but the effect of organic ligands and possible hydrolytic formation of colloids has not been addressed. The calculations demonstrate that inorganic ligands such as carbonate, fluoride, and phosphate may have a profound effect on the mobility of actinide ions, yet it is known that a number of organic ligands complex these ions even more readily. This issue and that of colloids needs to be addressed both theoretically and experimentally. Neglecting such effects reduces the confidence in calculations such as those under discussion.

Finally, the author reported only data for a single groundwater composition, which limits the general utility of the calculations. However, the complete description of the author's approach and the detailed, graphical display of results may make this report useful to those who wish to evaluate the effects of altering various parameters in this groundwater system. Regrettably, because of the paucity of experimental data on equilibrium constants for actinide reactions, there is little new in this report except for the amount of detail.

#### REFERENCES

Allard, B. (1983). "Solubilities of Actinides in Neutral or Basic Solutions", in N. M. Edelstein, ed., Actinides in Perspective, Pergamon Press, 533-580.

KBS-3 (1983). "Final Storage of Spent Nuclear Fuel-III. Barriers", SKBF/KBS Safety Report.

Langmuir D., and Herman, J. S. (1980). "The Mobility of Thorium in Natural Waters at Low Temperatures", Geochim. Cosmochim. Acta 44, 1753-1766.

Lemire, R. J. and Tremaine, P. R. (1980). "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C", Can. J. Chem. Eng. Data 25, 361-370.

Phillips, S. L. (1982). "Hydrolysis and Formation Constants", Lawrence Berkeley Laboratory Report LBL-14313.

Stumm, W. and Morgan, J. J. (1970). Aquatic Chemistry, Wiley-Interscience.

Letter Report

TITLE: Review of: The organic geochemistry of deep ground waters and radionuclide partitioning experiments under hydrothermal conditions, ONWI-448, July 1983, 84 p., by J. L. Means, A. S. Maest, and D. A. Crerar.

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 two sets of experiments relating to the occurrence, stability, and complexing capabilities of certain kinds of organic matter which are found, or expected to be found, in groundwaters around a proposed high level waste repository.

In the first part of the study ground waters from the Permian basins in Texas, the Paradox basin in Utah, and the Nevada Test Site were analyzed for their total organic carbon contents. Experiments were also performed to identify the specific types of organic compounds present. Much of the data in this report is superceded by that reported in Means and Hubbard (1985), the subject of letter report 280-48. The later report states that in the subject report, inadequate sample preservation and unrecognized chloride interferences in the procedures led to inaccuracies in the reported data. For this reason data on the organic geochemistry of ground waters for the Permian basins, should be taken from Means and Hubbard (1985) and not the subject report. No data for the Paradox basin or for the Nevada Test Site are given in the newer report. As the Paradox basin is not one of the three sites now scheduled for more detailed characterization, this is not a serious problem. The Nevada Test Site ground waters, due to their low chlorinity are not subject to one of the experimental errors. The poor sample preservation infers that the data reported in the subject report should be viewed as a lower limit for the amount of total organic carbon present, and that the speciation of the organic compounds may also be somewhat different than reported, due to bacterial activity in the samples. The first part of the subject report has therefore been largely pre-empted by a later document.

The second part of the subject report documents a series of experiments with several clays (kaolinite, illite and montmorillonite), several metals (uranium, strontium, cesium, and

