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LETTER REPORT

Title: Review and Evaluation of A Report on the Status of Hydrothermal Testing of Fully Radioactive Waste Forms and Basalt Repository Waste Package Components, SD-BWI-TI-253, Sept., 1984, by Janet A. Schramke, Scott A. Simonson, and David G. Coles.

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OVERVIEW

This report describes the initial data obtained from three preliminary hydrothermal experiments (runs B-SF-02, B-SF-03, and B-SF-04) performed with two "fully radioactive" simulated waste forms: ATM 6 (borosilicate) glass and spent fuel from the Turkey Point reactor. The starting materials for the experiments were: run B-SF-02 - ATM 6 glass + GR-3 groundwater; run B-SF-03 - ATM 6 glass + Umtanum basalt + GR-3 groundwater; and run B-SF-04 - Turkey Point spent fuel + GR-3 groundwater. The overall objective of the tests was to obtain baseline data for subsequent tests with fully radioactive waste forms and various additional candidate waste-package materials (canister metal, cladding, etc.). In this preliminary report, the authors present data obtained on

the aqueous concentrations of radionuclides and the major-element geochemistries of the hydrothermal fluids sampled during runs B-SF-02, B-SF-03, and B-SF-04.

Solid Starting Materials

Two "fully radioactive" simulated waste forms were employed in the tests: ATM 6 glass and Turkey Point spent fuel.

ATM 6 Glass

ATM 6 glass is a simulated high-level waste glass that contains ^{244}Cm , ^{137}Cs , ^{237}Np , ^{238}Pu , $^{239,240}\text{Pu}$, ^{75}Se , ^{99}Tc , U, and ^{232}Th . The physicochemical properties of this glass have been described in detail by Mellinger and Daniel (1983). Schramke et al. obtained their sample of ATM 6 glass from the Materials Characterization Center (MCC) at the Pacific Northwest Laboratory. In run B-SF-02, the ATM 6 glass was used as received (the glass was received as an unwashed, -60 +115 mesh powder). However, in run B-SF-03, the ATM 6 glass was washed in deionized water prior to experimentation in order to remove any adhering fine particles that were produced during grinding of the glass.

Turkey Point Spent Fuel

The spent fuel used as a solid starting material in run B-SF-04 was spent LWR fuel from the Turkey Point reactor. Prior to experimentation, the spent fuel was separated from its cladding, ground to a powder, sieved to a mesh size of -60 +115, and then rinsed in deionized water to remove fine particles.

Umtanum (RUE-2) Basalt

The basalt used in the experiments, designated RUE-2 basalt, was collected from an outcrop of the entablature section of the Umtanum

flow. Like the ATM 6 glass and Turkey Point spent fuel, the basalt was crushed and sieved prior to experimentation. SEM examination of the crushed basalt (Coles, 1983) revealed that the particles of basalt were coated with electrostatically attached fine material in the size range 1-10 μm .

Fluid Starting Materials

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

Experimental Conditions

All three hydrothermal experiments were performed in Dickson-type rocking pressure vessels. Experimental conditions for the tests were: (1) P = 30 MPa; (2) T = 200°C; (3) a 10:1 (by weight) initial solution-to-solids ratio (this ratio decreased slightly during experimentation owing to periodic extraction of fluid samples); and (4) run duration, 40-60 days.

