European Commission - Joint Research Centre

Pyrochemical Research on Molten Salts
Electrochemistry of Actinides
Basic Studies / Separation Methods

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Part 1

MOLTEN SALT CENTRE OF EXCELLENCE IN ITU

• Present pyrochemical research in ITU
• Pyrochemical Advanced Nuclear Fuel Cycle
• Basic studies
• **New developed techniques**
**ITU mission:** … to protect the European citizen against risks associated with the handling and storage of highly radioactive elements…

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

**Nuclear Chemistry Hot Cell Technology**
- Hot Cells for irradiated material
- Lead shielded cells
- Glove boxes under pure argon or nitrogen
Pyrochemical research in ITU

• **Basic research on An electrochemical properties in molten salts**
  - electrochemical behaviour and thermodynamic data of pure An and An-Al intermetallic compounds in molten LiCl-KCl and LiF-CaF$_2$

• **Clean-up of nuclear fuels – recovery of all actinides**
  - un-irradiated material from the fuel production
  - irradiated target fuels (U-Pu-Am-Zr-Ln alloys with up to 5% An and Ln, MOX)

  ✨ Electrochemical techniques in molten chloride and fluoride salt media
  - **Electrorefining** and electrowinning in molten LiCl-KCl using solid Al cathodes
  - Direct electroreduction of oxide fuel in molten LiCl-Li$_2$O and LiF-CaF$_2$-Li$_2$O

  ✨ Recovery of actinides from An-Al alloys
  - chlorination route, separation of An from Al in form of chlorides

  ✨ Calcination and chlorination of HLLW from PUREX
  ✨ Molten salt-liquid metal reductive extraction process

  } bilateral cooperation with CRIEPI, Japan
Double glove-box with furnace and electrochemical set-up

- outer box: $N_2$
- inner box: purified Ar, $< 5$ ppm $O_2, H_2O$

Electrolyser inside the inner box

a) crucible and electrodes
b) water-cooled flange and a lift system

Scheme of an electrochemical cell in an alumina crucible

Working electrode

Mo counter electrode

Ag/AgCl (1 wt. % AgCl) reference electrode
Studied An: Th, U, Np, Pu, Am  Plans: Pa, Cm

Transient electrochemical methods are used to evaluate:
Reaction mechanisms – number of exchanged electrons
Electrochemical properties - apparent standard potentials, diffusion coefficients

Techniques: Cyclic voltammetry, Chronopotentiometry, Square-wave voltammetry,…

Examples of electrochemical characterisations of Np, U and Am in molten LiCl-KCl carried out on inert W working electrodes (Cyclic voltammetry, chronopotentiometry and square-wave voltammetry)
Studied actinides: U, Np, Pu, Am – determination of An-Al alloys deposition potentials

Summary of cyclic voltammograms measured in LiCl-KCl-AnCl₃ melts at 450°C on Al electrode

Reduction potentials of some actinides and lanthanides on different cathodic materials

Advantages of Al for recovery of actinides
- Enables selective An deposition (different activity coefficients of An and Ln in Al)
- Stable An-Al alloy formation prevents from further re-oxidation of An
- High capacity of Al to take-up An (lab-scale experiment: up to 2.3 g of An in 1 g of Al)
Recovery of Actinides from Spent Nuclear Fuel by Pyrochemical Methods

- **Metallic spent fuel:** An + FP
- **Nuclear reactor**
  - **Conversion to metals**
  - **Spent fuel**
  - **Electrorefining in molten LiCl-KCl on Al cathode**
    - **LiCl-KCl + AnCl\(_3\) + FPCI\(_x\)**
  - **Cathodes processing: Chlorination**
    - **An-Al alloy**
    - **Exhaustive electrolysis**
      - LiCl-KCl + FPCI\(_x\)
    - **An-Al alloy**
    - **Al recovery**

**An - actinides, FP - fission products, Al - aluminium**
**Electrorefining**

- **Selectivity & Efficiency**
  
  High efficient grouped separation of all actinides using Al cathode and un-irradiated METAPHIX fuel: $U_{61}Pu_{22}Zr_{10}Am_{3.5}Gd_{0.5}Y_{0.5}Ce_{0.5}$

- **Deposits characterization**
  
  Solid, compact deposits composed of An-Al alloys (mainly AnAl$_3$, AnAl$_4$)

- **Capacity of Al to take-up An:**
  
  Very high capacity of solid Al demonstrated: More than 2 g of An in 1 g Al

**Exhaustive electrolysis**

- Selective and efficient recovery of An from LiCl-KCl-AnCl$_3$-LnCl$_3$ melts up to 0.1 wt.% An (*under investigation*)