cobalt), and two organic compounds (EDTA and oxalic acid) over a range of temperature conditions (25°C to 250°C). The objective of this study was to test what effects these two types of organic matter have on the adsorption of these metals onto clays. The authors state that their four major findings are: (1) the extent of adsorption of Sr, Co and U, in some cases, increase with increasing temperature; (2) oxalic acid has little effect or increases the adsorption of Cs and Sr onto all three clays studied; (3) thermal degradation of natural organic compounds in the near field (high temperature) environment may be significant; (4) U, Co, Sr, and Cs adsorption onto kaolinite and montmorillonite reaches a steady-state in less than 1 hour at 25°C and 1 atm. The authors report too many experiments for them to be discussed in detail here, but certain limitations apply to their experiments. All of the experiments were done in distilled water with the addition of the metals as their nitrate salts, to a usual concentration of  $5 \times 10^{-6}$  M. Hence, in salt solutions, where other ions might compete for the sites on the clays and on the organic ligands, the results might be somewhat different. Also, the water/clay ratios are relatively high in the experiments compared to what might be expected, and this would effect the total amount of radionuclides adsorbed per volume of solution. At a lower water/clay ratio a higher percentage per unit volume of solution of the radionuclides might be adsorbed. The organics are always added at  $2 \times 10^{-3}$  M, which may or may not be realistic of a repository. Also these are "model" organics and organics actually present in a repository may behave differently. The time scales of the experiments are much shorter than what is expected for a repository, and this may have an affect on the decomposition of the organic compounds. In summary, the experiments are well done, and complete for what they are but are a very limited subset of what might be expected in a repository setting. They provide an indication of what might be expected, but a more "site specific" approach is needed for them to reliably predict what would happen under repository conditions.

09/11/86

## LETTER REPORT

Title: Review and Evaluation of Icelandic Basaltic Geothermal Field: A Natural Analog for Nuclear Waste Isolation in Basalt, SD-BWI-TI-257, Dec., 1984, by G. C. Ulmer and D. E. Grandstaff.

AUTHOR: J. G. Blencoe  
Chemistry Division  
Oak Ridge National Laboratory

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

## OVERVIEW

This report discusses various geochemical and hydrologic characteristics of: (1) Hanford site groundwaters and basalts, (2) the groundwaters and solid reaction products of DOE-Hanford basalt-groundwater experiments, and (3) the groundwaters and basalts in several geothermal fields in Iceland. The underlying theme of these discussions is that the natural and synthetic Hanford basalt-groundwater systems and selected Icelandic geothermal systems share many common geochemical features. The authors begin their discussions by reminding the reader that: (1) DOE-Hanford seeks to assess the feasibility of siting an HLW repository in the basalts that underlie the Hanford site; and (2) some of the key data relating to such feasibility have been obtained from hydrothermal experiments performed in Dickson rocking autoclaves. However, the DOE-

Hanford autoclave experiments have been conducted over periods of - at most - a few thousand hours, whereas a nuclear waste repository in basalt (NWRB) must isolate nuclear waste for thousands of years. Thus, it is uncertain whether short-term experiments can adequately simulate geochemical conditions and reactions which occur over much longer periods of time in an NWRB. This uncertainty has prompted a search for natural analogs that would provide key information on the long-term performance of an NWRB.

Due to the fact that Hanford groundwaters and basalts are similar compositionally to some of the low-salinity groundwaters and tholeiitic basalts in Iceland, there is considerable interest in determining the extent to which selected geothermal fields in Iceland might properly serve as natural analogs for an NWRB. This interest is heightened by the fact that there are abundant geochemical data for Icelandic geothermal fields. The Icelandic data base has been developed over two decades as a result of a concentrated effort to generate electricity from natural or injected geothermal wells. The data base contains a wealth of information on:

- (1) the geochemistry of Icelandic basalts,
- (2) the geochemistry of Icelandic geothermal waters,
- (3) redox equilibria in basalt-groundwater systems,
- (4) the acidity of Icelandic geothermal waters,
- (5) secondary (well-clogging) solid phases,
- (6) hydrologic parameters in Icelandic basalt flows,
- (7) ranges of temperature in Icelandic geothermal fields, and
- (8) variations in (1)-(7) above during both historic and recent geologic time.

