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Demonstration of Chemical Decladding and Disposition Options of Non-Al Clad Fuels at the Savannah River Site

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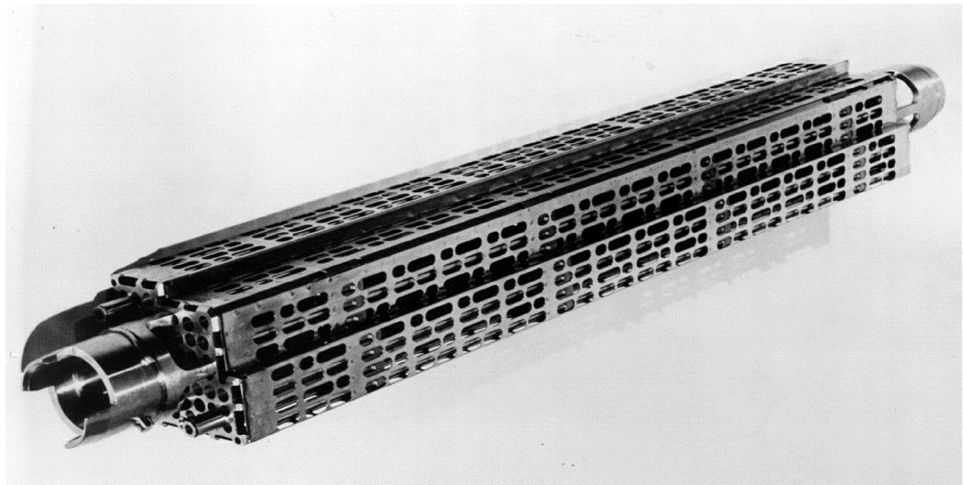
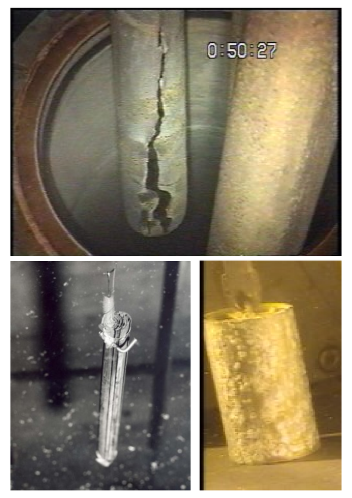
Abstract

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.

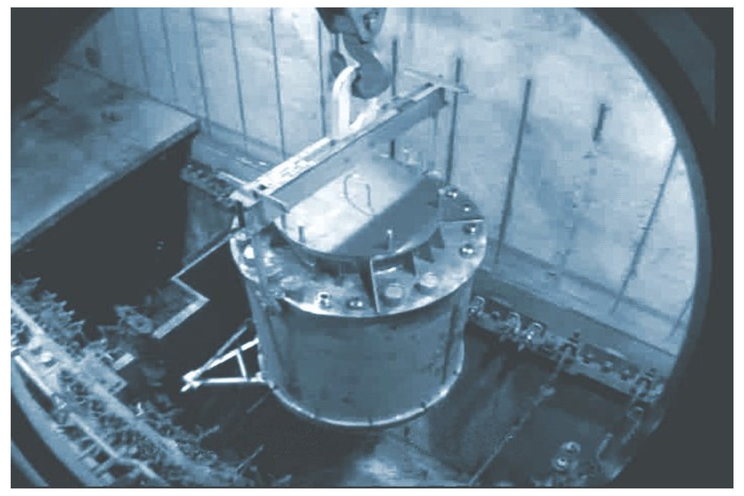
Objectives

- Demonstrate processes for chemical decladding of non-Al clad fuels
  - DAREX – refluxing HCl/HNO_3
  - SULFEX – refluxing H_2SO_4
  - ZIRFLEX – refluxing NH_4F/NH_4NO_3

  ← Stainless steels (e.g. 304L) [DAREX, SULFEX]

