



CETE Research at ORNL

February 2024

Changing the World's Energy Future

Jubin, Robert T.



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U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Materials Recovery and Waste Form Development
Campaign

CETE Research at ORNL

R. T. Jubin

Oak Ridge National Laboratory

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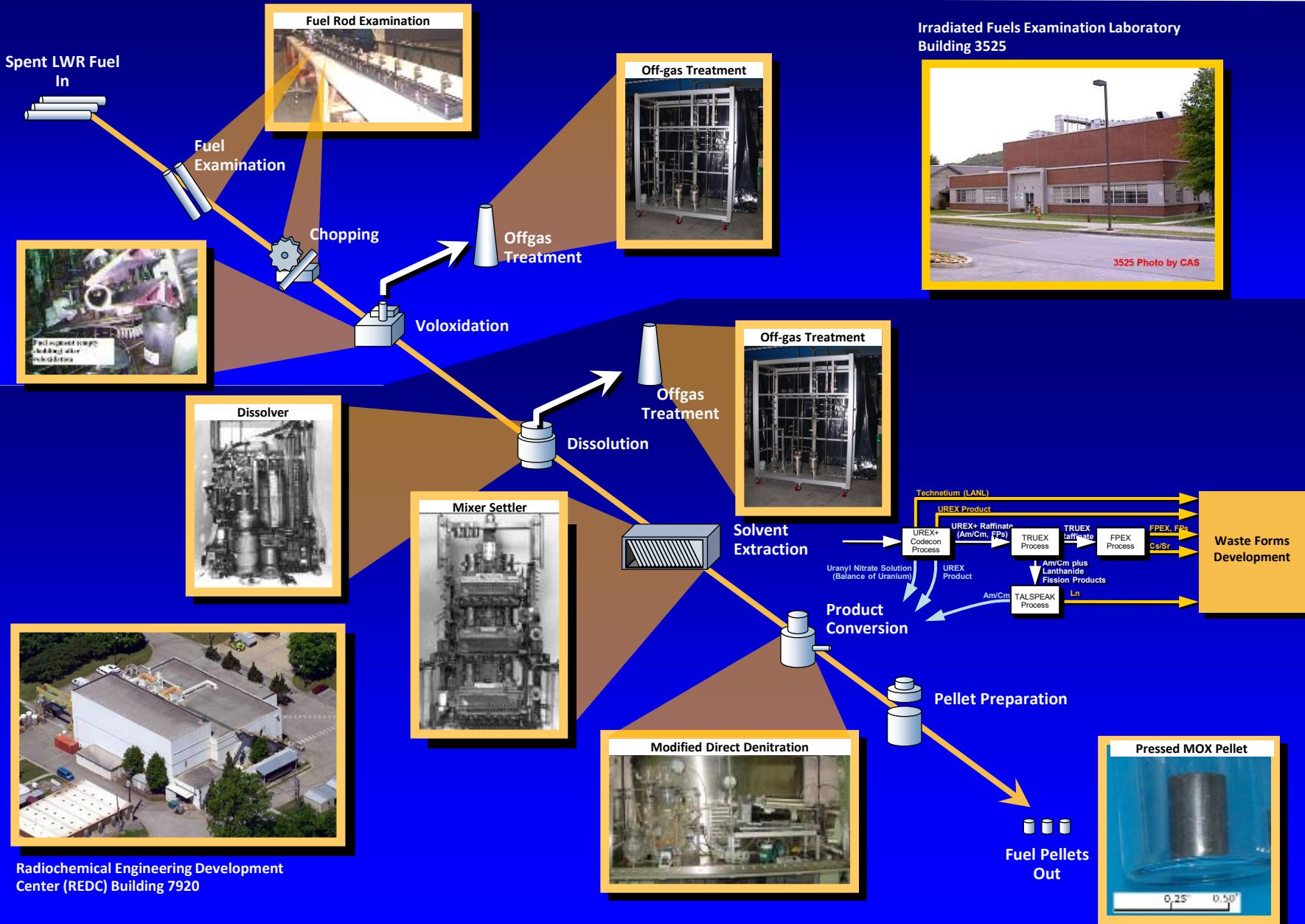
Nuclear Energy

- Overview of CETE R&D Program
- Summary of Run #1
- Review of CETE Voloxidizer Concept and Scale
- Run #2 – Voloxidation
 - Test Conditions
 - Qualitative Assessment of Product Powder and Hulls
 - General Observations on Processing Each Batch
 - Off-gas Evolution and Recoveries
- Campaign #2 – Dissolution
 - Off-gas Evolution and Recoveries
- Summary



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Coupled-End-to-End Demonstration Overview

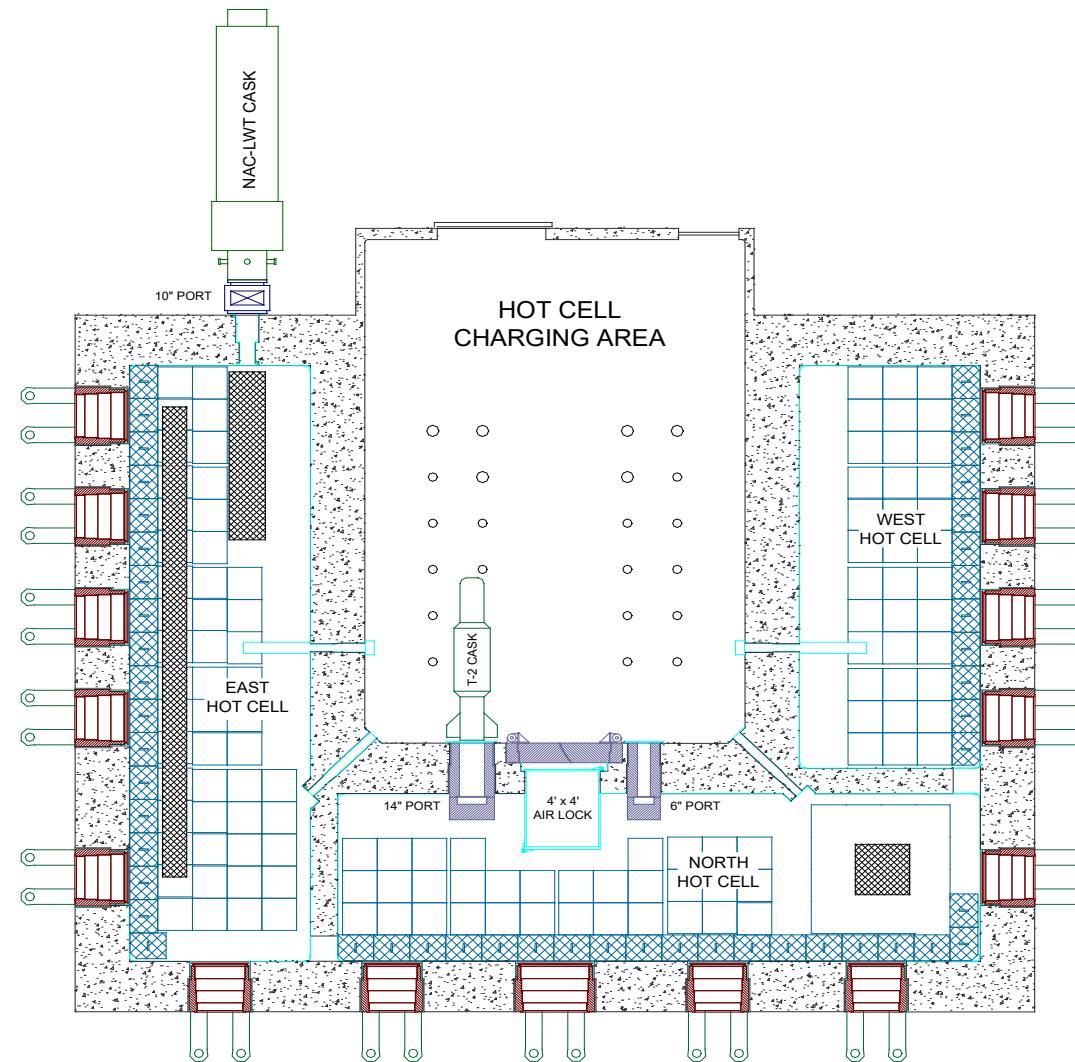




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Irradiated Fuels Examination Laboratory Building 3525





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Melton Valley- HFIR and the REDC



