

Purity of Uranium Product

from Electrochemical Recycling of Used Metallic Fuel

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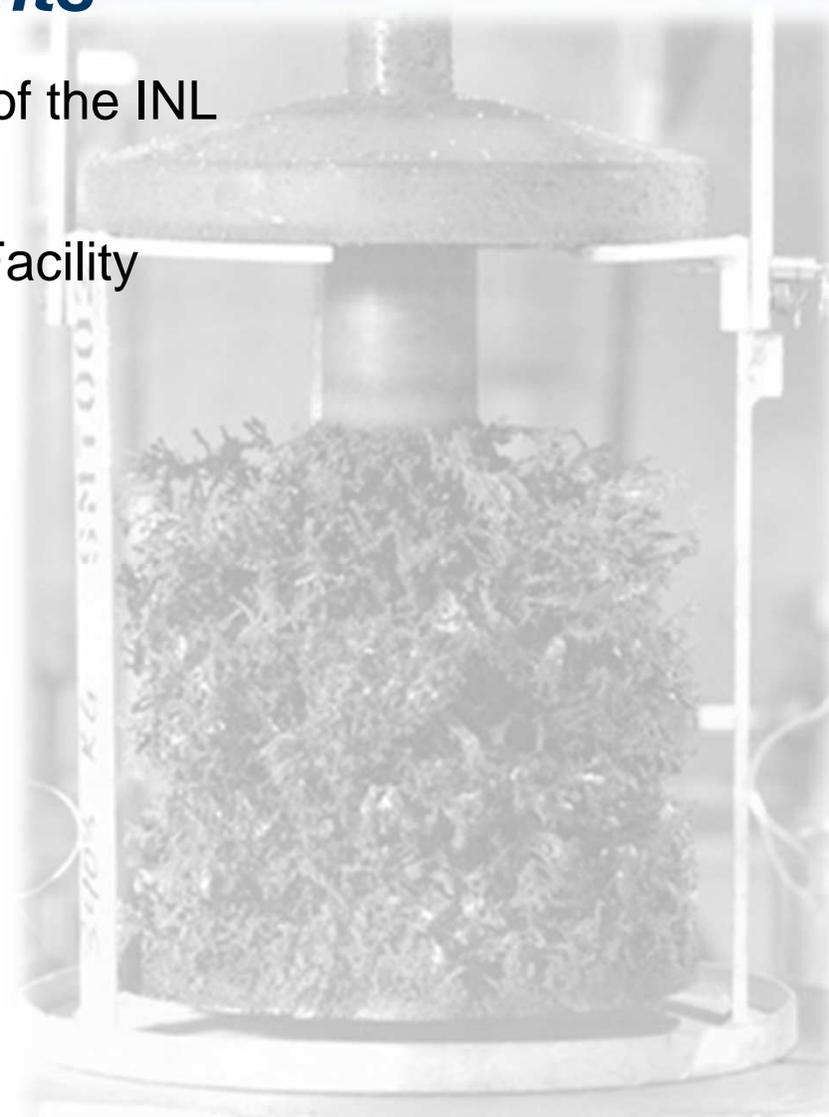
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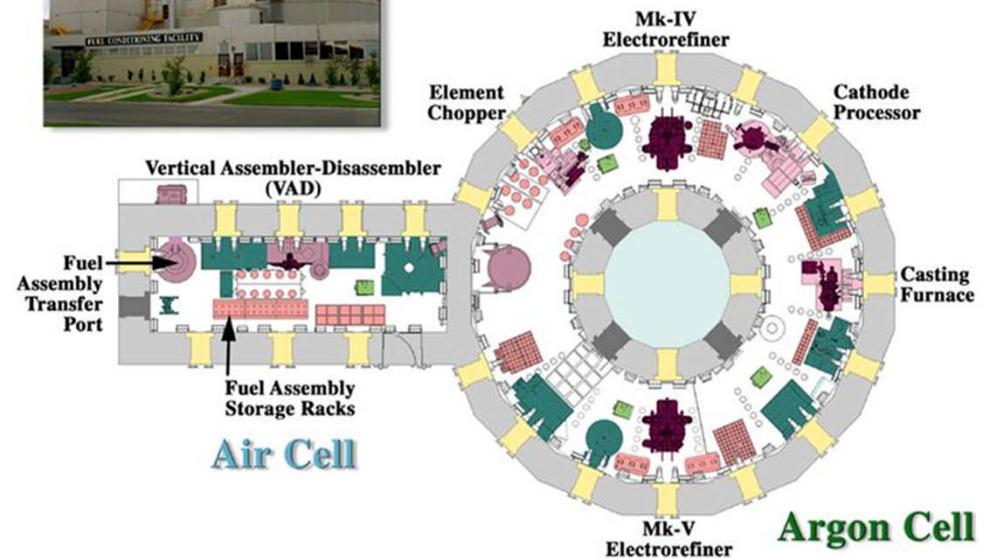
Materials and Fuels Complex (MFC) of the INL

