WSRC-MS-98-00450

Evaluation of Neutron Poison Materials for DOE SNF Disposal Systems

RECORDS ADMINISTRATION
R0078386

by

D. W. Vinson

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

G. R. Caskey Jr.

R. L. Sindelar

A document prepared for AMERICAN NUCLEAR SOCIETY THIRD TOPICAL MEETING DOE SPENT NUCLEAR FUEL AND FISSILE MATERIALS MANAGEMENT at Charleston, SC, USA from 9/8/98 - 9/11/98.

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

EVALUATION OF NEUTRON POISON MATERIALS FOR DOE SNF DISPOSAL SYSTEMS

Dennis W. Vinson
Westinghouse Savannah River Co.
Aiken, SC 29808
(803)725-1961

George R. Caskey, Jr.
ORISE[1]
705 Pin Oak Drive
Aiken, SC 29801

Robert L. Sindelar
Westinghouse Savannah River Co.
Aiken, SC 29808
(803)725-5298

ABSTRACT

Aluminum-based spent nuclear fuel (Al-SNF) from foreign and domestic research reactors is being consolidated at the Savannah River Site (SRS) for ultimate disposal in the Mined Geologic Disposal System (MGDS). Most of the aluminum-based fuel material contains highly enriched uranium (HEU) (>20% ^{235}U), which challenges the preclusion of criticality events for disposal periods exceeding 10,000 years. Recent criticality analyses have shown that the addition of neutron absorbing materials (poisons) is needed in waste packages containing DOE SNF canisters fully loaded with Al-SNF under flooded and degraded configurations to demonstrate compliance with the requirement that $k_{eff} < 0.95$.

Compatibility of poison matrix materials and the Al-SNF, including their relative degradation rate and solubility, are important to maintain criticality control. An assessment of the viability of poison and matrix materials has been conducted, and an experimental corrosion program has been initiated to provide data on degradation rates of poison and matrix materials and Al-SNF materials under repository relevant vapor and aqueous environments. Initial testing includes Al6061, Type 316L stainless steel, and A516Gr55 in synthesized J-13 water vapor at 50°C, 100°C, and 200°C and in condensate water vapor at 100°C. Preliminary results are presented herein.

I. INTRODUCTION

Approximately 50 metric tonnes heavy metal of aluminum-based spent nuclear fuel (Al-SNF), or 30,000 assemblies, are being consolidated at the Savannah River Site. Technologies are being developed at SRS to allow ultimate disposal of these fuels, most of which contain highly enriched uranium (HEU) (>20% ^{235}U), in the mined geologic disposal system (MGDS). These technologies are the direct/codisposal technology (DD) and the melt-dilute technology (MD). In both cases, the proposed waste package would codispose a canister containing either a direct or melt-dilute SNF form with several borosilicate glass logs of DHLW.

One aspect of spent nuclear fuel (SNF) disposal is the potential for achieving a criticality event. Analyses of degraded configurations of Al-SNF indicate that the reactivity of some configurations may be excessive [1,2]. Among the possible methods available to reduce the reactivity of the SNF forms is to limit the amount of fissile material disposed of in a single waste package and to load poisons with the HEU SNF. This paper considers criticality control through the implementation of poison materials added to the DOE SNF canisters to reduce the reactivity of the system. Attention is given to the issues associated with the selection of poison and matrix materials. The degradation rates of the poison matrix materials and the Al-SNF are important characteristics used to demonstrate their compatibility and long-term criticality control in the repository. A corrosion-testing program is being conducted at SRS to provide data o0n the corrosion rates of the poison matrix materials under vapor and aqueous conditions relevant to the proposed repository.

II. DISCUSSION

Criticality of candidate waste forms

Criticality control in waste packages for disposal at Yucca Mountain is governed by 10CFR60 [3]. It must be shown through analysis that there is no possibility (probability< 10^{-6}) of criticality for 10,000 years following disposal. Failure of containment is generally assumed to occur beginning several thousand years after emplacement. Therefore, both intact and degraded states of the waste package must be evaluated.

