Prospects for Safeguarding Pyroprocessing

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Contributors to this Talk

- University of Utah students
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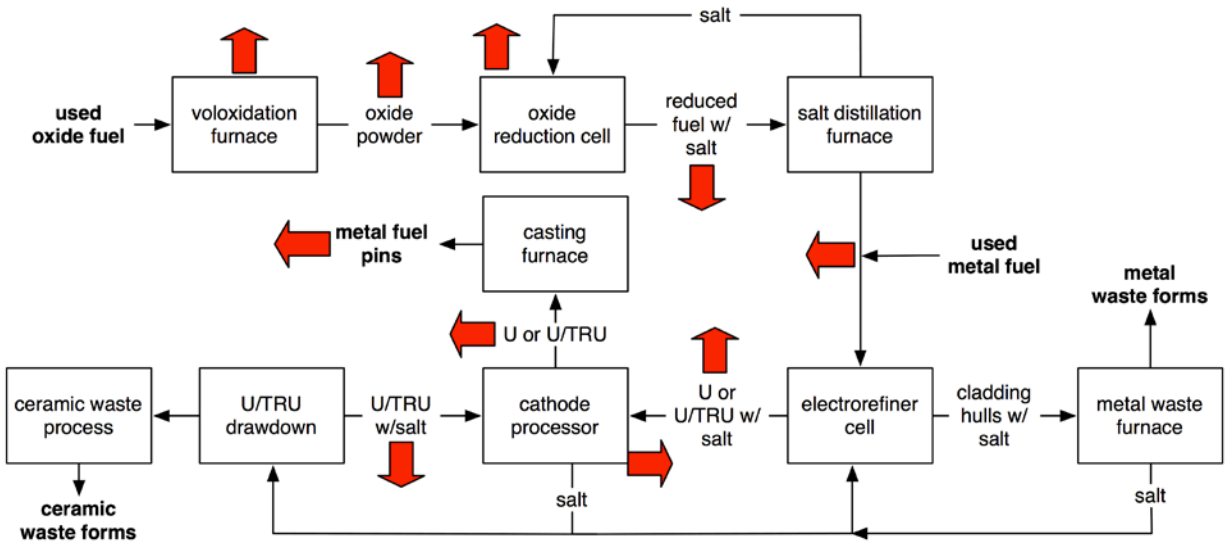
  - Mario Gonzalez
  - Lauryn Hansen
- Kerry Allahar (Boise State)
- Michael Shaltry (INL)
- Supathorn Phongikaroon (VCU)
- Ed Blandford & Phil Lafreniere (UNM)
- Arel Weisberg (ERCo)
- Rollin Lakis (LANL)

The Challenge to Safeguard

- Must protect against diversion of Pu-containing materials
- Multiple streams of batches
  - Salts
  - Metals
  - Oxides
- No input accountability tank
- Nuclear Material Accountancy will not yield sufficient confidence levels

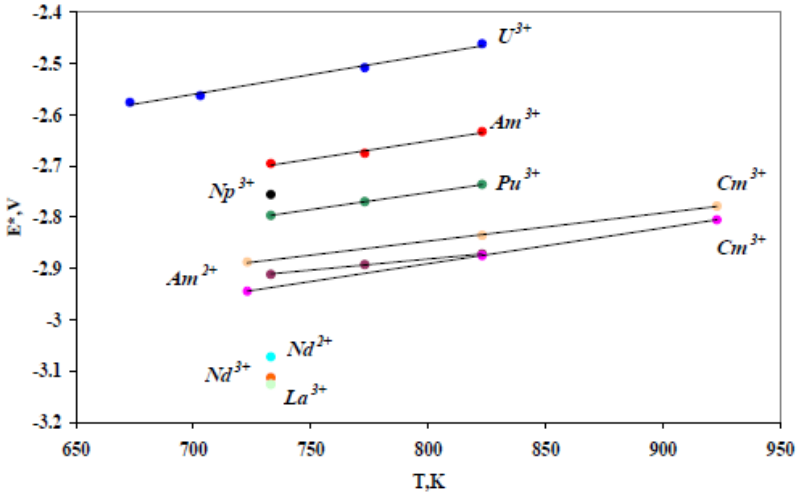


Pu SQ = 8 kg

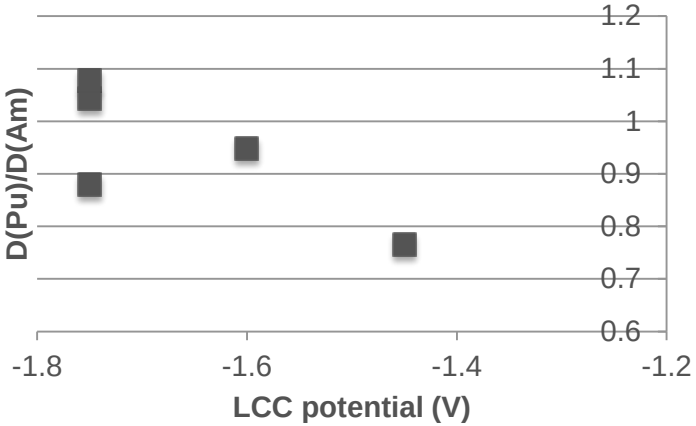
Neutron Balance Approach

- Cm-244 has much higher spontaneous neutron emission rate (4.19×10^6/sec-g) than any of the Pu isotopes (920/sec-g)
- Theorized by some that Cm will track Pu throughout the process
- Not supported by experimental data.
  - Standard reduction potentials are close, but not identical.
  - S. Li demonstrated the affect of cathode potential on separation factors.
- At U. of Utah, we used the ERAD model to simulate electrorefining of fuel with Pu and Cm to further assess.