**Chlorination**

- High efficient chlorination of UAI$_3$ alloy by Cl$_2$ and HCl(g)

- Demonstration of the complete process with U-Pu-Al alloys prepared by electrorefining in LiCl-KCl
Basic studies: New equipment

Electrochemistry of An and An alloys in molten fluoride salts

- new glove box under pure Ar atmosphere + HF line
- preparation and purification of fluoride salts
Electrochemistry of An and An alloys in molten fluoride salts

- electrochemical studies of An in molten fluorides up to 1000°C (incl. Th, Pa)
- electrochemical separation of An from FP (MSR fuel cycle)

An Inconel electrolyser for electrochemistry in molten fluoride salts
Preparation of actinide fluorides and chlorides
- installation of 2 horizontal furnaces and reactors to produce pure An fluorides and chlorides
- Available gases : HF, NF₃, Cl₂, HCl, Ar/H₂
- Chlor/fluorination of oxides, metals and/or chlorides, reduction reactions

**Aims:**
- To investigate basic thermochemical properties of the pure compounds (melting point, thermal capacity, viscosity, density…)
- Preparation of large amounts of ThF₄, UF₄ and PuF₃ (up to 50 g) for studies on Molten Salt Reactor fuel chemistry
Basic studies: New equipment

Combined electrochemistry – spectrometry in molten salts

- Installation of new furnace
- Miniaturized set-up for electrochemistry in a cuvette suitable for spectroscopy
- Optical fibers from UV-VIS, RAMAN, TRLF
- Exploring the possibility of EXAFS, NMR
Molten salt competence centre

ACSEPT
Preparation of An and Ln halides as starting materials

ITU molten salt centre of excellence

Basic electrochemical studies of actinides and Ln in molten fluoride and chloride media

Development of pyrochemical separation methods of An based on electrochemical techniques in chlorides and fluorides

ACSEPT
CNRS Toulouse
CEA Marcoule

Demonstration of pyrochemical separation methods for irradiated materials

EVOL
CNRS Toulouse
CNRS Paris

Molten salt / liquid metal extraction studies in fluoride medium. Pa studies

CNRS Orleans

Preparation and purification of salts for molten salt reactor studies

Thermochemical studies of pure An halides

Thermochemistry of molten salts / phase diagrams / modeling

ACSEPT
CNRS Toulouse
CEA Marcoule
CEA Valduc

Spectrophotometry box with furnace for uv-vis, RAMAN and TRLF for chlorides and fluorides

ACSEPT
CNRS Toulouse
CNRS Paris

NMR high temperature probe for molten salts

CNRS Orleans
Part 2

ELECTROCHEMISTRY OF Th IN MOLTEN SALTS

• Th in LiCl-KCl (Laurent Cassayre, ITU)
• Th in LiF-CaF$_2$ (Pierre Chamelot, CNRS Toulouse)
• Th in LiF-NaF-KF and LiF-CaF$_2$ (Martin Straka, NRI Řež)
**Electrochemistry of Th in LiCl-KCl**

**Melt preparation**
- chemical oxidation of Th metal by BiCl₃ in molten LiCl-KCl
- 5 different Th conc. used: 0.20, 0.43, 0.74, 0.96, 1.46 wt.%

**Electrochemical measurements**
- cyclic voltammetry, chronopotentiometry, chronoamperometry, open-circuit potential

**Electrodes**
- WE: W wire, Ø 1 mm, dipped 10 mm to the melt
- CE: Mo wire, Ø 1 mm, shape of a spiral
- RE: Ag wire in LiCl-KCl-AgCl (1 wt.% AgCl) in a Pyrex glass tube

**Working temperatures**
- 693, 733, 773, 798 and 823 K

**Aims**
- Reduction and nucleation mechanism, diffusion coefficient, apparent standard potential, activity coefficient
Reduction mechanism – cyclic voltammetry

**One-step process**

\[ \text{Th(IV)} + 4e^- \rightarrow \text{Th(0)} \]

1 stable Th electro-active specie

**Irreversibility indication**

Dependency of \( E_c \) on \( \log v \) is not constant

**Nucleation effect**

Progressive nucleation was detected
Electrochemistry of Th in LiCl-KCl

Diffusion coefficient - chronopotentiometry

\[ \log D_{\text{Th}} = -2.126 - \frac{1719}{T} \]

At 723K: \( D_{\text{Th}} = 3.15 \pm 0.15 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \)

Diffusion coefficient dependence on temperature follows the Arrhenius law

Calculated from CP using Sand equation

Verification: \( i \) is linear vs. \( \tau^{-1/2} \)
Apparent standard potential – open circuit potentiometry

