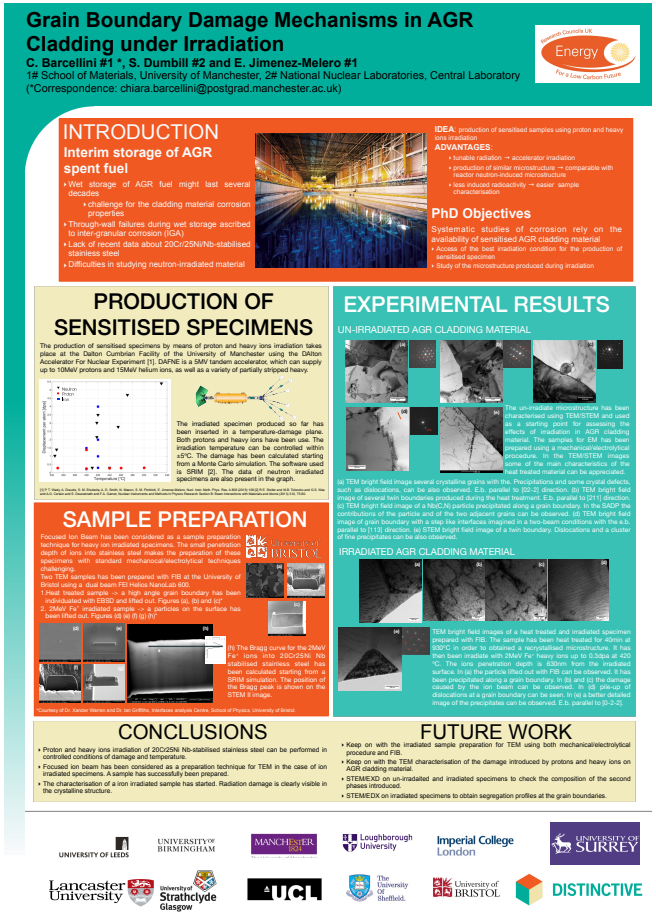
Grain Boundary Damage Mechanism in AGR Claddings under Irradiation

C. Barcellini*[1], S. Dumbill[2], and E. Jimenez-Melero[1]

[1]School of Materials, University of Manchester
[3]National Nuclear Laboratories, Central Laboratory
(*Correspondence: chiara.barcellini@postgrad.manchester.ac.uk)



DISTINCTIVE Theme 3rd Annual Meeting
National Railway Museum, York
5th - 6th April 2017

Sensitisation with charge particles

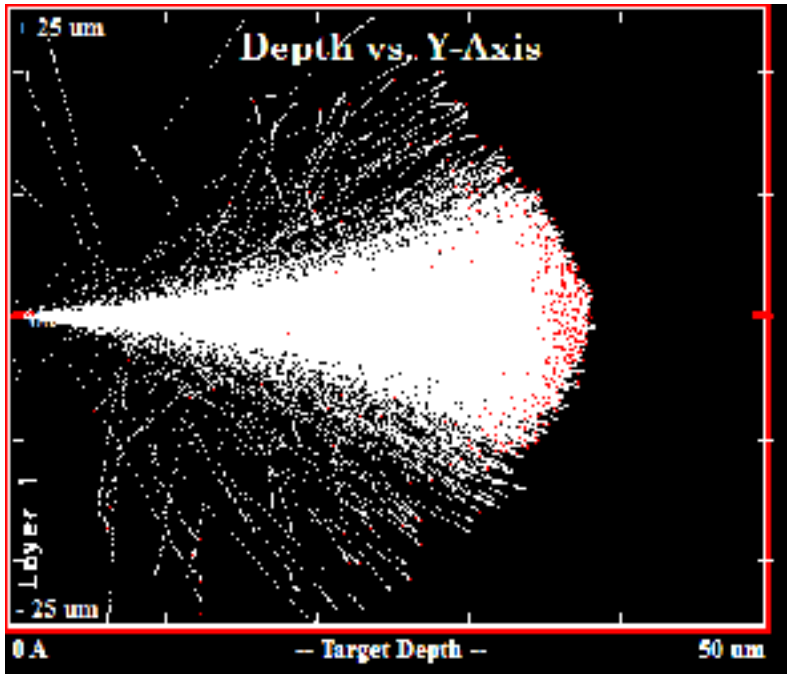
Sensitised specimens can be produced using intense beams of protons or heavy ions

ADVANTAGES:

- user-adjustable radiation
- similar microstructure
- reduced induced radioactivity

PhD main Objectives:

- access irradiation conditions
- study microstructures produced during irradiation



Irradiated AGR Cladding Material Preparation for TEM

C. Barcellini*[1], S. Dumbill[2], and E. Jimenez-Melero[1]

[1]School of Materials, University of Manchester
[3]National Nuclear Laboratories, Central Laboratory
(*Correspondence: chiara.barcellini@postgrad.manchester.ac.uk)

DISTINCTIVE Theme 3rd Annual Meeting
National Railway Museum, York
5th - 6th April 2017

Contents

Contents

Specimen Preparation

20Cr25Ni Nb-stabilised s.s.

- cold work
- 40min at 930°C

Annealed specimen → irradiation → Irradiated specimen

- austenitic matrix
  - composition -> SEM & TEM
  - g.b -> SEM/EBSD & TEM
  - texture -> SEM/EBSD
- second phases
  - composition -> SEM & TEM
  - texture -> SEM/EBSD

- austenitic matrix
  - composition -> SEM & TEM
  - g.b -> SEM/EBSD & TEM
  - texture -> EBSD
- second phases
  - composition -> SEM & TEM

Irradiated Sample Production

Ion Beam Facility

UNIVERSITY OF SURREY

MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

Dalton Cumbrian Facility

Energy

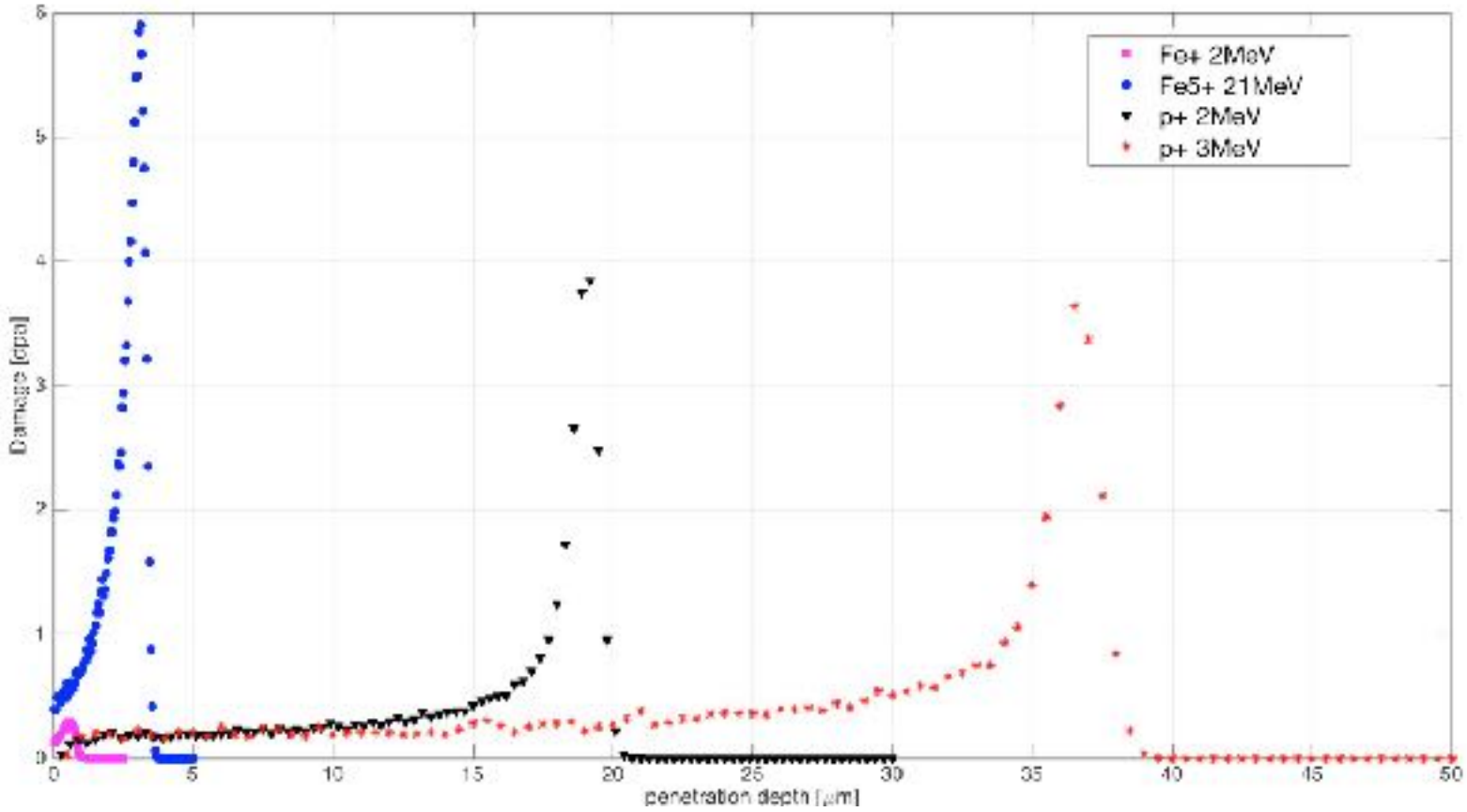
MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

EPSRC
Engineering and Physical Sciences Research Council

NATIONAL NUCLEAR LABORATORY

DISTINCTIVE

Examples of Bragg Curves



Specimen Preparation

20Cr25Ni Nb-stabilised s.s.

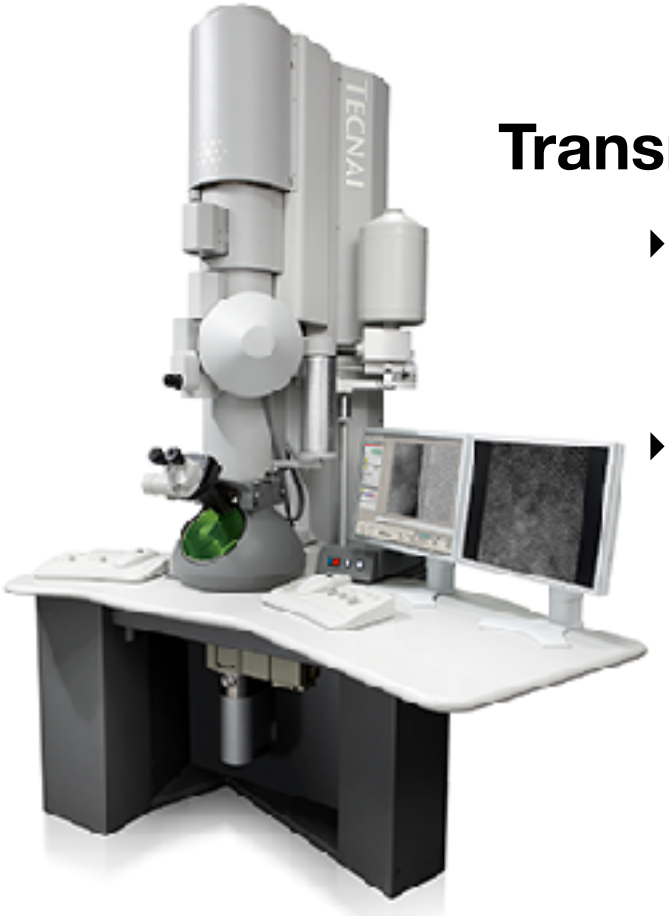
- cold work
- 40min at 930°C

Annealed specimen → irradiation → Irradiated specimen

- austenitic matrix
  - composition -> SEM & **TEM**
  - g.b -> SEM/EBSD & **TEM**
  - texture -> SEM/EBSD
- second phases
  - composition -> SEM & **TEM**
  - texture -> SEM/EBSD

- austenitic matrix
  - composition -> SEM & **TEM**
  - g.b -> SEM/EBSD & **TEM**
  - texture -> EBSD
- second phases
  - composition -> SEM & **TEM**

Characterisation of Irradiated Materials



Transmission Electron Microscopy (TEM)

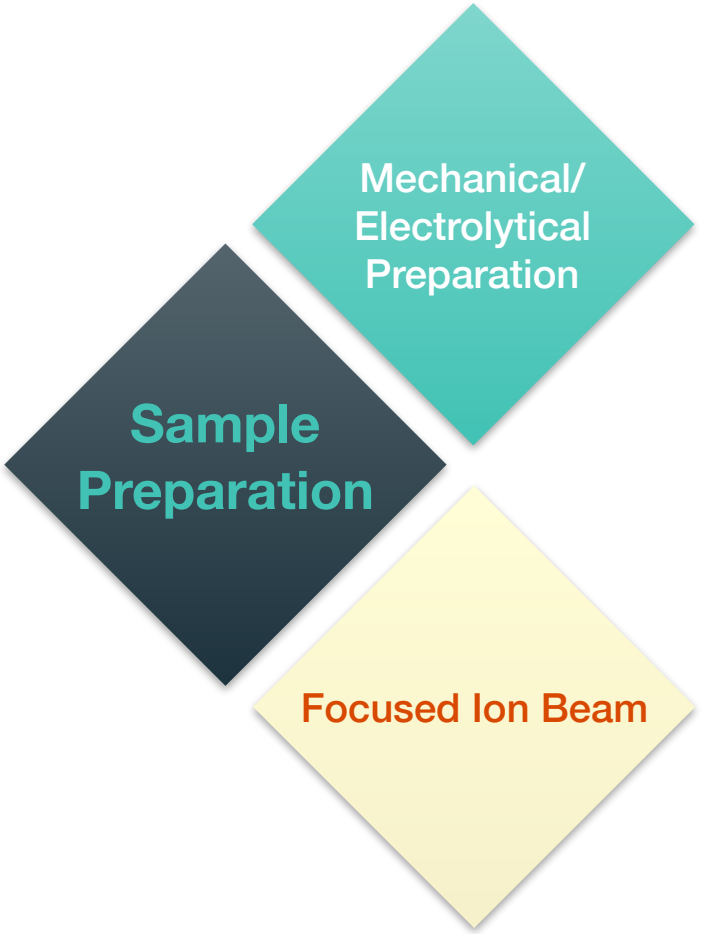
- Routine direct imaging
  - ≳10^5 magnification
  - ≲1nm resolution
  - structural changes
- EDX and EELS
  - local chemical changes
  - compositional changes

SAMPLE REQUIREMENTS

- electron-transparency

Contents

Sample Preparation Techniques



Advantages
- no damage
- cheap

Disadvantages
- difficult control of electropolishing parameters
- not site specific

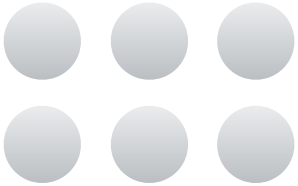
Advantages
- site specific
- control on the parameters

Disadvantages
- Ga beam damage
- expensive

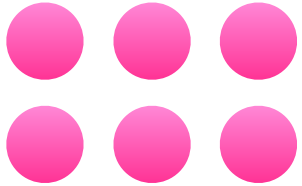
Mechanical/Electrolytical Procedure

Bulk Irradiated Sample

Pre back thinning with SiC paper



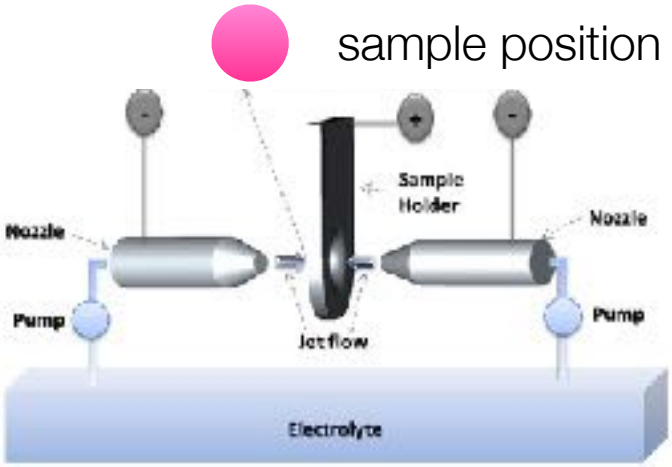
disks



paint the irradiated surface with Lacomit

Perchloric Acid	60%	6%
Methanol	99.99%	59%
2-Butoxyethanol	99.99%	35%

Temperature	-20°C
Voltage	20.5V
Flow Rate	20



Schematic of twin-jet electropolishing apparatus for 3mm TEM disks [1]

Focused Ion Beam

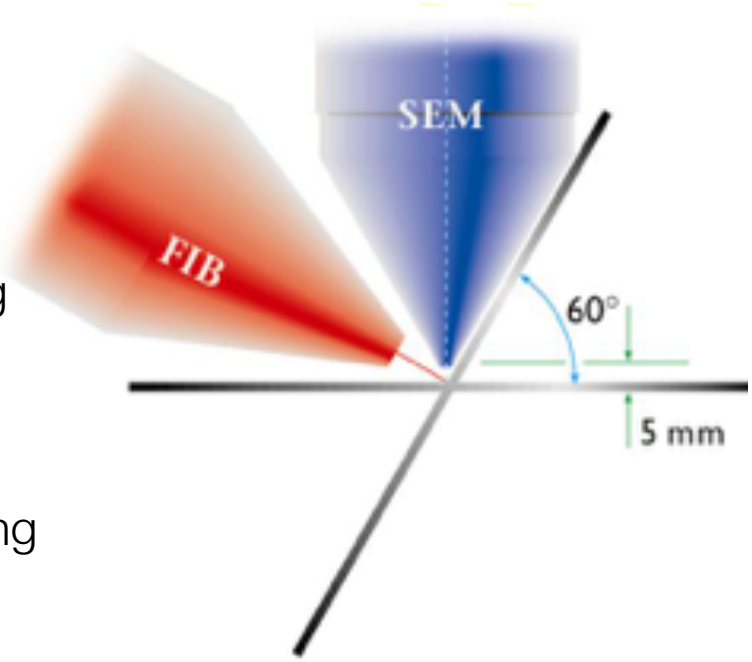
Dual Beam Focused Ion Beam:

Ga Ion Beam

- Emission of secondary electrons -> FIB Imaging
- Sputtering of substrate atoms -> FIB Milling
- Chemical interactions -> FIB deposition

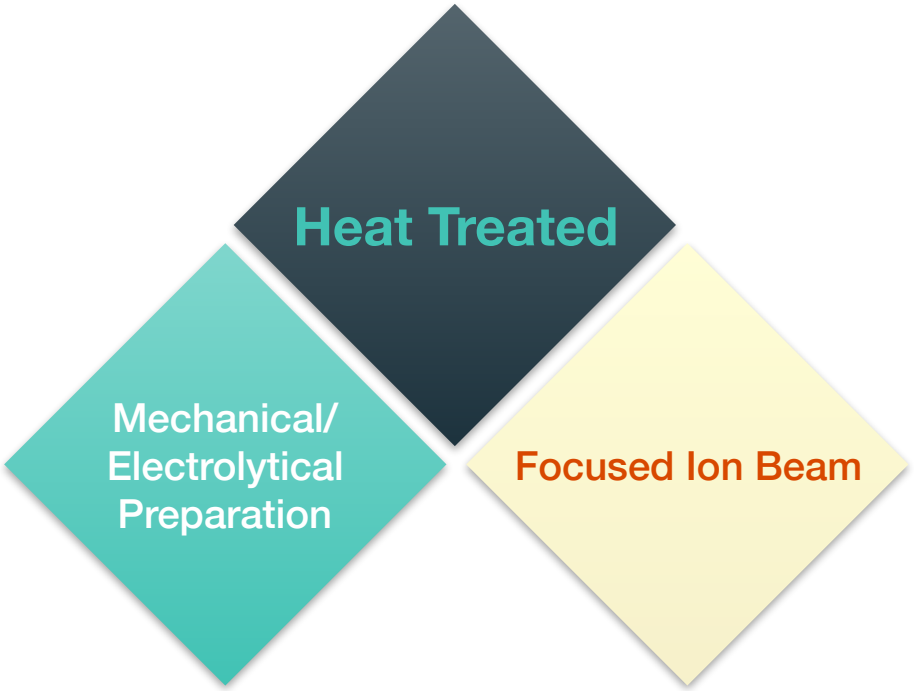
Electron Beam

- Emission of secondary electrons -> SEM Imaging
- Chemical interactions -> SEM deposition