  ← Zr alloys (e.g. Zircaloy-2) [ZIRFLEX]
- Determine suitability for H-Canyon implementation
  - Verify previous work done at ORNL and Hanford
  - Define waste streams and offgassing components/rates

L-basin storage pool



H-Canyon dissolver

Experimental Methods

• Flowsheet down-selection based on literature review

DAREX: (M = Fe, Ni)

$M + HNO_3 + 3HCl \rightarrow NOCl + MCl_2 + 2H_2O$

$HNO_3 + 3HCl \rightarrow Cl_2 + 2H_2O + NOCl$

$M + 2HNO_3 + 2HCl \rightarrow MCl_2 + 2H_2O + 2NO_2$

$M + 6HNO_3 \rightarrow M(NO_3)_3 + 3NO_2 + 3H_2O$

Analogous reactions for Cr

Chloride species are known to cause crevice corrosion and pinhole formation in stainless steels; therefore, DAREX is incompatible with process piping in H-Canyon and was not further explored in this project.

SULFEX: (M = Fe, Ni)

$M + H_2SO_4 \rightarrow MSO_4 + H_2$

$2Cr + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2$

Potentially suitable with new dissolver

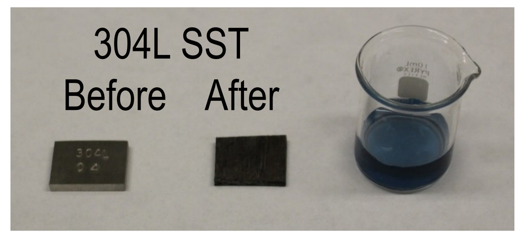
ZIRFLEX:

$Zr + 6NH_4F + 0.5NH_4NO_3 \rightarrow (NH_4)_2ZrF_6 + 5NH_3 + 1.5H_2O$

Potentially suitable (ensure offgas compatibility)

