The REFINE Research Consortium

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The University of Edinburgh

Leeds 3rd September 2013

REFINE Consortium

The University of Edinburgh

Manchester 1824 The University of Manchester

University of Cambridge

The University of Nottingham

UCL

National Nuclear Laboratory

REFINE Consortium

- The REFINE consortium
  - led by the University of Edinburgh
  - includes the Universities of Cambridge, Manchester, Nottingham and University College London, in partnership with UK National Nuclear Laboratory.
- a UK multidisciplinary programme
  - Chemistry, Engineering, Materials, Earth Sciences…..
- aimed at delivering essential pyrochemical
  - platform technologies
  - underpinning process development
  - training
- for safe, dependable and sustainable UK nuclear fuel reprocessing

REFINE programme

- REFINE is developing ……
  - specific sustainable spent fuel reprocessing technologies to produce a viable molten salts based, spent fuel treatment facility
    - minimizing waste
    - Legacy fuel reprocessing
    - for new Gen III+ and Gen IV reactor systems
    - delivering safe, reliable, economic and sustainable nuclear energy on the scale required in both the short and long term.

  - The programme is focussed on establishing the fundamental research, understanding and essential systems required.

REFINE Research Challenges

- Molten salt based technology synonymous with pyrochemical reprocessing worldwide
  - includes electrorefining (ANL, US)
  - electrowinning (Russia)
  - liquid/liquid extraction (France)
  - fluoride salt fuel (Czech Republic))
  - molten salt reactors
- Has the potential to be
  - strongly proliferation resistant
  - compact
  - compatible with a wide range of fuel types
    - high burn-up fuels and legacy fuels

REFINE Research Challenges

- molten salts have
  - a wide electrochemical window
  - can stabilize reactive species
  - can operate at temperatures where insulating oxide materials e.g. UO_2 become sufficiently conducting for processing
- BUT
  - their corrosive nature, particularly when containing highly reactive species at the required elevated temperatures offers real materials challenges for systems development.

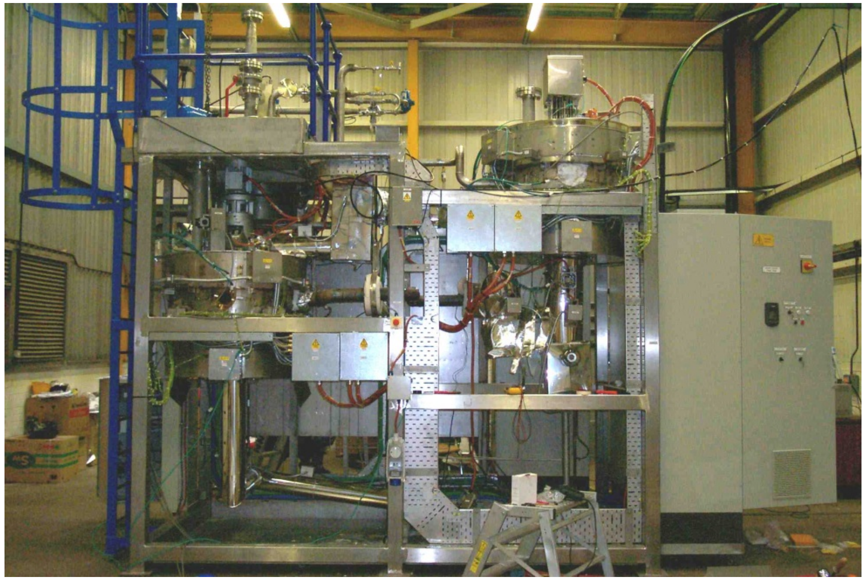
REFINE Academics

National Nuclear Laboratory

- Key Partner in REFINE
  - NNL contains a number of critical skills and facilities essential to support the nuclear industry in the UK
  - NNL has a key objective to help safeguard and develop nuclear expertise and multifunctional nuclear laboratory facilities
    - MSDR
    - Active experiments to benchmark surrogates

Molten Salts Dynamic Rig

- Designed, Tested and Commissioned by NNL Engineering Molten Salts Group
- Operating Temperature up to 500 °C
- 110 Kg Salt Inventory
- Argon Gas Atmosphere
- Range of Transfers Possible - Gas Lift, Fluidic, Mechanical Pump, Pressure, Gravity
- Pumping Rate > 4 m^3/hr
- Removable Sections for Testing In Line Components