GEOCHEMICAL AND HYDROLOGIC ANALOGIES BETWEEN ICELANDIC GEOTHERMAL FIELDS  
AND A POTENTIAL NWRB AT THE HANFORD SITE

The basis for employing Icelandic geothermal fields as analogs for an NWRB is that geochemical/hydrologic conditions in these fields may be similar to the geochemical/hydrologic conditions that develop in an NWRB during the post-closure period. In this regard, geochemical/hydrologic parameters of obvious interest include: temperature, basalt chemistry, host-rock permeability, and groundwater geochemistry. Ulmer and Grandstaff emphasize that each of these parameters would be similar for Icelandic basalts and a potential NWRB at the Hanford site. The arguments presented by these investigators are summarized below.

Temperature

The temperatures of the geothermal waters in Iceland range from 18 to 340°C. (Most reservoir temperatures are less than 250°C.) These temperatures encompass those that are anticipated to develop in an NWRB during the post-closure period.

Basalt Chemistry

The bulk compositions of Columbia River basalts are on the silica-rich side of the olivine tholeiite volume in the Yoder-Tilley basalt tetrahedron. The basaltic rocks of most analogous chemistry in Iceland are the Tertiary and Quaternary olivine tholeiites that are found in west Iceland (near Reykjanes) and in east Iceland. The Columbia River basalt flows of greatest current interest from the standpoint of HLW disposal (the Umtanum and Cohasset flows) are similar to each other compositionally, and are more similar in total chemistry to the Reykjanes lavas than to the east Icelandic lavas.

### Host-Rock Permeability

Columbia River basalts are typically thick and contain well-developed colonnade, entablature, and flow-top structural units. Hydrologically, these sub-units favor high horizontal flow along flow tops, low vertical flow across basalt interiors, and vertical "leakage" along structural discontinuities. Because Icelandic flows are usually less than 10 m thick, they often do not display the typical colonnade-entablature-flow top structure pattern that Columbia River basalts exhibit. Furthermore, Icelandic basalts are generally more rifted than Columbia River basalts (i.e., vertical flow of Icelandic geothermal waters tends to be associated with steeply-dipping faults and fissures). For these reasons, vertical flow of groundwater appears to be more common in Iceland than in many parts of the Columbia Plateau.

However, the range of reported groundwater residence times in Iceland is within the range of residence times reported for Columbia River basalts. The residence time of Icelandic geothermal waters is at least several tens of years and, in some cases, may be as long as 10,000 years. By comparison, in the Miocene flows of the Columbia River Plateau, groundwater residence times are believed to range from 500 to 5,000,000 years, with a median residence time of approximately 17,000 years (Clifton and Baca, 1984).

### Groundwater Geochemistry

The quantities of dissolved solids in Icelandic geothermal waters are highly variable, ranging from about 150 ppm to about 32,000 ppm (sea water salinity). The low-salinity groundwaters are produced by geothermal reactions between basalts and meteoric waters, whereas the high-salinity geothermal waters (in the vicinity of Reykjanes, for example) result from infiltration of sea water. The low-salinity geothermal waters in Iceland are usually slightly alkaline: room temperature pHs range from 6.1 to 10.1, with a median value of 9.1.

Sodium is the dominant cation: concentrations range from 26 to 500 mg/L (Arnorsson et al., 1983). Chloride is usually the dominant anion - concentrations range from 6 to 700 mg/L, but occasionally bicarbonate (approximately 15 to 200 mg/L), and/or sulfate (6 to 300 mg/L), are predominant.

Calculations performed by Arnorsson et al. (1983) indicate that low-salinity Icelandic geothermal fluids in basalt generally achieve equilibrium with respect to chalcedony (or quartz at temperatures above -180°C), calcite, albite, K-feldspar, fluorite, smectite (or chlorite above -200°C), marcasite (or pyrite), pyrrhotite, iron hydroxides, and at the highest temperatures, anhydrite and epidote.

The compositions of groundwaters in the Pasco Basin of the Hanford area are also somewhat variable. For example, the concentration of total dissolved solids varies from approximately 150 to 700 mg/L. In most samples sodium is the dominant cation, and either chloride or bicarbonate are the dominant anions. Most samples are also quite alkaline: pHs typically range between 9 and 10. Therefore, groundwaters in the Hanford area are similar geochemically to low-salinity Icelandic groundwaters.