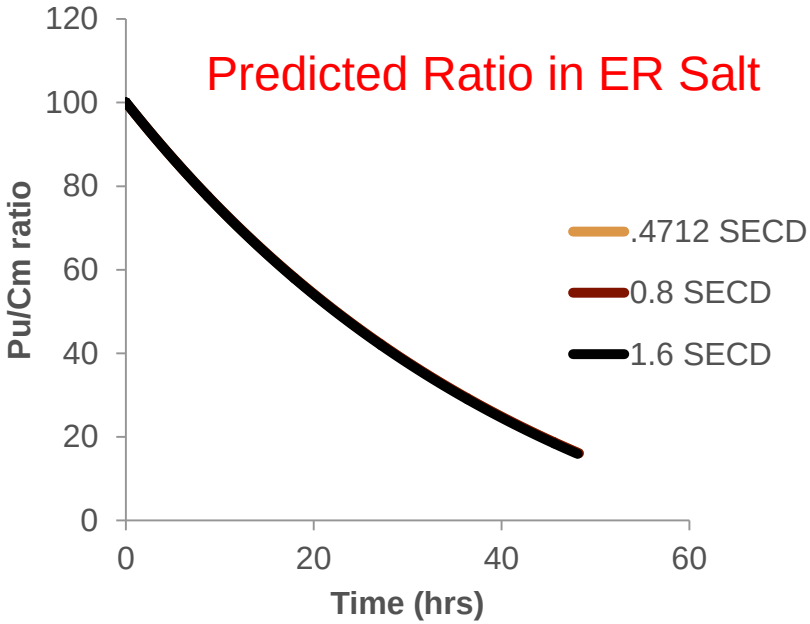
A.G. Osipenko (RIAR) - 2012

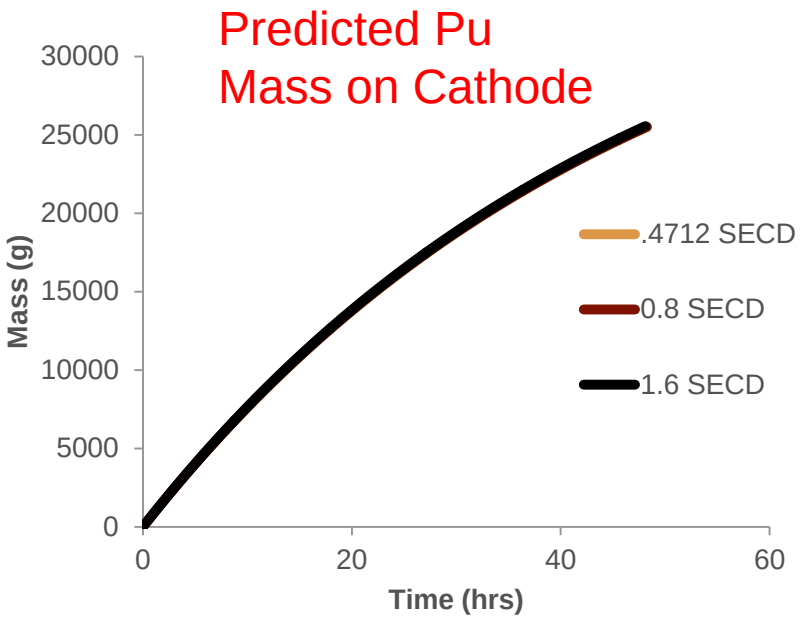


Shelly Li (INL) - 2009



Simulated U-Pu-Cm Electrorefining (ERAD)



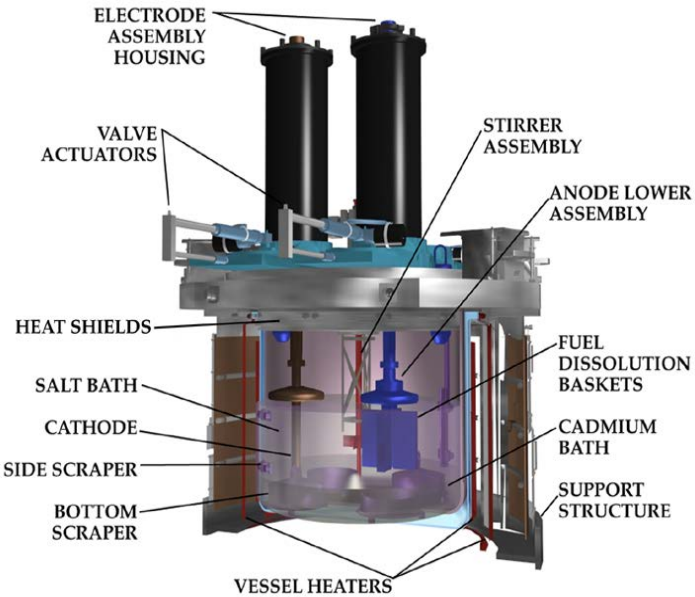


from CV fit

a

Electrorefiner Monitoring

- 50 kg of Pu in each pool of salt.
- INL systems are under “domestic safeguards” using a Mass Tracking System
- This approach will not satisfy timeliness requirements established by the IAEA.
- International safeguards requires ability to independently validate user declarations.
- One potentially practical approach is to use real time process monitoring data to evaluate whether the user declarations are likely to be true.

