OAK RIDGE NATIONAL LABORANPETOCKET CONTROL OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC. CENTER

86 FEB 18 P12:39

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:

Please find enclosed the Letter Reports referenced in the January Monthly Progress Report for B0287.

Sincerely,

Gary K. Jacobs Environmental Sciences Division

GKJ/

Enclosure:

Letter Reports, LR-287-21 through LR-287-27

cc:

Office of the Director, NMSS (Attn: Program Support Branch) Division Director, NMSS Division of Waste Management (2) M. R. Knapp, Chief, Geotechnical Branch K. C. Jackson, Geotechnical Branch J. W. Bradbury, Geotechnical Branch Branch Chief, Waste Management Branch, RES G. F. Birchard, Waste Management Branch, RES J. G. Blencoe A. D. Kelmers A. P. Malinauskas G. D. O'Kelley WM Recor K. L. Von Damm **GKJ File**

attachment in packet # 7B

8603140061 860212 PDR WMRES EXIGRNL
--

WM Project 2011/16 Docket No. . PDR LPDR

Distribution:

(Return to WM, 623-SS)

13-0287

POST OFFICE BOX X OAK RIDGE, TENNESSEE 37831

February 12, 1986

B - 0387 LR-287-21 01/21/86

W the dod 2/12/86 To: D. J. Brook Im: Bary K. Jacob

LETTER REPORT

TITLE: Review of the paper, "The Chemical State of the Fission Products in Oxide Fuels", J. Nucl. Matl. 131, 221-46 (1985), by H. Kleykamp, Kernforschungzentrum Karlsruhe, Karlsruhe, Federal Republic of Germany

AUTHOR: A. D. Kelmers

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL 41 88 54 92 4 (FIN B0287)/NRC 50 19 03 01

SUMMARY

Fission products are present in a limited number of phases in oxide fuels UO_2 or U, PuO_2) after irradiation. The paper summarizes the current information on fission product chemistry and distribution in the fuel pin. Both the chemistry and distribution are important to repository assessment efforts since these may control the rate of release of the fission products from spent fuel waste to groundwater in a high-level waste repository.

1. DESCRIPTION OF THE PAPER

This paper gives a review and summary of the existing information on the chemical state and spatial distribution of fission products in oxide fuel elements. Information is drawn from the extensive literature on both light water reactor (LWR) fuels (UO₂ fuel matrix), and fast breeder reactor (FBR) fuels (U,PuO₂ fuel matrix). The paper is comprehensive and thorough; it contains a listing of 201 references. The style is lucid, and the paper is particularly well suited for the reader who is unfamiliar with spent fuel but would like a general understanding of fission product chemistry.

2. SUMMARY OF THE PAPER

The most important property of oxide fuels, e.g. UO_2 and U,PuO₂, which affects the fission product chemistry is the partial pressure of oxygen in the gas phase of the fuel pin. Another important factor is the complexity of the system resulting after fission; more than 20 fission products can be detected after even moderate burnups. The chemistry of the fission products after irradiation is complicated by the following phenomena:

- (a) the fission product concentration increases gradually during irradiation,
- (b) the beta-active fission products change their chemical properties due to decay during and after irradiation,
- (c) the oxygen-to-metal ratio (0/M, where M = U + Pu) changes during burnup with an increase in the 0/M ratio,
- (d) axial and radial temperature gradients in the fuel pin result in material transport phenomena and thermal diffusion processes which cause compositional changes,
- (e) at higher operating temperature, reactions of fission products with the cladding become important, and
- (f) in the case of failed pins, reactions of the coolant with the fuel and fission products become important.

As a result of these factors, thermodynamic assessment of the fission product-fuel system is aggravated since the resulting multi-component system has a high number of degrees of freedom; i.e., the number of resulting phases is low relative to the number of components.

The information in the paper on fission product chemistry and distribution in the fuel and fuel assembly is summarized in Table 1. The fission products are present in nine different phases:

- noble gases The noble gases, Kr and Xe, are present both in the fuel and the fuel pin plenum;
- (2) halogens The halogens are present primarily in elemental form, I and Br, although the chemistry indicates they should be combined with cesium as CsI and CsBr; the halogens diffuse more easily in fuel than noble gases and are found primarily in the fuel-cladding gap;
- (3) alkali metals The alkali metals, rubidium and cesium, have complex chemistries and form several different compounds which are found in the fuel and the fuel-cladding gap;
- (4) molybdenum-ruthenium-noble metal alloys A five-element series of metal alloys containing Mo, Tc, Ru, Rh, and Pd are found primarily as small (<10 μ) particles in the fuel;
- (5) palladium intermetallic compounds and phases Palladium intermetallic and mixed phases form inclusions in the fuel containing Pd, Ag, Ca, In, Sn, and Sb;
- (6) complex tellurium compounds Tellurium is very reactive chemically and is found in a number of complex compounds which are distributed throughout the fuel and fuel-cladding gap; tellurium may also react with the cladding;
- (7) a zirconium and barium complex phase Zirconium and barium react with other fission products and with fuel to form a mixed oxide phase in the fuel;
- (8) uncertain niobium phase(s) Little is known about niobium chemistry since the fission yield is low; and

(9) fission products dissolved in the fuel - A number of the remaining fission products form oxides which are in solid solution in the fuel; these are: Sr, Y, Ce, Pr, Nd, Pm, and Sm.

3. HIGH-LEVEL WASTE REPOSITORY CONSIDERATIONS

The potential for the release to the environment of radioactivity associated with a given radionuclide in emplaced waste is controlled by five major criteria. These are:

- (a) The inventory of the radionuclide in the waste form at the time of the hypothetical repository event under assessment,
- (b) The rate of release of the radionuclide from the waste form into the groundwater,
- (c) The maximum concentration of the radionuclide attainable in the groundwater,
- (d) The retardation of the radionuclide in migrating groundwater by the engineered facility and geologic site components, and
- (e) The groundwater travel time to the environment and the radionuclide half-life (decay during travel).

The chemical form and distribution of the radionuclides in the spent fuel waste will play a determining role in the release of the radionuclide from the fuel (criterion b). Several generalized conclusions can be reached with regard to the potential for release of the fission products in the nine phases identified by the paper.

<u>FP Group 1 - Noble Gases</u>. While noble gas radionuclides may not be of major significant in the post-1000-year period, i.e., after the regulatory time for canister integrity, noble gases could be significant in events occurring at shorter times. An appreciable fraction of the Kr and Xe will be in the oxide fuel lattice. This fraction will be in the emplaced waste even if the fuel element end pieces are sheared and the gas plenum is ruptured during disassembly and the gases contained therein are released. Noble gases would have low solubility in groundwater and, if released by rupture of a waste canister during repository operations, would mix with the repository atmosphere.

<u>FP Group 2 - Halogens</u>. Most of the iodine would be in the fuel-cladding gap and thus would be readily available for dissolution by intruding groundwater. The fraction of halogens released to the groundwater would likely be much greater than the fraction of fuel oxide released.

FP Group 3 - Alkali Metals. The portion of the alkali metals present as salts in the fuel-cladding gap may be readily solubilized by intruding groundwater, while the fraction dissolved in the fuel as a complex oxide

3

might be less readily available for solubilization. Thus, cesium might show a bi-phasic release curve, an initial portion rapidly solubilized and then the remainder much more slowly released.

FP Group 4 - Metal Alloys. Of the fission products combined in the metal alloy particulates, technetium is by far the most important for repository assessment purposes. It is generally assumed that 9^{9} Tc is the most significant fission product due to it's long half-life, inventory, and potentially poor retardation by the geologic site. The release of technetium to intruding groundwater could be controlled by the availability of the inclusions to the groundwater, and the rate of oxidation and dissolution of the metal alloys. Due to the noble metal components, Rh and Pd, it seems possible that these metal alloy inclusions could be quite resistant to solubilization by groundwater. Possibly the most important questions for the assessment of repository performance of technetium in spent fuel may be: "Are the metal alloy inclusions accessible to intruding groundwater, and, is the geochemical environment oxidizing enough to oxidize these metal alloys and form soluble TcO4 ions?". Possibly the usual approach of asking: "Is the repository geochemical environment reducing enough to reduce TcO4"?" may not be exploring the release rate limiting process.

