THE UNIVERSITY OF UTAH

MONITORING PYROPROCESSING VIA UV-VIS ABSORPTION SPECTROSCOPY

International Pyroprocessing Research Conference 2014

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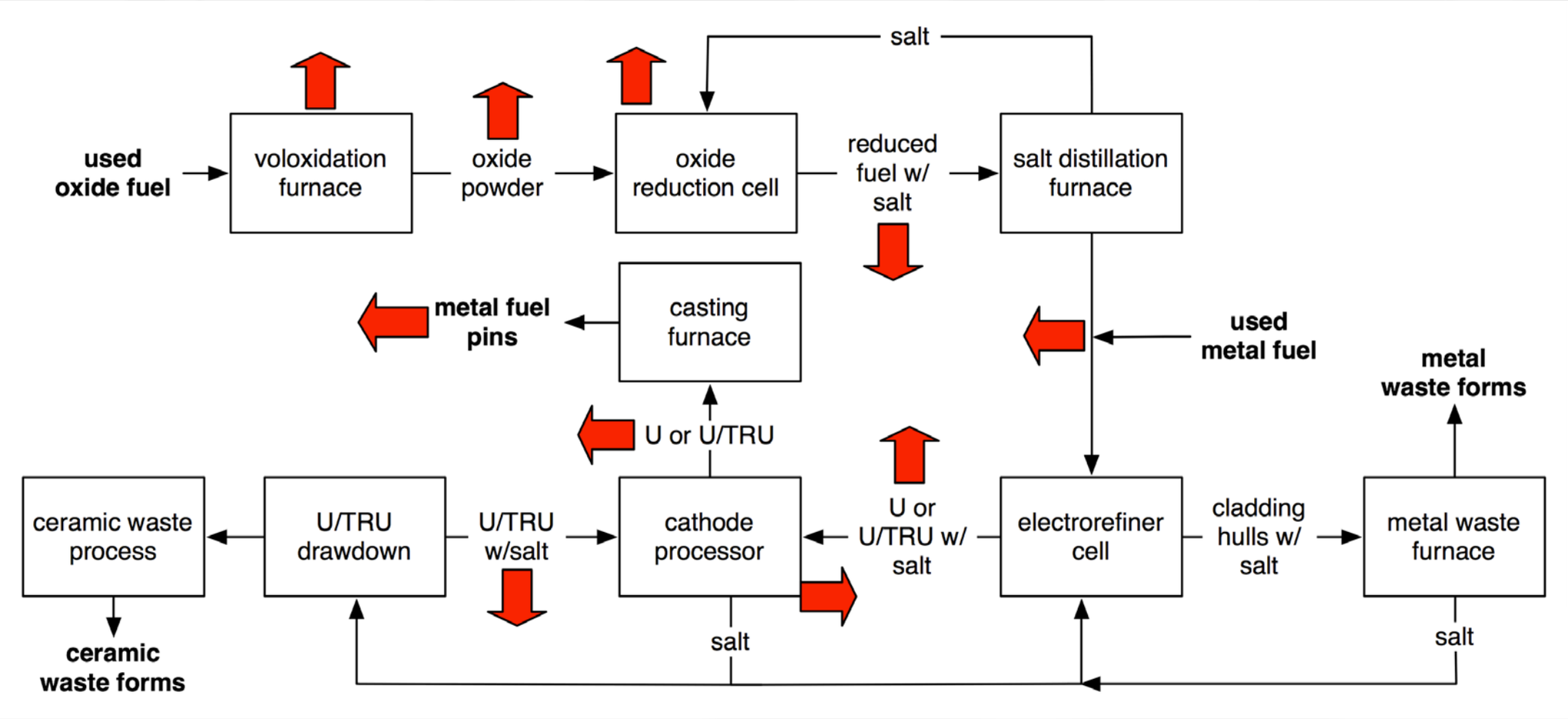
Nuclear Pyrometallurgy Laboratory

Pyroprocessing Safeguards

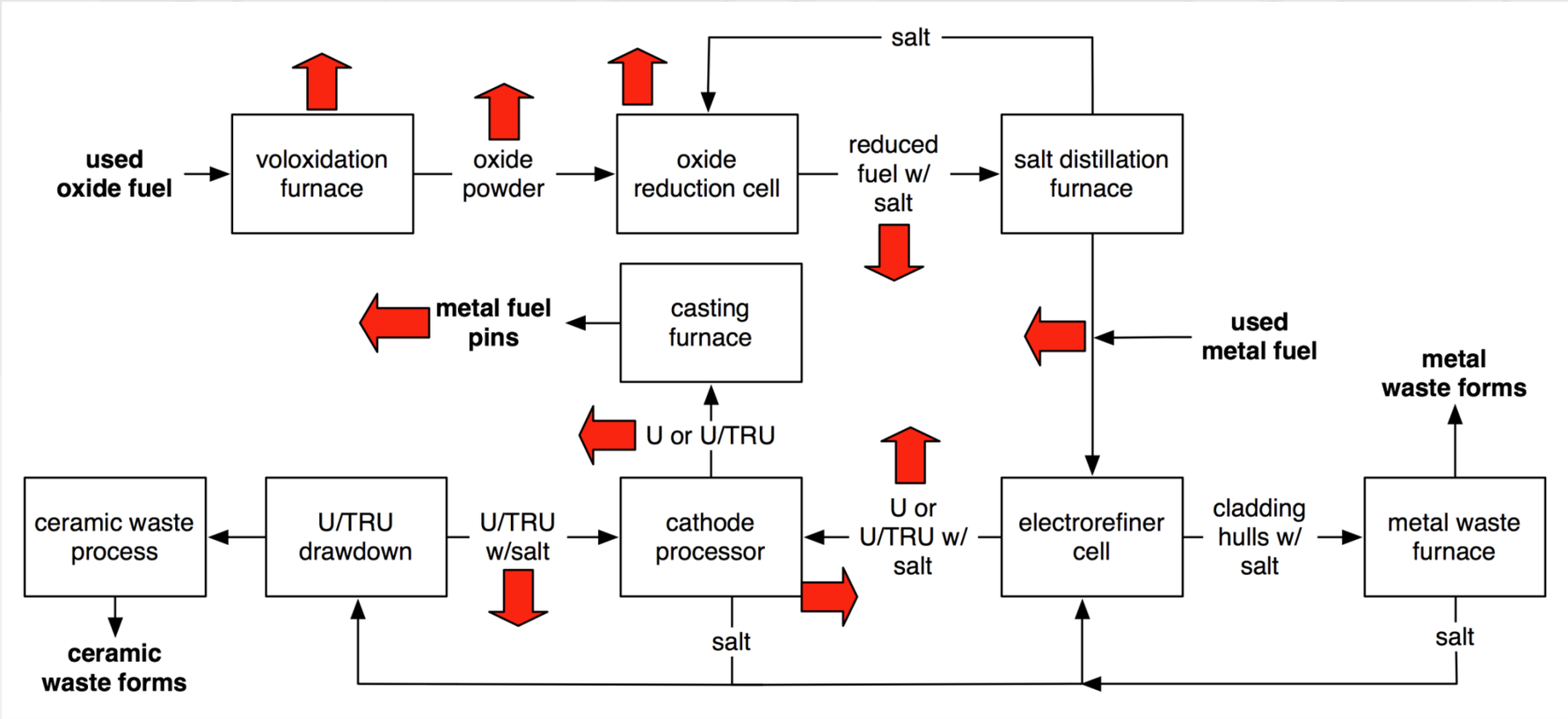
- Design not to produce a Pu product
- Safeguard Methodology Undeveloped



Simpson, M. F. *Science and Technology of Nuclear Installations* **2013**, *2013*, 1–8.

