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Reactor Chemistry, Materials and Plant Life Extension (PLEX)

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Reactor Operations Support
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Overview

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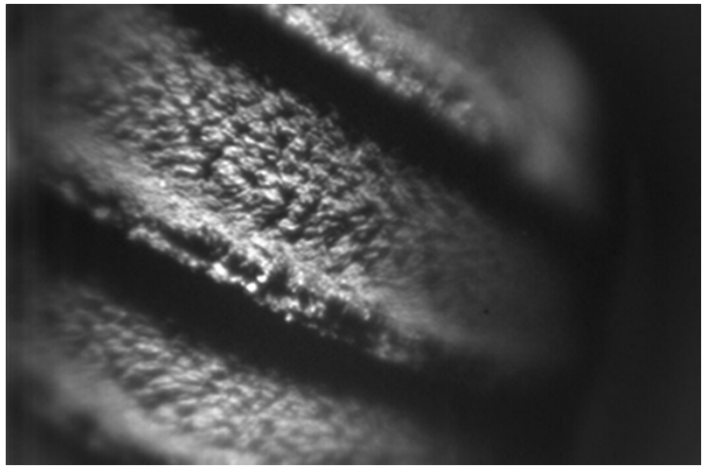
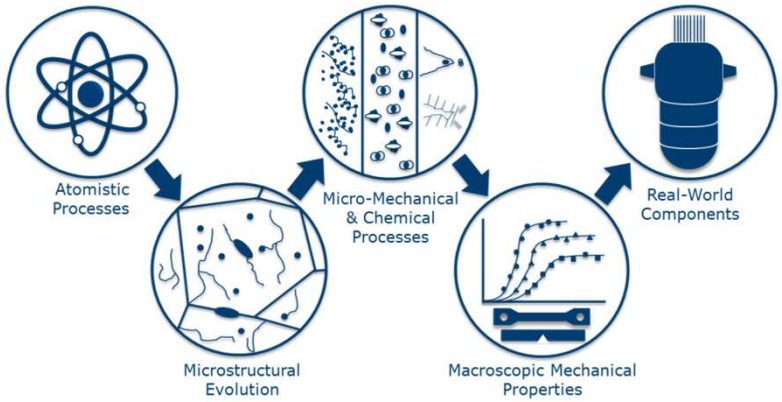
- Reactor Chemistry and Materials Team
- Reactor Chemistry and Corrosion
- Materials Science and PLEX
- Knowledge Management





Reactor Chemistry and Materials

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Materials and Corrosion

- **Radiochemists, metallurgists, physicists and corrosion scientists**.
  - Effect of **irradiation on nuclear materials**.
  - Use of **electrochemical techniques** to elucidate corrosion.
  - **Oxide characterisation** using diffraction techniques.

Radiation Chemistry and Modelling

- Modelling chemistry (thermodynamics/kinetics) in **PWR/AGR/BWR Nuclear reactor systems**.
- **Fission product chemistry** in PWR severe accidents.
- Metal and oxide solubilities in PWR primary coolant, corrosion, activity transport modelling.
- Radiation chemistry: iodine chemistry (PWR faults), PWR and AGR coolant chemistry.

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Customers

HSE
ONR
ROLLS ROYCE
EDF ENERGY
AWE
BETTIS LABORATORY
NATIONAL NUCLEAR LABORATORY
MINISTRY OF DEFENCE
amec foster wheeler
CRIEPI Central Research Institute of Electric Power Industry
Sellafield Ltd
NDA Nuclear Decommissioning Authority
Magnox
EPRI

Collaborators/Universities

OAK RIDGE National Laboratory
UNIVERSITY OF OXFORD
CCFE CULHAM CENTRE FOR FUSION ENERGY
MANCHESTER 1824 The University of Manchester
University of BRISTOL
Imperial College London

External Facilities

ESRF The European Synchrotron
Réacteur Jules Horowitz Reactor
MANCHESTER 1824 The University of Manchester Dalton Nuclear Institute
NEUTRONS FOR SCIENCE
OxfordMaterials
diamond
Science & Technology Facilities Council ISIS

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Reactor Chemistry and Corrosion