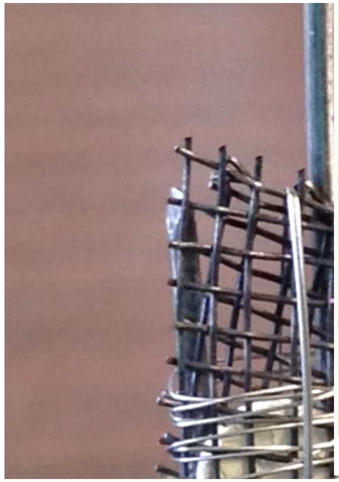


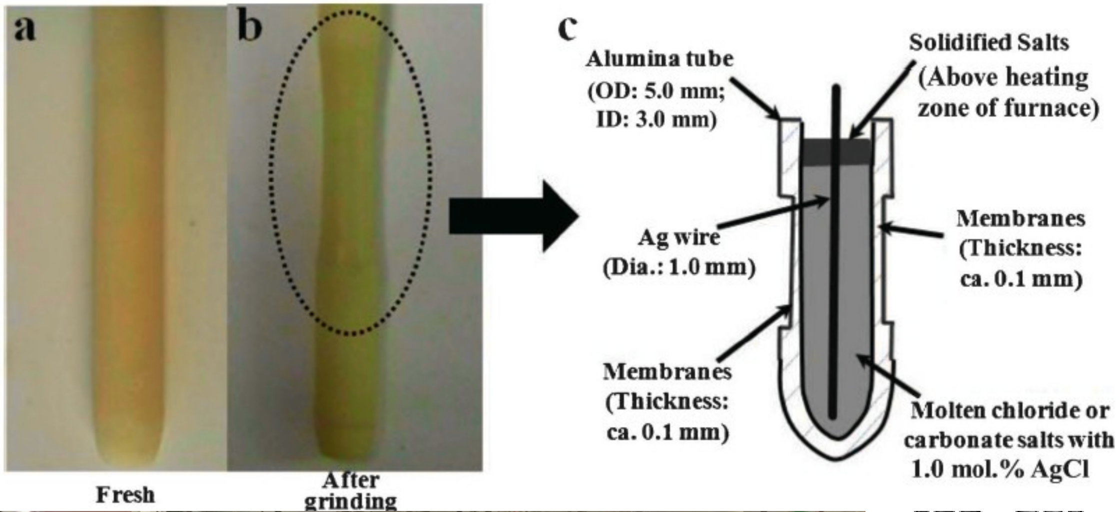
MSDR held in a quiescent state for several years. Under REFINE, it is being re-commissioned, characterised and used to underpin in-line analytical tools.

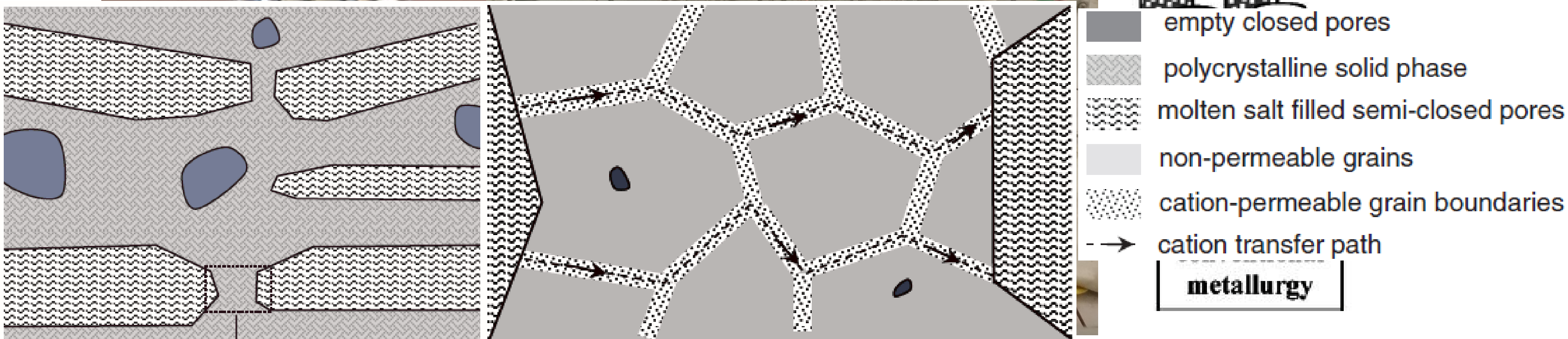
REFINE Technical Objectives

- Nearly 3 years into 4-year programme:
- 3 key themes, workpackages, *objectives*
- Direct Electrochemical Reduction (DR): *Understanding and controlling reduction in molten salts, forming solid state materials cleanly and efficiently, specifically electroactive materials for enhanced electrochemical separation in the electrorefiner*
- Electrorefining & Speciation (ES): *Specific solid state materials production by dissolution and deposition of selected species with controlled composition and morphology, specifically ensuring proliferation resistance. Dissolution of stable materials, specifically Gen IV fuels (ceramic, nitride and carbide fuels) and production and characterisation of the MS soluble species;*
- Analysis (AN): *Establishment of molten salt analysis techniques, specifically the in-line sensing technology required for PR systems with modelling to understand molten salt materials processes.*

Direct reduction







G. Chen, E. Gordo and D. Fray, *Metallurgical and Materials Transactions B*, **35**, 223 (2004).

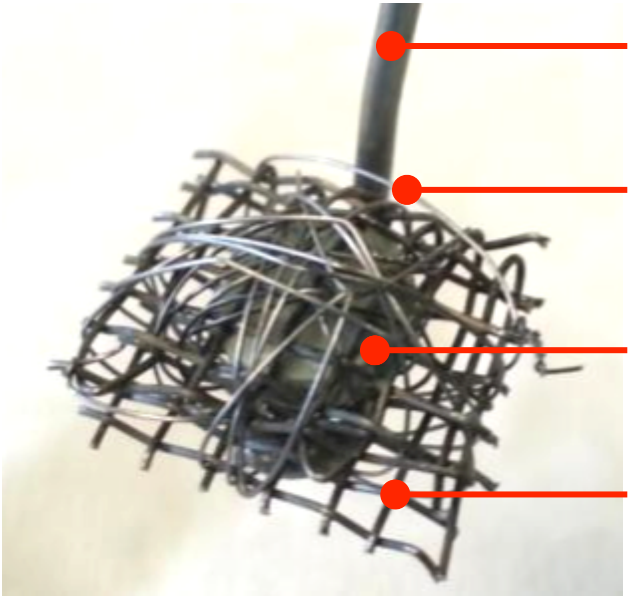
H. Wang, N. J. Siambun, L. Yu and G. Z. Chen, *Journal of The Electrochemical Society*, **159**, H740 (2012).

