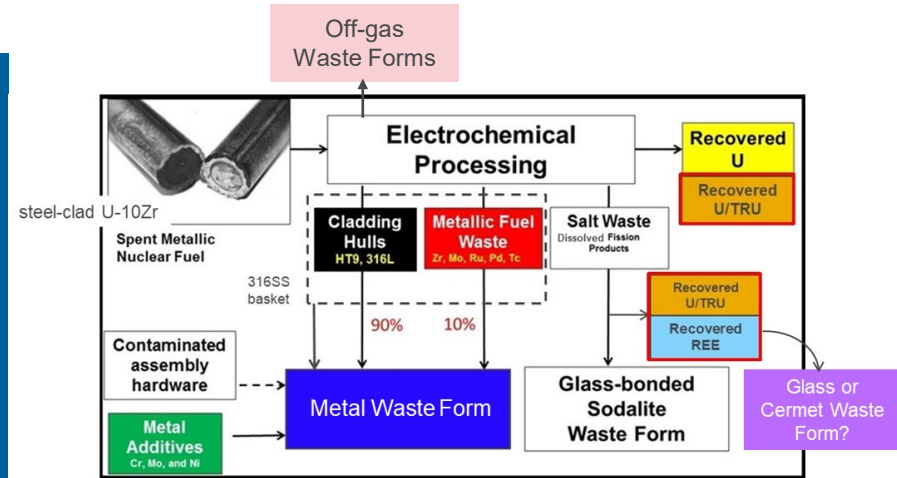


WASTE FORM DEVELOPMENT

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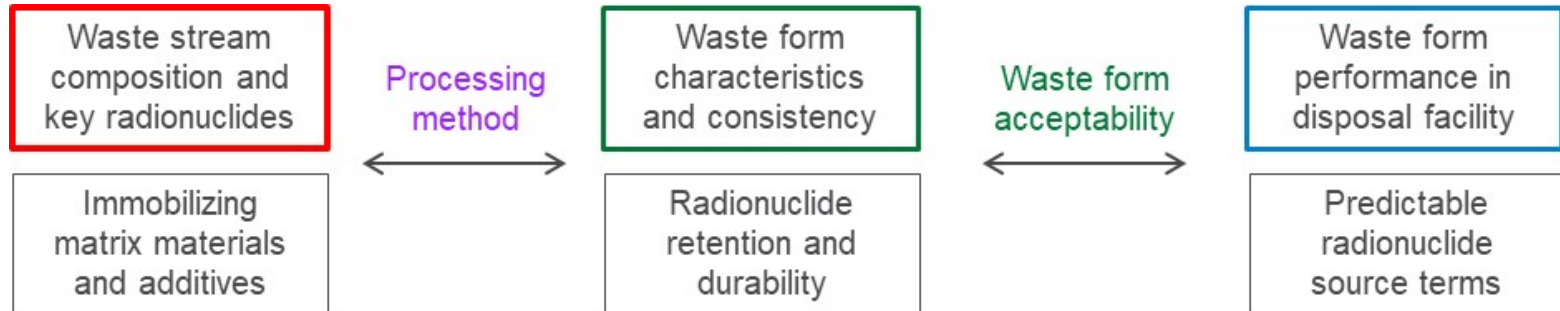
Merits and Viability of Different Nuclear Fuel Cycles and Technology
Options and Waste Aspects of Advanced Nuclear Reactors
National Academy of Sciences Review Panel
December 8, 2020

WASTE FORM DEVELOPMENT APPROACH

- Developing durable waste forms for waste streams generated during fuel production and reprocessing operations and mechanistically-based degradation models to optimize formulations and performance
 - Selecting immobilizing matrix based on waste stream composition and processing limitations
 - Formulating waste forms that immobilize radionuclides in host phases that are durable over wide range of environmental conditions representing potential disposal options (pH, redox, Cl^-)
 - Utilizing multiphase materials to optimize waste loading, durability, and radionuclide retention
 - Utilizing processing controls to achieve consistent waste form products
 - Developing mechanistic understanding of waste form corrosion behavior using material-specific testing to provide confidence in predicted long-term durability and radionuclide source terms
 - Developing source term models for radionuclide release in performance assessment calculations that capture key dependencies on waste form composition and disposal conditions
 - Developing characteristics-based approach for achieving product acceptance