Criticality of Al-SNF directly loaded in a canister was evaluated using the MCNP4A computer code, by the Civilian Radioactive Waste Management System [1,2]. Results for Al-SNF assemblies degraded to a worst case configuration and homogenized with water that had flooded the free volume in the canister, indicate that

[1] Oak Ridge Institute for Science and Education

reactivity would be excessive, and that poisons would be required in the canister to meet criticality requirements. Analyses of several scenarios for degradation of both the DHLW and Al-SNF within the waste package have been conducted using the EQ3/6 geochemistry computer program [2]. Criticality calculations indicate that the resulting configurations are less reactive than the case of a flooded, intact canister with degraded fuel.

The product of the melt-dilute technology option was evaluated using the SCALE 4.3 family of computer codes, by Westinghouse Safety Management solutions [4]. Preliminary results for degraded configurations of Al-SNF that has undergone the melt-dilute treatment to produce an SNF form of U-Al alloy at ≤ 20% ^{235}U enrichment indicate that criticality is precluded by moderator exclusion in a flooded DOE SNF canister. Analysis of the melt-dilute SNF form in a waste package, in which the DOE SNF canister has degraded, has not yet been completed.

Poison Options

Poisons are needed to maintain $k_{eff} < 0.95$ in desired packaging configurations of Al-SNF directly loaded in canisters. Candidate poison materials include isotopes and compounds of boron, gadolinium, hafnium, europium, and zirconium. The following is a brief summary of the current understanding of potential poison materials as described by Anderson and Theilacker [5] and by McDonell and Parks [6].

The most predominantly utilized poison materials are boron and borated metals. Boron used in a boron-stainless steel alloy has been used for discreet burnable poison and control rod applications. This is primarily due to the availability and excellent nuclear characteristics associated with boron. An advantage of boron is that its reaction products, helium and lithium-7, are not radioactive. Further, the cross section of the neutron absorbing isotope of boron, ^{10}B, is inversely proportional to the velocity of the incident radiation, which simplifies boron burnable poison physics calculations when compared with those for silver, hafnium, europium, or indium which have relatively complicated resonance absorption cross sections.

While the reaction products of boron are not radioactive, the production of helium and lithium-7 can cause metallurgical problems in a metal matrix. Boron has low solubility in structural materials such as stainless steel or aluminum. The result of irradiation of metal-boron alloys is accelerated embrittlement of the alloys. The helium gas generated when ^{10}B captures a neutron is extremely mobile and tends to accumulate at points of stress concentration. The lithium generated by neutron capture in ^{10}B puts additional stress on the metal matrix.

Gadolinium has the highest absorption cross section of any element. Gadolinium, however, has very poor corrosion resistance and high solumbility. Typically, it is used as an oxide dispersion in a metal matrix, however, Gadolinia (Gd_2O_3) dispersions are limited for practical purposes to about 40 percent by volume. Gadolinia has been used in transport/shipment casks as a criticality control material.

Silver-base alloys were first considered for power reactor application in 1950. Early work was based on alloys of silver containing 20 to 40 percent cadmium, which has good corrosion resistance, plus small amounts of other elements, such as copper, to add strength. These early alloys exhibited poor corrosion resistance in high temperature water and tended to lose weight during corrosion and, thus, release their high activity nuclides to the coolant. Europium has also found use as a control material in power reactors. Europium has the unique quality that capture of a neutron by ^{151}Eu begins a chain of four daughter isotopes that each have relatively high absorption cross sections. This quality provides for a relatively long-lived absorber material. Problems with europium include cost and scarcity. Further, due to its high vapor pressure and relatively low melting point, europium is difficult to alloy with common reactor materials such as stainless steel and zirconium. Zirconium alloys have found extensive use in light water reactors based entirely upon their excellent high temperature mechanical properties and their good corrosion resistance. Zirconium has a very low absorption cross section, and this is its major disadvantage with respect to criticality control. Of the materials considered for control rod application, hafnium is the least complicated metallurgically. In its pure form, hafnium has about the strength of Zircaloy-2 and about one third its corrosion rate in 500 to 600 °F water. Hafnium, therefore, requires no cladding or protective plating for water-cooled reactor application. The disadvantages of hafnium are primarily economic rather than difficulties with performance. The only significant source of hafnium is from zirconium ores that contain only about 2 percent hafnium by weight. However, the absorption cross section of hafnium is more than 500 times that of its sister element, zirconium.