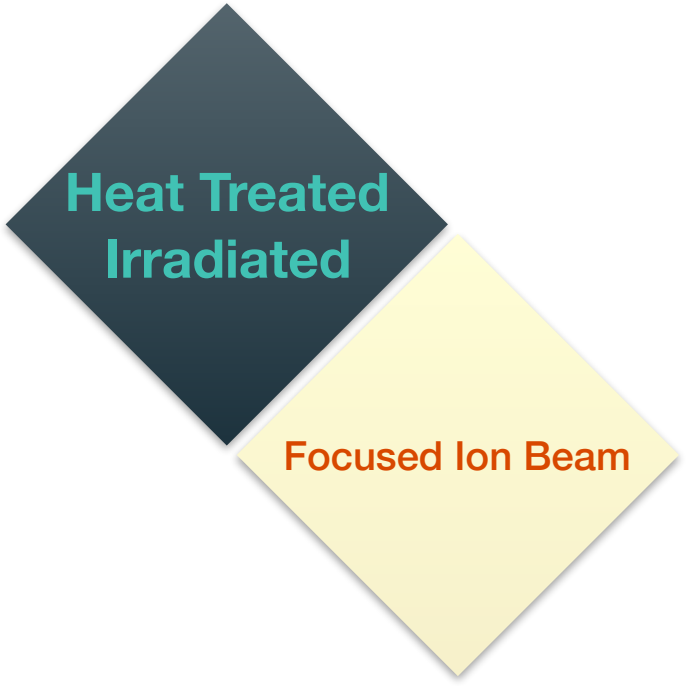
Contents

Overview of the Samples Prepared



Several Disks

1 samples



1 samples

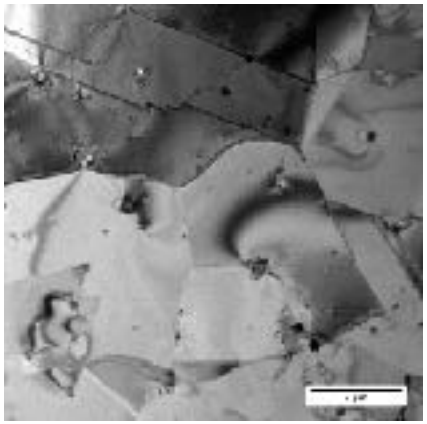
Overview of the Samples Prepared

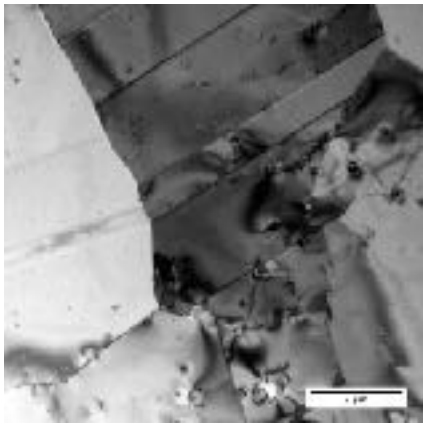
Several Disks

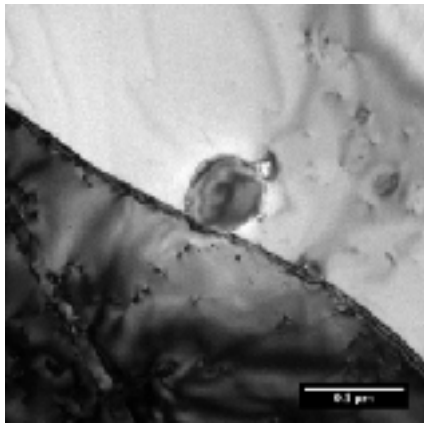
1 samples

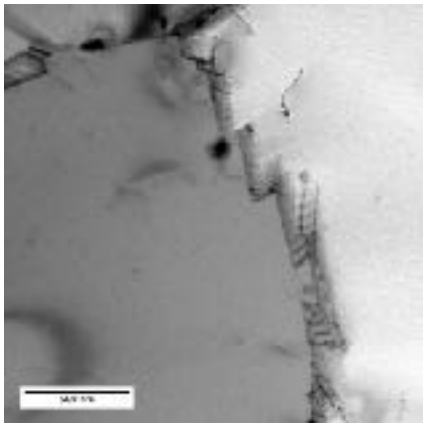
1 samples

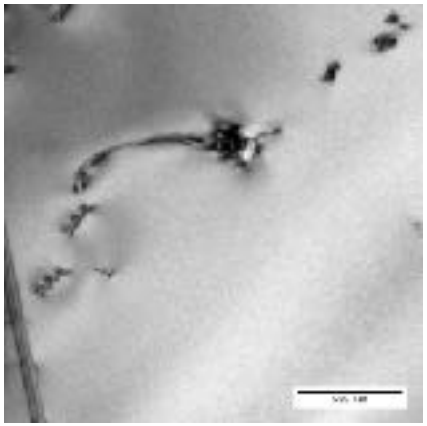
Characterisation of Heat Treated Specimen

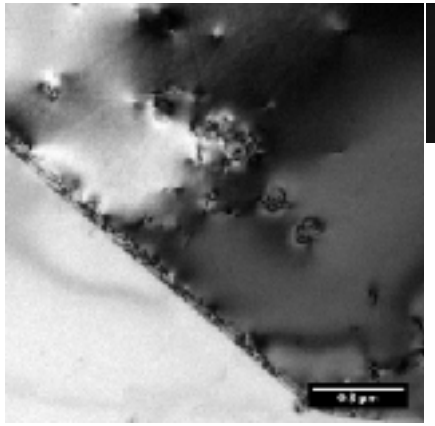


[110]


[012]





[013]



[013]



Overview of the Samples Prepared

Several Disks

1 samples

1 samples

Focused Ion Beam on Irradiated Material

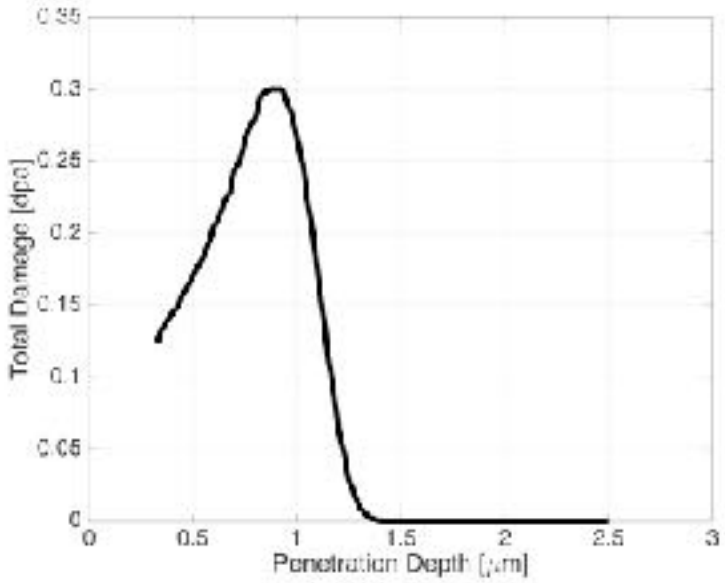
University of BRISTOL

UNIVERSITY OF SURREY

20Cr25Ni Nb-stabilised s.s.
heat treatment: **40min 930ºC**
irradiation: **0.3dpa at 420ºC**

FEI Helios NanoLab 600 with three-axis micromanipulator, Oxford Inst X-Max50 EDS, 7nm resolution platinum deposition and force measurement.

It can be used for the preparation of **active samples**



Energy

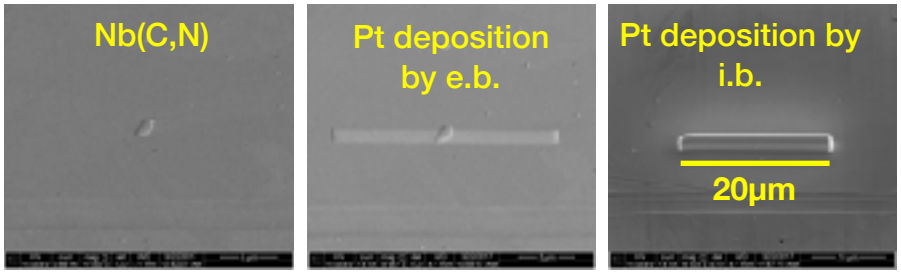
MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

EPSRC
Engineering and Physical Sciences Research Council

NATIONAL NUCLEAR LABORATORY

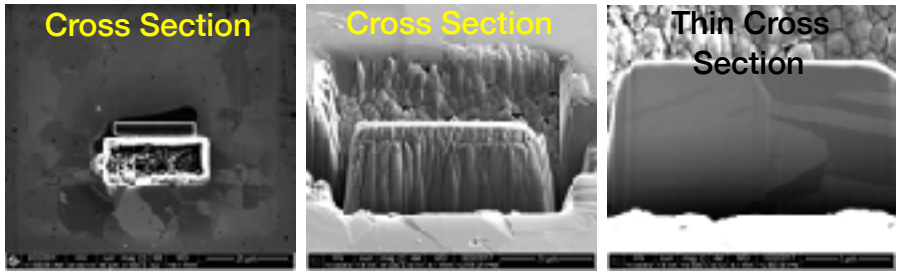
DISTINCTIVE

Focused Ion Beam on Irradiated Material



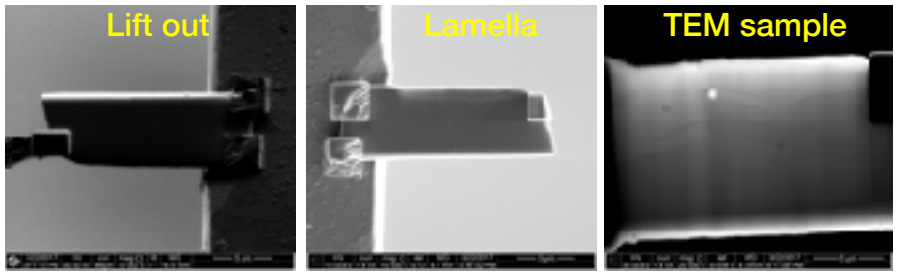
Second Phase: Nb(C,N)

- 0° 100nm of Pt by e.b. 10kV 1.4nA
- 52° 100nm of Pt by i.b. 30kV 26pA



Cross Section and Thinning

- 52° with i.b. 30kV 20nA for all sides
- 53.5° or 50.5° with i.b. 30kV 9nA

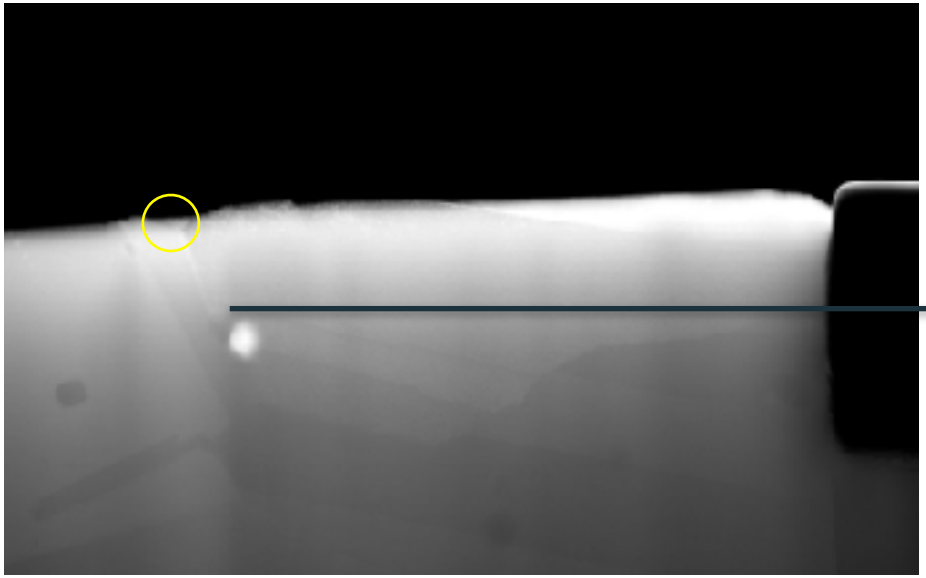


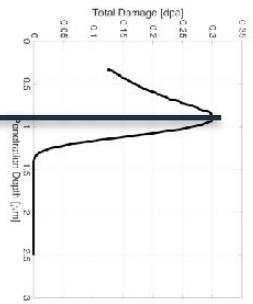
Lift Out & Final Cleaning

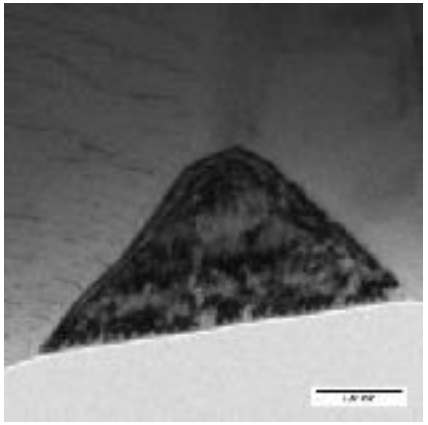
- 0° undercut with i.b. 30kV 2.7nA
- 0° lamella attached to the grid
- 53.5° with i.b. 30kV 0.9nA
- 60.4°with i.b. 5kV 71pA

SEM images courtesy of D. Xander Warren and Dr. Ian Griffiths, Interface Analysis Centre, School of Physics, University of Bristol

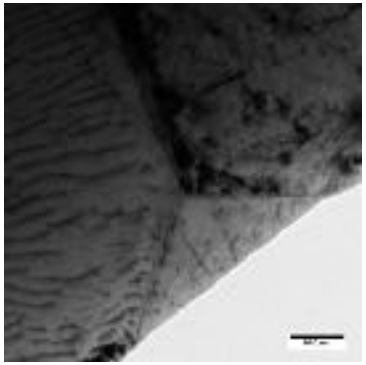
Characterisation of Irradiated Sample

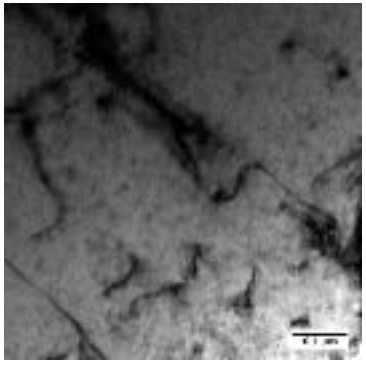


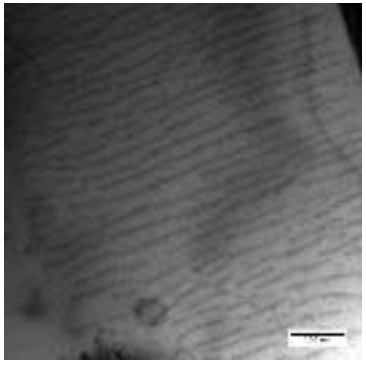




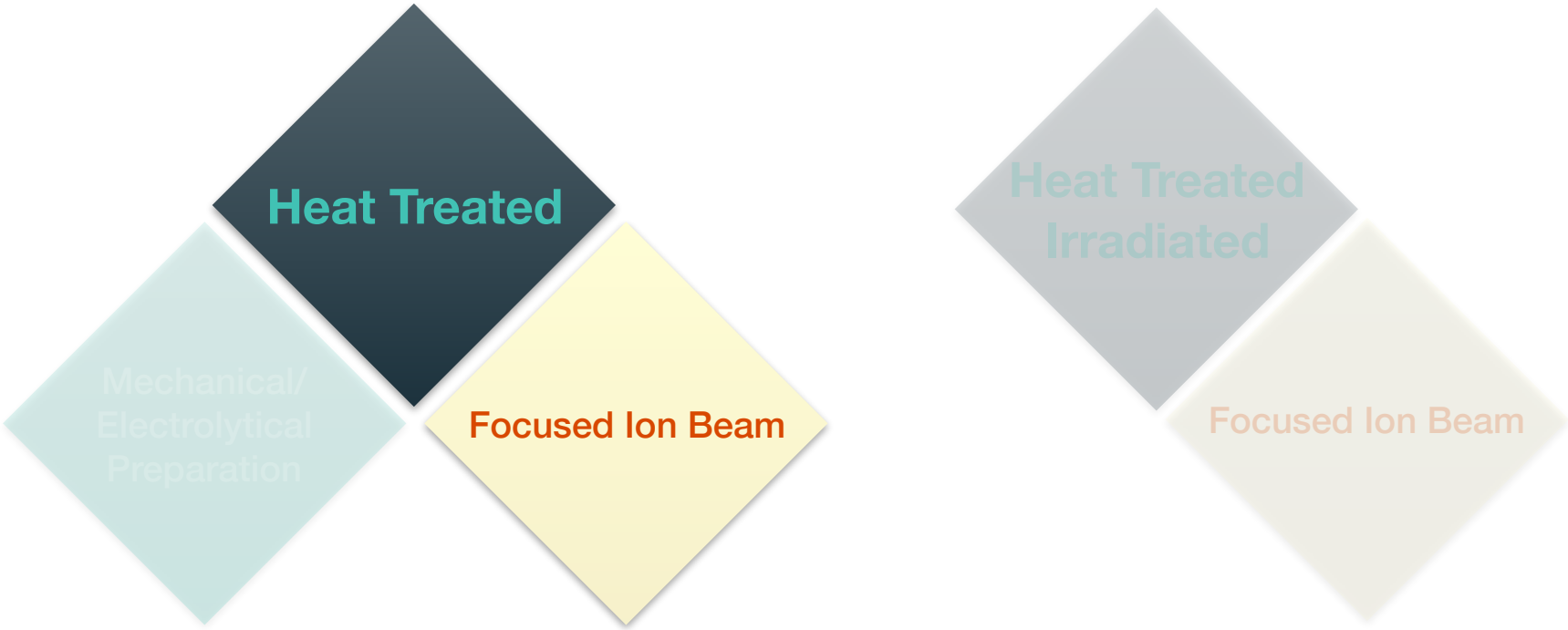
[013]







Overview of the Samples Prepared



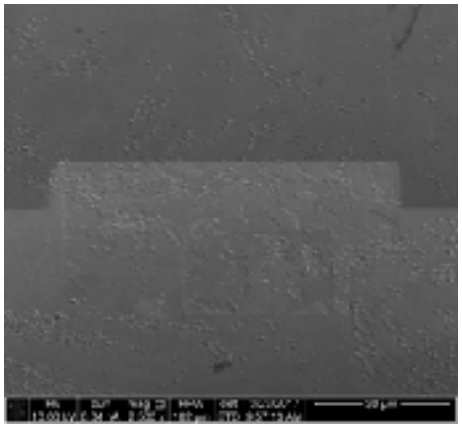
Several Disks

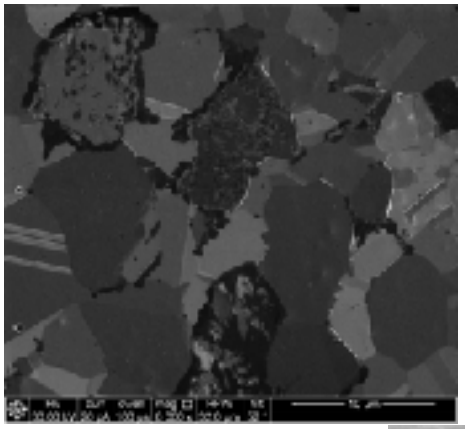
1 samples

1 samples

Focused Ion Beam on Un-irradiated Material

University of BRISTOL

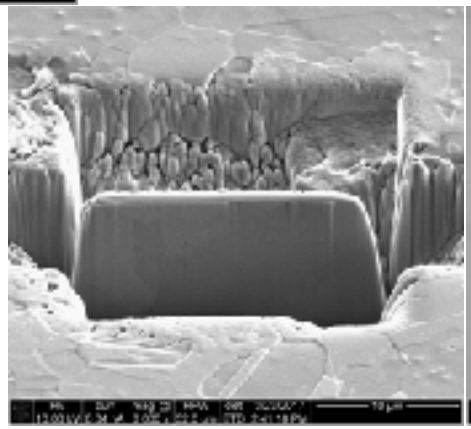


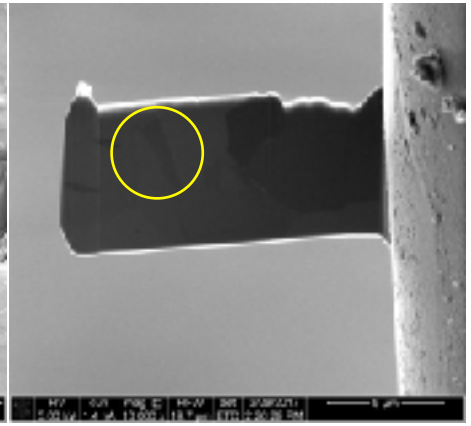


Heat Treaded Specimen:
as a benchmark for assessing the damage introduced by the Ga beam

High Angle Grain Boundary

- Pt deposition
- cross section
- lift out
- final cleaning





SEM images courtesy of D. Xander Warren and Dr. Ian Griffiths, Interface Analysis Centre, School of Physics, University of Bristol