FP Group 5 - Palladium Intermetallics. The radionuclides in this group can exist in a number of phases. The release rate of these radionuclides might be variable in different situations, depending on the phases present and their distribution in the fuel. These radionuclides are not usually considered to be of major concern in repository performance assessment efforts.

<u>FP Group 6 - Tellurium</u>. The unstable isotopes of tellurium have short half-lives and are not usually considered of importance in repository assessment efforts. Tellurium occurs in numerous phases and reaction products, and its release rate into intruding groundwater could be complex.

<u>FP Group 7 - Zirconium and Barium</u>. Zirconium and barium are present as a complex phase in fuel containing several other elements. This phase is enriched in the outer region of the fuel, thus dissolution of the zirconium-barium phase might be more rapid that of the fuel matrix. Again, these two elements are not generally considered of major importance for repository assessment efforts.

<u>FP Group 8 - Niobium</u>. The fission yield of niobium is very low and it generally is not considered of major importance for repository assessment purposes.

FP Group 9 - Fission Products Dissolved in Fuel. A number of elements are present as oxides dissolved in solid solution in the fuel matrix. These might be expected to be released to groundwater no more rapidly that the dissolution rate of the fuel matrix.

Table 1. Fission product chemical form and distribution in oxide fuel

FP GROUP 1: NOBLE GASES - KRYPTON AND XENON

Chemical Form: Kr, Xe.

Distribution:

- (1) In solution within the oxide lattice.
- (2) In closed intragranular and intergranular bubbles within the fuel.
- (3) In open porosity of the fuel and in the fuel element plenum.

Comment:

As fuel burnup and/or temperature is increased, migration from oxide lattice to bubbles to plenum is enhanced.

FP GROUP 2: HALOGENS - BROMINE AND IODINE

Chemical Form: Mainly as I, (Br); small amounts as CsI, (CsBr).

Distribution: Mainly outside fuel in fuel-cladding gap.

Comments:

- (1) Chemistry suggests form should be CsI, but mobility is like I (not I_2 or CsI).
- (2) Diffusion coefficient for I in fuel is two orders of magnitude greater than for Xe.

FP GROUP 3: ALKALI METALS - RUBIDIUM AND CESIUM

Chemical Form and Distribution:

- As (U,Pu,Cs,FP)O_{2-x} dissolved in the fuel, where FP represents a mixture of Sr, Y, Zr, Ce, Pr, Nd, Sm, Eu, and Gd.
- (2) As gas molecules CsOn in bubbles and closed pores in the fuel.
- (3) As $Cs_2(U, Pu)O_{3,5}$ in the fuel-cladding gap.

Table 1. (Continued)

Comm	ents:
	(1) Different isotopes of Cs are distributed differently due to different mobilities and half-lives of the precursors.
	(2) Alkali metals are reactive and react with fuel, cladding, and other fission products.
	(3) The fraction remaining in the fuel is dependent on the $0/M$ ratio (ratio of oxygen to $U + Pu$) of the fuel.
	(4) Some Cs also is with the zirconium-barium "grey phase".
	FP GROUP 4: MOLYBDENUM-RUTHENIUM-NOBLE METAL ALLOYS
Chem	ical Form: "White inclusions", metal alloys of Mo, Tc, Ru, Rh, and Pd
Dist	ribution:
(1) (2)	As up to 10 size precipitates in fuel. Larger particles slowly diffuse to cooler regions of the fuel.
Comm	ents:
(1)	The five-element composition varies with O/M ratio, temperature,
(2)	Depending on the temperature and fission product composition, several immiscible metallic phases can exist.
	FP GROUP 5: PALLADIUM INTERMETALLIC COMPOUNDS AND PHASES
Chem	ical Form: A variety of intermetallic compounds and mixed phases of Pd, Ag, Ca, In, Sn, and Sb.
Dist	ribution:
(1) (2)	In the fuel. In the fuel-cladding gap.
Comm	ents:
(1)	These elements have a high vapor pressure at operating temperatures
(2)	The intermetallic compounds are reactive and may combine chemically

-

· _ /

 \smile

~

Table 1. (Continued)

FP GROUP 6: TELLURIUM

Chemical Form:

Te is reactive toward fuel, fission product, and cladding components, and the resulting chemistry is quite complex; depending on the fuel composition, burnup, O/M ratio, temperature, etc., Te has been found in compounds such as: $(U,Pu,Te,FP)O_{2-x}$ where FT = various fission products, $(Ba_{1-x}Sr_x)TeO_0$, Pu_2O_2Te , a complex $(U,Pu)O_{2-x}$ -Te-Cs phase, etc.

Distribution: Throughout the fuel and fuel-cladding gap.

<u>Comments</u>: The article states: "the multiplicity of tellurium-containing phases prevents a self-contained description of the chemistry".

FP GROUP 7: ZIRCONIUM AND BARIUM

<u>Chemical Form</u>: "Grey phase", $(Ba_{1-x-y}Sr_xCs_y)$ (U,Pu,Zr,Mo,RE)O₃ where RE represents rare earth elements.

Distribution: Inclusions in fuel.

<u>Comments</u>: Vapor pressure is sufficiently high so that Ba is mobile and may be enriched in inclusions in cooler regions of the fuel.

FP GROUP 8: NIOBIUM

<u>Comments</u>: (1) Little information on Nb since fission yield is low. (2) May be in solid solution in the fuel.

FP GROUP 9: FISSION PRODUCTS DISSOLVED IN FUEL

<u>Chemical Form</u>: Sr, Y, La, Ce, Pr, Nd, Pm, and Sm are in solid solution in the fuel as oxides.

Distribution: Throughout the fuel.

LETTER REPORT

TITLE: Review of the Report: Derivation of a Waste Package Source Term for NNWSI from Results of Laboratory Experiments, UCRL-92096 (September 1985), by Virginia M. Oversby (Lawrence Livermore National Laboratory) and Charles N. Wilson (Westinghouse Hanford Company); this paper was presented at the Materials Research Society 1985 Symposium on the Scientific Basis for Nuclear Waste Management, at Stockholm, Sweden, September 9-11, 1985

AUTHOR: A. D. Kelmers

PROJECT TITLE: Technical Assisstance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL 41 88 54 92 4 (FIN B0287)/NRC 50 19 03 01

SUMMARY

Data from hot-cell leaching of LWR spent fuel in deionized water and in J-13 well water are reported. A favorable (compared to the NRC 10^{-5} per year release limit) uranium source term or fractional release of 6.4×10^{-8} per year was calculated from the leach information, after making a number of assumptions concerning the canister integrity and groundwater flux for a repository at Yucca Mountain. This source term was assumed to apply to all radionuclides whose release is controlled by fuel matrix dissolution. The leach tests showed that cesium and technetium were released more rapidly than uranium. The actinides, plutonium, americium, curium, and neptunium, were released at about the same rate as uranium, and were primarily present as particulates in the leach solution. A groundwater infiltration rate of 1 mm/y was assumed for Yucca Mountain; this value was a key factor in the calculation of the favorable source term.

1. DESCRIPTION OF THE REPORT

This report is a preprint of a paper given in Sweden at the 1985 Symposium on the Scientific Basis for Nuclear Waste Management and, as such, contains an abbreviated description of the leaching methodology. Nonetheless, the report is important for the NRC evaluation of the Yucca Mountain candidate repository since it contains the first public reporting of actinide and fission product dissolution data from the spent fuel leach experiments being conducted by NNWSI. The report also details the assumptions used in the calculation of a source term for uranium and some other radionuclides for a repository at Yucca Mountain.

2. ASSUMPTIONS FOR THE SOURCE TERM CALCULATIONS

A number of assumptions were made in order to allow calculation of a source term for spent fuel emplaced in a repository at Yucca Mountain. Obviously, the accuracy (or conservatism) of the calculated source term is totally dependent upon the corresponding accuracy (or conservatism) of the underlying assumptions. The assumptions given in the report are summarized in the following sections. (ORNL commentary is included within brackets.)

2.1 Canister Integrity

Corrosion rates for stainless steel under Yucca Mountain geochemical conditions are sufficiently low so that the container remains intact for more than 10,000 years. Localized corrosion mechanisms, possibly near the final closure weld, result in small breaches that could allow water to enter the canister. [ORNL Comment: This assumption seems to be highly favorable; the NRC Waste Package Section might wish to consider this assumption.]

