Management of Salt within Plutonium Electrorefining

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Introduction

- Electrorefining in molten salts used to recycle Pu
  - Plutonium has a limited ‘Shelf Life’ owing to radioactive decay
  - Purification required to produce metal for manufacturing
  - Pyrochemical processing very efficient for metal recycle
- Developed in early 1960’s at LANL
  - Focus was on metal recovery
  - Other factors are becoming increasingly important such as by-product management
- Originally carried out in equimolar NaCl-KCl
- Previous work in $CaCl_2$ at LANL, LLNL and AWE
- This work refers to electrorefining in $CaCl_2$

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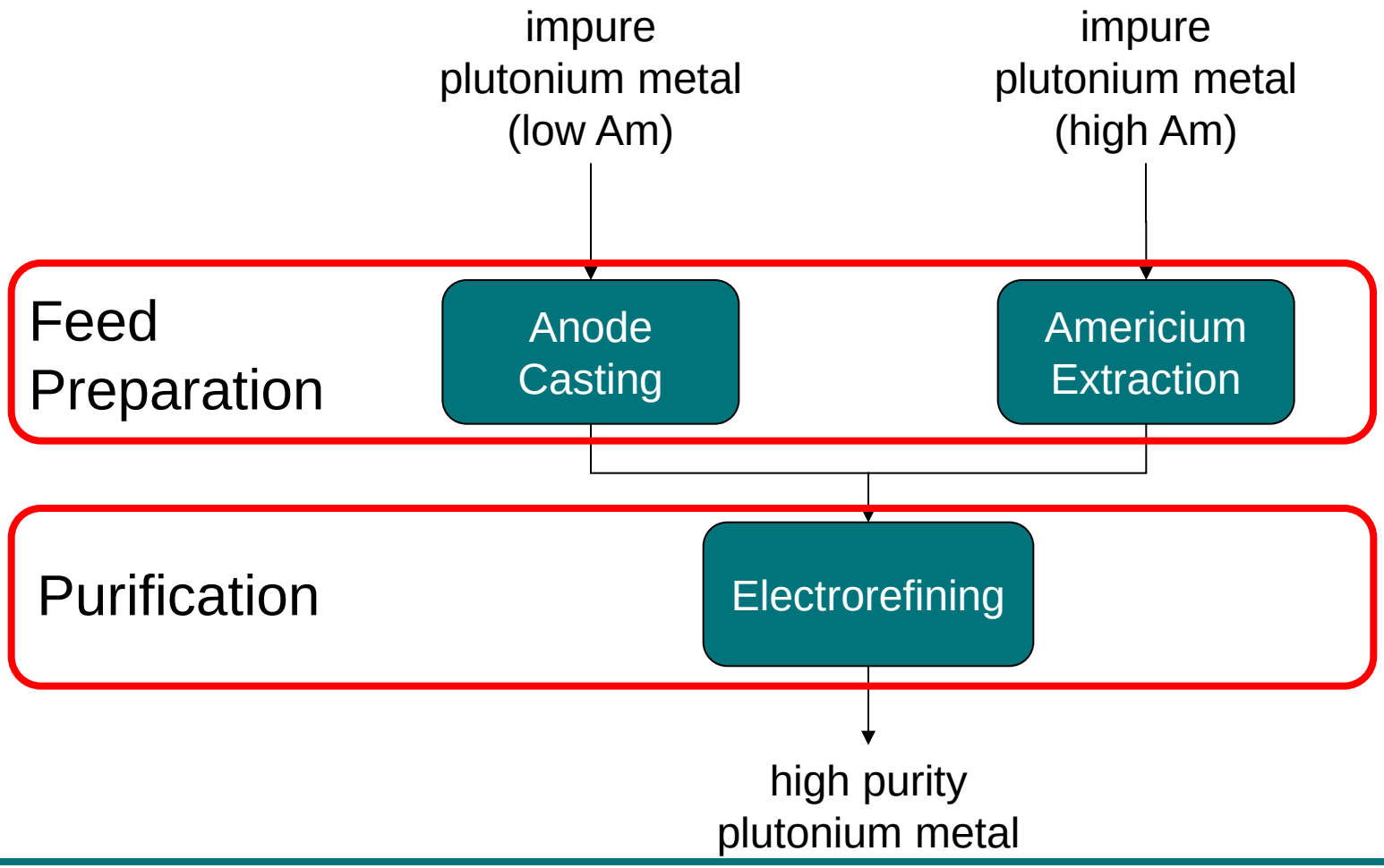
Simplified flowsheet