Energy

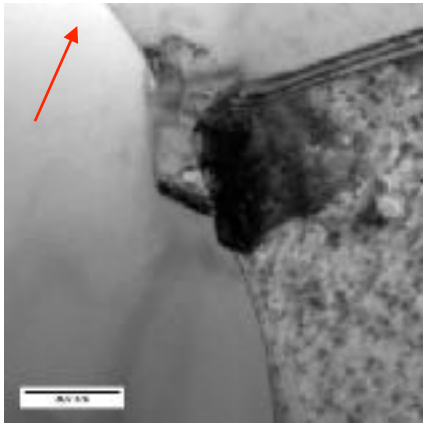
MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

EPSRC
Engineering and Physical Sciences Research Council

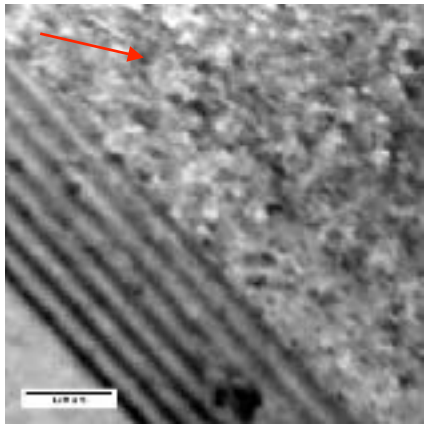
NATIONAL NUCLEAR LABORATORY

DISTINCTIVE

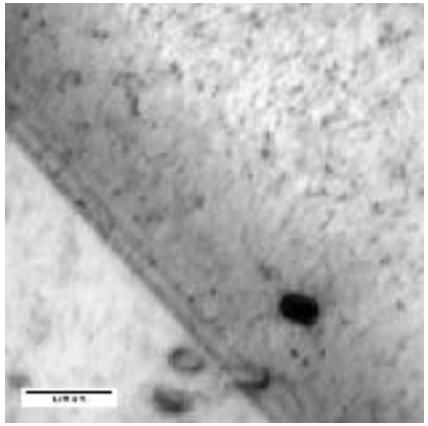
Characterisation of Heat Treated Specimen



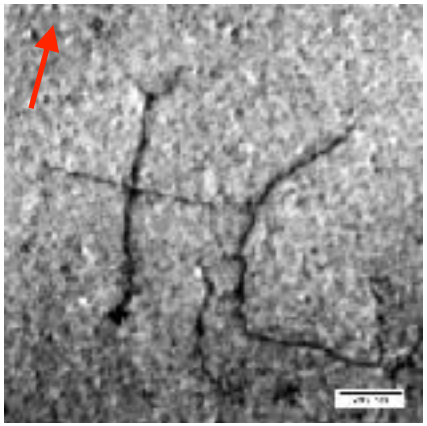

[112]



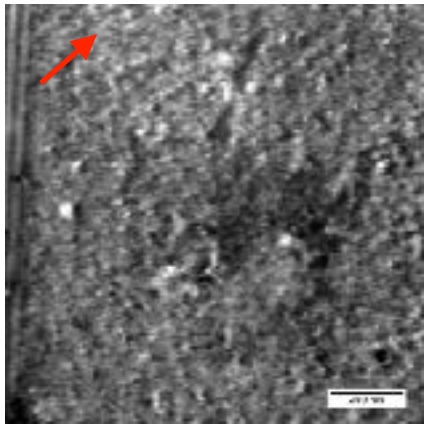
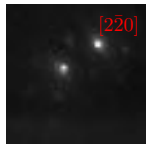

[001]



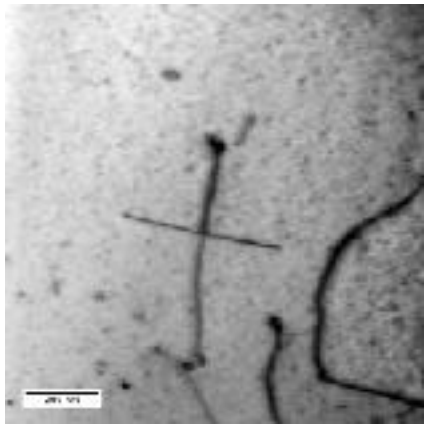
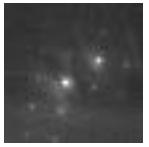
[001]




[001]

[001]



[001]

Contents

Conclusions

- State-of-the-art techniques has been combined in order to produce, prepare and analyse radiation damage in AGR cladding material.
- The feasibility of FIB preparation for heavy ion irradiated specimen has been investigated
  - a heavy ion irradiated TEM sample has been prepared and the characterisation has started
  - a heat treated TEM sample has been prepare and it will be use to characterise the Ga beam damage

Contents

Energy

MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

EPSRC
Engineering and Physical Sciences Research Council

NATIONAL NUCLEAR LABORATORY

DISTINCTIVE

Future Work

- Keep on working on the FIB preparation of heavy ion irradiated specimens.
  - find the perfect “recipe” for AGR cladding material in order to minimise the induced damage.
- TEM/EDX to check local changes in composition
  - does the Ga beam induce segregation?
- Preparation of proton irradiated TEM specimen using mechanical/electrolytical preparation
- Keep on with the characterisation of the radiation damage

Acknowledgments

NATIONAL NUCLEAR LABORATORY

MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

University of BRISTOL

UNIVERSITY OF SURREY

Energy

MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

EPSRC
Engineering and Physical Sciences Research Council

NATIONAL NUCLEAR LABORATORY

DISTINCTIVE

Thank you for your attention

Energy
MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute
EPSRC
Engineering and Physical Sciences Research Council
NATIONAL NUCLEAR LABORATORY
DISTINCTIVE

Questions?

Direct mass analysis of water absorption onto ceria and urania thin films

Dominic Laventine
Colin Boxall
Lancaster University

Distinctive April, 2017
Annual Meeting, York

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Lancaster University

Plutonium storage

- ~250 tonnes of separated Pu currently stockpiled worldwide.
- ~50% in long-term storage in UK whilst the Government develops its options
- Interim storage of PuO_2 involves sealing in inert steel containers.
- Under certain circumstances, these gas cans may pressurise; this must be avoided in practice.
- Need to understand how the structure and properties of PuO_2 change with time under storage conditions (e.g. in the presence of H_2O).

Plutonia interaction with water

- 5 routes to gas production have been suggested:

  (i) Helium accumulation from α decay
  (ii) Decomposition of polymeric packing material;
  (iii) H_2O desorption (steam) from hygroscopic PuO_2
  (iv) Radiolysis of adsorbed water
  (v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

- The last 3 processes all involve PuO_2/H_2O interactions and are complex, inter-connected & poorly understood.

- Haschke has suggested a reaction: $PuO_2 + H_2O \rightarrow PuO_{2+x} + H_2$
  This has been disputed on thermodynamic grounds.

- Experimental methods have been employed to determine extent of H_2O adsorption, typically through measurement of pressure changes and use of the ideal gas equation to indirectly determine water adsorption at the plutonium oxide surface.

Aims

Current models suggest water is initially absorbed onto metal oxides as a chemi-absorbed monolayer followed by multiple, physi-sorbed layers (with possible intermediate layers of differing binding energies).

- Study the interactions of plutonium oxide and analogues with water.
  - Ceria
  - Urania
  - Thoria
  - Plutonium oxide
- Use of quartz crystal microbalance methodology to experimentally determine:
  - The number of monolayers of water bound to the surface
  - The enthalpy of binding of the different layers.

Quartz crystal microbalance (QCM)

- The QCM measures in-situ mass changes at the surface of a piezoelectrode. Changes in mass, due to oxide formation or dissolution at the electrode surface or adsorption/desorption of gases, result in resonant frequency changes of the quartz crystal.
- Changes in frequency can be related to changes in mass through the Sauerbrey equation:

$$\Delta f = -\left(\frac{n{f_0}^2}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

- Knowing the surface area of the metal oxide layer and the mass of water absorbed allows the number of layers to be accurately calculated.
- The differences in temperature at which water absorption/desorption occurs allows the thermodynamics to be determined, indicating which layers are chemi- or physio-sorbed.

Ceria films on high temperature crystals: QCM

Uncoated crystal $F_{21ºC}$ = 5833918 Hz

Coated crystal $F_{25ºC}$ = 5826468 Hz

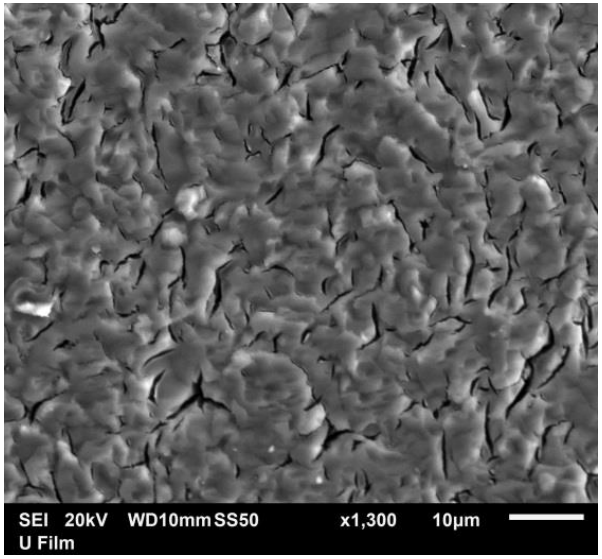
$$\Delta f = -\left(\frac{n{f_0}^2}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

$\Delta F_{25ºC}$ = –7450 Hz

Δ m = 42 μg

vol = 5.5 x 10^{-6} cm^3

Thickness = 125 nm



ρ_q = 3.570 $g.cm^{-1}$ n = 1

μ_q = 2.147 x 10^{11} $g.cm^{-1}s^{-2}$

Coated area = 1.33 cm^2

Active area = 0.46 cm^2

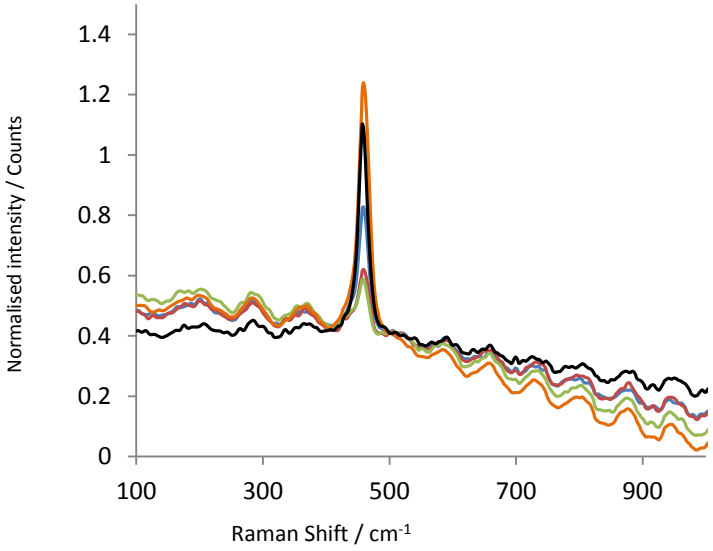
d_{CeO_2} = 7.65 $g.cm^{-3}$

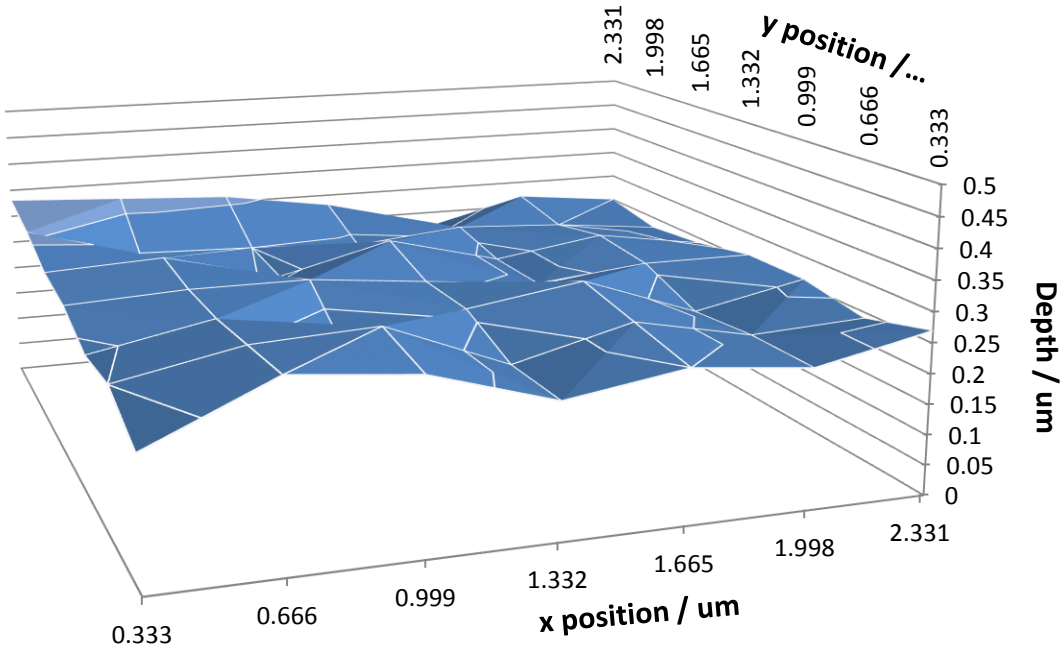
nF_0^2 = 3.409x 10^{13} Hz^2

$(Pgxug^{0.5})$ = 8.755 x 10^5 $gcm\text{-}1s\text{-}1$

Cf = 3.89 x 10^7

Ceria films on $GaPO_4$ crystals: SEM and XRF





$\Delta \quad F_{25ºC} = -7450$ Hz

Δ m = 42 μg

h (QCM) = 125 nm

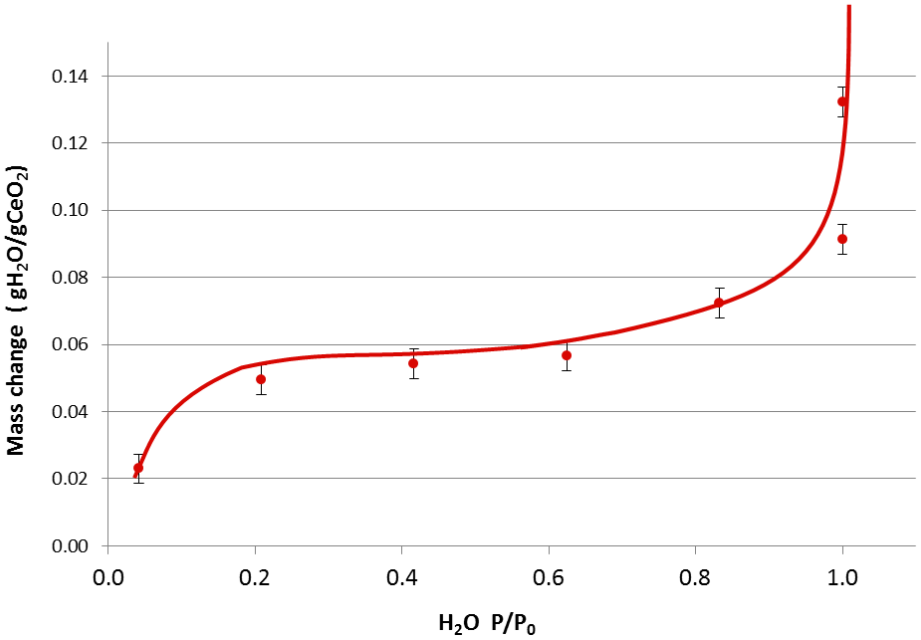
XRF map in a 7 x 7 grid (49 points) gives an average ceria thickness of 261 nm (SE = 29 nm).

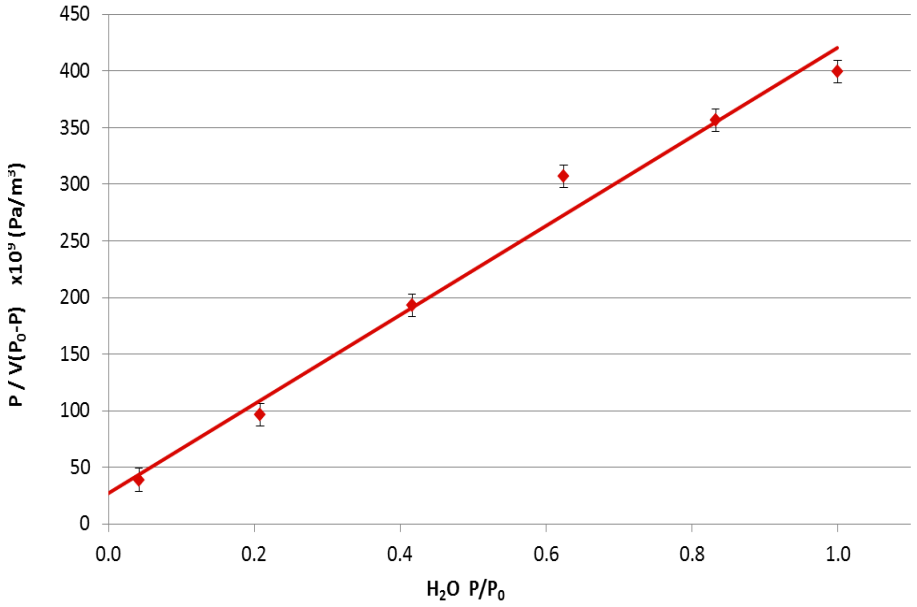
This gives a piezoactive volume of 8.9 x 10^{-6} cm^3 and therefore a porosity of 54%.

Ceria films on $GaPO_4$ crystals: BET

The BET equation allows the volume of a monolayer and the enthalpy of absorption to be calculated:

$$1/\left[Va\left(\frac{P0}{P}-1\right)\right] = \left(\frac{C-1}{V_M C}\right)\left(\frac{P}{P_0}\right)+\frac{1}{VmC} \qquad C = e^{(\Delta H_{ads} - \Delta H_{liq}/RT)}.$$





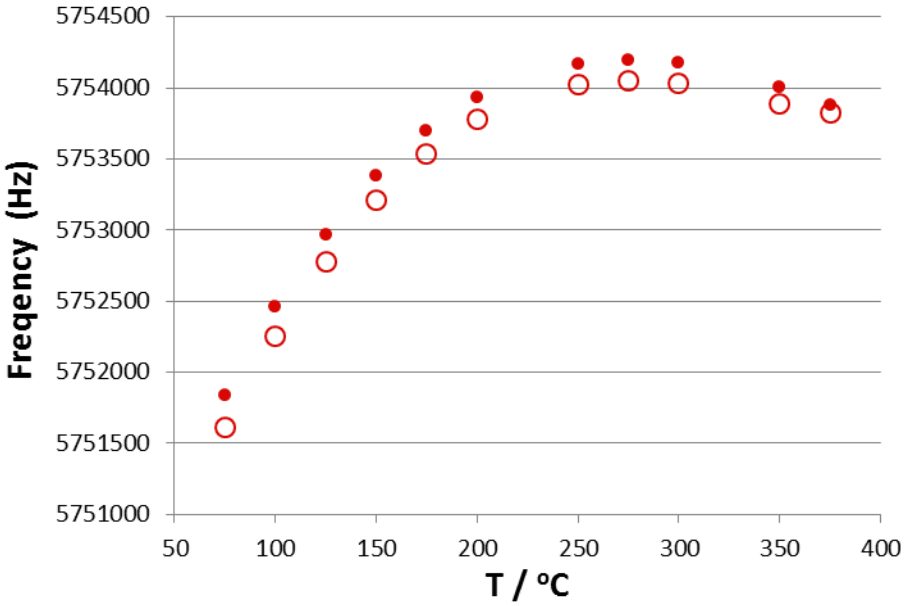
A plot of P/V(P_0-P) against P/P_0 gives an intercept of 1/VmC and a gradient of $(C-1)/(V_M C)$, therefore we can calculate:

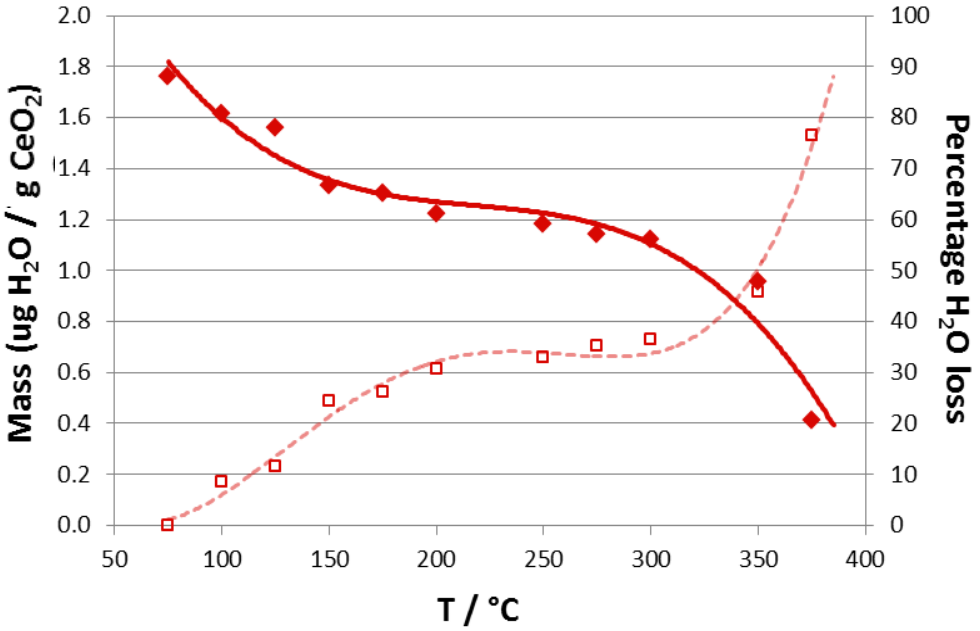
V_m = 2.43 x 10^{-12} m^3 SA = 4.46 m^2g^{-1}