2.2 Fuel/Water Ratio During the Dissolution Event

The spent fuel canister is placed in a vertical hole. The hole is lined with a carbon steel liner, which allows water to collect around the canister. (In the absence of such a liner, water would drain away and not surround the canister.) The container has a breach large enough to allow free access of the standing water in the lined hole. The volume of this water is approximately 1800 L, based on the geometry of the hole and canister (see Sect. 2.6). The weight of the fuel in the canister is 3140 kg. Thus, the fuel/water ratio is 1.74 kg/L. [ORNL Comment: This assumption seems to imply that use of a hole liner is potentially unfavorable. It is not clear then, why a liner was employed in the model.]

2.3 Groundwater Composition

The composition of the groundwater in contact with the spent fuel is equivalent to J-13 well water, a dilute bicarbonate solution. The J-13 well water composition is representative of water to be encountered in the repository formation. [ORNL Comment: This is the standard NNWSI assumption regarding groundwater composition in the repository. It does not consider possible changes in composition due to hydrothermal effects or radiolysis. These could be particularly important since the water is in the hole liner for a number of years (see Sect. 2.7.).

2.4 Uranium Solubility

The solubility (steady-state saturated solution concentration) of uranium in the groundwater in contact with the spent fuel is 5 mg/L. This conservative number is derived from the leach test results described in the report (see Sect. 3 of this letter report), as well as literature information reported by others on uranium solubility over spent fuel solids. This concentration of uranium in solution controls dissolution of the UO₂ fuel matrix.

2.5 Fuel Matrix Stability

The spent fuel emplaced in the repository is not degraded by oxidation or other mechanisms, which are not observed in short-time laboratory experiments. [ORNL Comment: This assumption may be valid only as long as the canister does not seriously degrade prior to the groundwater ingress event.]

2.6 Groundwater Infiltration Rate

A flow rate of 1 mm/y of water moves evenly through the repository at Yucca Mountain, and all of the water that intersects the emplacement drift collects in the canister emplacement holes. The delivery rate of new water to an emplacement hole is 40 L/y. [ORNL Comment: As a result of the assumptions given above, the rate at which the fuel matrix will dissolve, over time, depends linearly on the rate of delivery of groundwater to the fuel. Thus, the groundwater infiltration rate becomes a major controlling parameter in the source term calculation, and the groundwater flux becomes the key modeling parameter that results in the favorable source term obtained. Since the accuracy of the groundwater flux used in the calculation, the NRC Hydrology Section might wish to examine this assumption.]

2.7 Time of First Release

It would take 45 y to fill the volume between the canister and the bore hole liner, and no release from the hole would occur during that time. [ORNL Comment: This time of release is directly connected to the infiltration rate value assumed, see Sect. 2.6.].

2.8 Release Rate Controlling Mechanism

The fuel matrix (UO_2) release rate is controlled by the uranium solubility and groundwater flux; thus, the uranium release rate can be calculated from these two values. All other radionuclides whose release is controlled by matrix solubility would exhibit the same release rate. [ORNL Comment: Many radionuclides are either in solid solution or physically dispersed through out the spent fuel pellet (see ORNL Letter Report LR-287-21), thus this assumption may be true for many, but not all, radionuclides.]

2.9 Radioactivity Releases Not Accounted For by this Model

Four types of release are described in the subject report which are not dealt with by the release model developed. These are:

2.9.1 Release of ${}^{14}C$ - Some of the ${}^{14}C$ in the Zircaloy cladding will be released to air as soon as the canister is breached.

2.9.2 Activation Products - The release of activation products in the fuel cladding and assembly parts would be controlled by corrosion of the respective parts, not by UO_2 matrix dissolution.

2.9.3 <u>Radionuclides in the Fuel-Cladding Gap and/or at the Fuel</u> <u>Grain Boundary</u> - Radionuclides which have migrated during irradiation or storage to the fuel-cladding gap or to fuel grain boundaries will be more readily accessible to groundwater that those distributed through the fuel matrix. These radionuclides may dissolve more rapidly than the fuel and may not be controlled by uranium solubility. Radionuclides in this category may include 135Cs.

2.9.4 <u>Degradation of the Fuel Matrix</u> - Oxidation and/or disaggregation of the fuel matrix would provide a mechanism for accelerated release of soluble long-lived radionuclides such as 99 Tc. 135 Cs, 129 I, 237 Np, 79 Se, and 14 C. Uranium release would not be accelerated since the groundwater is already assumed to be saturated with uranium(VI) species or compounds.

2.10 Data Needed to Improve the Model

The report lists several types of needed information, which could help improve the accuracy of the release model. These are:

- (a) dependence of uranium solubility on temperature,
- (b) rate of canister failure,
- (c) rate of breach of fuel cladding, and,
- (d) rate of oxidation of UO_2 fuel matrix.

[ORNL Comment: Need for improved knowledge of the groundwater flux was not listed.]

3. SOURCE TERM CALCULATED

Using the assumptions and values described above, the uranium source term was calculated to be a fractional release of 6.4×10^{-8} per year. This source term value was assumed to also apply to all radionuclides whose release rate is controlled by the matrix solubility.

4. RESULTS OF SPENT FUEL LEACH EXPERIMENTS

The report contains the first public release of some of the information being obtained in the NNWSI spent fuel leaching project underway in hot cells at Westinghouse Hanford. Spent fuel from two commercial LWR units (H. B. Robinson and Turkey Point) have been leached in deionized water or J-13 well water. The fuel has been leached in four configurations: bare fuel, slit cladding, laser-drilled hole in cladding, and undefected (control). Uranium, ²³⁹⁺²⁴⁰ Pu, ²⁴¹Am, ²⁴⁴Cm, ²³⁷Np, ¹³⁷Cs, and ⁹⁹Tc were measured in the leachate. Data were expressed as release rate and fractional release from the fuel, rather than groundwater concentrations, since some radionuclides were primarily present as particulates rather than in solution at the completion of the test. A number of significant observations were made.

4.1 Effect of Fuel Exposure

Much higher release rates were observed for all radionuclides when bare fuel was leached, as compared to fuel in defected fuel pin cladding. This behavior may result both from limited diffusion of the leachant through the cladding defects, as well as fuel pellet disaggregation during removal from the cladding. [ORNL Comment: Leaching of bare fuel would seem to represent a worst case situation. If the canister (stainless steel?) and the Zircaloy fuel pins remain generally intact over the 1,000- to 10,000-yperiod, diffusion of water through canister and pin defects could be the rate limiting process for radionuclide release. Consideration of diffusional limitations could lead to the calculation of even lower release rates.]

4.2 Effect of Solution Concentration

Deionized water was a more aggressive leachant than J-13 well water. [ORNL Comment: It is not clear why deionized water should be a more agressive leachant. Possibly the final pH was lower without the buffering effect of the bicarbonate in the J-13 well water.]

4.3 Uranium Release

The fractional release measured for uranium corresponded to a solution concentration of about 2 mg/L. Half or more of the uranium released was in solution (not present as particulates) at the completion of the test. [ORNL Comment: A solubility limit of about 2 mg/L seems reasonable. Many investigators have measured experimental solubility values of around 1 to around 5 mg/L for uranium(VI) in near-neutral solutions in the absence of a complexant. The assumption seems to be that uranium(VI) species and compounds control the observed uranium release, even though the bulk of the uranium is present in this system as uranium(IV) in a UO₂ solid phase.]

4.4 Actinide Element Release

The fractional releases for plutonium, americium, curium, and neptunium were similar to those for uranium; the report suggested that this was reasonable since the actinides are in solid solution in the UO_2 matrix. Most of the actinides (>80%), however, were present as particulates at the completion of the test. [ORNL Comment: Particulate behavior for plutonium and americium is the rule rather than the exception.]

4.5 Cesium Release

Cesium was released more rapidly than uranium, and cesium fractional release for the defected fuel pins was much higher than the uranium fractional release. [ORNL Comment: This observation seems reasonable, since much of the cesium may be present in the fuel-cladding gap (see ORNL Letter Report LR-287-21) and thus could be readily available for dissolution in groundwater.]

