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Partitioning of Fission-Product Iodine During the Electrochemical Treatment of Used EBR-II Fuel

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Partitioning of Fission-Product Iodine During Electrochemical Treatment of EBR-II Fuel

Background
- Importance of the Capture and Immobilization of Fission-Product Iodine
- Experimental Breeder Reactor-II and EBR-II fuel treatment

Iodine Mass Balance in the Electrorefiner

Iodine Partitioning in EBR-II Fuel

Iodine Off-gas During Pyroprocessing
- Iodine off-gas during salt distillation operations
- Iodine off-gas during ceramic waste form production

Iodine Off-gas During Electrochemical Reduction of Oxide Fuels

Summary

Capture and Immobilization of Fission-Product Iodine during Used Fuel Reprocessing

- Iodine has high fission product yield
- ^{129}I very long half life ~ 16 x 10^6 yr
- Extremely mobile in biosphere (very soluble and volatile iodine species)
- Significant biological hazard due to rapid accumulation in thyroid tissue
- Strict regulatory release limits would require extremely efficient capture of iodine from reprocessing facility

Experimental Breeder Reactor-II

- EBR-II was a sodium-cooled, fast reactor located at the INL
  - Operated from 1963 to 1995
  - Highly enriched uranium-10 wt % zirconium driver fuel
  - Depleted uranium blanket fuel for plutonium production
  - Sodium-bonded fuel
  - High burnup experimental fuels (~20 atom % burnup)

- Demonstration test reactor for Integral Fast Reactor Program (1984 to 1995)
- EBR-II Spent Fuel Treatment Demonstration Project performed by ANL from 1996 to 1999
- Pyroprocessing selected by DOE as preferred technology for treating Na-bonded fuel
- Performed at Fuel Conditioning Facility (FCF), Materials and Fuels Complex (MFC), INL
- Inventory treatment of 22.4 tons blanket and 3.1 tons driver fuel initiated 2000 to present
- Cladding breach during reactor operations: ~ 1% iodine-131 escaped into primary Na coolant, 99% retained in fuel, iodine-131 not detected in secondary coolant, cover gas, or steam system.

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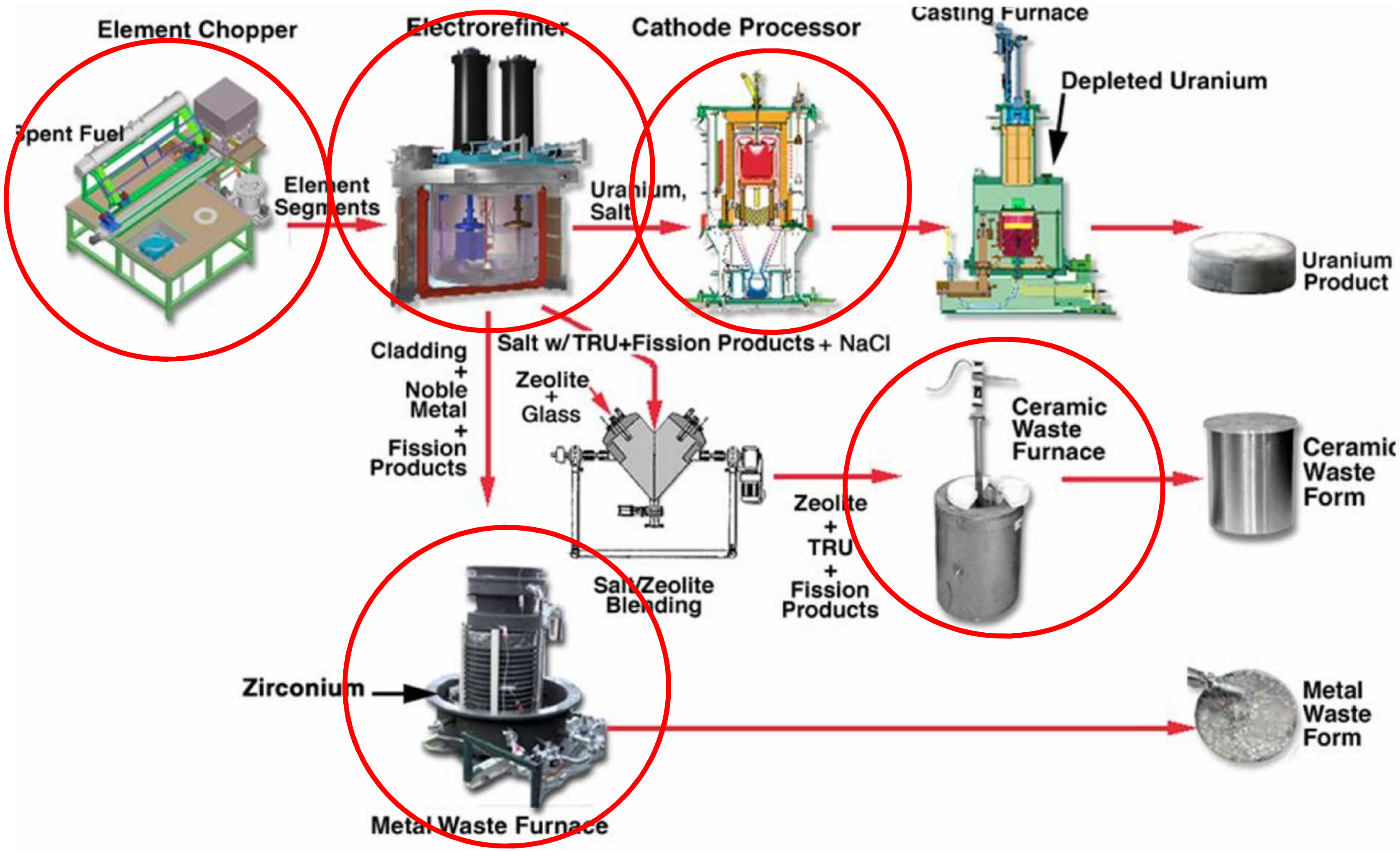
Iodine-129 Release During EBR-II Used Fuel Treatment from the Fuel Conditioning Facility