Reactor Chemistry Modelling

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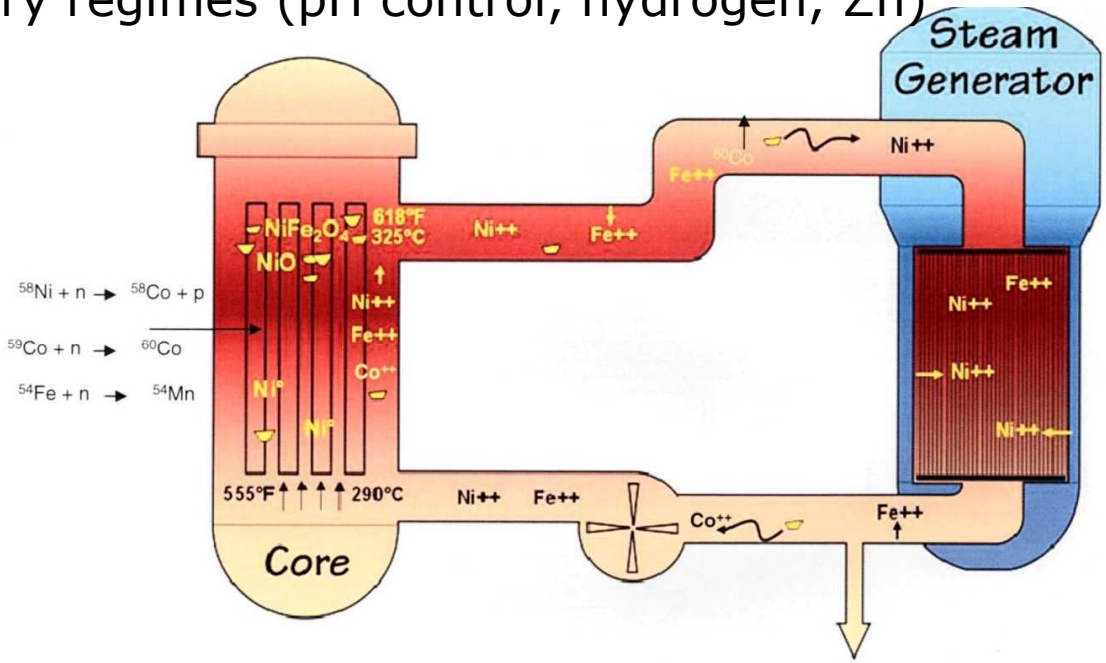
- Primary coolant chemistry in Pressurised Water (PWR) and Boiling Water (BWR) Nuclear Reactor Systems
  - Material release, transport, activation & deposition
    → operator dose, radioactive discharges, decommissioning costs
  - Fuel crud accumulation → power shifts, fuel failures
  - Assessment of material choices in new plant
  - Water chemistry regimes (pH control, hydrogen, Zn)



Boiling Water Reactor Vessel Internals Application (BWRVIA)

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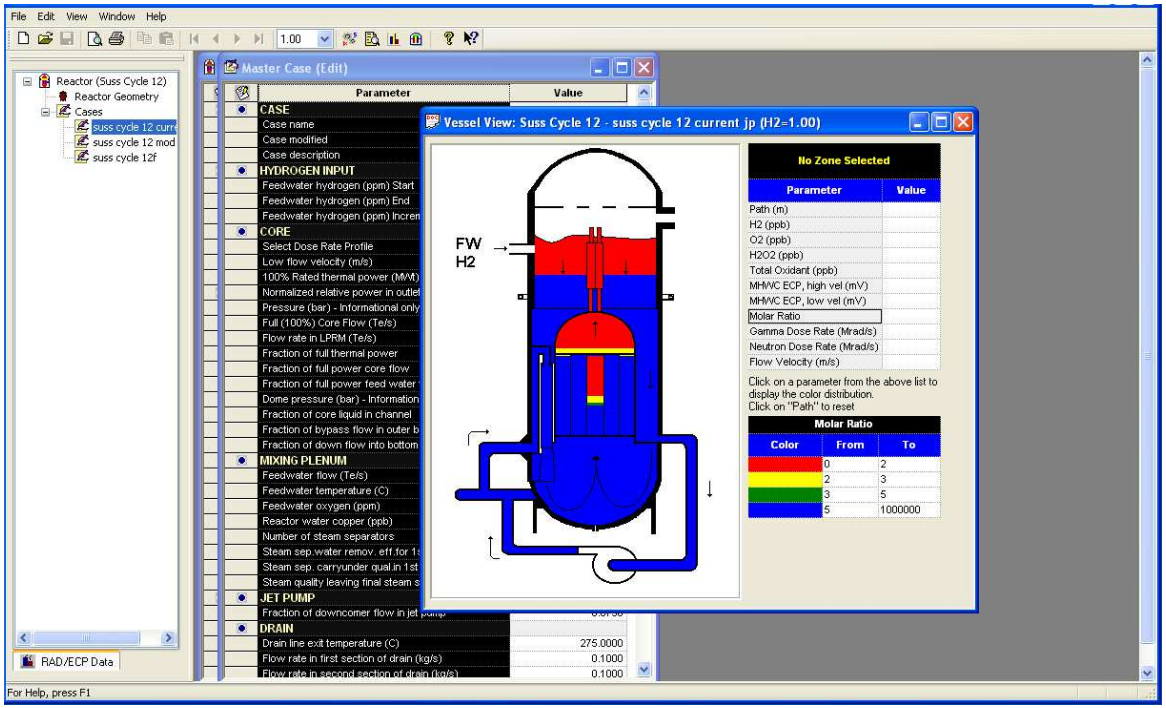
- Calculates radiation chemistry of water and corrosion potentials around BWR circuit
  - Potential for stress corrosion cracking
  - Used by BWR plant chemists around the world
  - Plant life extension analysis



