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LETTER REPORT

Title: Review and Evaluation of The Effect of Basalt on the Release of ^{99}Tc , ^{237}Np , and ^{239}Pu from Borosilicate Glass Under Hydrothermal Conditions, SD-BWI-TI-190, Dec., 1983, by David G. Coles.

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OVERVIEW

This report describes the initial data obtained from four hydrothermal experiments (runs B-48-01, B-48-02, B-48-03, and B-48-04) performed with two "tracer-doped" simulated waste forms: (1) a ^{99}Tc -doped, 76-68 (borosilicate) glass, and (2) a ^{237}Np - and ^{239}Pu -doped 76-68 glass. The starting materials for the experiments were: run B-48-01 - ^{99}Tc -doped glass + GR-3 groundwater; run B-48-02 - ^{99}Tc -doped glass + Umtanum basalt + GR-3 groundwater; run B-48-03 - ^{237}Np - and ^{239}Pu -doped glass + GR-3 groundwater; and run B-48-04 - ^{237}Np - and ^{239}Pu -doped glass + Umtanum basalt + GR-3 groundwater. The experiments were conducted to determine how basalt affects: (1) the dissolution/alteration behavior of 76-68 glass; (2) the solubilities/concentrations of ^{99}Tc , ^{237}Np , and ^{239}Pu ; (3) the major-element geochemistries of altered GR-3

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groundwaters; and (4) the formation of secondary minerals in hydrothermal systems that contain a simulated borosilicate-glass waste form. The overall objective of the tests was to obtain baseline data on tracer solubility and secondary mineral formation for comparison with data to be obtained later from tests with fully radioactive waste forms and various additional candidate waste-package materials (canister metal, cladding, etc.).

Due to the large amount of data obtained from the experiments, it was determined that the experimental results would be described in a series of reports. The present document is the first report in the series, and it is primarily concerned with initial data obtained on the radionuclide and major-element geochemistries of the hydrothermal fluids sampled in the four tests.

Solid Starting Materials

Two "tracer-doped," 76-68 (borosilicate) glasses (Bradley et al., 1979) were employed in the tests: (1) a ^{99}Tc -doped glass; and (2) a ^{237}Np - and ^{239}Pu -doped glass. Because these glasses were available in only limited quantities, and because they contained more than a sufficient amount of radioactivity, each glass was mixed with an approximately equal weight of undoped MCC 76-68 glass prior to experimentation. The undoped glass was obtained as a monolith, and was subsequently crushed, sieved, and cleaned in a manner identical to that for the two tracer-doped glasses. Prior to experimentation, the doped and undoped glasses were thoroughly blended by a mechanical mixing technique. SEM examination of the crushed glasses revealed that the surfaces of the glass particles were free of electrostatically attached fines.

^{99}Tc -doped 76-68 Glass

The ^{99}Tc -doped 76-68 starting glass consisted of 57.8% doped glass and 42.2% undoped glass. After crushing and sieving, the glass was washed

for two minutes in distilled water at 25°C. Next, the glass and wash water were analyzed for ^{99}Tc . By summing the amounts of ^{99}Tc in the cleaned glass and the wash water, it was determined that 43% of the ^{99}Tc in the unwashed glass was lost to the wash water during cleaning. Coles attributes this observation to dissolution of NaTcO_4 from breached vesicles in the glass. The final calculated radioactivity of the glass was 12.5 $\mu\text{Ci } ^{99}\text{Tc/g}$ glass, and the final concentration of ^{99}Tc was 0.7 mg $^{99}\text{Tc/g}$ glass.

^{237}Np - and ^{239}Pu -doped Borosilicate Glass

The ^{237}Np - and ^{239}Pu -doped starting glass consisted of 50% doped glass and 50% undoped glass. After crushing and sieving, the glass was washed for two minutes in distilled water at 25°C. Subsequent analysis of the wash water indicated only minor concentrations of ^{237}Np and ^{239}Pu . The final calculated radioactivity of the glass was 1.4 $\mu\text{Ci } ^{237}\text{Np/g}$ glass and 13 $\mu\text{Ci } ^{239}\text{Pu/g}$ glass. The final concentrations of ^{237}Np and ^{239}Pu were 2.0 mg $^{237}\text{Np/g}$ glass and 0.2 mg $^{239}\text{Pu/g}$ glass.

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 76-68 glass starting materials, the basalt was crushed and sieved prior to experimentation. SEM examination of the crushed basalt 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 four experiments, the starting groundwater was GR-3 synthetic groundwater (Jones, 1982). The pH of this groundwater was adjusted to 9.74 prior to experimentation.

Experimental Conditions

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

Analysis of Fluid Samples

Fluid samples were collected in plastic syringes at various stages during experimentation. After collection, each sample was immediately placed into an Ar-atmosphere box where pH was measured. Subsequently, aliquots of each sample were filtered through a 4000 Å filter, and/or an 18 Å filter. The purpose of filtration through a 4000 Å filter was to remove all particulates from the fluid samples. Therefore, it was assumed that the radionuclides and other solubilized elements in 4000 Å filtered solutions were associated with colloids and species in true solution. The purpose of filtration through an 18 Å filter was to remove all colloids from the fluid samples. Accordingly, it was assumed that the radionuclides and other solubilized elements in 18 Å solutions were associated with species in true solution.

