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# Recovery of Actinides from Irradiated Metallic Fuel by Electrorefining Using Solid Aluminum Cathodes

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Institute for Transuranium Elements

# Main ITU activities

- Fundamental and Applied Actinide Research
- Safety of Conventional/Advanced Nuclear Fuels
- Nuclear Waste Disposal
- Advanced Nuclear Fuel Cycle
- Forensic Analysis and Combating Illicit Trafficking
- Nuclear and Trace Analysis for Safeguards
- Alpha-Immunotherapy

## Advanced Nuclear Fuel Cycle

- Preparation of advanced experimental nuclear fuels (e.g., metallic, inert matrix fuels…)
- Investigation of specific properties and irradiation performance testing
- Development of efficient processes for the recovery of long-lived radionuclides
  - hydrometallurgical extraction separation processes
  - pyrochemical separation processes

…in the nuclear fuel cycle research to contribute to European efforts:

- to improve the spent fuel behavior under intermediate and final storage conditions
- to reduce the amount and the toxicity of radioactive waste (P&T)

- **Basic research on An properties in molten salts**
  - *electrochemical behaviour of pure An and An-Al intermetallic compounds in molten chloride and fluoride salts*
  - *combined spectroscopy-electrochemistry of An in molten chloride salts (UV-VIS, Raman, TRLF spectroscopy techniques)*
  - *synthesis and characterisation of actinide fluorides and chlorides (HF gas line)*
- **Processes for recovery of actinides from spent nuclear fuels**

  ☙ Materials
  - *un-irradiated and irradiated target fuels (An-Zr-Ln alloys, MOX)*

  ☙ Separation techniques in molten chloride and fluoride salt media
  - ***Electrorefining*** *and electrolysis* ***in molten LiCl-KCl using solid Al cathodes***
  - *Direct electroreduction of oxide fuel in molten LiCl-$Li_2O$ and LiF-$CaF_2$-$Li_2O$*
  - *Molten salt – liquid metal reductive extraction (MSR fuel cycle – under preparation)*

# Pyrochemical Advanced Nuclear Fuel Cycle

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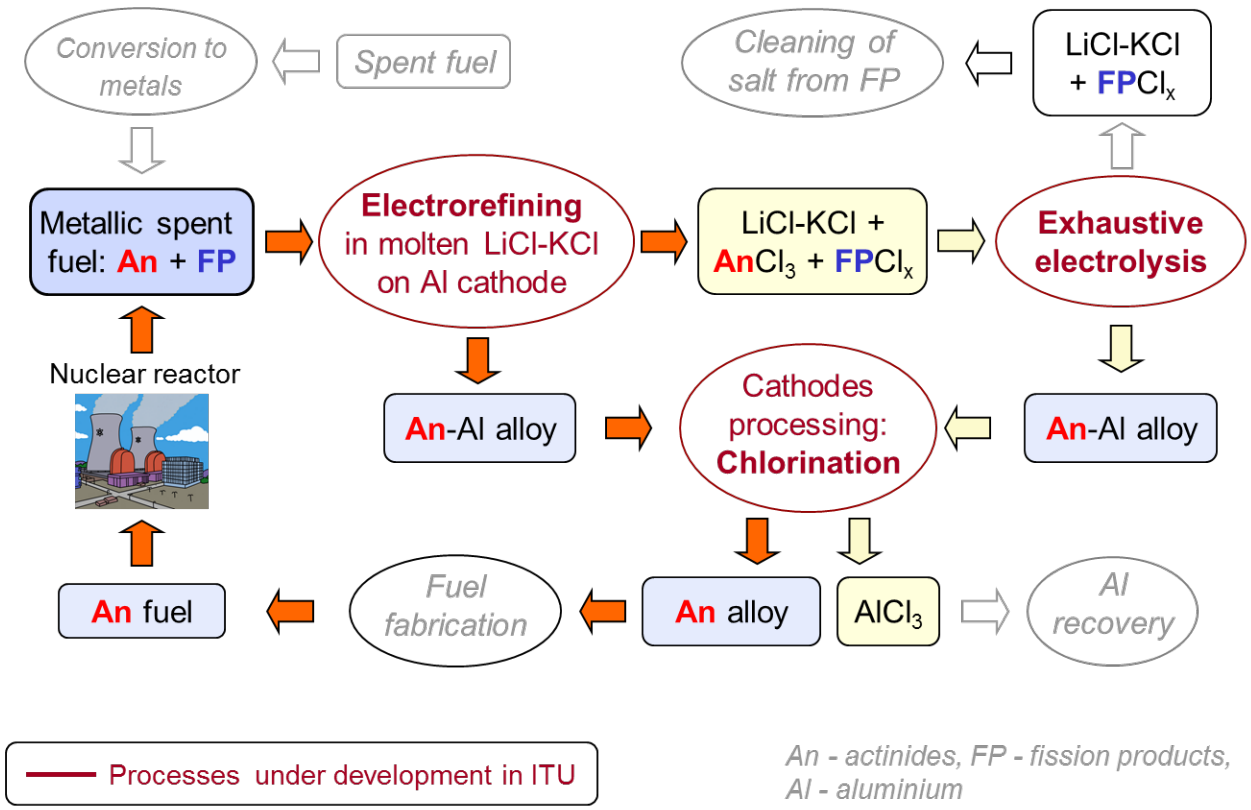
- Investigation on **core processes** of pyrochemical routes for recovery of An from spent nuclear fuel in lab scale
- **No full process development** (no flow-sheeting, not all steps / fate of not all elements investigated)