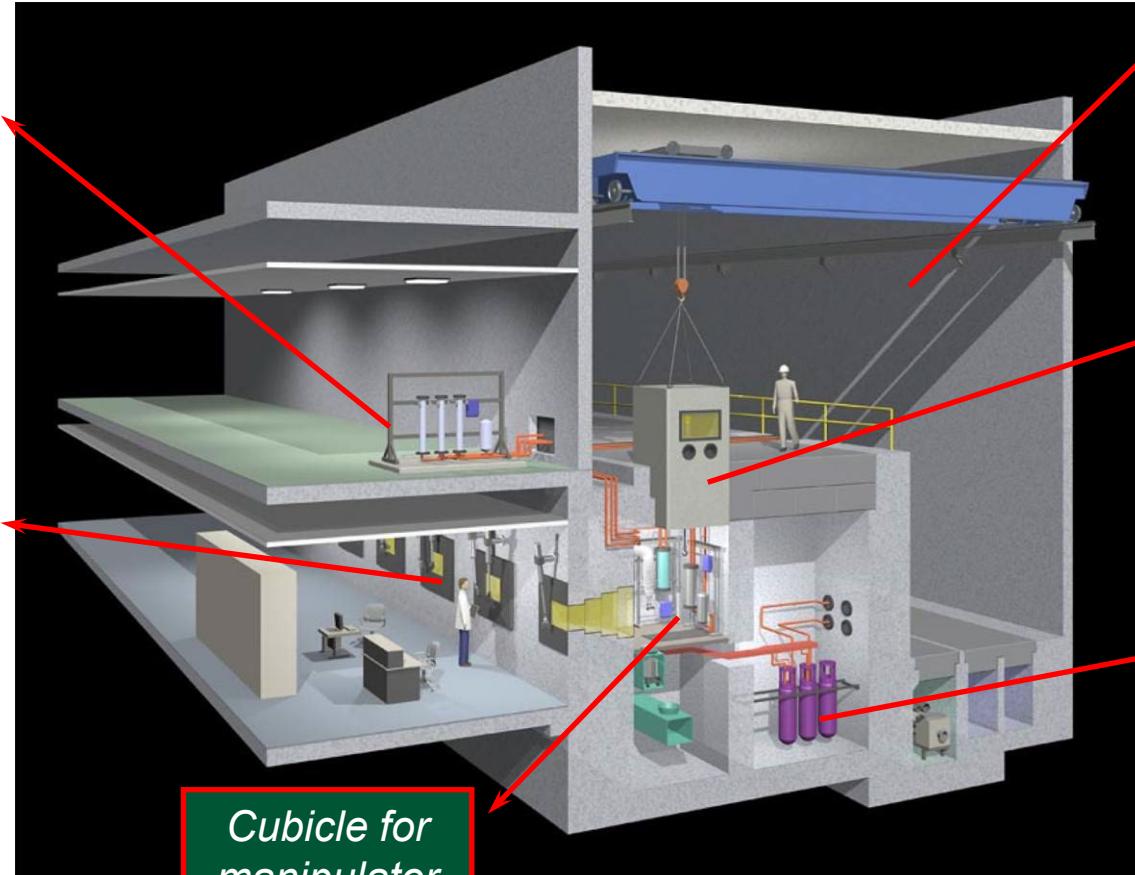


Overview of 7920 Hot Cell Facility

*Racks for
chemical
makeup &
additions*

*Nine shielded
hot cells for
remote
processing*

*Cubicle for
manipulator
operated
equipment*



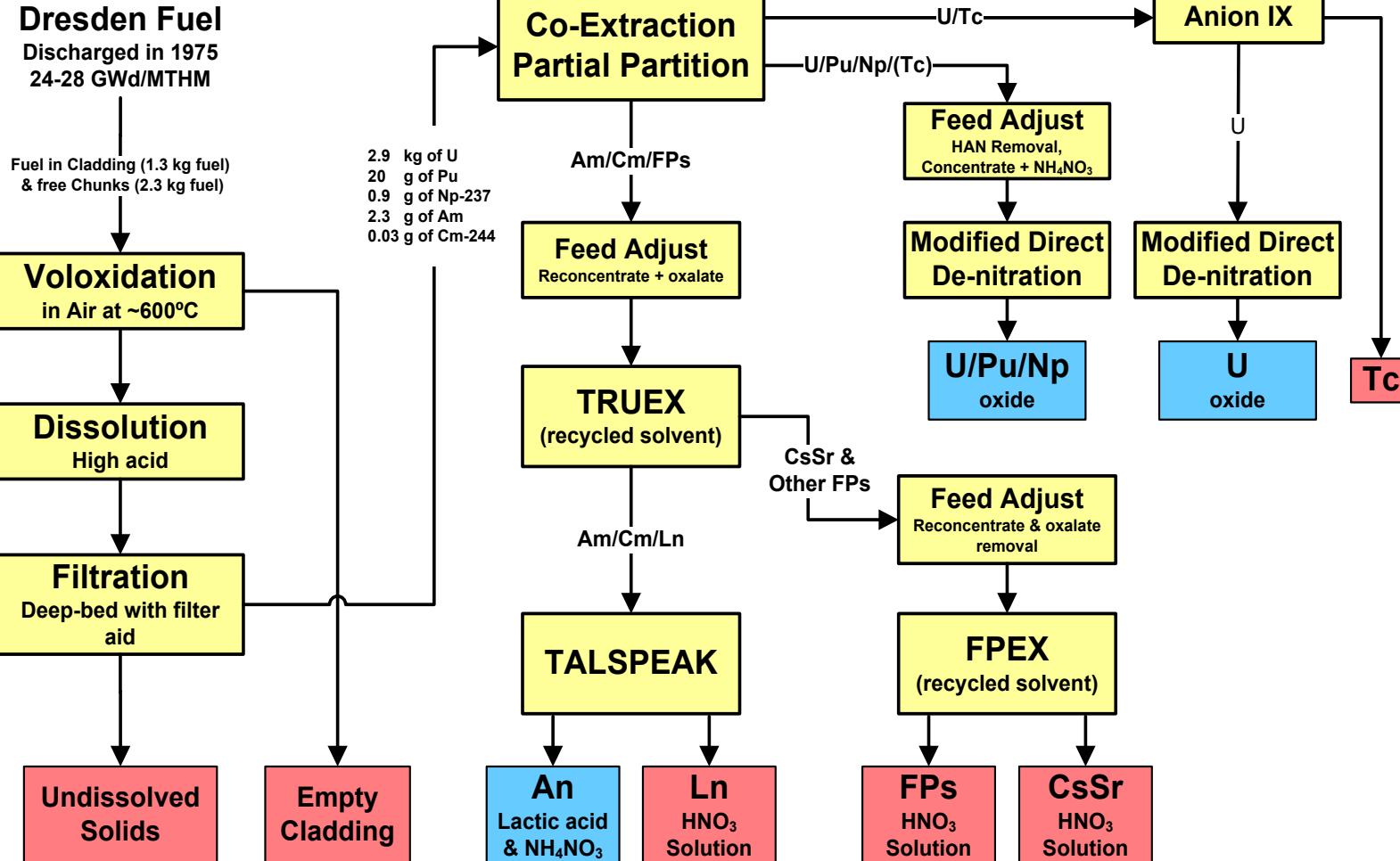
*High-bay
area for cask
receipt*

*Transfer case
for equipment
installation*

*Tank pit for
processing and
collection tanks*



CETE Used Fuel Processing - Run 1

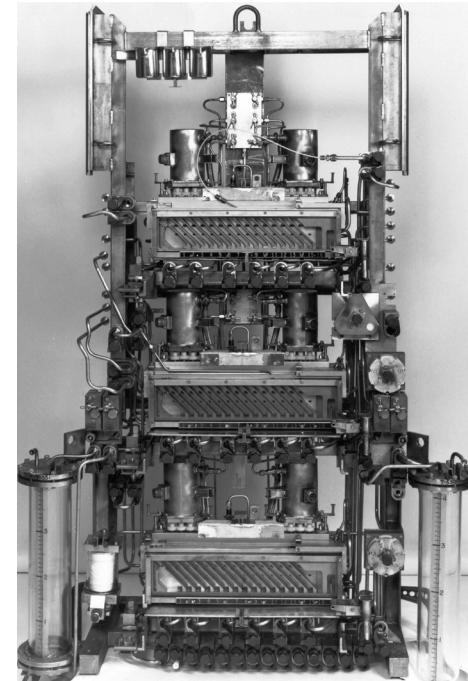
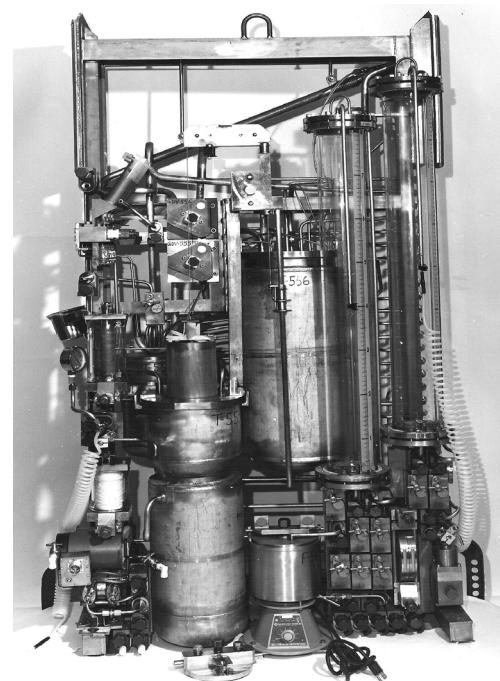




Radiochemical Engineering Development Center (REDC)

■ Building 7920

- Multipurpose hot cell facility
- Nine heavily shielded hot cells
- Equipment mounted on removable racks
- Offers flexibility in adding new processes and incorporating improvements



- *14 L jacketed dissolution tank, 25 L feed adjustment, 2 x 8 L metering tanks*
- *Three banks of 16-stage mixer/settler contactors, open top for reagent additions and stage sampling, 30/50mL M/S volumes, 5 L/h total flow throughput*



Product Conversion

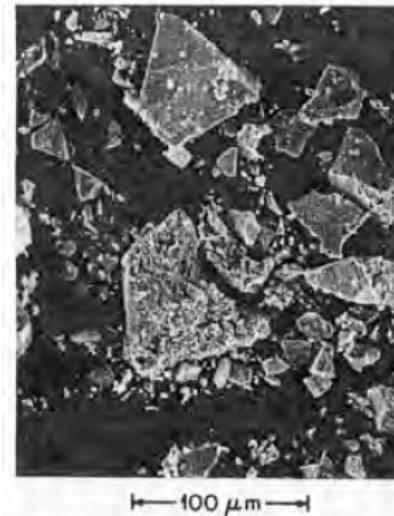
- **Direct Denitration**

- Thermally decomposes metal nitrates to oxide
- Mastic stage which leads to glassy, low surface areae product

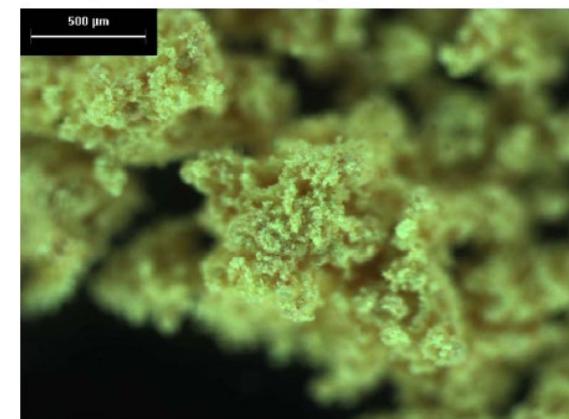
- **Modified Direct Denitration**

- Addition of inorganic nitrate salt to metal nitrate
- Uses rotary kiln to thermally decompose double salt to metal oxides
- Avoids the formation sticky mastic phase
- Resulting products have higher surface area
- Produces a powder with good ceramic properties for pellet fabrication

Traditional Direct Denitration
(Picture from P. Haas report)



Modified Direct Denitration
(Picture of MDD-produced DU)