ΔH_{abs} = 44.3 $kJmol^{-1}$ ΔH_{bind} = 2.5 $kJmol^{-1}$

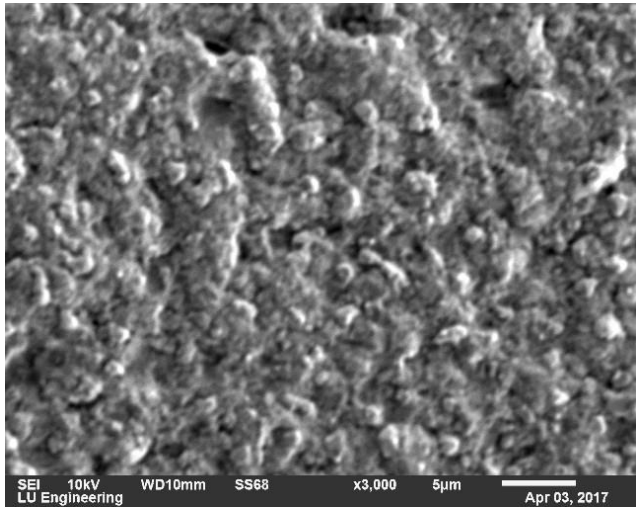
Ceria films on $GaPO_4$ crystals: High temperature

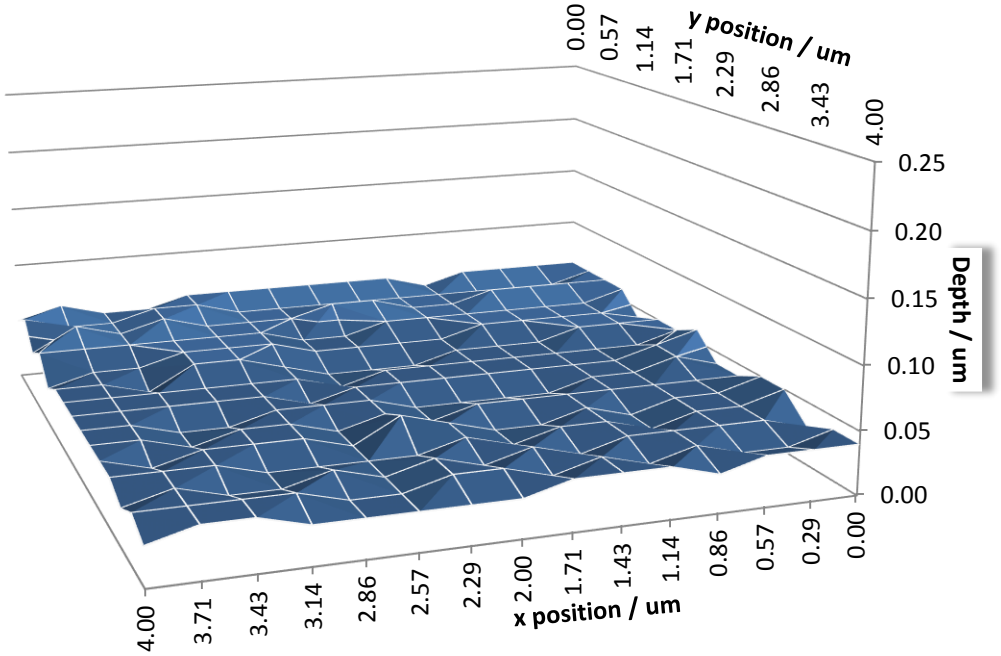
The BET equation allows the volume of a monolayer and the enthalpy of absorption to be calculated:





Urania films on $GaPO_4$ crystals: SEM and XRF





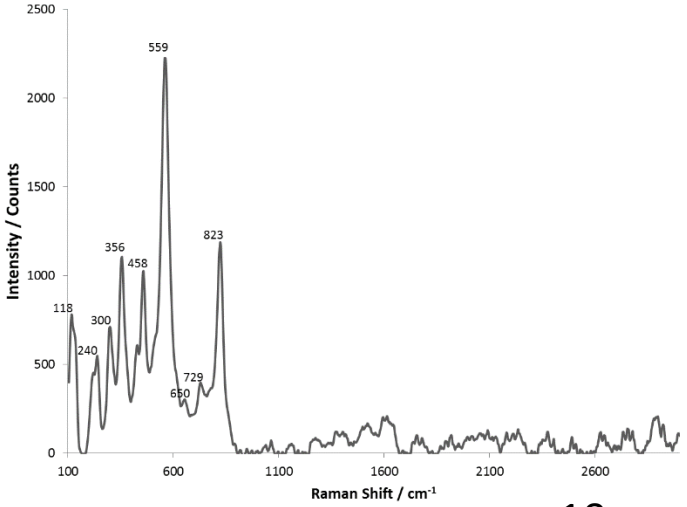
Δ $F_{25ºC} = -2352$ Hz

Δ m = 18 µg

h (QCM) = 27 nm

XRF map in a 15 x 15 grid (225 points) gives an average urania thickness of 42 nm (SD = 9 nm).

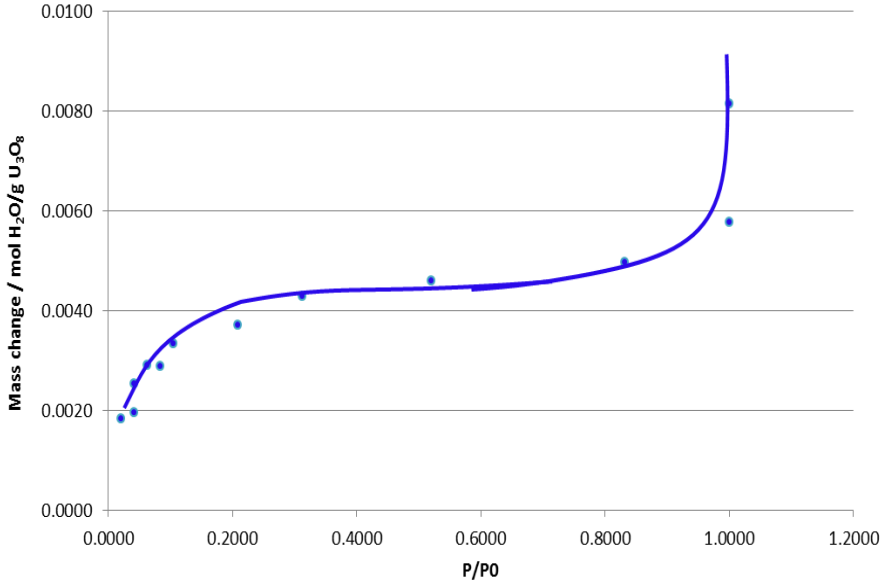
This gives a volume of 2.52 x 10^{-6} cm^3 and therefore a porosity of 35%.

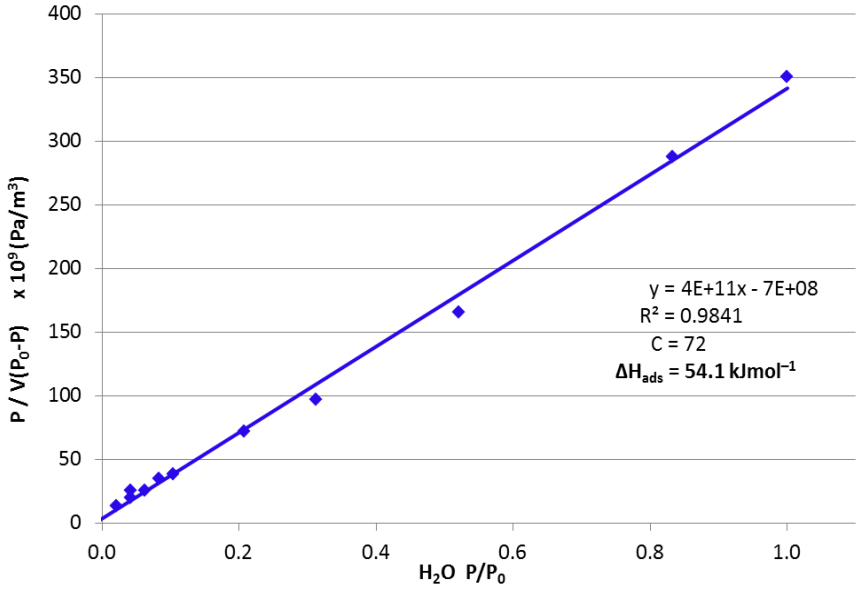


Urania films on $GaPO_4$ crystals: BET

The BET equation allows the volume of a monolayer and the enthalpy of absorption to be calculated:

$$1/\left[Va\left(\frac{P0}{P}-1\right)\right] = \left(\frac{C-1}{V_M C}\right)\left(\frac{P}{P_0}\right)+\frac{1}{VmC} \qquad C = e^{(\Delta H_{ads} - \Delta H_{liq}/RT)}.$$



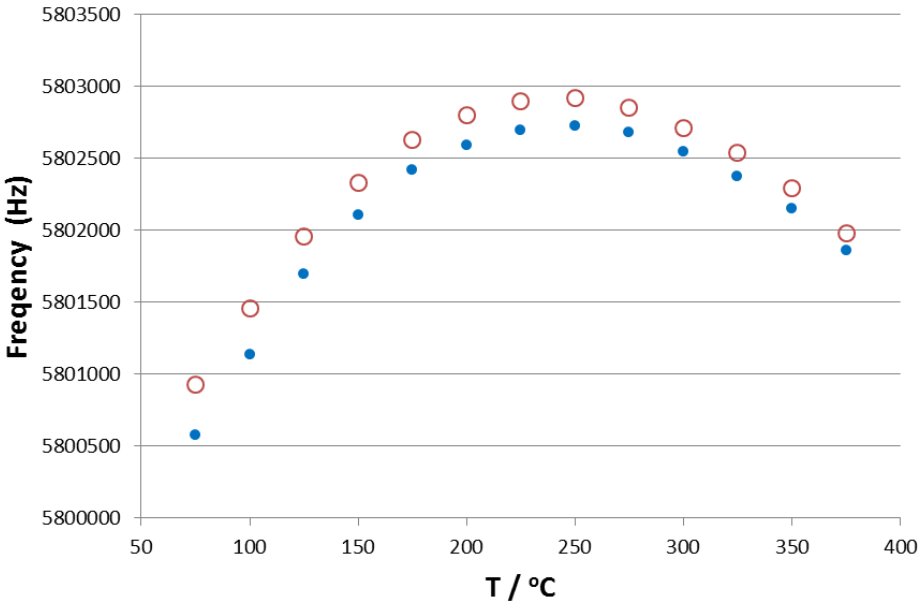


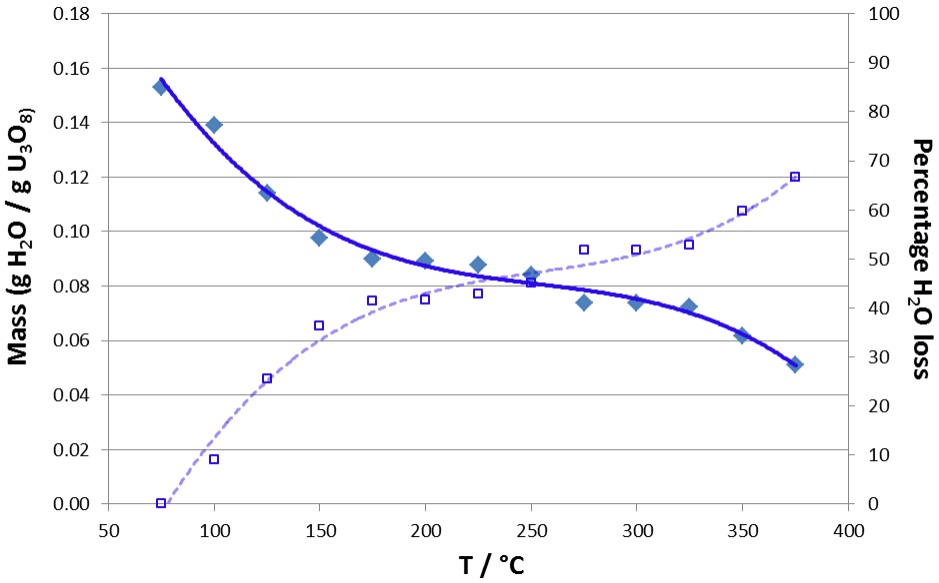
A plot of P/V(P_0-P) against P/P_0 gives an intercept of 1/VmC and a gradient of $(C-1)/(V_M C)$, therefore we can calculate:

V_m =	1.50 x 10^{-12} m^3	SA = 4.7 m^2g^{-1}	Calc.: 1000°C
ΔH_{abs} =	48.1 $kJmol^{-1}$	ΔH_{bind} = 6.5 $kJmol^{-1}$	
V_m =	3.10 x 10^{-12} m^3	SA = 8.92 m^2g^{-1}	500°C
ΔH_{abs} =	54.1 $kJmol^{-1}$	ΔH_{bind} = 12.5 $kJmol^{-1}$	

Urania films on $GaPO_4$ crystals: High Temperature

The BET equation allows the volume of a monolayer and the enthalpy of absorption to be calculated:





Conclusions

- Coated quartz piezocrystals with ceria and urania layers of different porosities. Analysed the morphology and thickness by SEM, AFM, XRF.
- Measured the absorption of water onto the ceria and urania films by direct mass analysis at different humidities.
- Calculated the surface area of the ceria and urania films, and the volume and number of absorbed monolayers at room temperature.
- Varied the temperature of the ceria-water systems, showing the desorprtion of water up to 400°C.
- Synthesis of thoria-coated $GaPO_4$ crystals.
- Increase the temperature of the systems, showing the desorprtion of water up to 500°C.

Acknowledgments

Lancaster University

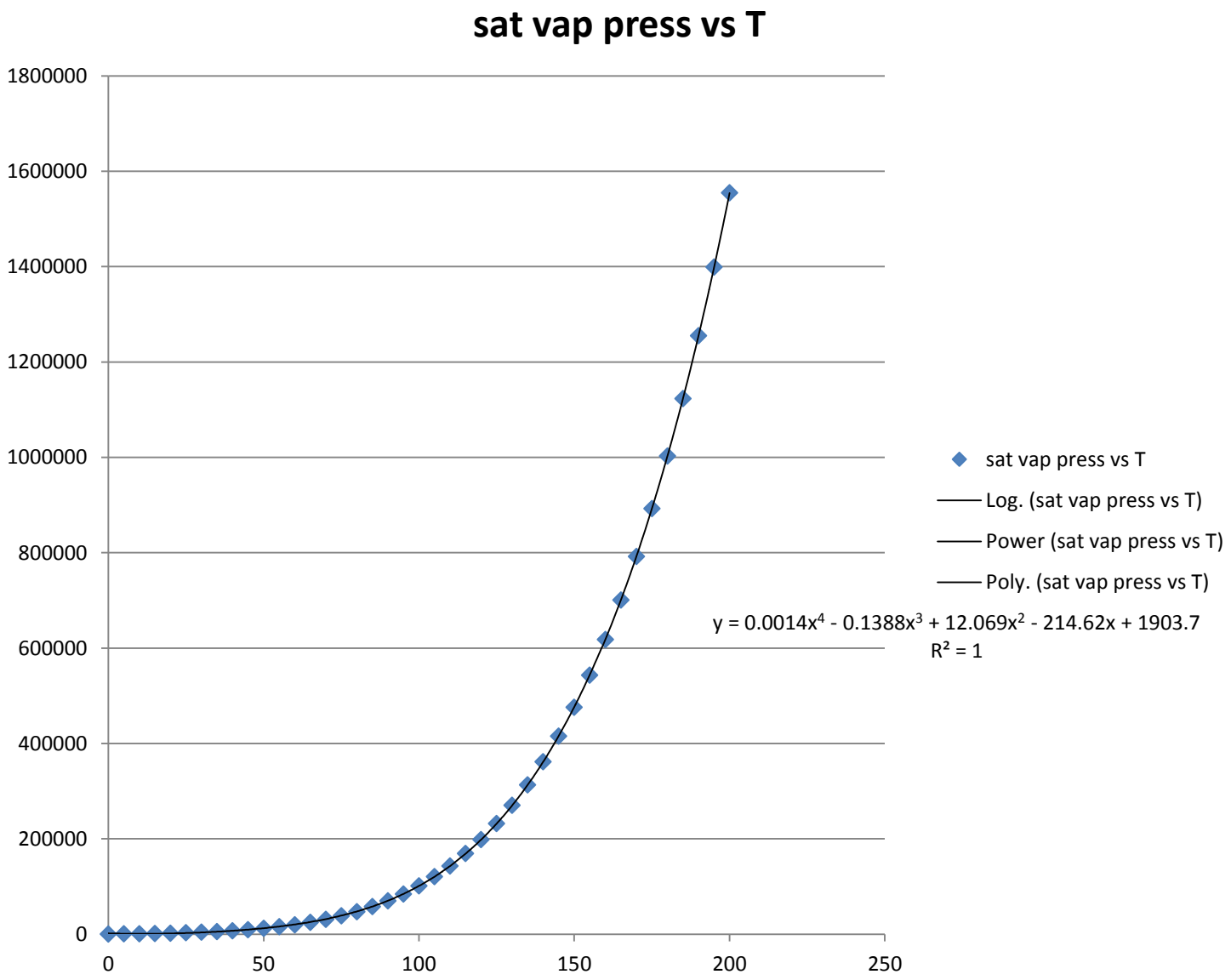
- Pat Murphy
- Richard Wilbraham
- Fabrice Andrieux

NNL

- Robin Taylor
- Robin Orr
- Dave Woodhead

Thanks for your attention

Saturated vapour pressure water



Nuclear Technologies

Choose certainty.
Add value.