AGR fuel storage

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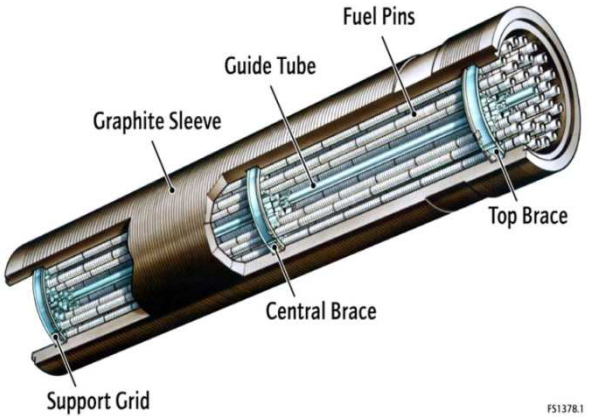
The Fuel Element

- A graphite outer sleeve, a structural component.
- A central guide tube (SS) to guide the tie bar.
- 36 pins filled with UO_2 pellets.
- Pins clad in SS.



Spent fuel, dismantled and pins in a slotted can.

- Cans are stored in ponds to dissipate heat and shield from radiation and provide access.

Corrosion implications

- In the very earliest days of pond storage of AGR spent fuel at pH 7, it took a few years before anything obvious was noted.
- Then fuel cladding corrosion led to failure.
- On the basis of tests which showed a beneficial effect, it was decided (1986) to increase the pH of the storage pond water to 11.4.
- This had the effect of inhibiting corrosion; no more fuel failures were observed in-pond.
- The catch is, we don't know if the rate of corrosion is now zero, or an immeasurably low value.

Underpinning work on validation of storage options for AGR Fuel

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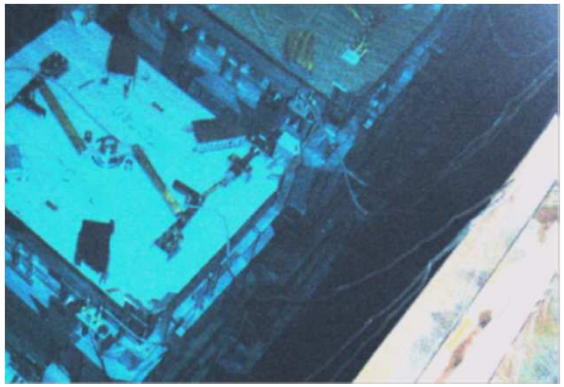
Several examples of NNL work in this area (ie irradiation assisted corrosion):

- Post-storage examination programme – current work
- Electrochemical Noise corrosion monitoring for AGR fuel cladding
- Mechanistic work on dry storage crack growth rates
- Radiation chemistry of cover gases for dry storage options
- Accelerator simulation of Radiation Induced Segregation (RIS) to provide non-active samples
- Modelling of RIS to predict effects of high burnup
- Measurement of contemporary RIS
- Measurement of high temperature effects of pH-based inhibitors



