



U.S. DEPARTMENT OF  
**ENERGY**

**Nuclear Energy**

Fuel Cycle Research and Development

## **Demonstration of Integrated Voloxidation and Dissolver Off-gas Treatment Systems**

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- **Basic Volatile Radionuclide Control Requirements**
- **Overview of CETE R&D Program**
- **Descriptions of the CETE Voloxidizer and Dissolver Off-Gas Systems**
- **Head – End Test Conditions for the Second CETE Campaign**
- **Off-gas Evolution and Recoveries**
- **Current R&D Efforts across DOE complex**
- **Summary**



# Regulatory Drivers of Off-Gas Capture: 10 CFR 20, 40 CFR 61

10 CFR 20	Air (Ci/m <sup>3</sup> ) at site boundary	Water (Ci/m <sup>3</sup> )
Tritium ( $t_{1/2} = 12.31$ yr)	$1.0 \times 10^{-7}$	$1.0 \times 10^{-3}$
Carbon-14 ( $t_{1/2} = 5715$ yr)	$3.0 \times 10^{-5}$	---
Krypton-85 ( $t_{1/2} = 10.76$ yr)	$7.0 \times 10^{-7}$	N/A
Iodine-129 ( $t_{1/2} = 1.57 \times 10^7$ yr)	$4.0 \times 10^{-11}$	$2.0 \times 10^{-7}$

**40 CFR 61.92: 10 mrem/yr dose equivalent to any member of the public**



## Regulatory Drivers (cont): 40 CFR 190

- (a) The annual dose equivalent does not exceed 25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ of any member of the public as the result of exposures to planned discharges of radioactive materials, radon and its daughters excepted, to the general environment from uranium fuel cycle operations and to radiation from these operations
- (b) The total quantity of radioactive materials entering the general environment from the entire uranium fuel cycle, **per gigawatt-year of electrical energy produced by the fuel cycle, contains less than 50,000 curies of krypton-85, 5 millicuries of iodine-129, and 0.5 millicuries combined of plutonium-239 and other alpha-emitting transuranic radionuclides with half-lives greater than one year**

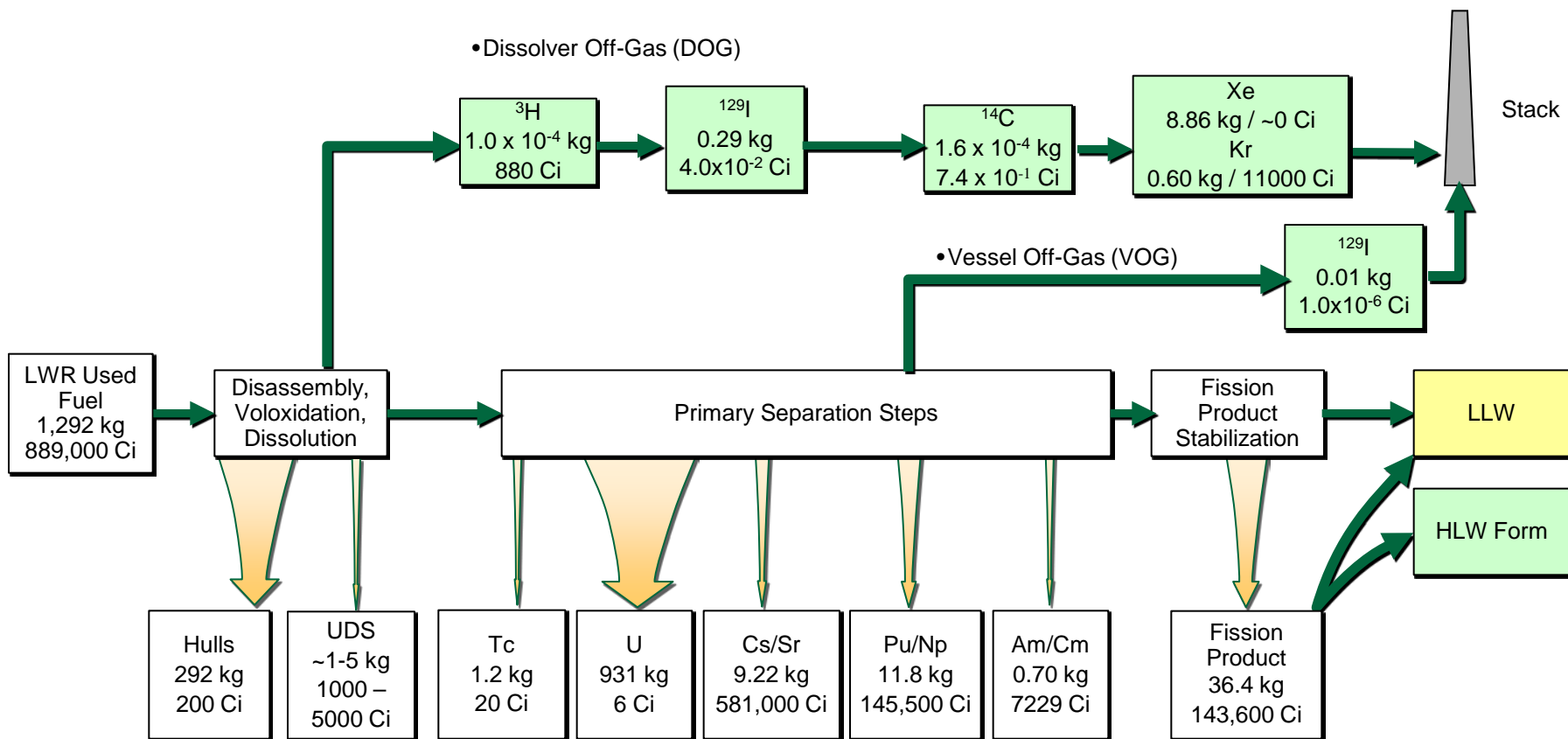
Isotope	Ci/MTIHM	Ci/GW(e)-yr	Min Required DF
<sup>129</sup> I	0.02648	0.89	178
<sup>85</sup> Kr (5 year cooled)	7121	239,000	4.77
<sup>85</sup> Kr (10 year cooled)	5154	173,000	3.45
<sup>85</sup> Kr (30 year cooled)	1414	47,000	0.95