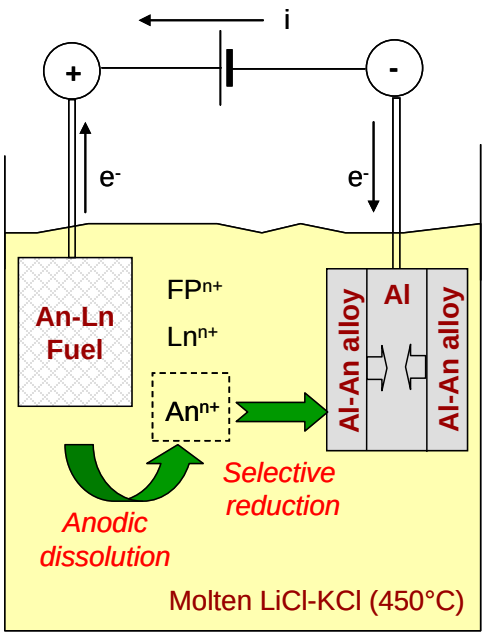
## Performance of the solid Al cathode in the electrorefining process using irradiated metallic fuel

**Main aim:** *To demonstrate selectivity and efficiency of the electrorefining process on **irradiated fuel** using solid Al cathode for homogeneous recovery of all An*

**Experiment:** *Galvanostatic runs at different current densities on plate and rod cathodes*
*Potentiostatic runs with different times on plate cathodes*

**Set-up:**
- *Biological shielded hot cell under purified Ar atmosphere (<10 ppm of $H_2O$ and $O_2$)*
- *Cathodes: Al plates 0.3 × 0.1 cm, rods ∅0.3 cm dipped 1.1 – 1.5 cm*
- *Anode: METAPHIX-1 fuel pieces (3.176 g) in a stainless steel basket*
- *Reference electrode: U metal deposited on W wire ($U/U^{3+}$ ref.)*

# Experiment description




**Principle:** *Group-selective deposition of all actinides on solid Al as An-Al alloys, anodic oxidation of the fuel controlled to avoid co-dissolution of Zr*

**Melt:** *LiCl-KCl with dissolved An (5.64 wt.%) and Ln (0.22 wt.%) from previous experiments*

**Analyses:** *Deposits cut, observed by optical microscopy, analysed by ICP-MS*

*Salt samples analysed by ICP-MS*

**Fuel:** ***METAPHIX-1*** *with initial composition U67-Pu19-Zr10-MA2-RE2 (wt.%, MA = Np, Am, Cm, RE = Nd, Ce, Gd, Y) and burn-up 2.5 at.% (PHENIX reactor)*

The **details of the irradiation and the fuel characterisation** before and after irradiation:

- Ohta, H. et al., "*Development of Fast Reactor Metal Fuels Containing Minor Actinides*", Journal of Nuclear Science and Technology **48**(4) (2011) p. 654-661
- Ohta, H. et al., "*Low-Burnup Irradiation Behavior of Fast Reactor Metal Fuels Containing Minor Actinides*", Nuclear Technology **165**(1) (2009) p. 96-110