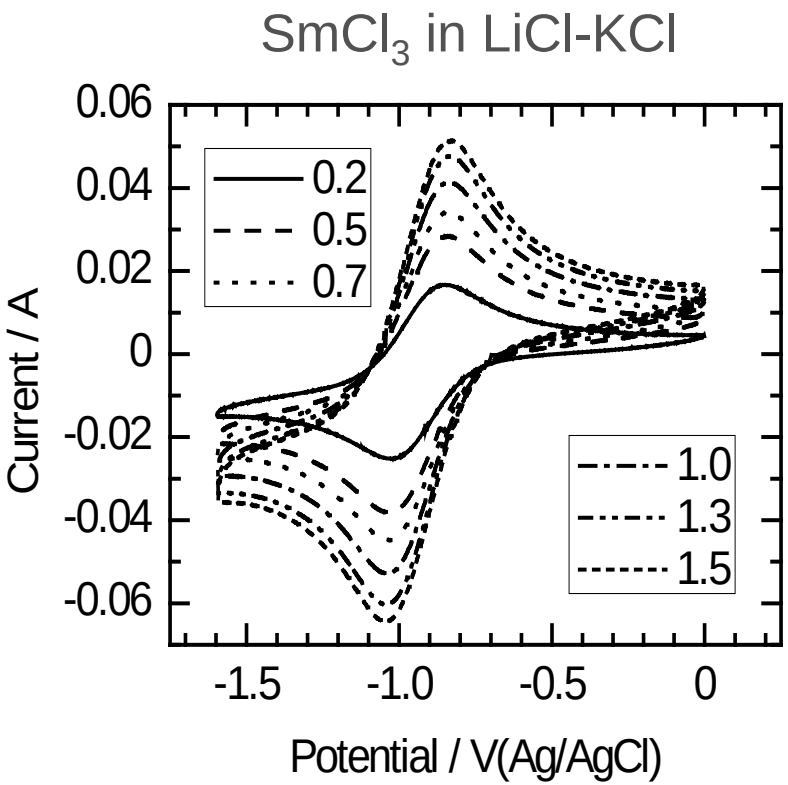


U cathode deposit

Salt Monitoring via CV

Allahar et. al. 2014

- Continuous measurement of actinide concentrations in the salt can be helpful for validating user declarations.
- Diversions from the ER can be picked up via changes in salt composition.
- Cyclic voltammetry (CV) is a simple electrochemical method that has been studies for this purpose.
- Peak current density can be related to concentration and diffusivity using Randles-Sevcick Equation.

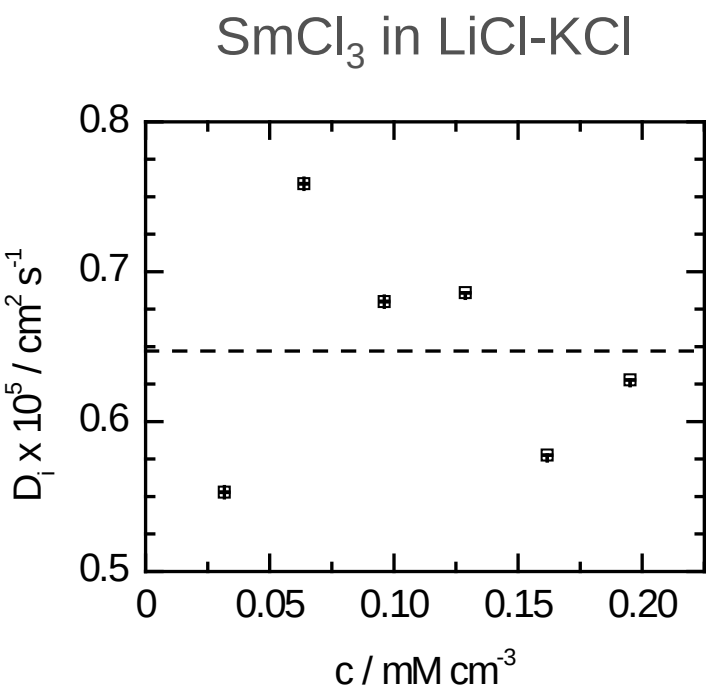


$$I_p = 0.4463nFSc_0\left(\frac{nF}{RT}\right)^{0.5}\nu^{0.5}D^{0.5}$$

If *D* is known, this method can be used for online monitoring of actinide concentrations in an ER.

Variability of Diffusivity

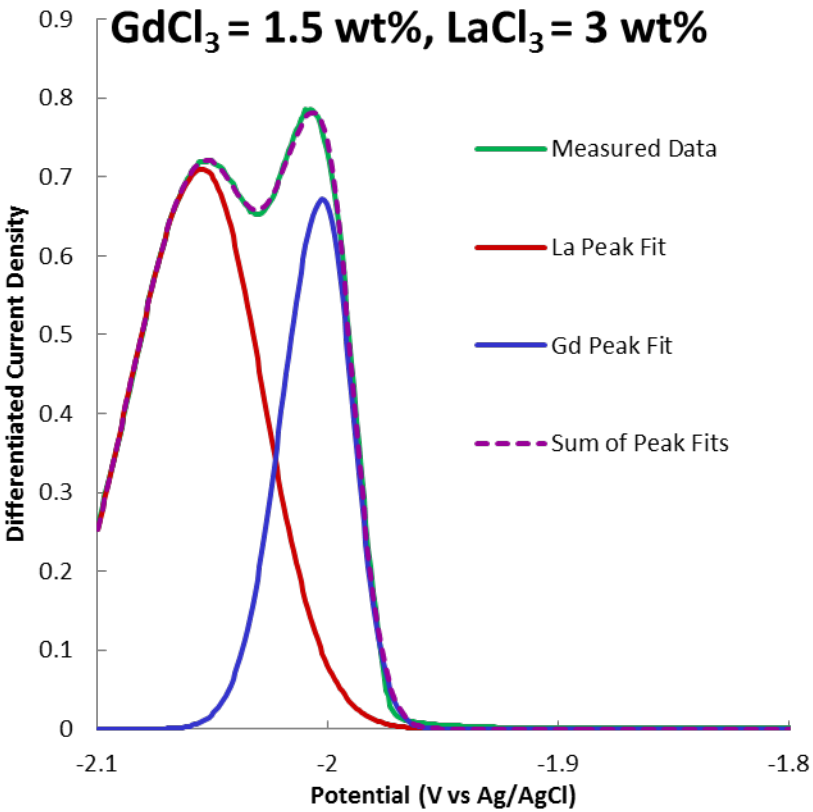
- Using the Randles-Sevcick equation, known concentrations, and measured peak heights, D was calculated and plotted versus concentration.
- Greater than 10% variability, thus limiting precision of concentration measurement.
- Variability expected to be even more unpredictable in multi-component solutions. $D = F(x_i)$
- No way to separately determine diffusivity and concentration for these systems.
- What we can determine is $c_o D^{1/2}$