Corrosion of AGR Fuel Cladding - Studentships

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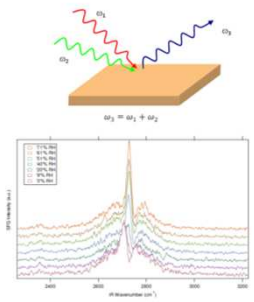
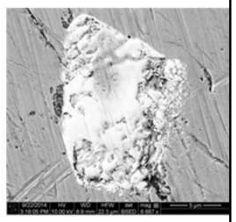
- **Francis Lydiatt (Manchester) -**NNL funded work on dry store corrosion fundamentals.
- **Choen May Chan (Manchester) -**NDA funded work on wet store corrosion mechanisms.
- **Ronald Clark (Swansea) -**NDA funded work on mapping corrosion sites on AGR cladding.
- **Mike Pugh (Newcastle) -**NDA funded work on crack growth rates on dry stored AGR cladding.
- **Elizabeth Howett (Lancaster) -**NNL funded work on fuel and cladding corrosion in pondwater chemistry.
- **DISTINCTIVE programme (DCF) -**NDA funded work on artificial radiation sensitisation of AGR cladding material.

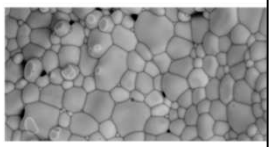
- Used vibrational sum frequency spectroscopy to determine the number of water monolayers on a surface, before that absorbed water begins to exhibit electrolyte characteristics.
- Very difficult experiment – built a one-of-a-kind controlled humidity VSFS instrument to look at oxide surfaces.



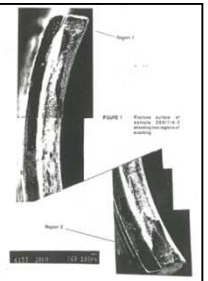
- Using electrochemical techniques to investigate different pH / chloride environments on thermally sensitised stainless.
- Microscopy of pit sites to characterise nucleation sites.
- Using strain testing to investigate effect of chemistry on crack propagation.



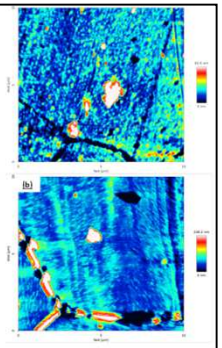
- Electrochemical corrosion testing using thermally sensitised stainless steel
- Investigating high temperature corrosion effects.



- Using strain testing to investigate the effect of humidity on thermally sensitised SS.
- Aimed at underpinning dry storage design parameters



- Using vibrating scanning electrode technique (VSET) to map active corrosion sites on thermally sensitised SS.
- Using time lapse microscopy to identify features of corrosion sites ***before*** corrosion initiates.



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Strategic Research

Internal Research & Development

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- Rationale for R&D
  - Development of Relevant Nuclear Skills & Capability
  - Development of opportunities for commercial growth
  - Address customer problems that are too fundamental for them to fully fund
  - Technical reputation

- Strategic Research (£1.5-2m)
  - Longer term projects (~3 yrs) typically £50-150k p.a.

- Signature Research (£0.6m)
  - Short term projects (<1yr) typically ~£10-£30k

- Entrepreneurial (£0.4m)
  - New products and services

Topic Areas:
- Nuclear Energy/Fuel Cycle
- Waste Management & Decommissioning
- Security
- Cross Cutting Topics

Current Strategic Projects

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- Uranium based accident tolerant fuels
- Development of new fuel manufacturing route (3D Printing)
- **Plant Lifetime Extension and Degradation of Cladding**
- Understanding the Formation and Behaviour of 14C in Reactor Graphite
- Spent Fuel Storage
- Fast Reactor Fuel PIE: Phenix Treasure
- Fast Reactor Fuel Performance Modelling
- Advanced Separations and recycle (aqueous)
- Thermal Treatment of ILW
- Photonics Based Remote Characterisation
- Colloid Formation, Stability and Transport in engineered systems and the environment
- Biogeochemical research applied to near surface and geological waste disposal
- Immersive and Augmented Design Modelling
- Fuel Cycle Scenario Assessments
- **Reactor Chemistry and Corrosion**