Note: Burn-up: 33 GWd/MTIHM



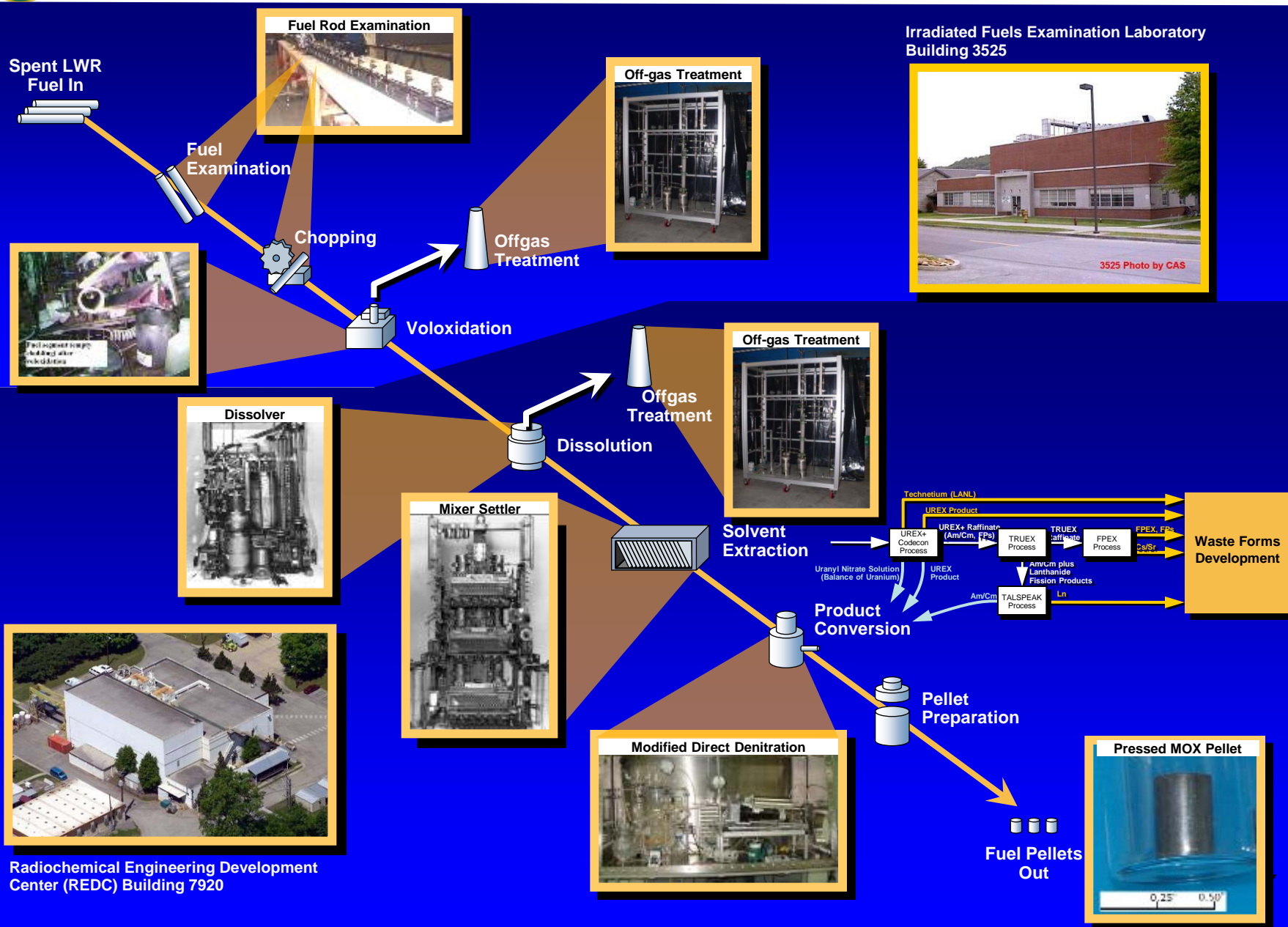
# Simple Reprocessing Block Diagram

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



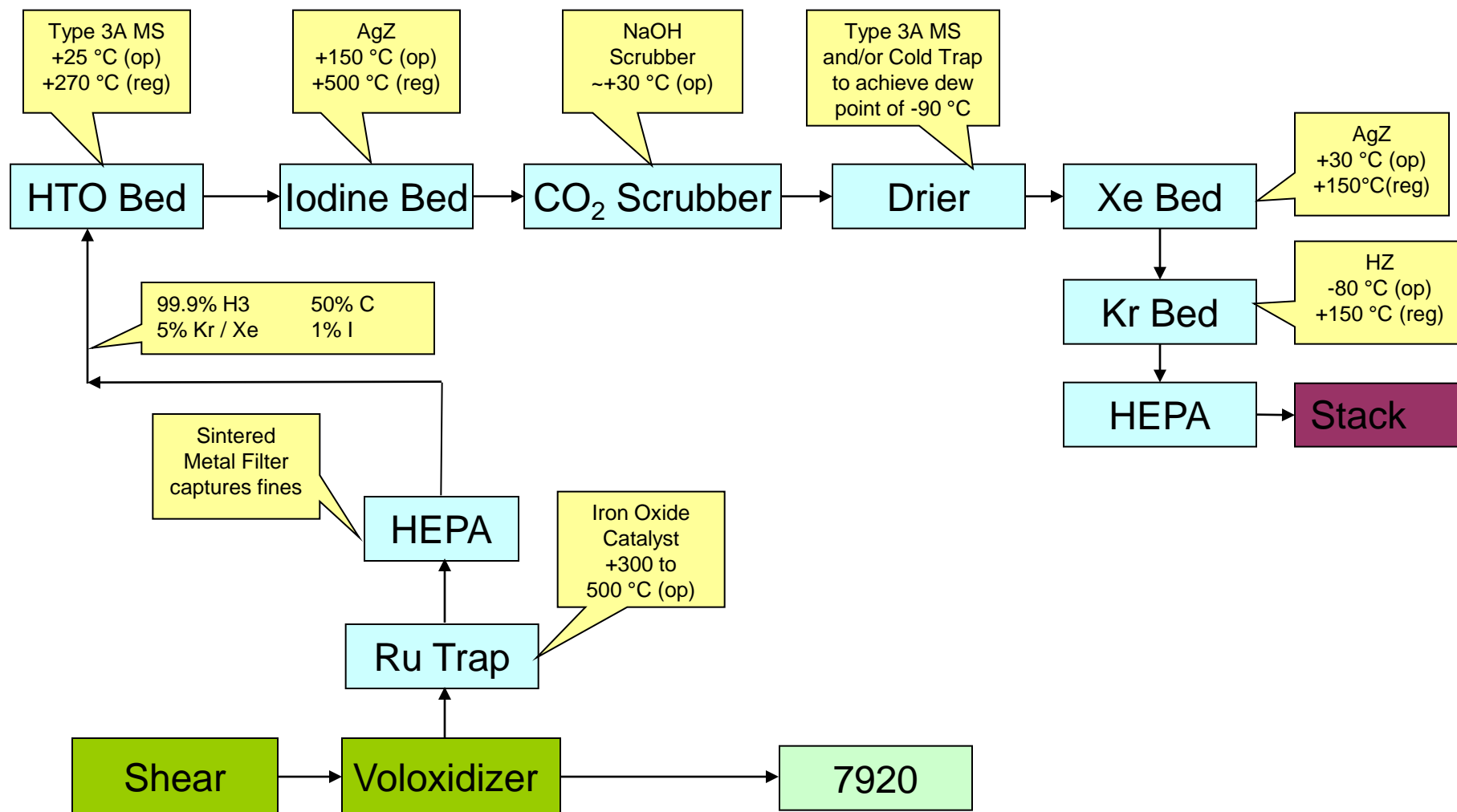