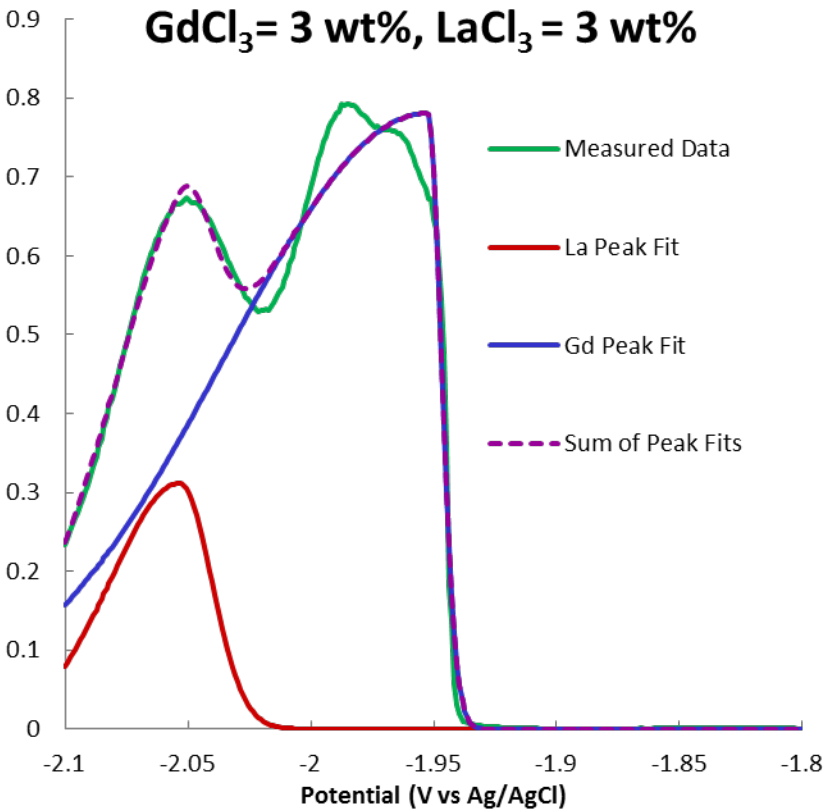


Literature value for $D = 1.3 \times 10^{-5}$ cm^2/sec

Allahar et. al. 2014

Peak Fitting Multi-Component Salts



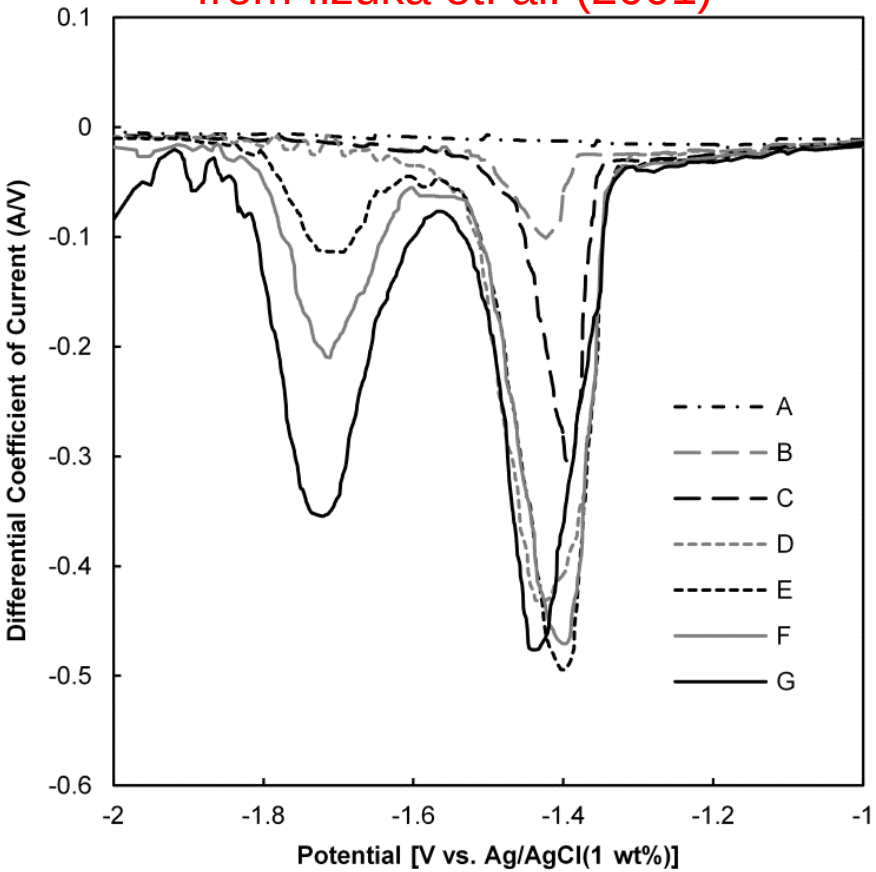


Principle Component Regression (PCR)

- Uses all the data, does not require knowledge of diffusivity or peak separation
- Identify main contributors to variance from a training set (principal components)
- Regress the PCs with concentration
- Predict unknown composition
- D. Rappleye will present results of applying this analysis to $LaCl_3/GdCl_3$