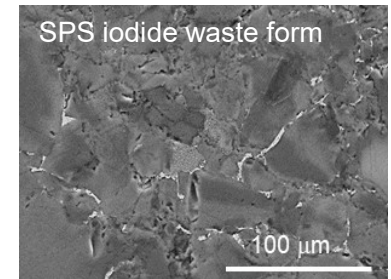
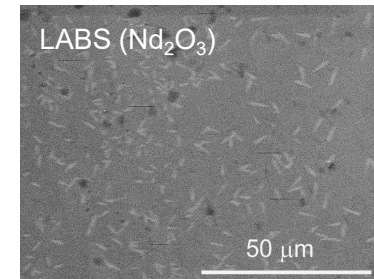
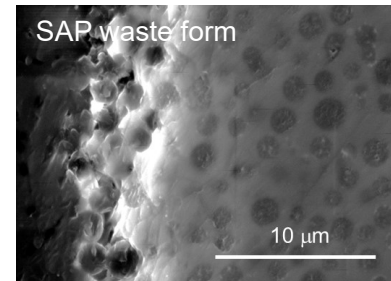
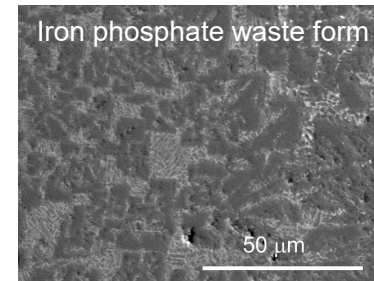
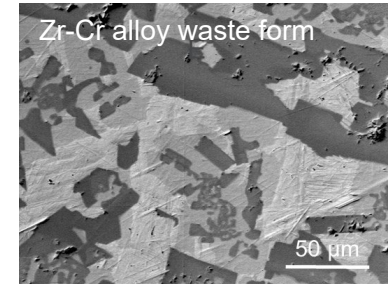
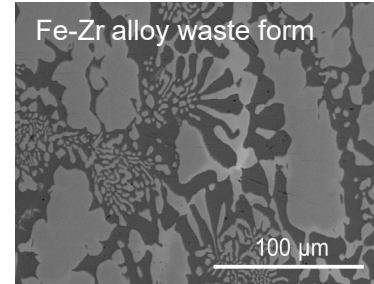
ITERATIVE METHOD AND INTERFACES

- Iterate to meet waste form formulation, production control, and performance objectives
 - Retain radionuclides in waste stream during processing
 - Immobilize radionuclides in durable host phases
 - Control processing variables to achieve consistent waste form products and accommodate anticipated variances in waste streams
 - Ensure characteristics meet storage, transport, and disposal requirements (e.g., thermal loading)
- Interfaces with **fuel reprocessing teams**, **repository development team**, **accountancy**, and **NRC**