- ~ 45 km west of Idaho Falls, ~800 employees
- Location of former EBR-II reactor
- Two hot cell facilities and multiple laboratories for research with irradiated materials
 - Irradiated Material Characterization Laboratory (IMCL)
 - Electron Microscopy Laboratory (EML)
 - Hot Fuel Examination Facility (HFEF)
 - Fuel Conditioning Facility (FCF)



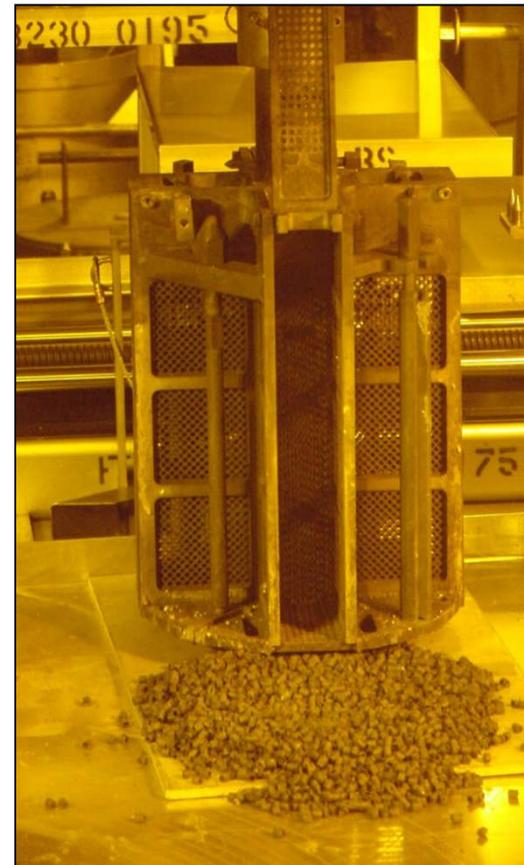
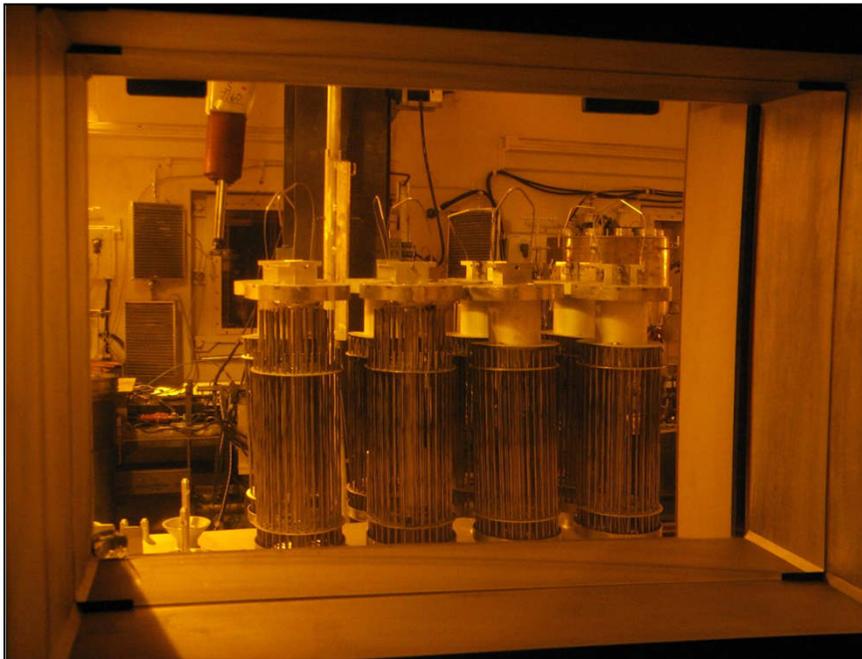
Fuel Conditioning Facility (FCF)

