

LETTER REPORT

Title: Review and Evaluation of Examination of Solids from  
200°C Hydrothermal Tests with Spent Fuel, SD-BWI-TI-  
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REVIEW

This report describes the solid starting materials and the solid reaction products of three DOE/Hanford hydrothermal experiments--designated runs BSF-08, BSF-10, and BSF-11--which were conducted to determine the hydrothermal reactivity of ATM-101 spent fuel, a reference light-water-reactor fuel from the H. B. Robinson reactor. Starting materials for the experiments were: runs BSF-08 and BSF-10--ATM-101 spent fuel plus BWIP reference groundwater GR-4; and run BSF-11--ATM-101 spent fuel plus RCE-3 reference Cohasset basalt plus GR-4 groundwater. All three experiments were performed in Dickson-type rocking autoclaves. The ATM-101 spent fuel used in the tests was sieved to -60/+115 mesh and rinsed in deionized water prior to autoclave loading. The basalt was sieved to -120/+230 mesh and was not washed after grinding and sizing. Initial solution/solids ratios were 10:1 by weight, with equal weights of spent fuel and basalt in run BSF-11.

Tests BSF-08 and BSF-10 were performed at 25 MPa, 200°C, and were terminated prematurely at 1400 and 2059 hours, respectively, when the reaction vessels were found to be leaking. Test BSF-11 also was performed at 25 MPa, 200°C, but it ran for its planned duration, 4362 hrs. As in similar earlier experiments (Thomas et al., 1985), solid reaction products were obtained by sampling materials from the gold-bag reaction vessels after each test was completed. Samples were selected on the basis of differences in appearance (color and texture) and location in the gold bag. Typical sampling locations were: (1) the bottom of the gold bag; (2) the middle of the gold bag near the final solution level; and (3) just above the final solution level, whenever solid material was present at this location. Identification of solid phases 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) (Schramke et al., 1984).

## Results

### Tests BSF-08 and BSF-10 (ATM-101 spent fuel plus GR-4 groundwater)

SEM examination of the reaction products of runs BSF-08 and BSF-10 at low magnifications showed that the particles of spent fuel had worn surfaces, but there was no evidence of dissolution or leaching of the spent fuel particles, and no secondary solid phases were observed. However, examination of the spent fuel particles at high SEM magnifications revealed that they are covered with 0.1- $\mu\text{m}$ - to 1.0- $\mu\text{m}$ -diameter "fines." These fines--apparently minute particles of spent fuel ( $\text{UO}_2$ )--exhibited irregular surfaces, indicating that they were not "attacked" extensively during experimentation. The fines apparently result from tumbling of the spent fuel in the rocking autoclave during experimentation. Significantly, similar experimental results were obtained previously from run BSF-04 with Turkey Point spent fuel and GR-3 groundwater (Thomas et al., 1985).

### Test BSF-11 (ATM-101 spent fuel plus RCE-3 Cohasset basalt plus GR-4 groundwater)

Results obtained from run BSF-11 differ significantly from the results obtained from runs BSF-08 and BSF-10. In run BSF-11 it was observed that the particles of reacted spent fuel and basalt, as well as the inside of the gold bag reaction vessel, were coated with smectite clay. SEM examination of particles of reacted spent fuel revealed that a large fraction of the smectite associated with these particles was concentrated in the narrow cavities between individual  $\text{UO}_2$  crystals. SEM/EDS analyses of these clay particles indicate that they contain Fe, Mg, K, and Ca, but no uranium or fission products.

The close spatial association notwithstanding, it is uncertain whether the smectite adhering to spent fuel particles formed during experimentation or was contributed by the basalt starting material. XRD analysis indicates that the smectite coating spent fuel and basalt reaction products is essentially identical to the smectite present initially in RCE-3 basalt. [RCE-3 basalt contains 5-8 vol. % secondary minerals, including smectite clay (Allen et al., 1985).] However, this observation does not prove that all of the smectite observed in the solid reaction products of run BSF-11 was present prior to experimentation.