## Coupled-End-to-End Demonstration Overview





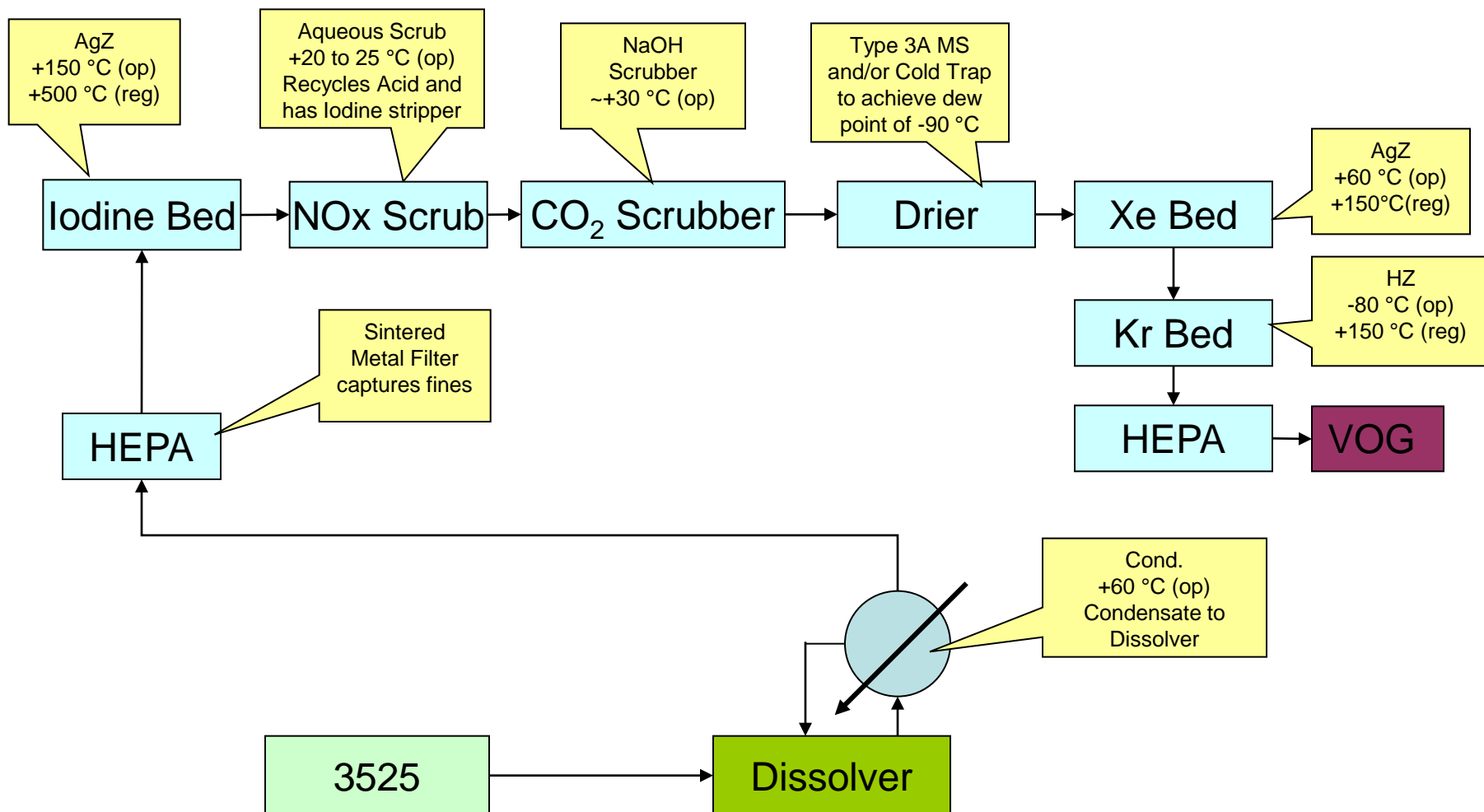
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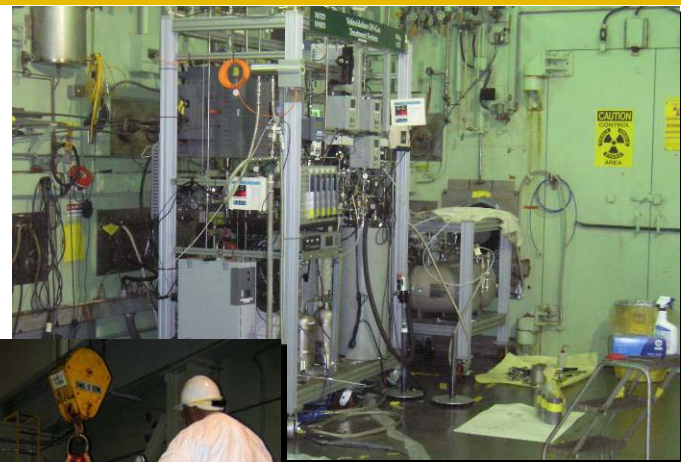
# Head-end Off-gas Capture Systems in Hot Operation