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Feed preparation

Anode Casting

- Casts anodes for ER
- Removes insoluble material such as oxide

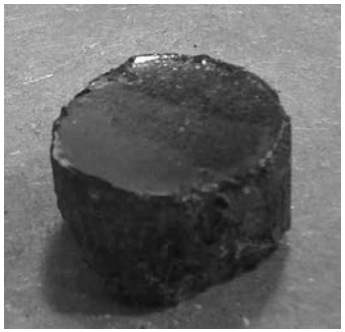
→

+

Americium Extraction

- Removal of americium from plutonium metal

$$Am + {}^{x}/_{2}MgCl_2 \rightarrow AmCl_x + Mg$$



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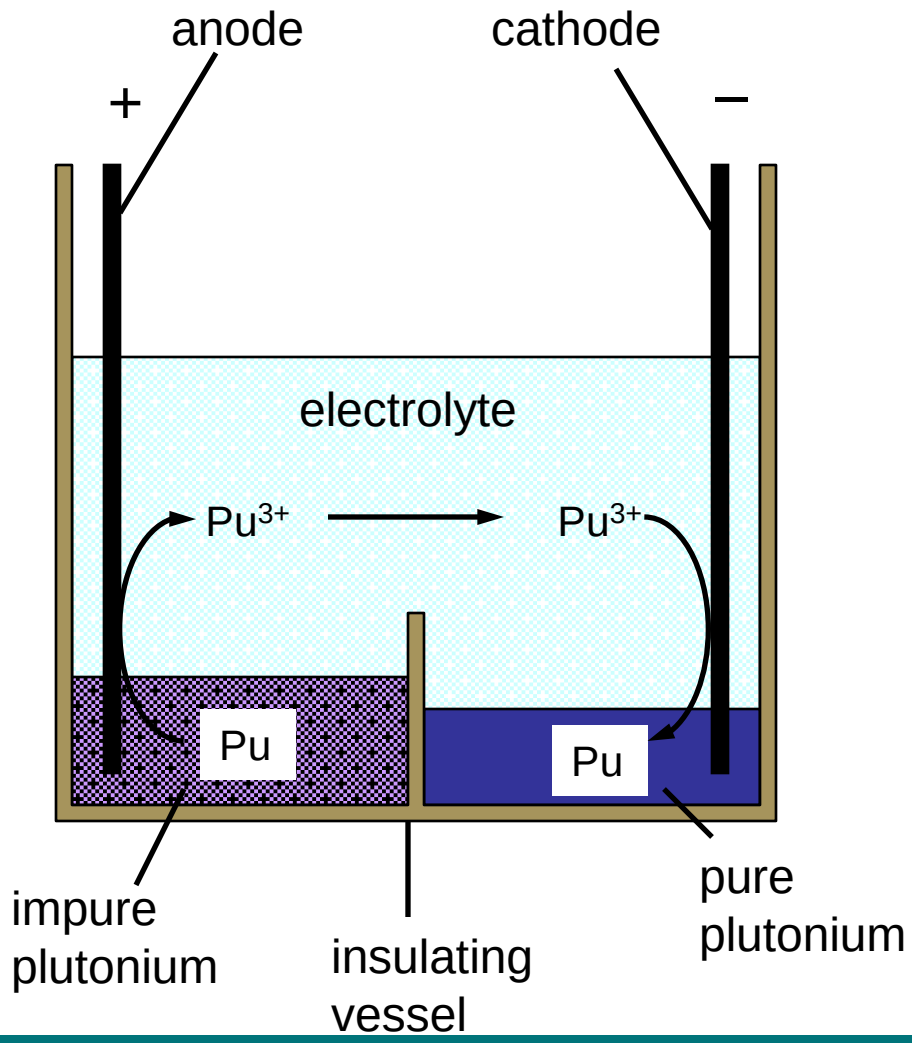
Electrorefining (ER)