Nuclear Material Accountancy (NMA)

- Significant Quantity (SQ): 8 kg Pu
- Material Unaccounted For (MUF)
- Sampling and Destructive Analysis



Process Monitoring (PM)

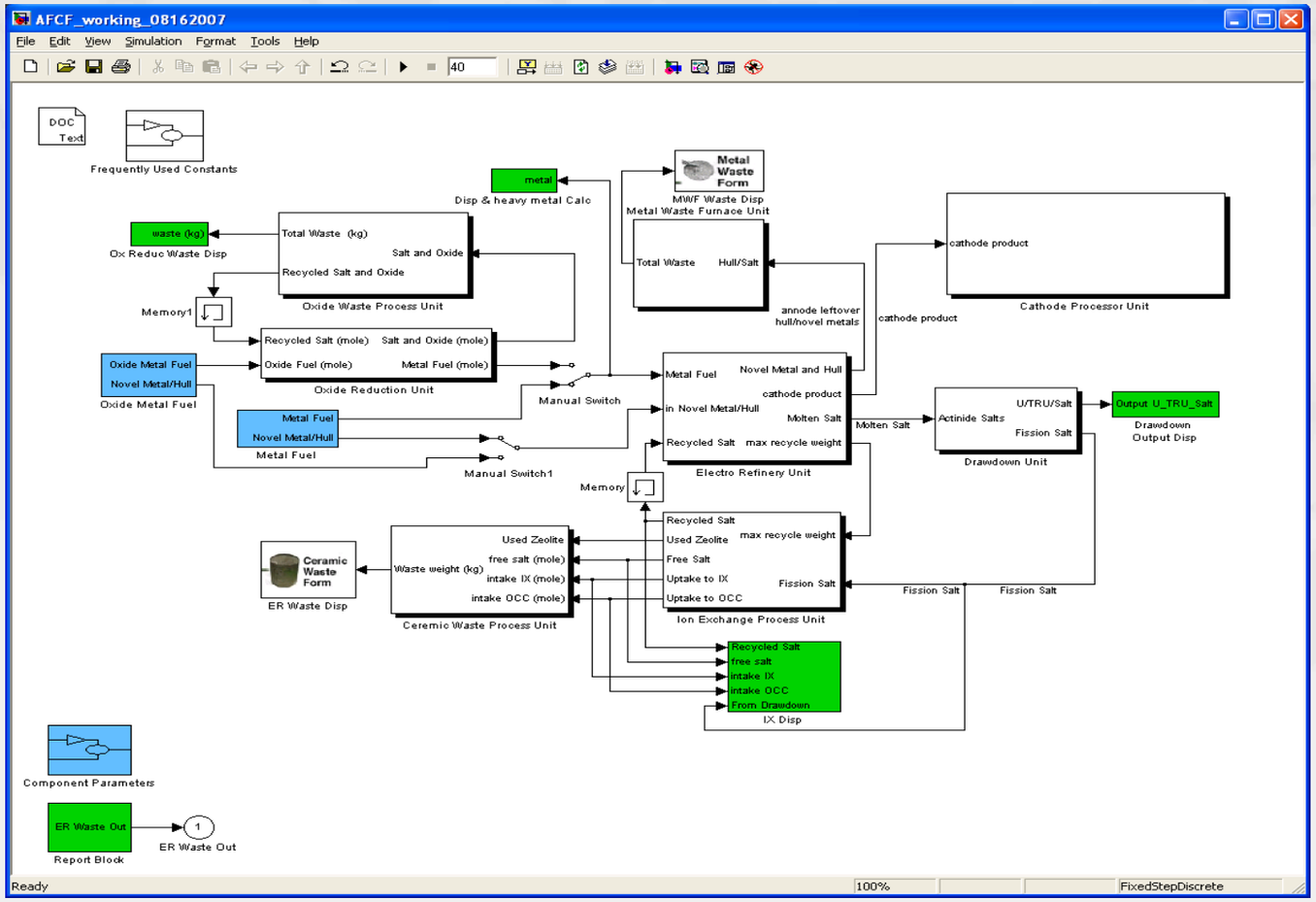
- Using processing signals (density, flowrate, temperature, potential, etc.)

- Signals can be analyzed via statistical algorithm

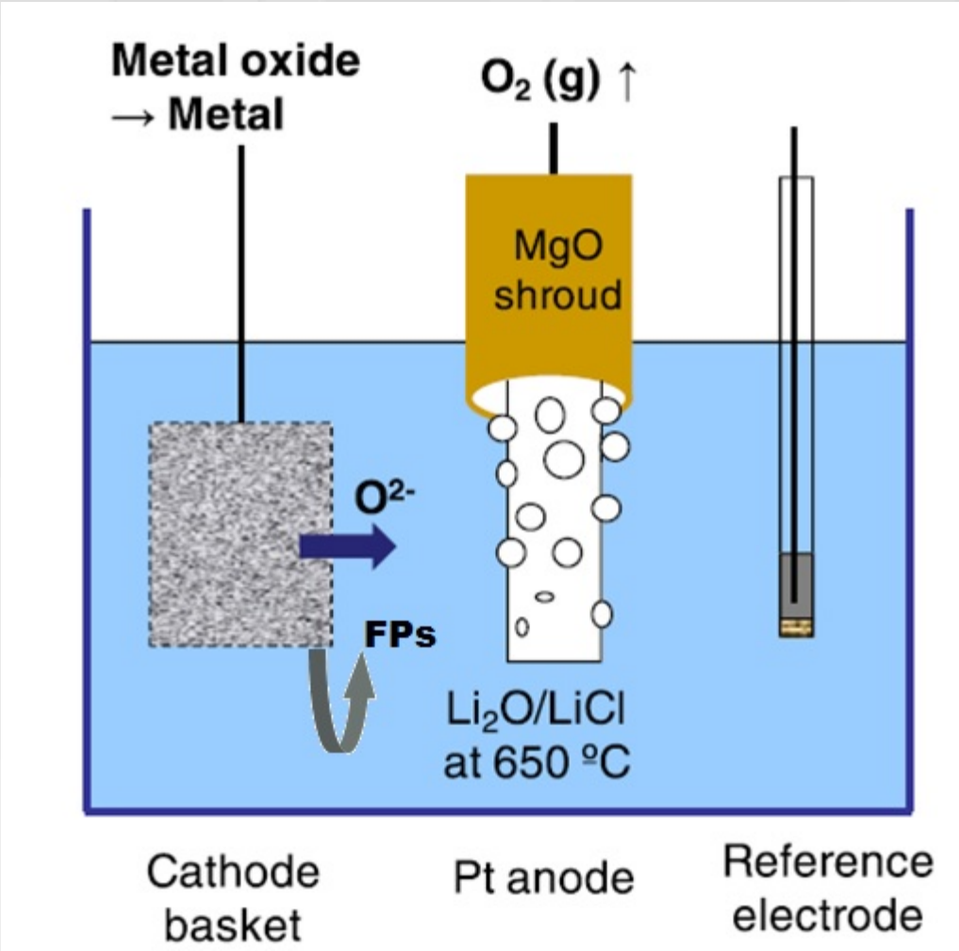
Signature Based Safeguards (SBS)

- Using processing signals, neutron count, electrochemical parameters, etc.