Direct reduction

Mixed oxide fuel surrogates

	Reaction	ΔG / kJ	V_d / V
★	$2NiO = 2Ni + O_2(g)$	284.434	0.737
	$4CeO_2 = 2Ce_2O_3 + O_2(g)$	457.639	1.186
	$PuO_2 = Pu(l) + O_2\ (g)$	851.940	2.207
★	CeO2 = Ce(l) + O2(g)	867.645	2.248
	ZrO2 = Zr + O2 (g)	896.103	2.322
	$UO_2 = U + O_2\ (g)$	899.168	2.330
	$2Ce_2O_3 = 4Ce(l) + 3O_2(g)$	1506.471	2.602
	$2CeClO = 2Ce(l) + Cl_2(g) + O_2(g)$	1527.341	2.638
	$2CaO = 2Ca + O_2(g)$	1045.427	2.709
	$CaCl_2 = Ca + Cl_2(g)$	635.339	3.292

Direct reduction



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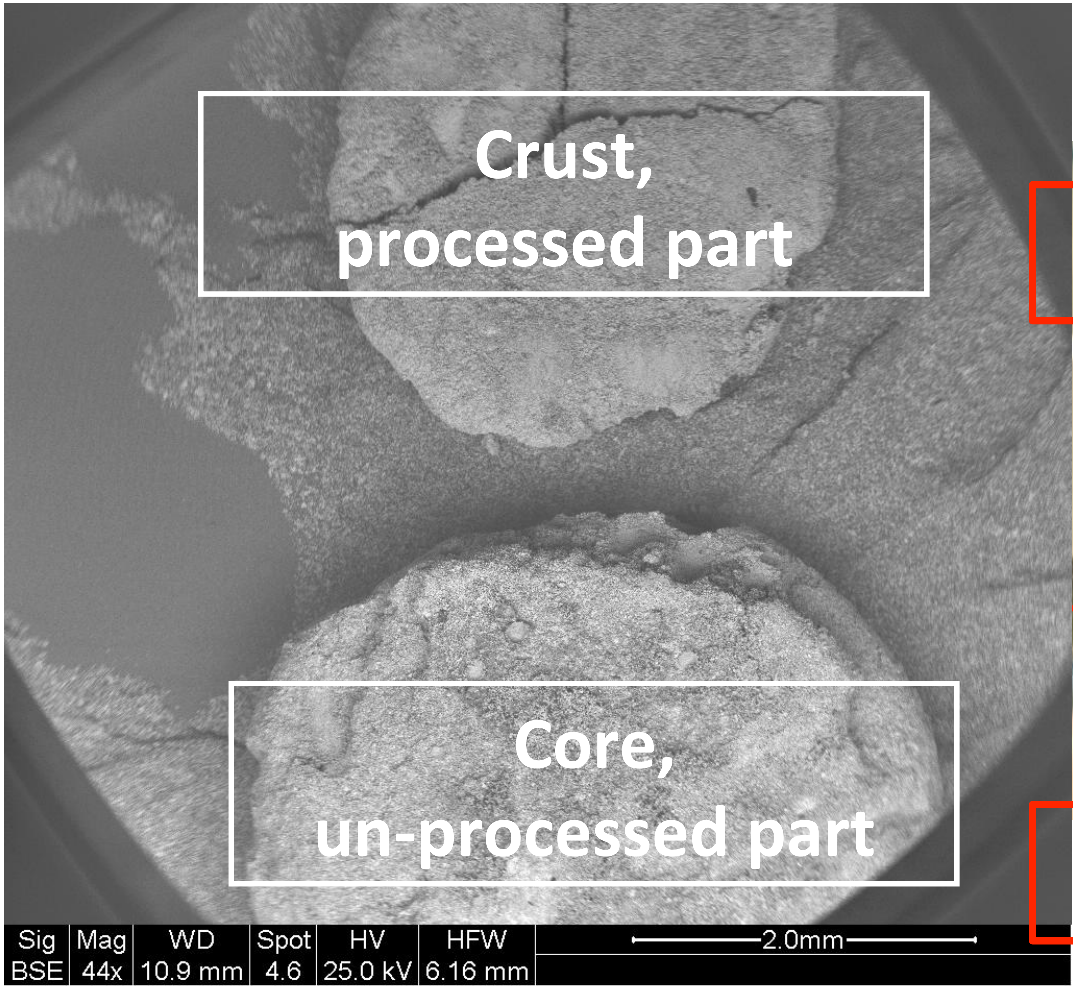
Before reduction

After reduction

Direct reduction

- **WP1: Reduction of mixed oxides**



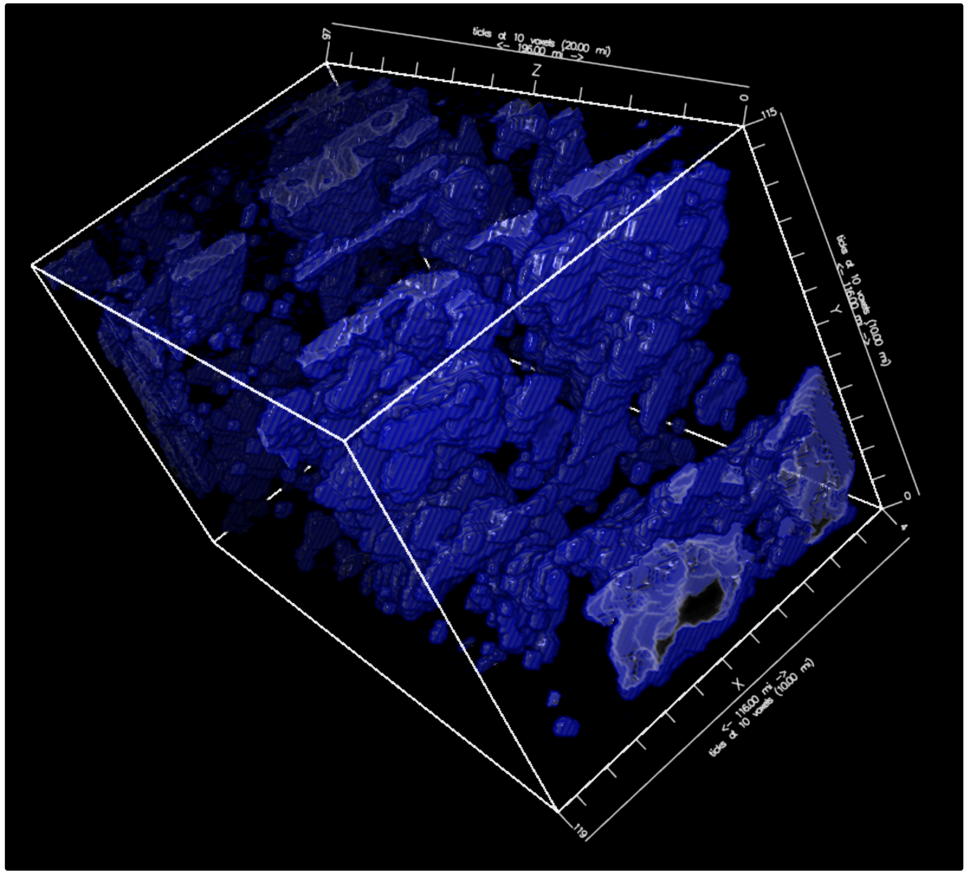
Element	*Wt%*	*At%*
OK	20.80	65.87
ClK	00.34	00.49
CaK	00.36	00.46
CeL	68.93	24.93
NiK	09.57	08.26
Matrix	Correction	ZAF

