Modified Direct Denitration-Product Conversion and the CETE Demonstration

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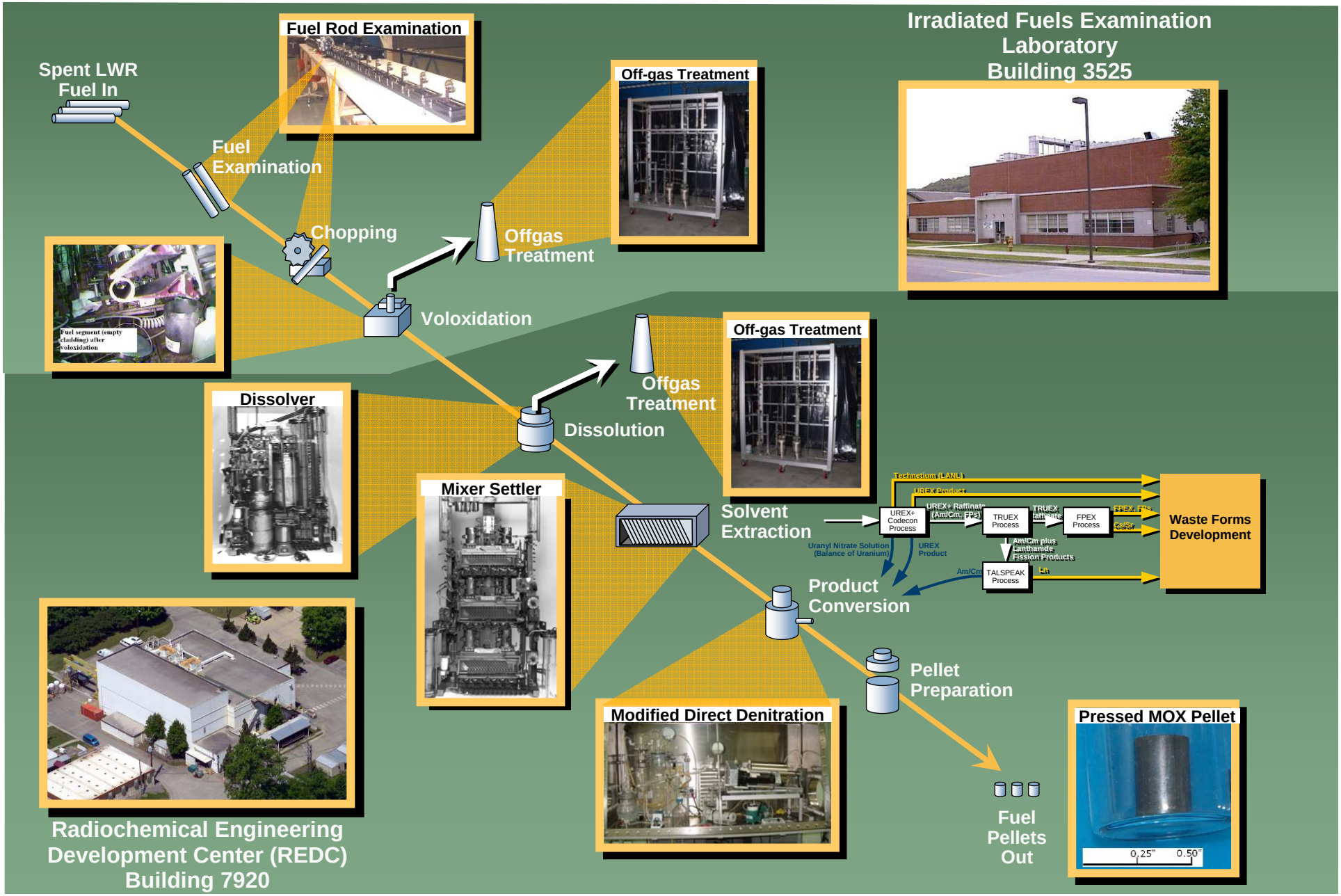