- Analysis signals via physics-based algorithm



Oxide Reduction (OR)



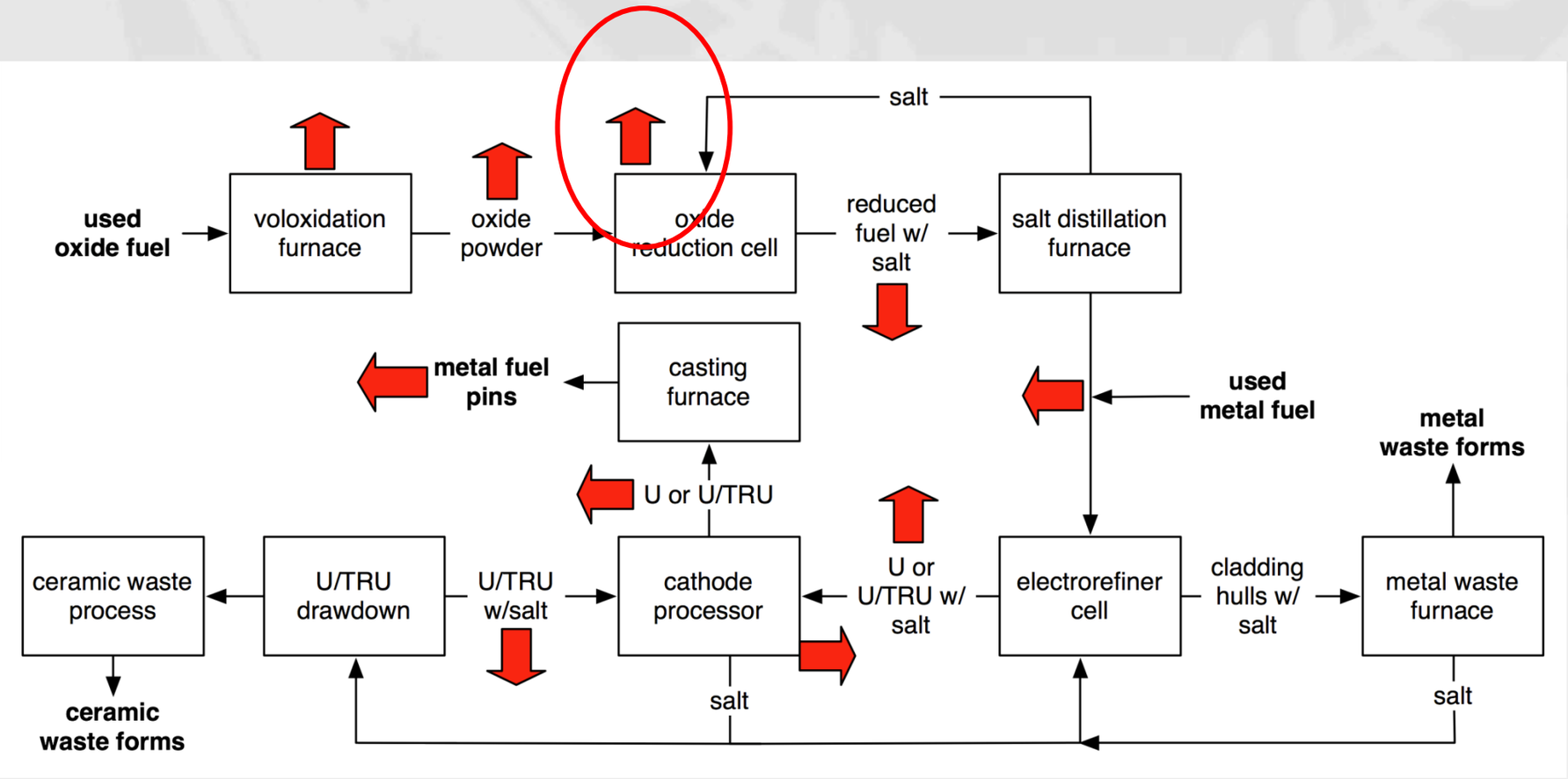
- Oxide feed contained in metal cathode basket
- Cathode: Reduction
  $M_xO_y + xe- \rightarrow M + yO^{2-}$
- Anode: Oxidation
  $2O^{2-} \rightarrow O_2(g) + 4e^-$ (inert anode)