- Purification of plutonium metal
  - Electrochemical process
  - Impure plutonium at anode converted to pure plutonium at cathode
  - Impurities remain in anode
- Typical yield 85-90%
- Typical purity 99.9%



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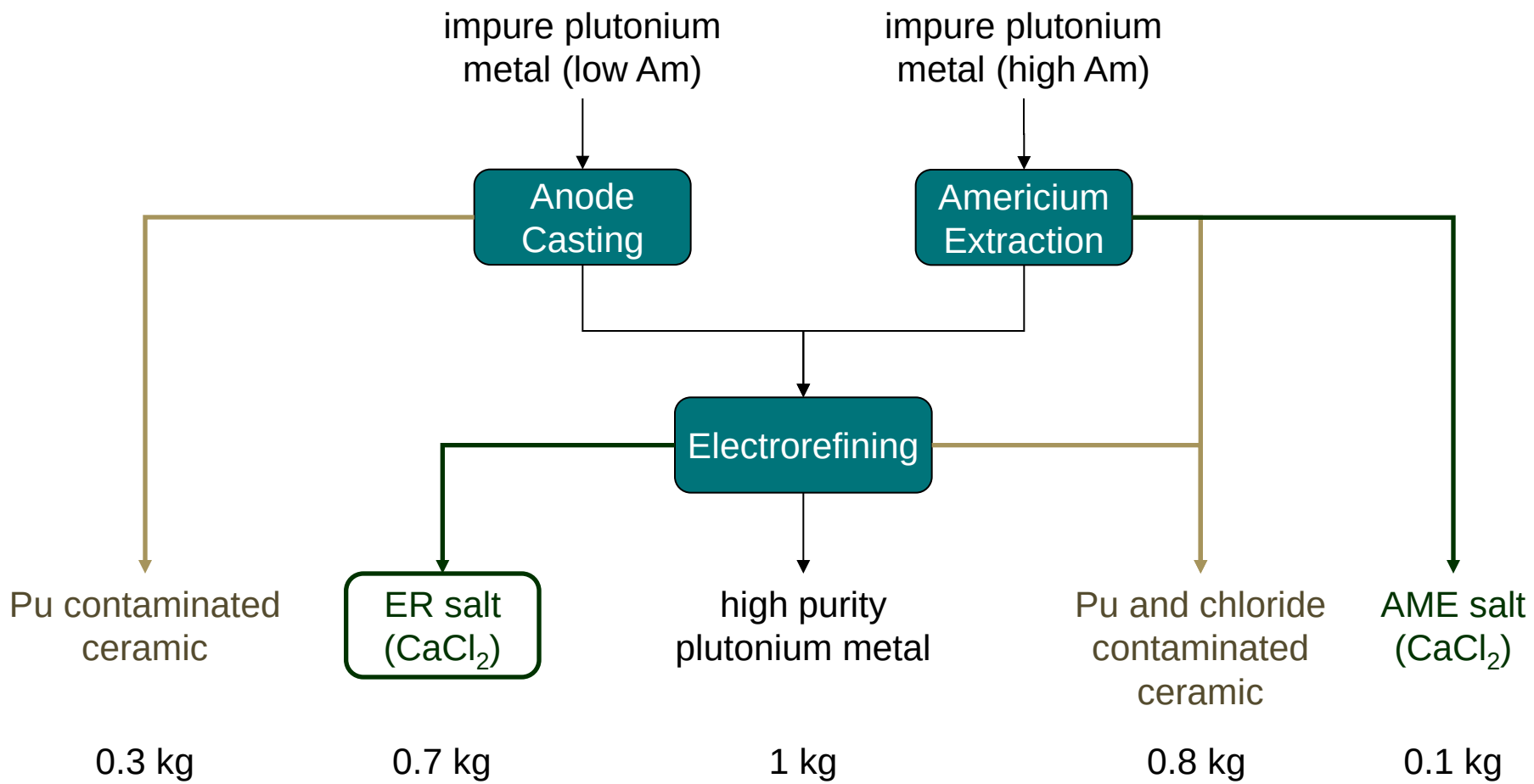
Residue generation