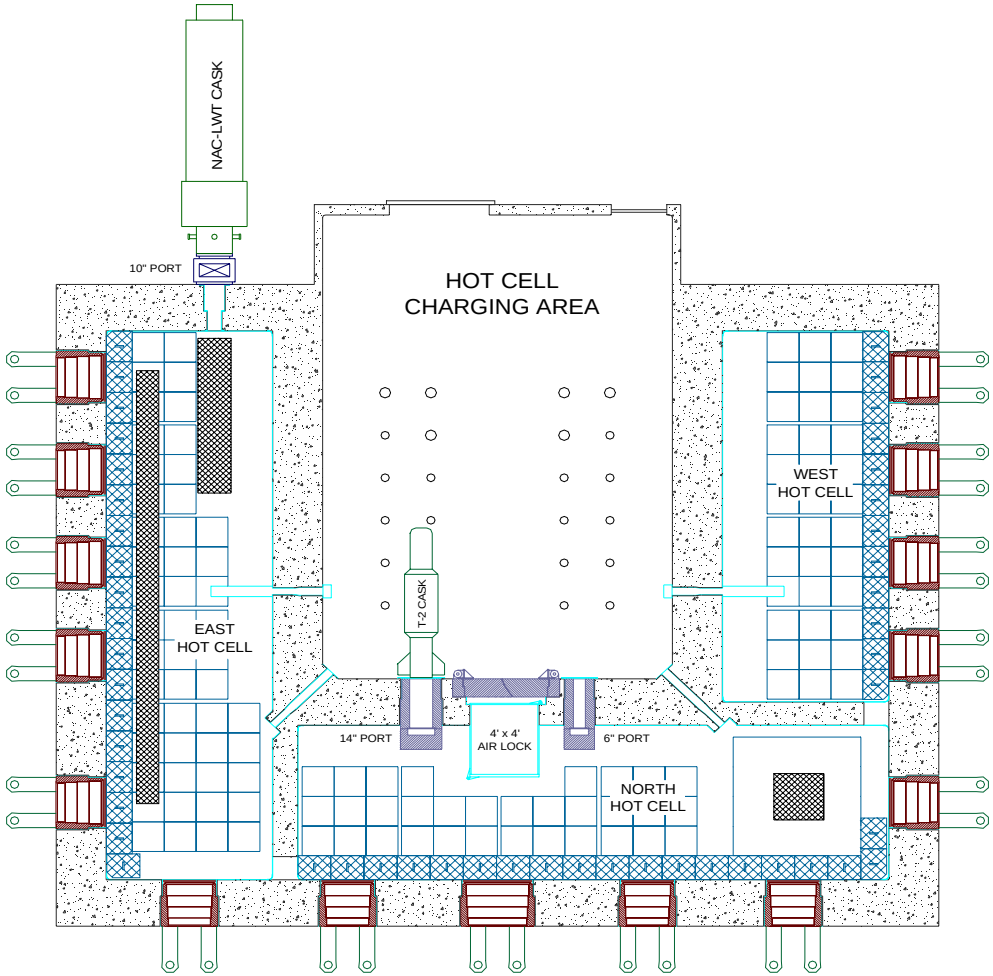
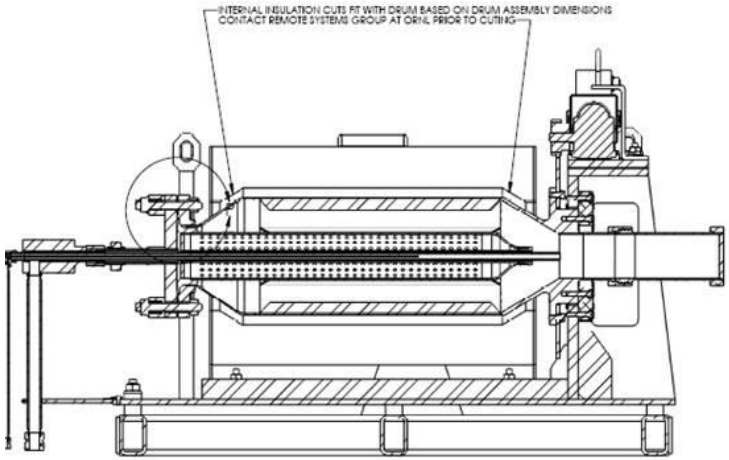
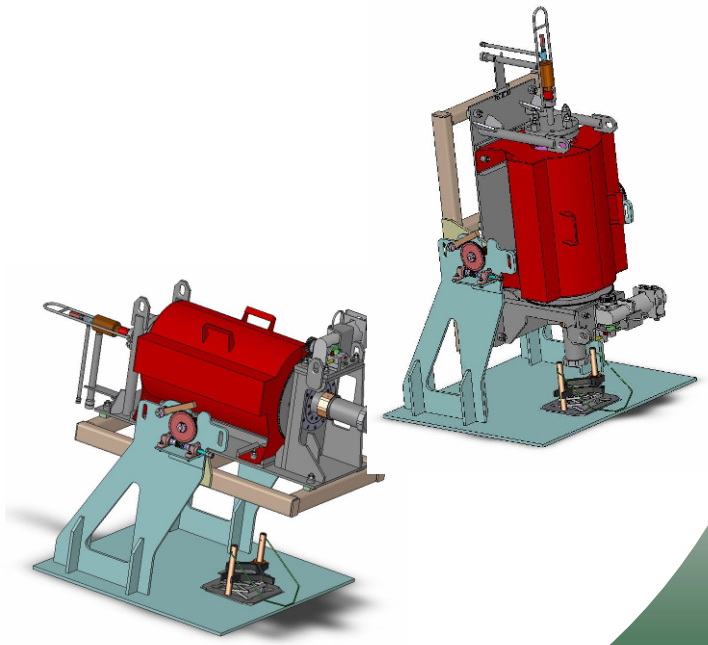
What is the Coupled-End-to-End Demonstration?