Reactor Chemistry and Corrosion

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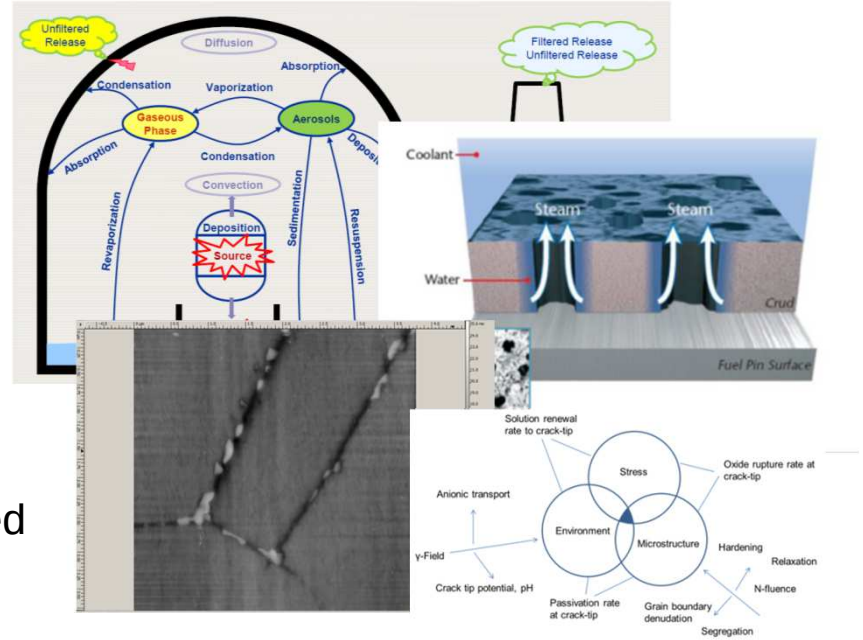
Vision: Maintain and further develop a world leading capability in reactor chemistry and corrosion



•Iodine (Severe accident) Chemistry

- •Aim to rejuvenate the severe accident iodine chemistry capability through involvement in international programmes including OECD Nuclear Energy Agency (NEA) projects, Behaviour of Iodine Project (BIP-3) and the Source Term Evaluation and Mitigation project (STEM-2).

• Environmentally Assisted Cracking (EAC) – localised degradation in nuclear materials

- •Development of High Speed – Atomic Force Microscopy (HS-AFM) for study of localised degradation processes in nuclear materials (PhD Studentship at Bristol).

•Future areas currently being scoped:

- •Hot water chemistry, radiation chemistry and corrosion facilities
- •Reactor chemistry and corrosion modelling
- • Irradiation Assisted Stress Corrosion Cracking (IASCC)

Highlight: NNL are the UK representatives on international iodine chemistry programmes BIP-3 and STEM-2, endorsed and funded in part by EDF and ONR

APT of Oxidised Grain Boundaries

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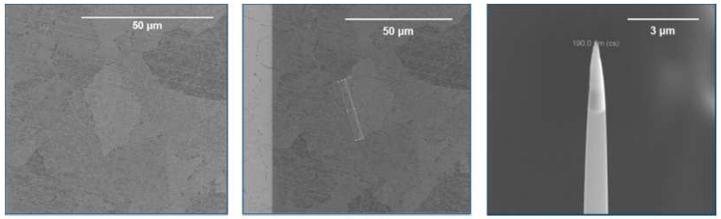
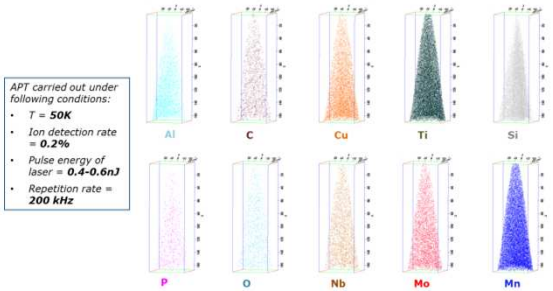
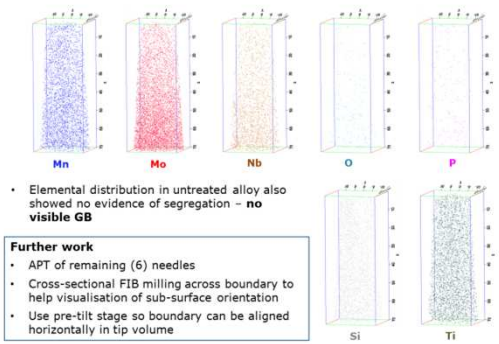
- Use of internal research funding to develop capability.
- Some Ni based alloys are susceptible to PWSCC, need to understand potential implications of PLEX for Alloy 690 susceptibility.
- Investigating the effect of initial heat treatments on SCC susceptibility in Alloy 600.