#### GEOCHEMICAL DATA FROM DOE-HANFORD BASALT-GROUNDWATER EXPERIMENTS VS. CORRESPONDING DATA FROM ICELANDIC GEOTHERMAL SYSTEMS

To further establish the analogy between expected geochemical conditions in an NWRB and corresponding conditions in Icelandic geothermal systems, Ulmer and Grandstaff compare the data obtained from DOE-Hanford basalt-groundwater experiments with corresponding data for Icelandic groundwaters and basalts.

### Groundwater Composition

Ulmer and Grandstaff note that groundwaters sampled from DOE-Hanford experiments with Umtanum and Cohasset basalt are very similar compositionally. This observation indicates that differences in basalt composition, glass composition, mineralogy, and differences in the compositions of the starting groundwaters (GR-3 and GR-4) had minimal effects on the geochemistries of the synthetic groundwaters. These experimental results are consistent with the contention of Arnorsson et al. (1983) that variations in salinity and basalt composition do not have major effects on the activities of neutral species and the cation/hydrogen activity ratios of basalt-hosted groundwaters. It is also noteworthy that, in most cases, the values of geochemical parameters for synthetic groundwaters from DOE-Hanford basalt-groundwater experiments lie in or near the ranges of corresponding data for Icelandic geothermal systems.

### Redox Equilibria vs. Temperature

Ulmer and Grandstaff emphasize that calculated redox conditions (Eh) for Icelandic geothermal systems form a congruent and coherent envelope in  $f_{O_2}$ -T space. This observation supports the contention that salinity does not greatly affect redox conditions. More importantly, however, calculated redox conditions for Icelandic geothermal systems are in excellent agreement with corresponding calculated redox conditions for groundwaters coexisting with Umtanum or Cohasset basalt in DOE-Hanford basalt-groundwater experiments. Thus, despite differences in salinity, in total chemistry, and geochemical environment, redox conditions appear to be very similar in DOE-Hanford basalt-groundwater experiments and in Icelandic geothermal systems.

### Hydrothermal pHs

Calculated high-temperature pHs for Icelandic geothermal waters are neutral to slightly alkaline, ranging from approximately 6 to 8. In comparison, calculated high-temperature pHs for synthetic groundwaters produced during DOE-Hanford basalt-groundwater experiments range from approximately 7 to 7.8. Therefore, low-salinity Icelandic geothermal waters and the groundwaters sampled from DOE-Hanford basalt-groundwater experiments appear to have similar pHs.

### Secondary Minerals

Assemblages of secondary minerals in Icelandic basalts appear to be correlative with temperature. Clay minerals (smectites) are the most voluminous secondary minerals. Iron-rich saponites are observed at shallow depths in Icelandic geothermal fields. At temperatures just below 200°C, mixed-layer smectite-plus-chlorite starts to form. Mixed-layer smectite-plus-chlorite remains dominant in the temperature range 200-230°C. Finally, at 230-250°C, chlorite becomes the dominant sheet silicate.

Zeolites are also common in Icelandic basalts. At rock temperatures below 100°C, two groups of zeolites occur: (1) mordenite, heulandite, stilbite, and epistilbite, which are common in tholeiitic basalts; and (2) chabazite, thomsonite, and mesolite-scolecite, which are found in olivine-tholeiite basalts. When temperatures reach 100-120°C, laumontite replaces other zeolites. Wairakite crystallizes at 180°C, and all other zeolites disappear at temperatures of about 200°C.

to be very similar in DOE-Hanford basalt-groundwater experiments.

Other common secondary minerals in Icelandic basalts include: chalcedony, quartz, epidote, actinolite, pyrite, pyrrhotite, anhydrite, and calcite.

The secondary minerals formed in DOE-Hanford autoclave experiments include smectite-chlorite, cristobalite, illite, K-feldspar, heulandite, and wairakite. Significantly, no secondary mineral observed to form in DOE-Hanford basalt-groundwater experiments is absent from the list of alteration minerals found in Icelandic basalts.