- Rectangular air cell with annular argon-atmosphere cell
- Operational in early 1960s
- Current generation of pyrochemical processing equipment installed in early 1990s
- Processing has included
 - ~3 MT of EBR-II blanket
 - ~1 MT EBR-II U-10Zr fuel
 - ~250 kg of FFTF U-10Zr fuel
- Preparations underway to process ~2 MT of EBR-II fissium alloy fuel



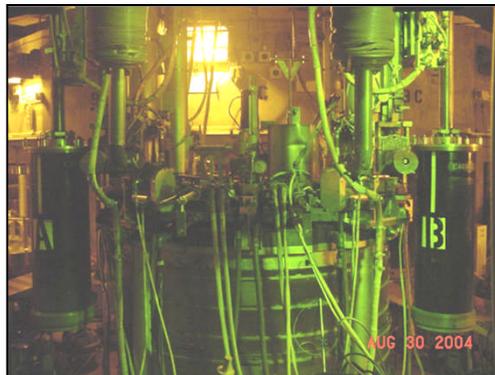
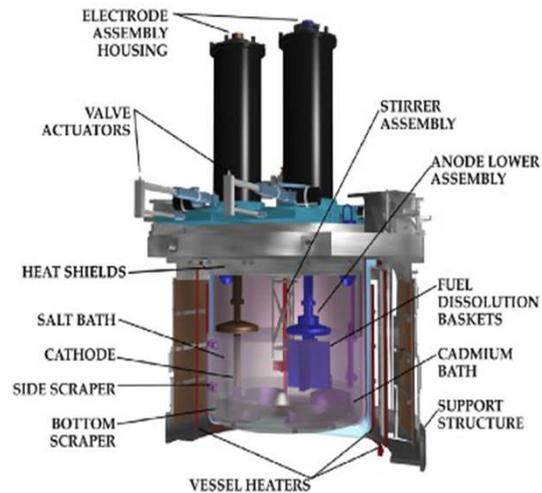
Processing at the Fuel Conditioning Facility (FCF)

- Fuel is removed from bundle in preparation for processing
- Fuel-bearing portion of fuel is chopped and loaded into anode baskets



Processing at the Fuel Conditioning Facility (FCF)

- Anode baskets are inserted into electrorefiner

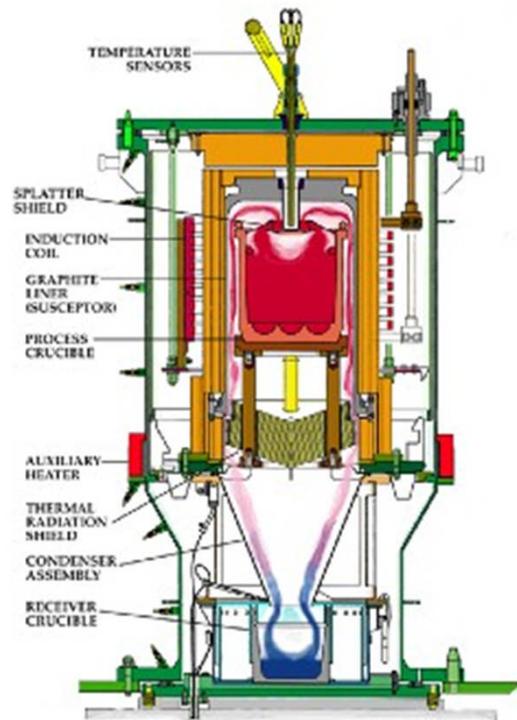


- Used fuel is electrochemically dissolved and purified uranium collected at the cathode.