The PhD after-life: Working for the supply chain

Dr Carlos De La Fontaine
DISTINCTIVE consortium – April 2017

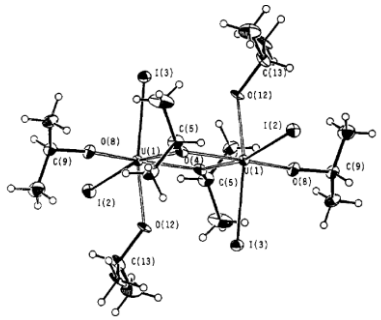
Content

Nuclear Technologies

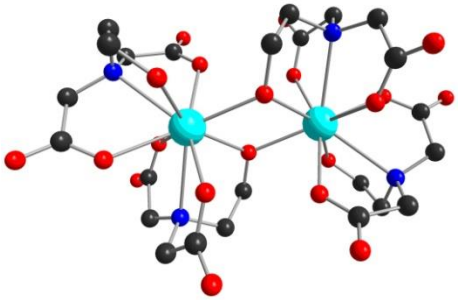
1. Background – insight on my PhD studies
2. Examples of careers in the nuclear industry
3. Drivers to join the supply chain
4. Brief overview of projects
5. Conclusion

Background – 'Controlled Hydrolysis and Solid State Chemistry: Two Approaches to the Synthesis of Actinide Oxide Materials'

Nuclear Technologies



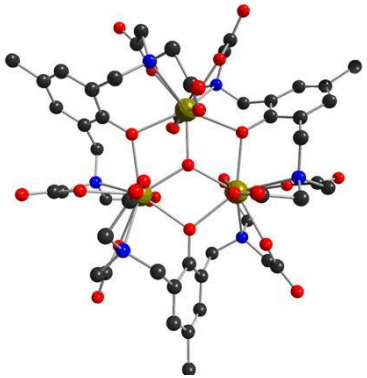
$U_2I_4(O\text{-}i\text{-}Pr)_4.(HO\text{-}i\text{-}Pr)_2$



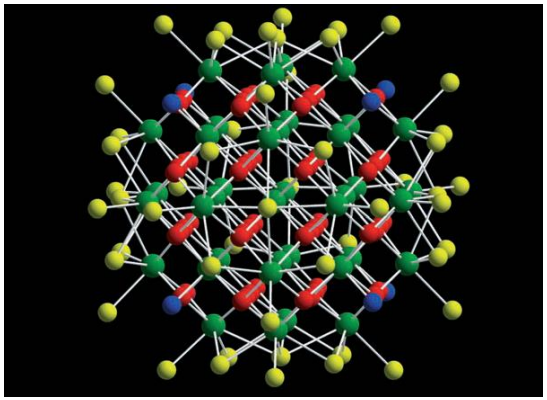
$[Th_2(C_6H_8NO_5)_4]^{4-}$

Ceramic wasteform

UO_2 fuel pellets



$[M_3O(C_{17}H_{17}N_2O_5)_3]^{5-}$ where
M = Th(IV) and U(IV)



Pu_{38} compound obtained by controlled hydrolysis[1]

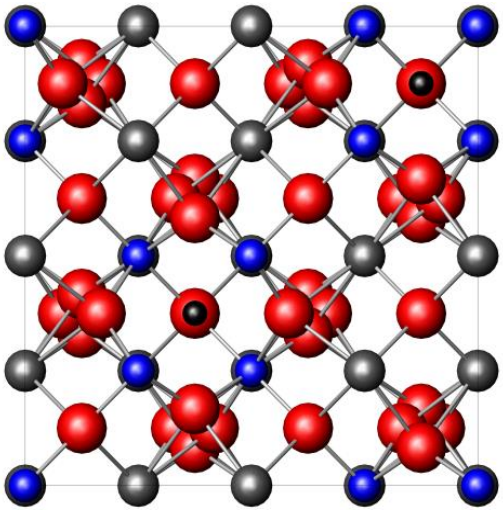
[1]L. Soderholm, Angew Chem. Int., 2008

Background – 'Controlled Hydrolysis and Solid State Chemistry: Two Approaches to the Synthesis of Actinide Oxide Materials'

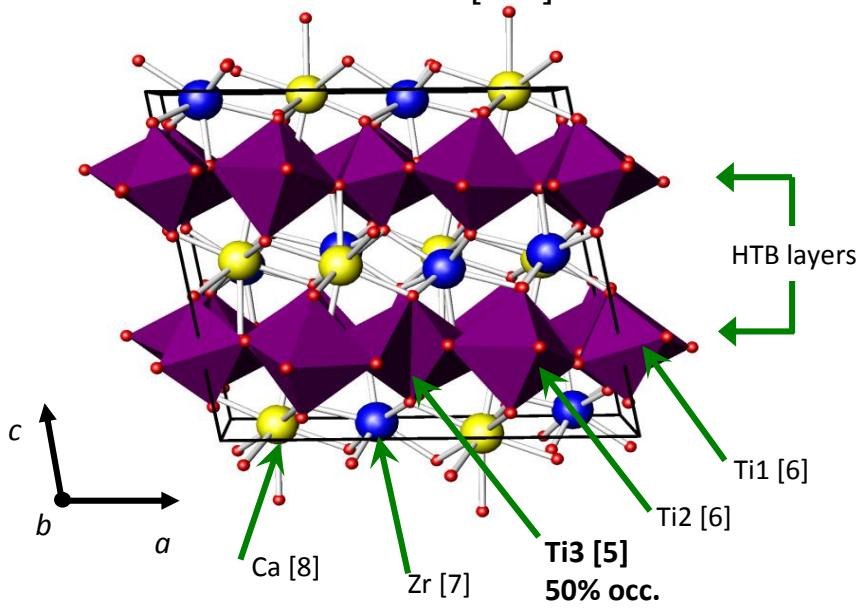
Nuclear Technologies

Side project at Sheffield University: Synthesis and characterization of new pyrochlore solid solutions for actinide immobilisation

Pyrochlore: $A_2B_2O_7$ (Fd-3m)



Zirconolite 2M [100]



Formulations studied:

$Y_2Ti_{2-2x}Fe_xNb_xO_7$

$Y_{2-x}Ce_xTi_{2-x}Fe_xO_7$

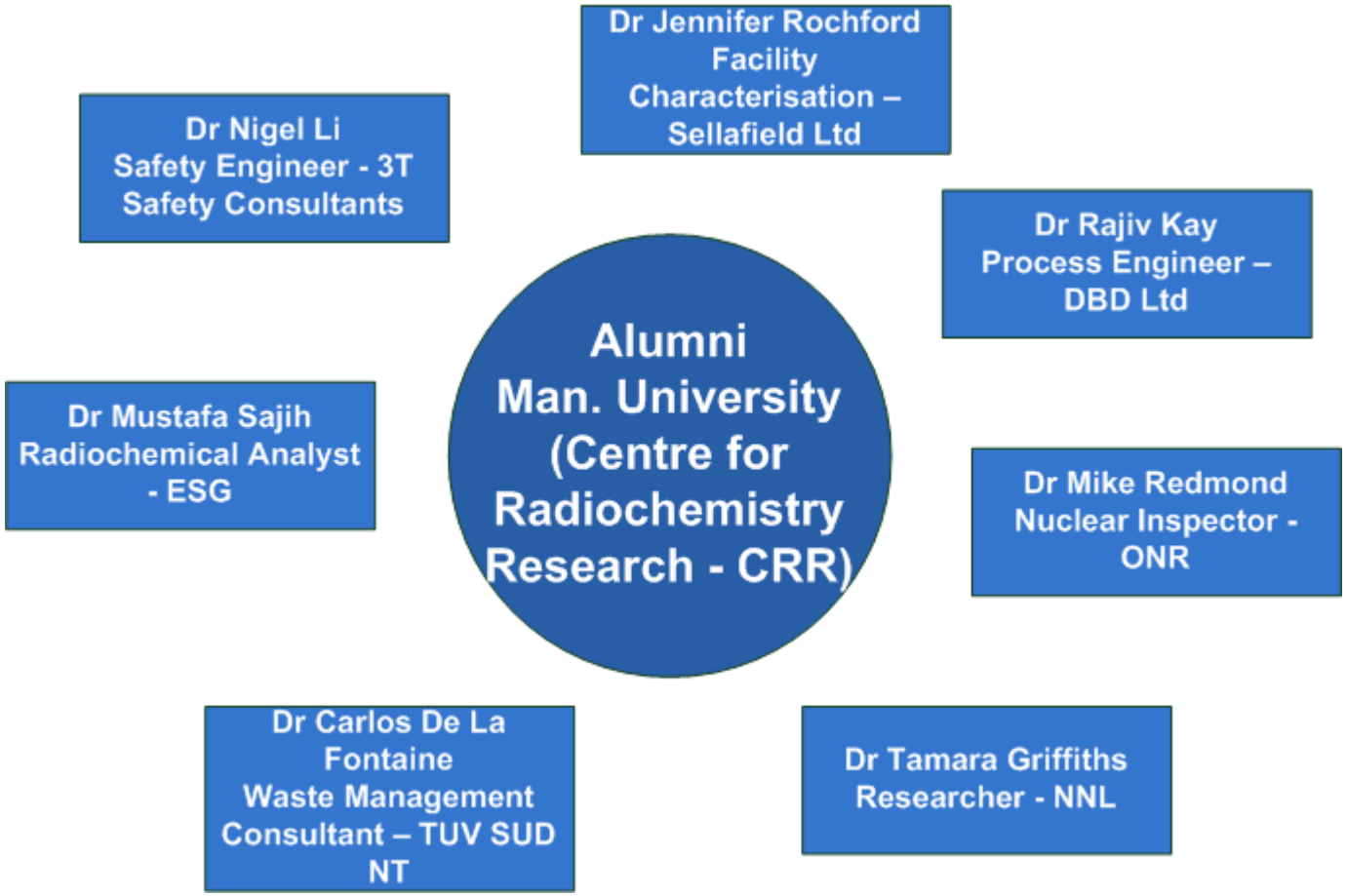
And what's next after your PhD ?

Nuclear Technologies

Examples of alumni from Manchester Uni.

Nuclear Technologies

Alumni that graduated between 2010 – 2013...



Why join the supply chain ?

Nuclear Technologies

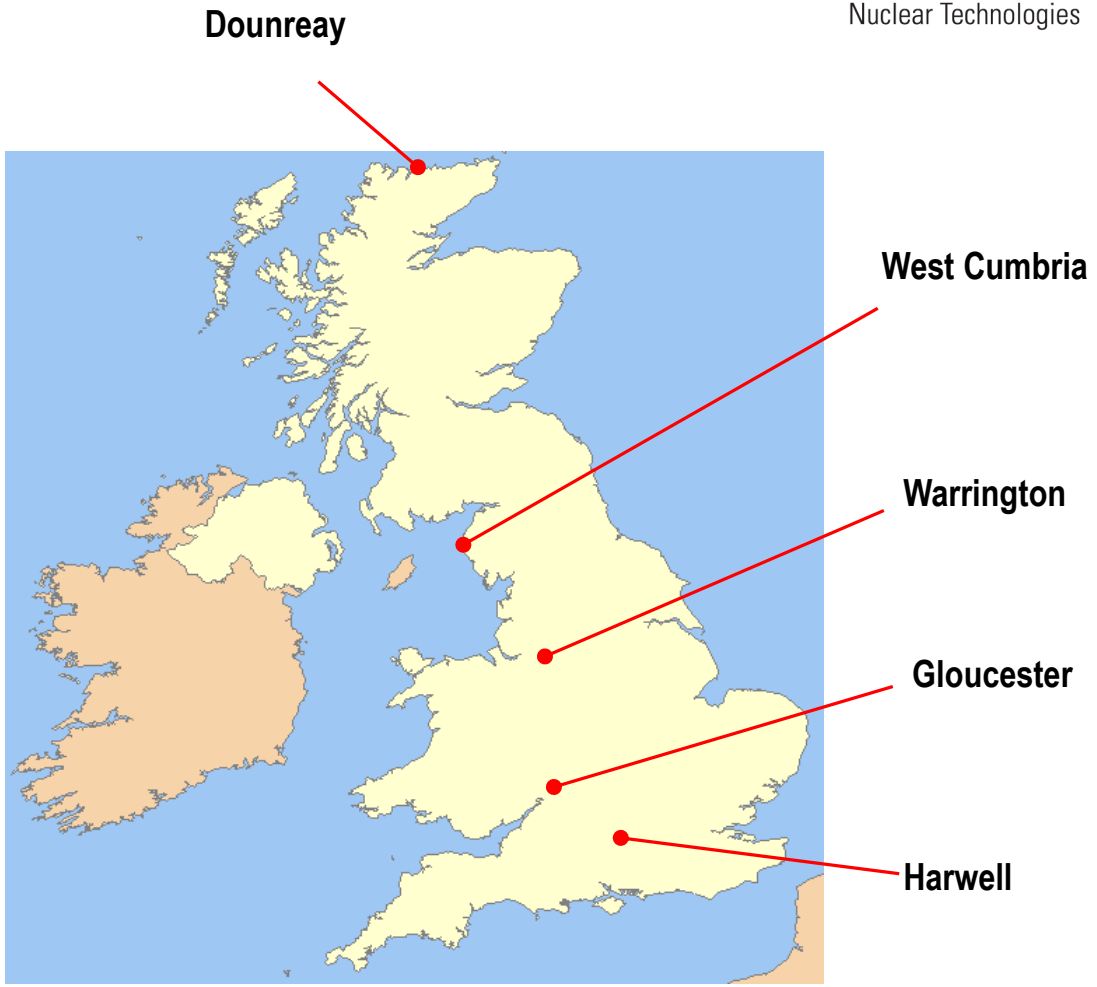
Consultancy...
Broad range of tasks within a relatively short timescale

- Variety of technical work
  - » Process Engineering, Radioactive Waste Management, Optioneering studies, Structuring R&D programmes, Market Reviews, Knowledge Management...
- Work in different sites
  - » Sellafield, La Hague, Magnox, GDF (both on the French & British projects)...
- Commercial
  - » Preparation of bids, production of ITTs and task specifications, review of proposals
- Business awareness
  - » Business development in the UK and abroad (mainly the French market), recruitment

TUV SUD Nuclear Technologies

Nuclear Technologies

- Consultancy specialised in the nuclear industry
- Company funded in 1994
- Acquired by TÜV SÜD in (2006)
- ~100 Staff/Associate Staff in UK



Why do Site Licence Companies (SLCs) award contracts to the supply chain?

Nuclear Technologies

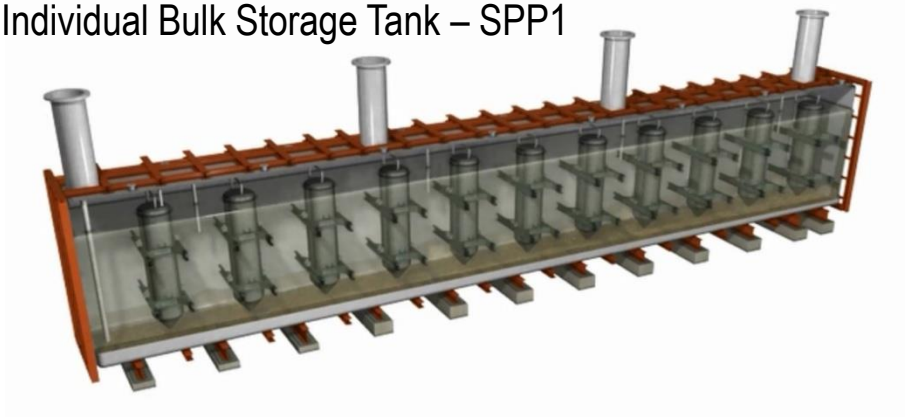
- Lack of expertise in a particular area
- Independent view – Peer review
- Resource constraints
- Enable innovation ...
- And many more reasons

Variety of technical work

Nuclear Technologies

Process Engineering – Support to the Sludge Packaging Plant 1 (SPP1)

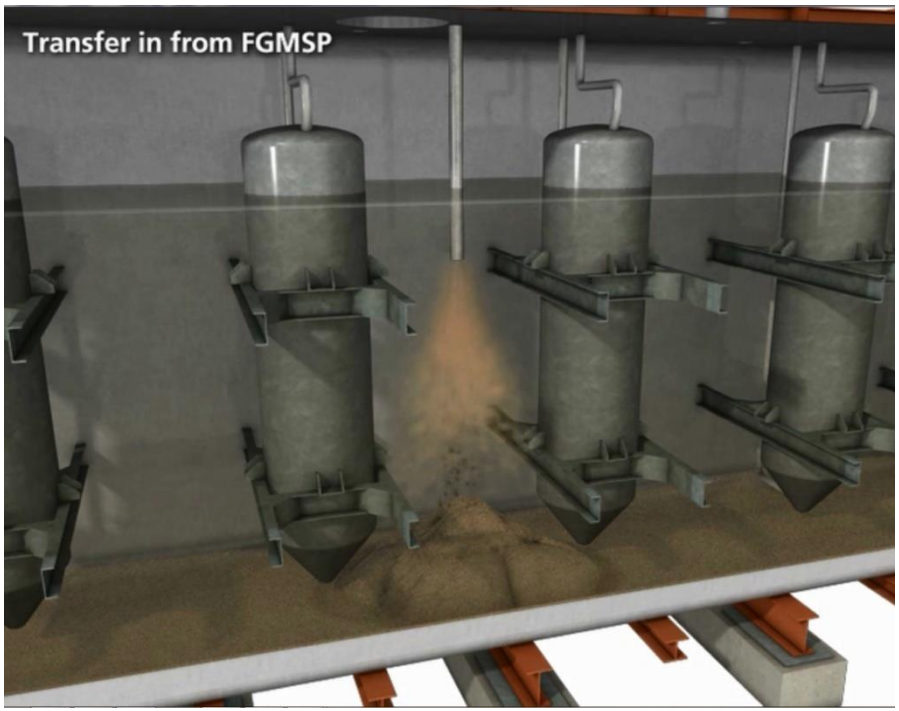
Individual Bulk Storage Tank – SPP1



- R&D conducted on ½ and ¼ scale pilot plants mimicking SPP1

- Engineering support and underpinning technology performance

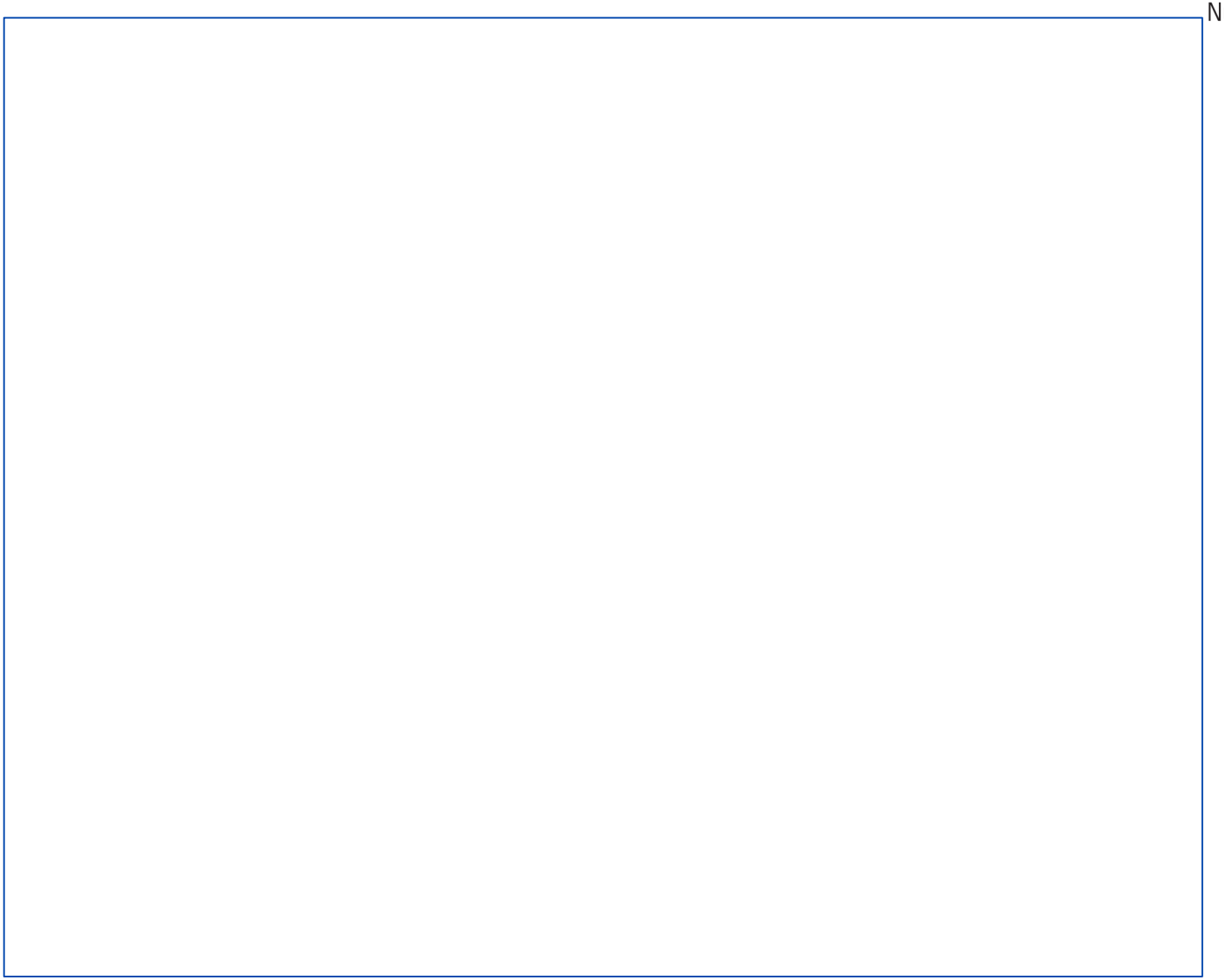
Pulse Jet Mixers



Variety of technical work (2)