# Galvanostatic runs

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**Approach:** *To deposit maximum possible amount of An in a form of An-Al alloys without formation of An metals at different current densities (except runs 1 and 7)*

| Run | Current | Current density | Norm. curr. dens. | Charge | Exp. deposit | Loading |
|---|---|---|---|---|---|---|
| | (mA) | ($mA/cm^2$) | ($mA/cm^2$/wt.% An) | (C) | (mg) | (% / $UAl_3$) |
| 1 | 50 | 40.7 | 6.6 | 43 / 459 * | 35.2 / 379 * | 10.0 / 106.1 * |
| 2 | 28 | 30.8 | 5.0 | 115 | 95.0 | 36.0 |
| 3 | 18 | 16.8 | 2.7 | 335 | 276.9 | 89.0 |
| 4 | 23 | 23.2 | 3.8 | 263 | 217.0 | 76.0 |
| 5 | 28 | 28.3 | 4.6 | 250 | 165.4 | 58.0 |
| 6 | 22 - 20 | 18.3 - 16.6 | 3.0 - 2.7 | 464 | 383.1 | 56.9 |
| 7 | 12 | 10.8 | 1.8 | 637 | 526.0 | 85.2 |

* *In run 1, the numbers X / Y are values before reaching the U metal deposition potential (X) and a sum of the complete run (Y).*

# Galvanostatic runs

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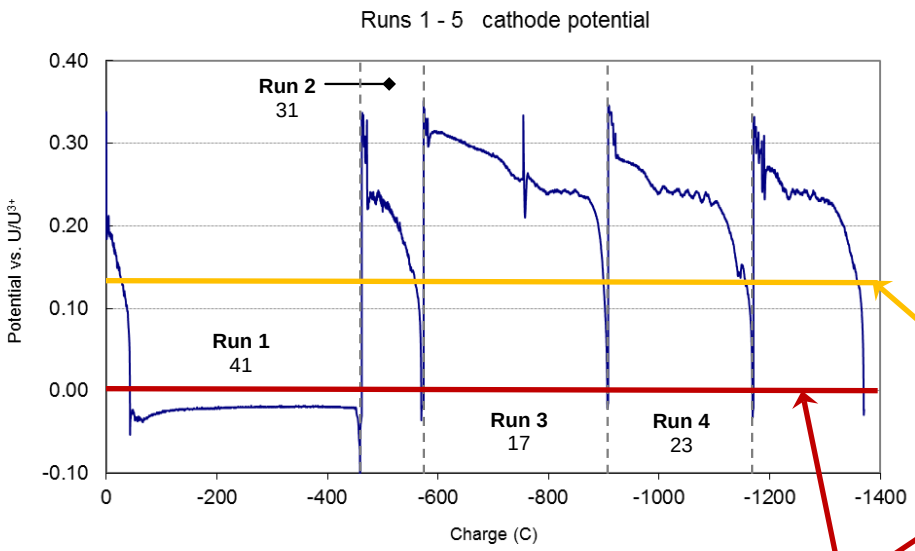
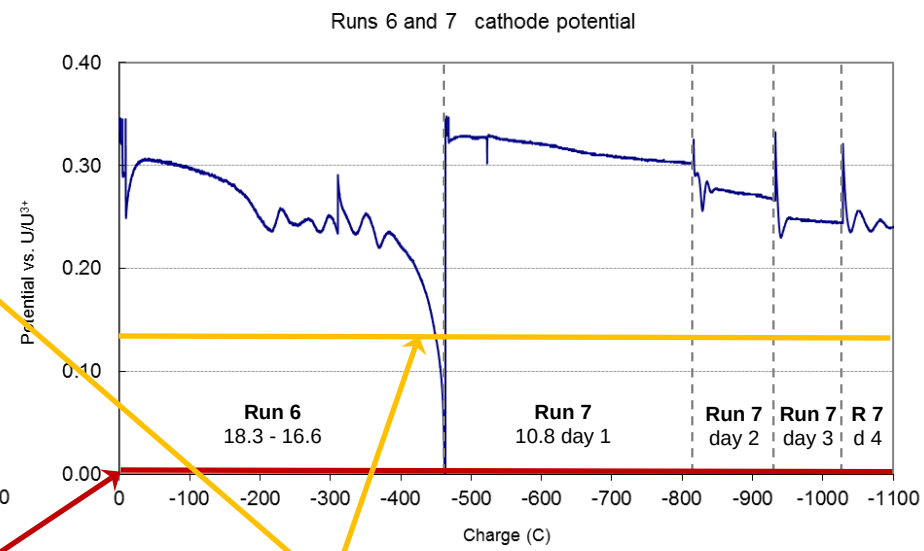
## Development of cathodic potentials during runs 1-5 (Al plates) and runs 6-7 (Al rods)