	Uranium			Plutonium		
Method	*Peak Height*	*PCR*	*PLS*	*Peak Height*	*PCR*	*PLS*
Slope	0.829	0.953	0.980	0.798	0.966	0.965
Intercept	0.233	0.053	0.020	0.039	0.033	0.037
R^2	0.860	0.989	0.992	0.986	0.993	0.991

$LiCl-PuCl_3-UCl_3$ CV data taken from Iizuka et. al. (2001)



Monitoring Cathode Deposition

- What about monitoring of the cathode composition?
- Variety of process conditions can lead to co-deposition of U and Pu
- Can we directly determine when Pu is reducing onto the cathode?
- Combining Nernst & Butler-Volmer equations can yield equation for partial current of each depositing species

$$I_{j,k} = i_{o,j}\left[\frac{a_{s,j}^{ox}}{a_{b,j}^{ox}} e^{-\frac{(1-\alpha_j)n_jF}{RT}(\eta_{j,k})} - \frac{a_{s,j}^{red}}{a_{b,j}^{red}} e^{-\frac{\alpha_j n_j F}{RT}(\eta_{j,k})}\right] \quad \text{(BV)}$$

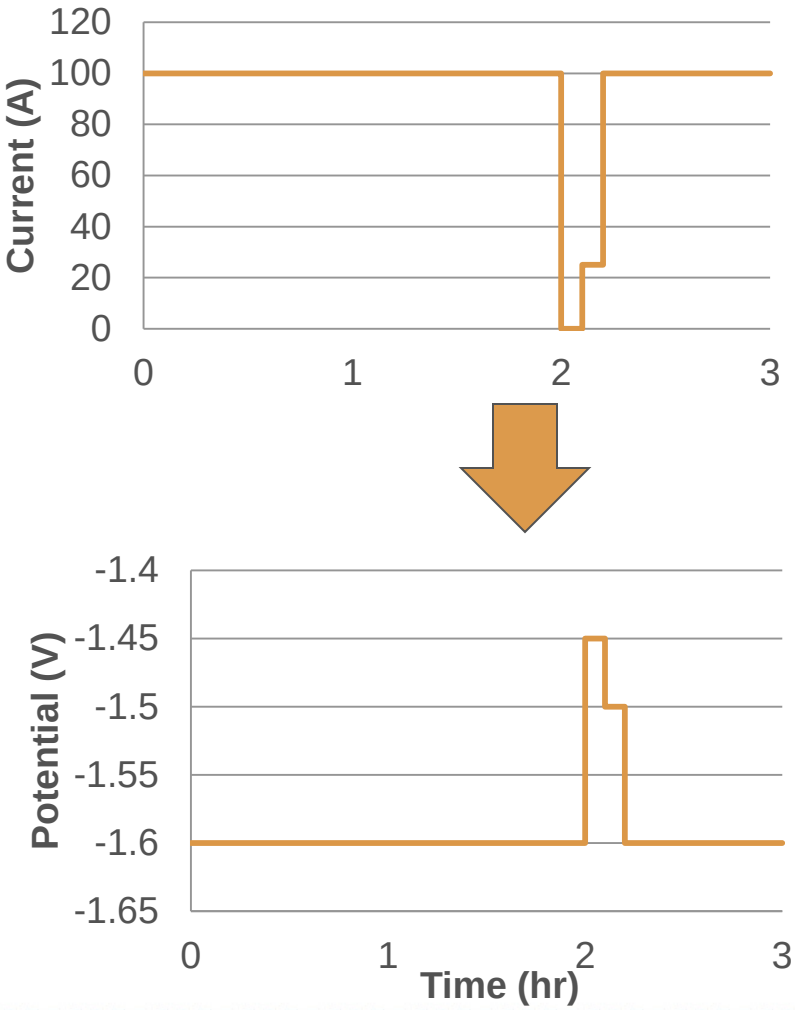
$$E_{eq,j} = E_j^o - \frac{RT}{n_jF} ln\left(\frac{a_{b,j}^{red}}{a_{b,j}^{ox}}\right) \quad \text{(Nernst)}$$

$$I_{j,k} = n_jFAh_j\left(c_{b,j}^{ox} - c_{s,j}^{ox}\right) \quad \text{(mass transfer)}$$

$$I_{j,k} = \frac{i_{o,j}^o A\left[\frac{\gamma_j^{ox} c_{b,j}^{ox}}{c_{tot}} e^{-\frac{(1-\alpha_j)n_jF}{RT}(E_k - E_j^o)} - e^{\frac{\alpha_j n_j F}{RT}(E_k - E_j^o)}\right]}{\frac{i_{o,j}^o \gamma_j^{ox} e^{-\frac{(1-\alpha_j)n_jF}{RT}(E_k - E_j^o)}}{n_jF\,h_j c_{tot}} + 1}$$