4.6 Technetium Release

For bare fuel, the fractional release of technetium was greater than for uranium. The report suggests that disaggregation of the fuel pellet during removal from the pin may have exposed technetium-containing phases at the fuel grain boundary to the groundwater leachant. The data for defected samples are sparce, but the technetium release exceeded that for uranium. [ORNL Comment: Technetium is often considered to be a key radionuclide for repository performance modeling due to its long half-life, inventory in spent fuel, and potentially poor retardation by site components. The technetium release data given in the report are the first such information publicly available from the NNWSI hot-cell experiments and, therefore, is of particular interest. Technetium is present as metal alloy inclusions in spent fuel (see ORNL Letter Report LR-287-21), thus, preferential release seems difficult to reconcile with the chemical nature of the fission product in fuel. The fuels for these tests have been out-of-reactor since 1974 and 1975. The individual fuel pins may have been sheared and stored in a hot cell since about 1976 or 1977; people at ORNL worked with samples of these fuels during that period. Thus, it is possible that the technetiumcontaining alloy inclusions may have partially oxidized during storage. Technetium likely will continue to be a key radionuclide for repository release modeling.]

LETTER REPORT

TITLE:	Review of: "Appendix B, Spent Fuel Dissolution", in Monthly Progress Report, Report Period: November 1985, from The Aerospace Corporation, Washington, D.C., NRC Contract FIN A-4165-5	
AUTHOR:	A. D. Kelmers	
PROJECT TITLE:	Technical Assistance in Geochemistry	
PROJECT MANAGER:	G. K. Jacobs	
ACTIVITY NUMBER:	ORNL 41 88 54 92 4 (FIN BO287)/NRC 50 19 03 01	

SUMMARY

Appendix B presents a conceptual model of spent fuel properties and a mathematical model of spent fuel dissolution kinetics. Some technical inaccuracies in the conceptual model of spent fuel are noted and discussed below. The mathematical model of dissolution kinetics, however, seems not to have been derived from the spent fuel conceptual model. A separate review of the mathematical model is given by H. C. Claiborne in Letter Report LR-288-2.

REVIEW OF APPENDIX B

This review is limited to Appendix B, "Spent Fuel Dissolution", by Robert B. Moler. Appendix B describes a conceptual model of spent fuel and a mathematical model of fuel dissolution kinetics for repository assessment purposes. The mathematical model appears to be a simplified description of waste dissolution; however, it does not appear to be based on the conceptual model of spent fuel as given in Appendix B. Some comments on specific statements on pages 1 and 2 of the appendix which define the spent fuel conceptual model are included below. A separate review of the mathematical model is given in Letter Report LR-288-2 by H. C. Claiborne.

Page 1, paragraph 1, sentence 1: "Few studies have been carried out on the kinetics of disolution of spent fuel." <u>Comment</u>: An extensive literature has been developed over decades by work in numerous countries which describe the dissolution of spent fuel for fuel recycle purposes. Such work is generally in nitric acid solution, however, and is not directly applicable to the near-neutral pH environments encountered in repositories. Nonetheless, such work has contributed to the general understanding of fuel dissolution kinetics. DOE repository projects are now conducting spent fuel leach experiments utilizing typical LWR spent fuel in groundwater-type solutions. For example, considerable source term data have become available from the NNWSI work at Westinghouse Hanford; see ORNL Letter Report LR-287-22, a review of LLNL Report UCRL-92096 (1985), by Oversby and Wilson.

Also, leach test results in typical groundwaters from work in foreign countries are available; see for example, Forsyth et al., in KBS Technical Bulletin 83-76 (1984) or Johnson, AECL-6837 (1982).

Page 1, paragraph 2, sentence 1: "Spent fuel is thermodynamically stable and, hence, does not undergo a (virtually) irreversible reaction in the presence of water as does CHLW." Comment: This statement may be incorrect for the geochemical conditions likely to be encountered in some geologic repository environments, since UO_2 , the main component of spent fuel, may be thermodynamically unstable with respect to UO_3 or other uranium(VI) compounds or species in some cases. Under the oxidizing redox condition expected at the Yucca Mountain site, uranium would be oxidized to U(VI) compounds and species; see, for example, Sinnock et al., Sandia Report SAND84-1492 (1984). However, under the very reducing redox condition expected to exist in the Hanford Site repository due to reduced iron species in basalt, the soluble uranium may be present as U(IV) species; see Early et al., Hanford Report RHO-BW-SA-282-P (1983). The important point is that the thermodynamic stability of uranium is a function of the geochemical conditions of the specific repository, thus generalized statements about thermodynamic stability may not be appropriate. Although UO_2 may be thermodynamically unstable under some groundwater Eh conditions, spent fuel may, however, still be a favorable waste form since the dissolution rate may be slow. Slow dissolution could result both from the high density of fuel pellets (restricted diffusion of water into the pellets), and from limited availability of oxygen in the groundwater to oxidize the UO₂.

Page 1, paragraph 2, sentence 2: "However, the process of dissolution of the surface of the UO_2 is the same process that results in hydrolyzed silica from CHLW glass entering into solution." Comment: Only in the very general sense that dissolution of either fuel or glass is a 'dissolution' process can this sentence be considered as correct. The dissolution of a silicate glass matrix is a complex process involving a number of reactions of groundwater with the glass surface, an underlying altered layer, and the unaltered silicate matrix. Considerable controversy surrounds the explicit reactions which may be involved; see, for example, the many papers on glass dissolution in the MRS series Scientific Basis for Nuclear Waste Management published annually since 1978. The dissolution of UO_2 and important actinides and fission products in the fuel and fuel pin may involve quite different reactions, depending upon whether the radionuclide of interest is in solid solution in the UO_2 , at the fuel grain boundary, in the fuelcladding gap, etc.

Page 1, paragraph 3, sentence 1: "The spent fuel case is less complex than the glass waste form case because of the lack of complicating chemical reactions of groundwater with the waste form."; and Page 1, paragraph 3, sentence 3: "Consequently, except for the initial release of material that has diffused to grain boundaries or is held in interstitials, the release of all materials will be congruent to the dissolution of UO_2 ." Comment: Properties of spent fuel have been extensively studied for decades; a good review of the chemistry of fission products in fuel has recently been published [Kleykamp, J. Nucl. Mater. 131, 221-246 (1985); see also ORNL Letter Report LR-287-21]. Fission products and actinides are distributed

۰.

in nine different phases in spent fuel. These phases may be generally distributed throughout the fuel assembly or segregated in specific regions. Chemical properties of the phases can be quite different. Actinides are in solid solution in the UO_2 matrix, thus the dissolution of americium, plutonium, etc. could be described by a model which correctly models UO2 dissolution. The actinides other than uranium, however, may be present primarily as particulates rather than true solution species in groundwater [see Oversby and Wilson, UCRL-92096 (1985)]; thus, their migration from waste to the environment cannot be described by uranium behavior. Technetium is probably the most important fission product. Technetium is present in spent fuel in the "white inclusions," discrete particles of metal alloys of Tc+Mo+Ru+Rh+Pd [see Kleykamp (1985)]; thus, the dissolution of technetium may be very poorly related to UO_2 dissolution kinetics. Cesium, another important fission product, is present primarily in the fuel-cladding gap as salts of uranium or as CsO_n bubbles in the fuel [see Kleykamp (1985)]. Cesium generally is rapidly solubilized in leaching tests. The approach of congruent dissolution taken in the appendix may have only limited application to some specific radionuclides such as technetium or cesium.

LR-287-24 02/03/86

LETTER REPORT

Title: Review and Evaluation of <u>Analysis of Solids from</u> Initial 200°C, 30 MPa Hydrothermal Tests with "Fully-Radioactive" Waste Glass and Spent Fuel, SD-BWI-TI-278, Sept., 1985, by L. E. Thomas, B. Mastel, and E. D. Jenson.

AUTHOR: J. G. Blencoe

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

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

REVIEW

This report describes the solid starting materials and the solid reaction products of three preliminary hydrothermal experiments--designated runs BSF-02, BSF-03, and BSF-04--which were conducted to determine the reactivity of two distinctly different "fully radioactive" waste forms: (1) a simulated high-level borosilicate waste glass labeled ATM-6 (developed by Pacific Northwest Laboratory's Materials Characterization Center), and (2) spent fuel from a lightwater reactor (Turkey Point spent fuel). The experiments were performed in Dickson-type rocking autoclaves at 30 MPa, 200°C for 1364, 1823, and 1338 hrs, respectively. The starting materials for the experiments run BSF-02--ATM-6 glass plus GR-3 groundwater; run BSF-03--ATM-6 were: glass plus RUE-2 Umtanum basalt plus GR-3 groundwater; and run BSF-04--Turkey Point spent fuel plus GR-3 groundwater. Solid reaction products were obtained by sampling material from the gold bag reaction vessels after each test was completed. Specifically, samples were taken from the bottom of the gold bag, the walls of the bag, and from the titanium closure head, whenever solids were present at these locations. Phase identification was accomplished by X-ray powder diffractometry (XRD), and selected solid reaction products were analyzed by scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS).