CETE Demonstration Run 1- Dresden Fuel

- Voloxidized fuel in 7920 hot cells, minimal off-gas capture

- Dissolved fuel in two batches



- Performed MDD run to co-convert U/Pu/Np and bulk U streams

- U/Pu/Np Conversion Feed

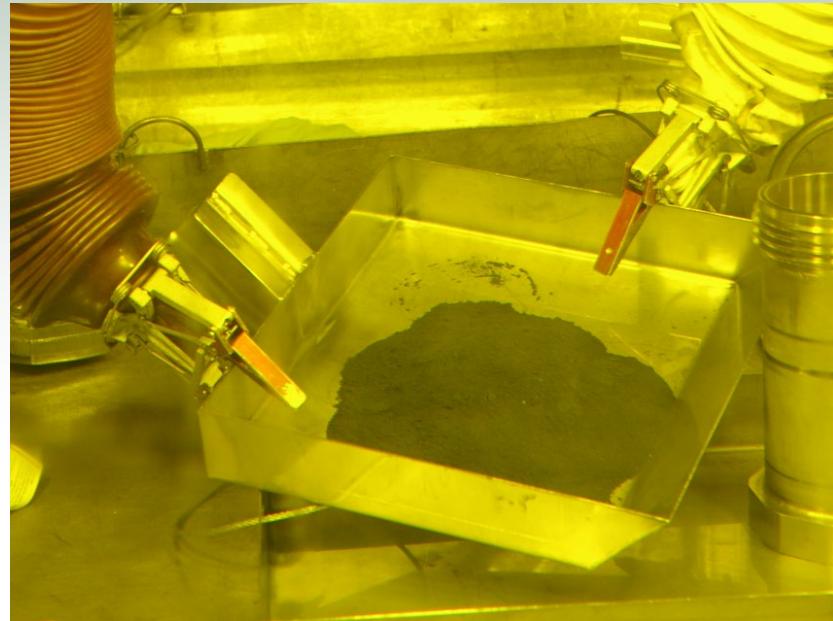
- 164 g U, 13.2 g Pu, 0.72 g Np, U:Pu ratio=12.4





CETE Demonstration Run 2

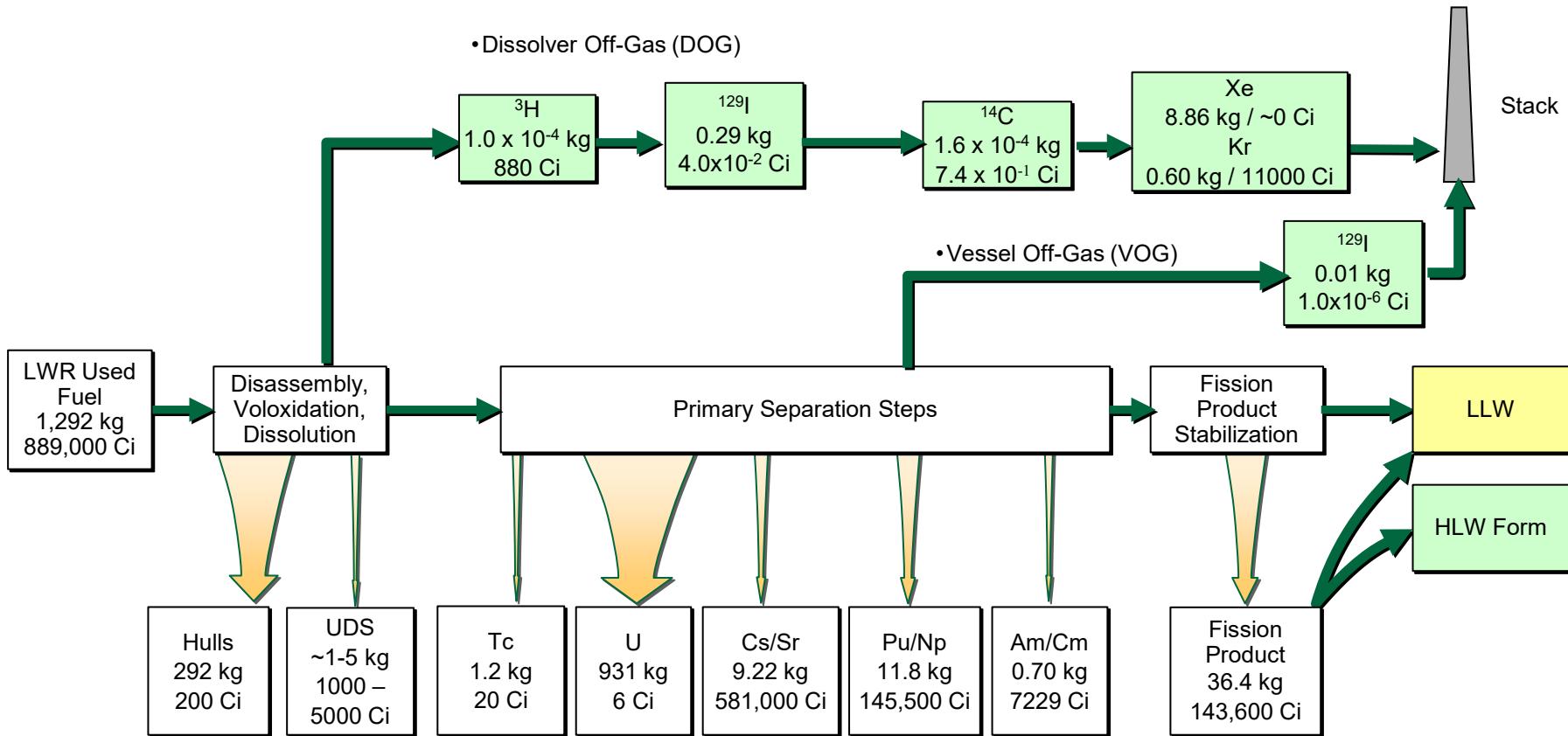
- 4 kg North Anna fuel + 1 kg Surrey fuel
 - N. Anna: 72 GWd/MTU burnup, 4 year short cooled
 - Surrey-2: 36 GWd/MTU burnup
- Three batches of Voloxidation completed
- Off-gas capture racks installed for Voloxidation and Dissolution
- The rest of this talk





Simple Reprocessing Block Diagram

(Mass Basis: 1 MT SNF; 55 GWD/MTIHM; 5 year Cooling)





Tritium

- Tritium recovery is primarily a drying operation
- DF of ~100 to 800 may be required depending on capacity of reprocessing facility and age of fuel processed
- Disposal as LLW requires relatively clean separation of the HTO without iodine
 - Mix of a short-lived radionuclide with a very long-lived radionuclide could complicate disposal
- HTO also has permit limits for a LLW site



Iodine

- The primary recovery technology is applied to the DOG
- DF's of greater than 1000 are probably required
- Virtually all other off-gas / vent streams must also be treated to recover ^{129}I , e.g., vessel off-gas, cell off-gas, etc.
- The distribution of ^{129}I in gas and liquid process streams has been measured at the Karlsruhe reprocessing plant (WAK) (Herrmann, et al., 1993) and predicted for the BNFP (Hebel and Cottone, 1982)
 - About 94% to 99% of the ^{129}I reports to the DOG
 - Remaining is distributed among the aqueous high, medium and low-level waste
- Iodine remaining in the waste solutions may also be released during waste immobilization
- Iodine is also present in Echem waste salt



¹⁴C Recovery

- The bulk of the ¹⁴C found in the irradiated nuclear fuel is assumed to be evolved as CO₂ into the DOG during fuel dissolution
- Diluted 1000-5000x by ¹²CO₂ by dissolver air sparge
 - To reduce the impact of nonradioactive CO₂, the process could be designed to remove the CO₂ from air prior to sparging the dissolver, minimizing sparge gas flow or using nitrogen in place of air
- If standard voloxidation is used then approximately 50% of the ¹⁴C will be released in the voloxidizer
- Caustic scrub followed by immobilization as grout may meet LLW standards, but similar to tritium may be limited by disposal facility permit
- Depending on regulatory limits and plant location, recovery may not be required



- DF of ~30 to 80 may be required depending on capacity of reprocessing facility and age of fuel processed
- Most ^{85}Kr (>99%) remains in SNF until it is sheared and dissolved
- Substantial fraction of the ^{85}Kr would be released during voloxidation, if used
- ^{85}Kr is released in the DOG in the range of hundreds of parts per million
- Since krypton is chemically inert recovery processes are based on physical separation from the off-gas
- ~95% of Kr is stable
- Xenon, a chemically stable fission product is also recovered by these processes
 - Xenon is present at about 10 times the krypton concentration in the gas stream
 - Complicates Kr recovery and immobilization
 - May possibly have commercial value if clean enough



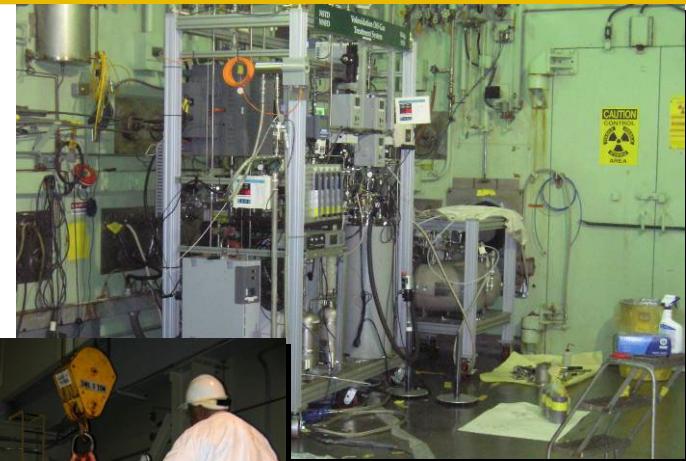
Head-end Off-gas Capture Systems in Hot Operation

■ Objective:

- Close material balance for volatile components
- Investigate release of volatile components during voloxidation and dissolution

■ Operations:

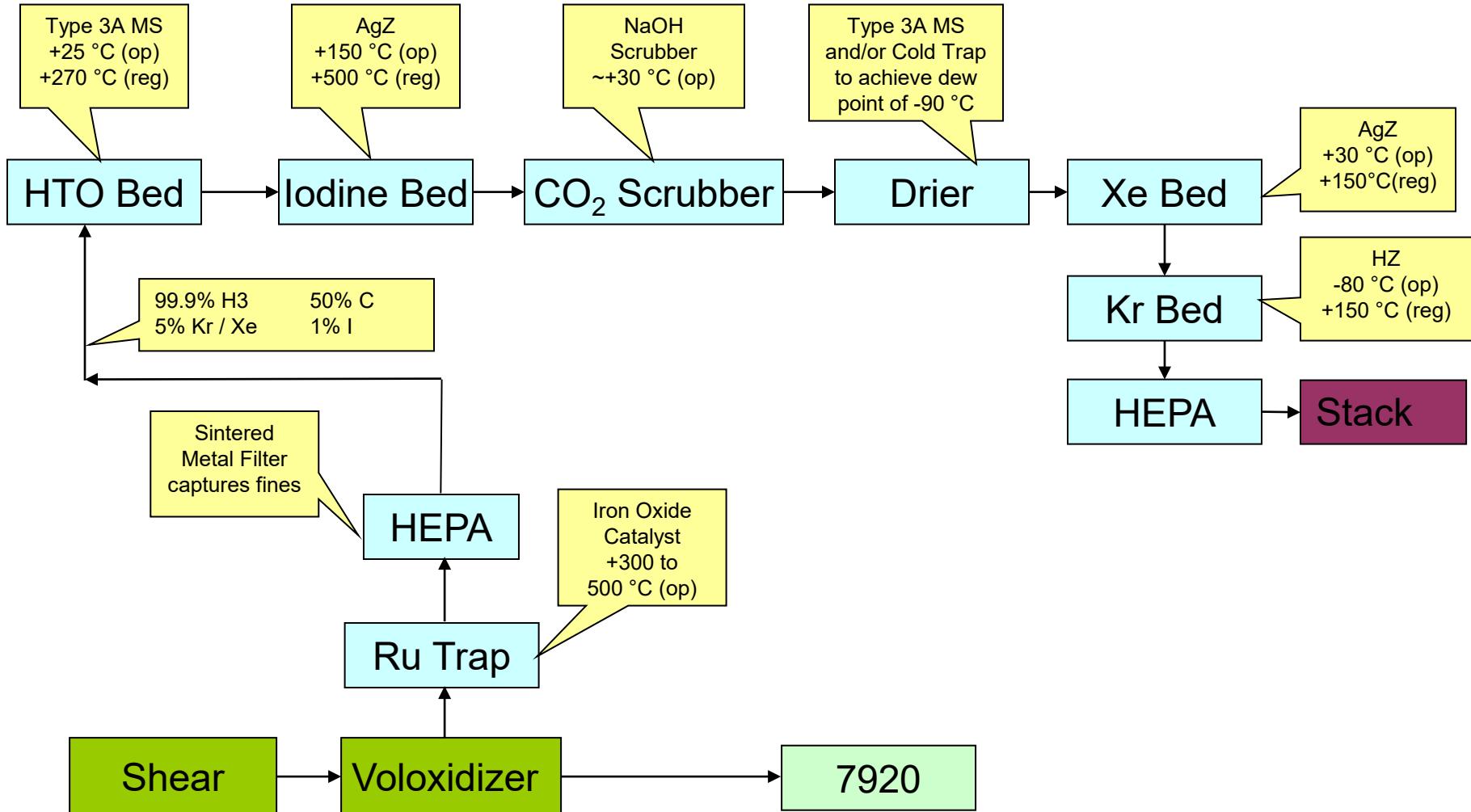
- Initial Voloxidation run completed Sept 30, 2008
 - *Three batches of fuel processed*
- Dissolver Off-gas capture system and powder feeder installed and in operation
- Initial Hot operation in June 2009
 - *Two batches of voloxidized fuel powder dissolved*





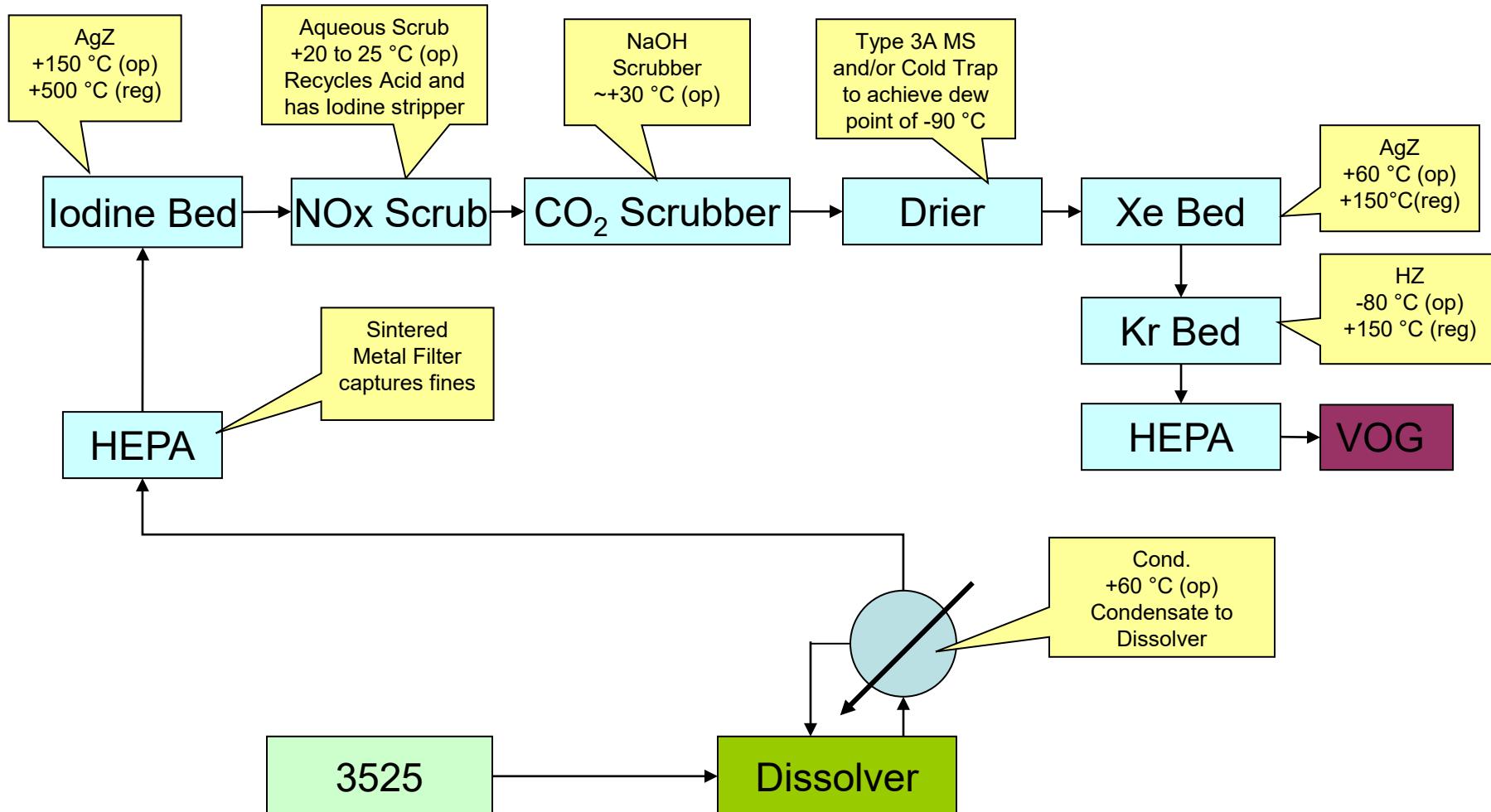
CETE VoxOG System

Nuclear Energy



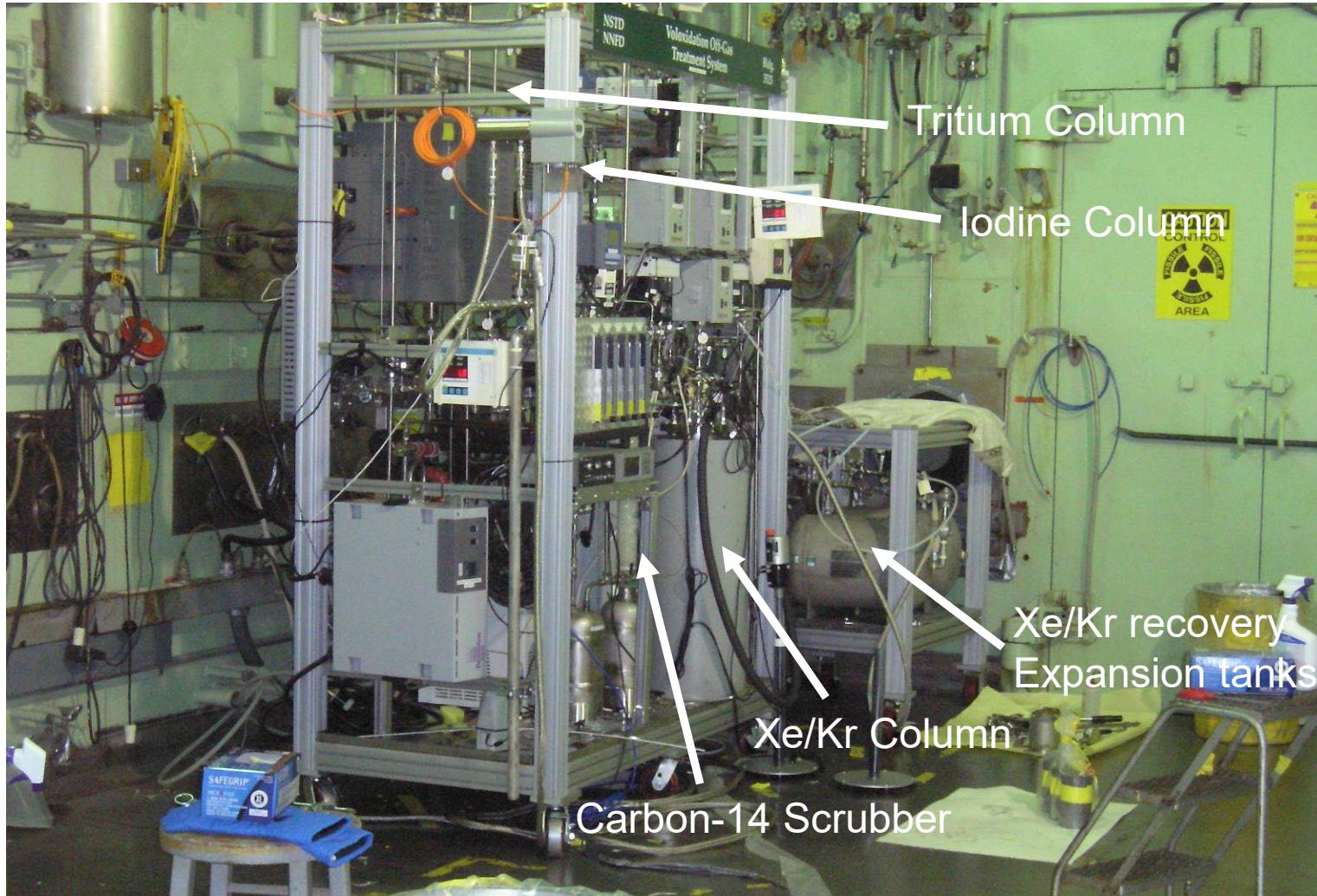


CETE / DOG System





Volox Off-Gas Rack as Installed in Bldg 3525





Voloxidation Process Description

■ Dry head-end process to oxidize spent fuel oxide

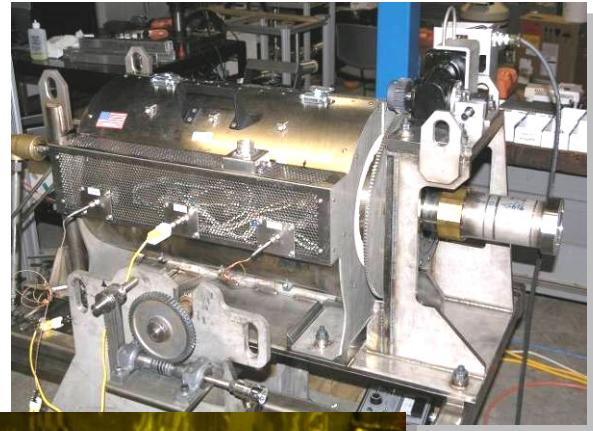
- Release fuel from cladding
- Release tritium from fuel prior to aqueous portion of processing plant

■ Process condition:

- Normal (Standard) is air at 450°C to 650°C
- Resulting reaction: $3\text{UO}_2 + \text{O}_2 \rightarrow \text{U}_3\text{O}_8$
- 99.9% of tritium released
- 99% of fuel reduced to small μm -size particles
- Portions of the C, I, and Kr also released

■ Controls

- Temperature
- Oxidizing environment, e.g., air, oxygen, ozone, etc.