#### OTHER POTENTIALLY USEFUL AVENUES OF INVESTIGATION

In addition to making more detailed comparisons between geochemical data obtained from DOE-Hanford basalt-groundwater experiments and corresponding data obtained from Icelandic geothermal systems, Ulmer and Grandstaff suggest several other potentially useful avenues of investigation. These possible research areas are summarized below.

##### Mineral Deposition

Ulmer and Grandstaff believe that the data which have been accumulating for wet-steam and dry-steam mineral deposition in Icelandic geothermal fields should be examined for their relevance to near-field and far-field mineral deposition in an NWRB. It is possible that the Icelandic data will shed light on mineral deposition associated with decreases in temperature in basalt-groundwater systems.

##### Higher than Planned Temperatures

Data from "high-temperature" wells (wells with downhole temperatures as high as 400°C) should be examined for their relevance to premature ("high-temperature") breaching of canisters in an NWRB.

##### Flow and Conductivity of Heat

Patterns of heat flow in Icelandic geothermal fields should be examined for their potential relevance to heat flow in an NWRB during the post-closure period.

### Geochemistry at Low Temperatures

Low-temperature data obtained from Icelandic geothermal fields should be analyzed for their potential relevance to the long-term, post-peak-temperature geochemistries of the rocks and groundwaters in an NWRB. Because the durations of laboratory experiments are limited by practical constraints, and because rock-water reactions are typically sluggish at "low" temperatures ( $T < 200^{\circ}\text{C}$ ), laboratory investigations of basalt-groundwater systems have emphasized high-temperature experiments. The nature of rock-water reactions at "low" temperatures, and over long timeframes (hundreds of years), have been largely inferred by extrapolating high-temperature data down to lower temperatures. Therefore, in view of the fact that Icelandic geothermal fields have developed over many thousands of years, low-temperature geochemical data from Icelandic geothermal fields may be uniquely useful for evaluating sluggish, low-temperature rock-water reactions in an NWRB.

### The Role of Glass

One major question that detailed analog studies of Icelandic geothermal fields might answer is whether mesostasis glass is effective in controlling the groundwater geochemistry and secondary mineralogy of natural basalt-groundwater geothermal systems. It is well known from DOE-Hanford basalt-groundwater experiments that basalt glass dissolves more rapidly than the crystalline silicate phases that are typically present in tholeiitic basalts (pyroxene, plagioclase, etc.). Therefore, as long as it is present in more than minor amounts, basalt glass will probably have a significant influence on groundwater geochemistry and the secondary minerals that form in basalt-groundwater systems.

In this regard, it is of some interest that basalt glass is always observed to be present in the solid reaction products of DOE-Hanford basalt-groundwater experiments. This persistence of basalt glass, which

may in turn promote the crystallization of metastable solid phases, raises the question of whether closed-system hydrothermal experiments properly simulate long-term geochemical conditions in an NWRB. Ulmer and Grandstaff hypothesize that, once the mesostasis glass is largely leached away and/or devitrified in a natural basalt-groundwater system, the compositions of other - more slowly dissolving - crystalline phases will control the formation of secondary phases. Furthermore, in this event, greater numbers of secondary minerals might crystallize than would be the case in "static" (closed-system) basalt-groundwater systems wherein, as noted above, glass invariably persists to the end of experimentation. For this reason, it would be worthwhile to determine whether the mesostasis glass in Icelandic basalt-groundwater geothermal systems has been completely leached away or devitrified.