*Start potential of U metal deposition* *Start potential of Ln deposition as Ln-Al alloys*

Run 1: *U metal deposition allowed – U reacted forming U-Al alloys up to saturation*

Run 7: *Run had to be stopped to prevent Zr co-dissolution (anodic cut-off reached)*

**Outcome:** *separation factors (selectivity demonstration), characterisation of the deposits*

# Galvanostatic runs

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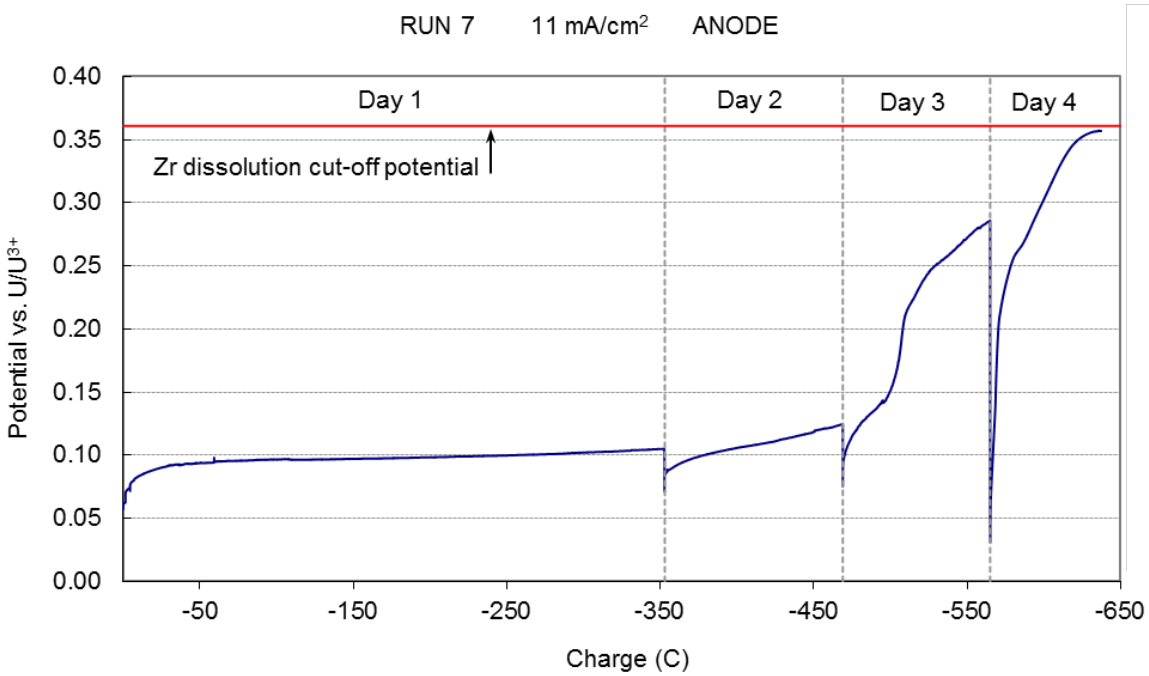
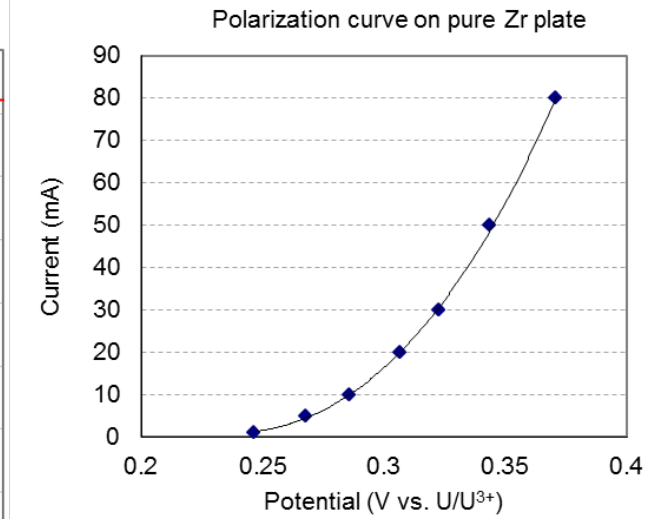
## Development of anodic potential during run 7