The analytical methodology yielded four different types of samples: an unfiltered, undiluted sample; an undiluted sample filtered through a 4000 Å filter; a 10:1 diluted sample filtered through a 4000 Å filter; and a 10:1 diluted sample that was first filtered through a 4000 Å filter and subsequently filtered through an 18 Å filter. The resulting aliquots of unfiltered and filtered groundwater were analyzed chemically using a variety of techniques. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) was used to obtain the aqueous concentrations of Na, K, Ca, Mg, Fe, Al, Si, B, Mo, and Zn. Concentrations of the anionic species F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , and NO_3^- were obtained by Ion Chromatography. Concentrations of aqueous ^{99}Tc , ^{237}Np ,

and ^{239}Pu were determined by radiochemical analysis of both unfiltered and filtered solutions. Coles suggests that the ICP and IC results are reproducible to better than ± 10 percent.

Results

In runs B-48-01, B-48-03, and B-48-04, pH rose from an initial value of 9.74 to -10 during the early stages of experimentation. Thereafter, pH remained steady until experimentation was concluded. In run B-48-02, however, pH initially dropped to 9.34, then rose to approximately the same pH as in the other three experiments (-10). This aberrant behavior of pH in run B-48-02 remains unexplained at the present time.

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

The paragraphs below describe the behavior of: (1) ^{99}Tc in runs B-48-01 and B-48-02, and (2) ^{237}Np and ^{239}Pu in runs B-48-03 and B-48-04.

Run B-48-01 (^{99}Tc -doped 76-68 glass + GR-3 groundwater)

The concentration of ^{99}Tc , initially 0 mg/L, increased sharply to -27 mg/L after 19 hr, and then gradually rose to an apparent steady-state concentration of -53 mg/L after 1629 hr. In all fluid samples it was observed that the aqueous concentration of ^{99}Tc was largely unaffected by filtration. This observation indicates that ^{99}Tc was in true solution, probably in the form of the anion TcO_4^- . At the conclusion of experimentation, nearly 65% of the ^{99}Tc in the starting glass had been partitioned into coexisting groundwater.

Run B-48-02 (⁹⁹Tc-doped 76-68 glass + Umtanum basalt + GR-3 groundwater)

The concentration of ⁹⁹Tc, initially 0 mg/L, increased to an apparent steady-state concentration of ~2.5 mg/L after 22 hr, remained essentially constant through 644 hr, and thereafter declined to a negligibly small concentration (<0.01 mg/L) after 1311 hr. Through 1647 hrs of experimentation, it was observed that the aqueous concentration of ⁹⁹Tc was essentially unaffected by filtration. After that time, however, filtration through a 4000 Å filter appeared to significantly decrease the aqueous concentration of ⁹⁹Tc. This observation suggests that, after 1647 hrs, a substantial proportion of solubilized ⁹⁹Tc was associated with filterable particulates.

At the conclusion of run B-48-02, the aqueous concentration of ⁹⁹Tc was less than 0.1% of the total inventory. This figure is in sharp contrast to the 65% figure for run B-48-01. Comparing the results obtained from these two experiments, it is evident that the presence of basalt lowers the aqueous concentration of ⁹⁹Tc by approximately four orders of magnitude.

Coles hypothesizes that the strikingly different results obtained in runs B-48-01 and B-48-02 can be attributed to different redox conditions in the two experiments. In run B-48-01, redox conditions probably remained oxidizing throughout experimentation because the starting 76-68 glass and the starting GR-3 synthetic groundwater were both prepared under oxidizing conditions. By contrast, in run B-48-02, it is evident that basalt was able to lower redox conditions and, concomitantly, the solubility/concentration of ⁹⁹Tc. Evidently, in this run, TcO_4^- was electrochemically reduced and removed from solution in one or more solid phases. At present, it is uncertain whether this decrease in the aqueous concentration of ⁹⁹Tc can be attributed to a combined sorption-redox reaction, the formation of $\text{TcO}_2(\text{s})$, or incorporation of ⁹⁹Tc into a major secondary mineral.

Run B-48-03 (^{237}Np - and ^{239}Pu -doped 76-68 glass + GR-3 groundwater)

The concentration of ^{237}Np , initially 0 mg/L, increased sharply to 0.04 mg/L after 16 hr, and then decreased to an apparent steady-state concentration of -0.0025 mg/L after 840 hr. Results of filtration indicate that essentially all solubilized ^{237}Np was associated with filterable colloids.

The concentration of ^{239}Pu , initially 0 mg/L, increased to -0.0006 mg/L after 16 hr, then decreased to 0.0002 mg/L after 100 hr, and thereafter decreased slowly to an apparent steady-state concentration of -0.0001 mg/L after 840 hr. Results of filtration indicate that essentially all solubilized ^{239}Pu was associated with filterable particulates and colloids.