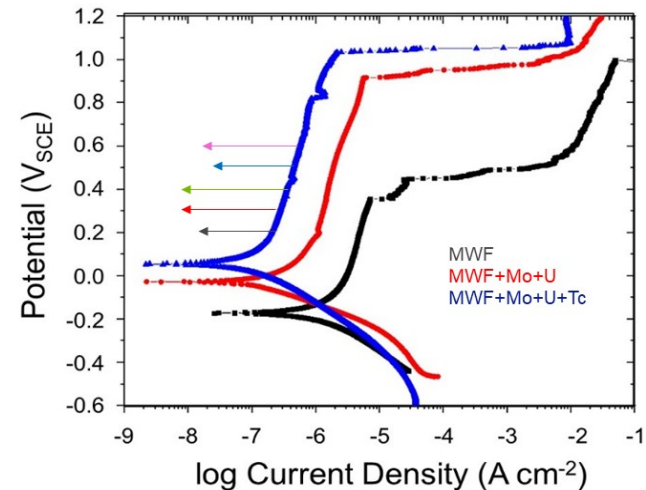
WASTE STREAMS & WASTE FORMS

- Cladding hulls and metallic fuel wastes
 - Multiphase Fe-Zr alloy for steel-clad fuel waste
 - Multiphase Zr-Cr alloy for Zircaloy-clad fuel waste
 - Multiphase Fe-Mo alloy for U-Mo fuel waste
- Chloride Salt wastes
 - Glass-bonded sodalite ceramic waste forms (CWF)
 - Tellurite glass
 - Silica-alumina-phosphate (SAP) glass (ROK)
 - Iron phosphate glass-ceramic
- Oxide wastes
 - Borosilicate glass
 - Lanthanide borosilicate (LABS) glass
 - Alloy-ceramic cermet
- Iodide wastes (captured from off-gas)
 - AgI-bearing composite materials
 - Ag-bearing glass (ROK)



METALLIC WASTE FORM (MWF)

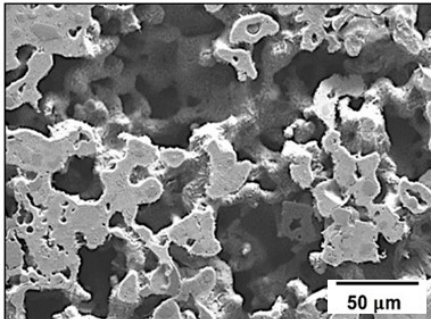
- Metallic waste streams dominated by cladding with small amounts of waste constituents that have high melting points by using eutectic mixtures and alloying to facilitate processing.
- Developed electrochemical test protocol to relate phase composition to corrosion behavior, including effects of passivation and galvanic couples.
- Protocol combines electrochemical methods with metallurgy, microscopy, and solution analyses to understand corrosion mechanism and effects of alloy composition and electrolyte properties to optimize corrosion resistance.
- Identified host phases and added trim metals to enhance durability of MWF made with steel cladding: increase corrosion potential voltage (E_{corr}) and maximize passivation stabilization. Added Mo stabilizes passivation films and improves corrosion resistance of MWFs 100-fold. →
- Passivation-based degradation model developed with terms for solution pH, redox, and chloride content.



Potentiodynamic scans of initial (black) and optimized (blue) MWF in pH 8 10 mM NaCl showing effects of trim and waste elements and benefit of passivation (arrows)

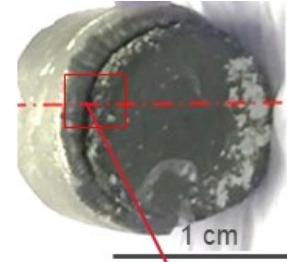
CERMET WASTE FORM

- Metal WF can accommodate oxide wastes as inclusion phases:
 - Residual oxides remaining in metallic fuel waste stream
 - Lanthanides and actinides removed from waste salt
- Oxide wastes are converted to alloys and insoluble zirconates during processing at 1600 °C
- Cermets made with HT9 and 20% mixture of lanthanide oxides + UO_2 generated U-bearing alloys and U-zirconate in durable product
- Porous ceramic lattice phase becomes filled with alloy and overlaid by excess alloy

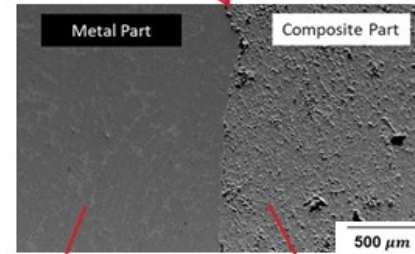


Microstructure of residual ceramic lattice after complete dissolution of alloy.

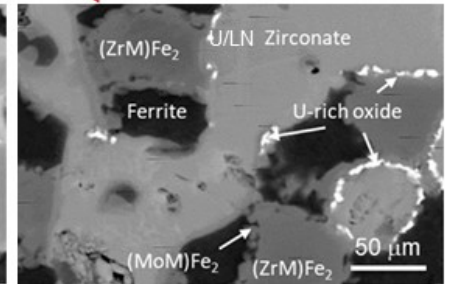
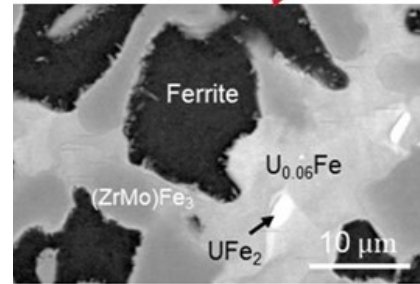
Ceramic lattice extrudes molten alloy as it densifies during production.