OR Diversion Scenario

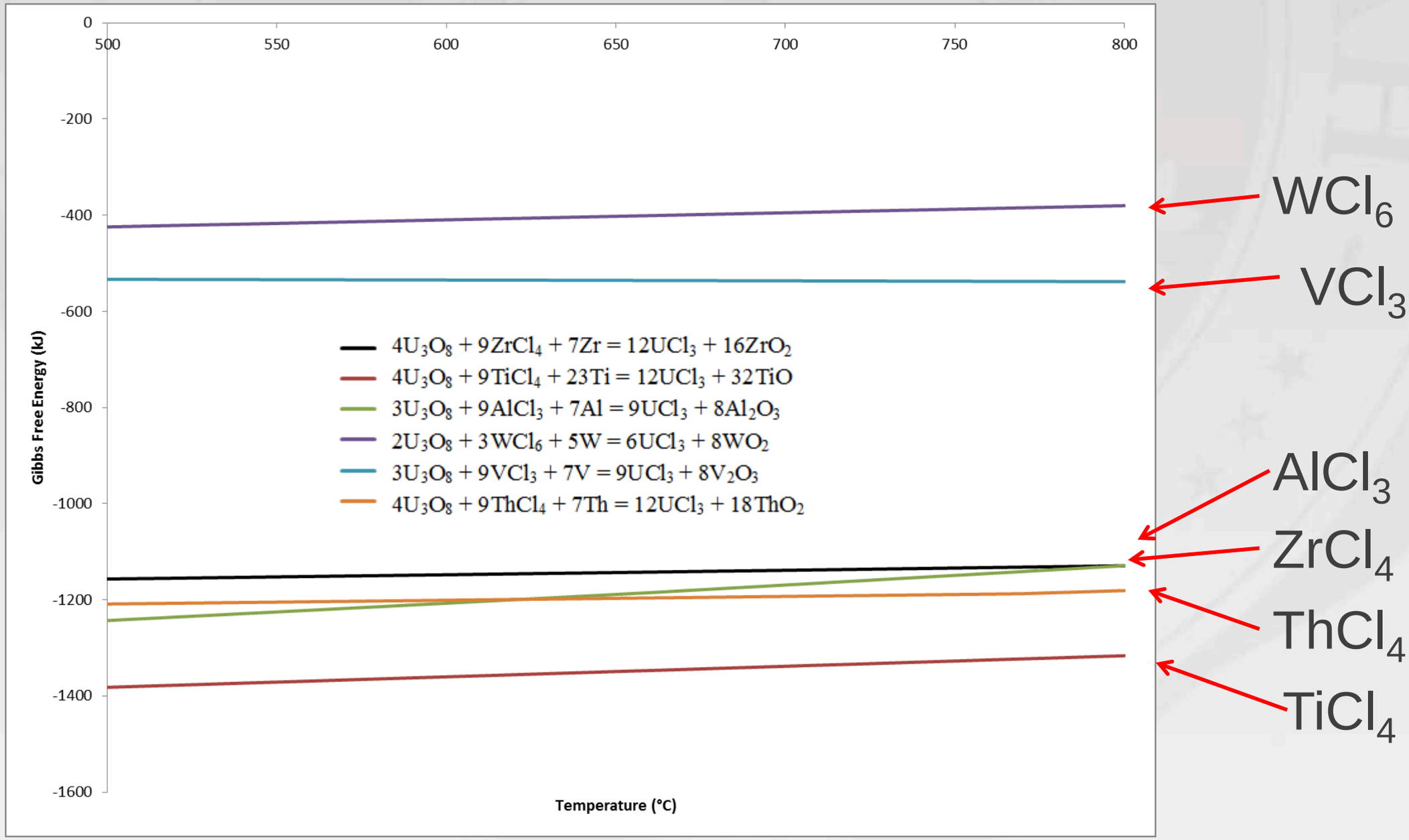
- Chlorination of actinide oxides

$$xUO_2 + yMCl_n + zM \rightarrow xUCl_3 + vM_aO_b$$

$$xPuO_2 + yMCl_n + zM \rightarrow xPuCl_3 + vM_aO_b$$

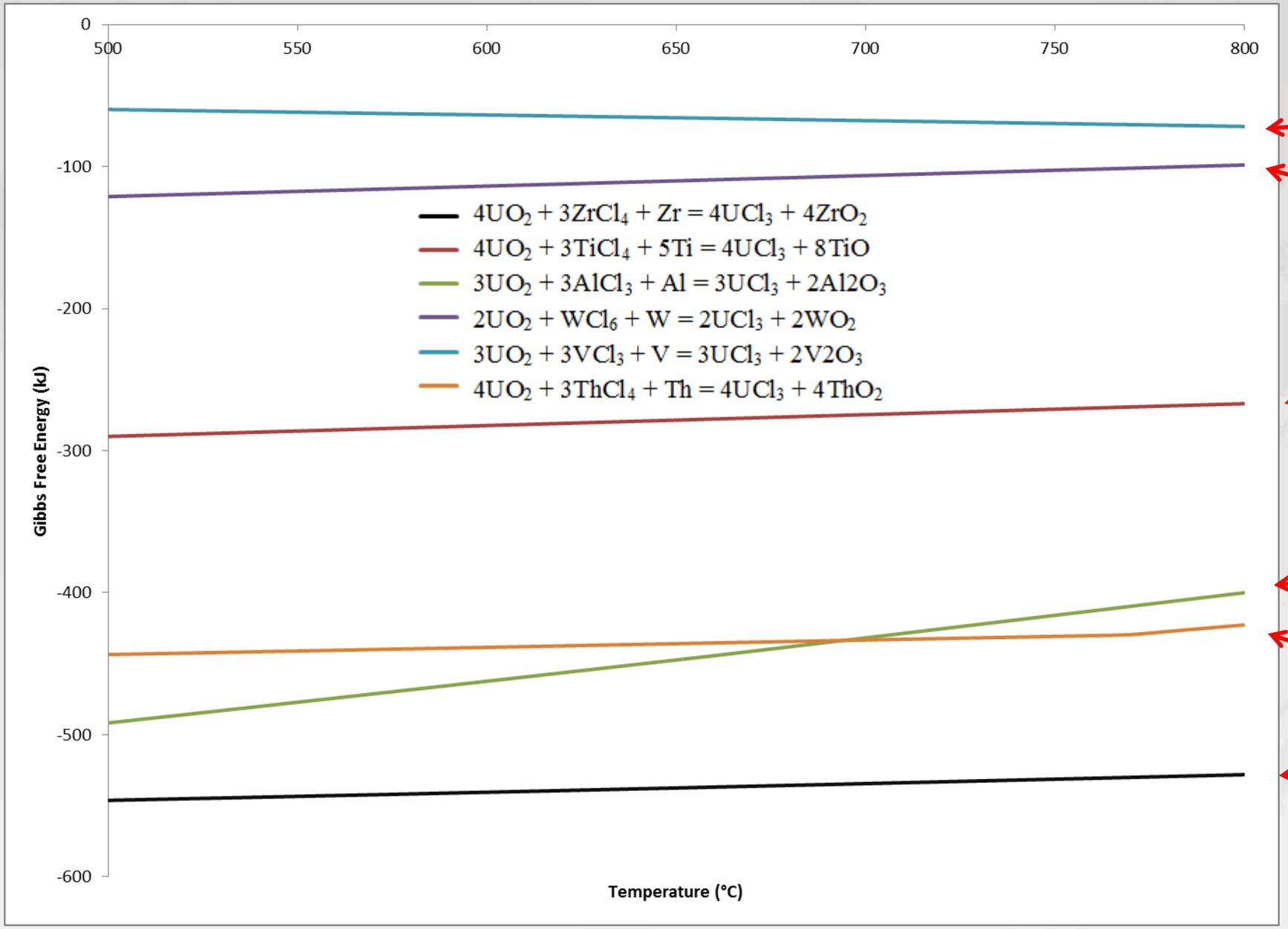


U_3O_8 Chlorination



HSC 7.1 Chemistry

UO_2 Chlorination



VCl_3

WCl_6

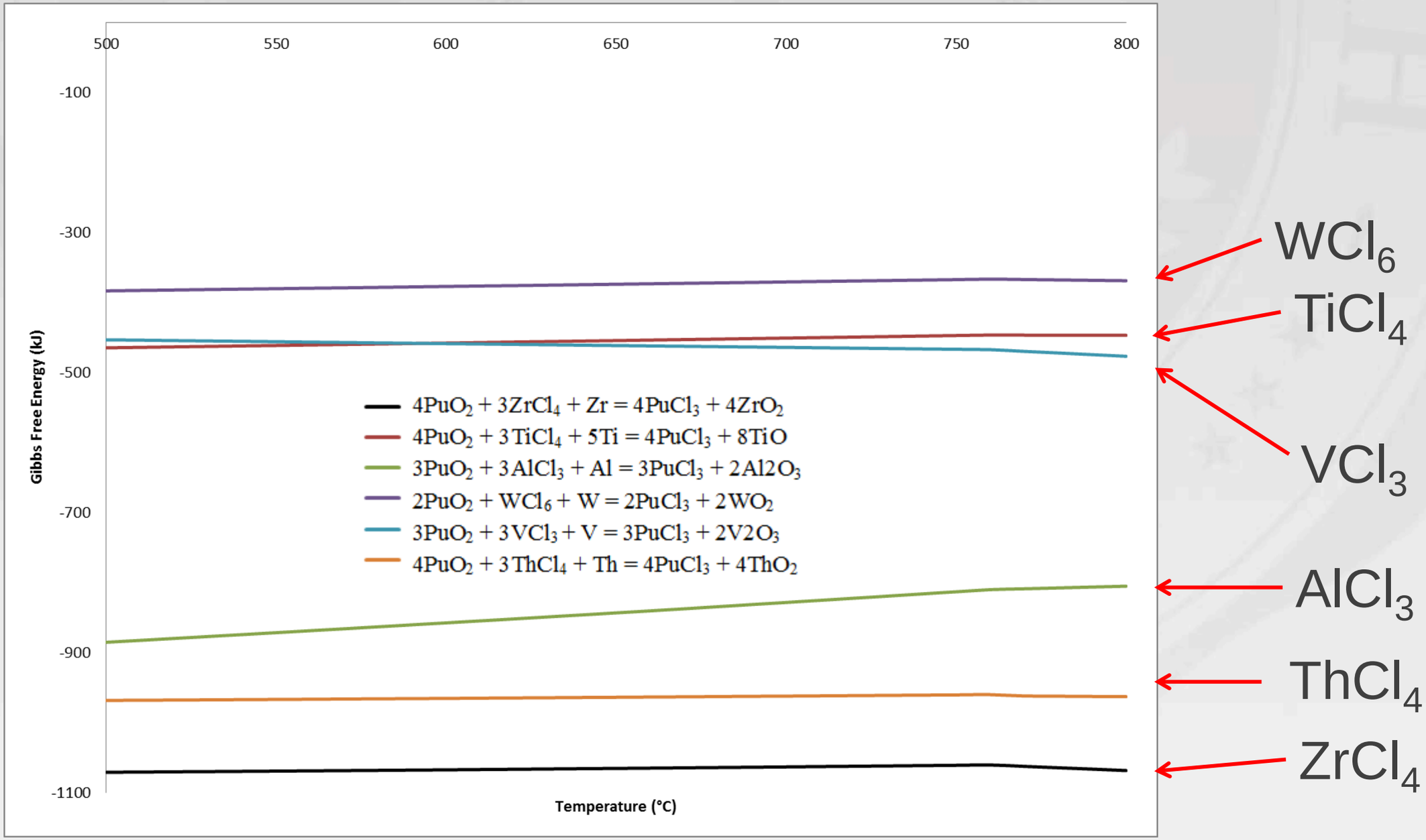
$TiCl_4$

$AlCl_3$

$ThCl_4$

$ZrCl_4$

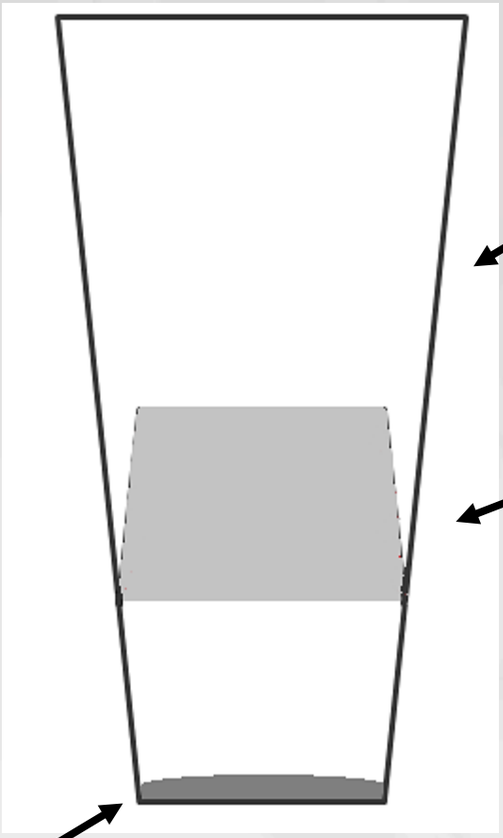
PuO_2 Chlorination



Chlorinating Agent	Oxide	ΔG @650ºC	Vp @ 650ºC (atm)
VCl_3	PuO_2	-4.61E+02	1.45E+00
	UO_2	-6.56E+01	
	U_3O_8	-5.36E+02	
$AlCl_3$	PuO_2	-8.43E+02	1.38E+01
	UO_2	-4.47E+02	
	U_3O_8	-1.19E+03	
WCl_6	PuO_2	-3.74E+02	4.82E+01