DREP Model

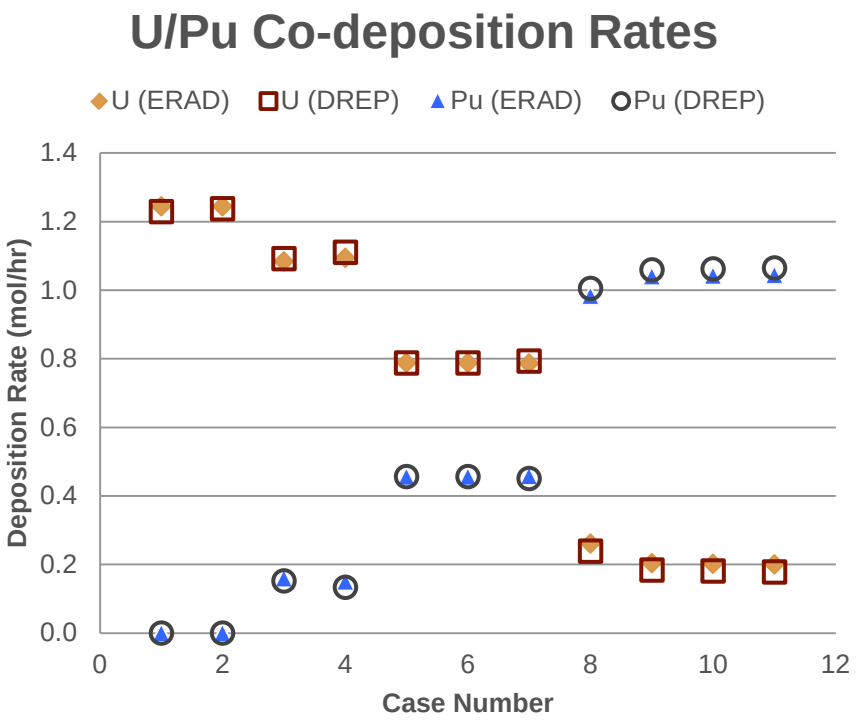
- Unknowns:
  - E_k – cathode potential
  - $C_{b,j}^{ox}$ – bulk salt concentration of
- Measured:
  - E_k – cathode potential
  - I_{cell} – cell current
- Constraint: $$I_k^{cell} = \sum_j I_{j,k}\left(c_{b,j}^{ox}, E_k\right)$$
- Assume $C_{b,j}^{ox}$ to be constant
- # of steps (j) = # of components (k) to be solvable



DREP vs Simulated Electrorefining

- U/Pu electrorefining runs simulated with ERAD model
- Matrix of starting compositions considered
- Experimental validation study ongoing

Case	1	2	3	4
U (wt%)	7.567	2.567	2.234	2.234
Pu (wt%)	0.234	0.234	0.567	2.567
Case	5	6	7	8
U (wt%)	1.234	1.234	1.234	0.313
Pu (wt%)	3.234	5.567	7.567	4.234
Case	9	10	11	
U (wt%)	0.213	0.213	0.213	
Pu (wt%)	4.234	5.567	7.234	



Average Relative Error	
U	3.88%
Pu	2.84%

Monitoring Electrolytic Reduction

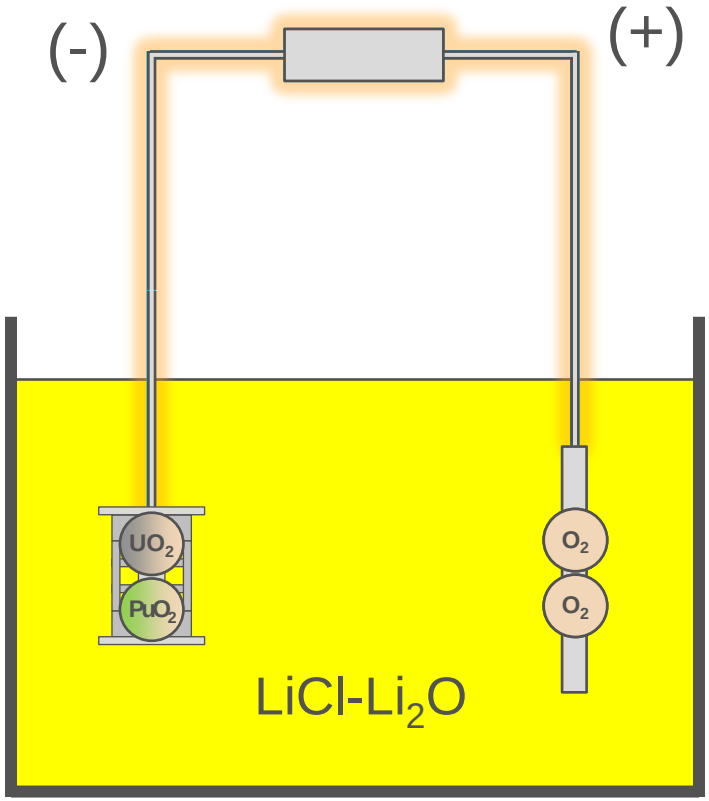
- Normal operations:

$$UO_2 + 4e^- = U + O^{2-}$$
$$PuO_2 + 4e^- = Pu + O^{2-}$$
$$2O^{2-} = O_2 + 4e^-$$

- Potential abnormal operations:

$$UO_2 + \tfrac{3}{4}\,ZrCl_4 + \tfrac{1}{4}\,Zr = UCl_3 + ZrO_2$$
$$PuO_2 + \tfrac{3}{4}\,ZrCl_4 + \tfrac{1}{4}\,Zr = PuCl_3 + ZrO_2$$

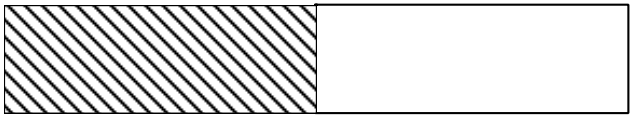
- How do we detect if this has occurred in a system?

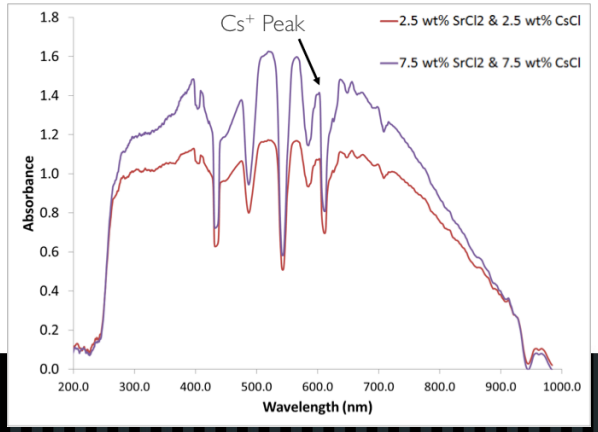


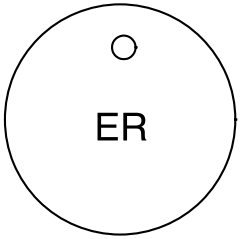
Spectroscopic Analysis of Salt Samples

- Inspector requests sample of electrolytic reduction salt
- Sample transferred remotely to sample chamber interfaced with light source + spectrometer
- Using fiber optics, both reflectance and transmission methods can be used.
- Variety of options for spectroscopy (LIBS, UV-Vis, HKED)