U-cermet cast from mixture of metal and oxide powders generates composite center with outer metal (top view)



SEM photomicrograph of interface shows continuity of alloy phases between metal and composite.

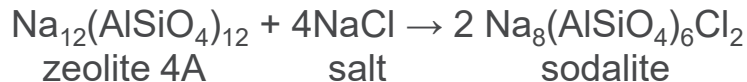


SEM analyses show microstructures of metallic (left) and composite (right) parts of cermet composed of same alloys and predominance of zircaloy.

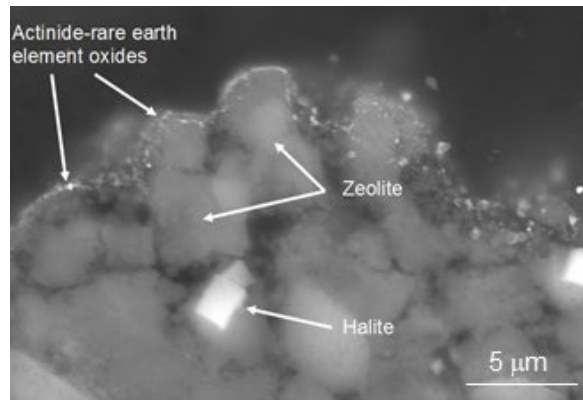
CERAMIC WASTE FORM (CWF)

- Glass-bonded sodalite waste form developed in 1990s for electrorefiner waste salt (LiCl/KCl) because borosilicate glass cannot accommodate chloride

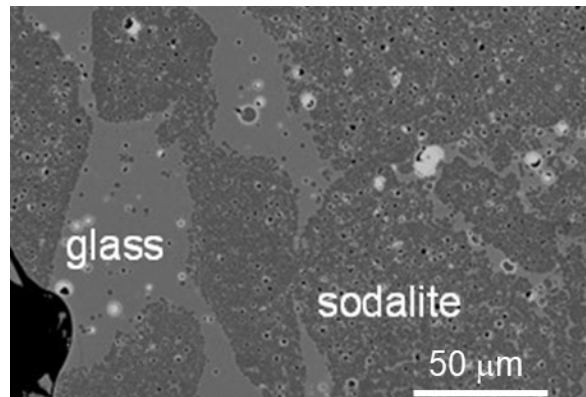
- Sodalite generated by reaction of zeolite 4A with NaCl



- Molten salt occluded in zeolite to facilitate reaction
- Salt-loaded zeolite then mixed with crushed borosilicate binder glass and vitrified
- ~75 vol% sodalite encapsulated in ~25 vol% glass
- Sodalite sequesters Cl, I, and most Na
- Other salt cations dissolve in glass; oxides and halite form inclusion phases
- Waste loading limited by stoichiometry of sodalite and volume of glass required to encapsulate it



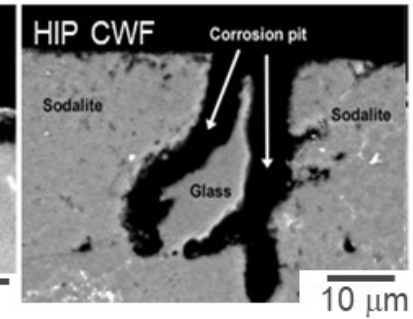
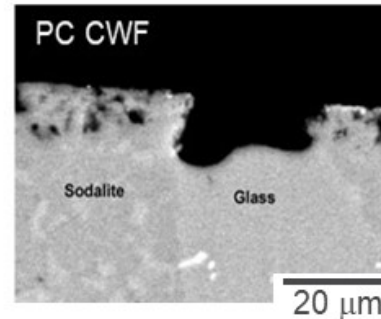
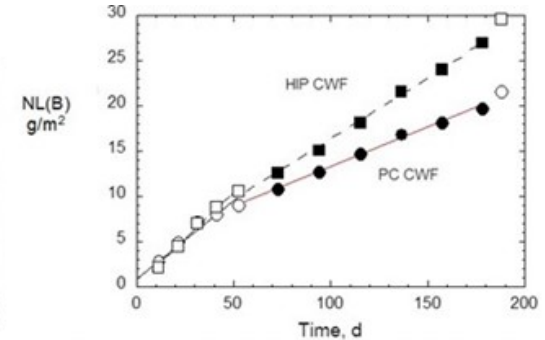
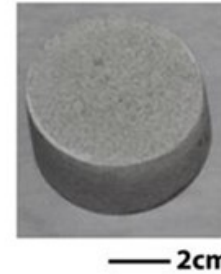
SEM photomicrograph of salt-loaded zeolite