Irradiated Fuels Examination Laboratory Building 3525

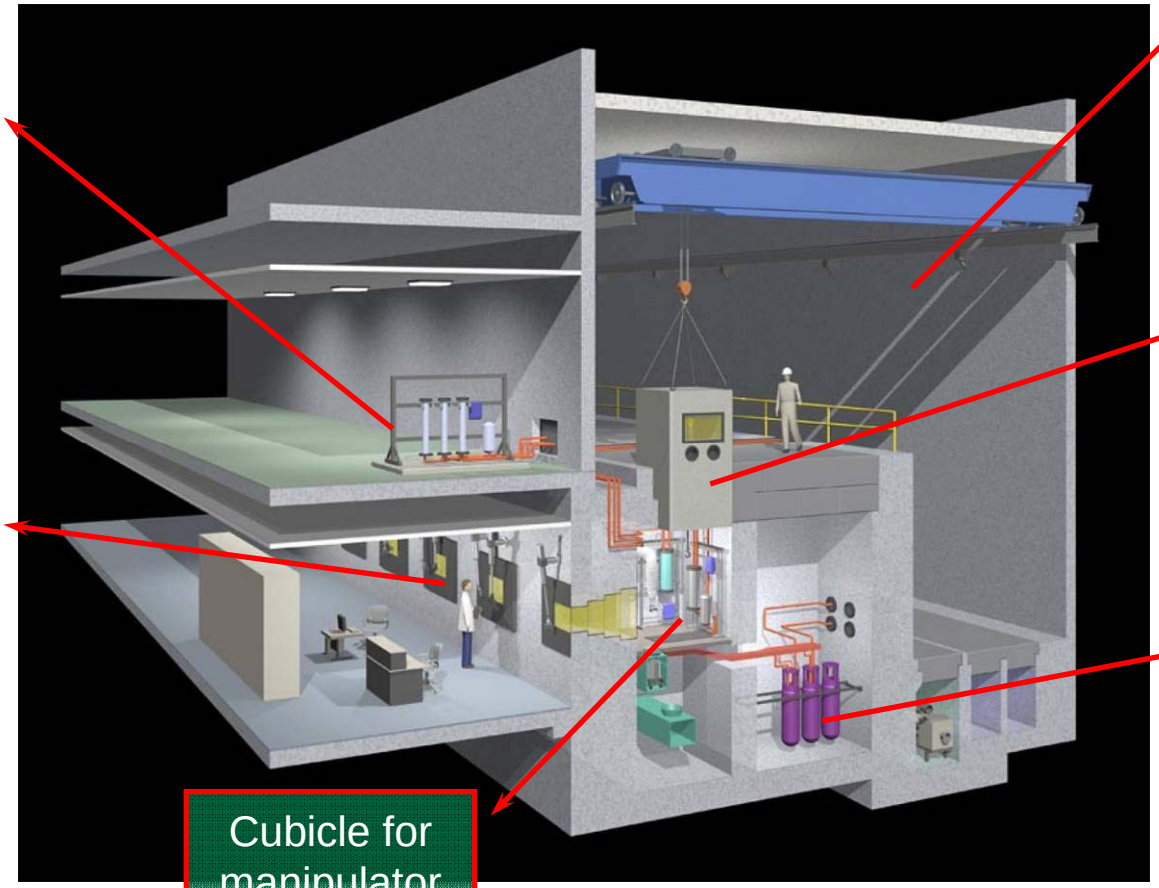






Melton Valley- HFIR and the REDC

Overview of 7920 Hot Cell Facility



Racks for chemical makeup & additions

High-bay area for cask receipt

Transfer case for equipment installation

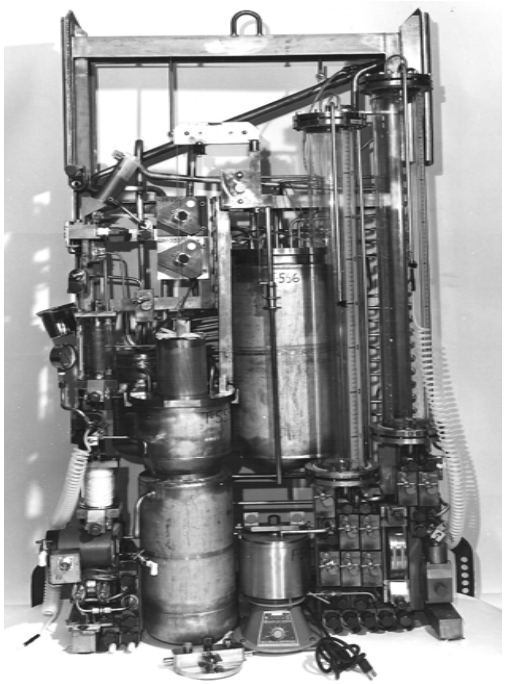
Nine shielded hot cells for remote processing

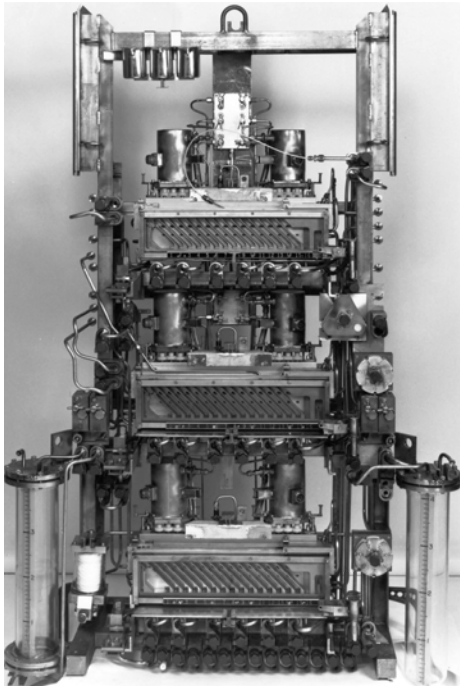
Tank pit for processing and collection tanks

Cubicle for manipulator operated equipment

Radiochemical Engineering Development Center (REDC)

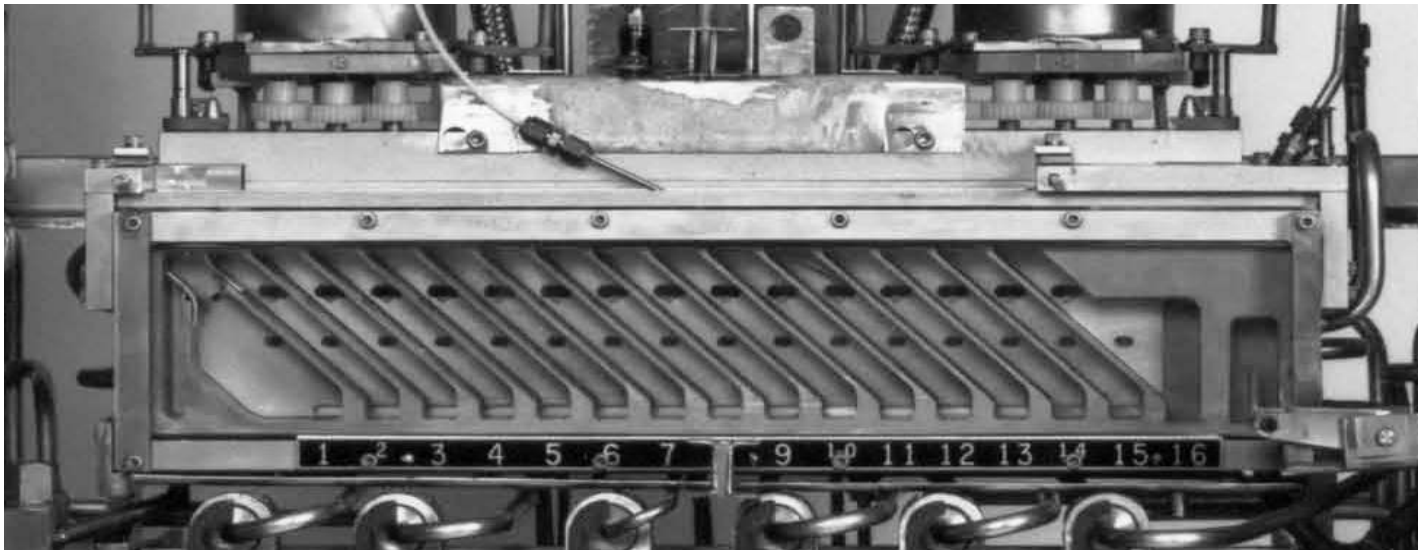
- **REDC**
  - **Multipurpose hot cell facility**
  - **Nine heavily shielded hot cells**
  - **Equipment mounted on removable racks**
  - **Offers flexibility in adding new processes and incorporating improvements**