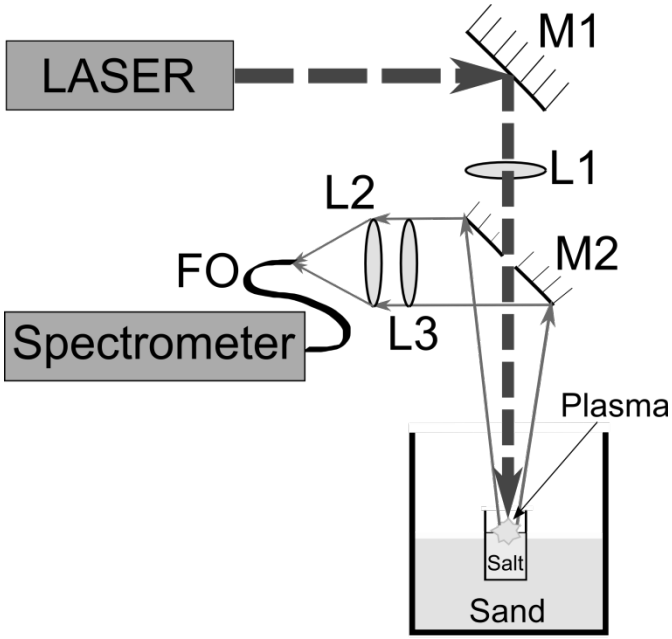
Compatible with LIBS, UV/Vis, etc.

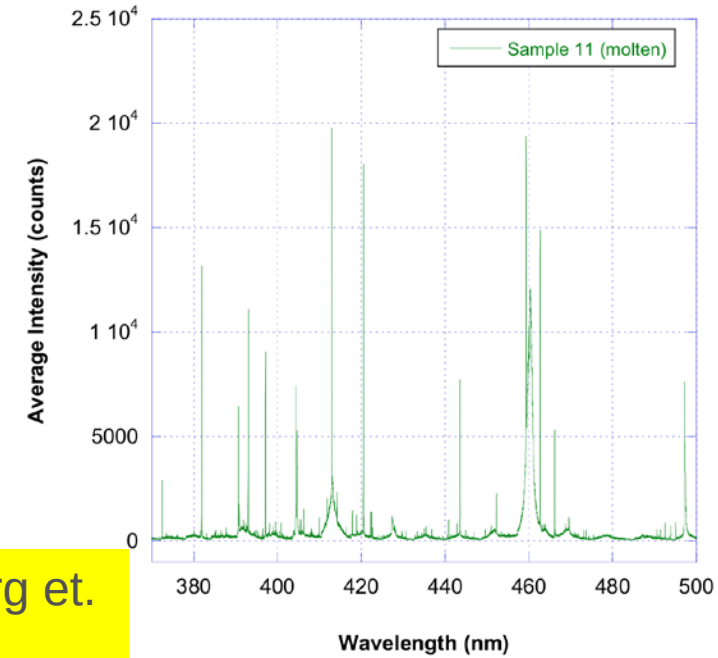




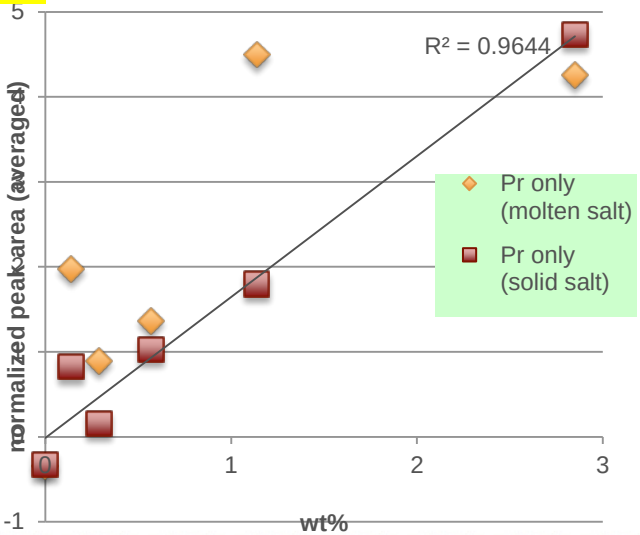


LIBS of LiCl-KCl-$PrCl_3$





Weisberg et. al. 2014



Solid salt samples exhibited superior correlation between peak height and concentration.

Signature Based Safeguards Approach

Build process model

Select, model, and place sensors

Systematic identification of normal and off-normal scenarios

Simulate abnormal processing and generate sensor output

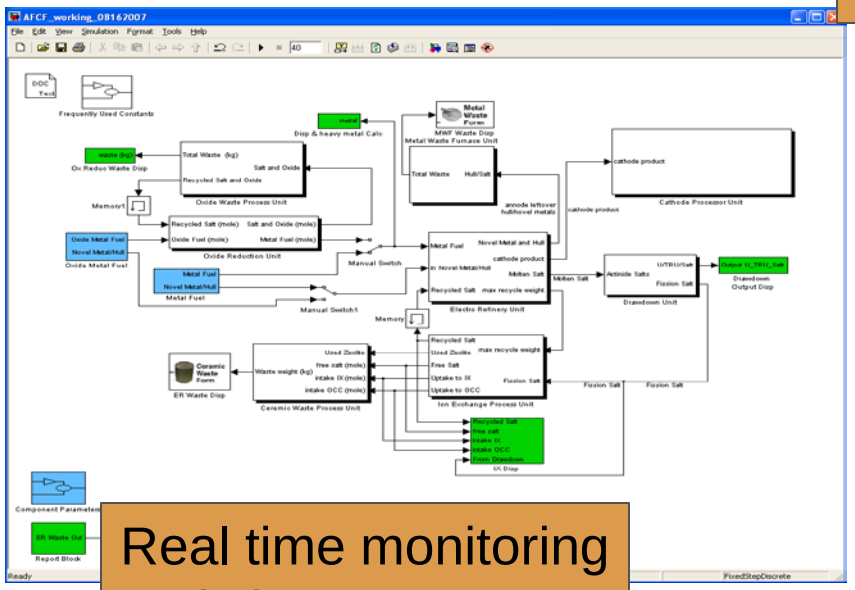
Simulate normal processing and generate sensor output