In an attempt to identify the source of the clay material intimately associated with the reacted spent fuel particles obtained from run BSF-11, both reacted and unreacted solid materials from this run were examined by XRD. The purpose of this exercise was to measure and compare the relative intensities of the (001) reflections of smectite in the two materials. Comparison of the intensities of these peaks indicates that some smectite may have formed during experimentation. However, the intensities of the two peaks are not markedly different and, therefore, the observed differences may be attributable to inhomogeneous distribution of smectite in the solid starting materials and/or in the solid reaction products.

### Discussion

Results obtained from runs BSF-08, BSF-10, and BSF-11 indicate that there is minimal reaction between ATM-101 spent fuel and groundwater in the presence or absence of basalt in hydrothermal experiments performed at 25 MPa, 200°C. Also, significantly, the results of these runs with real spent fuel contrast sharply with results obtained from earlier, similar experiments with simulated spent fuel (Woodley et al., 1981; Grandstaff et al., 1984). The disparities between the experimental results obtained with simulated spent fuel and real spent fuel under similar test conditions are plausibly attributed to significant physicochemical differences between the two materials. Spent LWR fuel typically consists of relatively dense, sintered  $\alpha$ -UO<sub>2</sub> in which most fission-product elements are either bound tightly in crystalline solution or are dispersed widely as small, discrete crystalline phases. (At the relatively low fuel temperatures attained during LWR operation, there is insufficient thermal energy available to cause fission products to migrate long distances in the fuel or to agglomerate as large discrete particles.) By contrast, the simulated spent fuel prepared by Grandstaff et al. (1984) is an unconsolidated admixture of several physically discrete chemical constituents (phases): viz., (1)  $\alpha$ -UO<sub>2</sub> powder containing minor to trace amounts of Th, Y, Ce, Pr, Sm, and Zr in crystalline solution; (2) metallic Pd, Re, and Mo; (3) the nondeliquescent oxides MoO<sub>3</sub>, SrO, and BaZrO<sub>3</sub>; and (4) the deliquescent Cs compounds CsI, Cs<sub>2</sub>MoO<sub>4</sub>,<sup>2</sup> and Cs<sub>2</sub>Te.<sup>3</sup> Thus, the relatively extensive reaction between simulated spent fuel and groundwater (Grandstaff et al., 1984) is reasonably attributed to the comparatively high free energy of the simulated spent fuel--a thermodynamic condition resulting from the inhomogeneous physicochemical make-up of the material. In view of the drastically different chemical reactivities of simulated and real spent fuel, results obtained from hydrothermal experiments with simulated spent fuel bear no relation to the results of hydrothermal experiments performed with real spent fuel.

## EVALUATION

This report emphasizes two important points concerning the reactivities of simulated and real spent fuel under hydrothermal experimental conditions that purportedly simulate geochemical environments in the very-near field of a basalt-hosted HLW repository during the early containment period.

1. Due to important differences in physicochemical make-up, simulated spent fuel is an unsatisfactory analogue for real spent fuel. Simulated spent fuel consists of an unconsolidated admixture of numerous, discrete crystalline phases and, therefore, it intrinsically possesses a relatively high free energy. The high free energy of simulated spent fuel helps to explain why it is extensively attacked and altered by groundwater during hydrothermal experiments (Grandstaff et al., 1984). By contrast, real spent fuel consists of comparatively dense, sintered  $\alpha$ -UO<sub>2</sub> in which most fission-product elements are either bound tightly in crystalline solution or are dispersed widely as small, discrete crystalline phases. Therefore, compared to simulated spent fuel of similar composition, real spent fuel possesses a relatively low free energy, and thus it is to be expected that real spent fuel will exhibit a greater resistance to chemical attack during hydrothermal experiments conducted at 25 MPa, 200°C.
2. Real spent fuel is essentially immune to chemical attack in spent fuel + groundwater and spent fuel + basalt + groundwater experiments performed at 25 MPa, 200°C. Therefore, future experiments conducted to explore the reactivity of real spent fuel under repository-relevant conditions should focus on the performance of real spent fuel under different geochemical conditions (e.g., at somewhat higher temperatures) and in systems containing additional candidate waste package components (e.g., carbon steel).

## REFERENCES

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