Characteristics of "Fully Radioactive" Solid Starting Materials

Unreacted ATM-6 glass

Starting ATM-6 glass consisted of 150-200 µm diameter particles that exhibited concoidal fracture surfaces. The particles contained few observable pores, and less than two vol. % crystalline phases--chiefly Ru, RuO₂, and at least one other unidentified phase. EDS microanalysis of the glass revealed that it is homogeneous and contains mainly Si, Al, Gd, Na, Zr, U, Ce, Cs, and Mo. (The composition of ATM-6 glass is nominally that of a Barnwell Nuclear Fuel Plant waste glass.) The composition of ATM-6 glass is somewhat different from that of PNL 76-68 glass used by Schramke et al. (1984a) in earlier hydrothermal interaction tests. The principal compositional differences between the two glasses are that ATM-6 glass contains substantial quantities of Gd and Li, and very little Fe and Zn.

Unreacted Turkey Point spent fuel

Spent fuel starting materials were 3-20 μm diameter grains of $\alpha-U0_{2}$. Microscopic examination of this material revealed extensive cracking along grain boundaries where 0.2 to 1 μm diameter pores were concentrated. No secondary crystalline phases or fission-product elements were detected by SEM/EDS; however, Turkey Point spent fuel is known to contain fission products at concentrations near the detection limits of this analytical method.

Results of Experiments With ATM-6 Glass

Test BSF-02 (ATM-6 glass plus GR-3 groundwater)

Solid reaction products from run BSF-02 included granular, green material from the bottom of the gold bag and a gray, gelatineous material from the walls and autoclave head. XRD analysis indicates that the material from the bottom of the gold bag is mostly residual ATM-6 glass, whereas the material from the wall of the bag is predominantly cesium- and uranium-bearing zeolite-P. (Zeolite-P is a synthetic Na, Al zeolite of the phillipsite group.) In addition to zeolite-P, the solid materials scraped from the wall of the gold bag contained minor quantities of "colloidal-sized" (<0.4 μ m diameter) crystals of pollucite and weeksite.

The foregoing results contrast with corresponding results obtained by Schramke et al. (1984a) in 200°C hydrothermal tests with PNL 76-68 glass. The single secondary crystalline phase produced in these experiments was not zeolite-P, but instead an Al-free, hydrated, iron-and zinc-bearing smectite clay.

Finally, another noteworthy observation concerning the solid reaction products of run BSF-02 is that optical examination of these materials revealed the presence of unaltered Ru and RuO, crystals protruding up to 5 μ m from the surfaces of many of the ATM-6 glass particles. This observation indicates extensive dissolution of the glass during experimentation.

Test BSF-03 (ATM-6 glass plus RUE-2 Umtanum basalt plus GR-3 groundwater

Material from the bottom of the gold bag was mostly remnant glass and basalt. SEM examination of the glass particles revealed that the outermost 2-4 μ m of these particles are altered. Optical examination of the basalt revealed that the glassy mesostasis is etched and pitted, but crystalline phases show no evidence of reaction. Material from the wall of the gold bag was principally cemented particles of clinoptilolite crystals.

Results of Experiments With Turkey Point Spent Fuel

Test BSF-04 (Turkey Point spent fuel plus GR-3 groundwater)

At low magnification in the SEM, the spent fuel particles from this run appeared slightly worn, but otherwise these particles appeared to be similar to unreacted spent fuel. However, SEM examination at a higher magnification revealed that many of the reacted particles are coated with extremely small "fines." These fines are apparently produced by abrasion during experimentation, because the larger "primary" spent-fuel particles show no rounding or surface etching that would indicate reaction with the groundwater. Furthermore, EDS analysis indicates that the fines contain no appreciable quantities of fission products. Collectively, these results imply that, during experimentation, the spent fuel was essentially immune to dissolution and other manifestations of chemical reaction. For this reason, it is believed that the actinide contents of the 0.4 μ m filtered solutions from this experiment are attributable mainly to the presence of colloidal-sized (1.8 nm to 0.4 μ m diameter), wear-produced particles of spent fuel.

Discussion

The results obtained from run BSF-02 with ATM-6 glass, when compared with corresponding results obtained previously with PNL 76-68 glass (Schramke et al., 1984a), seem to indicate that, in the absence of basalt, the fate of radionuclides released by glass dissolution and leaching is determined principally by the composition of the starting waste glass. Run BSF-02, with ATM-6 glass plus GR-3 groundwater. produced zeolite-P, whereas in the tests with PNL 76-68 glass the secondary crystalline phase produced was an aluminum-free hydrated ironand zinc-bearing smectite clay. By contrast, in run BSF-03, where the solid starting materials were ATM-6 glass plus Umtanum basalt, the secondary crystalline phase produced was clinoptilolite. Significantly, clinoptilolite with similar morphology and chemistry was also the solitary new crystalline phase produced in earlier 30 MPa, 200°C hydrothermal experiments with PNL 76-68 glass plus basalt (Schramke et al., 1984a). Collectively, these results suggest that, when basalt is added to the waste glass starting material of a hydrothermal experiment, dissolution of mesostasis glass in the basalt promotes the crystallization of clinoptilolite, regardless of the composition of the waste glass. On the other hand, in hydrothermal tests conducted at similar pressures and temperatures with just basalt plus groundwater (no waste glass present), iron smectite clay and illite are the predominant crystalline reaction products, and clinoptilolite is not formed (Lane et al., 1984, Grandstaff et al., 1984) Therefore, it is evident that the results obtained from waste glass/basalt/groundwater experiments are attributable to synergistic interactions between the glass and the basalt which apparently favor the crystallization of clinoptilolite, regardless of the composition of the waste glass.

EVALUATION

This interesting report provides useful information about the solid starting materials and the solid reaction products of recent DOE/Hanford hydrothermal experiments that were conducted to elucidate the reactivities of two "fully radioactive" waste forms: (1) a simulated high-level borosilicate waste glass designated ATM-6, and (2) Turkey Point spent fuel. A companion document (Schramke et al., 1984b) describes the compositions of the fluids sampled from the subject experiments. By analyzing both the solids and the fluids from hydrothermal experiments, DOE/Hanford is following through on its stated commitment to identify the "fate of radionuclides" under geochemical conditions that simulate those in the near field of a basalt-hosted HLW repository.

It is evident from this report and similar previous reports that DOE/Hanford and its contractors are obtaining very useful data from their hydrothermal experiments. For example, it is very significant that data obtained to date indicate that the types of solid reaction products, and hence the characteristics of partitioning of radionuclides between solid phases and groundwater, are highly dependent on the types and compositions of solid starting materials employed in the experiments. It is especially interesting and noteworthy that clinoptilolite habitually crystallizes in waste glass/basalt/groundwater experiments, regardless of the composition of the waste glass. Also, it is significant that DOE/Hanford has observed that spent fuel is essentially immune to hydrothermal alteration in experiments performed at 30 MPa, 200°C.

Finally, another commendable feature of this report is that it contains a section entitled "Recommendations for further work." In this section, the authors discuss: (1) current research activities (experiments in progress, ongoing analytical work, etc.); and (2) the directions in which future research is heading. It is clear from the commentary in this section that DOE/Hanford researchers are striving to ensure that their hydrothermal experimental work is completed in an efficient and timely manner, and that their analytical methods are close to state-ofthe-art.

Notwithstanding the great forward strides that DOE/Hanford has made in their hydrothermal testing program, several noteworthy deficiencies are evident in the work that has been completed to date. These apparent deficiencies are described in the discussion items below.

 Several key proposed components of basalt-hosted waste packages--most notably, canister metal, cladding material, and bentonite--have been excluded from the solid starting materials of hydrothermal experiments performed to date by DOE/Hanford and its contractors. Presumably, future DOE/Hanford hydrothermal experimentation will explore the effects of having one or more of these solids present in the starting materials.