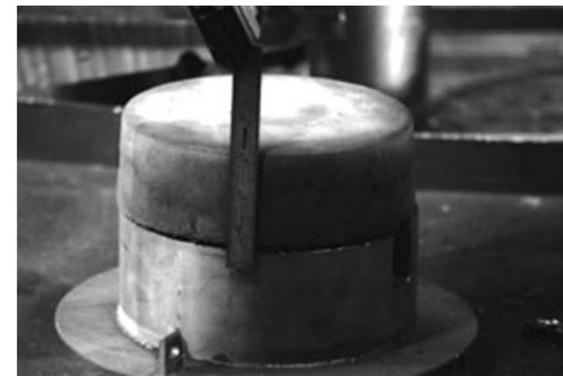
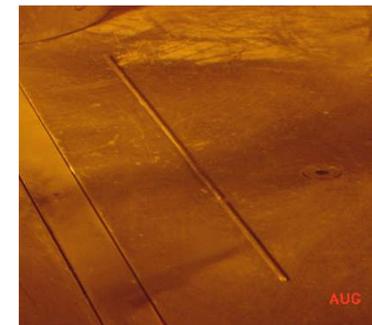
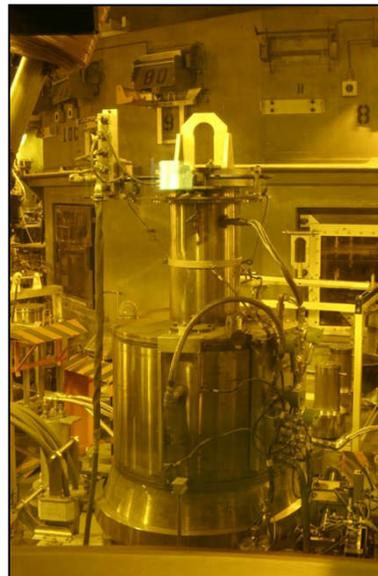
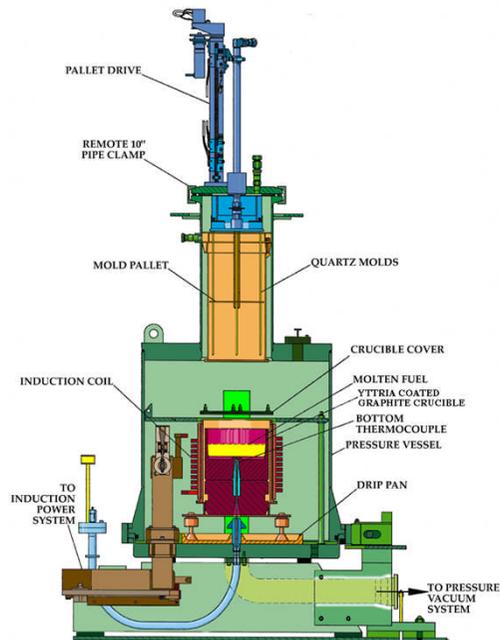
Processing at the Fuel Conditioning Facility (FCF)

- Cathode deposits are harvested and loaded into cathode processor
- Under high temperature and vacuum, salt is distilled and metal dendrites consolidated



Processing at the Fuel Conditioning Facility (FCF)

- Metal ingots remelted for final dilution to $<20\%$ ^{235}U and liquid sampling



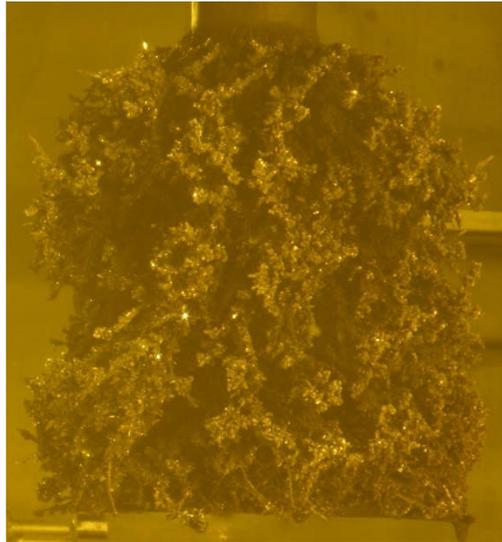
Uranium Product Purity

- Several options exist for uranium use, including feed for off-specification LWR fuel.
 - Off-spec LWR fuel program currently exists for down-blended HEU.
- However, facilities preparing uranyl nitrate solution for LWR fuel fabrication have low tolerance for TRU contaminants.
 - Acceptable level is 10s of ppm or lower.
- Driver Treatment Project considering process modifications to meet specifications of potential recipients.
- Efforts to clarify TRU contamination mechanisms restarted.