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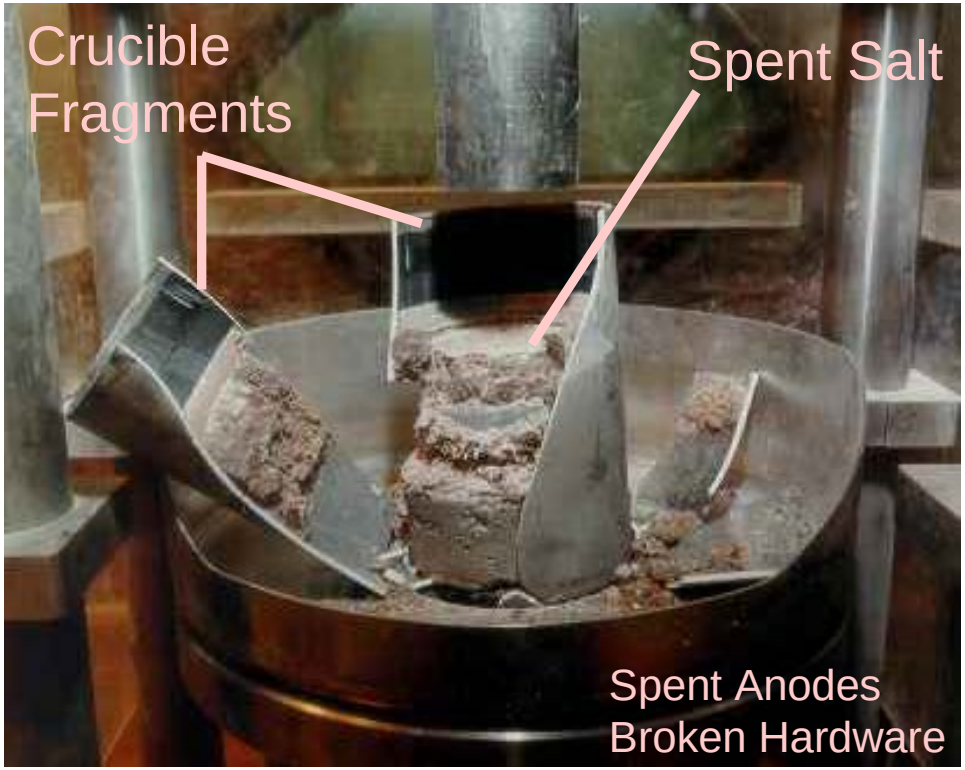
Molten salt residues – disposal challenge



- Levels of actinides require long term solutions
- Levels of chloride raises corrosion issues
- Separation of actinides from chloride desirable for long term waste disposal
- Pu contaminated residues require safe and secure storage pending treatment

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What can we do about residues generation?