	UO_2	-1.10E+02	
	U_3O_8	-4.02E+02	
$TiCl_4$	PuO_2	-4.54E+02	4.01E+03
	UO_2	-2.78E+02	
	U_3O_8	-1.35E+03	
$ThCl_4$	PuO_2	-9.64E+02	3.75E-03
	UO_2	-4.36E+02	
	U_3O_8	-1.20E+03	
ZrCl4	PuO_2	-1.07E+03	9.29E+02
	UO_2	-5.37E+02	
	U_3O_8	-1.14E+03	

HSC 7.1 Chemistry

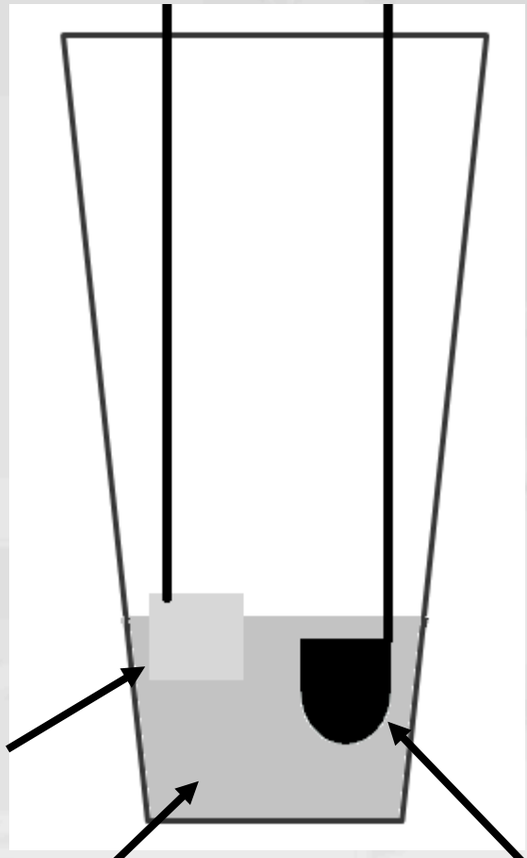
$ZrCl_4$ Addition



Glassy Carbon Crucible

LiCl-CsCl-SrCl Ingot

$ZrCl_4$ Powder



Zr Foil

$LiCl\text{-}CsCl\text{-}SrCl_2$

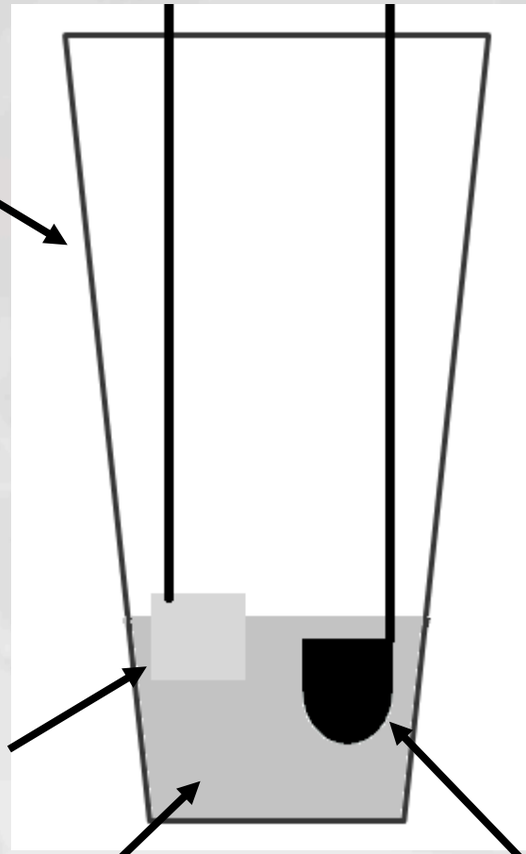
Cup with $ZrCl_4$

$ZrCl_4 + Zr = ZrCl_{4-x}$

Electric Furnace:
650°C (240°C/hr)

Hoover, R.O. PhD. Dissertation, University of Idaho, 2014.
Basile, F. *Journal of the Less-Common Metals* **1984**, *98*, 1.