- Release limits for INL at site boundry (40 CFR 61): total dose of 10 mrem/yr
- Historical release ~0.05 mrem/yr for whole INL site
- Actual radionuclides monitored at FCF stack monitor (contributor of 10% or more total dose emission):
  - H-3
  - Kr-85
  - Total alpha
  - Total beta
- Estimated total I-129 release from FCF during EBR-II used Fuel Treatment:* 8.2×10^{-12} Curies (3.2×10^{-8} g)

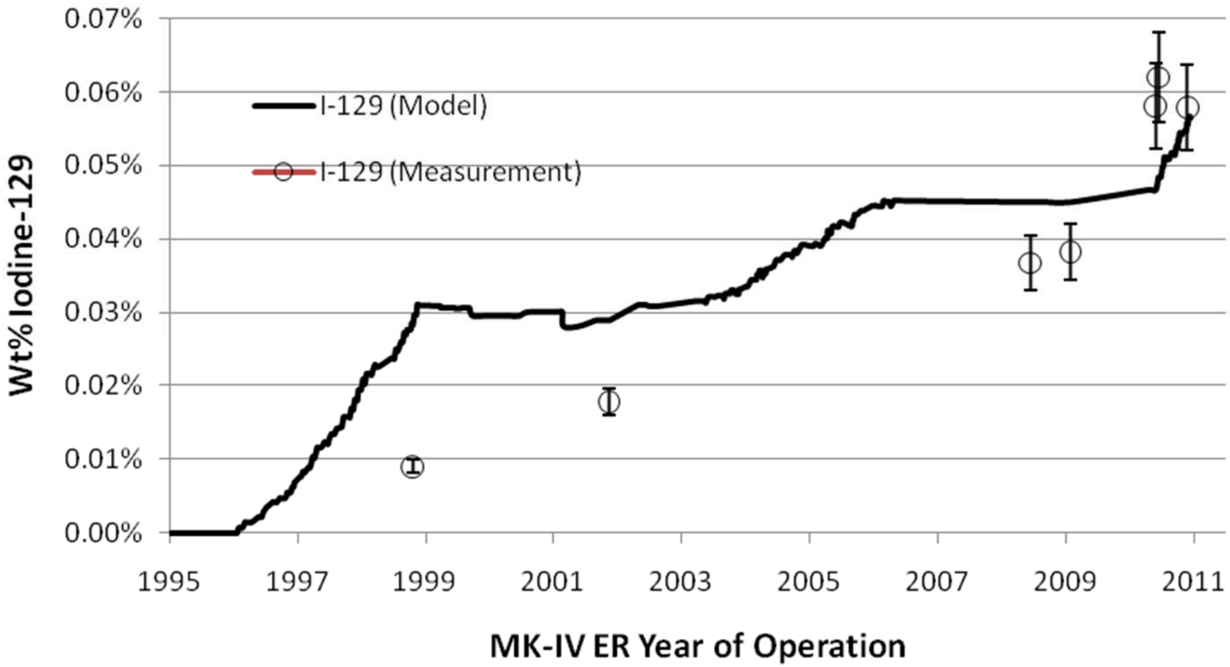
***Final Environmental Impact Statement for the Treatment and Management of Sodium-Bonded Spent Nuclear Fuel, Vol. 2, DOE/EIS-0306, 2000.**

Electrochemical/Pyrometallurgical Treatment of Sodium-Bonded EBR-II Fuel – Potential Points of Iodine Release



Iodine Mass Balance in the Electrorefiner Salt

- Comparison of Mass Tracking System predicted ^{129}I concentration to measured ^{129}I concentration in MK IV Electrorefiner (periodic salt measurements)
- Good agreement between predicted and measured iodine inventory in MK-IV ER
  - Predicted value estimated 20% confidence interval, or greater for ^{129}I. Measurement uncertainty for iodine is ± 10% (2σ)
- MTS also predicts that fission-product iodine will migrate to bond-Na of fuel element.