Crust,
processed

Element	*Wt%*	*At%*
OK	17.49	51.23
ClK	02.04	02.69
CaK	02.19	02.56
CeL	40.88	13.67
NiK	37.40	29.85
Matrix	Correction	ZAF

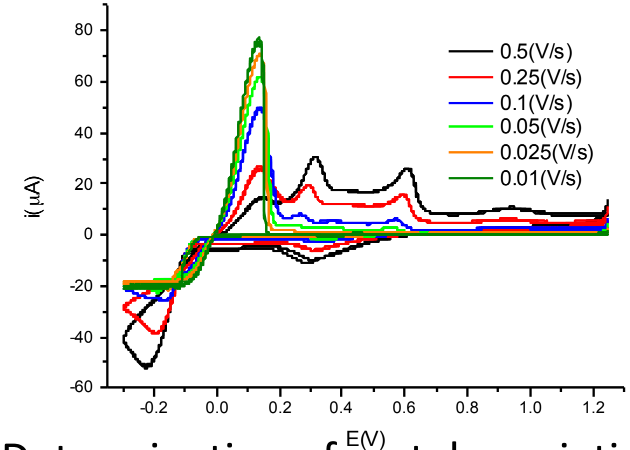
DR Highlights

- FIB Tomography: Thin film studies of progression of oxide reduction



ER Highlights

Liquid and Solid Cathode: fundamental electrorefining studies and characteristics



Powder XRD for quenched melt analyses

Some metal carbides can be converted to the oxide in molten salts (e.g. Cr_3C_2)

- Determination of metal speciation of carbide material (cf. UC fuel) in chloride melts to gain understanding of the behaviour of the metal:
  - Characterization of inert matrix fuel candidates and coated fuel surrogate material.
  - Elucidation of the fate of carbon in chloride melts from the chemical and anodic dissolution of carbide material.
  - Development of spectroscopic and analytical techniques for the identification of species formed during the chemical and anodic dissolution of UC in chloride melts.

AN highlights

The ability to monitor the salt composition in real time is of paramount importance for process control.