Surprisingly, it is not presently known whether the interstitial glass in Icelandic basalts is "exhausted" either generally or locally. The possibility of "exhaustion" of basalt glass can be investigated readily by examining thin-sections of drill core from Icelandic geothermal fields. The value of such a study would be that it will provide useful information regardless of what is discovered. If it is found that mesostasis glass is completely absent in most Icelandic basalt-groundwater geothermal systems, then the secondary mineralogy of the basalts in these systems should exhibit features which reflect this fact. Also, it will be important to establish whether "exhaustion" of basalt glass has any significant effects on groundwater geochemistry. Finally, it may be found that mesostasis glass is invariably present in Icelandic basalt-groundwater geothermal systems. If so, then explanations other than "exhaustion" of basalt glass must be entertained in order to account for the diversity of secondary minerals in Icelandic basalts.

## REFERENCES

Arnorsson, S., Gunnlaugsson, E., and H. Svarsson. 1983. The Chemistry of Geothermal Waters in Iceland. II. Mineral Equilibria and Independent Variables Controlling Water Compositions. Geochim. Cosmochim. Acta, 47, pp. 547-566.

Benson, L. V., and L. S. Teague. 1979. A Study of Rock-Water-Nuclear Waste Interactions in the Pasco Basin, Washington. Part I. Distribution and Composition of Secondary and Primary Mineral Phases in Basalts of the Pasco Basin, Washington. LBL-9677, Lawrence Berkeley Laboratory, Berkeley, CA.

Benson, L. V., and L. S. Teague. 1982. Diagenesis of Basalts from the Pasco Basin, Washington - I. Distribution and Composition of Secondary Mineral Phases. J. Sediment. Petrol., 52, pp. 595-613.

Clifton, P. M., and R. C. A. Baca. 1984. Stochastic analysis of groundwater traveltime for long-term repository performance assessment. In G. L. McVay, ed. Scientific Basis for Nuclear Waste Management VII, Materials Research Society Symposia Proceedings, v. 26, pp. 161-170.

Schramke, J. A., Thomas, L. E., McKinley, S. G., Simonson, S. A., and D. G. Coles. 1984. A Final Report on Hydrothermal Testing of <sup>99</sup>Tc-Doped Glass Waste Form and Waste Package Components. SD-BWI-TI-229. Rockwell Hanford Operations, Richland, WA.

## EVALUATION

This report focuses on selected geochemical characteristics of: (1) the groundwaters and solid reaction products of DOE-Hanford basalt-groundwater experiments, and (2) the groundwaters and basalts of selected geothermal fields in Iceland. Ulmer and Grandstaff emphasize that the DOE-Hanford experimental systems and the Icelandic geothermal systems have many common geochemical features. Most notably, there are numerous similarities between the pHs, redox conditions, and compositions of groundwaters and the kinds of secondary minerals that crystallize in these two types of basalt-groundwater systems. In view of these numerous shared geochemical features, the authors propose that Icelandic geothermal systems may be used as natural analogs for a nuclear waste repository in basalt (NWRB).

Taken together, the arguments presented by Ulmer and Grandstaff strongly support the contention that Icelandic geothermal systems can serve as natural analogs for an NWRB. However, examined individually, there are serious flaws in several of the arguments presented by these investigators. Moreover, the authors fail to raise some appropriate questions concerning the degree to which active basaltic geothermal systems can serve as natural analogs for an NWRB. These matters are addressed in the discussion items below.

1. Ulmer and Grandstaff suggest that groundwaters in equilibrium with basalt have roughly the same pH, Eh, silica content, etc., regardless of the composition of the basalt. This argument is bolstered by the finding that groundwaters sampled from DOE-Hanford autoclave experiments with Umtanum and Cohasset basalt have very similar geochemical characteristics. However, the Umtanum and Cohasset basalts have nearly identical bulk compositions, and there are some significant compositional differences between these two Columbia River basalts and Icelandic basalts. Specifically, the latter basalts contain significantly greater amounts of Mg and Ca,

and significantly less Si. Therefore, it would be useful to perform autoclave experiments with one or more Icelandic basalts and GR-3 or GR-4 groundwater to further test the suggestion that "minor" variations in basalt composition have minimal effects on the pH, redox state, and composition of coexisting groundwater.