- 2. 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.
- DOE/Hanford may wish to consider using a more systematic approach in 3. its attempts to determine how the presence of basalt affects the results obtained from hydrothermal experiments. Up to the present time, DOE/Hanford has performed parallel hydrothermal experiments with "excess" basalt present and with no basalt present. The difficulty with this approach is that the methodology is too crude to determine definitively how the presence of basalt influences the experimental results. The effects of the presence of basalt would be more clearly elucidated if the quantities of basalt in solid starting materials were varied systematically between the extremes of "excess" basalt present and no basalt present. Results of experiments performed to date indicate that "excess" basalt profoundly influences the formation of secondary crystalline phases. However, at present it is uncertain that the same results would be obtained if the quantity of basalt present in the solid starting materials is minor compared to the quantity of the solid waste form. For this reason, it would be useful to perform a limited number of experiments in which only a small amount of hydrothermally altered basalt was present. The results of these experiments would elucidate the extent to which basalt is able to control the formation of particular types of radionuclide-bearing secondary crystalline phases (e.g., clinoptilolite).
- 4. Finally, a minor point. Prior to reading this report, I was under the impression that the quantities of key radionuclides in a "tracer-doped" glass would always be smaller, and usually much smaller, than the corresponding quantities of these radionuclides in a "fully radioactive" glass. Evidently, however, this is not the case. I say this because, in examining table 1 of the subject report, I see that there is significantly more Np and Pu in the Np/Pu "tracer-doped" glass than there is in the so-called "fully radioactive" ATM-6 glass. Therefore, at least for Np and Pu, the adjectives "tracer doped" and "fully radioactive" are very misleading indeed.

REFERENCES

Grandstaff, D. E., G. L. McKeon, E. L. Moore and G. C. Ulmer. 1984. "Reactions in the System Basalt/Simulated Spent Fuel/Water," pp. 137-145 in G. L. McVay, ed., <u>Materials Research Society Proceedings</u>, Vol. 26, North Holland, New York.

Lane, D. L., M. J. Apted, C. C. Allen and J. Myers. 1984. "The Basalt Water System: Considerations for a Nuclear Waste Repository," pp. 95-103 in G. L. McVay, ed., <u>Materials Research Society Symposium</u> Proceedings, Vol. 26, North-Holland, New York.

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

Schramke, J. A., S. A. Simonson, and D. G. Coles. 1984b. <u>A Report on</u> the Status of Hydrothermal Testing of Fully Radioactive Waste Forms and Basalt Repository Waste Package Components. SD-BWI-TI-253. Rockwell Hanford Operations, Richland, WA.

LR-287-25 1/31/86

LETTER REPORT

TITLE: Review of: <u>Reaction of Bullfrog Tuff with J-13 Well</u> <u>Water at 90°C and 150°C</u>," UCRL-53442, September 15, 1983, by V. M. Oversby and K. G. Knauss.

AUTHOR: K. L. Von Damm

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

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

The subject report documents a study of the interaction between Bullfrog Tuff from the Yucca Mountain site, Nevada and J-13 well water. Most experiments were done with crushed tuff at temperatures of 90 and 150°C, water/rock mass ratios of 10:1 to 120:1 and durations of from 1 to a maximum of 63 days. An additional set of experiments was done with wafers of Bullfrog Tuff at 150°C to test the effects of sample preparation on the water-rock interactions. Data for the elements Al, B, Na, Li, K, Fe, Si, Ca, Mg, F, Cl, NO₃ and SO₄ are presented. The major conclusions are:

1. Increasing the rock/water ratio increases the rate of approach to steady state concentrations.

These rock samples, which were obtained from outcrop, not drill core, contain a highly soluble caliche-type material.
Erratic results for Al and Fe are due to the presence of sub-0.1µ particles which dissolve after sample acidification.
The crushed rock and wafer samples give similar results, inferring that the method of sample preparation does not have a large effect.

Three potential problems exist with the results presented in the subject report.

1. The erratic behaviour of Al and Fe has another potential source not addressed in this report. Aluminum, at low levels, is often found to be a contaminant from storage in plastic bottles. It is often used as a "filler" in the manufacture of plastics and tends to be progressively leached into samples from the bottles, especially acidified samples, with time. Iron may also be a residual problem from the fabrication of the bottles. Storing an acidified J-13blank in a bottle and analyzing it over time for these elements would test if this is the source of some of the erratic results. 2. Calcium and magnesium decrease in the blank solution, as well as in the experiments with rock present. This observation is not adequately discussed. Decrease of calcium is attributed to precipitation of $CaCO_3$ in the blank and to removal onto plagioclase phenocrysts in the water/rock experiments. Removal of Mg is not discussed except as a result of interaction with the rock. The alkalinity or carbonate data for the solutions are not presented, hence solubility with respect to carbonate phases cannot be examined. Solubility with respect to sulfates should also be considered. The lower values observed in solution for calcium in the <u>blank</u> compared to the experiments with rock, suggest that calcium may actually be leached from the rock, and another controlling mechanism exists. The solution data should be run through a thermodynamic model to test for saturation, and hence solubility controls, for calcium and magnesium.

3. The third comment is a general one with respect to interpretation and discussion of the data. This comment may be addressed in a companion report on the solids, but no mention of it is made here. With the data presented, some mention should be made of mass balance in two separate aspects of these experiments. Much emphasis is placed on the leaching of a "soluble" material from the rocks. As electroneutrality is required, a check should be made that what is attributed to this soluble material actually balances for the sum of the anions and cations involved. Is it predominately NaCl and $CaSO_4$ for example, based on the mass balance? The second place where mass balance should be discussed is with respect to the wafer experiments. Since the composition of the fluid is known before and after, and the solids are analyzed before and after, does the net gain or loss in solution balance with the net loss or gain in the solid? While the balance does not need to be "exact" a major discrepancy would indicate a potential experimental problem. This may be addressed in another report, but mention should be made of it here.

LR-287-26 2/2/86

LETTER REPORT

TITLE:Review of "Hydrothermal interaction of Columbia
Plateau basalt from the Umtanum flow (Washington,
U.S.A.) with its coexisting groundwater," Chemical
Geology 49 (1985) 53-71, by E. L. Moore, G. C. Ulmer,
and D. E. Grandstaff.

AUTHOR: K. L. Von Damm

<u>PROJECT TITLE</u>: Short-Term Technical Assistance in Geochemistry, Task Order No. 26

PROJECT MANAGER: G. K. Jacobs

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

The review of the subject report was requested to evaluate the uncertainty of the observed rock/mineral changes and the changes in water chemistry and redox conditions.

Redox Conditions

The redox changes in the reported experiments are poorly defined due to the reliance on the formation of H_2S in order to determine the fugacity of oxygen $(f-O_2)$, and the SO_4-H_2S couple. In two of the experiments H_2S was not detected, hence the redox state could not be determined. It is suggested in future experiments that another redox couple be measured. $Fe^{2+}-Fe^{3+}$ is one couple which, at the right concentration levels is not very difficult to measure. A better choice would be H_2 , which can be used directly in the equation $H_2O \rightarrow H_2$ + 0.5 O_2 , to determine the $f-O_2$. Most experimentalists studying seawater-basalt interaction now use this couple. No detailed mention is made of the method, but determination of sulfide by specific ion electrode is subject to interferences by iron, which can be overcome with special procedures. The authors should state the method in more detail. Redox at 200°C is important to know because of the maximum predicted waste package temperature of 250°C.

Another potential problem is the starting O_2 . The authors do not describe their procedures in sufficient detail to determine what the starting O_2 was. An effort must be made to exclude O_2 from the starting solutions, unless saturation with atmospheric oxygen is the condition which is to be tested.

Examination of the redox results for the other 300°C experiments at different water/rock ratios would clarify the issue of reproducibility and uncertainty of redox conditions.