Current techniques

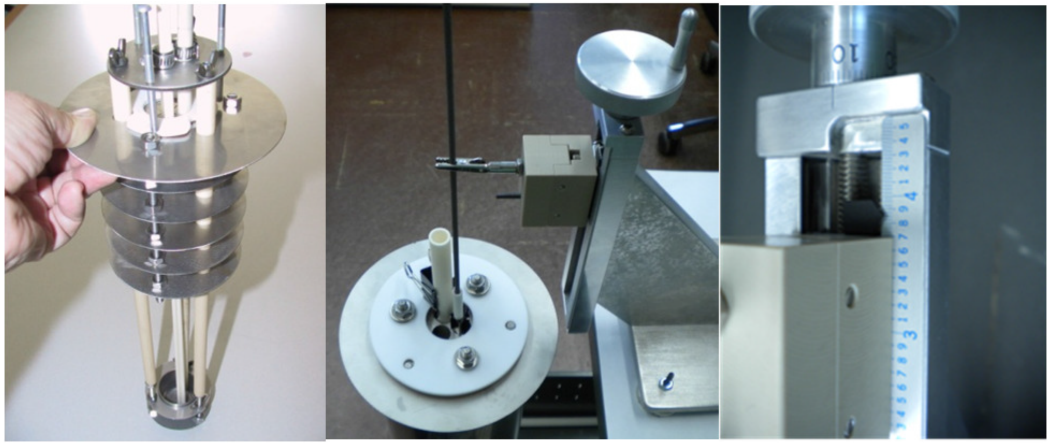
Ex situ techniques

- HPLC analysis of recovered salt

In situ techniques

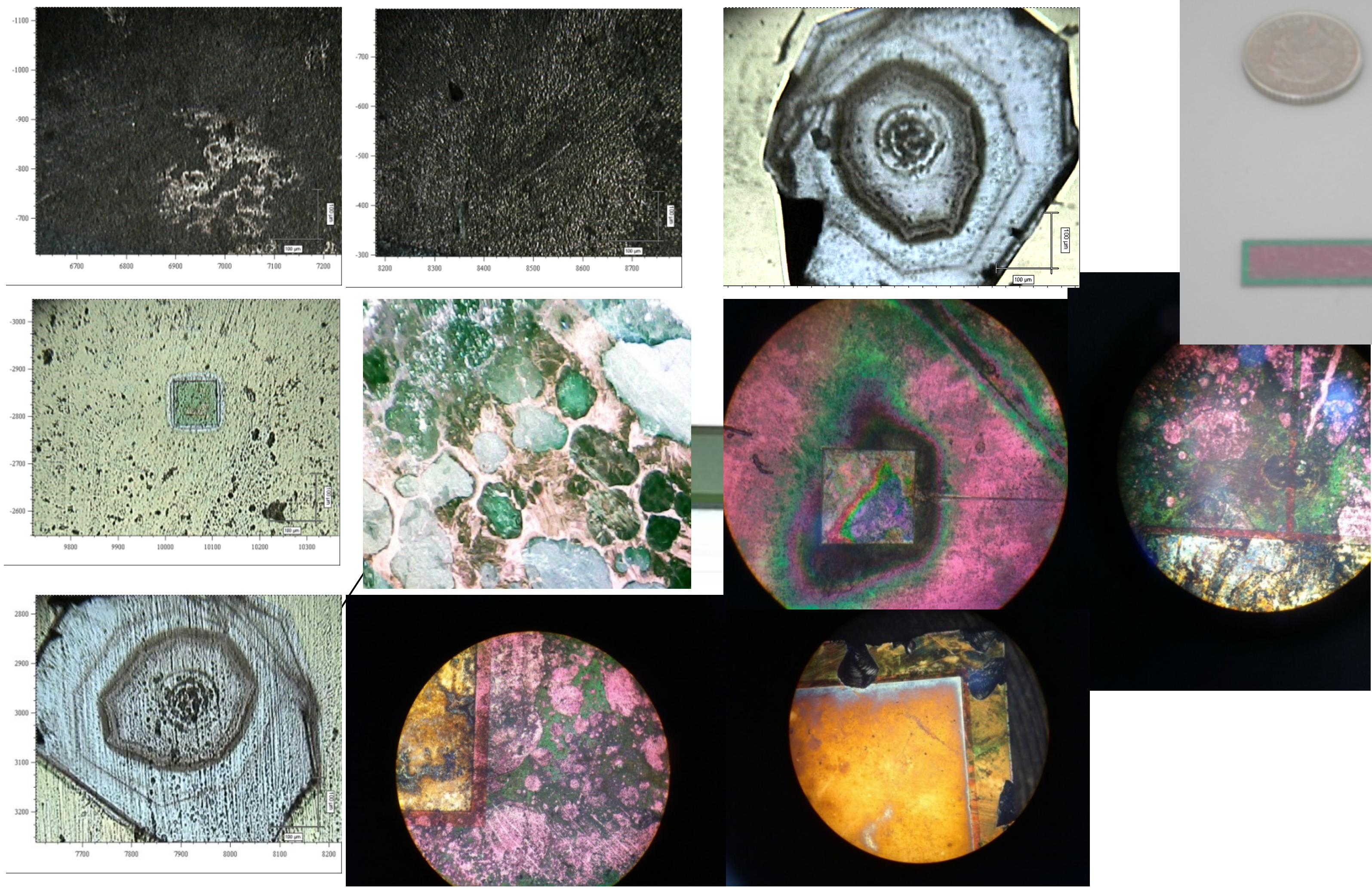
- Spectrophotmetric monitoring
- Electroanalysis
- Laser induced breakdown spectroscopy
- Off gas measurements
- Differential scanning calorimetry
- NMR?

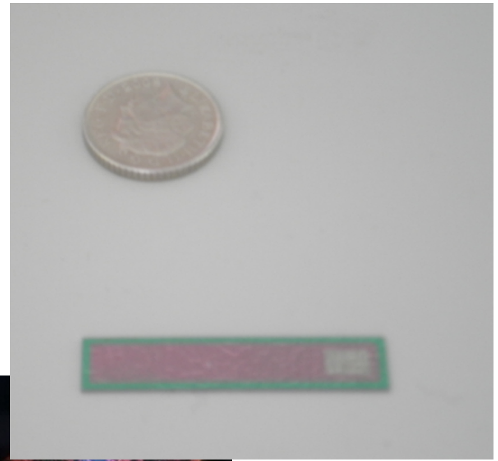
Electroanalysis in Molten Salts



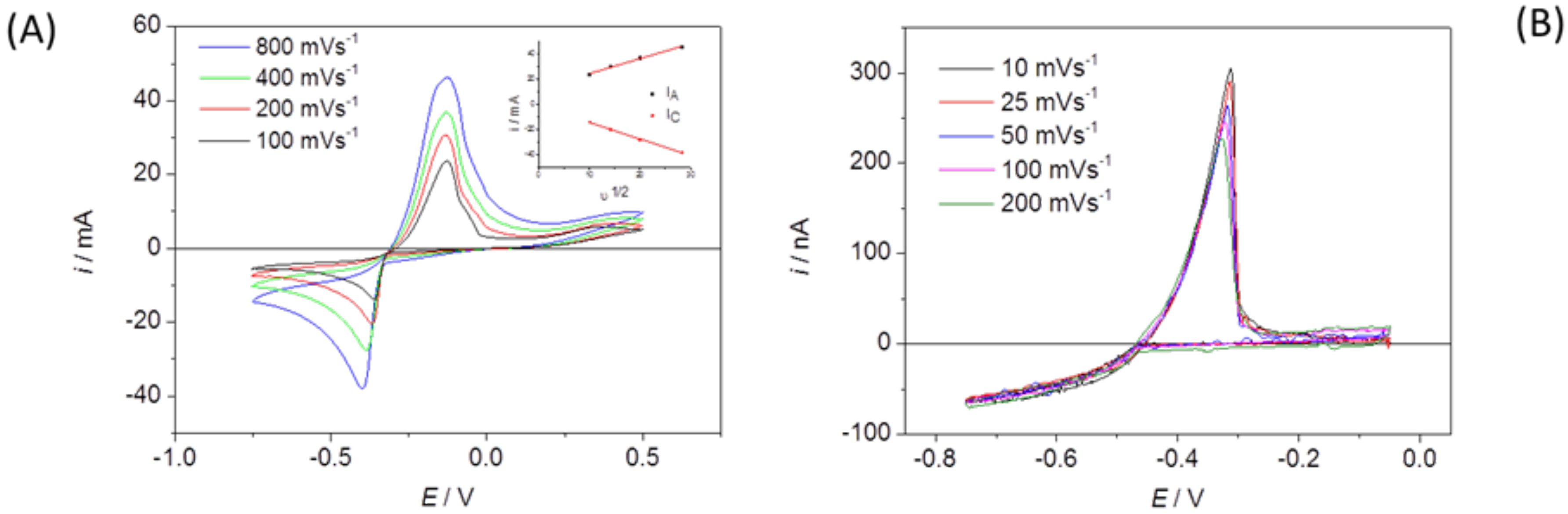
- Currently performed using large wire electrodes e.g. W or Pt.
- Electrode surface requires pre-treatment.
- Accurate estimation of area required for quantitation.
- Requires substantial effort to engineer in suitable sampling points.
- Large electrodes subject to analytical disadvantages such as high iR drop and sensitivity to convection.
- Disadvantages potentially overcome by microelectrodes BUT

The Materials Challenge!