Iodine Partitioning in EBR-II Fuel and Off-gas Studies

- Due to strict iodine release requirements in US, additional studies are being performed to determine minor iodine release during EBR-II fuel pyroprocessing operations
  - Iodine partitioning in EBR-II fuel
  - Iodine off-gas during salt distillation
  - Iodine off-gas during ceramic waste form production
  - Iodine off-gas during electrolytic oxide reduction

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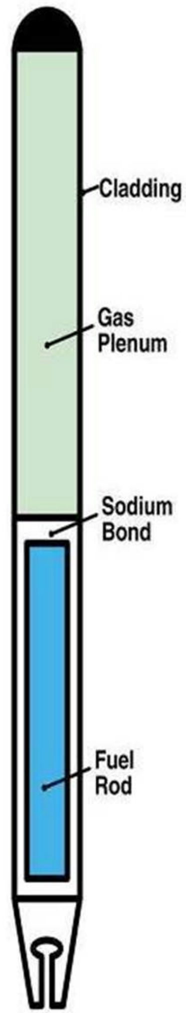
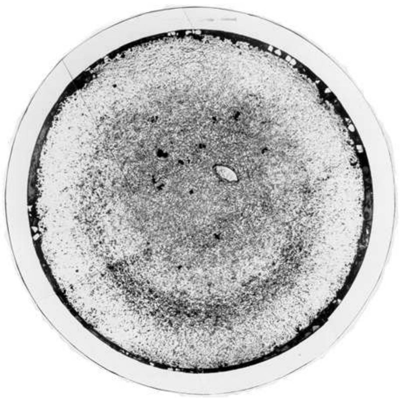
Iodine Partitioning in EBR-II Sodium-Bonded Fuel

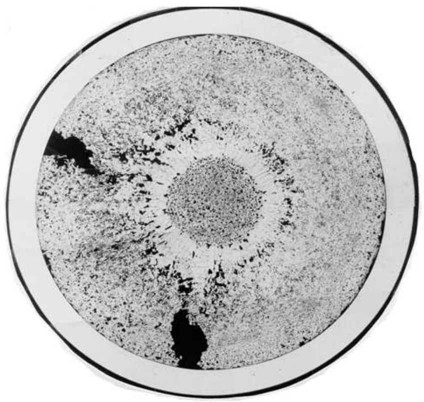
- Driver fuel ~ 10 at% burnup, assume that fission product iodine migrates to bond sodium
- Actual distribution of iodine between fuel and bond sodium unknown