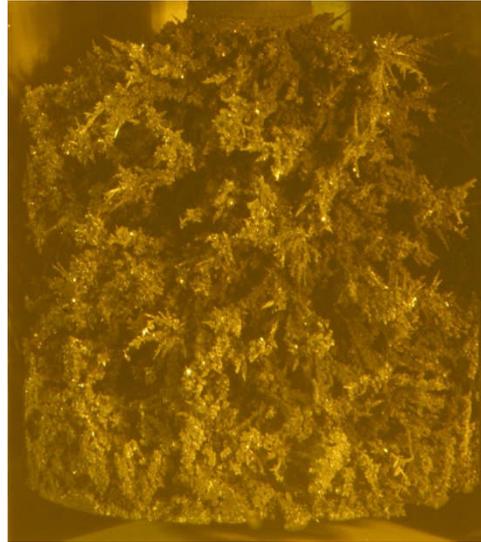
- This work: An effort to clarify “intrinsic” contamination of U dendrites as electrochemically deposited in the electrorefiner.
 - If primary contamination path is addressed, can specifications be met
 - Primary interest in major TRU species
 - Also interested in behavior of lanthanides, which may serve as indicators or follow similar trends

Dendrite Samples

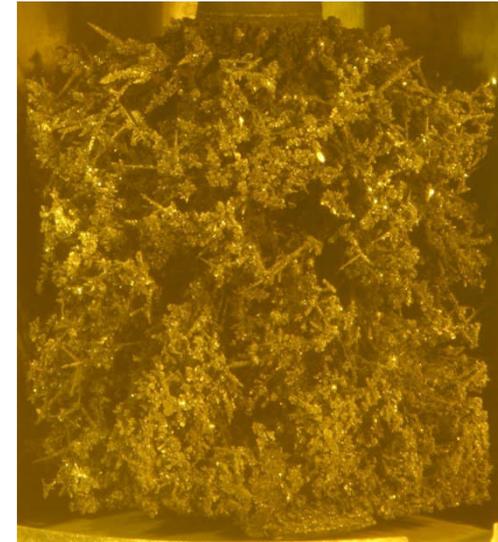
- Two samples were pulled from cathodes during the processing of 3 batches of FFTF (Fast Flux Test Facility) fuel



Cathode 9.01



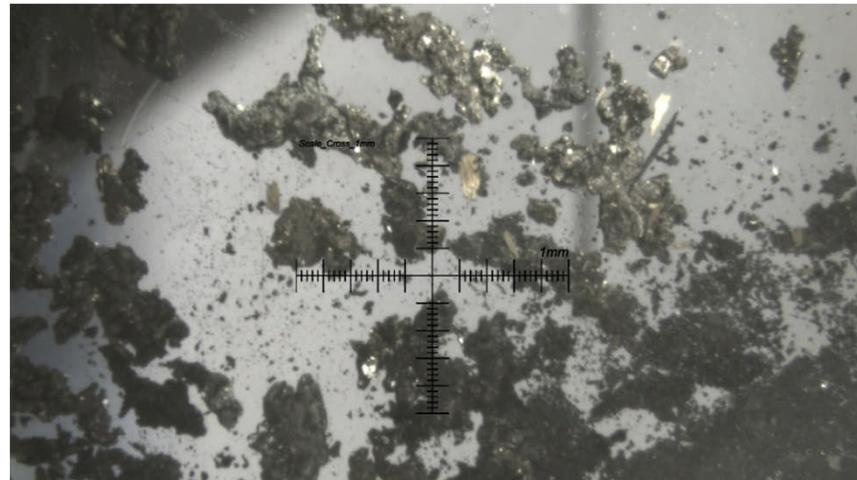
Cathode 10.01



Cathode 11.01

Dendrite Samples

- It is known that electrorefiner salt is occluded macroscopically (within the cathode mass) and microscopically (within the dendrite itself)
- Contaminants within salt complicate analysis of metal dendrite
- Two dendrite sample from each cathode: one sent as-is for destructive, and one crushed
 - Manual impact hammer for crushing
 - Crushing was performed to evaluate potential to reduce occluded salt