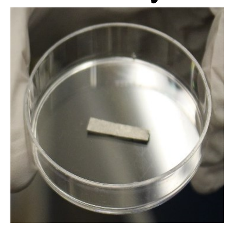
• Small-scale testing to ensure safety

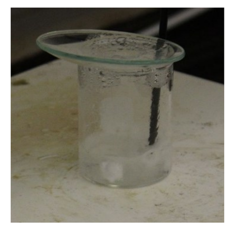
SULFEX dissolution waste



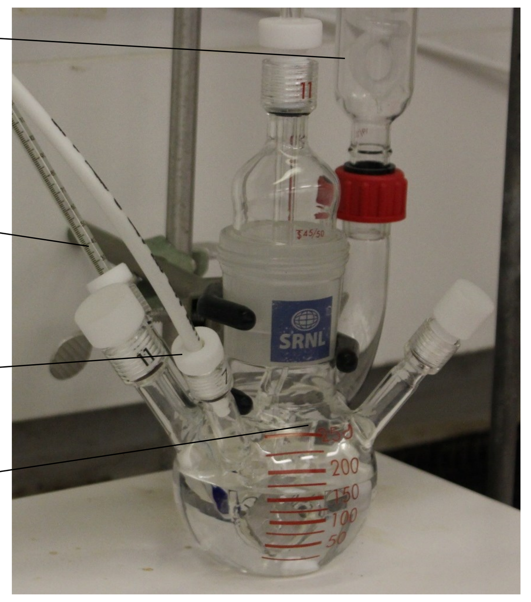
Zircaloy-2

ZIRFLEX dissolution in progress



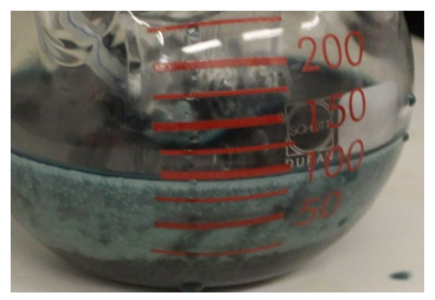


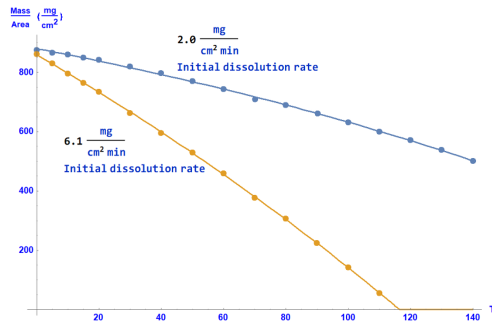
• Design of glass dissolver



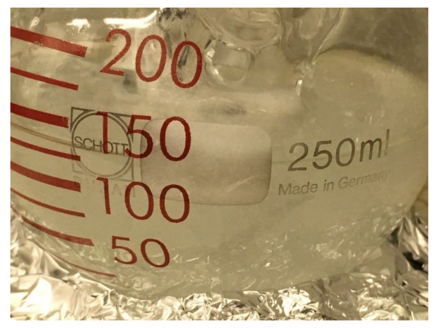
Results and Discussion

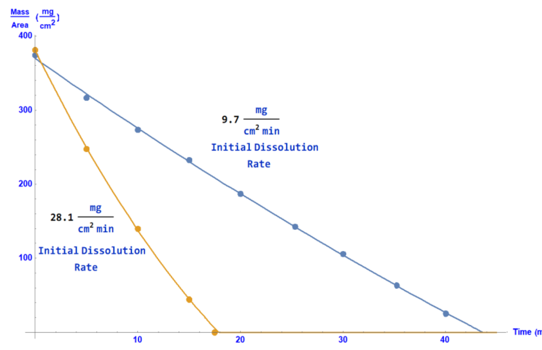
• Dissolution rates at 100 °C (slightly below reflux)





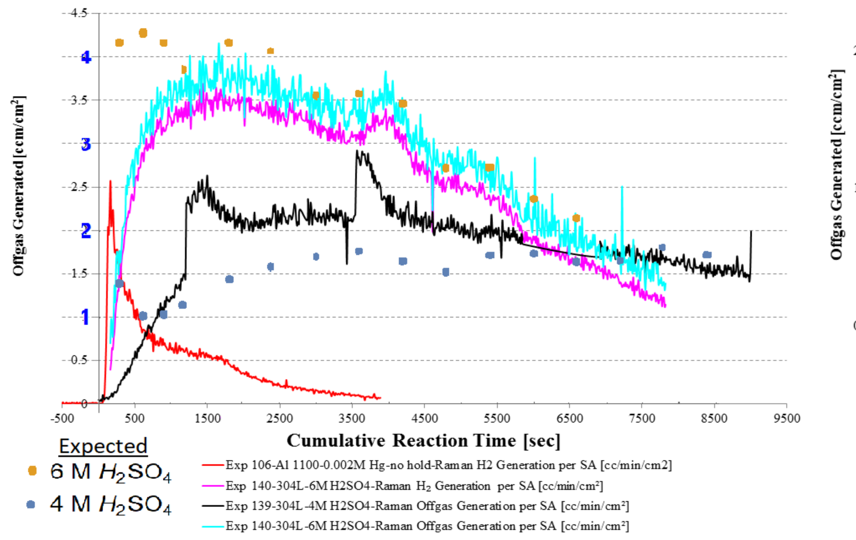
SULFEX dissolution resulted in a deep blue solution of iron/metal sulfates. At 4M and 6M H_2SO_4, a 20-mil 304L cladding (e.g. Consolidated Edison fuel) would be fully dissolved in **2h10m** and **45m**, respectively.