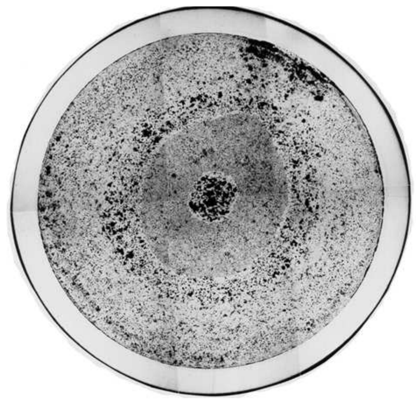
EBR-II Experimental U-20Pu-10Zr Fuel



X423A at 0.9% BU



X419 at 3% BU



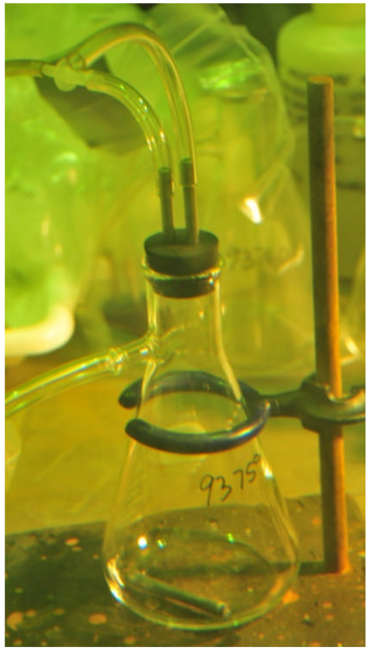
X420B at 17% BU

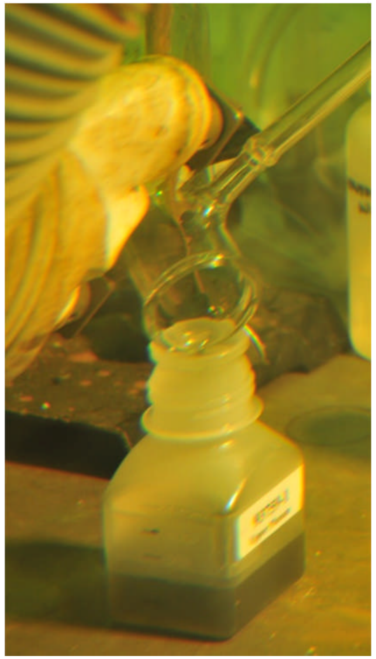
Redistribution of U, Pu and Zr occurs early

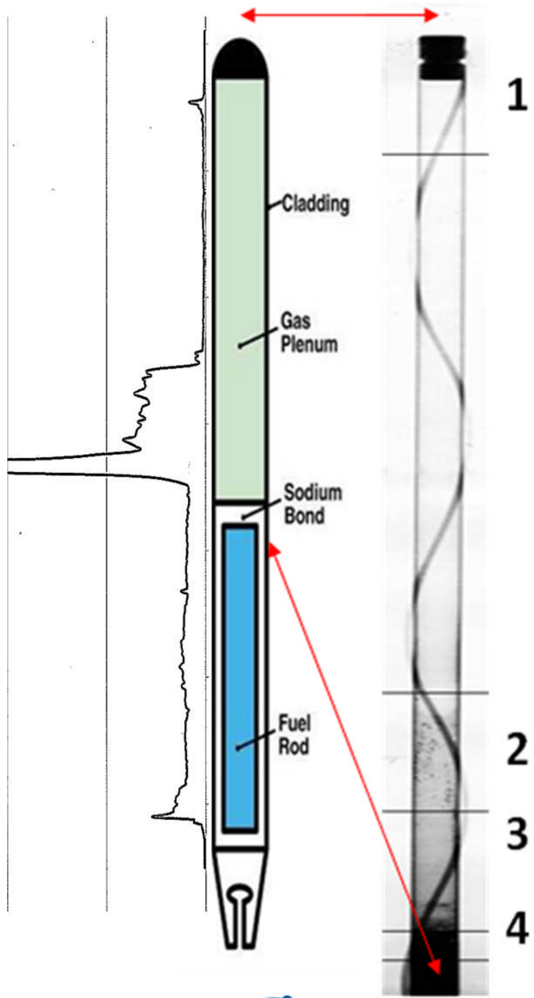
Inhomogeneity doesn't affect fuel life

Iodine Partitioning in EBR-II Sodium-Bonded Fuel

- Current effort directed at measurement of bond sodium region of experimental fuel X430
- Four regions of plenum sampled: top-cap, upper sodium plenum, lower sodium plenum, and fuel/sodium interface
- Sodium dissolved in water
    - Iodine, cesium and lanthanide elemental analysis performed







Iodine Partitioning in EBR-II Sodium-Bonded Fuel

Iodine measurement X430 experimental fuel elements T650 and T660

Fuel Element	Fuel	Lower Plenum Sodium	Upper Plenum Sodium	Plenum End Cap	Plenum Gas	Total Iodine measured	Total Iodine Expected
T659	NA	356 µg	801 µg	5750 µg	NA	6.9 mg	104 mg
T660	Under method development	427 µg	2052 µg	4810 µg	22 µg in plenum fission gas	7.3 mg	104 mg