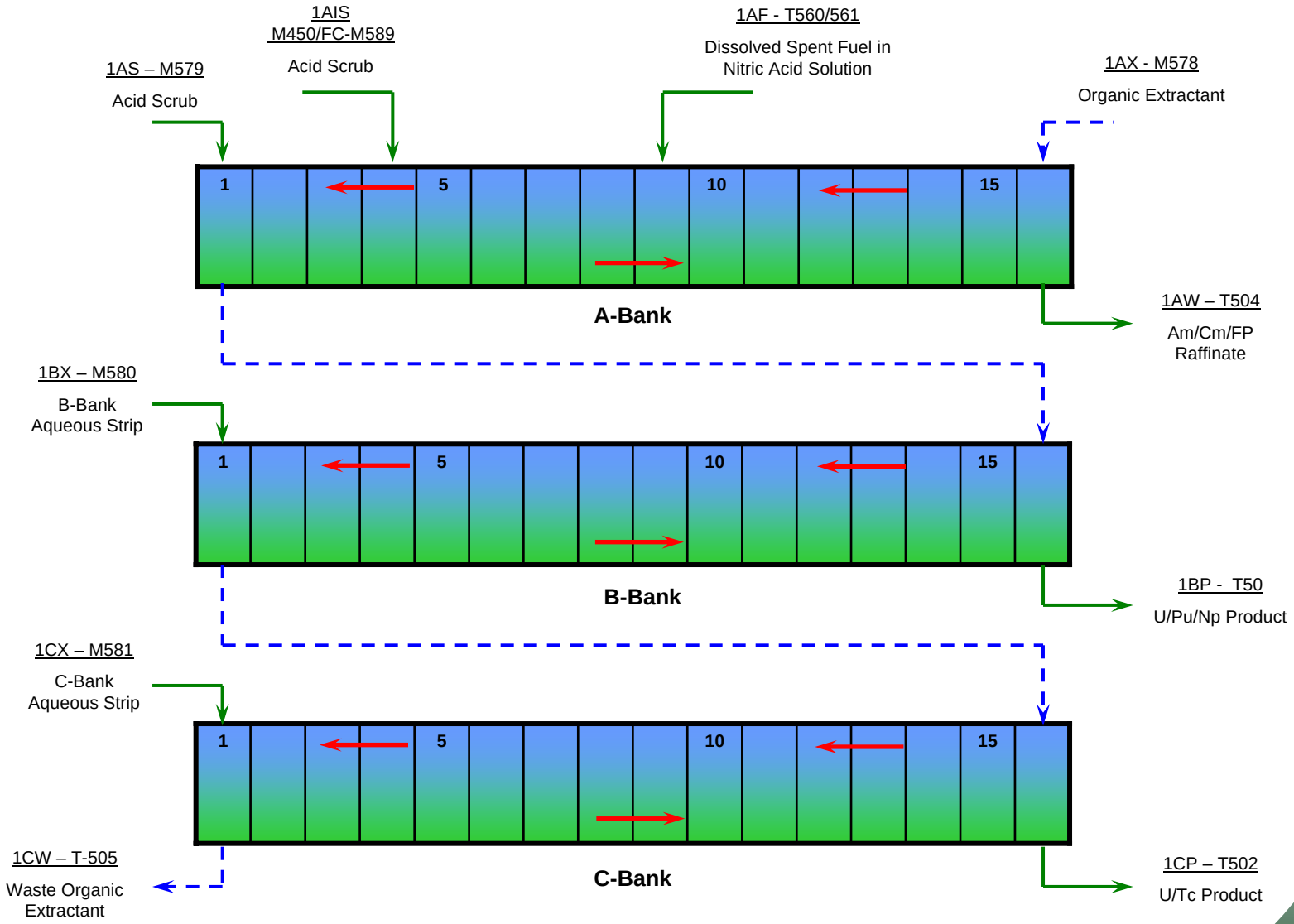
- **14 L jacketed dissolution tank, 25 L feed adjustment, 2 x 8 L metering tanks**
- **Three banks of 16-stage mixer/settler contactors, open top for reagent additions and stage sampling, 30/50mL M/S volumes, 5 L/h total flow throughput**

Solvent Extraction Equipment



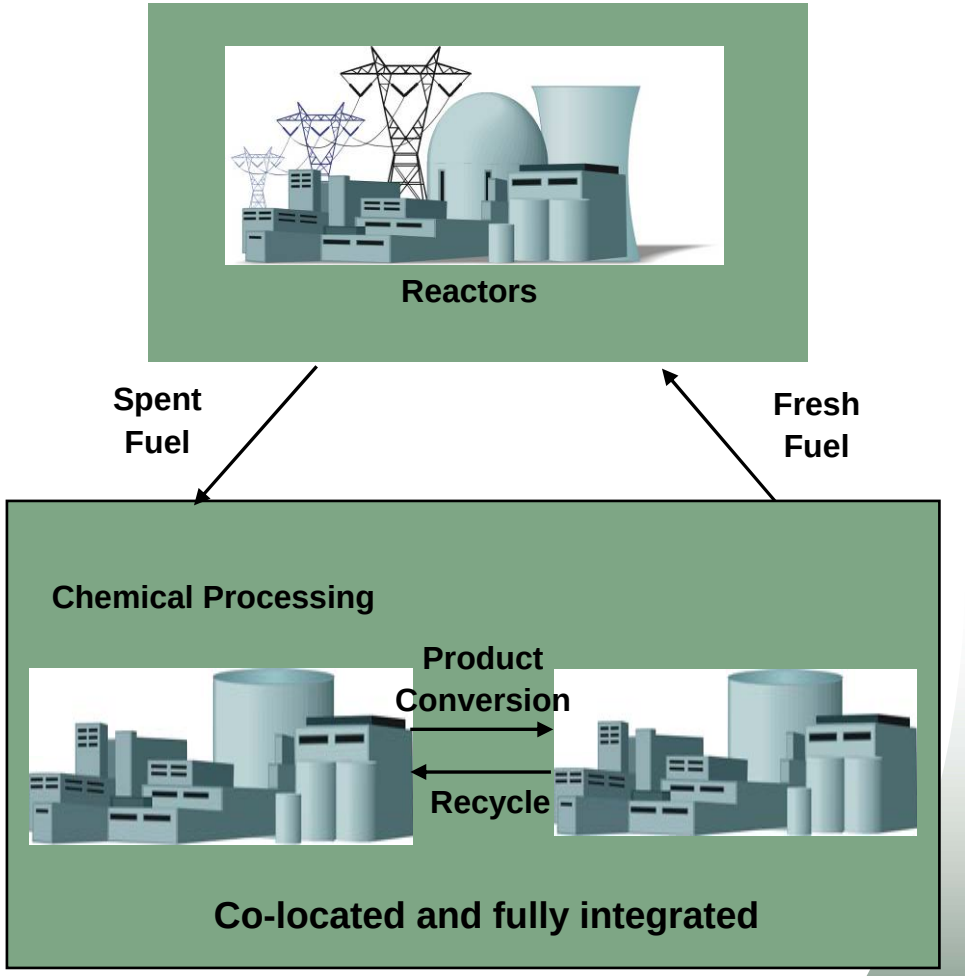
- **Quartz window allows viewing of settling stages**
- **Contactors are open on the top for reagent additions and stage sampling**
- **Mixer/settler volumes are 30/50 mL, respectively**
- **Throughput: up to 5L/h total flow**