Water Chemistry

While the trends in solution chemistry are correct it is difficult to determine if the magnitudes are. Specifically, there is more variation in the chemical parameters than can be accounted for by the stated analytical error. This is especially troublesome in the case of chlorine. There is almost no chlorine in basalt, yet the reported values show a variability greater than the reported analytical error. including increases in the total concentration. Particularly disturbing is the large increase in the 300°C experiment between 4360 and 4361 hours (1 hour difference) for which no explanation is given. The authors state that results for the other water/rock ratio experiments at 300°C are similar, but the data is not included. Inclusion of this data would accomplish two purposes: the reader would be able to better evaluate the experimental variability, a lower water/rock ratio may be more representative of the natural situation and that water chemistry be more appropriate to consider - or the data may demonstrate that water/rock ratio does not make a major difference. There are several other disturbing statements with respect to water chemistry. First, it is well known that copper and lead cannot be determined in Dicksonon apparatus because these two elements amalgam with the gold; their stated detection limits thus have no meaning. A potential problem exists with the calculated pH. They state that they use the same species as given in Bischoff and Seyfried, 1978, table 3 - hopefully they mean table 5. Bischoff and Seyfried did not include H_2S , HS^- or S^{2-} in their case, while this study should. This may have an effect on their calculated pH.

Gold bags within the Dickson cell can develop holes, leading to exchange with the pressure fluid, usually distilled water. If the authors observed such large variations in chloride how did they check that their experiment was not leaking? <u>Increases</u> in chloride suggest this was probably not a problem, depending on the pressure fluid used.

Mineralogy

The reported mineralogy for 300° C looks quite reasonable when compared to literature data. The absence of epidote is not particularly troubling as it is very recalcitrant to precipitate in experimental studies with basalt. Very recently the <u>first</u> report of its formation (clinozoisite) in a basalt-seawater experiment was made, after approximately 10 years of studies! Although only chlorite is reported, smectite may also occur as an unstable phase at the high temperature. Presumably over time, an iron sulfide would be likely to form, depending on the f-O₂. The solid-solution nature of zeolites makes it difficult to evaluate if exactly the ones reported would form, but their presence is what is important.

At 200°C the absence of any zeolite phase is surprising, this may be a kinetic problem. Also the occurrence of scapolite at 100°C and 300°C, but not at 200°C is anomalous.

At 100°C the formation of a sulfide, suggested to be pyrrhotite is disconcerting. With no sulfide present in the solution and the

reduction of SO₄ being very slow at this temperature, its presence is surprising. If it is important to know if pyrrhotite was formed in this experiment, characterization of the solids and possibly the experiment should be repeated.

Aspects of the treatment of quartz and other silica polymorphs are inconsistent. It is not very surprising that quartz did not precipitate. If amorphous silica was present it should show up in the x-ray as a broad hump; no mention is made if this was observed. However, if no quartz was observed, the quartz geothermometer should not be applied to these solutions since its basic assumption is that the solutions are saturated with and in equilibrium with quartz, not one of the other silica phases.

Again, results from the other 300°C experiments would help clarify the issue as to whether a stable mineral assemblage was formed. As the authors note that small changes are still occurring in solution chemistry, this implies changes are still occurring in the solid chemistry. The good agreement with the Icelandic data suggests that these experiments have reached a reasonably stable assemblage.

As this paper is based on a master's thesis, some of the questions raised above may be addressed in the thesis, but are omitted in the published form.

LR-287-27 1/30/86

LETTER REPORT

<u>TITLE</u>: Review of "Aqueous Oxidation-Reduction Kinetics Associated with Coupled Electron-Cation Transfer from Iron-Containing Silicates at 25°C," by Art F. White and A. Yee (1985). <u>Geochim. et Cosmochim.</u> <u>Acta 49</u>, 1263-1275.

AUTHOR: G. D. O'Kelley

<u>PROJECT TITLE</u>: 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 OF REPORT

The weathering of primary silicates plays a major role in the geochemical cycling of iron. Considerable recent attention has been focused on the dissolution of iron-containing silicates, which, because of the low oxygen fugacities in magma, contain iron predominantly in the ferrous [Fe(II)] state. The oxygenated environments involved in the weathering process on the surface of the earth readily oxidize ferrous iron to ferric [Fe(III)], so aqueous solutions resulting from weathering can be expected to contain Fe(II), Fe(III), and reduced species of coexisting elements. The authors suggest that redox-controlled reactions involving iron silicates are very important in determining the aqueous transport characteristics of a number of multivalent elements in a variety of environmental settings.

As Fe(II) is oxidized to Fe(III), a coexisting species must also be reduced. However, the pathways of electron transfer between reduced silicate phases and the oxidizing aqueous environment are not well defined. The objective of this work was to define more clearly the mechanisms and kinetics of electron transfer from augite, biotite, and hornblende over a range of experimental conditions.

Experiments were carried out either as long-term reactions (up to 9 months) between the iron silicates and various aqueous media in a closed system, or as short-term (up to 24 hours) experiments in which the mineral phases were contacted with solutions containing FeCl₂ and FeCl₃, bubbling various proportions of O_2 , CO_2 , and N_2 through the solutions under open system conditions. The range of pH covered in this study was about 1 - 10. Mineral identification and characterization of the specimens employed the usual methods of thin-section petrography, x-ray diffraction, and electron microprobe analysis. The surface chemistry of the unreacted

and reacted augite, biotite, and hornblende was characterized by x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary-ion mass spectrometry (SIMS), which were capable of determining mineral compositions within 20 Å (2 nm) of the mineral surfaces. Methods for analyzing the aqueous phase were adequate for the purpose. Total iron and Fe(II) were analyzed spectrophotometrically, and concentrations of Fe(II) and Fe(III) were verified independently in some cases by cation chromatography. The temperature was generally not 25°C, as suggested by the title, but was allowed to vary between 23° and 26°C. However, temperature effects are expected to be negligible for measurements of the precision reported here. Studies of reaction mechanisms utilized 59 Fe³⁺ tracer to tag FeCl₃ solutions in contact with specimens to identify redox pathways for iron, and oxygen enriched in 18 O₂ was used to differentiate between dissolved oxygen loss and surface oxidation.

Concentrations of iron on mineral surfaces were either unchanged or slightly elevated after reaction at neutral to basic values of pH in oxic solutions. At low values of pH the iron loss was found to be a strong function of the mineral phase. At pH 2 nearly half of the surface iron on hornblende and augite was lost, while biotite at the same pH retained the initial iron concentration. As found previously by other investigators, XPS measurements showed that the iron on mineral surfaces was predominantly Fe(III).

Studies of the behavior of iron in solutions contacted with the mineral phases showed that the changes in concentrations of Fe(II) and Fe(III) were quite complex, especially the experiments with hornblende. Above pH 3.5, the concentration of Fe(II) increased rapidly at first, and then either remained constant or decreased. In oxic solutions the rate of decrease was greatly accelerated at or above neutral values of pH, due to the precipitation of ferric hydroxide or oxyhydroxide. It was also found that, following the onset of amorphous Fe(OH)₃ precipitation in oxic solutions as pH increased with silicate hydrolysis, solutions remained supersaturated with respect to FeOOH phases but became increasingly undersaturated with respect to amorphous Fe(OH)₃. This suggested to the authors that the amorphous hydroxide phase was being gradually converted to the crystalline form. Application of a speciation model indicated that the oxic solutions remained saturated with respect to Fe(OH)₃ to find the oxic solutions remained saturated with respect to solutions hydroxide phase was being with respect to Fe(OH)₃ down to about pH 3.5.

It was necessary to investigate the fate of Fe^{3+} in solution in the presence of silicate minerals, since the XPS studies suggested that dissolution of an oxidized iron silicate surface would contribute predominantly Fe^{3+} , but large concentrations of Fe^{2+} appeared quite rapidly and eventually dominated at long times. On the other hand, ferric iron in blank solutions at ph 3.0 were stable indefinitely, as expected. The introduction of a low-iron muscovite showed only a small effect on the behavior of a solution containing Fe^{3+} at ph 3.0; this experiment and another with biotite showed that the dramatic and rapid increase in Fe^{2+} was related to the iron concentration in iron silicate minerals.

The authors investigated three possible mechanisms to explain the observed decrease in Fe^{3+} and the corresponding increase in Fe^{2+} :

• . . •

_

- Fe³⁺ is reduced in solution due to the release of an oxidizable species during the silicate dissolution;
- (2) Fe³⁺ undergoes stoichiometric exchange with Fe²⁺ on the surface of iron silicates;
- (3) Fe^{3+} is reduced in solution by electron transfer during the <u>in</u> <u>situ</u> oxidation of surface iron.