- Use less salt (crucible redesign)
- Re-use salt directly
- Remove Pu from salt (salt scrub/strip)
- Convert salt to waste form

- $CaCl_2$ salt system has certain advantages over NaCl-KCl system
  - Less side reactions (no equivalent Na or K production)

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Crucible development

- Current design
  - Unchanged since 1960's
  - Good chemical compatibility

  - Lengthy breakout
  - Failures require significant re-work
  - Excess salt required
    - Volume of cathode compartment too large

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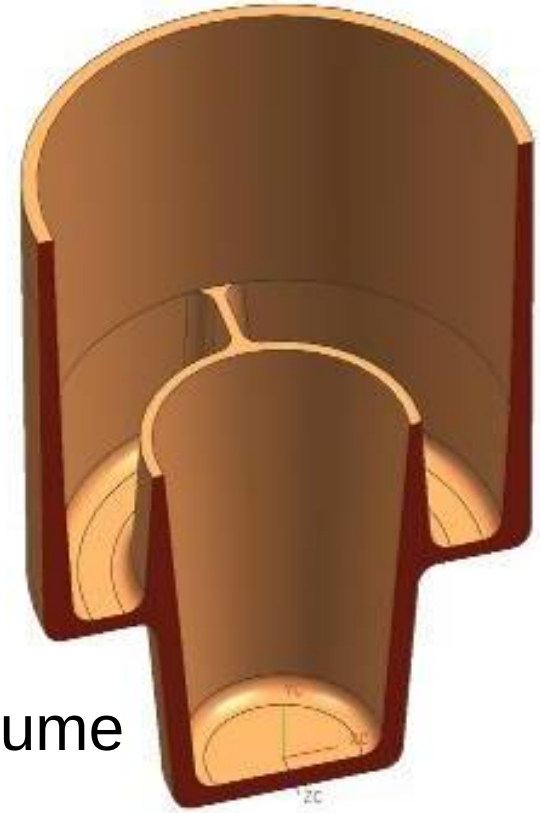
Crucible development

- Trials reported previously
  - ✓ 88% yield
  - ✓ Good product quality
  - ✓ Improved product break out
  - ✗ Teething troubles



- Minimisation of salt volume
  - Cathode section raised
  - volume of cathode and anode compartments equalised
  - 350 g saving in salt

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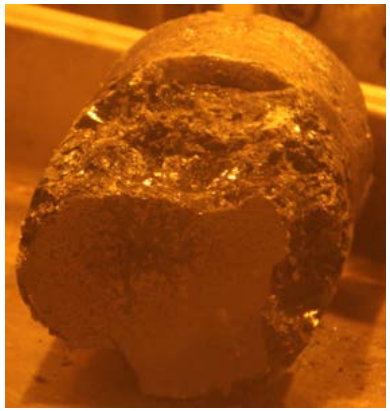
Salt re-use



- ER salt contains few impurities
  - Am, very small amounts of Np
  - Al_2O_3 from the break out process
- ER salt contains Pu charge carriers required for electrorefining
  - Less magnesium chloride required to oxidise Pu
- During breakout, approximately half of the salt segregated
  - only large lumps (< 1cm^3) of salt selected to avoid contamination with Al_2O_3 dust

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Salt re-use – results

Run No.	Salt (g)	Yield (%)	Anode efficiency (g/Amp.hour)	Cathode efficiency (g/Amp.hour)	Density (g/cm³)	Am content (ppm)
1	*929.3 868.9	88.1	2.82	2.69	19.58	100
2	*912.0 911.7	90.5	2.88	2.76	19.60	75
3	*778.4 1023.8	87.0	2.85	2.75	19.61	75
4	*897.0 912.1	90.4	2.96	2.67	19.61	75

* Re-used salt

$$Yield\ (\%) = 100 * \frac{Product\ metal\ wt}{Feed\ wt}$$

$$Anode\ efficiency = \frac{(Feed\ wt - spent\ anode\ wt)}{Charge\ passed\ (Amp.hr)}$$

$$Cathode\ efficiency = \frac{Product\ metal\ wt}{Charge\ passed\ (Amp.hr)}$$

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Salt strip

- Previous work at LANL, LLNL and AWE
  - Use Ca metal to reduce Pu species in the salt to Pu metal
  - Pu metal recovered as a metal button
  - Pu content of salt low enough to discard
  - Mixed results achieved with NaCl-KCl system at AWE
- Current set of experiments undertaken on $CaCl_2$ ER salt which is fragment free