Nuclear Technologies

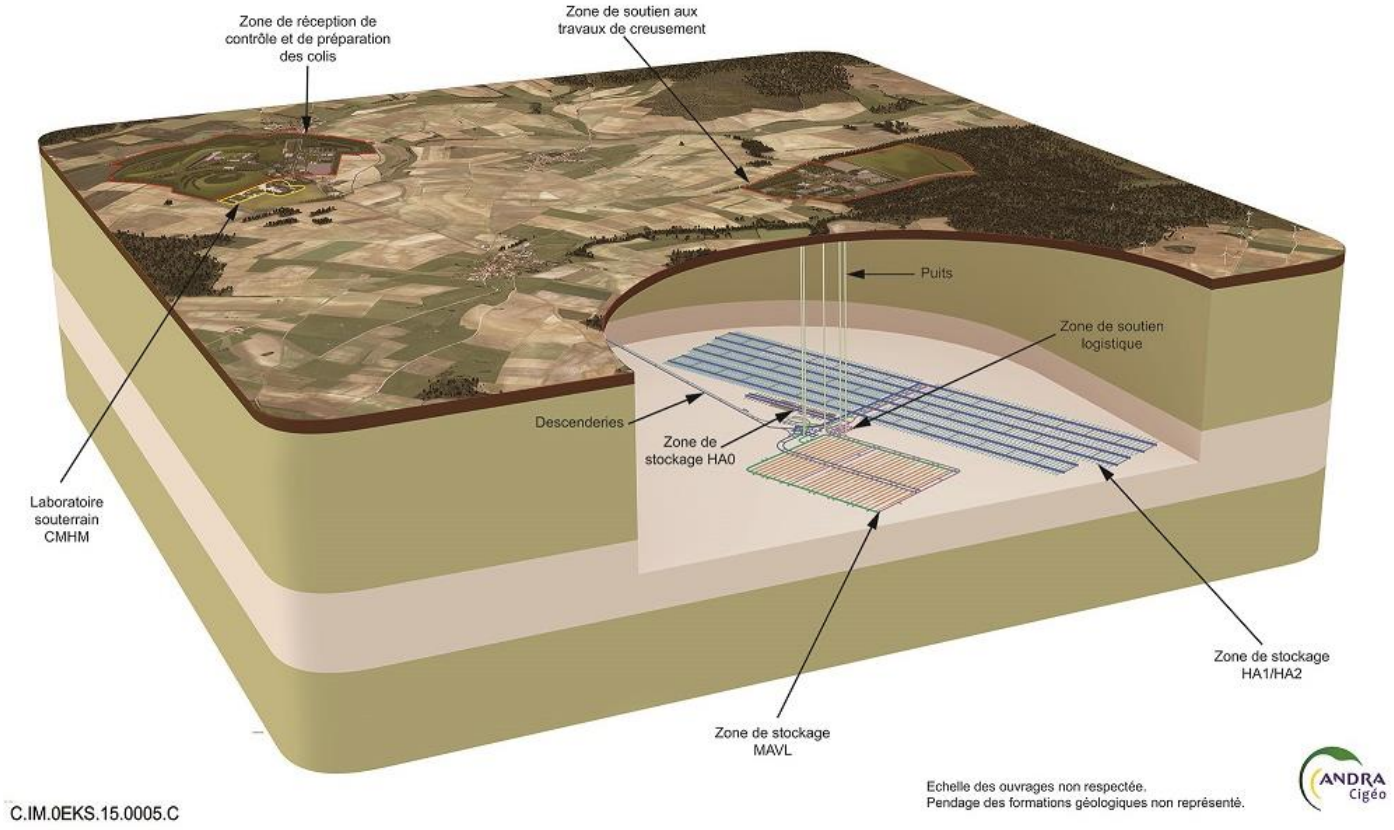
Process Engineering – Support to the Sludge Packaging Plant 1 (SPP1)



Variety of technical work (3)

Cigéo – Centre Industriel de Stockage Géologique – French GDF

Nuclear Technologies

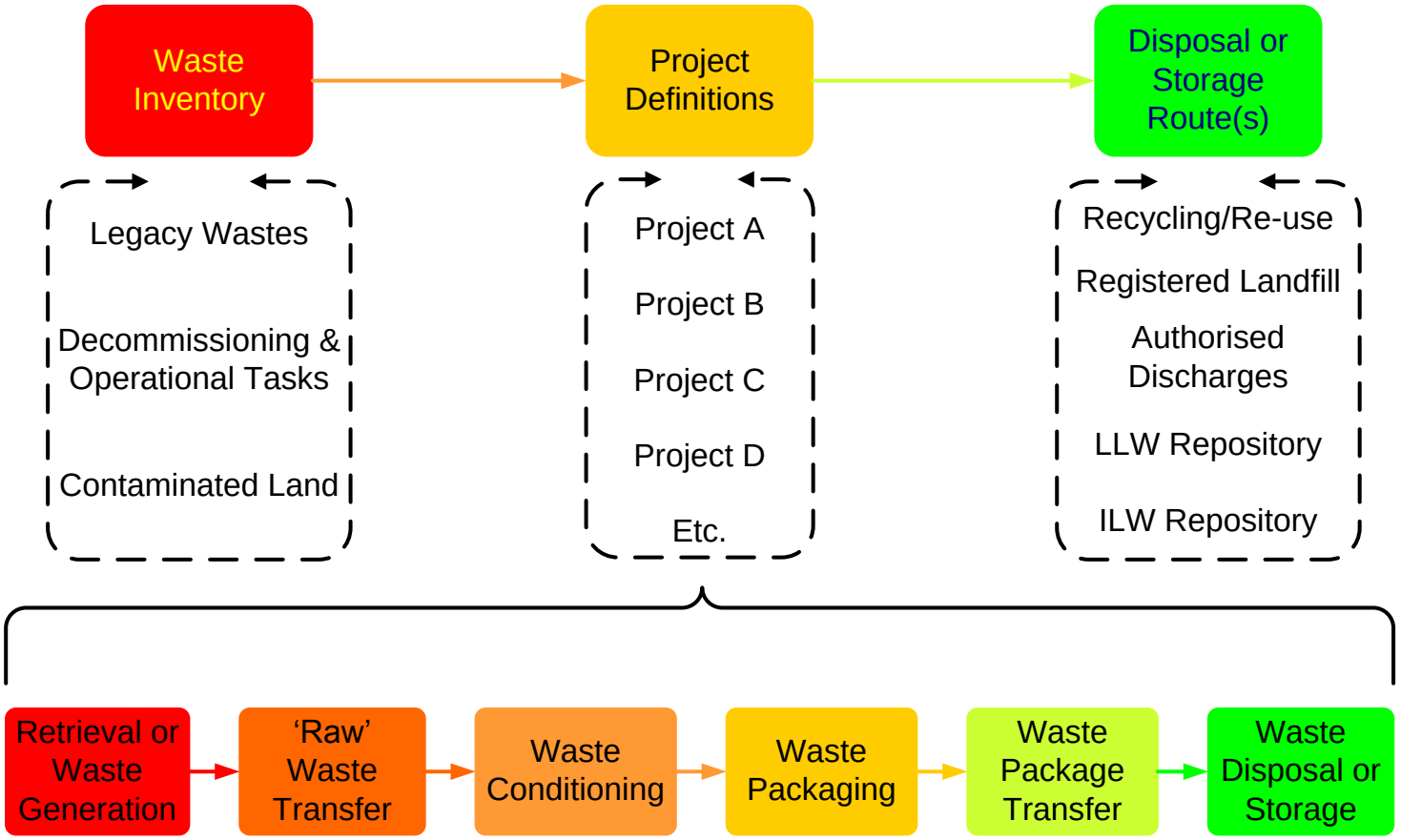


Peer-review of preliminary studies and early design of the French GDF

Variety of technical work (4)

Nuclear Technologies

Radioactive Waste Management – Waste Led Approach

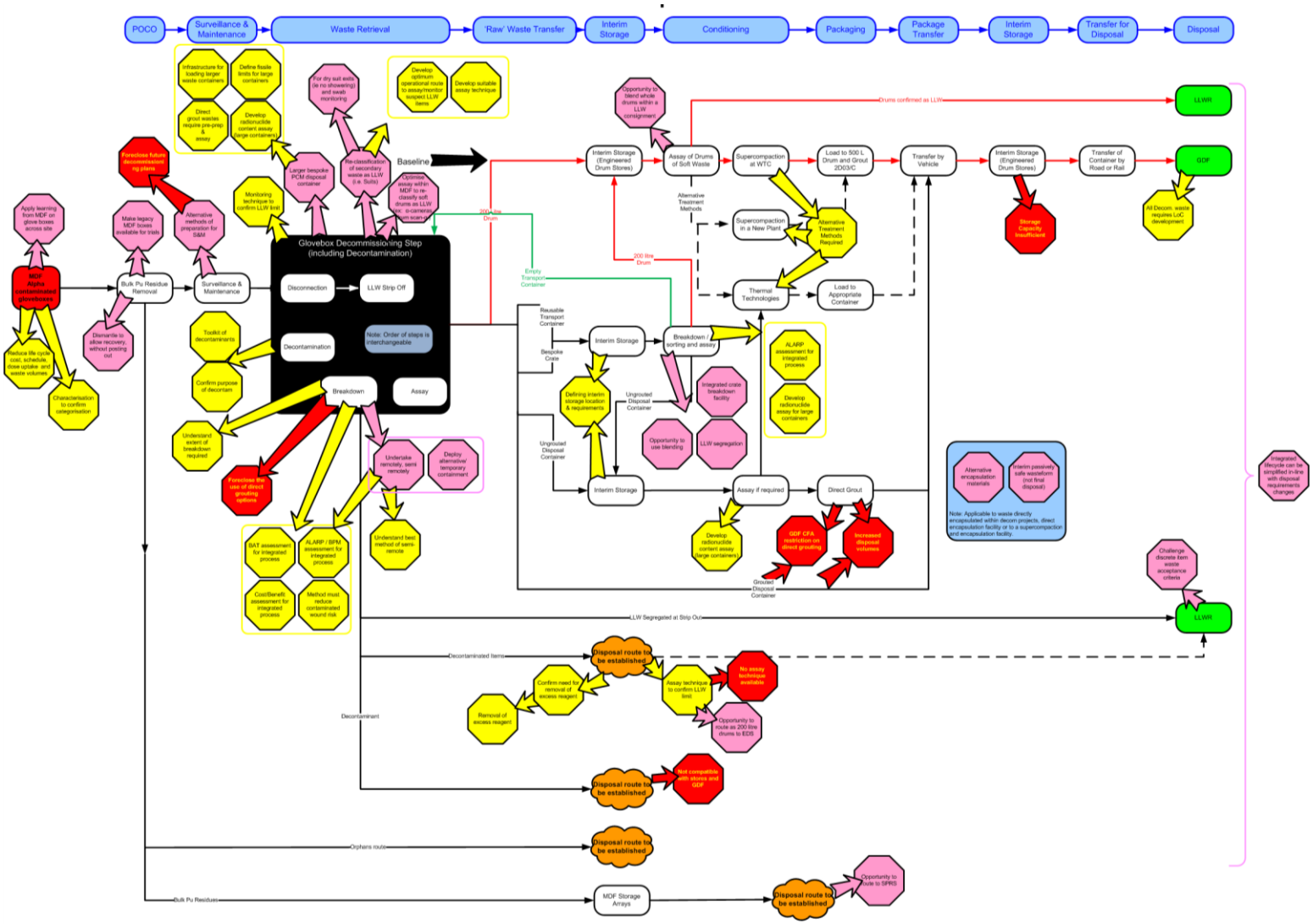


Examples: Orphan wastes (across the NDA estate), Aged TBP/OK (DSRL), Sludge - Flocs (La Hague), alpha contaminated gloveboxes (Sellafield) , Characterisation of sludge in RST (Sellafield)...

Variety of technical work (5)

Radioactive Waste Management – Waste Led Approach

Nuclear Technologies



Variety of technical work (6)

Strategy – Spent Fuel Management

Nuclear Technologies

- Technical support to the NDA on Fuel Management (Magnox, AGR, Exotics)

  - Support the development of the Spent Fuel strategy (review of baseline options, contingency plans, identifying gaps, production of Technical Roadmaps)
  - Support engagement with stakeholder
  - Production of task specifications and review of proposals

AGR sub-assembly

Conclusions

Nuclear Technologies

Just one of many profiles amongst former nuclear graduates...

Many opportunities within a growing industry...!

Any questions

carlos.delafontaine@tuv-sud.co.uk

Switching on Ion Exchange in Metal Germanates

Ryan George
School of Chemistry, University of Birmingham

Distinctive 2017 – 3rd Annual Meeting
5th-6th April
York

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Introduction

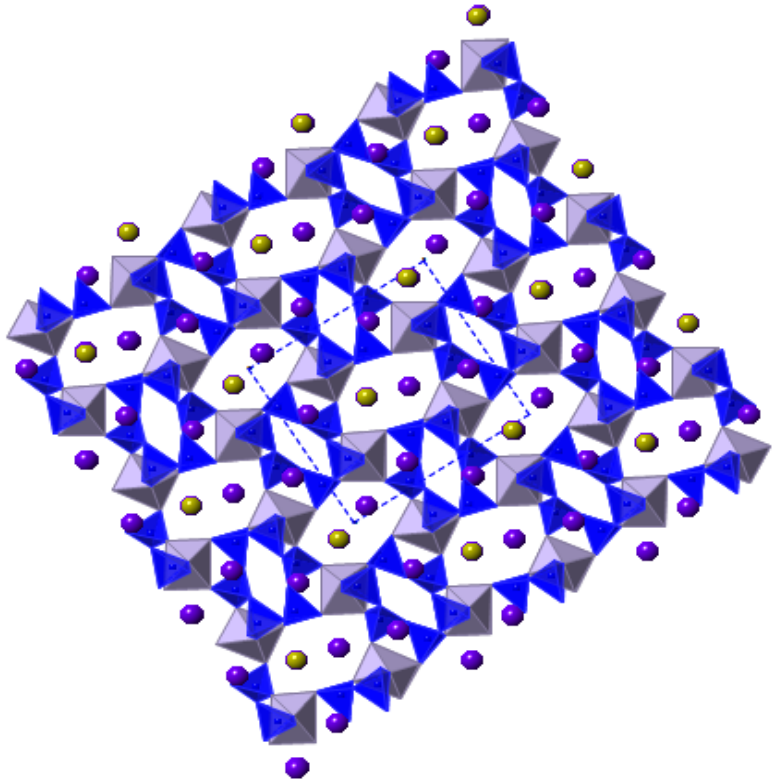
- Target ^{137}Cs and ^{90}Sr (Fission yields 4.5-6%, Half life ca 30 years).
- Both radionuclides are highly mobile and can be easily incorporated into the body.
- Design Principles
  - High thermal and chemical stability.
  - Potential thermal conversion to wasteform.
  - Medium sized pores (6-8 ring pore openings).
  - Hydrated cations located in channels, exchange K^+ for Na^+/H^+.

Research Councils UK Energy 2 For a Low Carbon Future

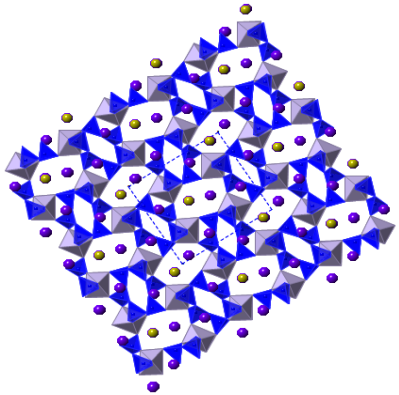
DISTINCTIVE

Octahedral-tetrahedral frameworks

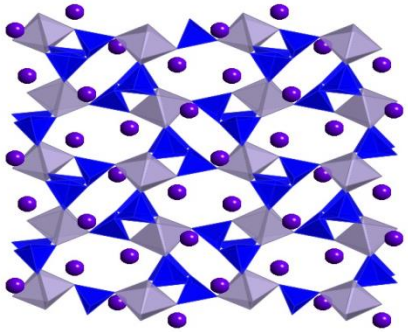
- Some of these materials are naturally occurring.
- A wide range of materials have been synthesised with various different metal octahedra and Si tetrahedra.
- These materials are microporous and have hydrated cations in the channels, commonly sodium and potassium. Hence the interest as potential ion exchange materials.



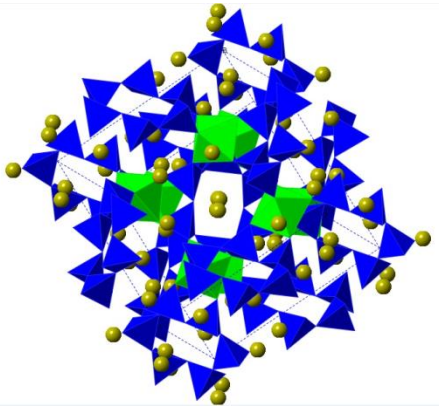
OT frameworks



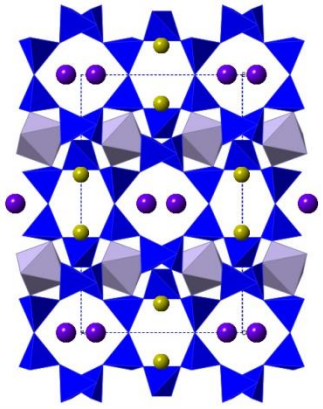
AV-7: $Na_{0.5}K_{1.5}SnSi_3O_9.H_2O$



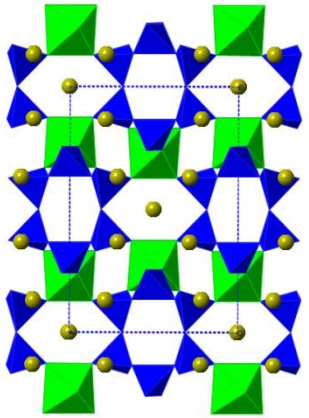
AV-6: $K_2(Sn/Zr/Ti)Si_3O_9 \cdot H_2O$



AV-13: $Na_{2.26}(Sn/Zr/Hf)Si_3O_9Cl_{0.26}.xH_2O$



EMS-2: $Na_4K_4Sn_4Si_{20}O_{52}.12H_2O$



AV-3: $Na_5Zr_2Si_6O_{18}(Cl,OH) \cdot 2H_2O$

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Ge vs Si

- Most of the published work covered focuses on changing the octahedral metal ion.
- Variation of the tetrahedral component may allow for further tunability.

Element	CN	Ionic radius
Si^{4+}	4	0.26 Å
Ge^{4+}	4	0.39 Å

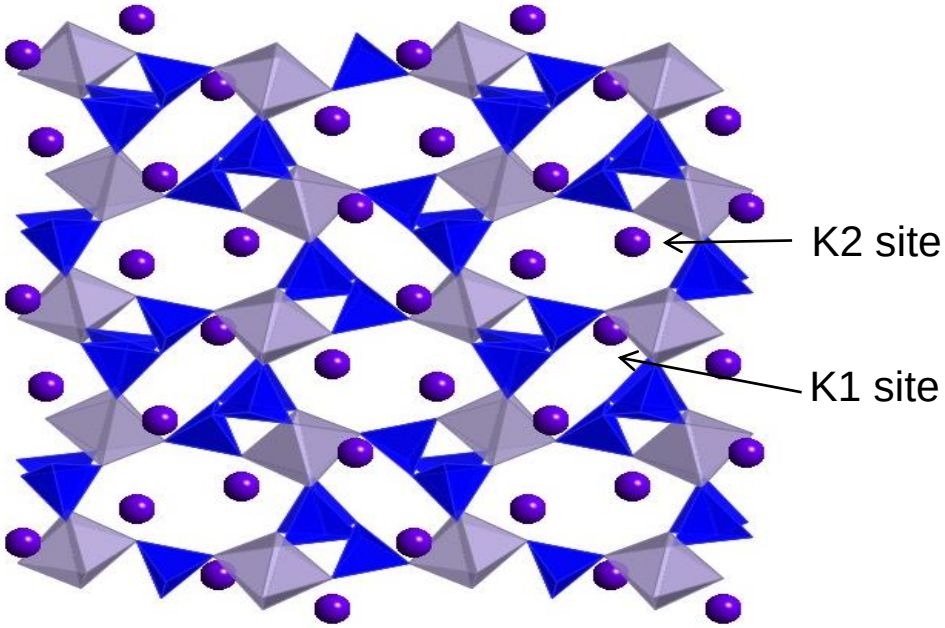
OT Germanate phases

- Small number of microporous germanates are known.
- First phase of interest is $K_2ZrGe_3O_9.H_2O$, originally reported by Plevert *et al*., *Inorg. Chem*, 2003, **42**, 5954-5959.
- This is a germanate derivative of the natural zirconosilicate mineral Umbite.
- Ion exchange properties not explored in the literature.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Umbite type materials



- $K_2MSi_3O_9.H_2O$ where M = Ti, Sn and Zr are all known with ion exchange properties explored.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

$K_2ZrGe_3O_9.H_2O$

- Hydrothermal synthesis optimised to produce multigram quantities (ca. 80% isolated yield) from GeO_2, $ZrOCl_2.8H_20$ and KOH at 200°C for 24 hours.
- Plevert *et al* recipe would yield around 0.3g per batch with a longer synthesis time.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

$K_2ZrGe_3O_9.H_2O$ Ion exchange

Element	Molar ratio	Molar ratio	Molar ratio
Ge	1	1	1
Zr	0.50	0.37	0.48
K	0.60	0.44	0.54
Sr	-	-	0.01
Cs	-	0.02	-

- Exchange using 0.1M Cs^+ or Sr^{2+} solutions with a 100:1 volume to weight ratio, shaken for 24 hours at ambient temperature. XRF analysis on loose powders.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Nb substitution