Analysis of Fluid Samples

Fluid samples were collected in plastic syringes at various stages during experimentation. After removal from the autoclave, each fluid sample was immediately placed into an Ar-atmosphere box where an unfiltered 0.5 ml aliquot was taken to measure the 25°C pH of the fluid. Next, all remaining fluid was filtered through a 4000 Å filter to remove particulate matter. This filtered fluid was subsequently split into the following aliquots for geochemical and radiochemical analysis: (1) an undiluted 5 ml aliquot - subsequently acidified with ULTREX HNO_3 - for standard radiochemical analysis (Leaf, 1984; Stromatt, 1984) and laser fluorimetry; (2) a 0.5 ml aliquot - subsequently diluted to 2.5 ml with deionized water - for ion chromatography (IC) analysis; (3) a 0.5 ml

aliquot - diluted to 5 ml with 2% ULTREX HNO_3 - for inductively-coupled plasma emission spectroscopy (ICP) analysis; and finally, in the case of fluid samples from run B-SF-04 (Turkey Point spent fuel + GR-3 groundwater), (4) an undiluted and unacidified 1.1 ml aliquot to analyze for ^{129}I and ^{14}C .

ICP analysis of experimental fluids yielded the aqueous concentrations of "key" cations (Na, K, Ca, Mg, Fe, Al, Si, B, Mo, and Zn), IC was used to measure the aqueous concentrations of anions (F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , and NO_3^-), laser fluorimetry was used to measure the aqueous concentration of U, and radiochemical analysis yielded the aqueous concentrations of radionuclides. In runs B-SF-02 (ATM 6 glass + GR-3 groundwater) and B-SF-03 (ATM 6 glass + Umtanum basalt + GR-3 groundwater), fluid samples were analyzed for ^{75}Se , ^{137}Cs , ^{99}Tc , ^{244}Cm , ^{238}Pu , $^{239,240}\text{Pu}$, and ^{237}Np . In run B-SF-04 (Turkey Point spent fuel + GR-3 groundwater), fluid samples were analyzed for ^{79}Se , ^{99}Tc , ^{134}Cs , ^{137}Cs , ^{237}Np , ^{238}Pu , $^{239,240}\text{Pu}$, ^{244}Cm , ^{241}Am , ^{90}Sr , ^{14}C , and ^{129}I .

The authors suggest that most of the data that they obtained from ICP, IC, and total carbon analysis are accurate to ± 10 percent. However, they also acknowledge that the reproducibilities of analytical data for several important elements and species - most notably B, K, and SO_4^{2-} - were very poor (i.e., greatly in excess of ± 10 percent).

Because all analyzed fluids were filtered through a 4000 Å filter prior to geochemical and radiochemical analysis, the analytical data obtained by Schramke et al. represent the combined concentrations of materials in colloidal suspension and in true solution. Separation of materials in colloidal suspension from materials in true solution requires an additional filtration step which was not performed in this investigation. However, Schramke et al. state that, in all subsequent BWIP/PNL/WHC hydrothermal experiments with fully radioactive waste forms, colloiddally-suspended and dissolved materials in aqueous solution will be segregated by 18 Å filtration.

Results

The following paragraphs summarize the experimental results obtained from runs B-SF-02, B-SF-03, and B-SF-04.

Run B-SF-02 (ATM 6 glass + GR-3 groundwater)

Listed below are key "solubility" data (mg/L) obtained from run B-SF-02.

pH: 9.74 (initial pH); 10.358 (306 hrs); 10.323 (642 hrs); 10.35 (978 hrs).

Na: 358 (initial concentration); 741 (306 hrs); 867 (642 hrs); 1067 (978 hrs).

SiO₂: 76.1 (estimated initial concentration); 1577 (306 hrs); 1782 (642 hrs); 2128 (978 hrs).

B: 230 (306 hrs); 325 (642 hrs); 491 (978 hrs).

Mo: 58 (306 hrs); 86 (642 hrs); 122 (978 hrs).

K: 3.43 (initial concentration); 12 (306 hrs); <5 (642 hrs); 25 (978 hrs).

Ca: 2.78 (initial concentration); <0.15 (306 hrs); 0.28 (642 hrs); 0.78 (978 hrs).

Mg: 0.0032 (initial concentration); 0.06 (306 hrs); 0.21 (642 hrs); 0.13 (978 hrs).

U: 5.8 (306 hrs); 7.5 (642 hrs); 8.1 (978 hrs).