2. Ulmer and Grandstaff emphasize that values of various geochemical parameters ( $-\log H_4SiO_4$ ,  $\log K/H$ ,  $\log Na/H$ , etc.) for groundwaters sampled from DOE-Hanford autoclave experiments are generally within the ranges of corresponding values for Icelandic basalts. However, it is also evident from diagrams provided by the authors (Ulmer and Grandstaff, 1984, Fig. 2) that the trends of these parameters with temperature are different from corresponding trends for Icelandic basalts. Therefore, the reader is left with the impression that Icelandic geothermal waters may not be strictly analogous to the groundwaters sampled from DOE-Hanford autoclave experiments.
3. Ulmer and Grandstaff argue from several lines of evidence that similar pH and redox conditions develop in autoclave experiments and in Icelandic geothermal systems. However, the authors' arguments are undermined by the fact that, in both autoclave experiments and natural geothermal systems, pH and redox conditions must be calculated because - at present - it is not possible to obtain direct measurements of these parameters. Therefore, the lines of evidence presented by Ulmer and Grandstaff do not rule out the possibility that the similar calculated pHs and redox conditions for synthetic and natural basalt-groundwater systems are an artifact of calculational methodology.
4. In discussing Icelandic geothermal systems, Ulmer and Grandstaff note that it is common to observe highly altered basalt immediately adjacent to essentially unaltered basalt. Unfortunately, however, Ulmer and Grandstaff do not attempt to explain this curious juxtaposition, nor do they propose that the phenomenon should be

studied. It would seem that such an unusual pattern of alteration is worthy of study, because the resulting data could provide important clues concerning why and how basalts alter to secondary minerals.

5. Ulmer and Grandstaff state that all of the secondary minerals observed in the solid reaction products of DOE-Hanford basalt-groundwater hydrothermal experiments with Umtanum and Cohasset basalts are also present in one or more geothermal systems in Iceland. This appears to be true, but it is curious that clinoptilolite is absent from both the DOE-Hanford basalt-groundwater experimental systems and the Icelandic geothermal systems. The absence of clinoptilolite from these systems is puzzling because this zeolite has been observed in the solid reaction products of DOE-Hanford experiments on the system <sup>99</sup>Tc-doped borosilicate glass + Umtanum basalt + GR-3 groundwater (Schramke et al., 1984), and clinoptilolite is a common secondary mineral in Hanford basalts (Benson and Teague, 1979, 1982). Therefore, it is surprising that clinoptilolite is not observed in either the solid reaction products of DOE-Hanford basalt-groundwater experiments or in Icelandic basalts.
  
6. At one point in the subject report (p. 31), Ulmer and Grandstaff attribute the wide variety of secondary minerals in Icelandic geothermal systems to: (1) differences in the bulk compositions of the basalts in these systems, and/or (2) the persistence of early-formed secondary minerals and the growth of new secondary minerals during changes in temperature and changes in the rates of leaching of rock constituents as the geothermal systems evolve. However, at a subsequent point in the report (p. 33), it is stated that the "diversity of alteration" in Icelandic basalts could also be explained by "exhaustion" (complete dissolution and/or devitrification) of mesostasis glass in the basalts. To test the latter hypothesis, Ulmer and Grandstaff suggest that Icelandic

basalts should be examined petrographically to see if all original glass has devitrified. The clear implication of this suggestion is that, if it is observed that all original glass is "exhausted", then this observation would help to explain why Icelandic basalts contain a wide variety of secondary minerals. However, Ulmer and Grandstaff do not state how the effects of the absence of glass will be sorted out from the effects of temperature and variable rates of "leaching" which the authors themselves have suggested could be influential in creating a large suite of secondary minerals in Icelandic basalts.