CETE UREX+ Flowsheet



Conversions

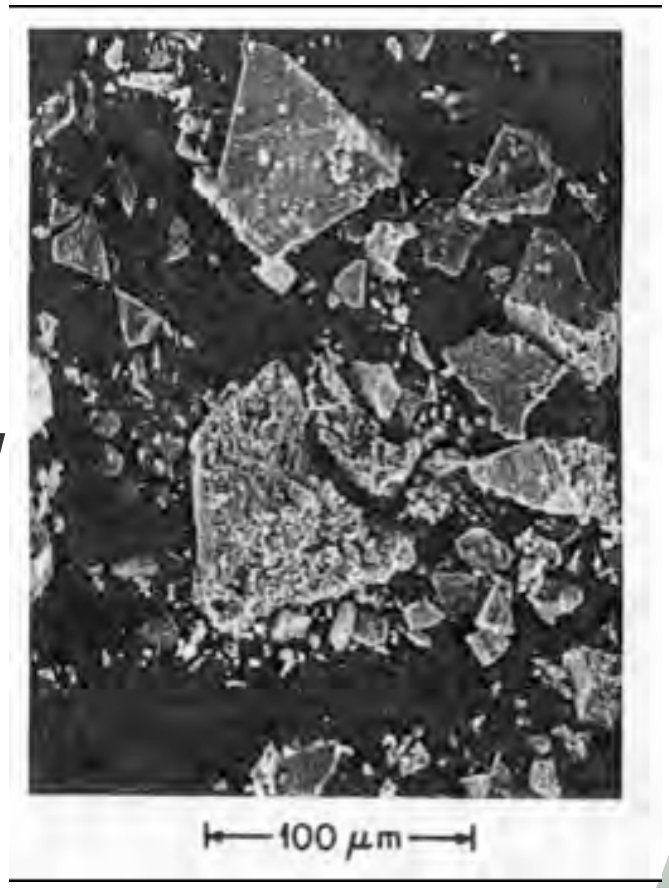
- **Processing of spent nuclear fuel produces a number of purified product streams**
- **Typical aqueous processing products are in nitric acid solutions**
- **Conversion to solid form needed for recycle, storage, or disposal**
- **<u>Direct conversion</u> to oxide with proper ceramic properties for recycle fuel fabrication ideal**
- **Product Conversion is the link between Separations and Fuel Fabrication**



Development of Modified Direct Denitration

MDD History

- **Conversion of aqueous processing products to solid form needed for recycle, storage, or disposal.**
- **Initial development work on uranyl nitrate conversion to uranium oxide**
- **Direct denitration produced a low-surface-area glassy product that requires further processing to obtain desired ceramic properties**
- **Ceramic properties should be comparable to oxide obtained by the ammonium diuranate (ADU) process**
- **Incorporation of an additive to the uranyl nitrate produced oxide with the desired ceramic properties; thus named the Modified Direct Denitration (MDD) process**

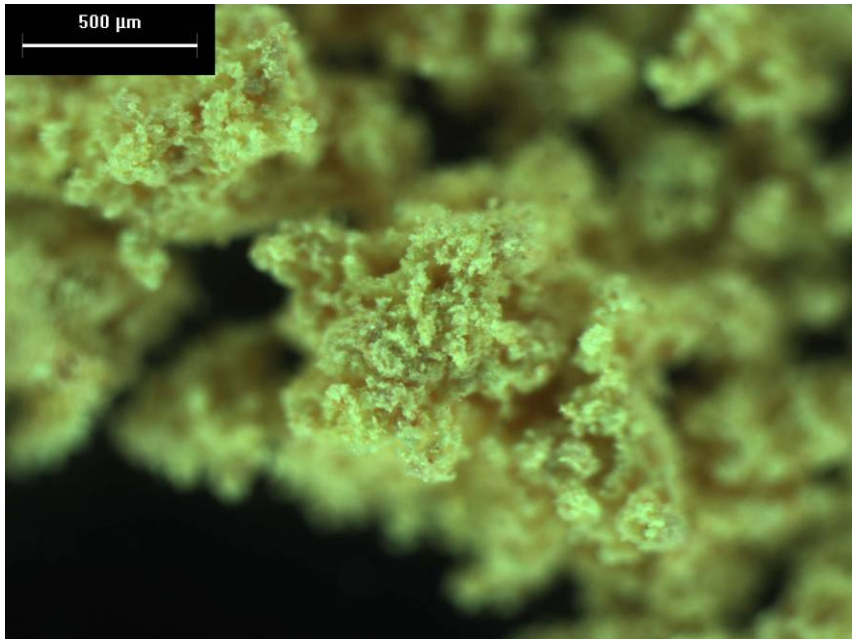


P. A. Haas, R. D. Arthur, W. B. Stines
ORNL-5735, 1981

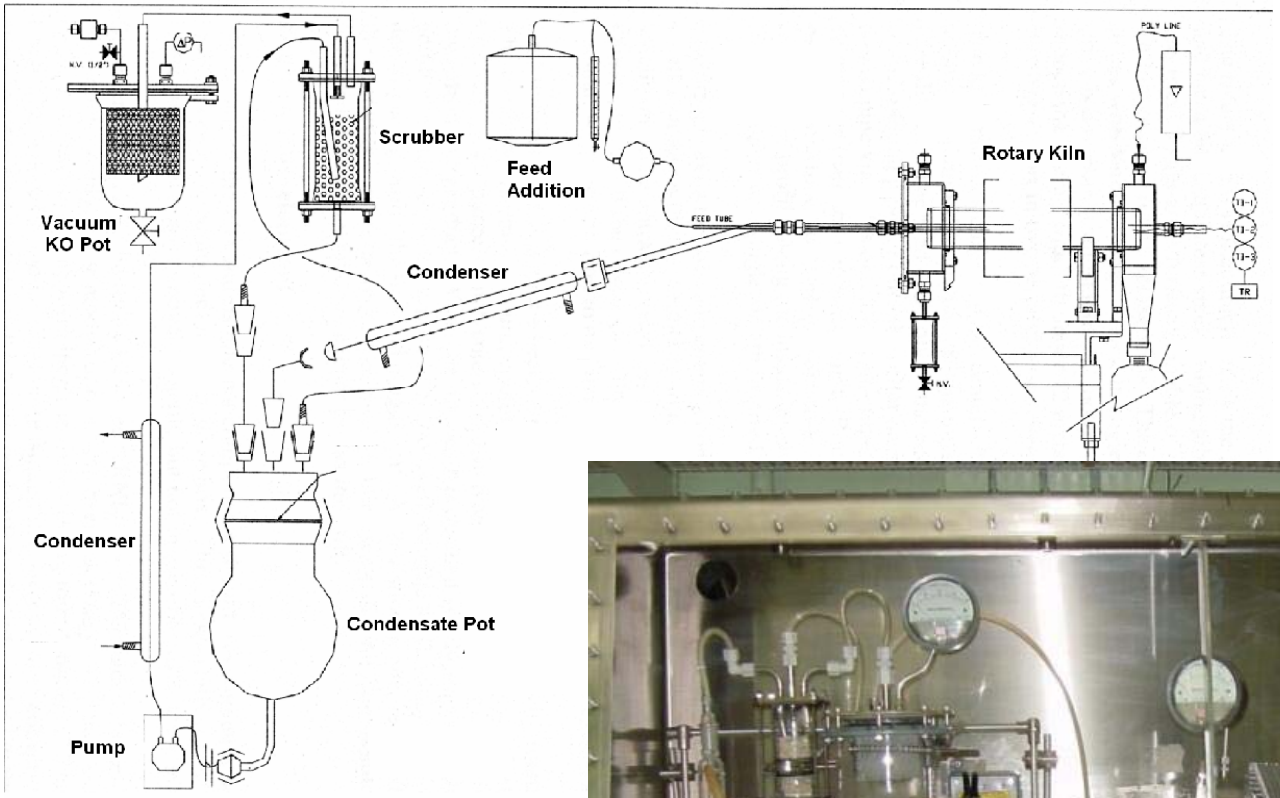
Development of Modified Direct Denitration