Empty Hull: Post Volox

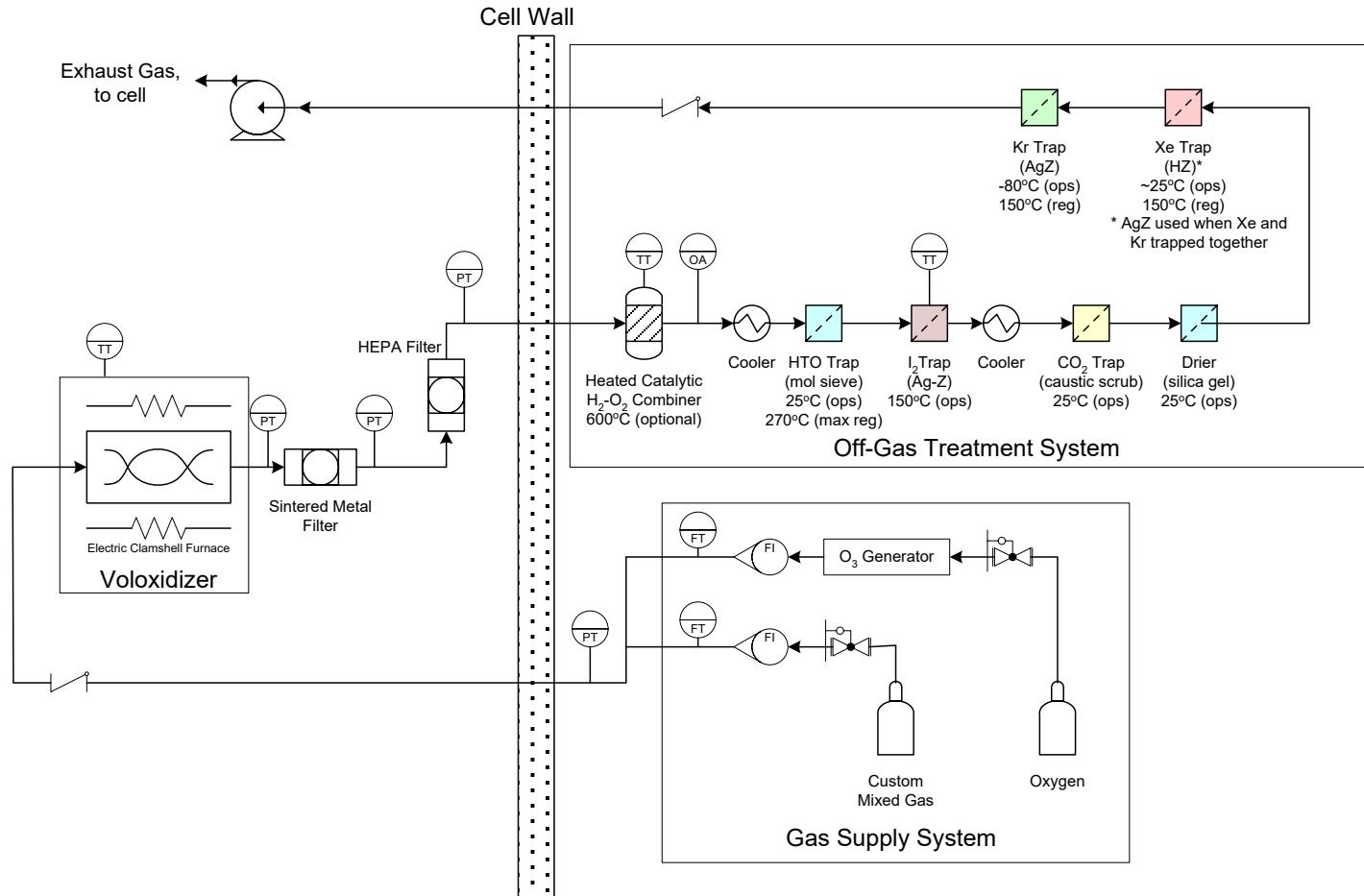


Fuel: Post Volox



Primary Voloxidation Process Concept

In-cell Voloxidizer with Out-of-Cell Off-gas Treatment





Test Conditions for Second CETE Run

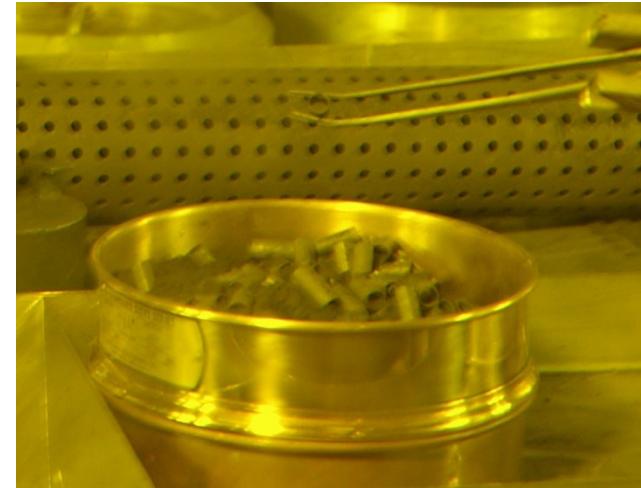
Batch	Fuel	Burnup (GWD/MT)	Batch Fuel/Total (kg/kg)	Segment Length (in)	Oxidation Gas	Nominal Temp. (°C)
1	Surry-2	36	1.2/1.7	1.0	Air	500
2	North Anna	63—70	2.1/2.9	0.88	Air	600
3	North Anna	63—70	2.0/2.8	0.88	Oxygen	600



Voloxidizer Products

■ When oxidation complete

- Cladding hulls completely cleared of monolithic fuel
- Fuel powder was very fine
 - *Flowed readily*
 - *Agitation resulted in dusting, required careful handling when in the open*
- Cladding and bulk powder separated readily
 - *Dust coating on hulls and equipment was visually evident—very small fraction of fuel*
 - *Effect seemed electrostatic in nature*
- Off-gases were captured for analysis
 - *Tritium, iodine, and noble gases on solid media*
 - *Carbon dioxide in a caustic scrubber*





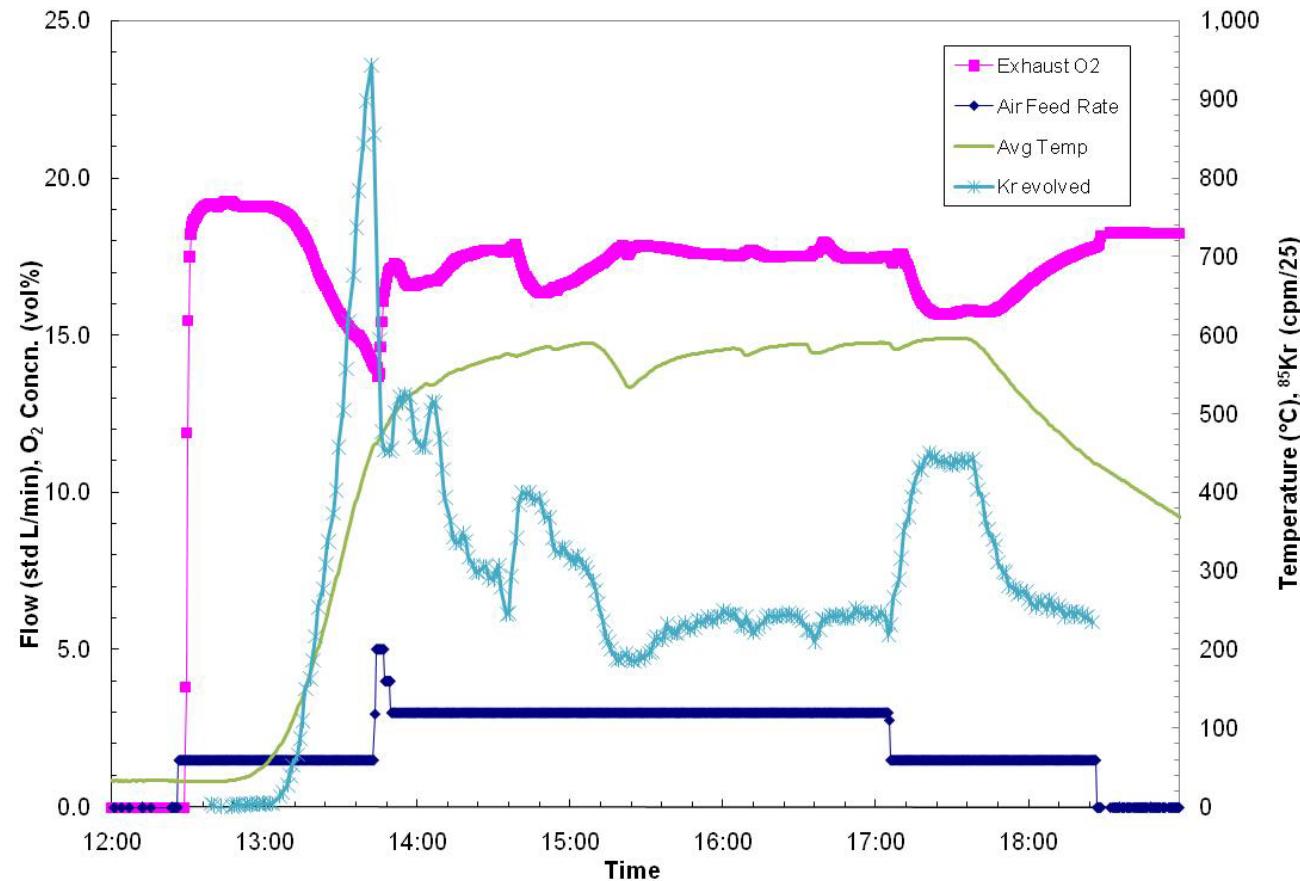
Batch 1: General Observations

- **Oxidation started at temperature of about 100°C**
 - Oxygen consumption and ^{85}Kr release observed via instrumentation
 - Initial rapid increases probably caused by reaction of fines from shearing operations
- **Run prematurely terminated**
 - Oxygen consumption and ^{85}Kr release decreased steadily
 - Drift in oxygen sensors made endpoint determination uncertain
- **Examination of fuel before reaction complete was very useful**
 - Fuel surface receded from hull openings, estimated about 2/3 was reacted
 - Fuel surface appeared smooth and flat within a hull
 - *It was thought that our ‘optimized’ shear caused little fracturing of the fuel throughout the segment*
- **Completed processing**
 - Reloaded all material to voloxidizer
 - Restarted and resumed at same temperature
 - ^{85}Kr measurements slowly approached zero; reaction complete
- **Processing time ~12.5 hrs**
 - Includes oxidation time during ramp to target temperature