## ■ Objective:

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

## ■ Status:

- Voloxidizer and Off-gas capture system in operation
- 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*





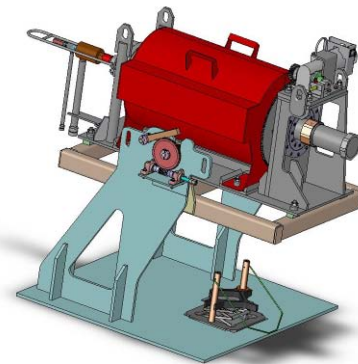
# Voloxidation Basics

## ■ Dry head-end process to oxidize spent fuel oxide

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

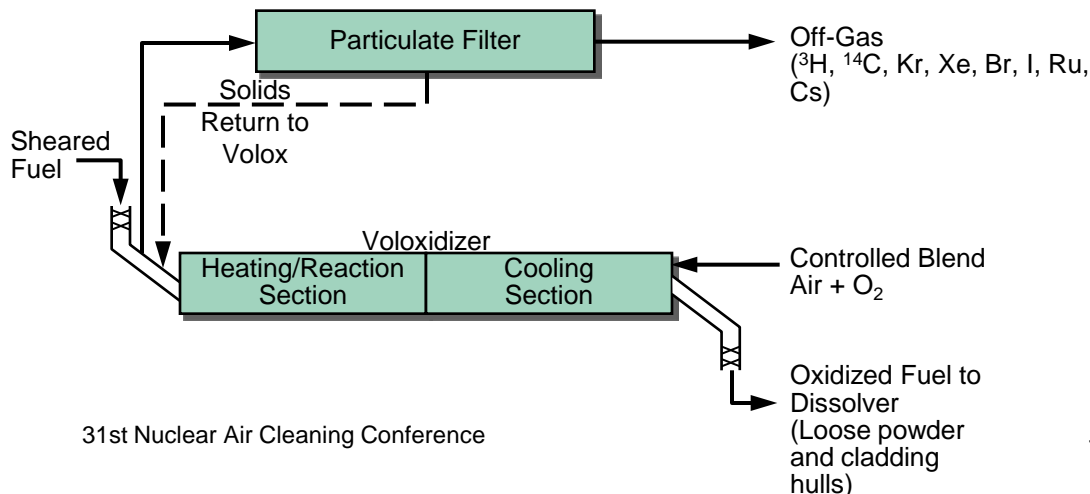
## ■ Process condition:

- 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 <44 µm particles
- ~ 50% of C, 1% of I, and 5% Kr also released



## ■ Controls

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





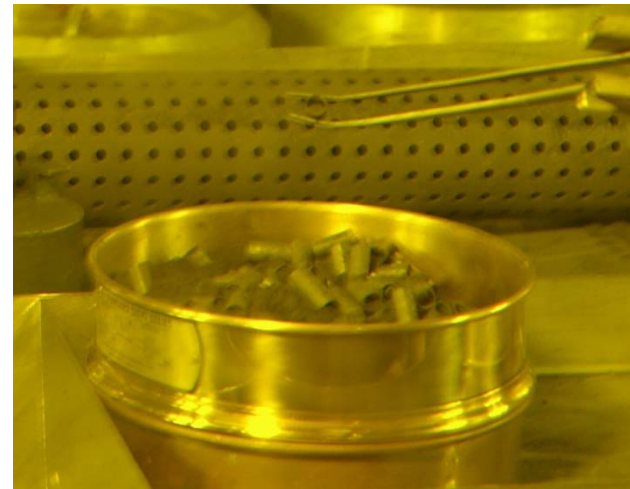
# Test Conditions for Second CETE Campaign

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



### ■ 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  $^{85}\text{Kr}$  release observed via instrumentation
- Initial rapid increases probably caused by reaction of fines from shearing operations

### ■ Run prematurely terminated

- Oxygen consumption and  $^{85}\text{Kr}$  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
- $^{85}\text{Kr}$  measurements slowly approached zero; reaction complete