The authors discarded mechanism (1), because careful measurements of chemical compositions and charge balances showed that no multivalent ions were present at concentrations comparable to those of Fe^{3+} . Tracer experiments with ${}^{59}Fe^{3+}$ demonstrated that the ${}^{59}Fe$ remained in solution after reduction to ${}^{59}Fe^{2+}$ and was not exchanged for ${}^{59}Fe^{2+}$ on the silicate surface. Thus, mechanism (2) was also rejected, leaving the last mechanism, electron transfer, as most likely.

The authors propose the transfer of an electron from the solid to the solution, coupled with the simultaneous transfer of a cation, which they represent as follows:

$$[Fe^{2+}, 1/z M^{Z+}]_{silicate} + * Fe^{3+} = [Fe^{3+}]_{silicate} + * Fe^{2+} + 1/z M^{Z+}, (1)$$

where M denotes a cation of charge z+, and the asterisks mark the iron ions in the aqueous phase. It is apparent that equation (1) maintains a balance of charge for the silicate and the solution phases. Thus, Fe^{2+} in the mineral phase is oxidized to Fe^{3+} on the surface, while Fe^{3+} , either initially in solution or dissolved from the oxidized surface, is reduced to Fe^{2+} , accompanied by a release of cations from the surface to the solution. This situation is complicated still further by the wellknown hydolysis of silicates, which is manifested as a loss of aqueous hydrogen ions. At low values of pH, the hydrolysis reaction can lead to an increased loss of surface iron. The authors present the results of several experiments to support their coupled electron-cation mechanism as described in equation (1), as well as the role of silicate hydrolysis.

Above pH 3.5 ferric hydroxide is instrumental in controlling both ferric and ferrous iron concentrations in oxic solutions. Representative equations for the processes are:

$$Fe^{3+} + 3 H_20 = Fe(0H)_3 + 3 H^+;$$
 (2)

$$Fe^{2+} + 1/4 O_2 + 5/2 H_2O = Fe(OH)_3 + 2 H^+.$$
 (3)

The reactions in equations (1) and (2) both serve to remove Fe^{3+} from solution. The precipitation of $Fe(OH)_3$ from aqueous Fe^{2+} is a reaction whose effect is opposite to that of surface oxidation, because Fe^{2+} is consumed from the solution. The removal of ferric iron by precipitation is very rapid at near-neutral values of pH, and the precipitation of $Fe(OH)_3$ is controlled by aqueous oxidation of of Fe^{2+} , as described in

equation (3). The rate law and rate constant for the oxidation of Fe^{2+} were determined and the rate constants for $FeCl_2$ solutions were in agreement with those tabulated by Davison and Seed (1983). In the presence of fresh hornblende, the rates were considerably enhanced, due perhaps to surface catalysis or to sorption effects.

The authors analyzed the surface oxidation-solution reduction in terms of half-cell reactions and experimental concentrations inserted into the Nernst equation. A range of values for the standard half-cell potential for surface oxidation of Fe²⁺ was calculated to be 0.33 to 0.52 V. This range was bracketed by the ability of the reaction to reduce Fe³⁺ in solution spontaneously, but not to reduce Fe³⁺ in precipitated Fe(OH)₃. This potential range makes surface oxidation of Fe²⁺ a slightly better reducing agent than aqueous oxidation of Fe²⁺, with the capability of reducing geochemically important species such as UO_2^{++} , VO_2^{++} , H_2SeO_3 , and Cu^{2+} . However, as pointed out in the Evaluation below, the upper bound of the half-cell should be about 0.65 V.

The uptake of dissolved oxygen was also very complicated. Although oxygen contents of closed, blank samples showed little or no change with time, the iron silicates studied by the authors were quite effective in consuming oxygen. Loss of oxygen above pH 3.5 can be attributed in part to dissolution of iron during silicate hydrolysis and precipitation as a hydroxide [equation (3)]. Under conditions for which oxyhydroxides may form, oxygen uptake can be described by the equation

$$Fe^{2+} + 1/4 0_2 + 2 OH^- = FeO \bullet OH + 1/2 H_2O.$$

^ .

At pH 7 the authors were able to verify the stoichiometry of equations (1) and (4) in a solution in contact with augite.

Another significant mechanism for oxygen uptake is surface oxidation of the iron silicates in which oxygen (not hydrogen as stated in the paper) is reduced to form water according to the coupled electron-cation transfer reaction

$$[Fe^{2+}, 1/z Mz+]_{silicate} + 1/4 0_2 + H^+ = [Fe^{3+}]_{silicate} + 1/z M^{2+} + 1/2 H_20$$
(5)

Several independent lines of evidence were used by the authors to argue for the significance of this mechanism. For example, the standard reduction potential for the half-cell reaction of O_2 and H⁺ to form H₂O is 1.23 V, which, when combined with the potential range of 0.52 to 0.33 V as given by the authors for the surface oxidation half cell, indicates a positive affinity for oxygen over all conditions measured here. Further, tracer experiments with ¹⁸O demonstrated that oxygen uptake was not due to incorporation of dissolved oxygen on the silicate mineral surfaces, as would be the case with hydroxide or oxyhydroxide precipitation. Thus, equation (5) was supported, in that dissolved O_2 was reduced to form water, where it remains in solution.

(4)

Several additional artifacts were discovered in the course of the experiments but will not be reviewed here, except to mention that solid-state cation diffusion controlled the oxidation depths in the minerals, which were estimated at 12 Å (1.2 nm), 28 Å (2.8 nm), and 80 Å (8.0 nm), respectively, for augite, biotite, and hornblende.

EVALUATION

This paper is a very lengthy account of a many-faceted study on weathering processes which operate on iron silicate minerals represented by augite, biotite, and hornblende. Multiple processes are required to account for the oxidation of Fe^{2+} to Fe^{3+} at mineral surfaces, the reduction of aqueous Fe^{3+} , and the loss of dissolved oxygen. The various possible reactions, their regions of applicability, stoichiometries, and in some cases, their physical consequences, were investigated in considerable detail. The quality of the work was greatly enhanced by the large number of analytical methods brought to bear on various aspects of the studies reported.

The authors make a compelling case for coupled electron-cation transfer as a significant mechanism in the weathering of the minerals studied. Indeed, the authors suggest that the rate-determining step in the oxidation of ferrous iron in the surface layers of the minerals is the cation diffusion process. This study adds a new perspective on the weathering of iron silicates; the authors may not be overstating the case in claiming that the mechanisms proposed constitute a new class of weathering reactions.

Although much information is presented graphically, it is not feasible in such an extensive work to publish much quantitative data. With this reservation, the experimental measurements appear to have been made with care. It does appear strange to read in the title that the work was conducted at 25°C, when the text states that temperatures ranged between 23° and 26°C.

The discussion of the surface oxidation potential presented this reader with some difficulties. Equation (11) was derived from equation (9) in the paper by use of the Nernst equation. Applying the stoichiometry of equation (9), the second term of equation (11) should be $-0.059 \log [M^{Z+}]^{1/Z}$ and not $+0.059 \log [1/ZM^{Z+}]$:

$$E = E^{\circ} - 0.059 \log [M^{Z+}]^{1/Z}$$

The cation concentration used by the authors was, apparently, $[Ca^{2+}] = 10^{-4}$ M, which leads to E - E° = 0.12 V, and not the value of 0.25 V used by the authors to bracket possible values for the surface oxidation half-cell potential. Thus, the bracketed range would become 0.33 to 0.65 V, which makes the surface of hornblende a little less effective as a reducing agent.

A surprising misunderstanding appears repeatedly in the last few pages of the paper. The authors state that a net reaction of the form

$$1/2 0_2 + 2 H^+ + 2 e^- = H_20; E = 1.23 V$$

•...

is a reaction in which "hydrogen ion is reduced to form water." To the contrary, hydrogen has a valence of +1 on both sides of the above equation. The oxygen is reduced from a formal valence of zero to -2 in water. In spite of this error, the general theme of the authors' interpretation seems correct, and the important role of electron-cation mechanisms in weathering of the iron silicates is well supported. However, the reduction of $H^+(aq.)$ to H_2 (g) is the reference half-cell reaction for all standard electrode potentials and has the standard potential of 0.00 V, not 1.23 V.

REFERENCE

Davison, W. and Seed, G. (1983). "The Kinetics of the Oxidation of Ferrous Iron in Synthetic and Natural Waters," <u>Geochimica et</u> <u>Cosmochimica Acta 47</u>, 67-79. See also letter report on this paper by G. D. O'Kelley, LR-287-16, November, 1985.