MDD Details

- **The thermal decomposition behavior and characteristics of the oxide are changed by the addition of an inorganic salt**
- **For uranium, a double salt is formed which produces a slurry, then a crystalline matrix, and finally a high-surface-area oxide**
- **The decomposition is accomplished in three distinct steps:**
  - **dehydration at 50°C**
  - **decomposition of the tetranitrate salt at 170-270°C**
  - **decomposition of the trinitrate salt at 270-300°C to UO_3 with crystallization at ~500°C**
- **This conversion is readily accomplished in a rotary furnace unit which lends itself to continuous operation**



Process Equipment Description

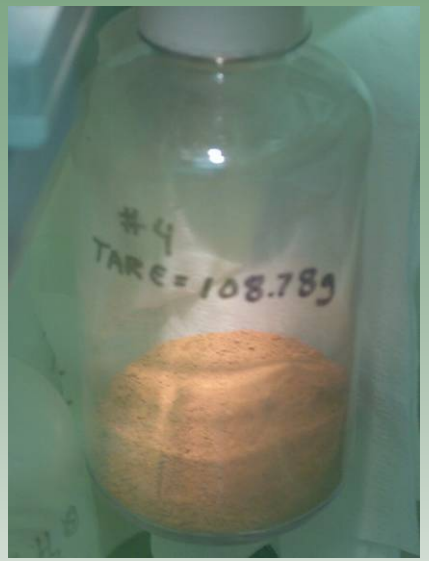


- **Condensate is used as scrubbing liquid for off-gas**
- **Air purge sweeps off-gas vapors from the furnace**

- **Heart of MDD process equipment is the rotary furnace**
- **Metal nitrate feed solution enters furnace and exits as converted oxide powder**

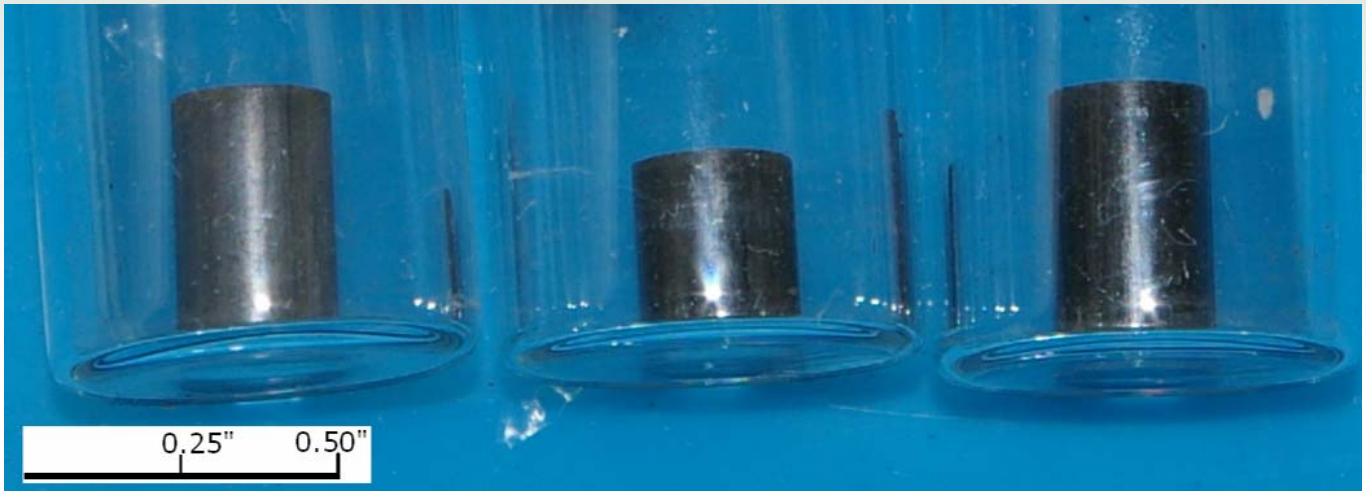
Pre-CETE MDD Glovebox Work

- **Cold testing with cerium**
- **Plutonium Conversion, 100% Pu**
- **Uranium Conversion, 100% U**
- **MDD Co-conversions**
  - **U/Pu- 90 wt% U & 10 wt% Pu**
  - **U/Pu/Np ratios of 90.4/9.1/0.5 wt% respectively**
  - **U/Pu/Np/Am ratios of 92.3/ 7.15/ 0.31/ 0.28 wt% respectively**
  - **Condensate from all co-conversion runs was collected**
    - *Decanted solids and fed as slurry*
    - *Ammonium hydroxide precipitation allows for condensate recycle*
- **Proof of Principle completed**



Pre-CETE Mixed Oxide Pellet Work

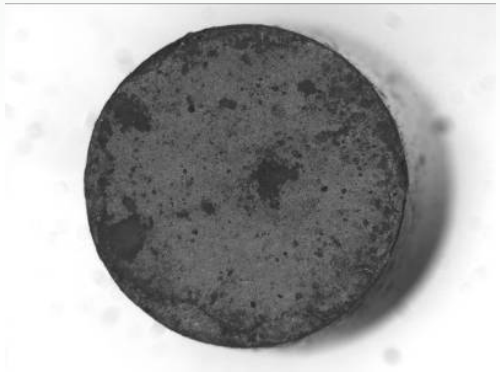
- **MDD U/Pu/Np/Am oxide- calcined/reduced, pressed pellets**
- **An organic binder was used, pressed to ~43,000 psi**
- **Green pellets- L/D values between 1.0 and 1.6**
  - **Pellet 1 D=0.251" L/D=1.6 %TD= 53.3%**
  - **Pellet 2 D=0.251" L/D=1.1 %TD= 54.0%**
  - **Pellet 3 The powder was pre-compacted/ ground before pressing D=0.251" L/D=1.6 %TD= 56.9%**