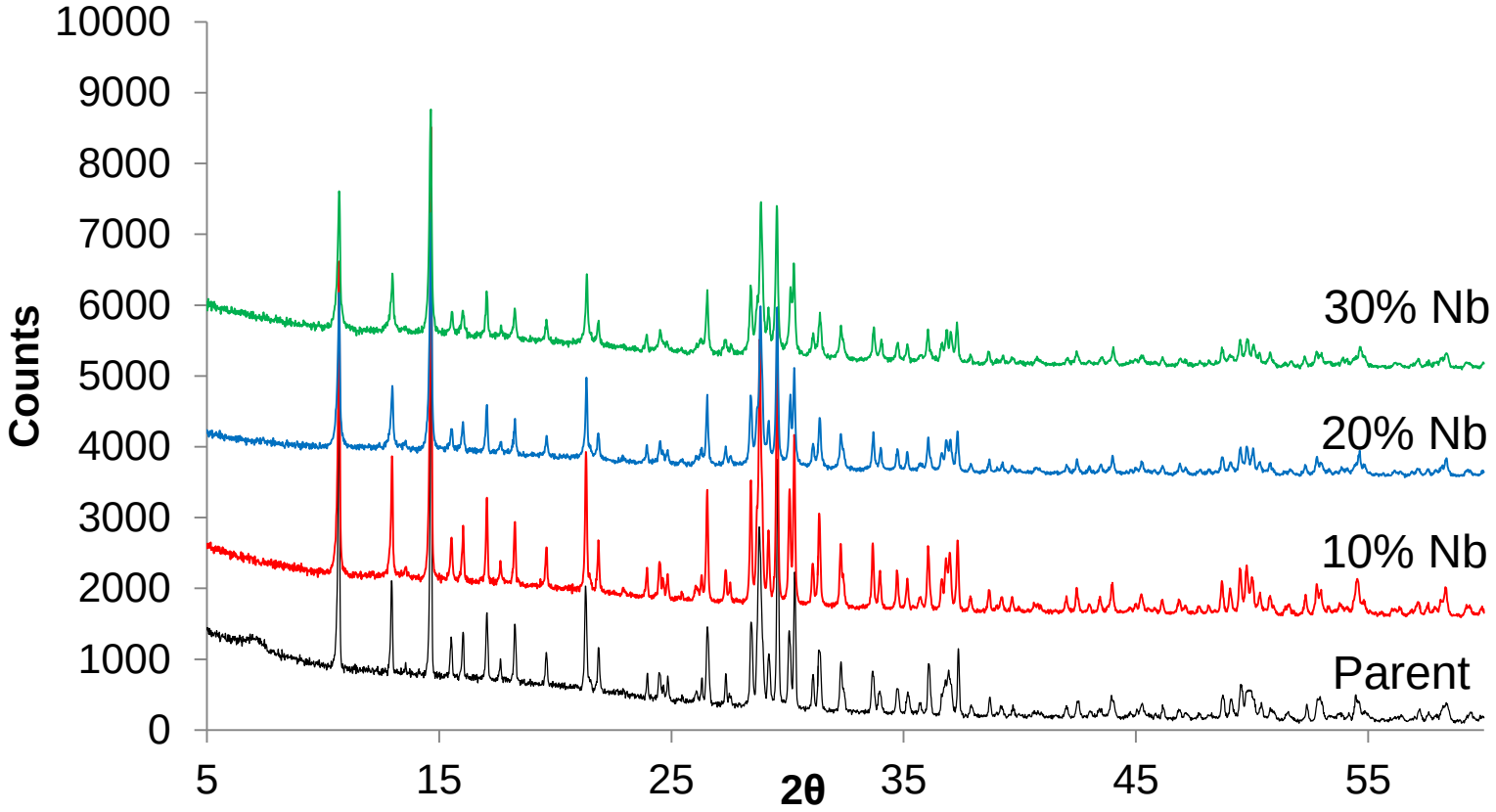
Element	CN	Ionic radius
Zr^{4+}	6	0.72 Å
Ti^{4+}	6	0.605 Å
Sn^{4+}	6	0.69 Å
Nb^{5+}	6	0.64 Å

- $Nb^{5+} \longrightarrow Zr^{4+} + K^{+}$
- Single phase up to 30% Nb^{5+} for Zr^{4+}

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Nb substitution



Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

$K_{2-x}Zr_{1-x}Nb_xGe_3O_9.H_2O$ Ion exchange

	10% Nb	20% Nb	30% Nb
Element	**Molar ratio**	**Molar ratio**	**Molar ratio**
Ge	1	1	1
Cs	0.29	0.37	0.63
Zr	0.37	0.33	0.30
K	0.38	0.33	0.25
Nb	0.04	0.08	0.11

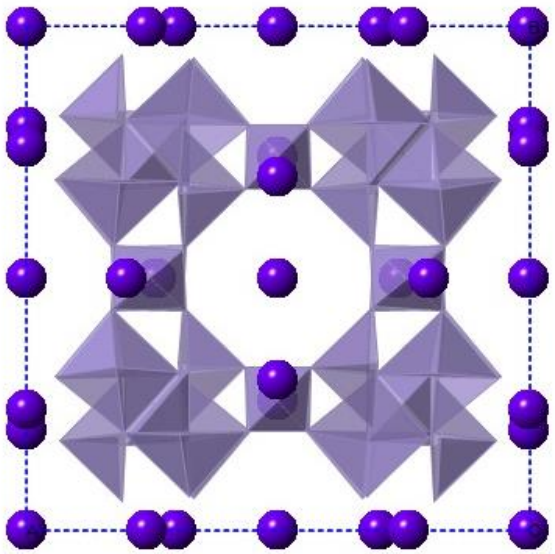
- XRF analysis on loose powders

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

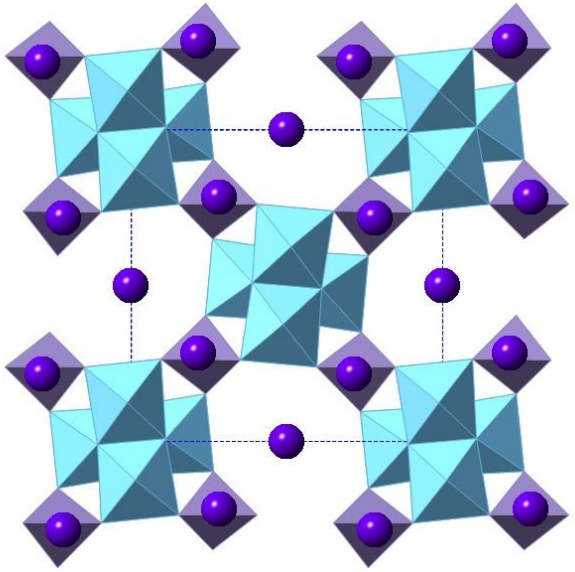
Pharmacosiderites

- Sn, Ti substitutions and Nb 40% doping result in the formation of pharmacosiderite phases.



$HK_3Ge_7O_{16}.4H_2O$

Sn and 40% Nb as impurity



$HK_3Ti_4Ge_3O_{16}.4H_2O$

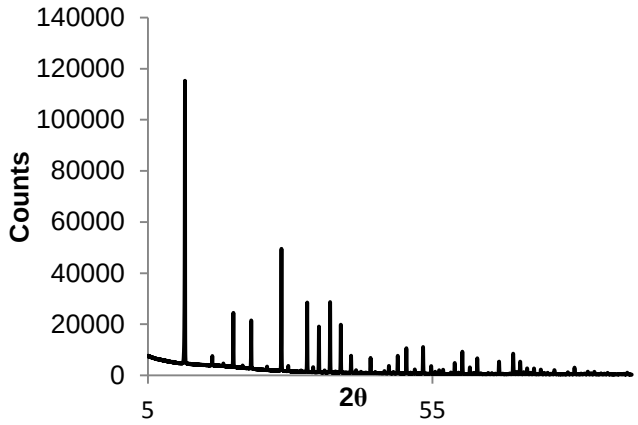
Ti source

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

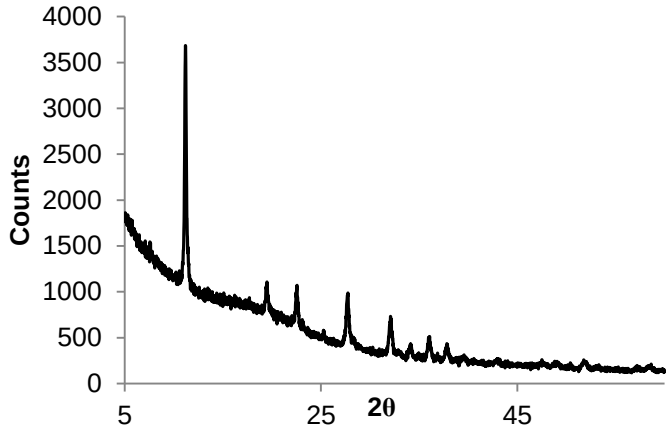
Pharmacosiderites

$HK_3Ge_7O_{16}.4H_2O$



	Parent	Cs	Sr
Element	**Molar ratio**	**Molar ratio**	**Molar ratio**
Ge	1	1	1
K	0.47	0.18	0.44
Sr	-	-	0.03
Cs	-	0.38	-

$HK_3Ti_4Ge_3O_{16}.4H_2O$



	Parent	Cs	Sr
Element	**Molar ratio**	**Molar ratio**	**Molar ratio**
Ge	1	1	1
Ti	1.12	1.08	1.13
K	0.86	0.21	0.29
Sr	-	-	0.28
Cs	-	1.05	-

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Summary

- Substitution of Ge for Si in the umbite structure does not improve ion exchange properties.
- Ion exchange can be switched on by doping Nb^{5+} for Zr^{4+}, with facile Cs^{+} uptake in $K_{2-x}Zr_{1-x}Nb_xGe_3O_9.H_2O$.
- Other framework substitutions result in the formation of pharmacosiderite phases, which have also been shown to be good exchangers.

Further work

- Further explore pharmacosiderite ion exchange, with potential further chemical modification.
- Measuring K mobility.
- Studying thermal decomposition products of umbite.
- Studying sodium exchange in ZrGeUmbite.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Acknowledgements

- Dr Joe Hriljac
- Dr Tzu-Yu Chen

EPSRC
Engineering and Physical Sciences Research Council

UNIVERSITY OF BIRMINGHAM

investing in your future
European Regional Development Fund
European Union

Advantage West Midlands
www.advantagewm.co.uk

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Characterization of cement based materials through atomic force microscopy

Luca Rizzo
University of Strathclyde

Distinctive Annual Meeting
5/04/2017
National Railway Museum - York

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Structure

1. Introduction to Atomic Force Microscopy

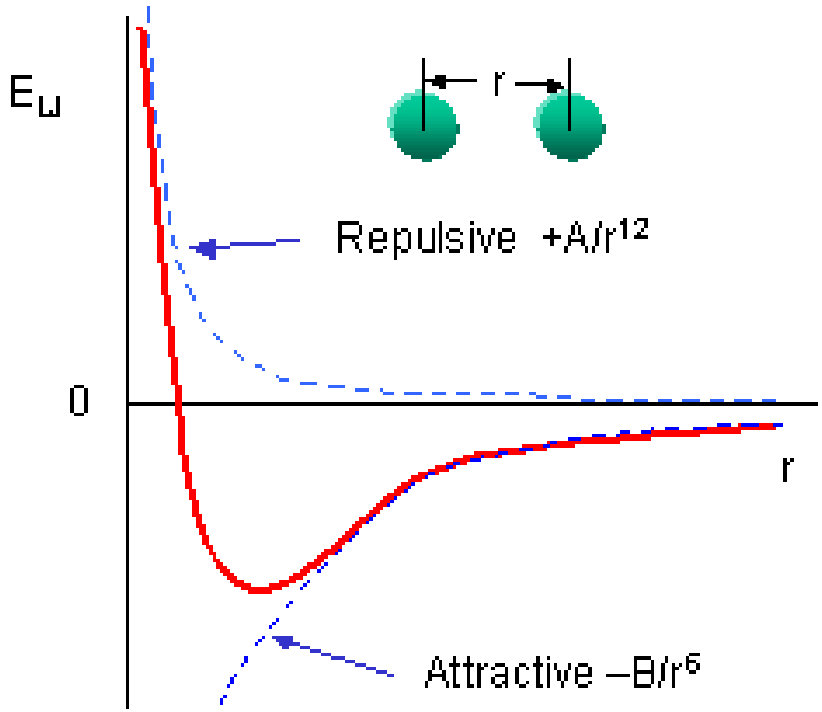
2. AFM/lab experiments

3. Further projects

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Atomic Force Microscopy

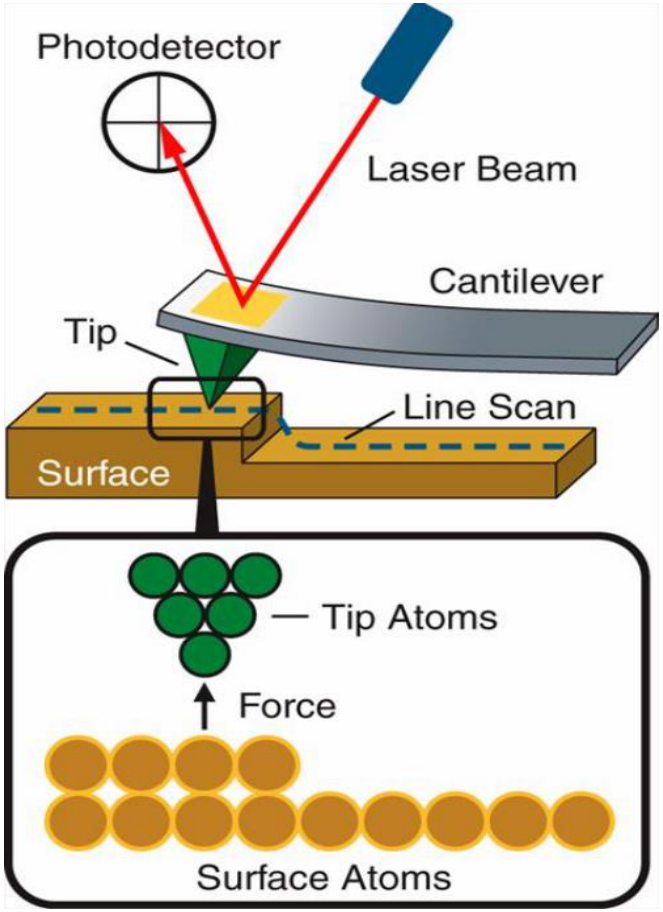


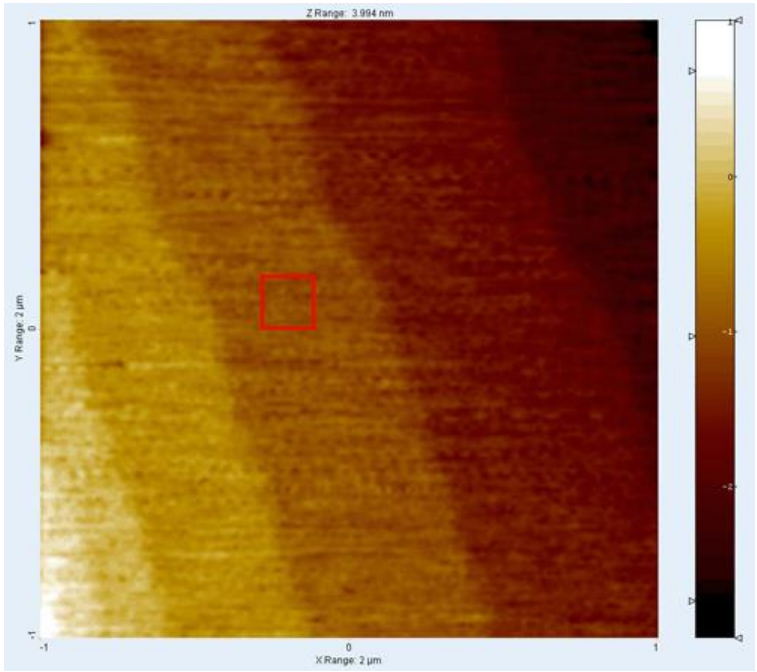
Lennard Jones potential energy diagram

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Atomic Force Microscopy





2D topographic image

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM topography

Modes of operation. There are 3 modes of AFM operation

1. Contact mode
2. Non-contact mode
3. Tapping mode

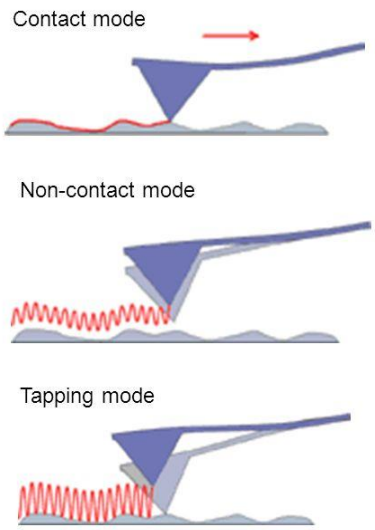
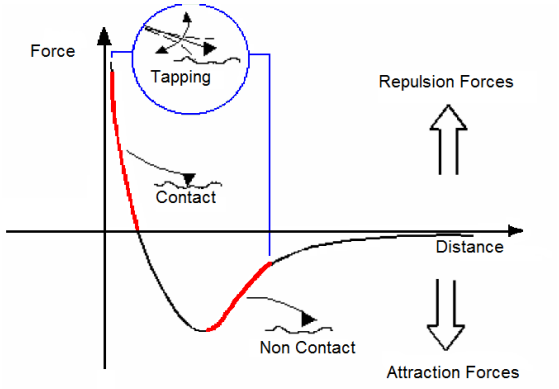


Fig. 7.3 Modes

1. Contact mode and lateral force microscopy (static)
2. Frequency modulation (dynamic)
3. Tapping mode (dynamic)

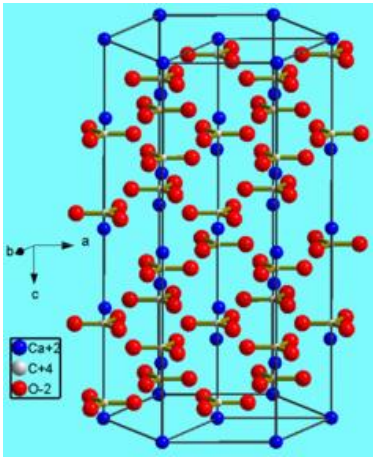


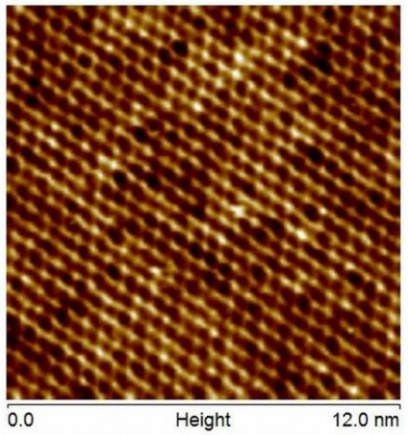
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

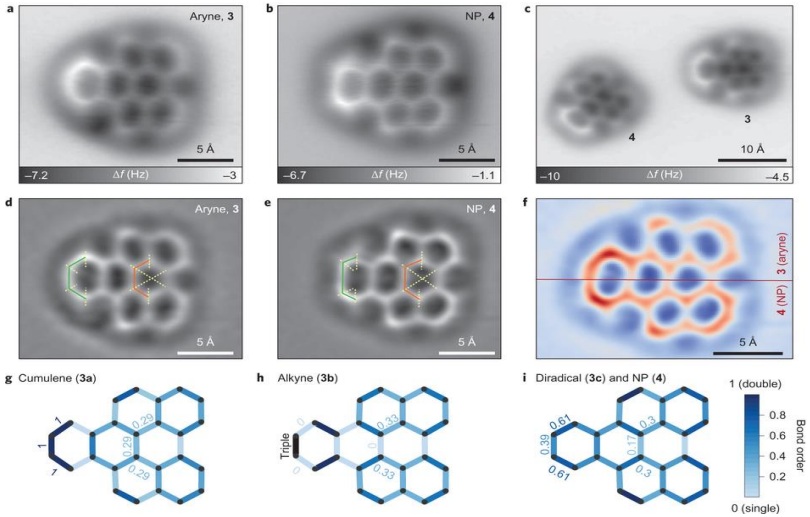
Atomic Resolution

Calcite





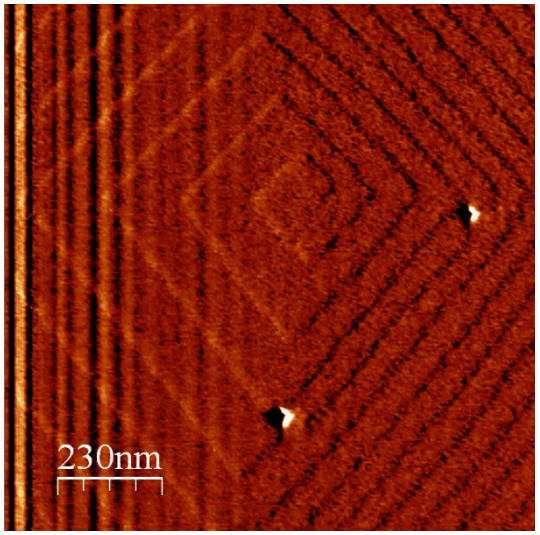
Aromatic Compounds (UHV-AFM)