Poison Viability Considerations

The governing regulations forbid the inclusion of pyrophoric, combustible, explosive, or chemically reactive materials in waste packages to be disposed at Yucca Mountain. Therefore, it is important to consider the chemical behavior of candidate neutron absorbing

material in expected repository environments. In addition, the chemical compatibility of candidate neutron poison material with the SNF form, the DHLW, and the waste package materials and components, including disposable canister materials and basket structural materials, must be evaluated.

The first approach is to have a poison material that will remain intact long after the aluminum base SNF has degraded, while the second approach is to have a poison material that will degrade concurrently with the SNF.

Neutron absorbing materials can be dispersed in stainless steel or some other corrosion resistant material or clad with stainless steel or other noble material (e.g., nickel plating of the silver-base alloys). These neutron-absorbing materials would be more corrosion resistant than the aluminum-base SNF meat and cladding materials. Based upon their relative positions in the galvanic series, these neutron absorbing materials would also be expected to be noble (passive) to the aluminum-base materials in the event of the development of a galvanic cell. Therefore, the neutron absorbing materials can be expected to remain intact as the aluminum-base SNF degrades and reconfigures.

In the second case, of the borated aluminum alloys, we would expect the corrosion rate of the neutron absorber material to be similar to the corrosion rate of the SNF material. Therefore, the poison material would degrade and perhaps reconfigure with the SNF. These two groups of poison materials represent two different approaches to criticality control in the SNF canister.

The first approach is easy to model with time since we know where the degrading materials are likely to collect. The second approach, however, requires a very complex modeling effort. In this scenario, the desire is that the neutron absorbers will degrade at a rate comparable to the SNF and that the degraded SNF will reconfigure in such a way that incorporates the poison material. However, using a neutron absorbing material that will degrade at the same rate as the fissile materials requires that the neutron absorbing material remain insoluble, with respect to the fissile material. Soluble material will be flushed from the waste package at a rate that corresponds to its relative solubility. Material with higher solubility is more likely to be dissolved in solution and washed from the waste package. Therefore, it is required that the neutron absorbing material used for criticality control be insoluble relative to the fissile constituents of the SNF. The result of using an insoluble neutron absorbing material would be criticality control within the waste package even after significant degradation of the SNF and the neutron absorbing material has occurred.

Neutron absorbing materials for loading in Al-SNF canisters have been assessed as a method for avoiding criticality with HEU SNF. Candidate materials include borated stainless steel, dispersions of europium oxide, gadolinium oxide, gadolinium phosphate, or samarium oxide in stainless steel, and cadmium. Chemical and mechanical properties, corrosion resistance, neutron absorption properties, cost, and availability are the major factors evaluated for narrowing the list of candidate materials to a manageable few candidate materials that are included in the experimental program described below. The reduced list of candidate poison materials being considered further include borated stainless steel, borated carbon steel, gadolinium oxide and gadolinium phosphate dispersions in carbon steel and in stainless steel, and boron and gadolinium forms in an aluminum matrix. Results of this testing program will provide input to the selection of the optimum poison material for the disposition of Al-SNF.

The efficacy of a specific poison material is controlled primarily by the material's degradation rate relative to the degradation rate of the Al-SNF and structural material under repository conditions. Other important properties include the material's susceptibility to selective leaching of the poison material from the structural material matrix and its susceptibility to enhanced corrosion due to galvanic cell formation. Further, it is important to identify the degradation products of the poison material and the relative solubility of these products at repository relevant oxygen potential and pH values with respect to the fissile constituents of the Al-SNF degradation products.

Estimation of the products formed by degradation of the waste package contents is a complex process that simultaneously considers many factors. Thermochemical and kinetic analyses must include all possible soluble species, chemical reactions among them, formation of complexes, precipitation of amorphous, colloidal, or crystalline substances, changes in water composition especially those that control pH and oxidizing potential, the influence of the radiation field, and temperature changes in the water as it moves into the waste WP. Unfortunately, reliable thermochemical data do not exist for all of the uranium or poison compounds of interest [7]. The most likely uranium and aluminum compounds would be the hydrated oxides and silicates of uranium and hydrated aluminum oxides or alumino-silicates. Little difference is between direct and melt-dilute products as the basic alloy phases are the same.