Batch 2: General Observations

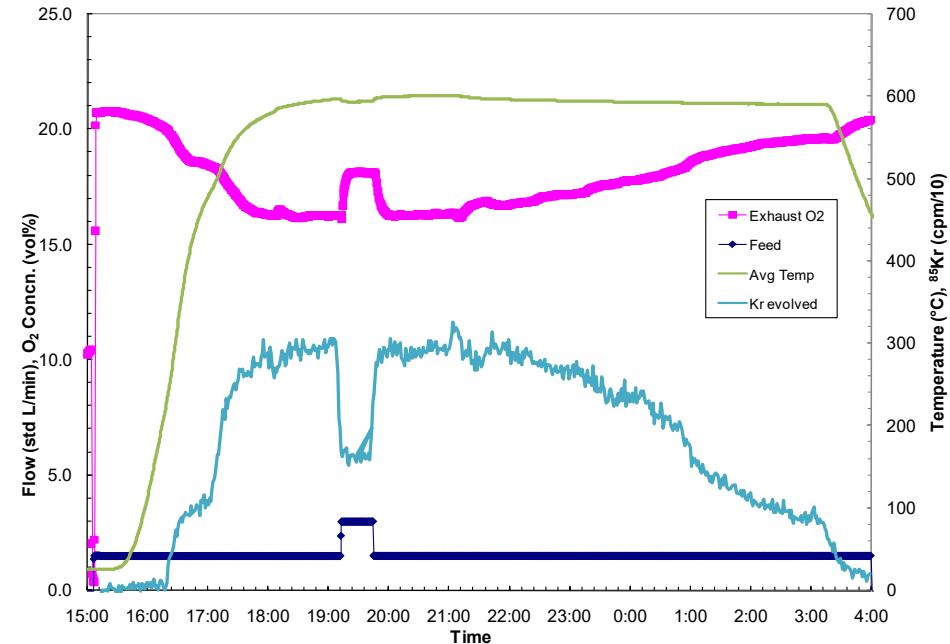
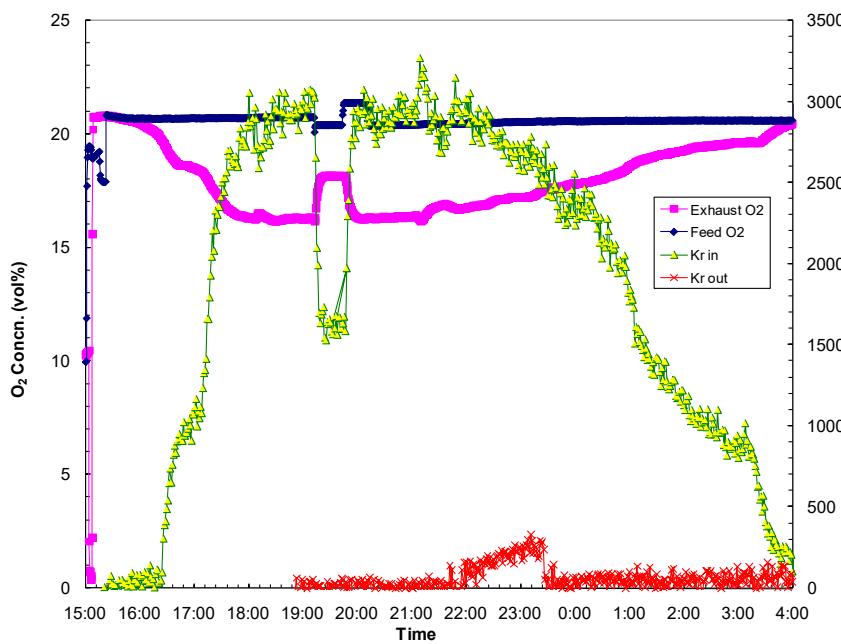
- **Conditions:**
 - Fuel: North Anna
 - $T = 600^\circ\text{C}$
 - Gas = Air
- **Oxidation starts at $\sim 100^\circ\text{C}$**
- **Kr trap saturated, required shutdown to replace**
- **Interim fuel condition**
 - Surface receded from hull opening
 - Some hulls, surface had not receded as much as others
 - Surface smooth and flat
 - Tapping hulls released additional fuel powder





On Line Monitoring of Voloxidation Process Effective and Insightful

North Anna Fuel – Air Oxidation part 3: O₂ Concentration, Kr-85, Air Flow, and Temperatures





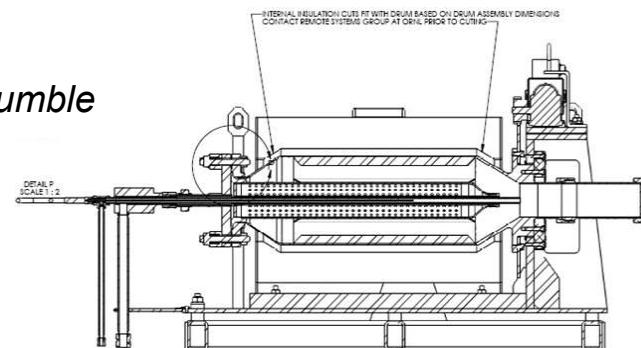
Batch 2: General Observations, & Process Changes

Condition of fuel led to changes in operation of equipment

- Minor fraction of hulls where fuel had not receded as much
 - *Fuel segments in cool zone near closure flange*
 - *FIX: Removal of basket*
 - Conical ends of main drum keeps fuel in hot zone of furnace
- Fuel released when hull is tapped
 - *Insufficient agitation or impact with vessel walls*
 - *Segments could roll within smooth basket rather than tumble*
 - *FIX: Removal of basket*
 - Fuel agitates in large diameter of outer drum
 - Outer drum equipped with lifting/mixing vanes

Processing time ~16 hrs

- Includes oxidation time during ramp to target temperature
- Includes ~2 hrs beyond completion of oxidation to observe Kr outgassing





Batch 3: General Observations

Conditions:

- Fuel: North Anna
- $T = 600^\circ\text{C}$
- Gas = Oxygen feed
- Inleakage of air keeps O_2 concn below 100%

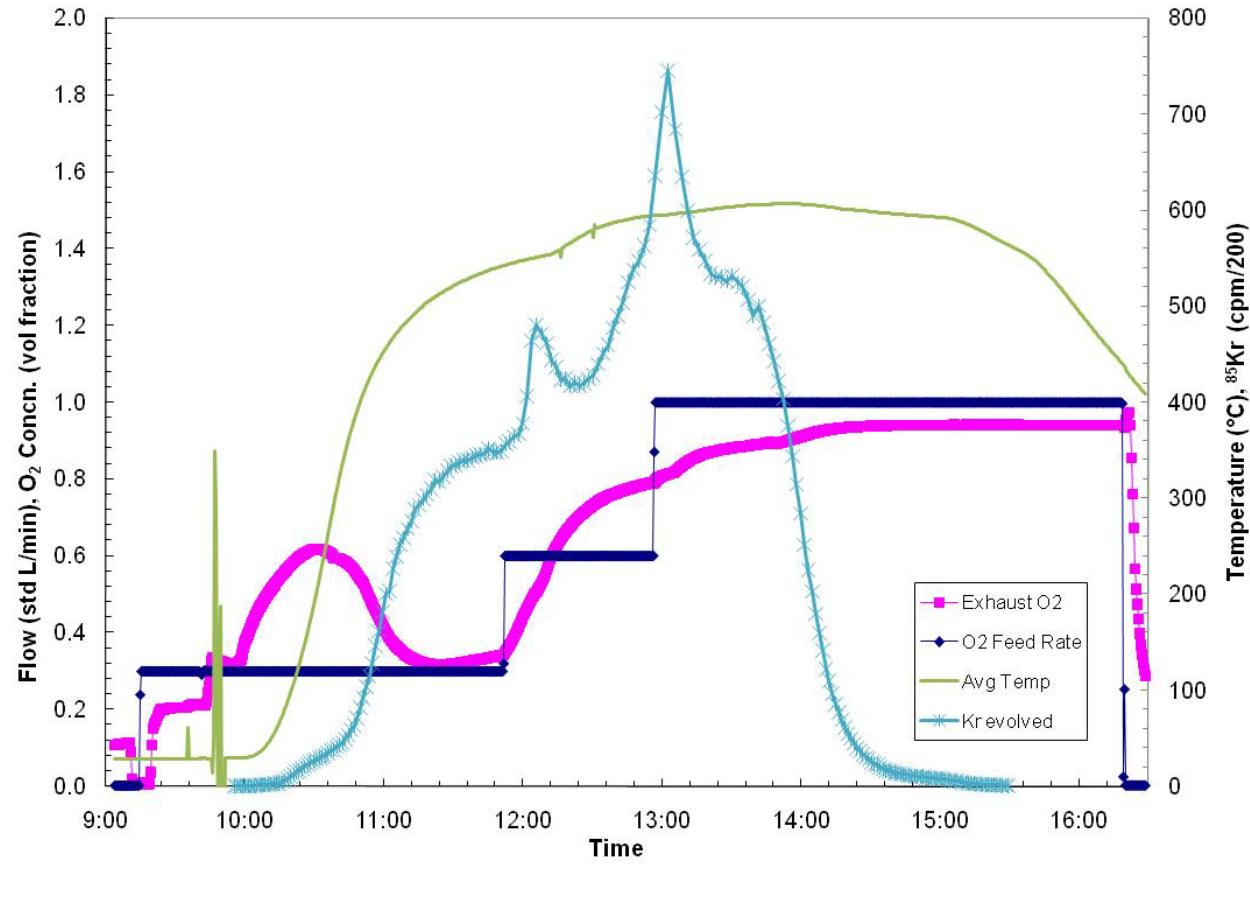
Oxidation starts at $\sim 100^\circ\text{C}$

Used two Kr traps—capacity for Xe & Kr off-gas

Completed processing batch in one phase

Processing time

- ~ 4 hrs
- Much shorter reaction time vs Batch 2 indicative of limiting step—gas film diffusion





Voloxidation Off-gas Recovery: ${}^3\text{H}$

- Tritium was desorbed and captured on cold finger with ethylene glycol backup trap
- Co-absorbed iodine and C-14 also recovered
- Up to ~60% of total tritium estimated by ORIGEN recovered
- Fraction remaining in cladding is a story for another time.