Silver (I) Chloride



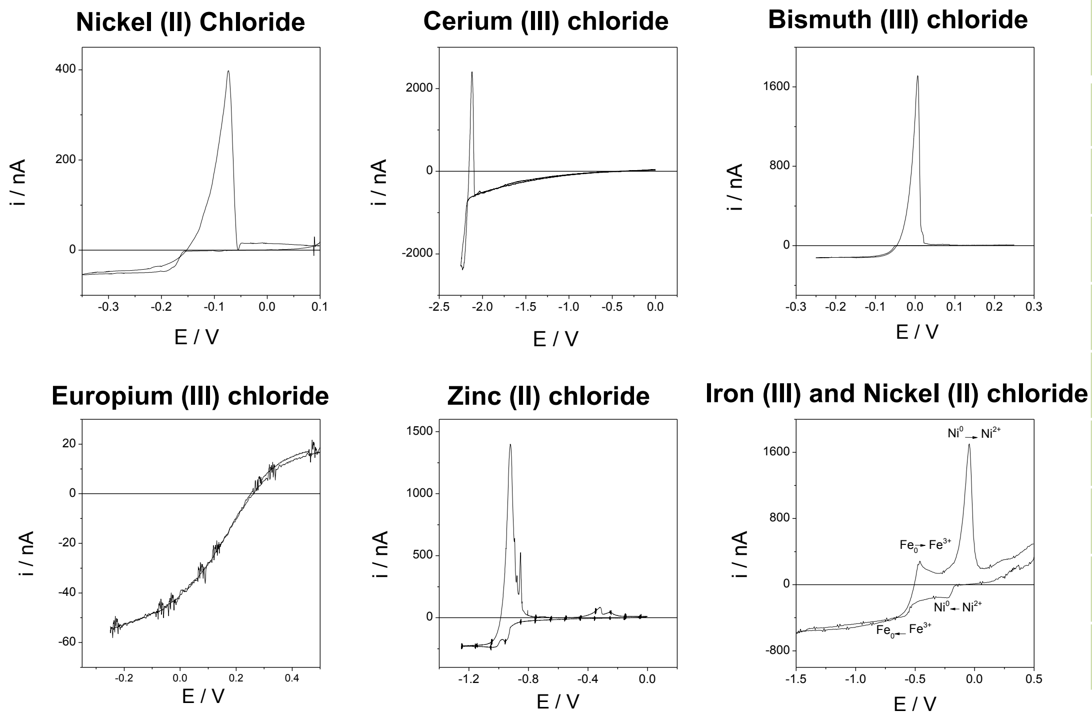
- Macroelectrode gives expected quantitative response,
  - square root dependency with scan rate and diffusionally limited peak currents
- Microelectrode also produces quantitative response

  plating wave and a sharp stripping peak independent of scan rate

Benchmark electroanalysis

$$i_L = 2.341nFDcL^{(1)}$$

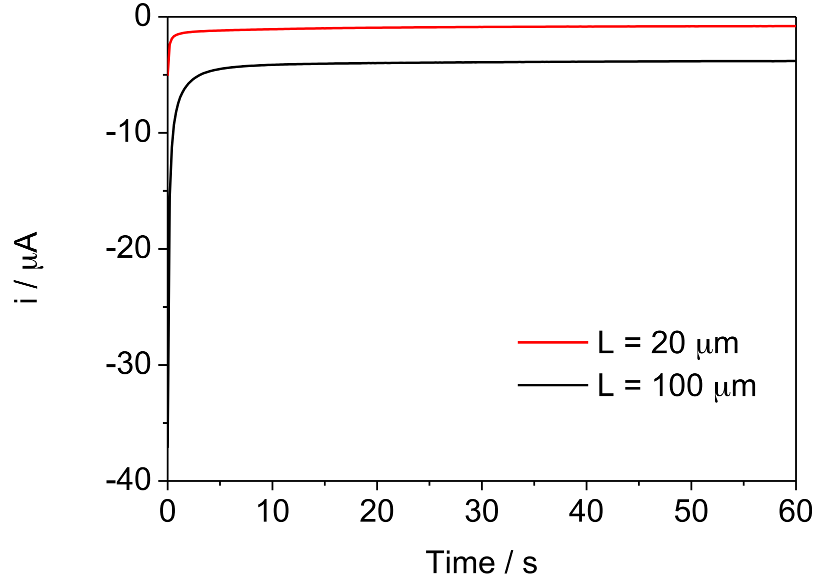
D = diffusion coefficient ($m^2\ s^{-1}$) c = concentration (mol m^{-3}) L = edge length (m)