Reference standard state: hypothetical supercooled liquid

![Graph showing equilibrium potentials for different concentrations and apparent standard potential](image)

Equilibrium potentials for different concentrations

**Activity coefficients**

\[
E_{\text{Th(IV)/Th(0)}}^{0*} = E_{\text{Th(IV)/Th(0)}}^0 + (2.303RT/nF) \cdot \log \gamma_{\text{Th(IV)}}
\]

Measured apparent standard potential \(E_{\text{Th(IV)/Th(0)}}^{0*}\) calculated from tabulated Gibbs energy

Standard potential \(E_{\text{Th(IV)/Th(0)}}^0\) calculated from tabulated Gibbs energy

Activity coefficient \(\gamma_{\text{Th(IV)}}\)

\[E_{\text{Th(IV)/Th(0)}}^{0*}(V \text{ versus } \text{Cl}_2/\text{Cl}^-) = -2.98 + 5.54 \times 10^{-4} \ T \text{ (K)}\]

\[\gamma_{\text{ThCl}_4} \text{ (723 K)} = 4.6 \times 10^{-4}\]
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- Electrochemical behaviour of ThF$_4$ in molten fluorides
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- Th in LiF-NaF-KF and LiF-CaF$_2$ (Martin Straka, NRI Řež)
Main research areas involving molten salt:

- Molten Salt Reactor concept (MSR): Thorium/Uranium cycle
- Basic electrochemical and TD properties of An/Ln in molten fluoride salts (fuel / coolant)
- Reprocessing of molten salts based liquid fuel

Electrochemistry of Th in molten LiF-CaF$_2$

Better knowledge on the chemistry and electrochemistry of Th in molten fluorides

⇒ Th behaviour in comparison with lanthanides
⇒ Efficiency of different extraction processes from fission products (e.g. lanthanides)
  • electrochemical process with use of:
    → inert cathode
    → reactive cathodes (nickel, bismuth)
  • precipitation process by strong oxide donor additions
**Experimental conditions**

- Molten media: LiF-CaF$_2$ eutectic (79.5-20.5 molar %) (FP : 762°C)
- Solutes: ThF$_4$ (CERAC 99.9%)
  CaO (MERCK 99.9%)
- Temperature range: 800 - 850°C
- Inert atmosphere : Argon (O$_2$ < 1ppm)
- Working electrodes: Tantalum
  Molybdenum
  Nickel
- Comparison electrode: Pt/PtO$_x$/O$^2-$
- Counter electrode: Glassy carbon

**Scheme of the cell:**
1: glassy carbon crucible, 2 and 3: graphite liner,
4: ss, 5: electrodes
Electrochemistry of Th in LiF-CaF$_2$

Reduction mechanism – cyclic voltammetry, square wave voltammetry

Cyclic voltammogram (100 mV/s$^{-1}$)
Substrate: Mo, $\theta : 840^\circ$C ,
[ThF$_4$] = 0.052 mol.kg$^{-1}$

Square wave voltammogram (25 Hz)
Substrate: Ta, $\theta : 840^\circ$C ,
[ThF$_4$] = 0.052 mol.kg$^{-1}$

$E = 0.49$ V / (LiF/Li)

ThF$_4$ + 4 e$^{-} = $ Th + 4F$^{-}$
Electrochemistry of Th in LiF-CaF$_2$

Nature of the reduction product / Limiting process - diffusion coefficient

Inverse chronopotentiogram
Substrate Ta, $\theta = 840^\circ$C, $[\text{ThF}_4] = 0.052$ mol.kg$^{-1}$

$\tau_{\text{ox}} / \tau_{\text{red}} = 1$

Formation of solid Th phase

Influence of the potential sweep
Substrate Mo, $\theta = 840^\circ$C, $[\text{ThF}_4] = 0.052$ mol.kg$^{-1}$

Limiting process: diffusion
$D_{\text{Th(IV)}} = 9.5 \pm 0.5 \times 10^{-6}$ cm$^2$.s$^{-1}$ at 840$^\circ$C
Electrochemistry of Th in LiF-CaF₂

Influence of oxide additions on Th precipitation

Square wave voltammogram (25 Hz)
Substrate: Mo, θ: 840°C, [ThF₄] = 0.068 mol.kg⁻¹
[CaO]: 0.079 mol.kg⁻¹

A: ThF₄ + 4e⁻ = Th + 4 F⁻
B: ThOF₂ + 2e⁻ = ThO + 2 F⁻

Presence of soluble thorium oxyfluoride (ThOF₂)

Th extracted from the melt by precipitation as ThO₂
Thorium behaviour on reactive electrodes