Analyze signatures for diversion based on sensor output

Reduce or increase # sensors for adequate confidence

Initiate operations

Real time monitoring and signature analysis



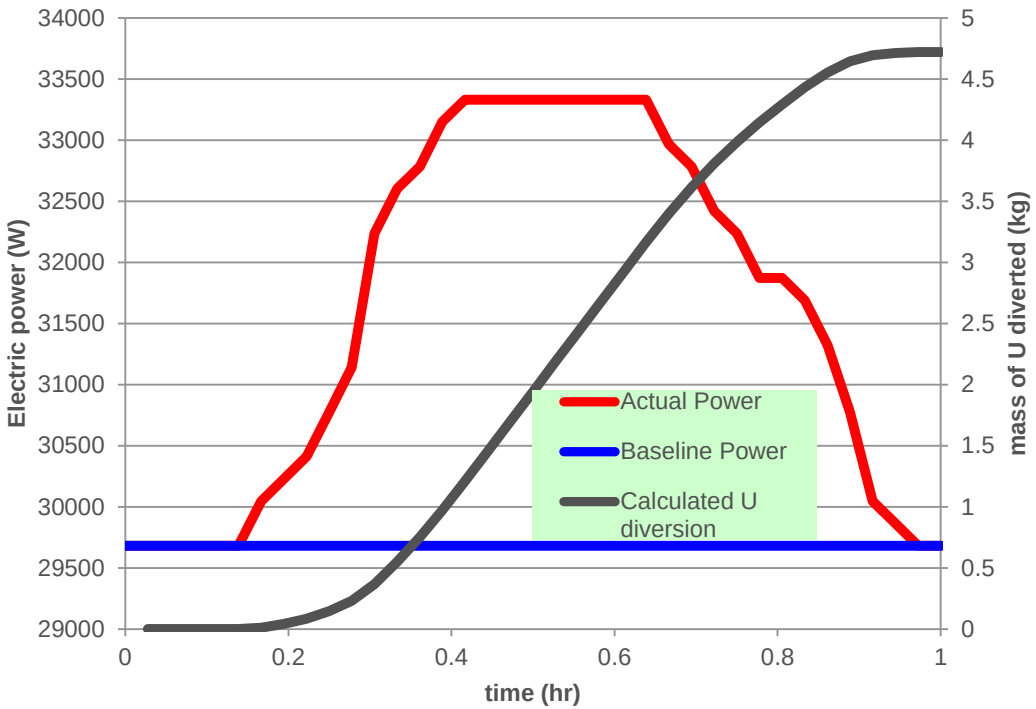
Simulated Voloxidation Sensor Output

- Investigated simple abnormal operation in which O_2 feed is shut off, resulting in no UO_2 oxidation.
- Result would be holdup of spent fuel in cladding hulls that could be diverted through waste disposal
- What if mass measurements cannot be trusted?
- Electric power supplied to the furnace could be used to catch diversion, because reaction is exothermic. Less reaction results in higher furnace power.

$$P = \frac{F(T) + \zeta \Delta H_{rxn}}{\varepsilon}$$

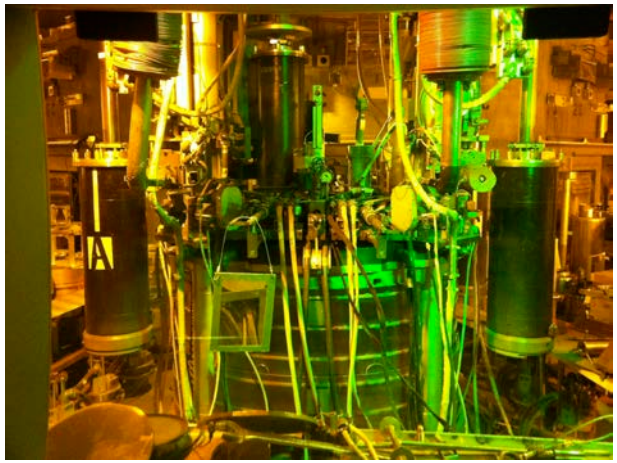
$$\Delta m_{power} = \int_{t1}^{t2} -\frac{3\varepsilon \Delta P (238\ g/mole)}{\Delta H_{rxn}} dt$$

$$\Delta m_{tot} = \Delta m_{power} + \Delta m_{gamma} + \ldots..$$



Many ER Sensor Options….

- Cell current/voltage
- Voltammetry
- Thermocouples
- Furnace power
- Density probe (double bubbler)
- Neutron counting/gamma spectroscopy
- Spectroscopic measurements
  - Laser Induced Breakdown Spectroscopy
  - UV/Vis Spectroscopy
  - HKED
- Sampling & destructive analysis (very slow)



Overall Conclusions

- While pyroprocessing poses unique challenges for implementation of safeguards, it is feasible based on an approach that seeks to verify the truth of facility declarations and identifies signatures of misuse.
- We need to continue development of pyroprocessing sensors and build open-source process models.
- Transparency is the key to achieving a rock-solid safeguards approach.