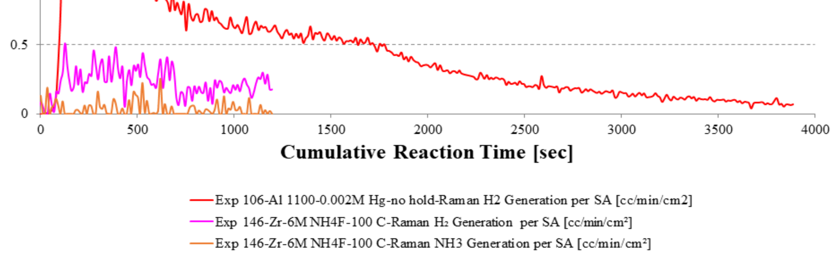


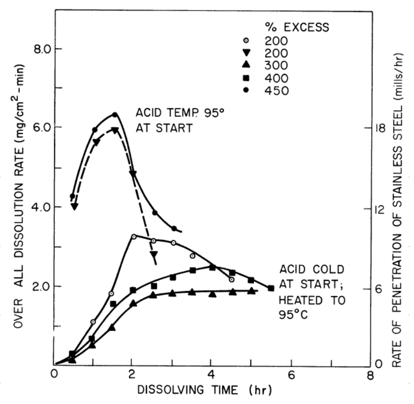


Rapid dissolution and significant offgassing were observed in the ZIRFLEX dissolution. At 4M/0.5M and 6M/1M NH_4F/NH_4NO_3, a 27-mil Zr-2 cladding (e.g. PWR blanket fuel) would be fully dissolved in **40m** and **17m**, respectively.

• Offgassing studies with Raman cell







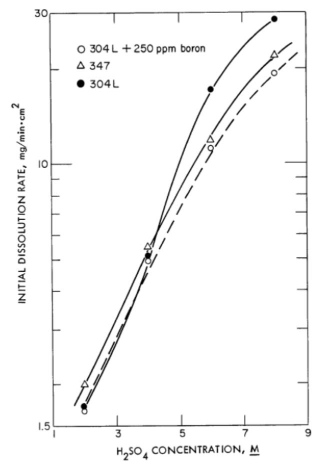
SULFEX experiments (left) indicated nearly pure H_2 offgas that tracked with theoretical offgassing rates expected from the dissolution rate plots. ZIRFLEX experiments detected NH_3 at lower concentrations than expected, likely due to it condensing in the cold condenser before reaching the Raman cell. These results are quantitatively consistent with data from ORNL[1] (top right).

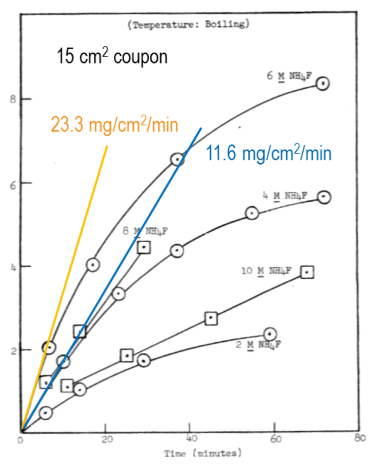
• Waste generation

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.

The ZIRFLEX process resulted in a clear neutral solution to which $Al(NO_3)_3$ was added to complex the residual F^- in solution The resulting slightly acidic solution was neutralized with caustic, producing a significant amount of white precipitate.

• 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.[3] 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 small damaged non-Al clad fuels in hot cells

SRNL is a U.S. Department of Energy National Laboratory operated by Savannah River Nuclear Solutions.

References:

1. Flanary, J.R. *et al.*, Development of the SULFEX Process for Decladding Stainless-Steel-Clad Power Reactor Fuel Elements with Sulfuric Acid. ORNL-2461, Oak Ridge, TN, 1959.
2. Ferris, L.M. and Kibbey, A.H. Laboratory Development of the SULFEX Process for the Dissolution of Consolidated Edison Power Reactor Fuel. ORNL-2714, Oak Ridge, TN, 1959.
3. Swanson, J.L. The ZIRFLEX Process. Second United National Conference on the Peaceful Uses of Atomic Energy. A/CONF.15/P/2429, Richland, WA, 1958.