### ■ Processing time ~12.5 hrs

- Includes oxidation time during ramp to target temperature





## Batch 2: General Observations

### ■ Conditions:

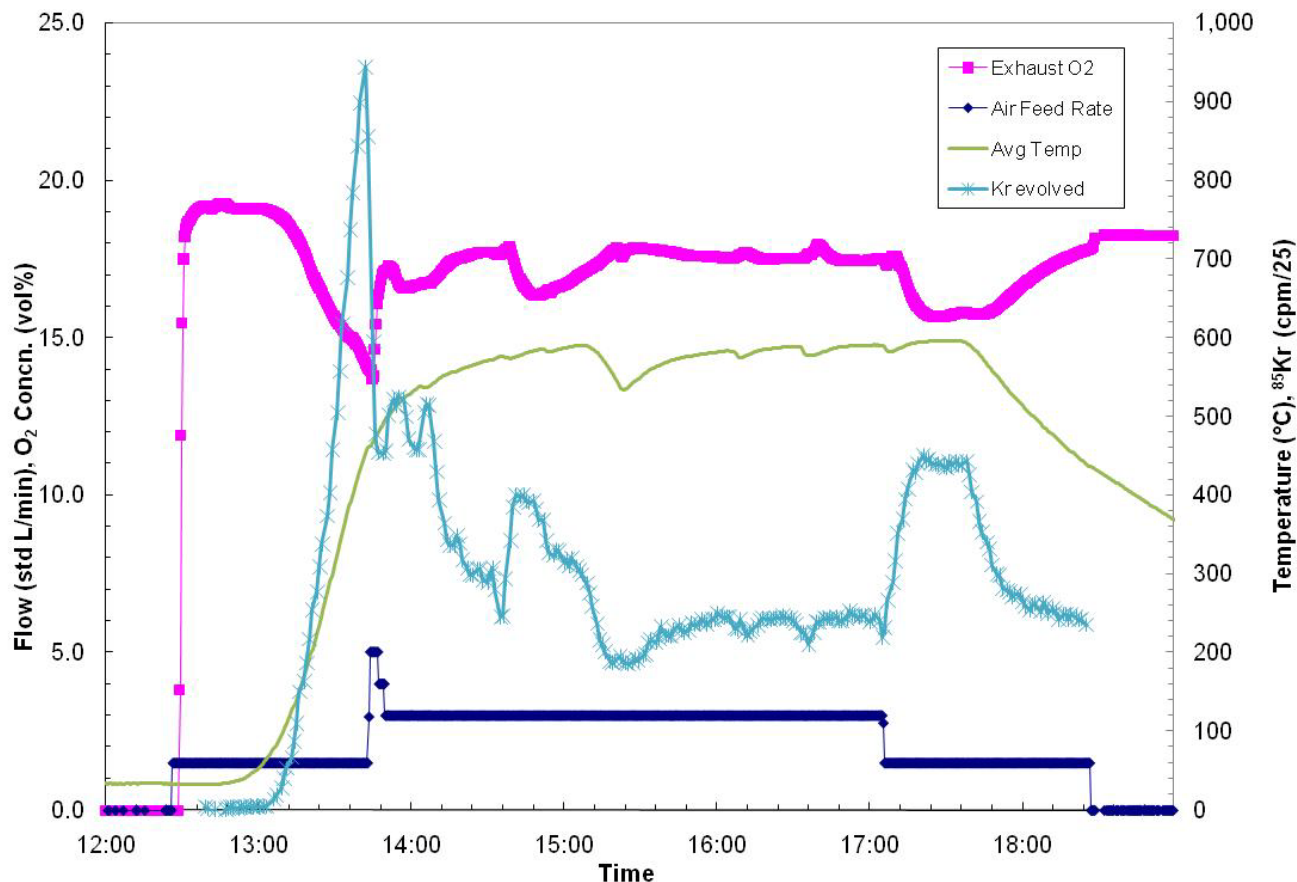
- Fuel: North Anna
- T = 600°C
- Gas = Air

### ■ Oxidation starts at ~100°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



*Progress of first processing phase*



## Batch 3: General Observations

### ■ Conditions:

- Fuel: North Anna
- $T = 600^{\circ}\text{C}$
- Gas = Oxygen feed
- Inleakage of air keeps  $\text{O}_2$  concn below 100%

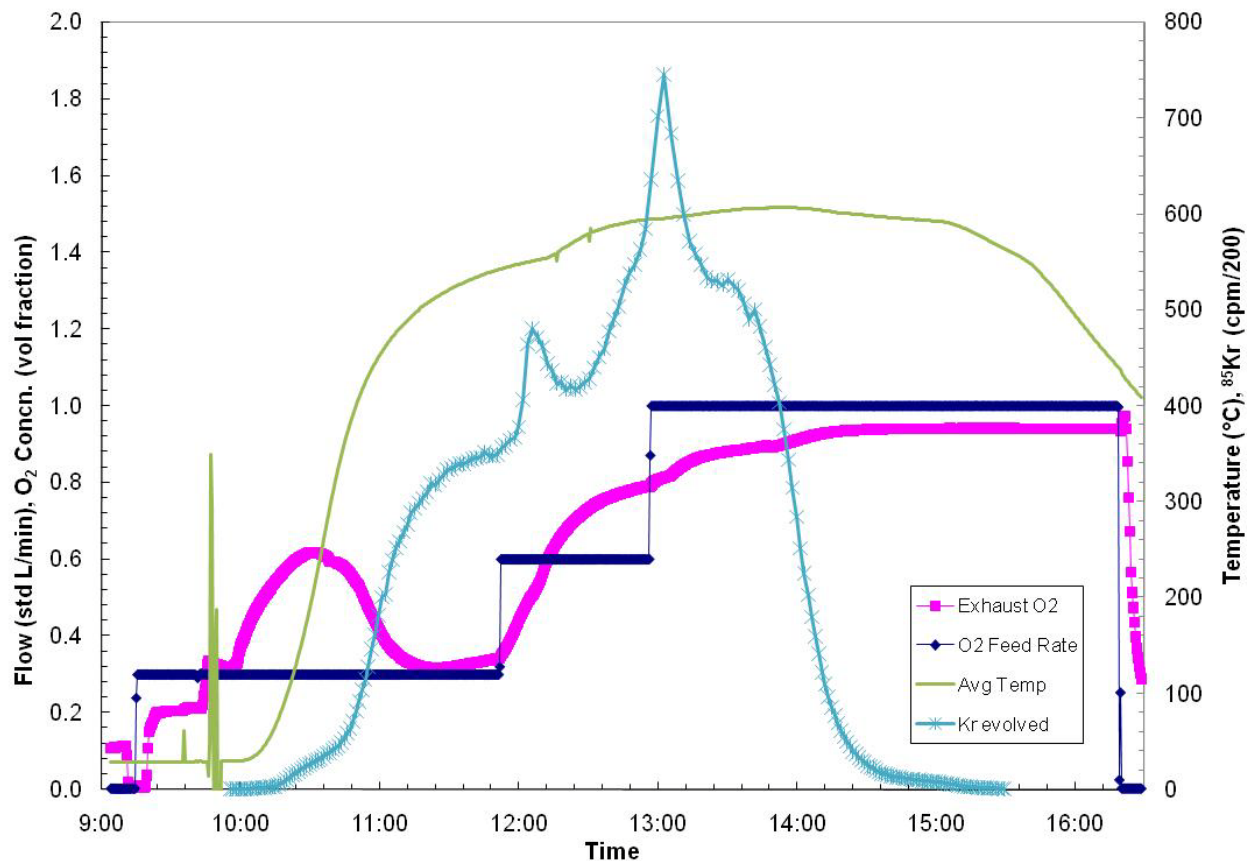
### ■ Oxidation starts at $\sim 100^{\circ}\text{C}$