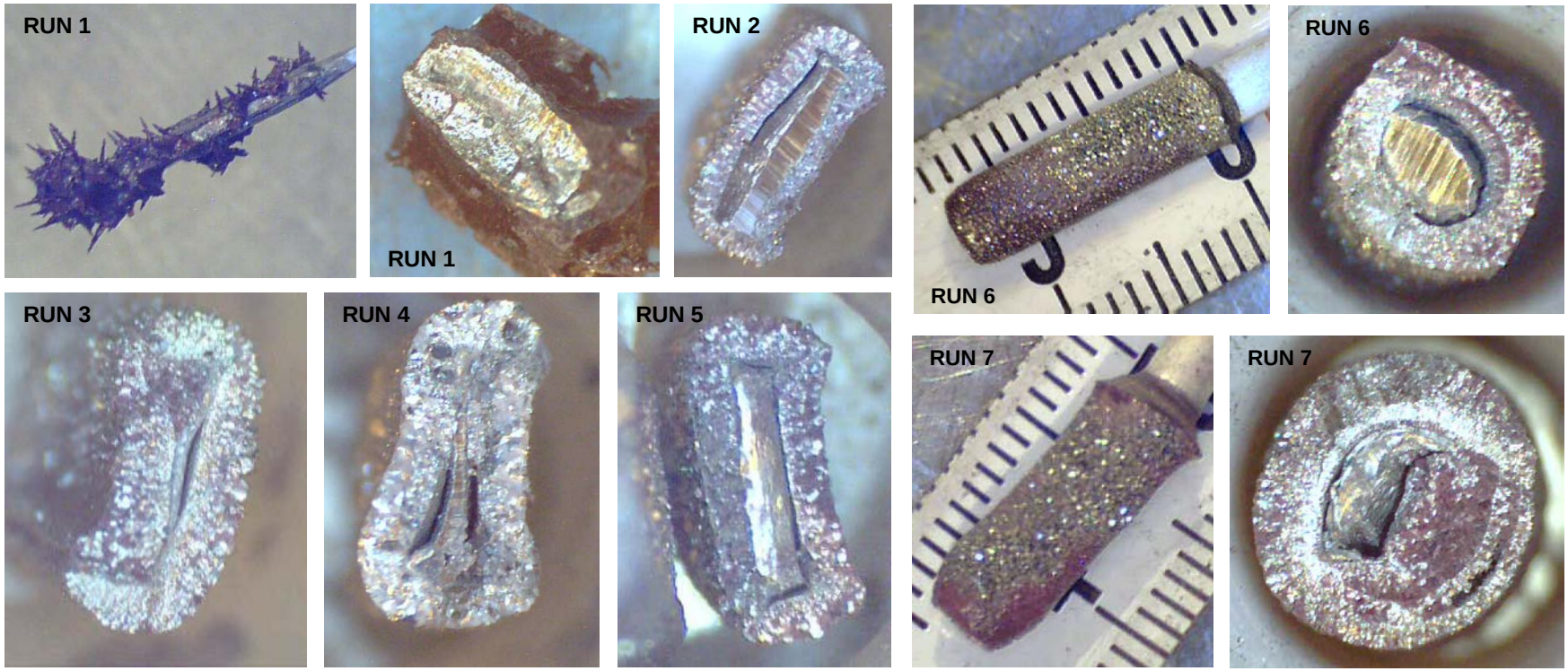




**Zr dissolution cut-off:** *Determined from polarisation curve measured on pure Zr plate in the same melt as used for the experiment*

*About **72% of An dissolved from the fuel without co-dissolution of Zr***
*(based on mass balance calculation, no ICP-MS of the anodic residue available)*

# Galvanostatic runs

**Deposits:** *Uniform, dense and well adhered surface alloy deposits*




Optical microscopy photographs taken after the runs without washing of the electrodes

# Potentiostatic runs

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**Approach:** *To deposit different amounts of alloys (different times of electrorefining)*
*The same constant potential used for all runs*
*Anode: U dendrites from previous experiments (no more fuel available)*

| Run | Potential | Time | Charge | Exp. deposit | Alloy layer thickness | Loading |
|---|---|---|---|---|---|---|
| | (V vs. $U/U^{3+}$) | (s) | (C) | (mg) | (mm) | (%/$UAl_3$) |
| 8 | + 0.11 V (= -1.26 V vs. $Ag/Ag^{+}$) | 5676 | 179.2 | 0.1480 | 0.45 | 56.5 |
| 9 | | 2914 | 126.8 | 0.1047 | 0.36 | 40.0 |
| 10 | | 8500 | 250.7 | 0.2070 | 0.58 | 79.0 |
| 11 | | 1500 | 62.7 | 0.0518 | 0.21 | 19.8 |

