**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

**Disclaimer:**

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.
Demonstration of Chemical Decladding and Disposition Options of Non-Al Clad Fuels at the Savannah River Site

Anthony B. Thompson, DeWayne Dick (co-presenters), Tracy Rudisill, Gene Daniel, Michael Devore, Martine Duff, Laura Tovo, Michael Bronikowski (PI/corresponding author)

Savannah River National Laboratory, Aiken, SC

Abstract

The Savannah River Site’s H-Canyon processes aluminum-clad fuels from foreign and domestic research reactors to recover enriched uranium. However, there is an extensive inventory of non-Al-clad fuels currently in the storage basin, many of which are damaged or at risk of failure. Most of these are clad with stainless steel or Zircaloy, which are incompatible with H-Canyon’s process chemistry. Development of decladding methods is therefore critical to the waste cleanup mission at SRS. Here we demonstrate the dissolution of stainless steel using the SULFEX process developed at Oak Ridge and the dissolution of Zircaloy using the ZIRFLEX process developed at the Hanford Site. Dissolution and offgassing rates are consistent with previous studies and show that these cladding materials can be processed even below reflux conditions. Waste streams have been treated and quantified, providing valuable information for potential future process development in H-Canyon. This study has demonstrated that the technology may be feasible in the near term for processing smaller damaged fuels in the SRS hot cells.

Saxton fuel (left) and various damaged fuels (right) are among the variety of fuels stored in SRS L-basin. Damaged or undamaged fuels can be processed by selective cladding dissolution.

Objectives

• Demonstrate processes for chemical decladding of non-Al clad fuels
  - DAREX – refluxing HCl/HNO3
  - SULFEX – refluxing H2SO4
  - ZIRFLEX – refluxing NH4F/NH4NO3
• Determine suitability for H-Canyon implementation
  - Verify previous work done at ORNL and Hanford
  - Define waste streams and offgassing components/rates

Experimental Methods

• Flowsheet down-selection based on literature review
  - DAREX: (M = Fe, Ni)
    M+HNO3+3HCl → NOCl+MCI2+2H2O
    HNO3+3HCl → Cl2+H2O+3NOCl

  - SULFEX: (M = Fe, Ni)
    M+H2SO4 → MSO4+H2
    2Cr2(OH)3+3HNO3 → Cr2O3+H2SO4+6H2O

  - ZIRFLEX
    Zr+6NH4F+0.5NH4NO3 → (NH4)2ZrF6+3NH4Cl
    Potentially suitable with new dissolver

• Small-scale testing to ensure safety
  - SULFEX dissolution waste
  - ZIRFLEX dissolution in progress

• Design of glass dissolver
  - Condenser w/ recirculating ice bath
  - Thermometer/ thermocouple
  - Air purge
  - Sample basket

Results and Discussion

• Dissolution rates at 100 °C (slightly below reflux)
  - SULFEX dissolution resulted in a deep blue solution of inorganic sulfates. At 4M and 8M H2SO4, a 20-ml SULFEX cladding (e.g. Consolidated Edison fuel) would be totally dissolved in 2h10m and 45m, respectively.

• Offgassing studies with Raman cell
  - SULFEX experiments (left) indicated nearly pure H2 offgas that tracked with theoretical offgassing rates expected from the dissolution rate plots. ZIRFLEX experiments detected NH3 at lower concentrations than expected, likely due to it condensing in the cold condenser before reaching the Raman cell. These results are quantitatively consistent with data from ORNL1 (top right).

• Waste generation
  - The SULFEX process resulted in a deep blue solution with a light blue deposit on the reactor walls. The solution produced large crystals of sodium sulfate upon neutralization.

• Comparison to existing data
  - Although SULFEX offgassing rates were consistent with ORNL data (see above), initial rates (left) were lower than those reported at ORNL.2 ZIRFLEX initial dissolution rates (right) were consistent to within 20% of Hanford data.2 Initial rate of dissolution is known to depend strongly on the extent of surface oxidation, and temperature was slightly lower in these studies (100 °C vs. reflux).

Conclusions

• SULFEX and ZIRFLEX are feasible routes for processing non-Al clad fuels
  - Corrosion studies needed to select new dissolver materials for H-Canyon
  - Process development needed for handling waste streams in H-Canyon
  - Data consistent with previous in-depth studies at ORNL and Hanford
  - Could be suitable for processing smaller non-clad fuels in hot cells

References