Iodine Partitioning in EBR-II Sodium-Bonded Fuel

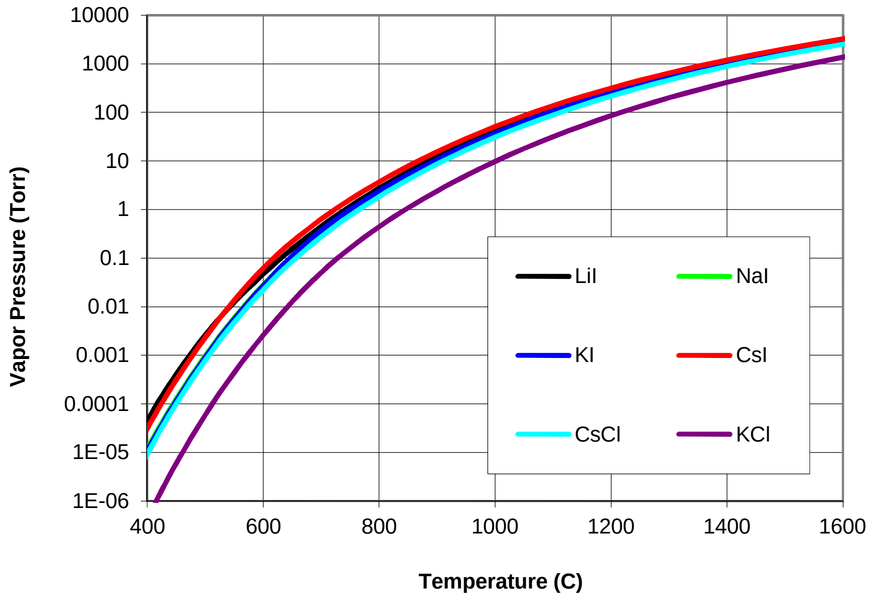
- Method development of iodine measurement in used EBR-II fuel
  - Potential Iodine species: NaI, CsI, AgI PdI_2, UI_3, ZrI_4, ^3HI
  - Goal: retain I^- in reducing or basic solution, or convert to stable IO_3^- for ICP-MS measurement
- Electrolytic dissolution of fuel
  - 6N HCl
  - 6N HNO_3/KF
  - Methanol/H_3NCl
- Experiment: stainless steel clad, U-10Zr fuel segments dissolved in Pt anode with a glass carbon cathode with:

$$I^- + 3H_2O \rightarrow 3H_2 + IO_3^- \text{ (but not: } 2I^- + 2H_2O \rightarrow H_2 + I_2 + 2HO^-\text{)}$$

- Appears that I^- is retained in acidic solutions as IO_3^-

Iodine Off-gas Measurements from LiCl-KCl Eutectic Salt

- Off-gas collected from molten LiCl-KCl eutectic salt spiked with 1000 ppm CsI at 500° C
- Off-gas trapped in dual HCl impingers
- No iodine detected in trap, only K detected



Analyte	Total Trap Concentration (ppm)	Detection Limit (ppb)
Li	ND	1.2
K	0.4	5.6
Cs	ND	0.01
I	ND	3.8

Salt Vapor Off-gas Measurements During Salt Distillation Operations

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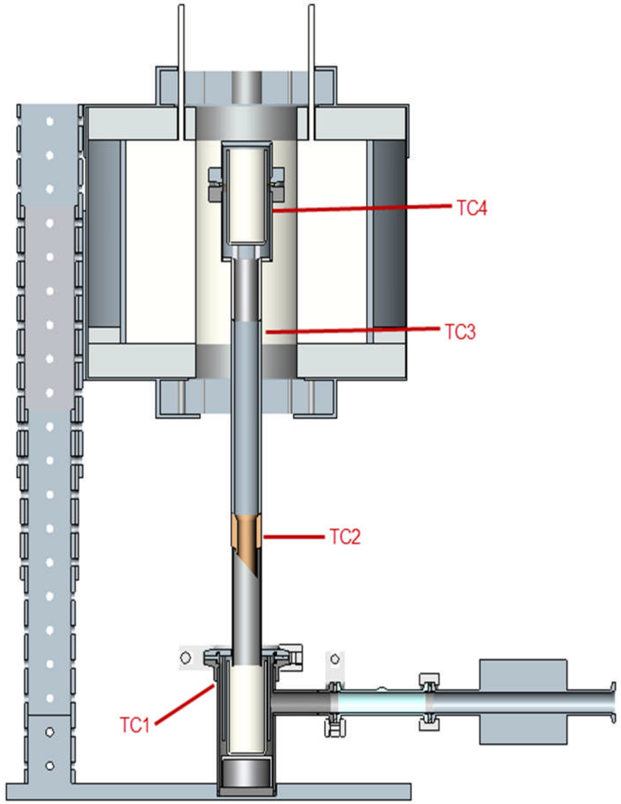
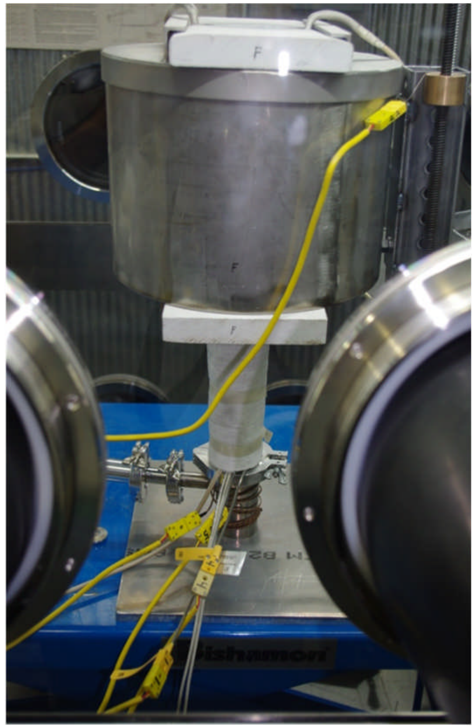
- Salt distillation operations
  - Cathode processer
  - Metal waste form furnace
- Recovered salt returned to ER
- Potential for volatile fission products (i.e. iodine) escape through vacuum system
- Salt distillation test apparatus
  - Salt crucible
  - Salt condenser
  - Halide trap (Ag zeolite)
  - Dual zone furnace with vacuum system
- Halide measurement
  - Leach Ag zeolite to release trapped halides (primarily Cl)