SEM photomicrograph showing CWF microstructure

CERAMIC WASTE FORM DEGRADATION

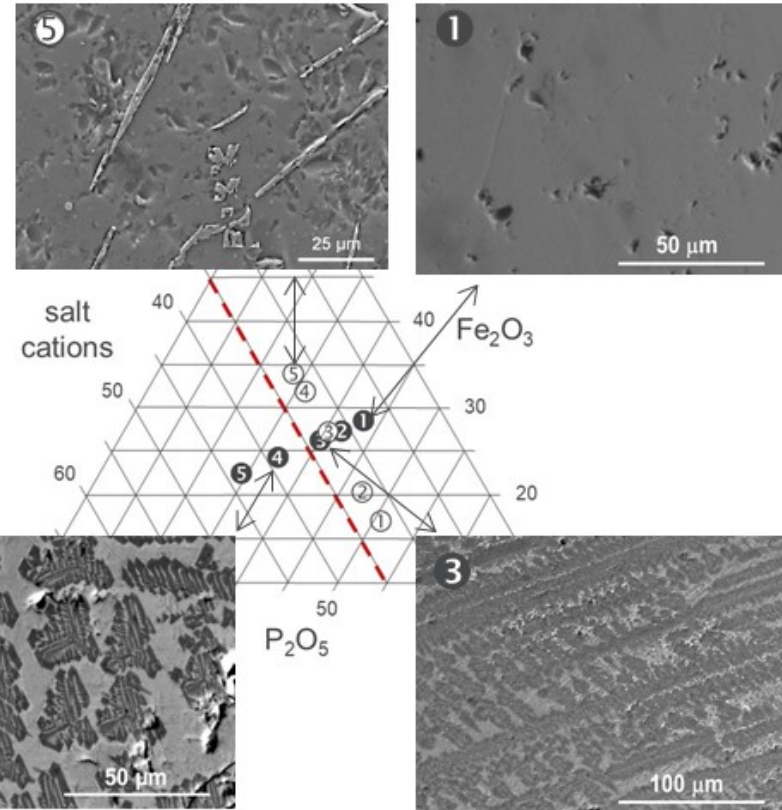
- Many 50-g developmental CWF lab samples made for testing by using hot isostatic press (HIP) and pressureless consolidation (PC) methods
- Several test methods used to understand the degradation mechanism, develop and parameterize degradation model:
 - instantaneous dissolution of halite when contacted by water, slow dissolution of sodalite and glass phases
- Sodalite and glass have similar kinetic dissolution rates, but sodalite dissolution is solubility limited →
- Long-term degradation modelled by using HLW borosilicate glass model (Stage 3 behavior due to zeolite precipitation and growth does not occur)



Photomicrographs of cross-sectioned PC CWF and HIP CWF after degradation in ASTM C1308 tests with 110 ppm H_4SiO_4

IRON PHOSPHATE WASTE FORM

- Iron phosphate waste form being evaluated as alternative to ACWF for salt waste
- Step 1: Reaction with phosphate to dehalogenate salt and immobilize salt cations in waste form by using $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, or H_3PO_4
- Recovery and recycle of NH_4Cl being evaluated
- Step 2: Add iron oxide and vitrify to improve durability
- Scoping studies to evaluate processing conditions and determine suitable composition range; study micro-structure, degradation behavior, and durability of final waste form
 - ASTM C1308 tests to measure kinetic rates
 - ASTM C1220 and ASTM C1285 tests to measure solution saturation effects
 - Borosilicate glass model probably appropriate