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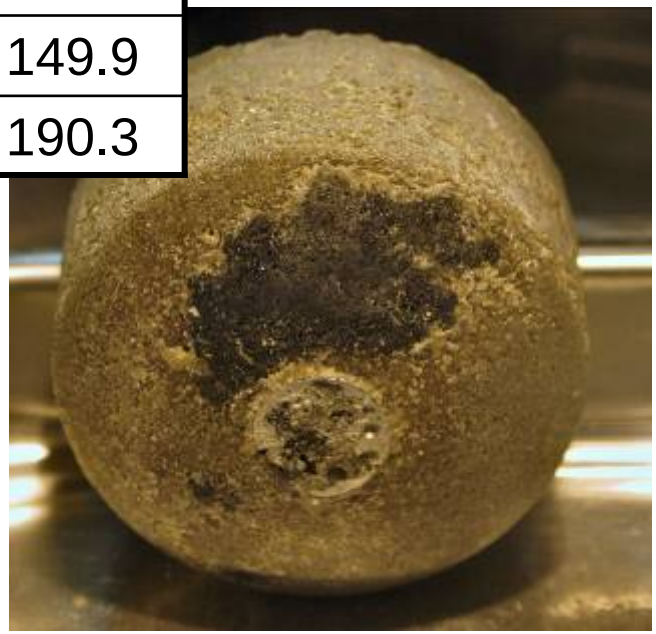
Salt strip – run data

Run No.	Feed Salt		Calcium		Pu product (g)
	Total wt (g)	Pu wt* (g)	Mass (g)	Excess‡‡ (%)	
1	1723.2	66.6	22.6	35	44.7
2	3297.5	146.1	47.5	30	149.9
3	3362.2	174.8	65.9	50	190.3

* High Resolution Gamma Spectroscopy and calorimetry
‡ estimated from Pu assay and assuming Pu^{3+}



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Salt strip –analysis of products

- Bulk of salt very low in Pu
- Metal product suitable for recovery

	Plutonium content			
	(g)		(wt%)	
Run	1	2 & 3	1	2 & 3
‘dirty’ salt *	17.0	0.20 – 0.45	1.85	0.04 – 0.06
‘clean’ salt *	3.3		0.43	
‘clean’ salt **	0.15		185 ppm	

* pncc
** chemical analysis

Metal product analysis

Pu (wt %)	Ga (ppm)	Am (ppm)	Fe (ppm)	Ni (ppm)	Ca (ppm)	Mg (ppm)	Ta (ppm)	Y (ppm)	Al (ppm)	Ti (ppm)	U (ppm)	Np (ppm)
97.50	42	5000	32	60	2900	16000	48	610	2700	230	260	65

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Epoxy encapsulation

- Salt and chloride contaminated ceramic requires immobilising to convert to waste
- Epoxy resins are compatible with chloride salts and have a track record in radioactive waste applications
  - e.g. UKAEA encapsulated MoD radium boxes at Harwell, UK