Corrosion Test Program

An experimental corrosion program is designed to evaluate the compatibility of boron and gadolinium poison material with Al-SNF materials in repository environments. The first stages of the program will address the relative corrosion rates of the matrix materials, stainless steel, carbon steel, and aluminum, in a vapor environment. The relative corrosion rates of the matrix materials will be evaluated for exposure durations of up to one year. The materials are being exposed to various water-vapor chemistries and at different temperatures. The current chemistries include synthetic J-13 and condensate water vapor, but will be expanded to include irradiated vapor and chloride chemistries. The current temperatures include 50, 100, and 200°C water vapor for the J-13 chemistry, and 100°C water vapor for the condensate chemistry.

This report presents the current state of experimental testing that is being carried out to determine the degradation properties of the modified list of candidate poison materials. These tests include vapor corrosion and aqueous corrosion tests. The tests utilize J-13 and modified J-13 water chemistry to simulate the chemistry effects due to the radiolytic decomposition of water, to the degradation of HLW glass logs, and the infiltration of chlorides into the waste package. Also, galvanic corrosion tests will be conducted in the test program. Aqueous corrosion tests include both static and flow tests as described below.

Static tests will be conducted to measure the following properties/behavior of candidate poison materials: selective leaching, dissolution rates, and corrosion. Static tests are commonly used for corrosion studies and are generally referred to as immersion or coupon testing. The American Society for Testing and Measurements has a standard practice for conducting such tests (ASTM G31-72 (reapproved 1985)). Various analysis techniques must be used in conjunction with the test to measure the desired properties.

Flow testing will be conducted to determine both the dissolution and corrosion characteristics of candidate poison materials for inclusion in a codisposal waste package. Flow tests had been used previously to study the dissolution response of commercial spent fuel. Flow test parameters included water composition, temperature, flow cell design, and flow rate. These parameters are expected also to effect both the dissolution rate and corrosion of candidate poison materials.

The corrosion and stability of candidate poison materials, which may impact the efficacy of the neutron absorbing material, will be assessed through accelerated electrochemical testing. The electrochemical technique, an accepted standard test method, identifies and characterizes the modes of corrosion for a given material/environment system. The electrochemical tests to be used involve controlling a potential applied to a sample and measuring the responding current. The relationship between the current and potential is a function of the active corrosion mechanisms. The electrochemical testing will be followed by metallographical analysis of the sample to characterize both the microstructural dependence of corrosion and the morphological changes from corrosion.

The current vapor corrosion experiments include 2-inch x 0.75-inch x 1/8-inch coupons. The materials include Al6061, A516Gr55, and SS316L. The coupons were obtained from Metal Samples. They have a 600-grit finish and have been given unique labels. The tests include coupled and uncoupled test specimens according to the test matrices provided in Table 1 and Table 2.

Table 1 Test Matrix for Uncoupled Specimens

Material	Temperature	Chemistry
Al6061	100°C	Condensate
	50°C	J-13
	100°C	J-13
	200°C	J-13
A516Gr55	100°C	Condensate
	50°C	J-13
	100°C	J-13
	200°C	J-13
SS316L	100°C	Condensate
	50°C	J-13
	100°C	J-13
	200°C	J-13

Table 2 Test Matrix for Coupled Specimens

Couple	Temperature	Chemistry
Al6061/Al6061	100°C	J-13
Al6061/A516Gr55	100°C	J-13
Al6061/SS316L	100°C	J-13
A516Gr55/SS316L	100°C	J-13
A516Gr55/A516Gr55	100°C	J-13
SS316L/SS316L	100°C	J-13

The uncoupled specimens are degreased, cleaned, and then weighed prior to exposure. They are then mounted in vapor corrosion capsules (see Figure 1 and Figure 2) in preparation for exposure. The capsules are EM welded, backfilled with the appropriate water chemistry, and then placed in an oven at the appropriate temperature.