F: 33.4 (initial concentration); 33 (306 hrs); 38 (642 hrs); 29 (978 hrs).

Cl: 312 (initial concentration); 362 (306 hrs); 347 (642 hrs); 354 (978 hrs).

SO₄²⁻: 174 (initial concentration); 256 (306 hrs); 193 (642 hrs); 285 (978 hrs).

⁷⁵Se: 0.000006 (306 hrs); 0.000005 (642 hrs); 0.000003 (978 hrs).

⁹⁹Tc: 13.6 (306 hrs); 22.1 (642 hrs); 27.1 (978 hrs).

¹³⁷Cs: 0.030 (306 hrs); 0.051 (642 hrs); 0.058 (978 hrs).

^{237}Np : 0.033 (306 hrs); 0.020 (642 hrs); 0.019 (978 hrs).
 ΣPu : 0.000101 (306 hrs); 0.000117(642 hrs); 0.000080 (978 hrs).
 ^{244}Cm : - (306 hrs); - (642 hrs); - (978 hrs).

Run B-SF-03 (ATM 6 glass + Umtanum basalt + GR-3 groundwater)

Listed below are key "solubility" data (mg/L) obtained from run B-SF-03.

pH: 9.74 (initial pH); 10.01 (331 hrs); 10.032 (667 hrs); 10.156
 (1175 hrs); 10.228 (1511 hrs)
 Na: 358 (initial concentration); 381 (331 hrs); 435 (667 hrs); 538
 (1175 hrs); 500 (1511 hrs).
 SiO_2 : 76.1 (estimated initial concentration); 768 (331 hrs); 1298 (667
 hrs); 1594 (1175 hrs); 1471 (1511 hrs).
 B: 24 (331 hrs); 60 (667 hrs); 70 (1175 hrs); 41 (1511 hrs).
 Mo: 1.1 (331 hrs); 2.2 (667 hrs); 4.4 (1175 hrs); 5.4 (1511 hrs).
 K: 3.43 (initial concentration); 47 (331 hrs); 70 (667 hrs); 63
 (1175 hrs); 60 (1511 hrs).
 Ca: 2.78 (initial concentration); 0.52 (331 hrs); 0.69 (667 hrs);
 0.82 (1175 hrs); 0.39 (1511 hrs).
 Mg: 0.0032 (initial concentration); 0.13 (331 hrs); 0.13 (667 hrs);
 0.13 (1175 hrs); 0.11 (1511 hrs).
 U: 0.83 (331 hrs); 0.54 (667 hrs); 0.41 (1175 hrs); 0.23 (1511
 hrs).
 F: 33.4 (initial concentration); 35 (331 hrs); 35 (667 hrs); 39
 (1175 hrs); 41 (1511 hrs).
 Cl: 312 (initial concentration); 342 (331 hrs); 342 (667 hrs); 355
 (1175 hrs); 357 (1511 hrs).
 SO_4^{2-} : 174 (initial concentration); 254 (331 hrs); 180 (667 hrs); 163
 (1175 hrs); 163 (1511 hrs).
 ^{75}Se : - (331 hrs); - (667 hrs); - (1175 hrs); - (1511 hrs).
 ^{99}Tc : 0.2038 (331 hrs); 0.0013 (667 hrs); 0.0003 (1175 hrs); 0.0013
 (1511 hrs).

^{137}Cs : 0.0137 (331 hrs); 0.0060 (667 hrs); 0.0191 (1175 hrs); 0.0097 (1511 hrs).
 ^{237}Np : 0.0033 (331 hrs); 0.0173 (667 hrs); 0.0147 (1175 hrs); 0.0051 (1511 hrs).
 ΣPu : 0.000334 (331 hrs); 0.001050 (667 hrs); 0.000816 (1175 hrs); 0.000339 (1511 hrs).
 ^{244}Cm : 0.000001 (331 hrs); 0.000005 (667 hrs); 0.000004 (1175 hrs); 0.000002 (1511 hrs).