**Outcome:** *Kinetic properties of An in solid Al*

# Potentiostatic runs

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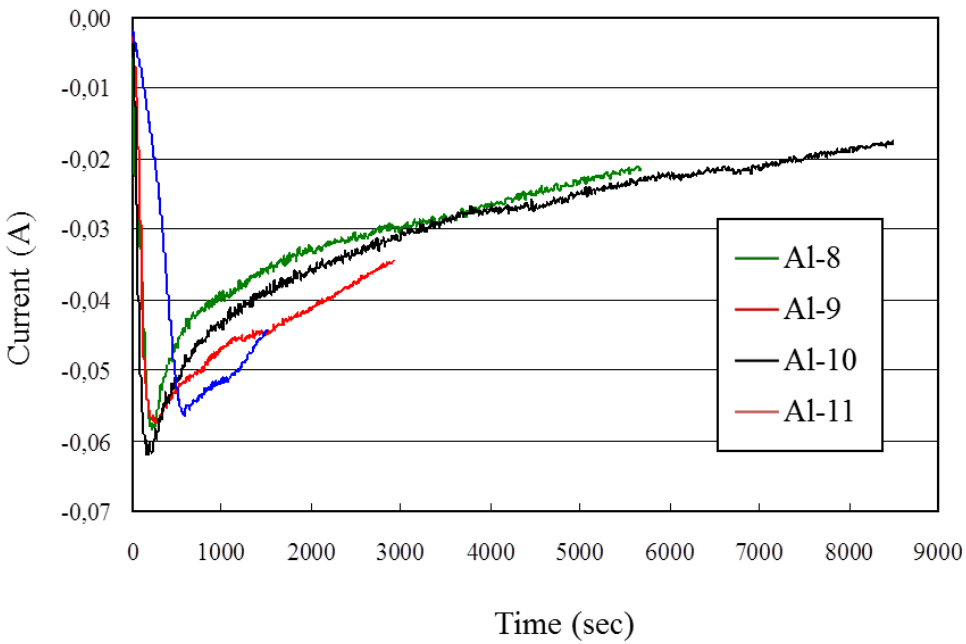
## Development of current during runs 8-11 …



**Decrease of current with time**
*increase of the alloy layer thickness*
*⇒ more difficult alloy formation*

**… and optical microscopy photographs of the cross-sections of the deposits** (without washing)

# Analyse of the deposits

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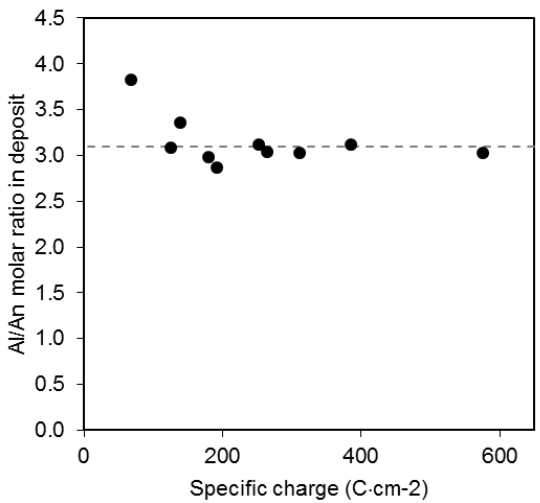
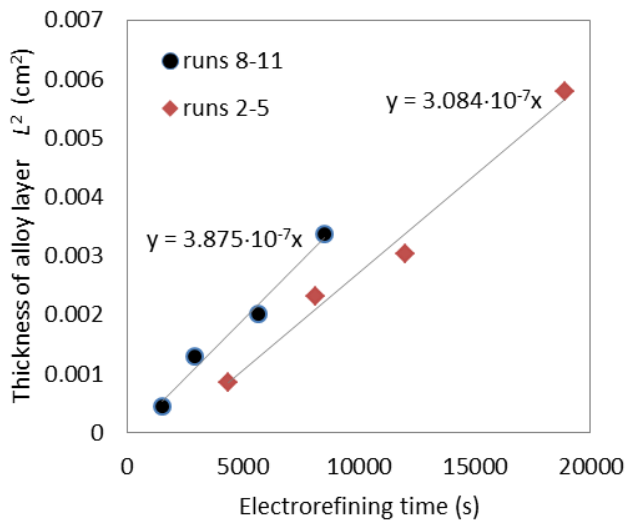
## Alloy formation kinetic properties