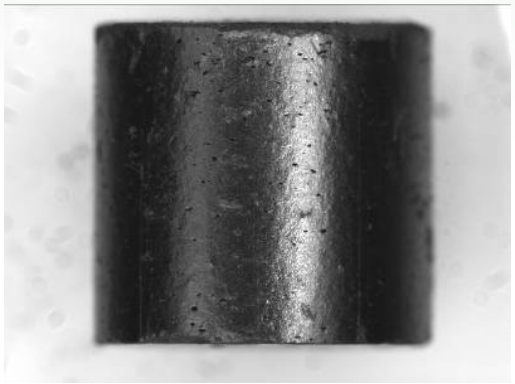


MDD DU Powder Characterization

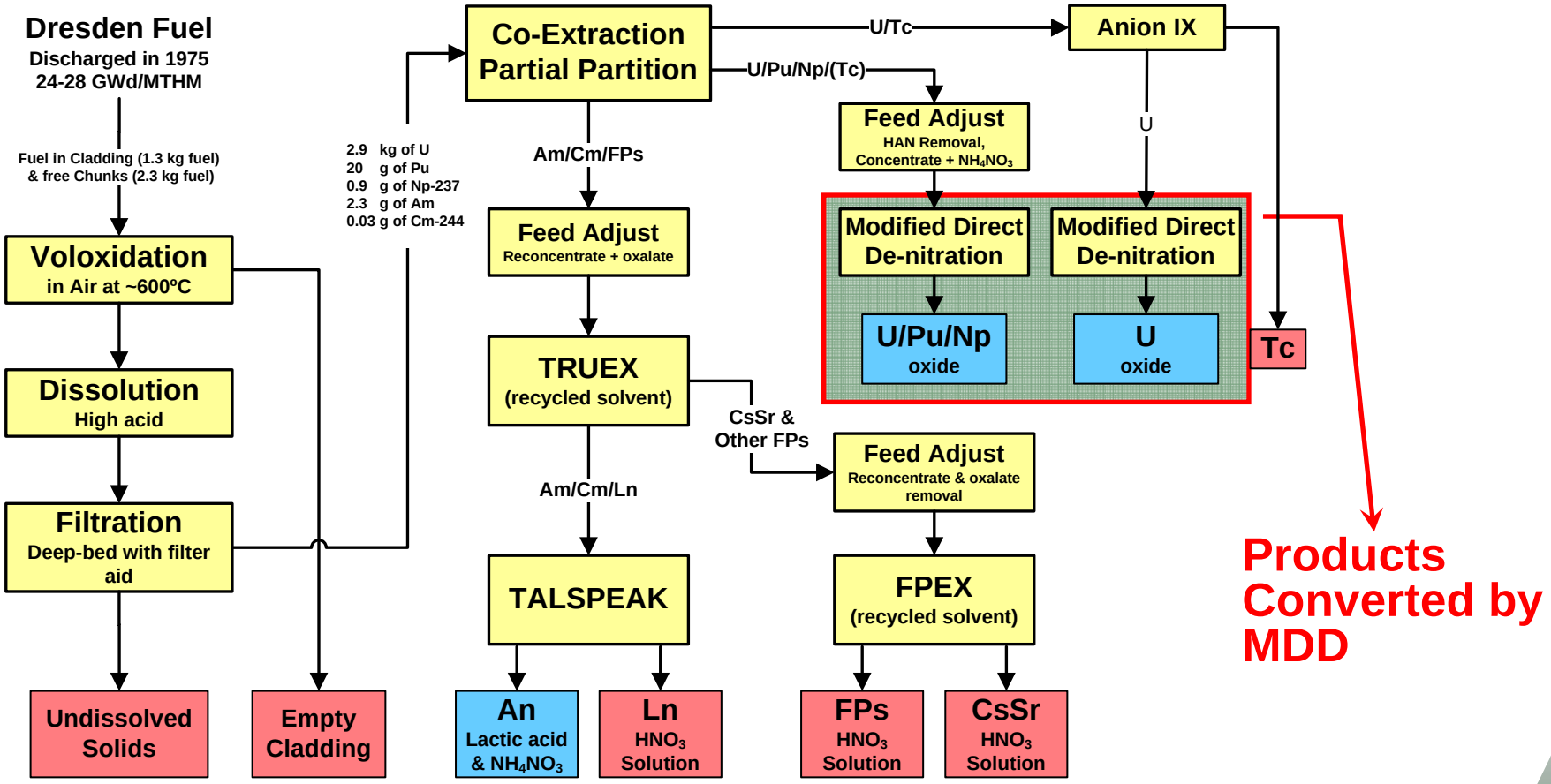
Calcination/reduction and sinterability studies on two runs with depleted uranium

Powder	Calcination/ Reduction	Surface Area	Green Pellet	Sintered Pellet
062507	Dry 4% H_2/Ar	3.0 m^2/g	49% TD	95% TD
	Moist 4% H_2/Ar	2.2 m^2/g	51% TD	91% TD
062707	Dry 4% H_2/Ar	1.8 m^2/g	54% TD	92% TD
	Moist 4% H_2/Ar	1.6 m^2/g	56% TD	90% TD



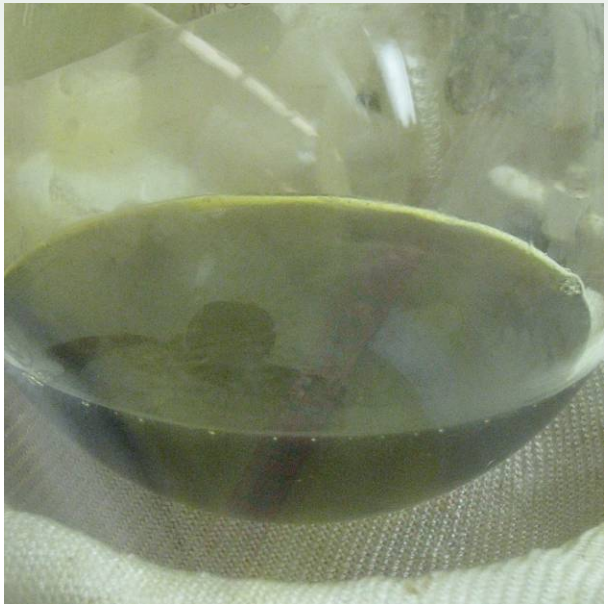


Coupled-End-To-End (CETE) Run 1 Spent Fuel Processing



CETE Demonstration Run 1- Dresden Fuel

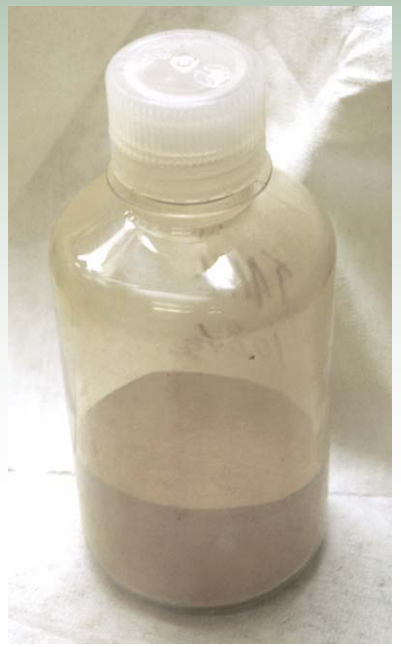
- **~3.5 kg Dresden-1 BWR spent fuel, discharged Sept. 1975 with a fuel burnup of 24-28 GWd/MTHM.**
  - **MDD run using "clean cut" of uranium from U/Tc separation to determine whether impurities/contamination from hot cell processing affect the rotary kiln operation**
  - **U/Pu/Np stream transferred from hot cells to glove box for final feed preparation and processing via MDD**
  - **11.7:1 U: Pu/Np in feed solution**