The following conclusions can be drawn from the various solubility/concentration data obtained during runs B-SF-02 and B-SF-03.

1. The aqueous concentrations of SiO_2 were systematically higher in run B-SF-02 (basalt-absent) than in run B-SF-03 (basalt-present).
2. The continuously increasing aqueous concentrations of B in run B-SF-02 suggest that ATM 6 glass was still being dissolved/alterd at the conclusion of run B-SF-02.
3. In view of the systematically higher aqueous concentrations of B in run B-SF-02, greater quantities of ATM 6 glass were dissolved/alterd in this run than in run B-SF-03.
4. With the exception of ^{237}Np , the aqueous concentrations of actinides were higher in run B-SF-03 (basalt-present) than in run B-SF-02 (basalt-absent).
5. The aqueous concentrations of ^{99}Tc , ^{75}Se , and ^{137}Cs were systematically higher in run B-SF-02 (basalt-absent) than in run B-SF-03 (basalt-present).

Run B-SF-04 (Turkey Point spent fuel + GR-3 groundwater)

Listed below are key "solubility" data (mg/L) obtained from run B-SF-04.

pH: 9.74 (initial pH); 7.803 (162 hrs); 7.194 (522 hrs); 7.788 (858 hrs); 7.96 (1194 hrs).

Na: 358 (initial concentration); 366 (162 hrs); 366 (522 hrs); 307 (858 hrs); 266 (1194 hrs).

SiO₂: 76.1 (estimated initial concentration); 113 (162 hrs); 103 (522 hrs); 176 (858 hrs); 38 (1194 hrs).

B: 17 (162 hrs); 10 (522 hrs); 20 (858 hrs); 14 (1194 hrs).

Mo: 2.9 (162 hrs); 4.6 (522 hrs); 4.8 (858 hrs); 5.0 (1194 hrs).

K: 3.43 (initial concentration); 30 (162 hrs); 23 (522 hrs); <5 (858 hrs); 31 (1194 hrs).

Ca: 2.78 (initial concentration); 2.05 (162 hrs); 0.74 (522 hrs); 0.66 (858 hrs); 0.67 (1194 hrs).

Mg: 0.0032 (initial concentration); 0.11 (162 hrs); 0.15 (522 hrs); 0.14 (858 hrs); 0.02 (1194 hrs).

U: 1.20 (162 hrs); 1.00 (522 hrs); 0.77 (858 hrs); 1.00 (1194 hrs).

F: 33.4 (initial concentration); 31 (162 hrs); 31 (522 hrs); 29 (858 hrs); 25 (1194 hrs).

Cl: 312 (initial concentration); 374 (162 hrs); 334 (522 hrs); 293 (858 hrs); 268 (1194 hrs).

SO₄²⁻: 174 (initial concentration); 165 (162 hrs); 155 (522 hrs); 124 (858 hrs); 110 (1194 hrs).

⁷⁵Se: <0.000975 (162 hrs); <0.000975 (522 hrs); <0.000975 (858 hrs); <0.000975 (1194 hrs).

⁹⁰Sr: 0.0173 (162 hrs); 0.0358 (522 hrs); 0.0549 (858 hrs); 0.0417 (1194 hrs).

⁹⁹Tc: <0.002660 (162 hrs); <0.000532 (522 hrs); <0.000532 (858 hrs); 0.000745 (1194 hrs).

¹²⁹I: <0.516 (162 hrs); <0.310 (522 hrs); <0.310 (858 hrs); <0.310 (1194 hrs).