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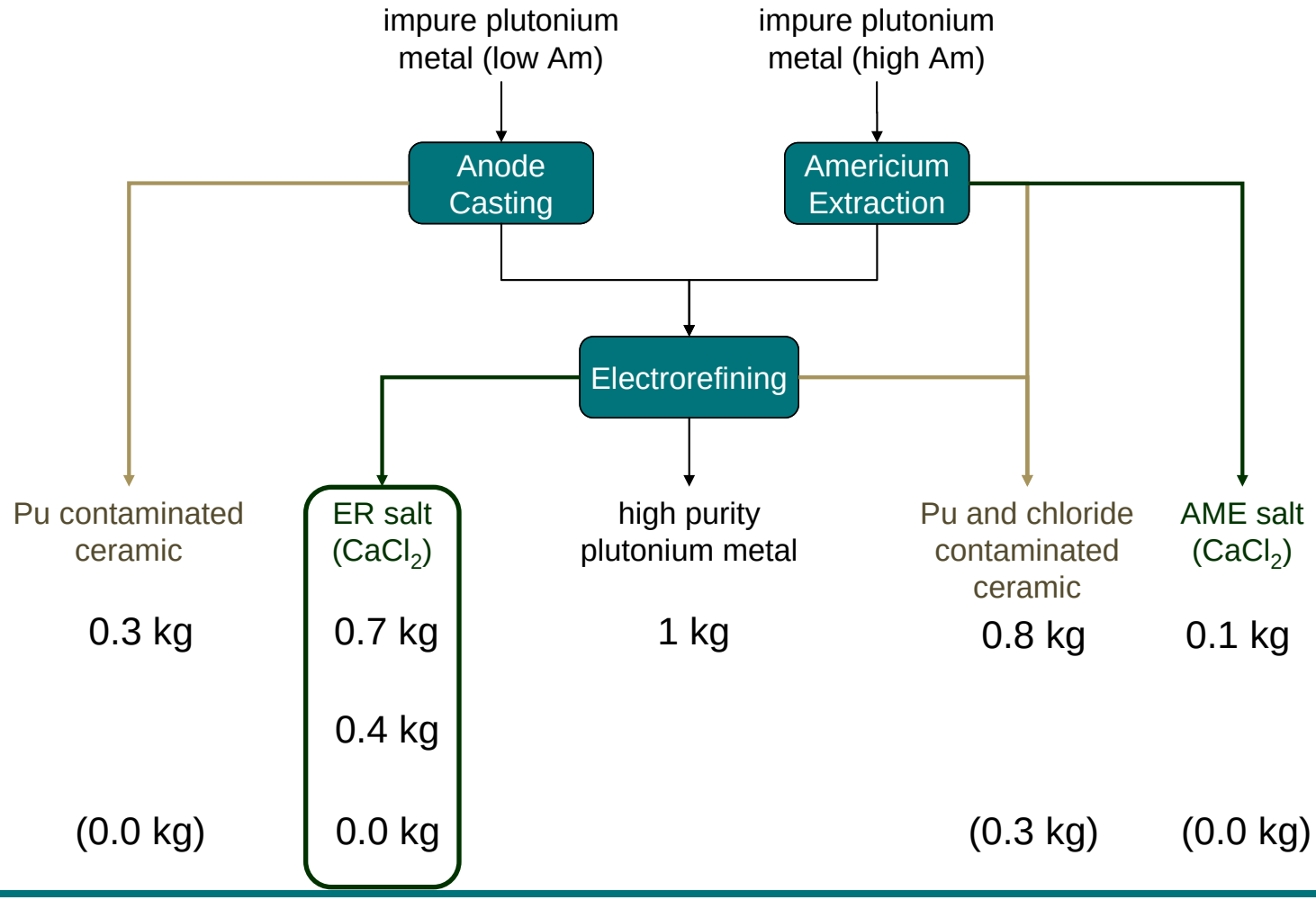
Residue reduction



	Pu contaminated ceramic	ER salt ($CaCl_2$)	high purity plutonium metal	Pu and chloride contaminated ceramic	AME salt ($CaCl_2$)
Current estimate	0.3 kg	0.7 kg	1 kg	0.8 kg	0.1 kg
With new crucibles and salt re-use		0.4 kg			
+ salt strip and encapsulation	(0.0 kg)	0.0 kg		(0.3 kg)	(0.0 kg)

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Summary

- Pyrochemical processing is efficient for the recovery of plutonium metal
- The management of the by-products (residues) from processing is becoming increasingly important
- AWE is developing its processing to eliminate residue generation where possible
- Further work is required to assess the tolerance of salt strip to Al_2O_3