CETE Demonstration Run 1- Dresden Fuel

- **Performed MDD run to co-convert U/Pu/Np stream**
- **U/Pu/Np Conversion Feed**
  - **164 g U, 13.2 g Pu, 0.72 g Np, U:Pu ratio=12.4**
- **U/Pu/Np Product**
  - **U/Pu/Np oxide by MDD = 183 g**
  - **Residuals at ~300°C = 3 %**
  - **Pressed pellets at 43,000psi using**

    0.3 wt% stearic acid as binder



MDD Powder Characterization

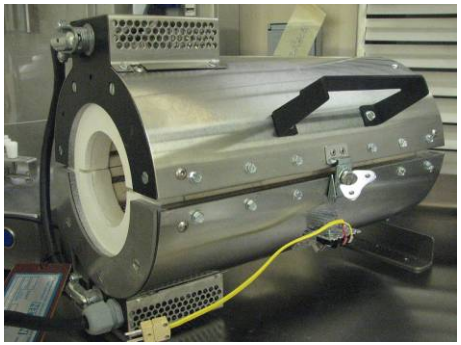
Equipment installation and testing in glove boxes is on-going.

Powder Rheometer

XRD

BET Surface Area Analyzer

Calcination/ Reduction Furnace



Laser-light Particle Size Analyzer

RIDGE National Laboratory

MDD Powder Characterization

Powder Characterization Laboratory

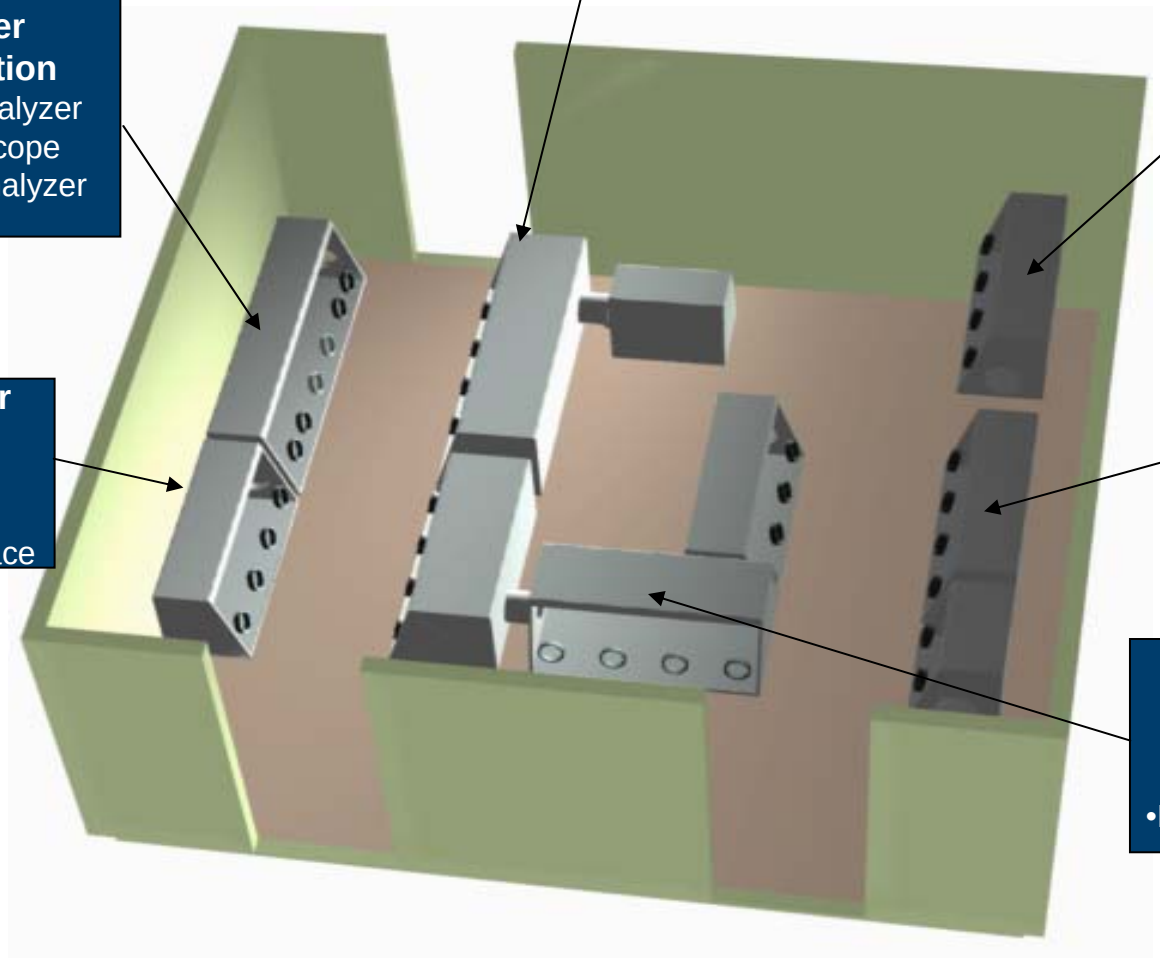
Pellet Production (Inert)

Final Powder Characterization
- Particle Size Analyzer
- Stereo Microscope
- Surface Area Analyzer

XRD
- Housed in 3 foot gb

Rough Powder
- Balance
- Rheometer
- Sieves
- Calcination Furnace

Wet Chemistry



Pellet QC (Inert)
- Stereo Microscope
- Laser Profilometer
- Pycnometer
- Misc Metrology Equipment

On-going Work…

- **Installation and operation of pellet fabrication glove boxes, press, and sintering furnace**
- **Continued characterization of Run 1 MOX**
- **Convert U and U/Pu/Np streams in glove box MDD unit from N. Anna fuel (Run 2)**