Σ Cs: 0.172 (162 hrs); 0.232 (522 hrs); 0.277 (858 hrs); 0.313 (1194 hrs).
 ^{237}Np : 0.000320 (162 hrs); 0.000256 (522 hrs); 0.000384 (858 hrs); <0.000640 (1194 hrs).
 Σ Pu: 0.0154 (162 hrs); 0.0104 (522 hrs); 0.0086 (858 hrs); 0.0118 (1194 hrs).
 ^{241}Am : 0.000511 (162 hrs); 0.000354 (522 hrs); 0.000329 (858 hrs); 0.000409 (1194 hrs).
 ^{244}Cm : 0.000019 (162 hrs); 0.000013 (522 hrs); 0.000011 (858 hrs); 0.000015 (1194 hrs).

Comparing the data listed above with corresponding data for runs B-SF-02 and B-SF-03, it is evident that - at 30 MPa, 200°C - groundwaters in contact with spent fuel contain greater quantities of dissolved/mobilized Cs and Pu than groundwaters in contact with fully radioactive borosilicate glass.

Summary

The discussion items below summarize the most important experimental results obtained from runs B-SF-02, B-SF-03, and B-SF-04.

1. Runs B-SF-02, B-SF-03, and B-SF-04 were of insufficient duration to achieve steady-state concentrations of solubilized radionuclides.
2. The concentrations of silica in the fluids sampled from run B-SF-03 (ATM 6 glass + Umtanum basalt + GR-3 groundwater) were systematically lower than those in the fluids sampled from run B-SF-02 (ATM 6 glass + GR-3 groundwater). Also, judging from the concentrations of boron in the fluid samples taken during these two runs, less glass was dissolved/alterred in run B-SF-03 than in run B-SF-02.

3. Comparing the aqueous concentrations of B with the aqueous concentrations of radionuclides in fluid samples taken during runs B-SF-02 and B-SF-03, it is evident that - after initial release - the aqueous concentrations of radionuclides were lowered significantly by precipitation and/or sorption.
4. The aqueous concentrations of actinides as a function of time in run B-SF-03 seem to reflect varying rates of release and removal of the actinides. Also, the concentration-versus-time data for ^{237}Np and ^{239}Pu in run B-SF-03 are quite similar to corresponding concentration-versus-time data for these elements obtained from experiments performed with tracer-doped glasses. This result suggests that radiolysis had little or no effect on the aqueous concentrations of ^{237}Np and ^{239}Pu in run B-SF-03.
5. The aqueous concentrations of ^{99}Tc , ^{75}Se , and ^{137}Cs in run B-SF-03 were lower than corresponding concentrations of these radionuclides in run B-SF-02. This observation suggests that, in the system ATM 6 glass \pm Umtanum basalt + GR-3 groundwater, the presence of basalt tends to lower the aqueous concentrations of ^{99}Tc , ^{75}Se , and ^{137}Cs .

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EVALUATION

This report describes initial geochemical and radiochemical data obtained from three preliminary hydrothermal tests on two "fully radioactive" simulated waste forms: ATM 6 (borosilicate) glass and Turkey Point spent fuel. The overall objective of the tests was to acquire baseline data for subsequent tests with fully radioactive waste forms and various additional candidate waste-package materials (canister metal, cladding, etc.). The principal findings of the experimentation, which have been corroborated by subsequent follow-up experimentation, are itemized below.

1. Hydrothermal experiments with fully radioactive waste forms must be conducted for lengthy periods of time (hundreds to thousands of hours) in order to achieve steady-state concentrations of solubilized radionuclides.
2. In the system ATM 6 glass + Umtanum basalt + GR-3 groundwater, the presence of basalt tends to lower the aqueous concentration of SiO_2 and diminish the quantity of glass that is dissolved/altered.
3. After being released from a fully radioactive waste form, most radionuclides are quickly removed from solution by precipitation and/or sorption.
4. In the system ATM 6 glass + Umtanum basalt + GR-3 groundwater, the presence of basalt tends to increase the aqueous concentrations of most actinides, but decrease the aqueous concentrations of ^{99}Tc , ^{75}Se , and ^{137}Cs .