Figure 1 Stainless steel capsule, constructed of two pipe caps

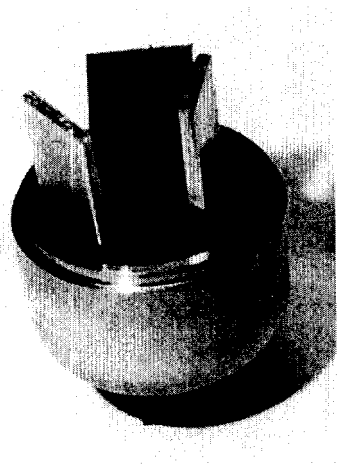

Figure 2 Three corrosion coupons are mounted in each capsule

Coupons for the coupled, vapor corrosion tests require additional machining in preparation for exposure. The coupons are sent to the machine shop at SRTC to have two 1/8-inch diameter holes drilled in them that are used to connect the coupons. The coupons are then degreased, cleaned, and weighed prior to exposure. The coupons are connected using two Carpenter 20b3 fasteners that are inserted through Teflon washers and spacers as depicted in Figure 3. The couple is then weighed and then mounted in vapor corrosion capsules in preparation for exposure. The capsules are EM welded, backfilled with J-13 water, and then in an oven at 100°C.

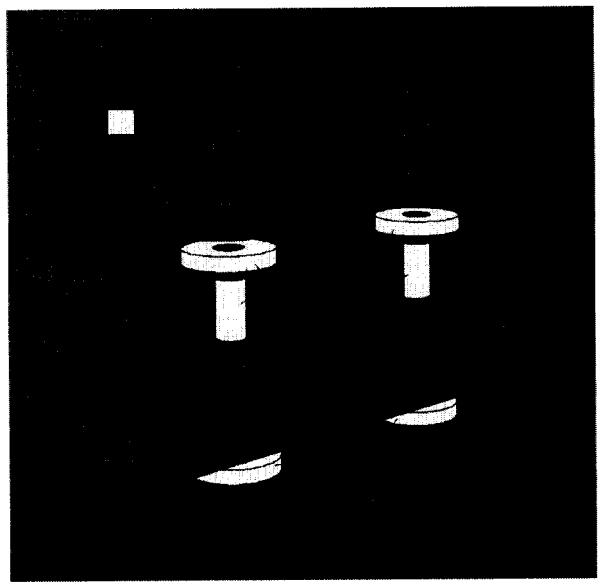

Figure 3 Schematic of the configuration of coupled coupons

The exposure capsules, with their contents are produced in quintuplicate to allow the periodic removal of samples at five predetermined time intervals. The time intervals being used in this program are 1 week, 1 month, 3 months, 6 months, and 1 year.

REFERENCES

1 *Evaluation of Codisposal Viability for Aluminum-Clad DOE-Owned Spent Fuel: Phase I Intact Codisposal Canister*, Document Identifier Number (DI#): BBA000000-01717-5705-00011 REV 01, Civilian Radioactive Waste Management System Management and Operation (June 9, 1997).

2 *Evaluation of Codisposal Viability for Aluminum-Clad DOE-Owned Spent Fuel: Phase II Degraded Codisposal Waste Package Internal Criticality*, Document Identifier Number (DI#): BBA000000-01717-5705-00017 REV 00, Civilian Radioactive Waste Management System Management and Operation (December 15, 1997).

3 *US Code of Federal Regulations, Chapter 10, Part 60.*

4 *Criticality Evaluation of DOE SNF Codisposal Canister with Melt and Dilute MTR Fuel*, S. M. Revolinski, Westinghouse Safety Management Solutions, WSMS-CRT-98-003, Rev. 03 (February 27, 1998).

5 W. Kermit Anderson and J. S. Theilacker, *Neutron Absorber Materials for Reactor Control*, p. 2, United States Atomic Energy Commission, Washington, DC (1962).

6 *Repository Emplacement Costs for Al-Clad High Enriched Uranium Spent Fuel*, **Proceedings of the Topical Meeting on DOE Spent Nuclear Fuel – Challenges and Initiatives**, W. R. McDonell, and P B. Parks, Salt Lake City Utah, pp. 507 – 528 (December 13-16, 1994).
7 *Alternative Aluminum Spent Nuclear Fuel Treatment Technology Development Status Report (U)*, Savannah River Technology Center, WSRC-TR-97-00345 (October 1997).