*Dependency of the achieved final alloy layer thickness L on current density – linear*

*Dependency of $L^2$ on time of electrodeposition – linear ⇒ rate determining step of the alloy layer formation is diffusion in the alloy layer ⇒ alloy growth according to* ***parabolic law***




$$L^2 = K_p \cdot t$$

***Molar ratio of Al to An in the deposits*** *from runs 2-10 plotted against the specific charge*

**Parabolic law constant:**

*Potentiostatic runs* $K_p = 3.9 \cdot 10^{-7}\ cm^2 \cdot s^{-1}$

*Galvanostatic runs* $K_p = 3.1 \cdot 10^{-7}\ cm^2 \cdot s^{-1}$

# Analyse of the deposits

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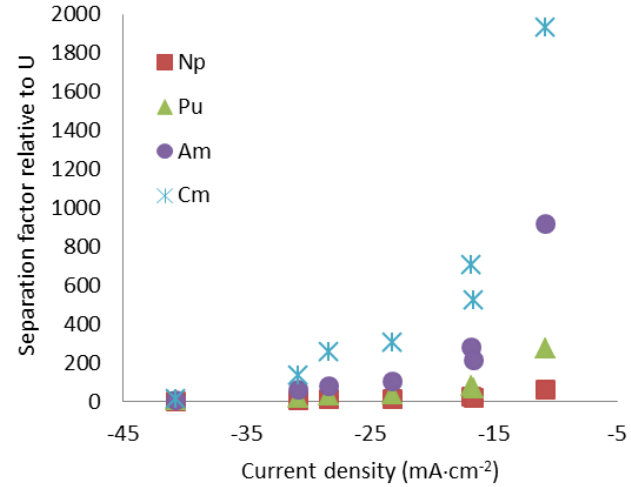
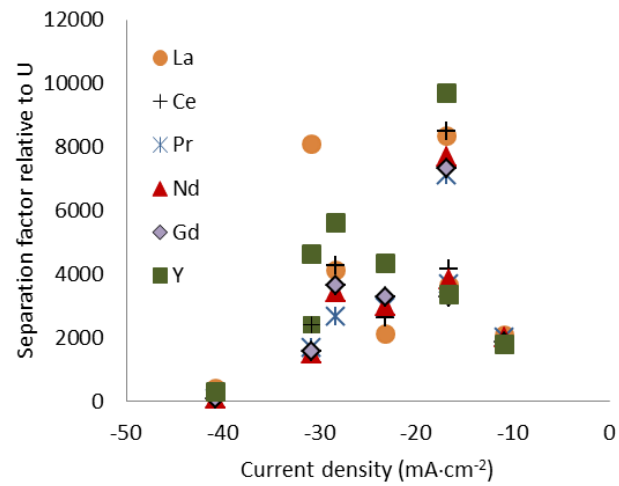
## Separation factors / deposit composition

$SF_M = (X_{M\ in\ salt} / X_{M\ in\ Al}) / (X_{U\ in\ salt} / X_{U\ in\ Al})$ – *relative to U*

| run | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| *j* (mA·cm$^{-2}$) | -31 | -17 | -23 | -28 | -18 | -11 |
| U | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Np | 7.43 | 23.8 | 12.9 | 10.4 | 19.1 | 62.4 |
| Pu | 20.3 | 78.8 | 39.6 | 31.8 | 65.9 | 274 |
| Am | 58.2 | 277 | 105 | 82 | 211 | 916 |
| Cm | 132 | 703 | 303 | 254 | 521 | 1930 |
| La | 8080 | 8347 | 2100 | 4111 | 3646 | 2078 |
| Ce | 2407 | 8507 | 2642 | 4276 | 4156 | 2001 |
| Pr | 1665 | 7098 | 2963 | 2669 | 3672 | 2005 |
| Nd | 1483 | 7692 | 2982 | 3432 | 3839 | 2013 |
| Pm | 4438 | 7927 | 3193 | 4888 | 3311 | 2063 |
| Sm | 5358 | 10402 | 3201 | 7371 | 3316 | 1857 |
| Eu | 8529 | 10849 | 3448 | 7449 | 3072 | 1520 |
| Gd | 1574 | 7309 | 3283 | 3644 | 3289 | 1864 |
| Tb | 1940 | 7059 | 3431 | 3328 | 3043 | 1736 |
| Dy | 1764 | 8419 | 3366 | 3499 | 3347 | 2447 |
| Y | 4618 | 9684 | 4352 | 5612 | 3365 | 1776 |