Cyclic voltammograms on Mo and Ni
\[ \theta : 840^\circ C, 100 \text{ mV/s}^{-1}, [\text{ThF}_4] = 0.069 \text{ mol.kg}^{-1} \]

Solid Ni-Th alloys formation
Depolarisation: \(~ 0.5 \text{ V}\)

Liquid Bi-Th alloys formation
Depolarisation: \(\text{ThF}_4 \Delta E = 0.45 \text{ V}, \text{LiF} \Delta E = 0.95 \text{ V}\)

Cyclic voltammogram on Bi
\[ \theta : 840^\circ C, 5 \text{ mV/s}^{-1}, [\text{ThF}_4] = 0.13 \text{ mol.kg}^{-1} \]

EDX Analysis of Bi pool after electrolysis (12h) in LiF-CaF\(_2\)
**Electrochemical behavior of Th in molten fluorides**

- Reduction into metal in one step (4 e⁻ exchanged)
- Limiting process: diffusion
- Formation of alloys with Ni, Bi – high depolarisation
- ThF₄ sensitive to oxide ions toward precipitation
  presence of oxyfluoride intermediate compound: soluble ThOF₂

**Apparent Potential scales in LiF-CaF₂ (840°C)**

- Inert cathode (Mo, Ta)
- Ni reactive cathode
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- Electrochemistry of ThF$_4$ in molten fluoride salts
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NRI – Nuclear Research Institute

Nuclear Research Institute Řež

- Nuclear safety, reliability and feasibility analyses and diagnosis
- NPP lifetime management
- Reactor R&D and services (LVR-15 and LR-0 reactors)
- GenIV Nuclear Fuel Cycle R&D and waste treatment
- Radiopharmaceuticals production and R&D

Department of Fluorine Chemistry

- Pyrochemical reprocessing for advanced fuel cycles
  - MSR online reprocessing
- Fluoride volatility method
  - Technological line „FERDA“
- Electrochemical separation methods
  - $\text{BeF}_2$-based and $\text{BeF}_2$-free systems
Electrochemistry at NRI Řež, plc

- 2 \( N_2 \) glove boxes with integrated electrolyser
- work up to 650°C and 950°C
- use of GC crucibles (counter electrode)

- elements of interest: U, Th, Lns

- \( Ni / INCONEL \) 625 body
- \( Ar \) atmosphere
- gas-tight electrode shift

- flange and electrode holders
Electrochemistry of Th in LiF-CaF$_2$

Th in LiF-NaF-KF and LiF-CaF$_2$ – reduction mechanism

CV of FLiNaK-ThF$_4$
W electrode, 550°C, sc. rate 100 mV/s

CV of LiF-CaF$_2$-ThF$_4$
Mo electrode, 900°C, sc. rate 25-250 mV/s

Insufficient electrochemical window, Th$^{4+}$ reduction prior the melt decomposition

Linear relationship of peak current with scan rate, slight peak potential shift ⇒ indication of irreversibility
Electrochemistry of Th in LiF-CaF\(_2\) – diffusion coefficient / behaviour on Ni reactive electrode

One-step mechanism of Th\(^{4+}\) reduction
Diffusion coefficient (Sand equation):

\[
\log D = -10435/T - 1.1406
\]

\(900^\circ C - 950^\circ C\)

SEM-EDX analysis of Ni electrode after electrolysis of LiF-CaF\(_2\)-ThF\(_4\) melt (30 minutes / \(j = 30 \text{ A} \cdot \text{m}^{-2}\)):

Th-Ni alloys observed
Summary

• Research on molten salt in Europe
  - Basic research of An and Ln in molten chloride and fluoride salts
    - Electrochemistry / spectroscopy / thermodynamic studies
    - Possibility to work with important amounts of An incl. minor actinides
  - An/Ln separation experiments
    - mainly in chlorides, in fluorides under development
  - MSR – different concept studies
    - Th-U breeder / TRU burner
    - fuel based on LiF-ThF₄, LiF-NaF-BeF₂, LiF-BeF₂
  - Cooperation within EC-EURATOM Framework Programmes
    - e.g., ACSEPT, EVOL
Conceptual flow-sheet of MSR on-line fuel reprocessing

MSR Th-breeder concepts:

- TRU burner using Th support in order to breed 233U
- Self sustainable Th breeder system or Th breeder with the breeding factor > 1

Flow-sheet

- Melt based on LiF-BeF$_2$
- Combination of extraction and electroseparation methods with changing of carrier melt
- Pa chemistry is crucial

Back-end proposed on the base of results from 5$^{th}$ EC-EURATOM FWP, project PYROREP