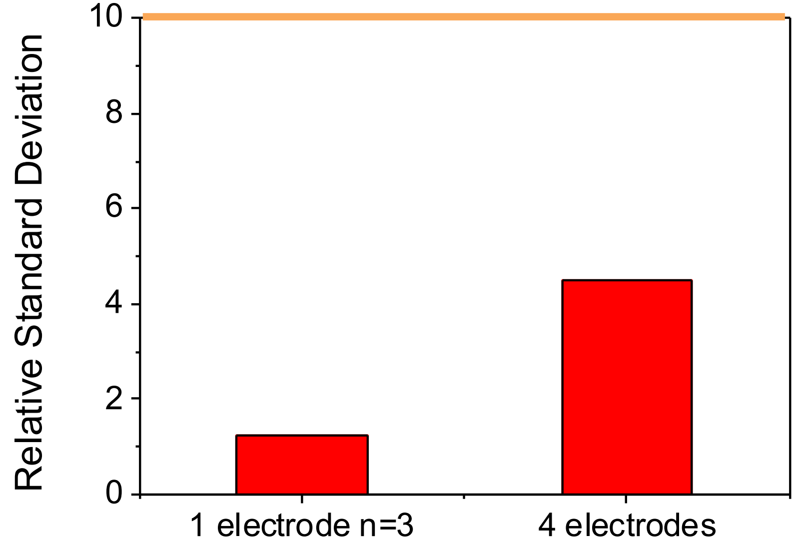


Redox couple	*D* at 698 K
	$\times 10^{-5}\ cm^2\ s^{-1}$
Ag(I)/Ag(0)	2.48 ± 0.07
Sm(III)/Sm(II)	0.92 ± 0.09
Eu(III)/Eu(II)	0.69
Ce(III)/Ce(0)	1.02
Zn(II)/Zn(0)	2.22
Bi(III)/Bi(0)	0.25
Ni(II)/Ni(0)	2.31
Fe(III)/Fe(0)	1.44

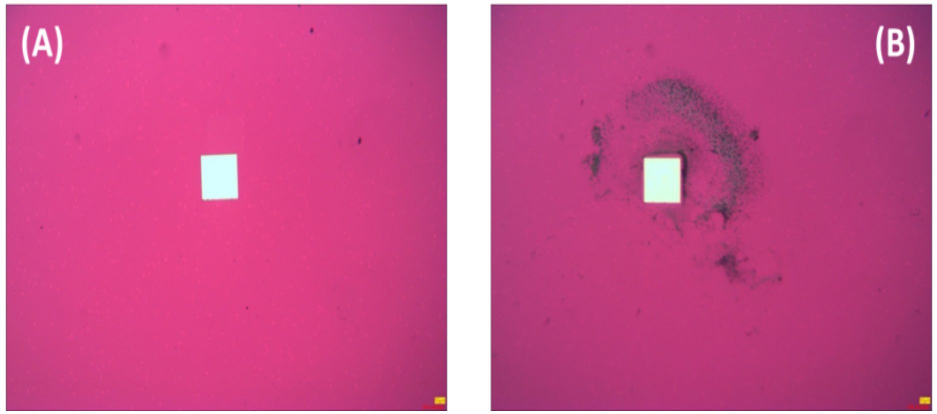
1) Woodvine, Mount *et al.*, (2010) Analyst

Electrode fidelity





- i_L varies with *L* as expected
- Error for ambient aqueous glass pulled microelectrodes ~ 10%



Corrigan, D.K., Blair, E., Terry, J.G., Walton A.J. and Mount A.R. Anal Chem (2014), submitted.

NMR

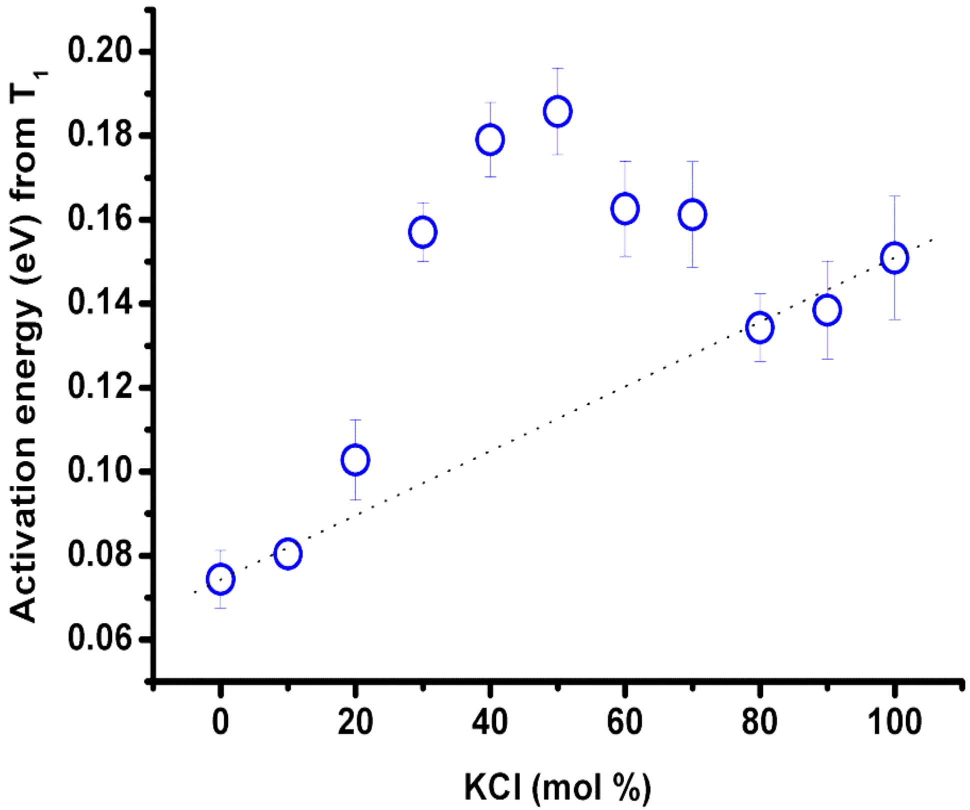
- Fundamental properties of molten salts and solutes