# Analyse of the deposits

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## Separation factors / deposit composition

| run | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| U | 72.13 | 92.92 | 98.05 | 96.16 | 95.36 | 97.78 | 99.39 |
| Np | 0.62 | 0.36 | 0.13 | 0.23 | 0.28 | 0.15 | 0.06 |
| Pu | 26.97 | 6.70 | 1.82 | 3.60 | 4.34 | 2.05 | 0.55 |
| Am | 0.14 | 0.02 | 0.00 | 0.01 | 0.01 | 0.01 | 0.00 |
| Cm | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| sum An | **99.89** | **99.99** | **100.00** | **100.00** | **100.00** | **100.00** | **99.99** |
| sum Ln | 0.11 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |

*Relative content of An and Ln in the deposits from galvanostatic runs*

**Comparison with the previous experiments with un-irradiated METAPHIX-1:**
*Even better selectivity in the present experiments, but lanthanides content in the melt is significantly lower (not possible to increase it – salt needed for future experiments)*

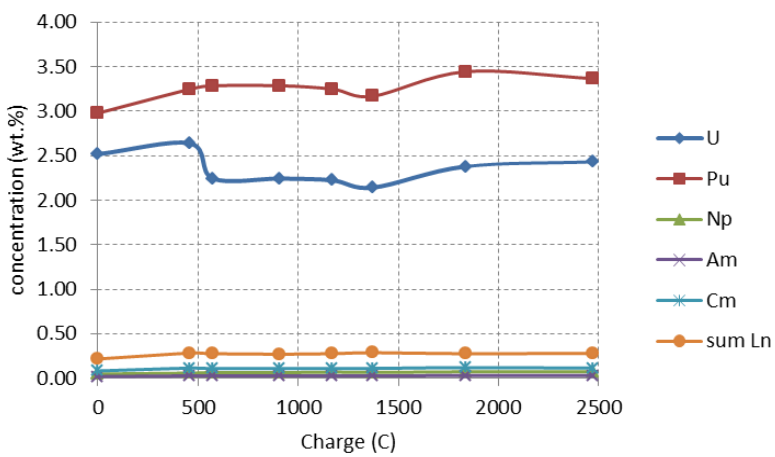
# Analyse of the runs

**Current efficiency** - *Comparison of the passed charge with a charge theoretically needed to deposit the molar amounts of elements analysed in the deposit*

$$R = \sum \left( \frac{m}{M} Fz \right) / Q_{passed}$$

*m* = mass of element as analysed by ICP-MS in the deposit [g]
*M* = molar mass of the element
*F* = Faradays constant (= 96485 $C \cdot mol^{-1}$)
*Q* = charge passed in each run [C]

| Run | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
| Current density / potential | -31 | -17 | -23 | -28 | -17 | -1.26 V vs. Ag/AgCl | | | |
| Current efficiency (%) | **83.9** | **95.5** | **86.1** | **89.6** | **94.1** | **97.2** | **85.0** | **92.4** | **91.5** |




| | U | Np | Pu | Am | Cm | La |
|---|---|---|---|---|---|---|
| $c_i$ | 2.52 | 0.05 | 2.98 | 0.02 | 0.08 | 0.22 |
| $c_f$ | 2.43 | 0.07 | 3.36 | 0.03 | 0.11 | 0.28 |

*Initial ($c_i$) and final ($c_f$) concentration of An and Ln in the melt during the experiment*

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## Summary

- Efficient separation of actinides over lanthanides from irradiated metallic fuel by electrorefining using solid Al electrode in a lab scale demonstrated
  - *relative content of actinides in the deposits > 99.9 % for all current densities*
  - *separation factors of lanthanides in the order of $10^3$-$10^4$ relative to U*
  - *uniform, dense and well adhered deposits composed of $AnAl_3$ alloys*
- Additional information from the experiment
  - *Rate determining step of the An-Al alloy growth is intermetallic diffusion of An and Al*
  - *Parabolic law constant evaluated from both potentiostatic and galvanostatic runs*
  - *possible problems with scale-up due to thin maximum layers of the alloys at studied current densities*

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