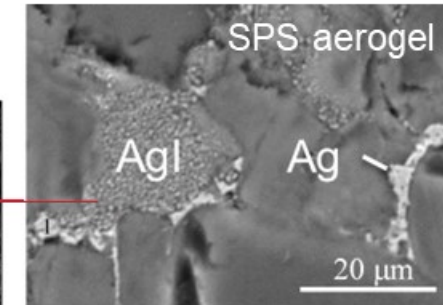
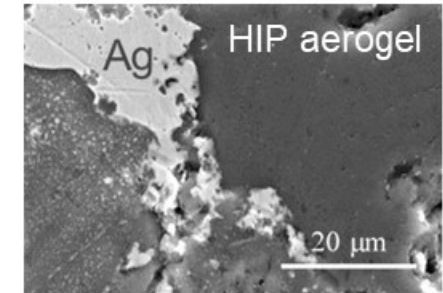
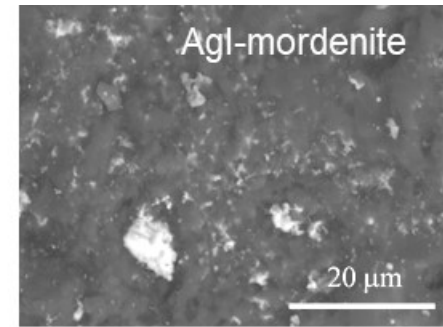
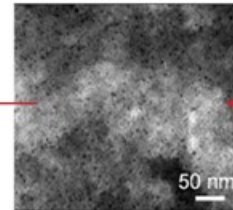
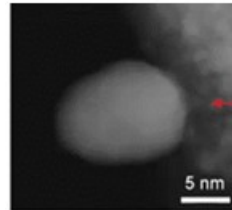
AgI-BASED WASTE FORMS

- Metallic silver dispersed on mordenite or silica aerogel substrates used to capture iodine by generating AgI
- I-loaded material processed by HIPing or spark plasma sintering (SPS) to encapsulate AgI in a densified matrix
- AgI-coated silver particles and excess metallic silver accumulate at grain boundaries; small amounts of AgI encapsulated in grains
- AgI dissolves by chemical and reductive dissolution



- Electrochemical tests being performed to quantify reductive dissolution of AgI under reducing conditions and galvanic couples with metallic silver and steel canister
- Immersion tests performed to quantify effectiveness of encapsulating phase

TEM and SEM images of AgI material microstructures.



STATUS OF WASTE FORMS DEVELOPMENT

Waste Form	Relative State of Development		Key Remaining Issues
Borosilicate glass		X	
Metallic		X	Parameterize model
Glass-bonded sodalite		X	Simplify processing steps
LABS glass		X	Demonstrate waste compatability and processing
Cermet	X		Develop and demonstrate process; parameterize model
Iron phosphate	X		Select, develop, and demonstrate process; complete model
AgI composite	X		Select, develop, and demonstrate process; develop model

CONCLUDING STATEMENTS

- Approach to developing durable waste forms considers compatibility of waste streams with immobilizing matrix, retention of radionuclides during processing, and sequestering of radionuclides in durable host phases.
- Waste form suitability based on waste loading capacity and flexibility, effectiveness of process controls, and predictions of acceptable long-term degradation resistance in disposal environments.
- Chemical durability and degradation behavior measured using tests selected based on degradation mechanism of host phases and modes of radionuclide release. Consensus standard test methods (ASTM) used when appropriate, new methods developed when necessary.
- Interfacing with colleagues developing disposal system models and applying insights gained from developing HLW and LAW glass to meet waste acceptance criteria and from developing waste form degradation models for Yucca Mountain License Application.
- Waste forms developed for pyroprocessing salt are probably suitable for chloride waste salts from MSRs; studies initiated to determine their suitability for fluoride waste salts from MSRs.

ACKNOWLEDGEMENTS

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- Government License Notice -the manuscript has been created by UChicagoArgonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357.