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

### ■ Completed processing batch in one phase

### ■ Processing time

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



*Progress of processing*





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

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. <sup>1</sup>
North Anna, Phases 1-3	2071	1.94	0.692	35.7	<sup>2</sup>
North Anna, Phase 1	2012	1.89	0.230	12.2	<sup>2</sup>

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

- 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. Analysis of product powder underway to corroborate results.



## Voloxidation Off-gas Recovery: $^{85}\text{Kr}$

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
<b>TOTAL</b>				<b>13.3</b>
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
<b>TOTAL</b>				<b>64.5</b>
North Anna, Phase 1	2012	25.2	13.4	53.2
<b>TOTAL</b>				<b>53.2</b>

- 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%).



# Voloxidation Off-gas Recovery: Iodine and $^{14}\text{C}$

## ■ Preliminary analysis of Iodine in catalyst bed and molecular sieves (tritium trap)

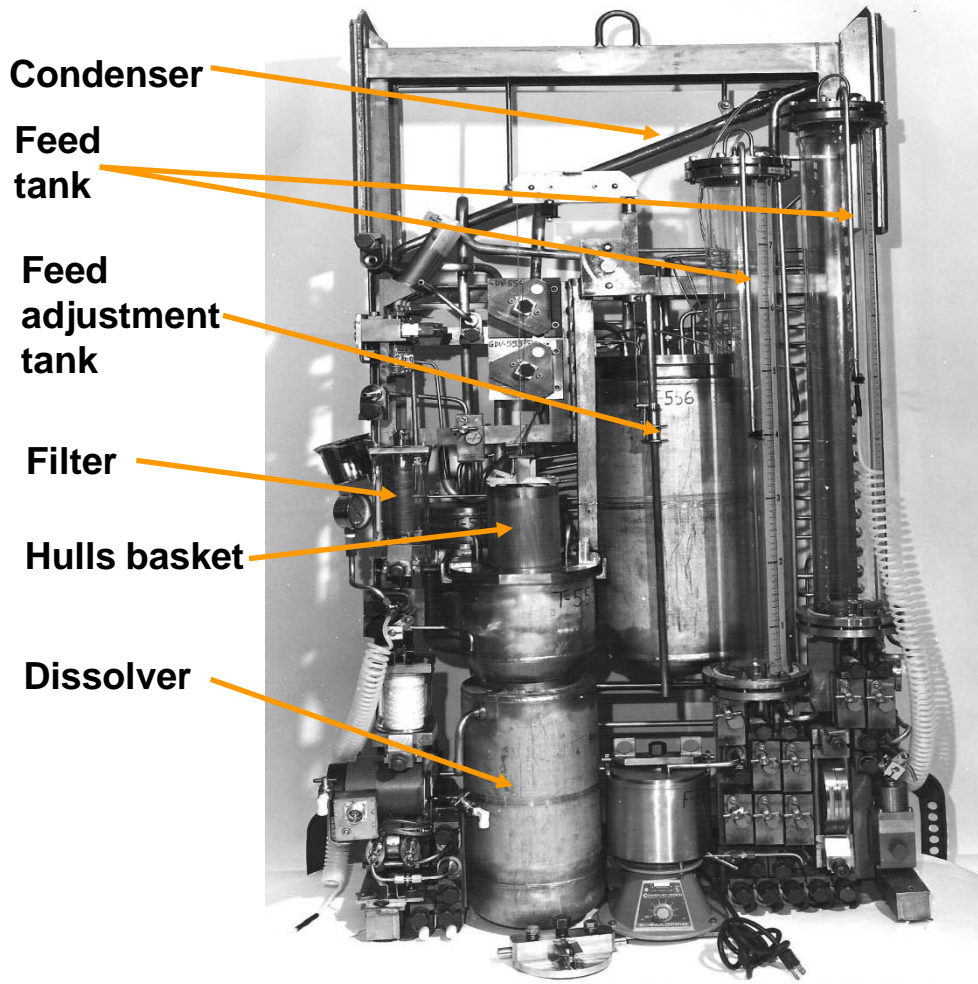
- ~0.04% recovered by voloxidation of Surry-2 fuel
- 0.05 to 0.13% recovered from North Anna fuel
- Lower than the 1% removals estimated from the literature