Sample 93676: Cathode 9.01, crushed

Dendrite Samples Inputs – ER Salt and FFTF Fuel

- Need to know ER salt constituents in order to back out their contribution to dendrite samples

ER Salt composition bounding dendrite samples

| Sample ID | Source | Li (wt%) | K (wt%) | La (wt%) | Pr (wt%) | Np (wt%) | Pu (wt%) |
|----------------|--------------------|--------------|--------------|---------------|---------------|----------------|---------------|
| 93586 | prior to batch 9 | 4.93 | 18.9 | 0.347 | 0.325 | 0.0406 | 1.01 |
| 93805, 93806 | Following batch 11 | 5.17 | 19.4 | 0.364 | 0.352 | 0.0453 | 1.14 |
| Average | | 5.05 | 19.2 | 0.356 | 0.339 | 0.0430 | 1.08 |
| <i>2σ</i> | | <i>0.253</i> | <i>0.958</i> | <i>0.0178</i> | <i>0.0169</i> | <i>0.00215</i> | <i>0.0538</i> |

- For reference, composition of used FFTF fuel

FFTF fuel constituents from burnup code*

| Source | La (wt%) | Pr (wt%) | Np (wt%) | Pu (wt%) |
|----------|----------|----------|----------|----------|
| batch 9 | 0.184 | 0.174 | 0.0528 | 1.34 |
| batch 10 | 0.183 | 0.174 | 0.0528 | 1.37 |
| batch 11 | 0.183 | 0.174 | 0.0527 | 1.34 |

*For information. Dendrites should not be a function of input fuel composition

Dendrite Samples

- Samples were water washed to remove as much surface salt as possible
- Washed samples dissolved and analyzed by ICP-MS and ICP-OES

| Sample ID | Sample Form | Source | Li (wt%)* | K (wt%)* | La (wt%)* | Pr (wt%)* | Np (wt%)* | Pu (wt%)* |
|---------------------------------|-------------|----------------------|-----------|----------|-----------|-----------|-----------|-----------|
| 93676 | Crushed | Cathode ERFF09.01 | 174E-04 | < 97 | 13.5E-04 | 11.8E-04 | 4.72E-04 | 61.1E-04 |
| 93678 | Crushed | Cathode ERFF10.01 | 85.0E-04 | < 0.137 | 4.05E-04 | 3.46E-04 | 2.69E-04 | 20.3E-04 |
| 93680 | Crushed | Cathode ERFF11.01 | 92.2E-04 | < 0.092 | 5.14E-04 | 4.25E-04 | 3.48E-04 | 25.4E-04 |
| 93677 | Uncrushed | Cathode ERFF09.01 | 261E-04 | < 0.151 | 19.5E-04 | 20.7E-04 | 10.9E-04 | 203E-04 |
| 93679 | Uncrushed | Cathode ERFF10.01 | 107E-04 | < 0.180 | 4.38E-04 | 3.77E-04 | 3.28E-04 | 22.4E-04 |
| 93681 | Uncrushed | Cathode ERFF11.01 | 147E-04 | < 0.170 | 8.25E-04 | 7.34E-04 | 3.82E-04 | 36.3E-04 |
| Average | | | 144E-04 | | 9.14E-04 | 8.55E-04 | 4.82E-04 | 61.4E-04 |
| Average w/o cathode 9.01 | | | | | 5.46E-4 | 4.71E-04 | 3.32E-04 | 26.1E-04 |
| <i>2σ</i> | | | 7.22E-4 | | .457E-04 | .428E-04 | 0.166E-4 | 1.31E-04 |