7. As noted above, Ulmer and Grandstaff argue that "exhaustion" of original glass might help to explain why Icelandic basalts contain such a wide variety of secondary minerals. This suggestion is plausible, but the situation is more complicated than Ulmer and Grandstaff seem to realize. For example, it should be recognized that it will be difficult to determine the distances over which basalt glass is in effective geochemical communication with groundwater. If this distance is great (say, tens of meters), then local exhaustion of basalt glass is liable to have only minimal effects on the geochemical properties of groundwater and the nature of secondary mineralization in basalt. On the other hand, if "glass-groundwater communication" is only effective over short distances (say, on a centimeter scale), then local glass "exhaustion" could have important geochemical effects on nearby groundwater and basalt.

In this regard, it is useful to recall that current conceptual designs of an NWRB at the Hanford site include strategies to impede the flow of groundwater near waste packages. Therefore, to the extent that this effort is successful, glass leaching and devitrification may be slowed considerably in the near field of the NWRB; i.e., glass "exhaustion" in the near field might not occur even over periods of hundreds to thousands of years. Furthermore,

it is noteworthy that, despite their considerable age (-16 million years), Hanford basalts still contain abundant mesostasis glass. Consequently, for expected post-closure geochemical conditions and events in an NWRB at the Hanford site, the possibility of anything but extremely local glass "exhaustion" seems highly unlikely. For this reason, if it is discovered that mesostasis glass is completely absent in Icelandic basalt-groundwater systems, then these systems may not be suitable geochemical analogues for an NWRB in Hanford basalt.

Finally, the foregoing comments suggest two potentially significant avenues of investigation in studies of Icelandic basalts. First, some effort should be made to correlate the nature of secondary mineralization with primary basalt mineralogy (and especially the presence or absence of mesostasis glass). Second, research efforts should focus on Icelandic geothermal fields where throughput of groundwater is relatively slow. These "low-permeability" geothermal fields would be more analogous to an NWRB than highly active geothermal fields.

LETTER REPORT

TITLE: Review of: T. W. Newton and J. C. Sullivan, "Actinide Carbonate Complexes in Aqueous Solution," in Handbook on the Physics and Chemistry of the Actinides, Volume 3, edited by A. J. Freeman and C. Keller, North-Holland, 1985, pp. 387-406.

AUTHOR: A. D. Kelmers  
Chemical Technology Division  
OAK RIDGE NATIONAL LABORATORY  
Oak Ridge TN 37831

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

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

The chapter by Newton and Sullivan contains a useful and thorough review of the published information on actinide complexes in carbonate solutions. Formal potentials for the (VI)/(V), (V)/(IV), and (IV)/(III) couples are given, as well as the association quotients for the respective carbonate complexes. Reference is also made to the limited spectroscopic data and kinetic information for these complexes.

Knowledge of the actinide carbonate complex chemistry is important to the NRC in understanding the predicted behavior of uranium, neptunium, plutonium, and americium in the high-level waste repository systems because the groundwaters at the Yucca Mountain or Hanford Site locations are primarily dilute bicarbonate-carbonate solutions. At the various salt sites, once the radionuclide-containing saline solution has migrated from the salt into an adjacent aquifer, it may also be similar in carbonate composition.

Unfortunately, actinide carbonate complexes have received limited attention and the available information may be incomplete and/or inaccurate for purposes of modeling migration of actinides in the candidate repository site groundwater systems. The chapter by Newton and Sullivan contain a number of pertinent statements. For example:

"Examination of the literature available in 1983 shows that although progress has been made, there remains a significant amount of work to be done and a number of inconsistencies need to be resolved."

"Most of the recent work on actinide carbonate complexes is based on the need to understand the behavior of actinides under environmental conditions. For this purpose, the chemistry of these complexes at low concentrations of both the actinide and carbonate or bicarbonate is particularly important. Because of experimental difficulties, however, most investigations have done at relatively high concentrations of carbonate. Very little has been reported on the temperature coefficients or the enthalpies of actinide carbonate complexation reactions."

"The ions of the various actinides in the same oxidation state have very similar radii. Thus it is reasonable to expect the values for the corresponding complexing constants to be similar insofar as the bonding is electrostatic. .... Unfortunately, data to check the qualitative validity of the idea of chemical similarity are sparse."