## ■ Preliminary analysis of $^{14}\text{C}$ removal/recovery

- $\sim 3 \times 10^{-4}$  Ci/kg of fuel dissolved (heavy metal basis) was recovered
- ~10 times more  $^{14}\text{C}$  recovered than estimated present in the fuel
- Difference caused by not including the contaminants (e.g.  $^{14}\text{N}$ ) in as-fabricated fuel in the ORIGEN calculations
- Seeking analysis of fuel used to verify it met specifications; will aid comparisons
  - $0.00615 \text{ gm } ^{14}\text{C} / \text{MT fuel if no } ^{14}\text{N present}$
  - $0.375 \text{ gm/MT at } 35\text{ppm } ^{14}\text{N}$
  - $0.8 \text{ gm/MT at the ASTM limit of } 75\text{ppm } ^{14}\text{N}$
- If all  $^{14}\text{C}$  was released quantity recovered equates to 0.085gm/MT or an estimated  $^{14}\text{N}$  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

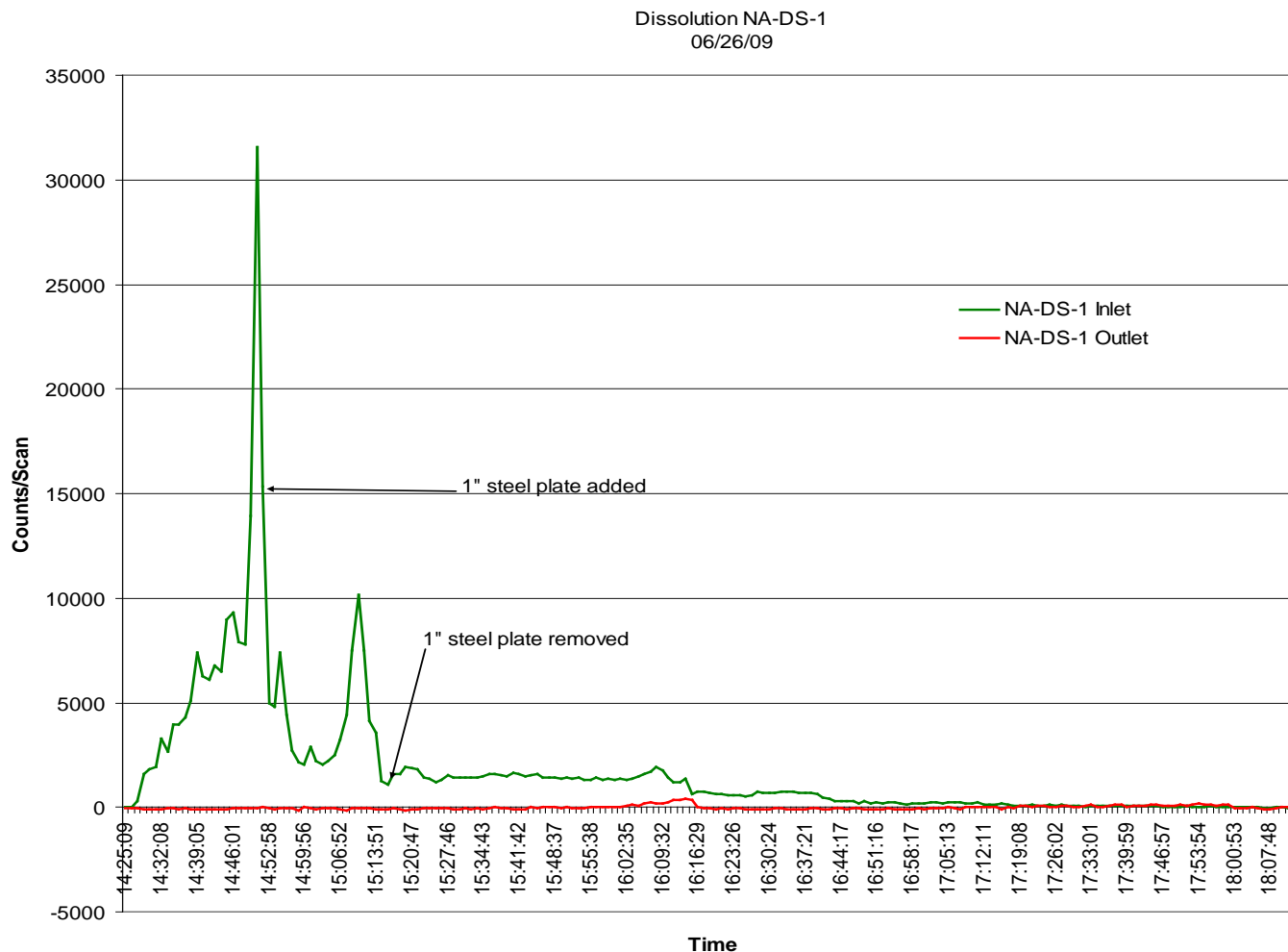
## ■ 1180 gm of Burn 2 North Anna fuel was dissolved on 15 July

- 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

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	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 - O2								
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 is still pending
  
- **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 still pending



# Dissolver Off-gas Recovery: $^{14}\text{C}$

## ■ Preliminary analysis of $^{14}\text{C}$ removal/recovery

- $\sim 3 \times 10^{-4}$  Ci  $^{14}\text{C}$  /kg of fuel dissolved (heavy metal basis) was recovered
- Again this is  $\sim 10$  times more  $^{14}\text{C}$  recovered than estimated present in the fuel
- $^{14}\text{C}$  releases from voloxidation and dissolution are roughly 50% - 50%.
- As in the voloxidation case, the difference attributed to ignoring contaminants (e.g.  $^{14}\text{N}$ ) 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  $^{14}\text{N}$  present*
  - *0.375 gm/MT at 35ppm  $^{14}\text{N}$*
  - *0.8 gm/MT at the ASTM limit of 75ppm  $^{14}\text{N}$*
- If all  $^{14}\text{C}$  was released during voloxidation and dissolution, the quantity recovered equates to 0.17gm/MT or  $^{14}\text{N}$  impurity of  $\sim 16$ ppm