- Development for in-line analysis in molten salt systems

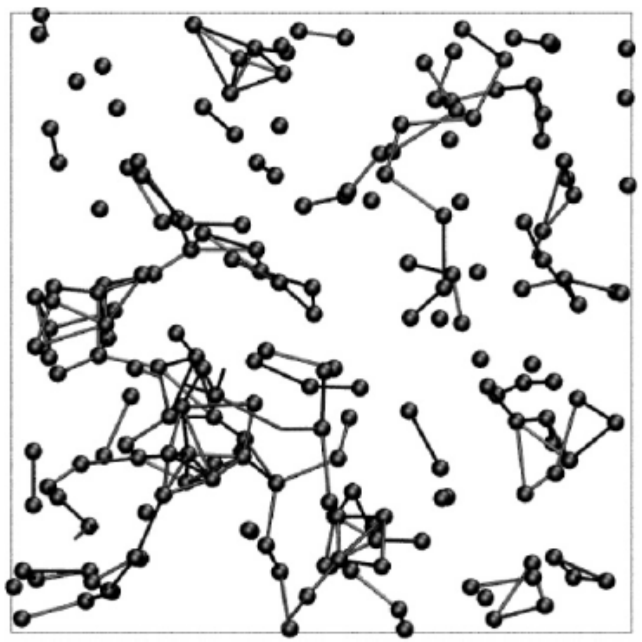
LiCl/KCl

Compositional effect

Activation energy vs composition

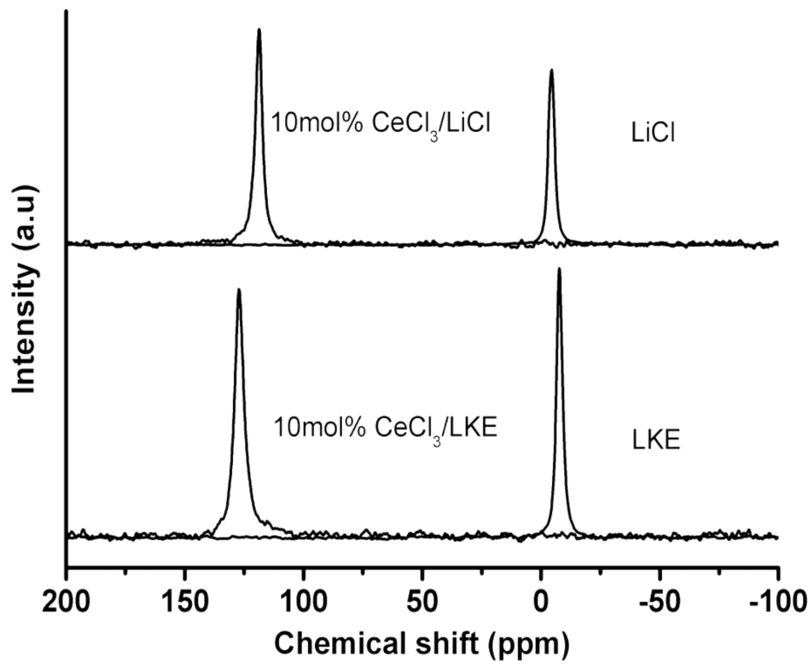


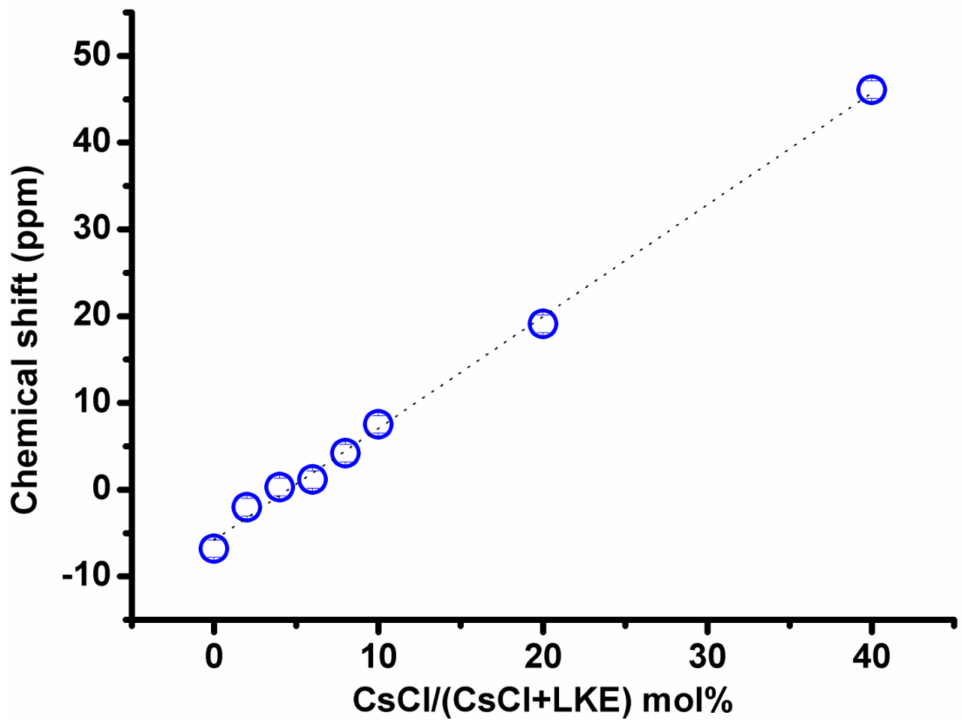
Intermediate range order complexes



M. Salanne, J. Phys: Condens. Matter 20 (2008) 332101

$CeCl_3$/LKE





Effect of $CeCl_3$ on ^{35}Cl chemical shift: shielding of the ^{35}Cl, indicate stronger interaction between Cl^- and cations.

Compositional effect of additions of alkali chlorides (e.g. CsCl) and surrogates of Uranium and Plutonium (e.g. $CeCl_3$) on chemical shift of ^{35}Cl can are being studied by NMR.

Potential for monitoring concentrations during the electrorefining process.

Summary

- The REFINE consortium is:
  - delivering essential molten salt (pyrochemical)
    - fundamentals
    - platform technologies
    - underpinning process development
    - training
  - for safe, dependable and sustainable UK nuclear fuel reprocessing
- Present focus: outputs, engagement, next steps....
- Outreach meeting: Royal Academy of Engineering, London, 16th December 2014
- www.refine.eng.ed.ac.uk Email: a.mount@ed.ac.uk