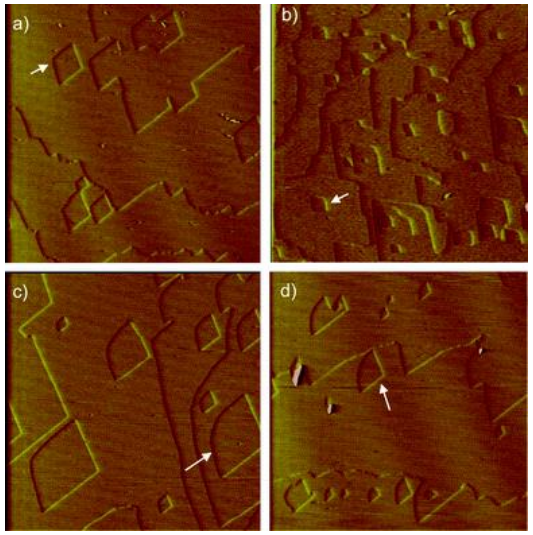
Research Councils UK
Energy
For a Low Carbon Future

In situ reaction: in air (gas), and in liquid

Example: crystal growth(spiral) and dissolution(layer by layer) of Calcite



$CaCO_3$ supersaturated solution



DI water

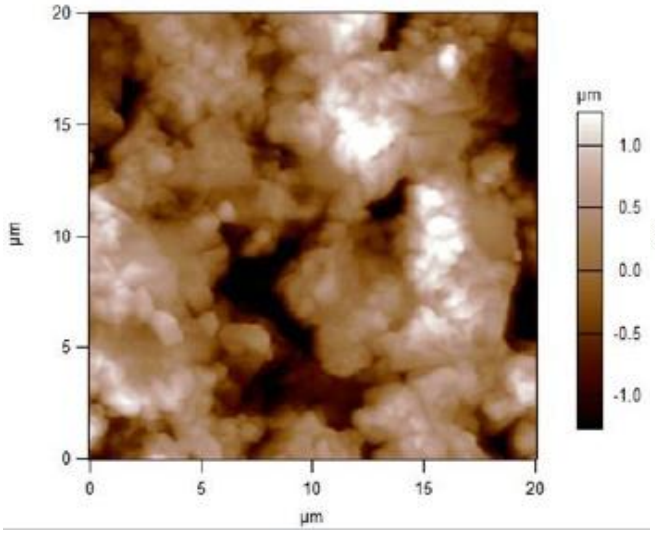
Research Councils UK Energy For a Low Carbon Future

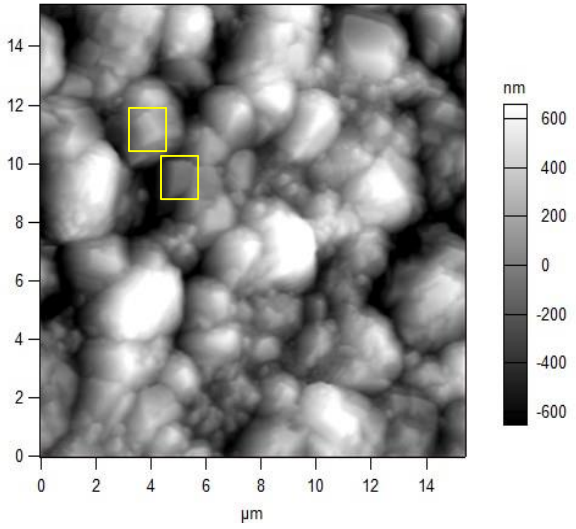
DISTINCTIVE

AFM tests: cement pastes

Comparison between Nano Silica(left) and Silica Fume(right) reactivity with Calcium Hydroxide (Tapping mode in air)

$Ca(OH)_2 + SiO_2 + H_2O \rightarrow$ C-S-H





Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests: cement pastes

Cement pastes preparation trough MICA replication method at different temperature to evaluate its effect on surface roughness.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests:

Interaction between strontium and calcite

Strontium 90 SR-90 half life 28.79 years

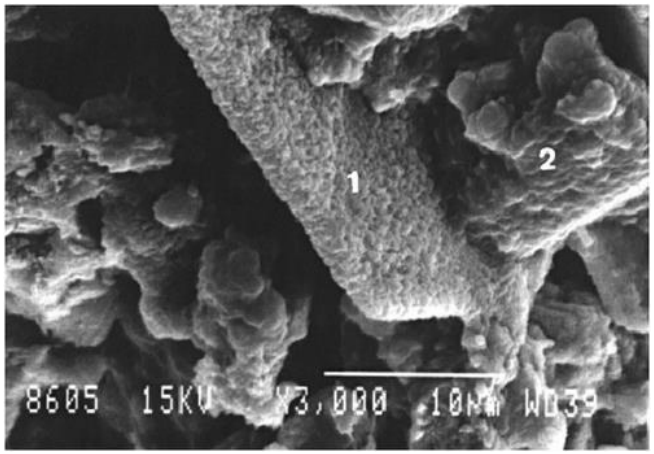
↓ β^- decay 0.546 MeV

Yttrium 90 Y-90 half life 64 hours

↓ β^- decay 2.28 MeV

Zirconium 90 Zr-90 Stable

$$Ca(OH)_2 + CO_2 \Rightarrow CaCO_3 + H_2O$$



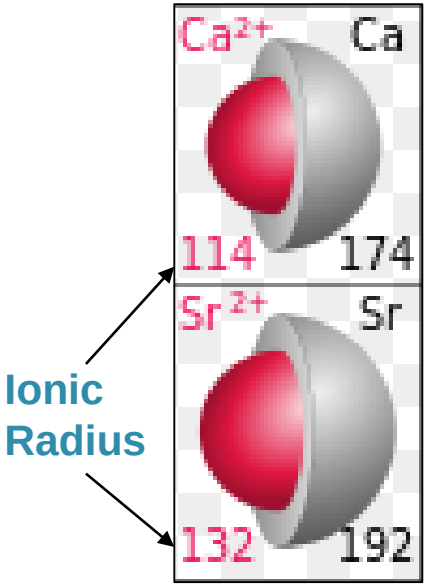
SEM image for portlandite crystal being covered by calcite

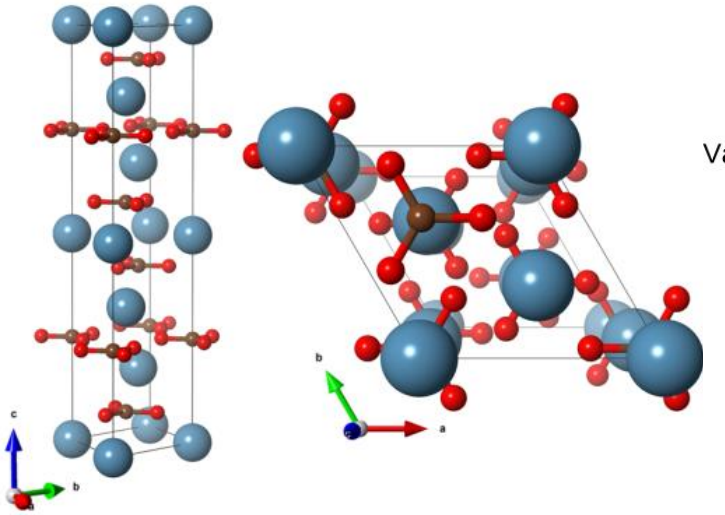
Research Councils UK Energy For a Low Carbon Future

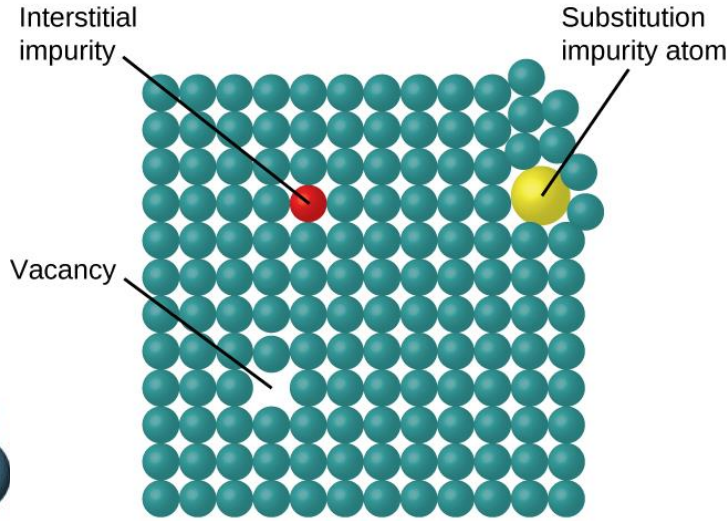
DISTINCTIVE

AFM tests:

Interaction between strontium and calcite







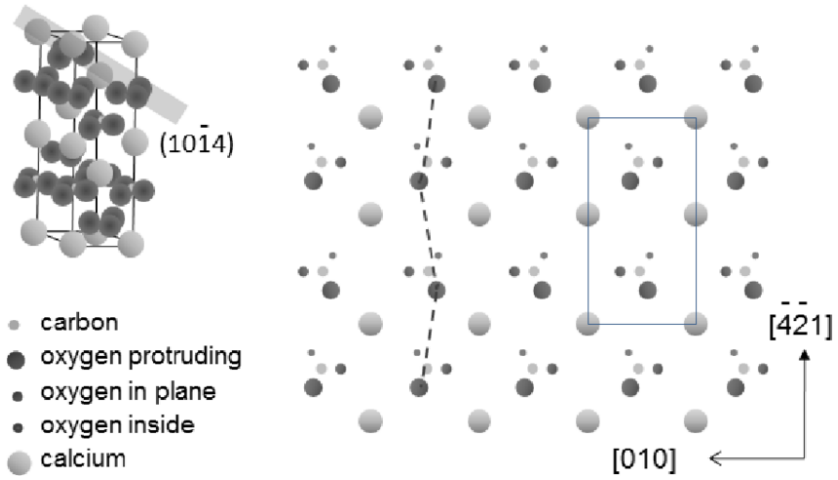
Calcite Unit Cell

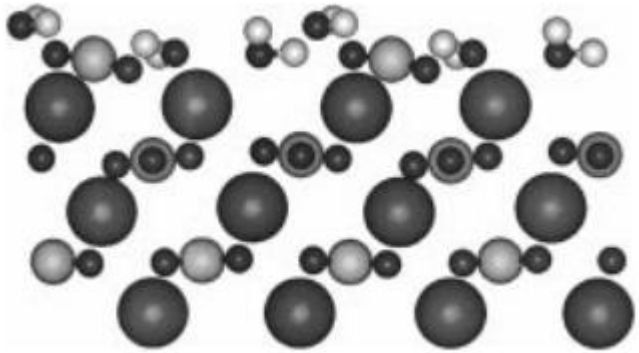
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests:

Interaction between strontium and calcite





Calcite (104)

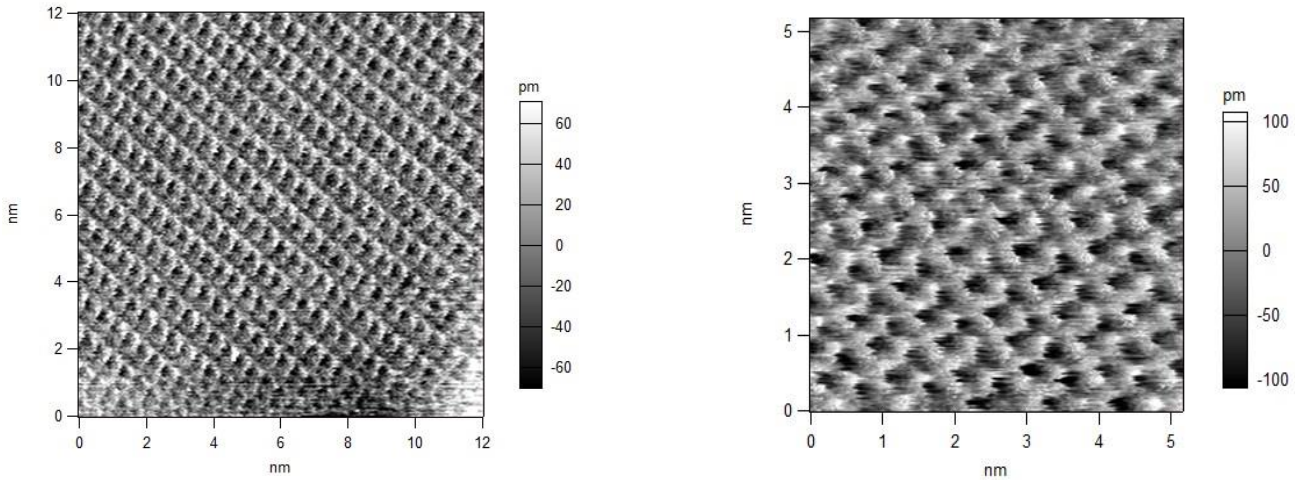
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests:

Interaction between strontium and calcite

Atomic Resolution of calcite in $SrCl_2$ 0.5 mM solution for 14 days. (tapping mode in liquid).



No differences detected in the crystalline pattern

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests:

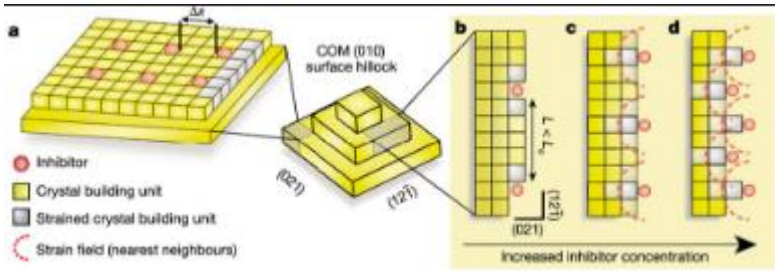
Interaction between strontium and calcite

Comparison between:

- Calcite crystal growth at fixed SI = 0.89 ($CaCl_2$ + Na_2CO_3) fixed pH = 10.2 (in equilibrium with atmospheric CO_2).

- Crystal growth with the addition of Sr^{2+} 0.2 mM

- Crystal growth with the addition of Sr^{2+} 0.6 mM



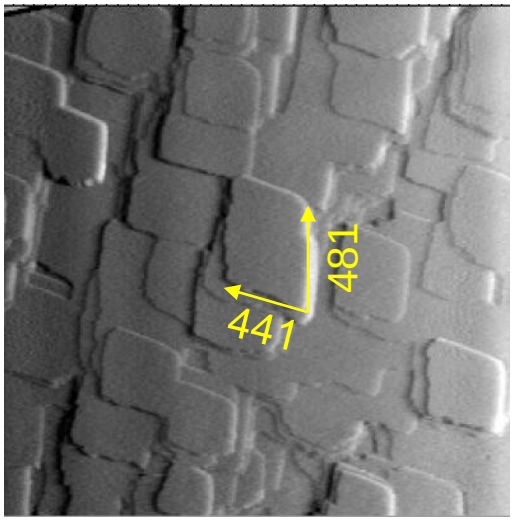
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

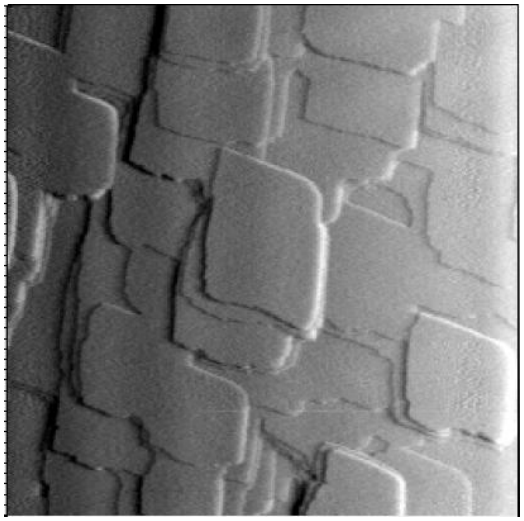
AFM tests:

Interaction between strontium and calcite

T1 = 0 s



T2 = 96 s



Flow rate: 18 ml/h

Contact mode

Scan frequency: 9.77 hz

Dimensions:
10.5 x 10.5 um

Channel: deflection retrace

Crystal growth over time on the [1014] surface of calcite. Steps velocity measured along the 441-481 directions as sections growing rates.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests:

Interaction between strontium and calcite

First data analyzed

Solution:	Section growth rate:
Calcite SI = 0.89	5.31 nm/s
+ 0.2 mM $SrCl_2$	4.93 nm/s
+ 0.6 mM $SrCl_2$	3.90 nm/s

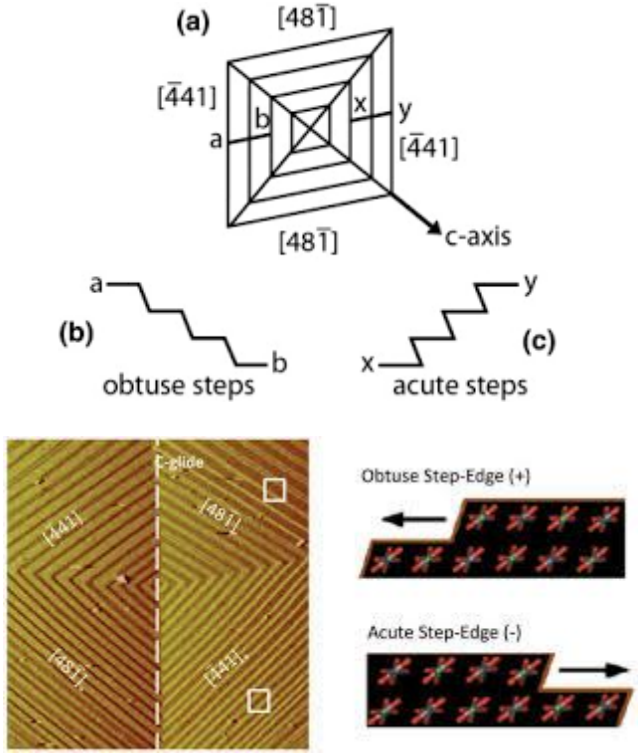
Need to increase the number of pitches anylized and to complete the experiment by trying other concentrations in the range 0.1-0.8 mM or $SrCl_2$

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

AFM tests:

Interaction between strontium and calcite



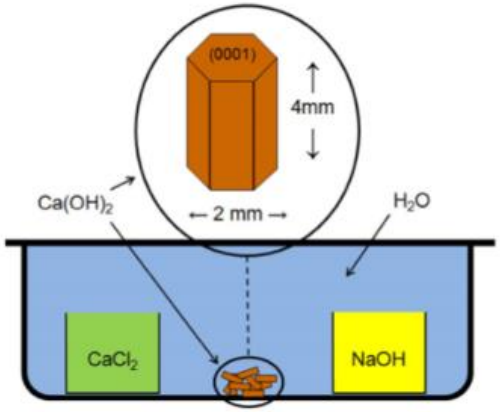
Same experiment using a supersaturated solution 1.20 SI to grow Spiral shaped pitches above the calcite surfaces.

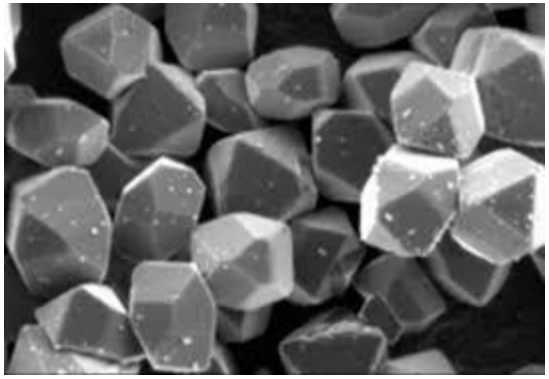
Then adding the 0.89 SI solution with strontium at different concentrations to monitor steps velocities with respect to acute and obtuse steps.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Portlandite Single Crystals Synthesis





Via slow counter-diffusion method by $CaCl_2$ + NaOH in very diluite solution SI = 0.40

XRD-fingerprinting to evaluate eventual carbonation.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Conclusions

- We reached a way to get cement paste surfaces to approach AFM characterization by MRM. We are studying how the temperature synthesis affect surface roughness.

Further works:

- Force distance curves on cement pastes (C-S-H surface characterizaion)
- Ettringite crystal growth (on cm sized crystals)

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Conclusions

National Nuclear Laboratory Collaboration

- Strontium inhibition of calcite CG is confirmed by our data and is proportional to its concentration. (try effect of caesium and zinc)
- Porlandite synthesis of mm sized crystals

Further experiments:

- Portlandite behaviour in presence of $Mg(OH)_2$ (Magnox) – Epitaxial Growth
- Radionuclide incorporation into C-S-H pastes [Europium – Caesium – Zinc – Rhenium]

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

PhD student: Luca Rizzo

Supervisor: Dr Andrea Hamilton

Email: Luca.rizzo@strath.ac.uk

University of Strathclyde Glasgow