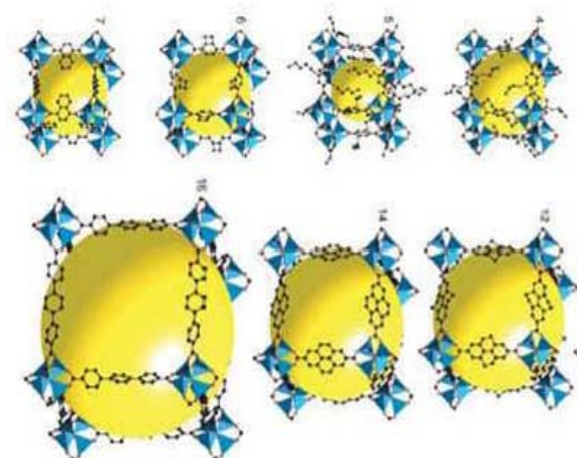
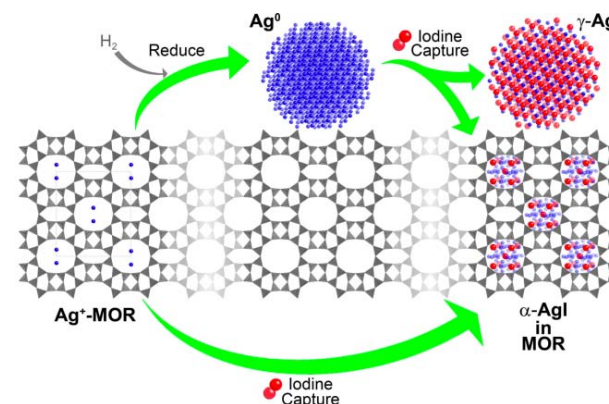




# Multi-lab Off-Gas “Sigma” Team Formed

- Transition of efforts to goal-driven, science-based R&D approach
- Multidisciplinary team from across the complex working collaboratively to solve a broad technical challenge
  - Understand and demonstrate technologies to meet regulatory requirements for recovery and disposal of volatile radionuclides from the processing of used nuclear fuels
- Develop viable methods to control radioiodine, krypton-85, tritium and, if needed, carbon-14 releases from used nuclear fuel recycle
  - Applicable to both aqueous, E-chem and advanced separation processes
  - Includes both capture and immobilization
- Understand the scientific basis for the capture and immobilization technologies

## *Understanding AgI phase formation*



*Metal organic frameworks for I and Kr immobilization*

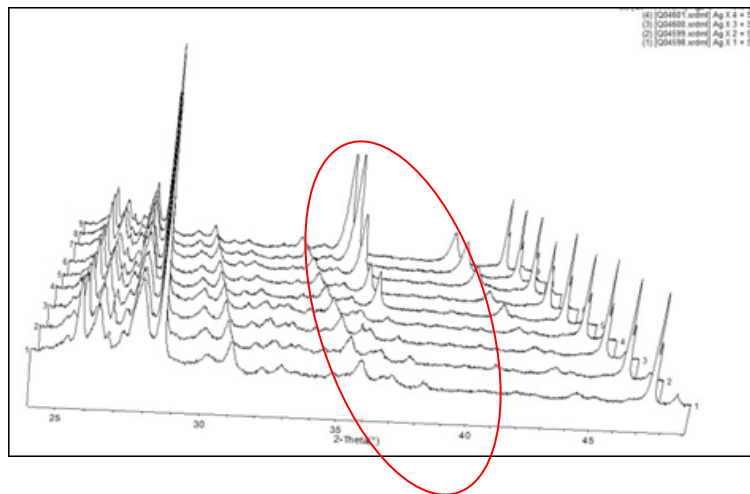


# Recent Accomplishments of Off-Gas Sigma Team Members

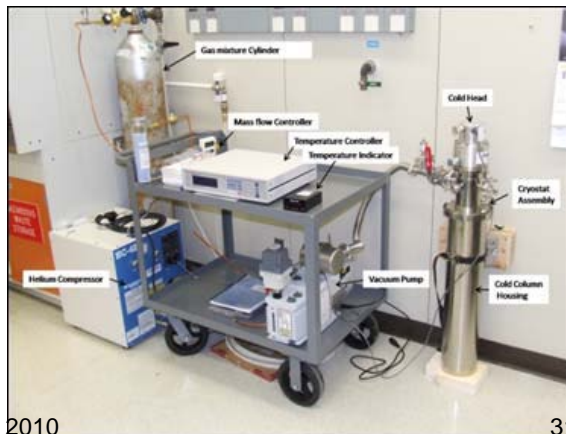


*Single AgZ pellet studies to elucidate reaction rates and mechanisms of I sorption*

*Aging of Ag<sup>0</sup>Z shows clear changes in Ag<sup>0</sup> content*



*Lab-scale Kr capture experiments*





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- **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
- **12% to 63% of total tritium released from fuel during voloxidation,**
  - Does not include tritium held in the cladding – analysis of hulls still pending
  - Significant fraction (40-60%) of total tritium estimated to be in hulls
- **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**



# Questions?

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- Comments?
- Snide Remarks?

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- **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**



- 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  $^{129}\text{I}$ , e.g., vessel off-gas, cell off-gas, etc.
- The distribution of  $^{129}\text{I}$  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  $^{129}\text{I}$  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



- **The bulk of the  $^{14}\text{C}$  found in the irradiated nuclear fuel is assumed to be evolved as  $\text{CO}_2$  into the DOG during fuel dissolution**
- **Diluted 1000-5000x by  $^{12}\text{CO}_2$  by dissolver air sparge**
  - To reduce the impact of nonradioactive  $\text{CO}_2$ , the process could be designed to remove the  $\text{CO}_2$  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  $^{14}\text{C}$  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  $^{85}\text{Kr}$  (>99%) remains in SNF until it is sheared and dissolved
- Substantial fraction of the  $^{85}\text{Kr}$  would be released during voloxidation, if used
- $^{85}\text{Kr}$  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