*1E-04 = 1 ppm

Dendrite Samples

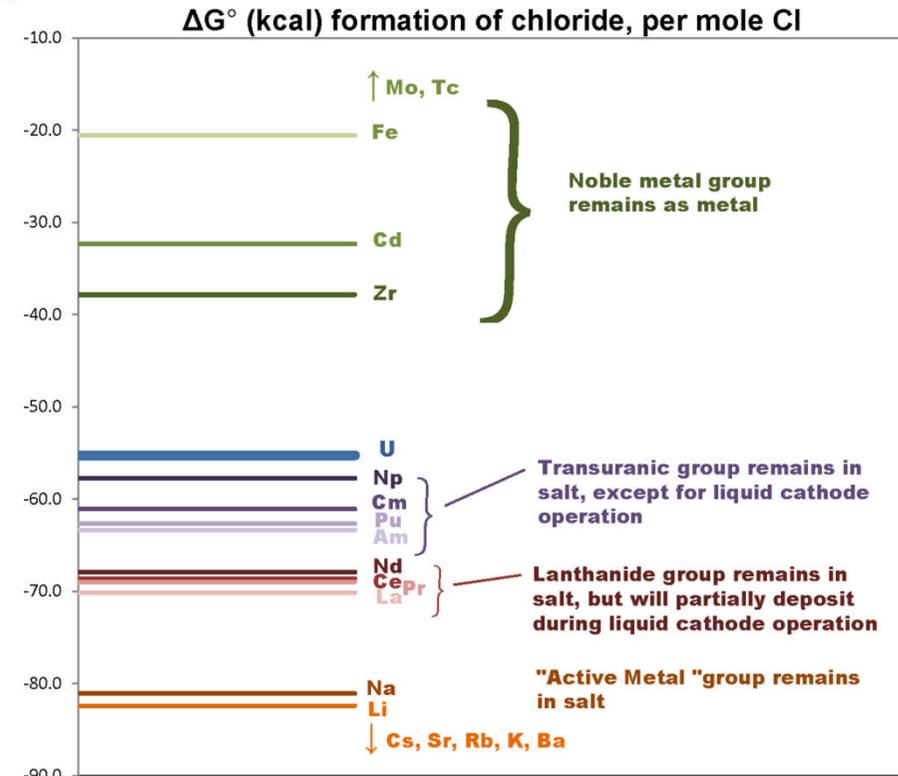
- Concentration of Li in washed dendrites used to estimate salt content
- Salt components subtracted from analysis to estimate “intrinsic” contamination levels
- Result shows no La or Pr, a few ppm of Np, and either ~0 or ~30 ppm of Pu

| Sample ID | Sample Form | Source | La (wt%)* | Pr (wt%)* | Np (wt%)* | Pu (wt%)* |
|---------------------------------|-------------|-------------------|-----------------|-----------------|------------------|-----------------|
| 93676 | Crushed | Cathode ERFF09.01 | 1.25E-04 | 0.33E-04 | 3.29E-04 | 25.5E-04 |
| 93678 | Crushed | Cathode ERFF10.01 | -1.93E-04 | -2.24E-04 | 1.97E-04 | 2.21E-04 |
| 93680 | Crushed | Cathode ERFF11.01 | -1.35E-04 | -2.03E-04 | 2.67E-04 | 5.07E-04 |
| | | | | | | |
| 93677 | Uncrushed | Cathode ERFF09.01 | 1.13E-04 | 3.49E-04 | 8.75E-04 | 150.E-04 |
| 93679 | Uncrushed | Cathode ERFF10.01 | -3.15E-04 | -3.40E-04 | 2.37E-04 | -.377E-04 |
| 93681 | Uncrushed | Cathode ERFF11.01 | -2.10E-04 | -2.67E-04 | 2.53E-04 | 3.89E-04 |
| Average | | | -1.03E-04 | -1.09E-04 | 3.60E-04 | 31.0E-04 |
| Average w/o cathode 9.01 | | | -2.13E-04 | -2.58E-04 | 2.39E-04 | 2.70E-04 |
| <i>2σ</i> | | | <i>6.10E-04</i> | <i>5.80E-04</i> | <i>0.730E-04</i> | <i>18.1E-04</i> |