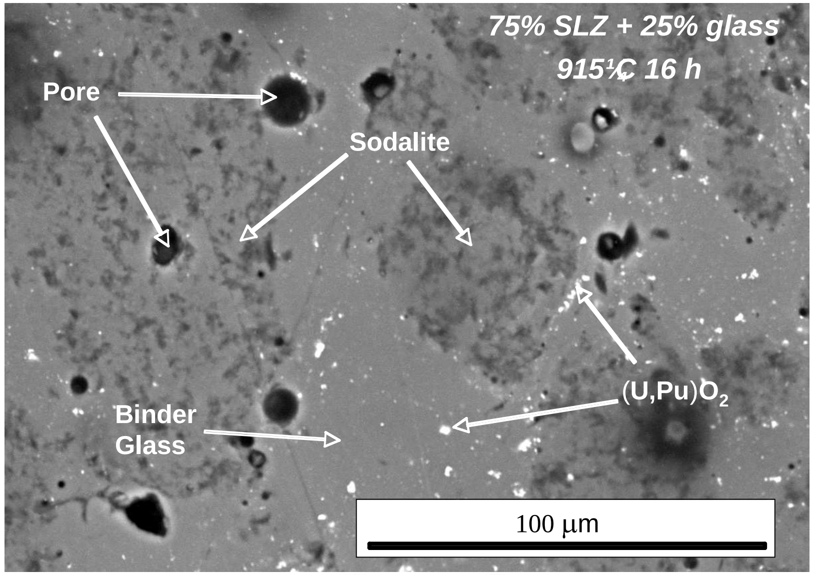
Salt Vapor Off-gas Measurements During Salt Distillation Operations

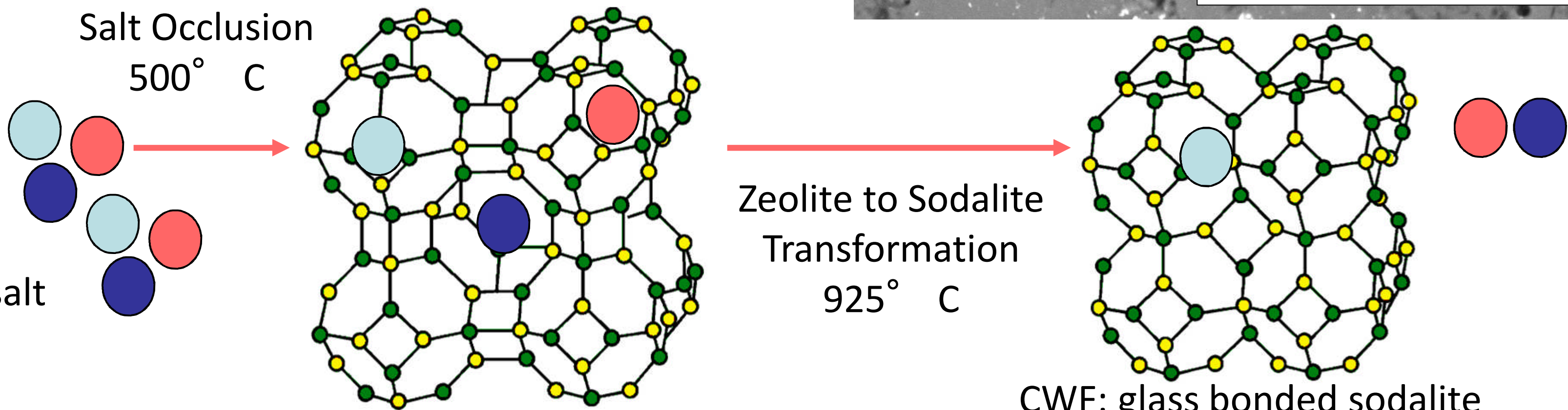
- Salt distillation of LiCl-KCl with 2 wt% CsI at 1100°C at ~100 mtorr
- Analysis of I, Cs and Li from collection chamber and Ag zeolite
  - Collection chamber rinse: I 205 ppm, Cs 12.4 ppm, Li 553 ppm
  - Vacuum line rinse: I 0.3 ppm, Cs 0.1 ppm, Li 3.4 ppm
  - Ag zeolite collected, leaching in 0.1 M Na_2S
    - Perform analysis for I, Cs and Li by ICP-MS