Chlorination Setup

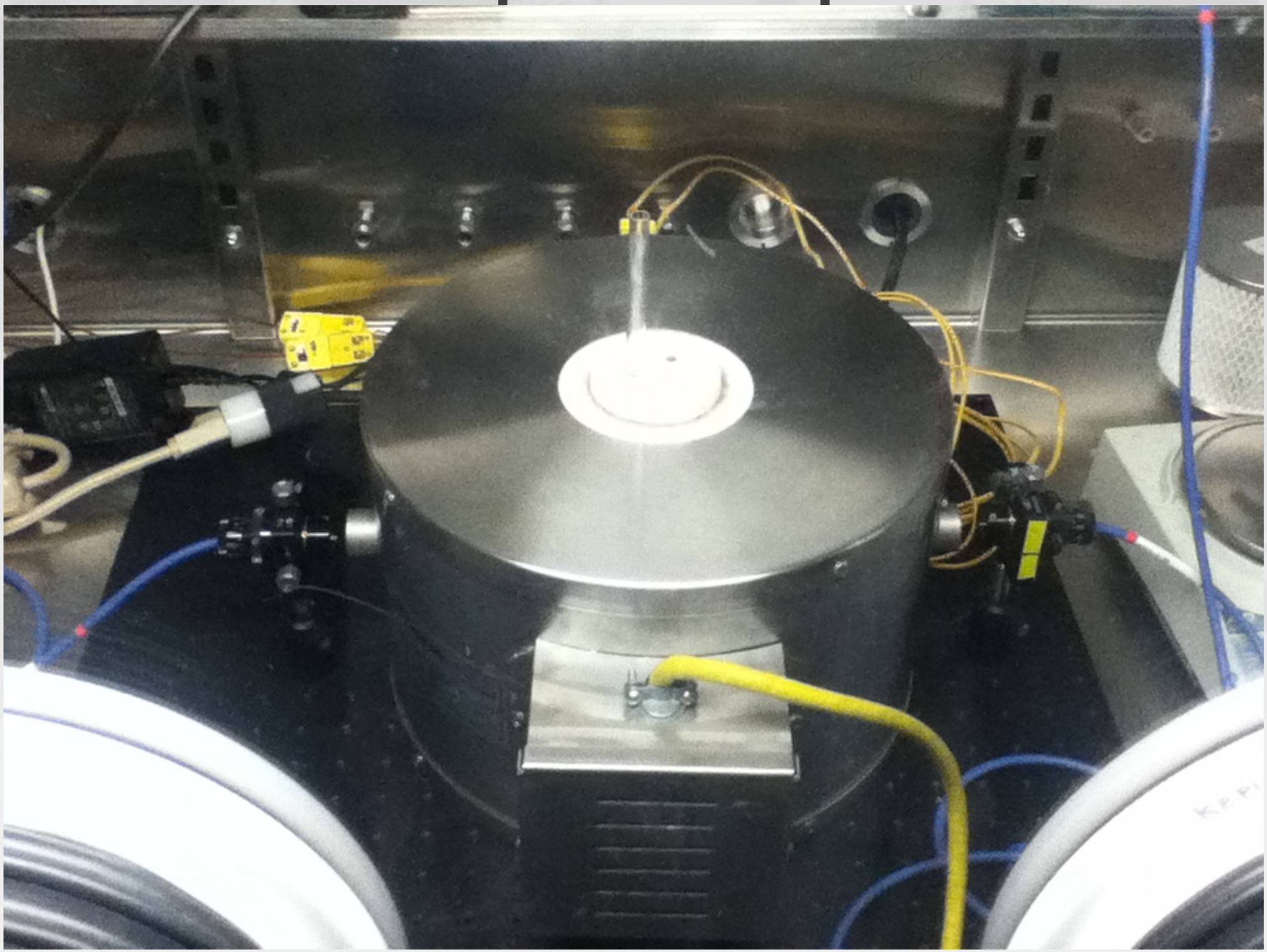


Salt Temperature: 650°C

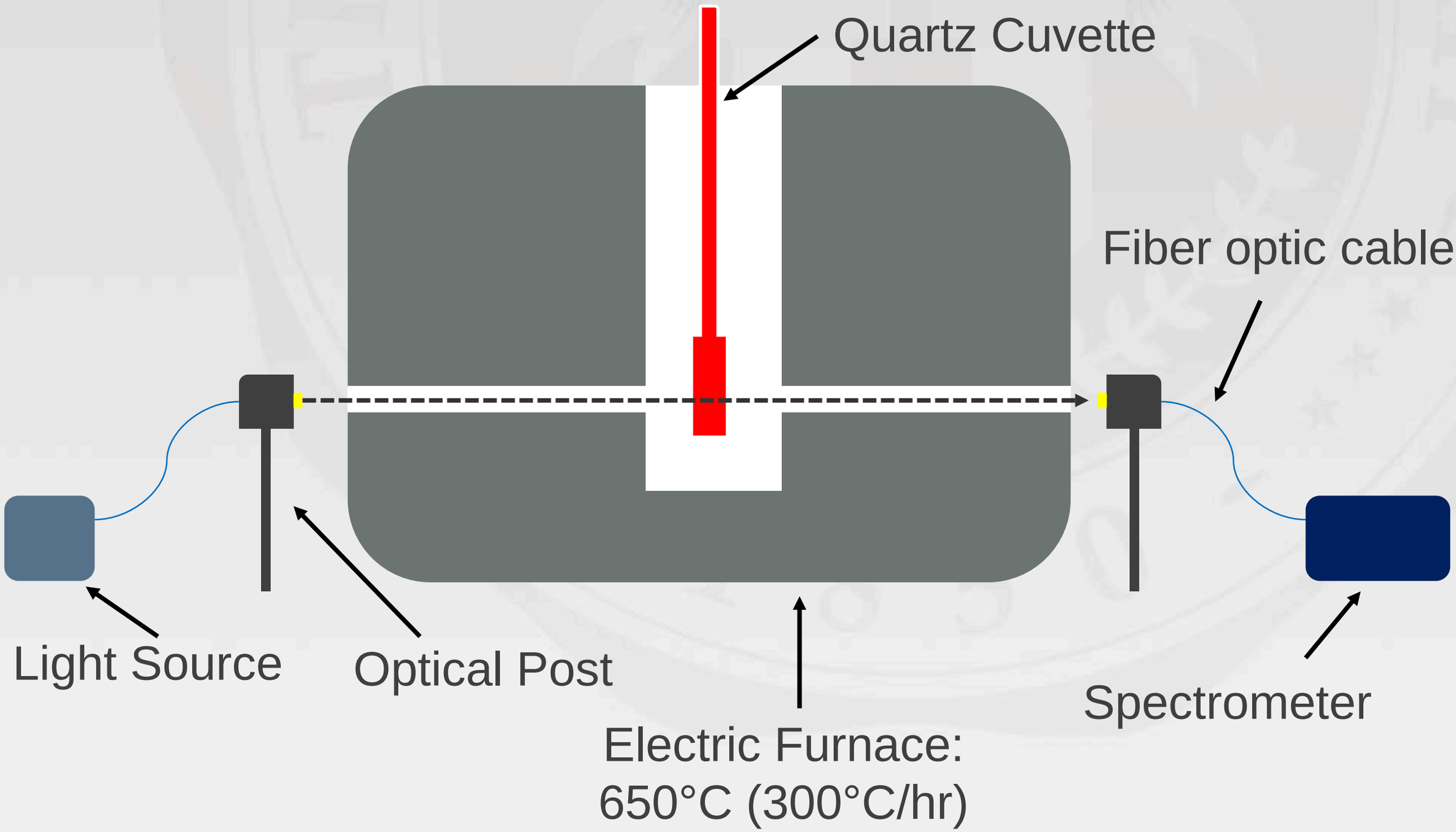
$$4U_3O_8 + 9/4ZrCl_4 + 7/4Zr = 3UCl_3 + 4ZrO_2$$

Sakamura, Y. *Journal of The Electrochemical Society* **2004**, *151*, C187.

UV-Vis Absorption Spectroscopy



UV-Vis Spectroscopy Setup



Absorption Spectroscopy as an inspection tool

- IAEA inspectors could have a small absorption spectrometer within a facility's hot cell.
- Quickly melt a salt sample and measure for abnormalities.
- Faster than external chemical assay.
- Results could be input into PM or SBS algorithm.