Fuel, oxidation #s	Fuel (g-HM)	Origen Estimate Initial (Ci)	Recovered in Traps (Ci)	Fraction of ORIGEN (%)	Fraction Remaining in Fuel (%)
Surry-2, Phases 1-2	1223	0.166	0.104	62.5	<24. ¹
North Anna, Phases 1-3	2071	1.94	0.692	35.7	²
North Anna, Phase 1	2012	1.89	0.230	12.2	²

1. Based on ICPMS analysis of voloxidation product powder and lower limit of detection for ${}^3\text{H}$.

2. Not Reported.

- The Zircaloy® cladding retains from 40% (Goode et. al., ORNL/TM-7103, 1980) to 60% (Uchiyama et. al., Rad Waste Mgmt & Nucl Fuel Cycle, 17(1), 1992).
- Thus, as little as 40% of the FP tritium remains in the fuel, which is available for removal by voloxidation.
- The first two experiments (above) are consistent with the literature.

Voloxidation Off-gas Recovery: ^{85}Kr

Fuel, oxidation #	Fuel (g-HM)	ORIGEN Estimate Initial (Ci)	Recovered from Off-gas Traps (Ci)	Released by Volox (%)
Surry-2, Phase 1	1223	2.26	0.228	10.0
Surry-2, Phase 2			0.0723	3.3
TOTAL				13.3
North Anna, Phase 1	2071	25.9	~11. (est)	~42. (est)
North Anna, Phase 2			1.51	5.6
North Anna, Phase 3			4.53	16.9
TOTAL				64.5
North Anna, Phase 1	2012	25.2	13.4	53.2
TOTAL				53.2

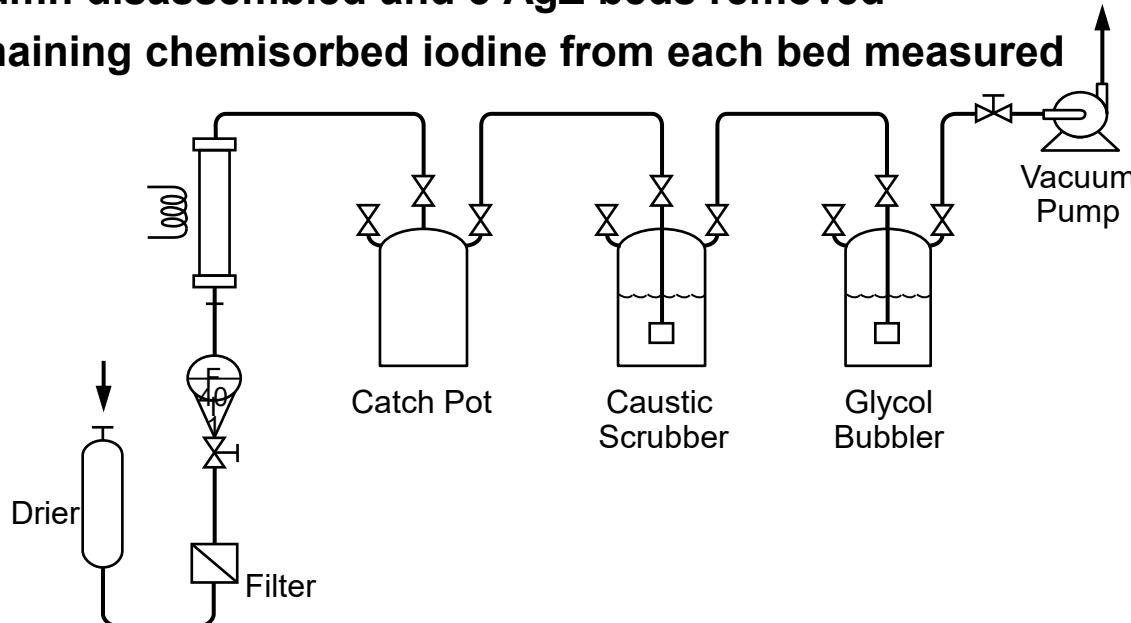
- Noble gases are not the primary target of Voloxidation.
- Noble gases not removed by voloxidation will be removed during dissolution. –together achieve 100% removal
- Usual practice is to combine voloxidizer and dissolver off-gas and capture the noble gases from combined stream.
- These data are collected as part of the overall mass balance
- Much higher release in voloxidation than expected based on literature (~5 - 10%).



Iodine Bed Analysis

Nuclear Energy

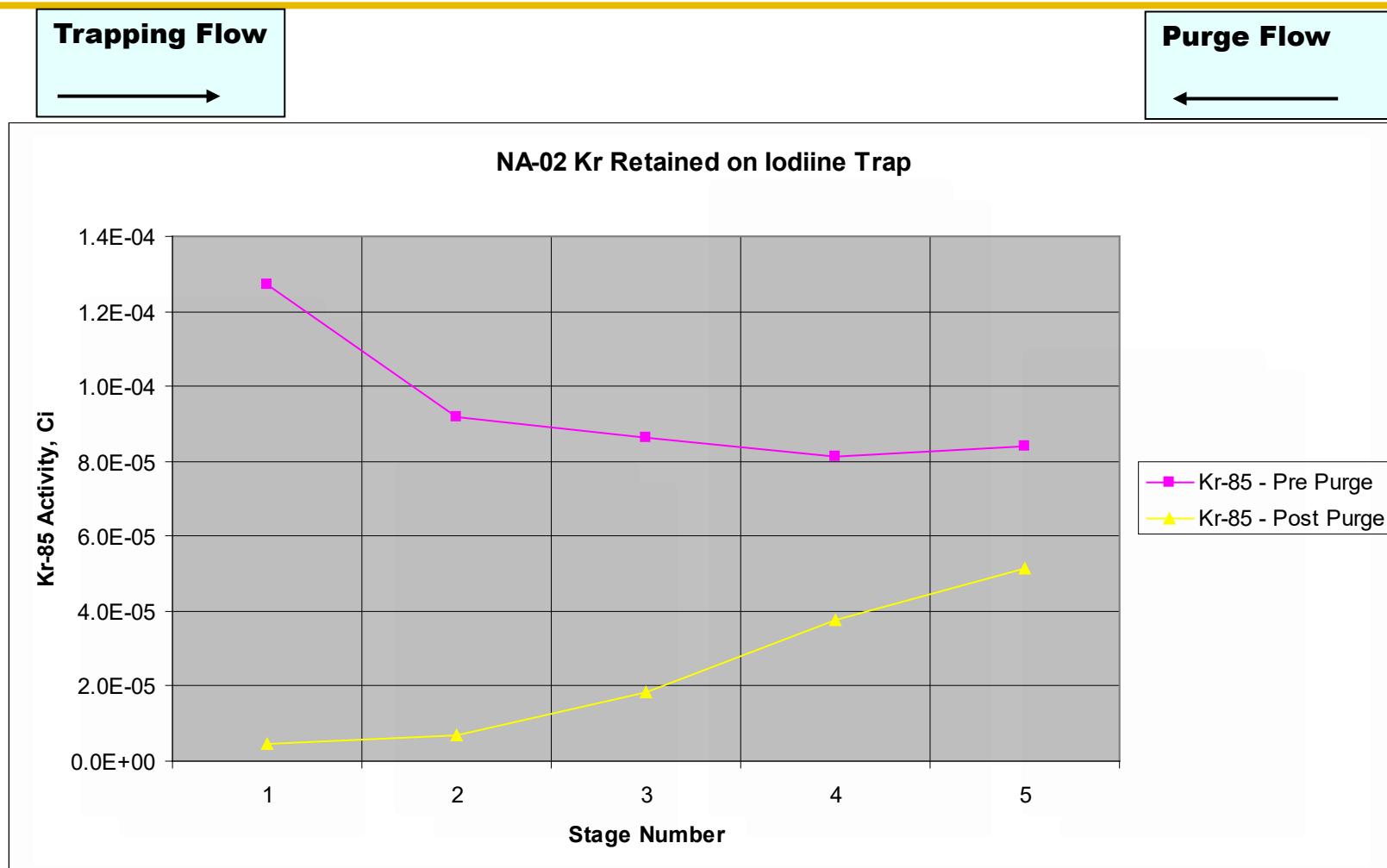
- Iodine trapping columns from each individual fuel batch were recovered
- Traps are purged to remove any physisorbed iodine
 - Any iodine removed from the beds is recovered
 - Bed heated to 150° C
 - Purge with 1 - 4L/min of dry air
 - Run time: ~24 hours
- Column disassembled and 5 AgZ beds removed
- Remaining chemisorbed iodine from each bed measured