Iodine Partitioning in the Ceramic Waste Form

- Chemistry of Waste Salt Processing
  - Zeolite is a crystalline aluminosilicate material containing microspores
  - Zeolite 4A absorbs salt at 500⁰ C
  - Salt occluded zeolite-A is then mixed with glass and heated to form glass-bonded sodalite CWF
  - Most salt is bound by sodalite, while some partitions into the glass phase





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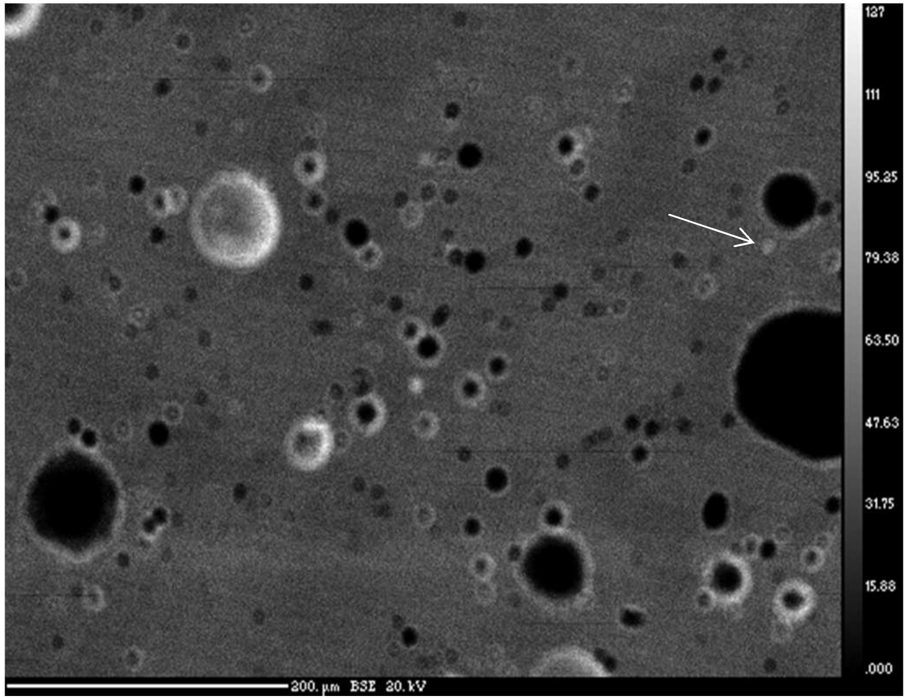
Iodine Partitioning and Iodine Off-gas in the Ceramic Waste Form

- Iodine behavior in the CWF from leaching studies performed by W.L. Ebert, et al. ANL-02/10.
  - I release correlates with Cl release – indicates that I and Cl are found in same phase distribution of CWF
- Measurement also indicates no loss of K and Cs between pre- and post-processed CWF (CsCl and KCl, NaI, KI and CsI have similar vapor pressures at CWF processing temperatures)

- Nominal salt-loaded CWF composition:
  - 10 wt% salt loaded zeolite (mixed at 500° C), ~2 wt% fission products
  - 75 wt% salt-loaded zeolite:25 wt% glass binder (processed at 925° C)
  - Iodine off-gas measurements during CWF processing with 500 ppm iodine loaded salt (~7.5 ppm iodine in CWF) no iodine measured in trap system (DL ~ 2 ppb).
- High-Loaded salt CWF composition for off-gas measurements
  - 17 wt%, high-fission product salt loaded zeolite (1:1 LiCl-KCl eutectic :CsI – 3.2 wt% I loading)
  - 75 wt% salt-loaded zeolite: 25 wt% glass binder
  - Processed inside tube furnace using nominal processing conditions (925° C) with dual HCl trap
  - Analyze for Li, Cs, I in traps, collected 400µg (0.2wt%)I in traps

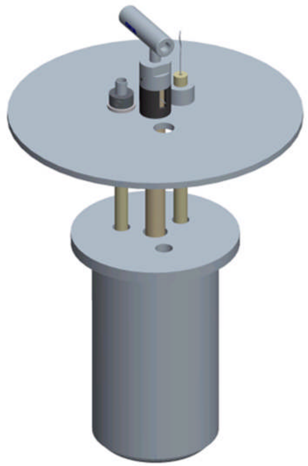
Iodine Partitioning in the Ceramic Waste Form