1E-04 = 1 ppm

Dendrite Samples

- Is this result reasonable?
- Possibly ... but more investigation needed
- Ratios of salt constituents shifted ... more samples needed to clarify
- However data is clear enough to indicate major Pu contamination occurs elsewhere



| Element | Apparent Standard Potential (vs Cl ₂ /Cl ⁻ at 723K) | Source |
|---------|---|-----------------------------|
| U | -2.498 | Roy, Grantham et al., 1996 |
| Np | -2.698 | Roy, Grantham et al., 1996 |
| Pu | -2.808 | Roy, Grantham et al., 1996 |
| Pr | -3.085 | Fusselman, Roy et al., 1999 |
| La | -3.146 | Fusselman, Roy et al., 1999 |

Final Product Samples

- What are La, Pr, Np, and Pu concentrations in final U product following CP and CF? Analysis of pin samples from ER batches 9, 10, and 11 are pending
- Historic data shows high level of contamination of Np and Pu occurs in CP. No previous data for La and Pr.
- Batches in the table below were processed when Np and Pu concentrations in salt were significantly lower than for FFTF batches 9, 10, and 11.

Typical Uranium Product[†] Analysis, Prior to FFTF Processing

| Sample Form | Source | Li (wt%) | K (wt%) | C (wt%)* | La (wt%)* | Pr (wt%)* | Np (wt%)* | Pu (wt%)* |
|----------------|---------------|----------|---------|----------|-----------|-----------|------------------|------------------|
| Cast Pin | Casting BF045 | ND | ND | 68 E-04 | NA | NA | 27.1 E-04 | 30.7 E-04 |
| Cast Pin | Casting BF046 | NDi | ND | 177 E-04 | NA | NA | 3.79 E-04 | 43.4 E-04 |
| Cast Pin | Casting BF048 | ND | ND | ND | NA | NA | 14.7 E-04 | 57.2 E-04 |
| Cast Pin | Casting BF049 | ND | ND | 63 E-04 | NA | NA | 12.4 E-04 | 32.7 E-04 |
| Cast Pin | Casting BF050 | ND | ND | 281 E-04 | NA | NA | 3.00 E-04 | 75.6 E-04 |
| average | | | | | | | 12.2 E-04 | 47.9 E-04 |

[†] Uranium dendrites are diluted with DU to produce cast LEU product for storage

* 1E-04 = 1 ppm

ND = Not Detected, NA= Not Analyzed

Other Information from Dendrite Samples

- Fraction of salt which was occluded in these samples was ~7% or ~3% when crushed.
- Or 0.34% or 0.23% mass of a washed dendrite was salt.

| Sample ID | Sample Form | Source | Approximate fraction of sample which was salt | Fraction of cathode which was salt* | Dendrite sample washed in DI water | |
|----------------|-------------|-------------------|---|-------------------------------------|------------------------------------|---|
| | | | | | Fraction of salt that is occluded | Mass fraction of dendrite which is salt |
| 93676 | Crushed | Cathode ERFF09.01 | 5.8% | 20% | 5.8% | 0.35% |
| 93678 | Crushed | Cathode ERFF10.01 | 24% | | 0.53% | 0.17% |
| 93680 | Crushed | Cathode ERFF11.01 | 7.4% | 22.6% | 2.2% | 0.18% |
| average | | | 12.4% | 21.3% | 2.8% | 0.23% |
| | | | | | | |
| 93677 | Uncrushed | Cathode ERFF09.01 | 3.7% | 20% | 14% | 0.53% |
| 93679 | Uncrushed | Cathode ERFF10.01 | 8.9% | | 2.2% | 0.21% |
| 93681 | Uncrushed | Cathode ERFF11.01 | 5.2% | 22.6% | 5.2% | 0.28% |
| average | | | 5.9% | 21.3% | 7.14% | 0.34% |

*From mass balance at CP

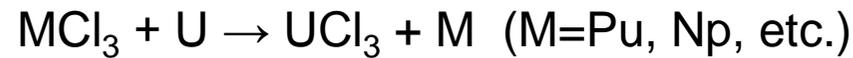
Conclusions, Future Recommendations

- Data suggests that electrochemical metal deposition continues to not be a significant contribution to Pu contamination
- Simple crushing may be an effective mechanism to reduce occluded salt
- Additional samples could further elucidate intrinsic contaminant levels

Backup Slides

CP Reaction

- It is believed that low vapor pressure species concentrate during distillation process
- At high temperature, a reaction



may occur with metallic products dissolved into bulk of molten uranium