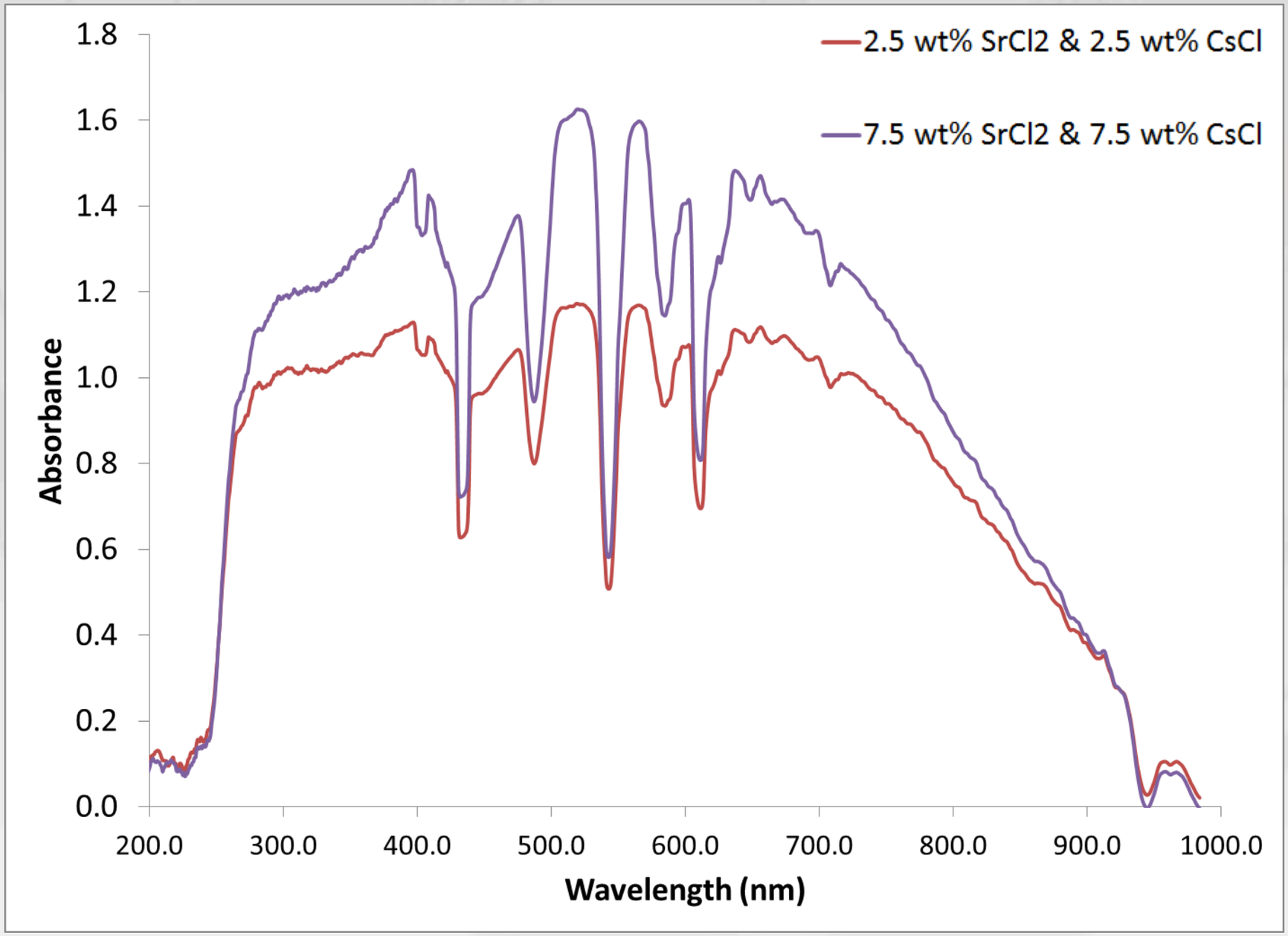
Oxide Reduction Salt

Salt	Mass fraction
LiCl	<0.99
Li_2O	0.01 – 0.03
RbCl	variable
$SrCl_2$	variable
CsCl	variable
$BaCl_2$	variable

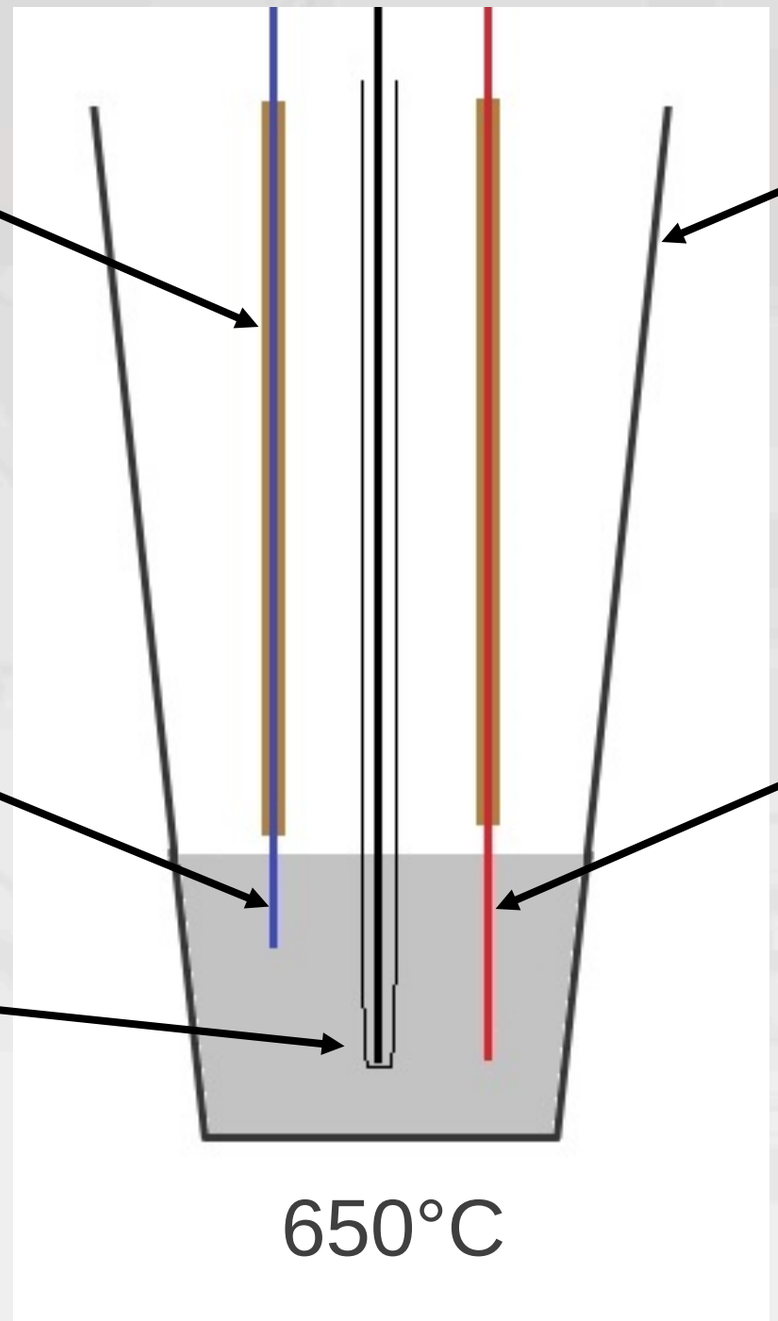
Electrorefiner Salt

Salt	Mass fraction
LiCl	0.199
KCl	0.253
NaCl	0.240
RbCl	5.02E-03
$SrCl_2$	1.37E-02
YCl_3	1.03E-02
CsCl	3.54E-02
$BaCl_2$	1.98E-02
$LaCl_3$	1.80E-02
$CeCl_3$	3.41E-02
$PrCl_3$	1.69E-02
$NdCl_3$	5.78E-02
$PmCl_3$	3.46E-04
$SmCl_3$	1.12E-02
$EuCl_3$	6.93E-04
$GdCl_3$	3.00E-04
$NpCl_3$	1.61E-03
UCl_3	4.68E-02
$PuCl_3$	3.50E-02
$AmCl_3$	4.69E-05