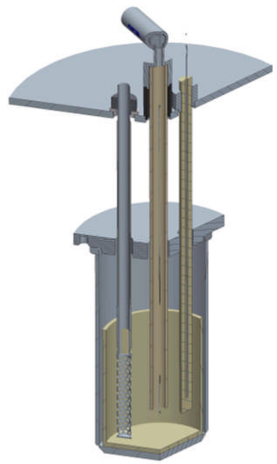
- Recently have performed direct measurement of iodine in CWF using electron probe micro-analysis (Cameca SX-100R Analyzer)
- Iodine measured in halite phase only, cesium balance deficient in halite phase

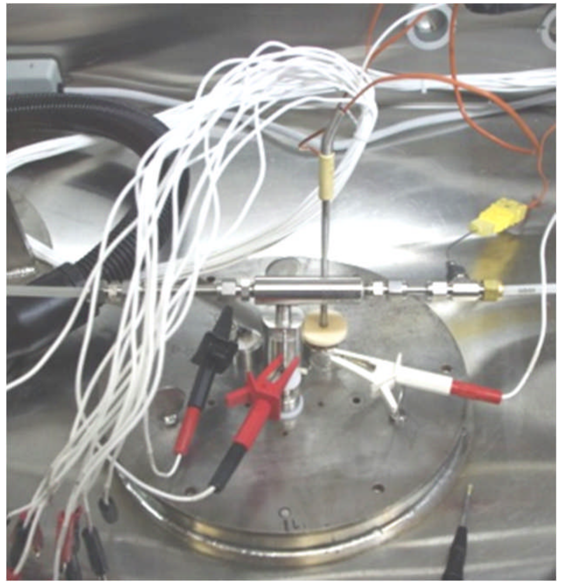


Iodine Off-Gas During Oxide Fuel Electrolytic Reduction

- Iodine off-gas capture during the electrolytic reduction of surrogate oxide fuel (MnO)
  - Assume iodine enters electroreduction vessel due to no head-end voloxidation process performed on used oxide fuel, or from incomplete iodine removal during voloxidation
- Experiments performed in molten salt furnace II (EDL) utilizing Integrated Recycle Test (IRT) proposed off-gas sampling apparatus
  - Cathodic reduction of surrogate oxide fuel (MnO)
  - Shrouded anode with both venturi and vacuum pump to remove process gases (O_2, Cl_2 and I_2) from anode region
  - Iodine captured using stainless steel tube trap, analyzed by ICP-MS
  - Tested online O_2 monitoring systems for process control







Iodine Off-Gas During Oxide Fuel Electrolytic Reduction

- **Electrolysis Conditions**
  - LiCl-1wt% Li_2O-2wt%CsI molten salt @ 650°C
  - 14 g MnO fuel stimulant at cathode
  - constant current reduction 0.5 A
  - cathode potential: -1.03 V, initial anode potential: 1.53 V ↑
  - anode shroud outlet Ar flow rate: ~500 mL/min

$$2Li_2O \rightarrow 4Li + O_2(g) \quad E° = 2.47\ V$$
$$2LiI \rightarrow 2Li + I_2(g) \quad E° = 2.47\ V$$
$$4LiI + Pt \rightarrow 4Li + PtI_4 \quad E° = 1.91\ V$$

Iodine Off-Gas During Oxide Fuel Electrolytic Reduction

- Analysis of I, Cs and Pt in electrolytic reduction salt and rinsed from components of experimental apparatus

Analyte	Salt Concentrations			Iodine Trap Rinse	Analyte Detection Limit
	After 1st Reduction	Intermediate (5 days @ 650°C)	After 2nd Reduction		
I		1.13wt% ± 0.02%	1.16wt% ± 0.02%	0.52 ppm	1.4 ppb
Cs		1.10wt% ± 0.02%	1.12wt% ± 0.02%	0.34 ppm	0.9 ppb
Pt	8.1 ppm	ND	1.2 ppm		0.07 ppb

Summary

- Iodine mass balance in the electrorefiner
  - Iodine-129 accountable in ER salt - good agreement between measured and predicted value
- Iodine partitioning in irradiated EBR-II fuel
  - Iodine-129 mass deficit from expected in bond-sodium – important to determine iodine partitioning between fuel, bond sodium, and plenum regions for operations and waste processing options
- Iodine off-gas from LiCl-KCl eutectic salt
  - Iodine not detected during off-gas of eutectic salt at 500° C – consistent with Fuel Conditioning Facility historical radionuclide emissions
- Iodine off-gas during high-loaded salt distillation operations
  - Iodine detected outside collection crucible
  - Iodine sorption on solid Ag-zelolite trap media under analysis
  - Ag-zeolite media effective at trapping iodine during distillation
- Iodine off-gas during CWF production
  - Iodine not detected at 500 ppm iodine salt concentrations
  - Iodine detected at high iodine salt loadings
- Iodine off-gas during electrolytic oxide reduction
  - Iodine released at anode during oxide reduction
  - Iodine corrodes Pt anode