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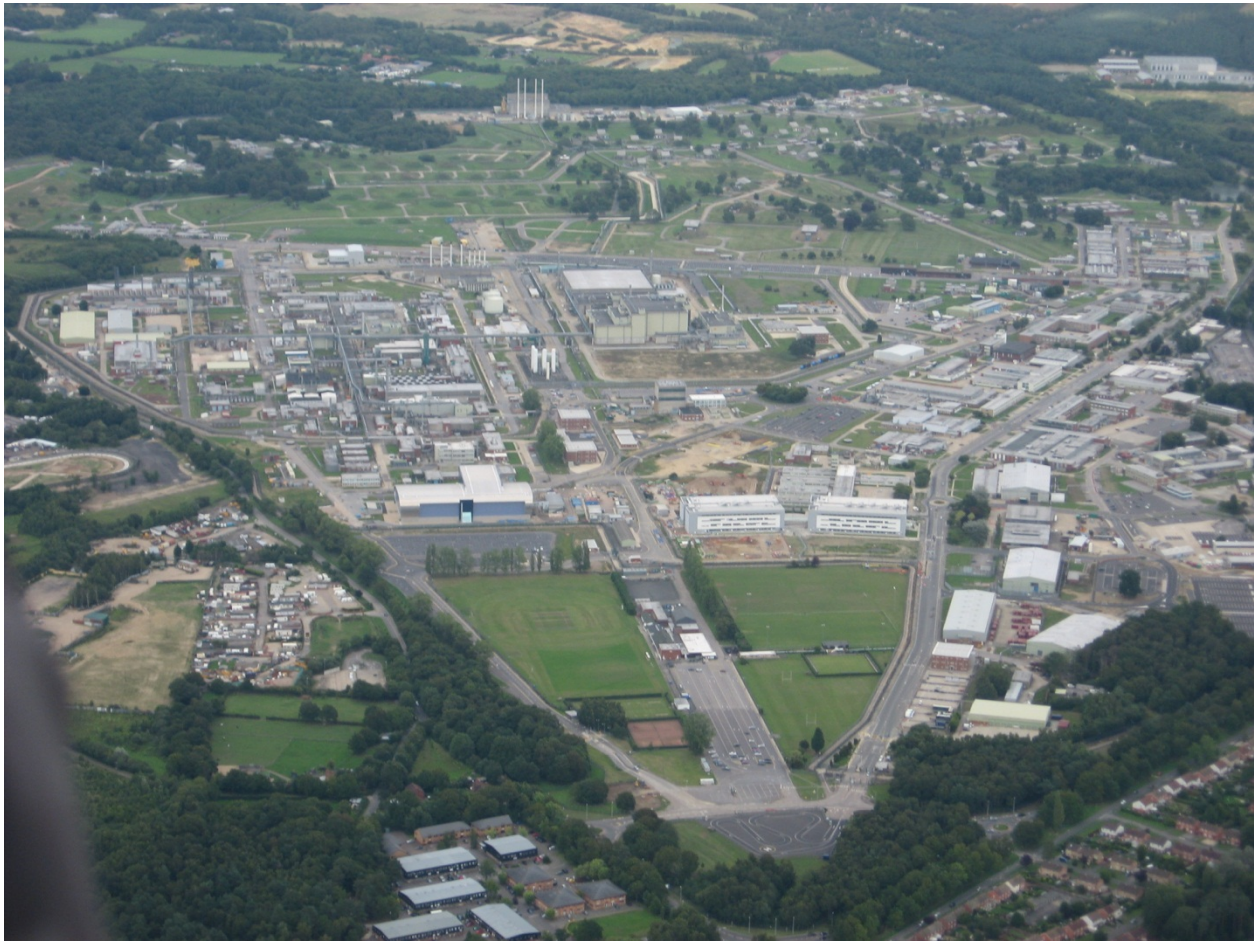
Thank you



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