LiCl-$SrCl_2$-CsCl UV-Vis Spectra



Electrochemical Setup



Alumina sheath

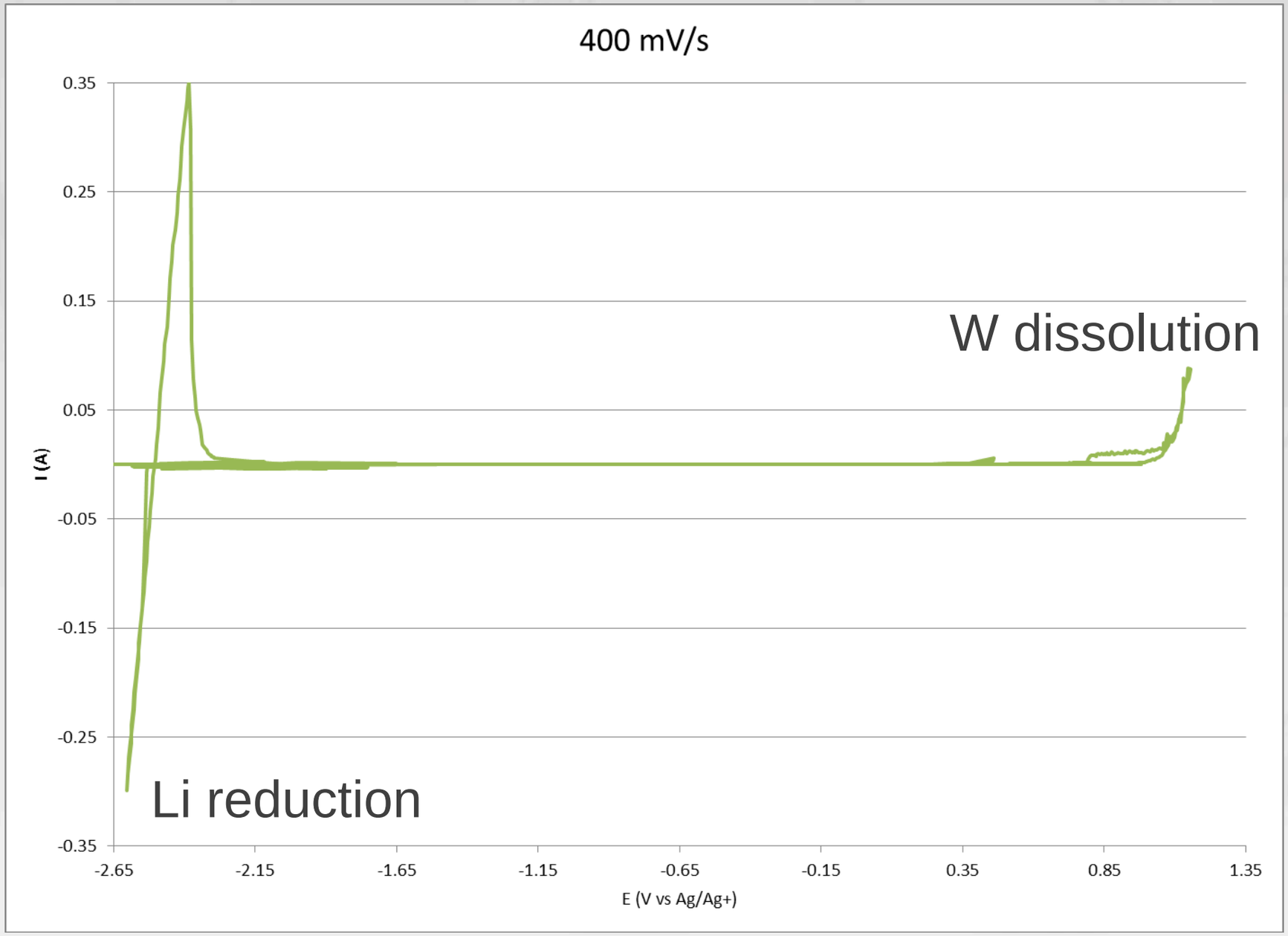
Glassy Carbon Crucible

Working Electrode:
0.5 mm 99.9% W wire

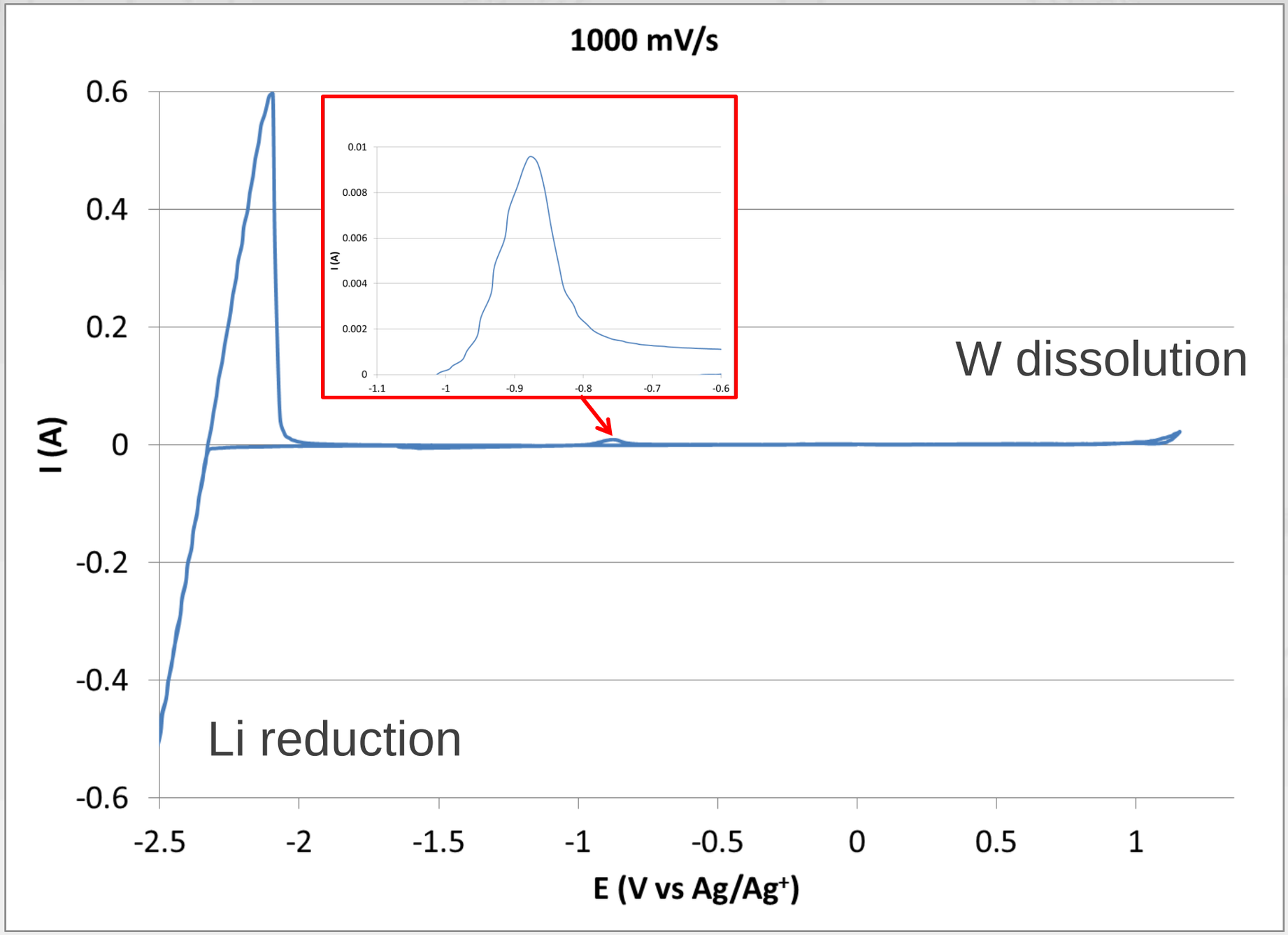
Counter Electrode:
0.5 mm 99.9% Pt wire

Reference Electrode:
LiCl-1%wt AgCl

LiCl-$SrCl_2$-CsCl CV



$LiCl-SrCl_2-CsCl-ZrCl_4$ CV



Future Work

- Analysis for $ZrCl_{4-x}$ via UV-Vis and CV
- Chlorinate uranium oxide
- Analysis for UCl_3 via UV-Vis and CV
- Repeat for other chlorinating compound if necessary

Conclusions

- Chlorination of actinide oxides is a credible diversion threat based on thermodynamic calculations.
- Addition of $ZrCl_4$ to molten LiCl is difficult because of the high vapor pressure. Other chlorinating species may need to be considered.
- UV-Vis absorption spectroscopy can be performed on molten salt samples from the oxide reduction process.

Nuclear Pyrometallurgy Laboratory

Thank You!

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