Base material:
MP Ionex®-Type Ag-900



Kr-85 Retained on AgZ Iodine Beds



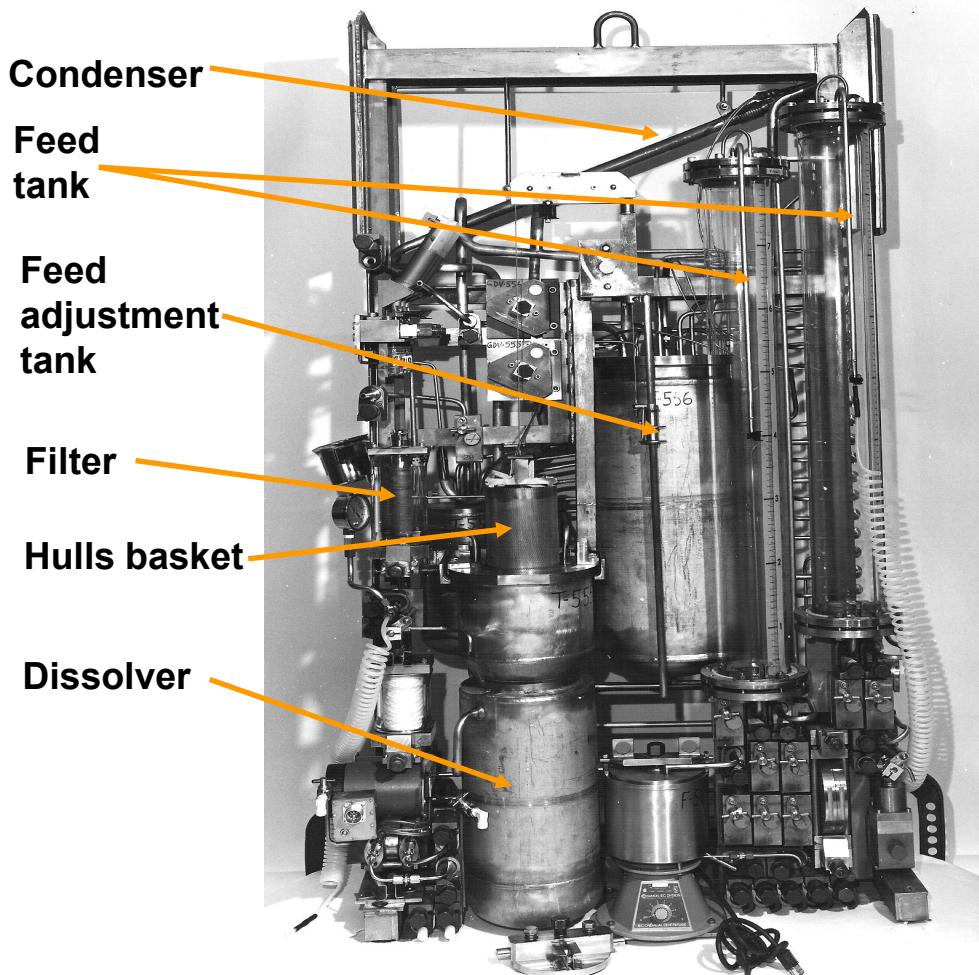


Voloxidation Off-gas Recovery: Iodine and ^{14}C

- Iodine levels were below level of detection on AgZ traps and in all purge traps
- Analysis of iodine in catalyst bed and molecular sieves (tritium trap)
 - ~0.04% recovered by voloxidation of Surry-2 fuel
 - 0.05 to 0.13% recovered from North Anna fuel
 - Lower than the 1% removals estimated from the literature
- Preliminary analysis of ^{14}C removal/recovery
 - $\sim 3 \times 10^{-4}$ Ci/kg of fuel dissolved (heavy metal basis) was recovered
 - ~10 times more ^{14}C recovered than estimated present in the fuel
 - Difference caused by not including the contaminants (e.g. ^{14}N) in as-fabricated fuel in the ORIGEN calculations
 - Seeking analysis of fuel used to verify it met specifications; will aid comparisons
 - $0.00615 \text{ gm } ^{14}\text{C} / \text{MT fuel if no } ^{14}\text{N present}$
 - $0.375 \text{ gm/MT at 35ppm } ^{14}\text{N}$
 - $0.8 \text{ gm/MT at the ASTM limit of 75ppm } ^{14}\text{N}$
 - If all ^{14}C was released quantity recovered equates to 0.085gm/MT or an estimated ^{14}N impurity of ~8ppm



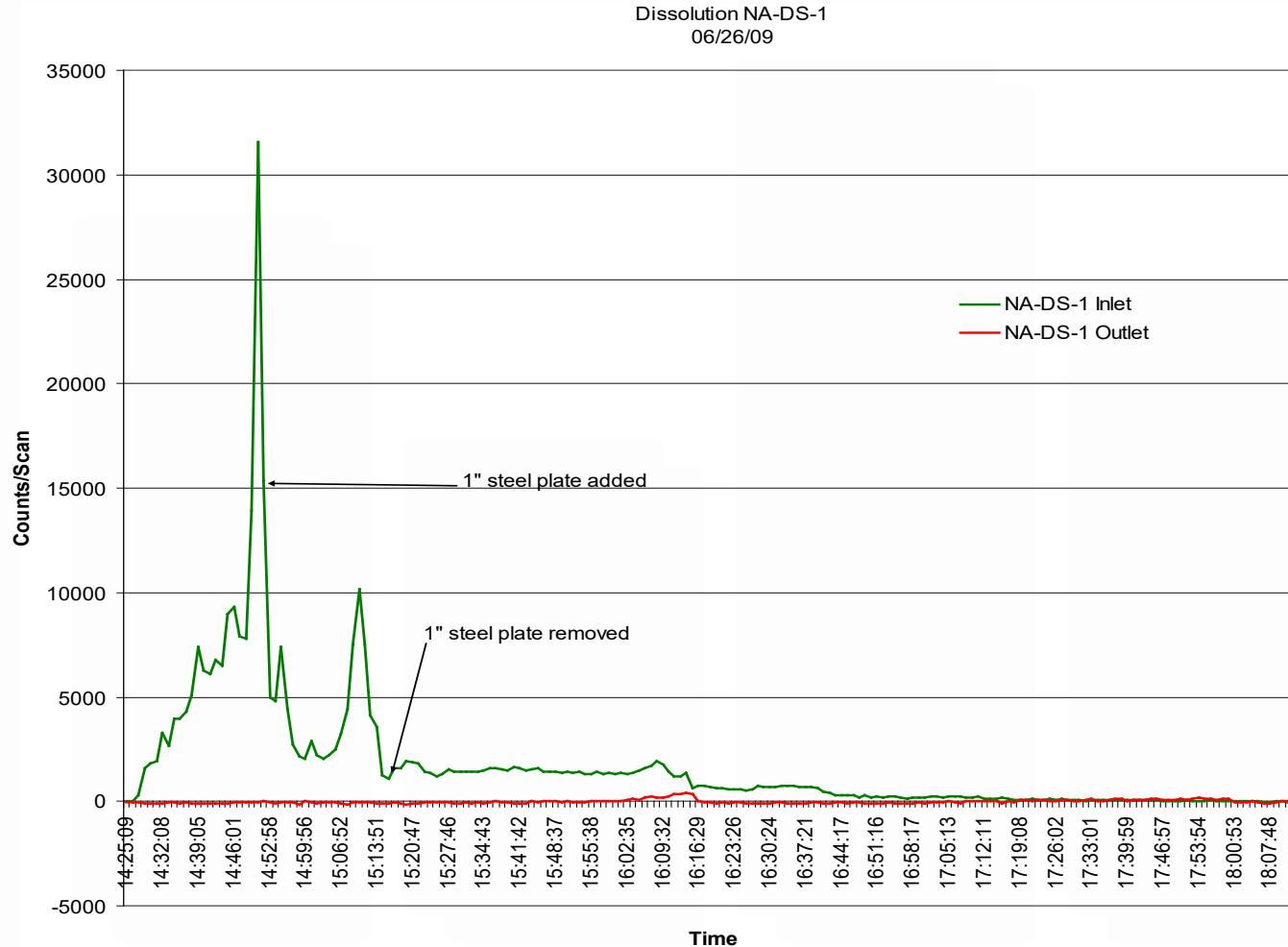
Dissolution of Voloxidized Fuel Powder



- **1180 gm of Burn 1 North Anna fuel was dissolved on 26 June**
 - Used new powder feeder
 - Fuel added to dissolver over ~ 30-minute period
 - Dissolver temperature raised to 90°C for 8-hour digestion period
 - Off-gas routed to DOG rack
 - Dissolver solution filtered through UDS filter system
- **1180 gm of Burn 2 North Anna fuel was dissolved on 15 July**
 - Fuel added to dissolver over ~ 60-minute period
 - Dissolver temperature raised to 90°C for 8-hour digestion period
 - Off-gas routed to DOG rack
- **Surry fuel was not processed**



Kr Evolution During Dissolution – North Anna – Air Voloxidized Powder





Total Krypton Release / Recovery

	Grams of Fuel Oxide	ORIGEN Estimate Initial (Ci)	Gamma Scan Inlet (Ci)	Gamma Scan Outlet (Ci)	Gamma Scan Trap (Ci)	Gamma Scan Vent (Ci)	Trap Loading Based on Desorption Gas Analysis (Ci)	% Recovered vs ORIGEN Estimate
North Anna - Air								
Dissolution	1180	12	3.93	0.0005	3.49	2.60	4.78	39.8%
Voloxidation								~65%
North Anna - O ₂								
Dissolution	1180	12	7.75	ND	8.06	9.34	Pending	67.0%
Voloxidation								53%



Dissolver Off-gas Recovery: Tritium and Iodine

- Trace quantities of tritium (~0.03% of estimated total) were recovered during the purging of the iodine traps from the first North Anna fuel dissolution
 - Fraction remaining in the dissolver solution was pending at end of program

- Preliminary analysis of iodine traps
 - Major fraction of the iodine released during the digestion phase of dilution
 - Good agreement on total iodine recovered from two dissolution operations
 - Fractions released during initial dissolution varied widely (6% to ~35% of total recovered)
 - Fraction of iodine remaining in dissolver solution was pending at end of program



Dissolver Off-gas Recovery: ^{14}C

■ Preliminary analysis of ^{14}C removal/recovery

- $\sim 3 \times 10^{-4} \text{ Ci } ^{14}\text{C} / \text{kg}$ of fuel dissolved (heavy metal basis) was recovered
- Again, this is ~ 10 times more ^{14}C recovered than estimated present in the fuel
- ^{14}C releases from voloxidation and dissolution are roughly 50% - 50%.
- As in the voloxidation case, the difference attributed to ignoring contaminants (e.g. ^{14}N) in as-fabricated fuel
- Seeking analysis of fuel used to verify it met specifications; will aid comparisons
 - *0.00615 gm C-14 / MT fuel if no ^{14}N present*
 - *0.375 gm/MT at 35ppm ^{14}N*
 - *0.8 gm/MT at the ASTM limit of 75ppm ^{14}N*
- If all ^{14}C was released during voloxidation and dissolution, the quantity recovered equates to 0.17gm/MT or ^{14}N impurity of $\sim 16\text{ppm}$



Summary

- **Three batches of fuel were voloxidized at various conditions in lots ranging from ~1 kg to ~2 kg each**
 - Total amount of fuel processed ~5.3 kg (heavy metal basis)
 - 2 kg were then dissolved in two batches
- **Large fraction of tritium released from fuel during voloxidation, nearly 100%**
 - Does not include tritium held in the cladding – a story for another time
- **10%–50% of the Kr was released from the fuel by voloxidation**
 - Significantly more than the 5%–10% reported in the literature
- **Carbon-14 releases from dissolution and voloxidation are approximately the same**
 - Similar to literature reported values
- **Bulk iodine releases occurred during the digestion phase of dissolution**
 - < 1% released during voloxidation
- **Further analysis of feed materials and dissolver solutions continues**

Coupled-End-to-End Nuclear Fuel Reprocessing Project