Run B-48-04 (^{237}Np - and ^{239}Pu -doped 76-68 glass + Umtanum basalt + GR-3 groundwater)

The concentration of ^{237}Np , initially 0 mg/l, increased sharply to 0.012 mg/L after 160 hr, decreased slightly to 0.008 mg/L after 496 hr, then rose fairly steadily to 0.070 mg/L after 1503 hr, and thereafter declined rather sharply to an apparent steady-state concentration of -0.031 mg/L after 1839 hr. Results of filtration indicate that ^{237}Np was predominantly associated with filterable particulates. Coles hypothesizes that these particulates (and accompanying colloids) are secondary minerals (e.g., clays) which form during experimentation. The increased association of ^{237}Np with filterable particulates and colloids in this run compared to run B-48-03 implies that basalt promotes the formation of particulates and colloids which sorb ^{237}Np .

The concentration of ^{239}Pu , initially 0 mg/L, increased sharply to -0.001 mg/L after 16 hr, then increased fairly steadily to a maximum value of 0.0072 mg/L after 1167 hr, and thereafter decreased slowly and

steadily to -0.0034 mg/L after 2173 hr. Results of filtration indicate that: (1) little or no ^{239}Pu existed in true solution, and (2) approximately 90% of the solubilized ^{239}Pu was associated with filterable particulates. Therefore, as in the case of ^{237}Np , the analytical data suggest that basalt promotes the formation of ^{239}Pu -bearing particulates which increase the mobility of ^{239}Pu . Comparing the results obtained from runs B-48-03 and B-48-04, it is evident that basalt increases the aqueous concentrations of ^{237}Np and ^{239}Pu by approximately an order of magnitude.

Finally, in run B-48-04 it was observed that the final concentration of ^{237}Np was approximately an order of magnitude higher than the final concentration of ^{239}Pu (-0.03 mg/L vs. -0.003 mg/L). However, it is also true that the concentration of ^{237}Np in the 76-68 starting glass was an order of magnitude higher than the corresponding concentration of ^{239}Pu . Therefore, the differing aqueous concentrations of ^{237}Np and ^{239}Pu in run B-48-04 may reflect differences in the concentrations of these radionuclides in the starting 76-68 glass.

Summary

The discussion items below summarize the most important experimental results obtained from runs B-48-01, B-48-02, B-48-03, and B-48-04.

1. During run B-48-01 (^{99}Tc -doped glass + GR-3 groundwater), approximately 65% of the ^{99}Tc inventory was released from the glass to the groundwater. Coles attributes this result to dissolution of tiny, highly-soluble crystals of NaTcO_4 from breached vesicles in the glass. Also, throughout this run it was observed that filtration had absolutely no effect on the aqueous concentration of ^{99}Tc . This observation is consistent with the hypothesis that ^{99}Tc was in true solution during the experiment, probably in the form of the anion TcO_4^- .

2. The final aqueous concentration of ^{99}Tc was four orders of magnitude less in run B-48-02 (basalt present) than in run B-48-01 (basalt absent). Coles suggests that this dramatic decrease in the solubility/concentration of ^{99}Tc is attributable to electrochemical reduction of TcO_4^- by aqueous Fe^{2+} solubilized from the Umtanum basalt.
3. In run B-48-02 (^{99}Tc -doped glass + Umtanum basalt + GR-3 groundwater), it was observed that a small fraction of the solubilized ^{99}Tc was associated with filterable particulates and colloids.
4. Data obtained from runs B-48-03 (^{237}Np - and ^{239}Pu -doped glass + GR-3 groundwater) and B-48-04 (^{237}Np - and ^{239}Pu -doped glass + Umtanum basalt + GR-3 groundwater) indicate that essentially all solubilized ^{237}Np and ^{239}Pu was associated with filterable colloids and particulates. Furthermore, the aqueous concentrations of ^{237}Np and ^{239}Pu were almost an order of magnitude greater in run B-48-04 (basalt present) than in run B-48-03 (basalt absent). Therefore, it appears that the presence of basalt enhances the aqueous concentrations of ^{237}Np and ^{239}Pu in the system 76-68 glass ± Umtanum basalt + GR-3 groundwater.

REFERENCES

Bradley, D. J., C. O. Harvey, and R. P. Turcotte. 1979. Leaching of Actinides and Technitium from Simulated High Level Waste Glass. PNL 3152, Pacific Northwest Laboratory, Richland, Washington.

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EVALUATION

This report relates three significant observations concerning the aqueous concentrations of ^{99}Tc , ^{237}Np , and ^{239}Pu in the system 76-68 glass \pm Umtanum basalt + GR-3 groundwater.

1. The addition of Umtanum basalt to the system 76-68 glass + GR-3 groundwater dramatically reduces the solubility/concentration of ^{99}Tc .
2. Regardless of the presence or absence of basalt, essentially all solubilized ^{237}Np and ^{239}Pu is associated with filterable colloids and particulates.
3. The addition of Umtanum basalt to the system 76-68 glass + GR-3 groundwater increases the aqueous concentrations of ^{237}Np and ^{239}Pu by almost an order of magnitude.