- After tip reconstruction, individual elemental species were isolated to see their distribution throughout analysed volume
- On the whole, a uniform distribution was observed for all species – **no visible GB**

32 NNL Commercial 31/01/2016



- Elemental distribution in untreated alloy also showed no evidence of segregation – **no visible GB**

Further work
- APT of remaining (6) needles
- Cross-sectional FIB milling across boundary to help visualisation of sub-surface orientation
- Use pre-tilt stage so boundary can be aligned horizontally in tip volume

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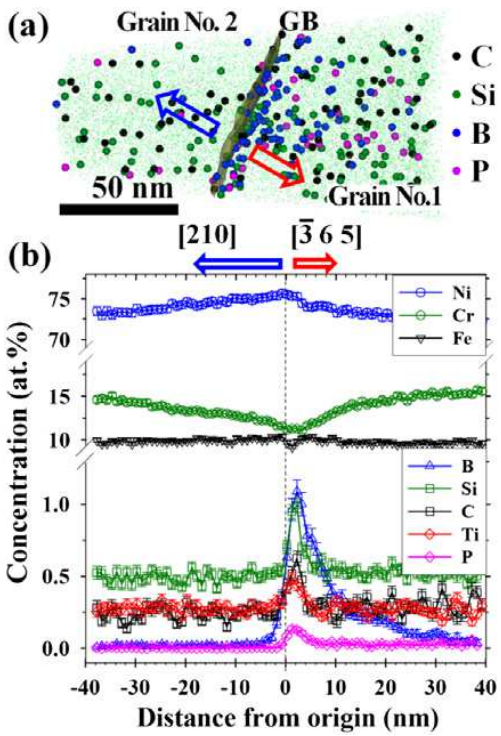

S. I. Baik at al., Scripta Materialia, vol. 66, pp. 809–812, 2012.

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Materials Science and PLEX

Materials Science and PLEX

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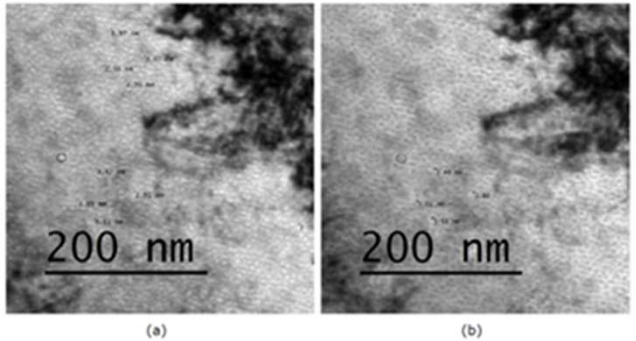
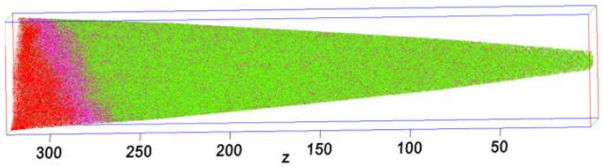
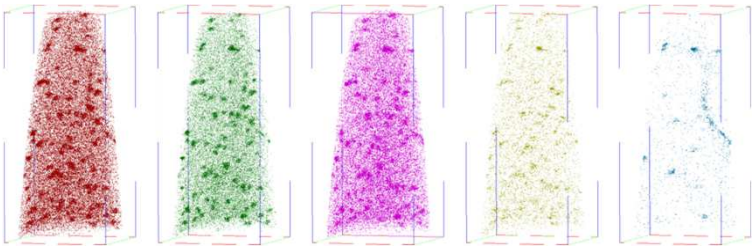
- Many plant are reaching the end of their design life and are being considered for life extension.
- New plant are being designed with significantly longer design lifetimes than current plant.



- Two main research themes:
  - Embrittlement of Pressure Vessel Steels
  - Degradation of Zircaloy fuel cladding

- Mechanistic understanding of these processes are evolving meaning these two areas are active areas of research worldwide.





Collaborations

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UNIVERSITY OF OXFORD

Jenni Zelenty
Long term thermal ageing of RPV Steels

James Sayers
Effect of water chemistry on H uptake in Zircaloys

MANCHESTER 1824
The University of Manchester

Matthew Topping
Proton irradiations of Zr-Fe alloys

Alex Carruthers
Characterisation of ion and neutron irradiated RPV steels

MUZIC 2

Mechanistic understanding of H pickup in Zircaloys

Industry:
Westinghouse, EdF, Studsvik, Rolls-Royce, Amec, PSI, Sandvik, EPRI
Universities:
Oxford, Manchester, Imperial, Chalmers, Penn State

EU NUGENIA+
2 projects:

NUGENIA
NUclear GENeration II & III Association

AGE60+ – AREVA, CIEMAT, MTA EK, UJV Rez a. s

APLUS – Rouen University, SCK-CEN

PWR Cladding Research

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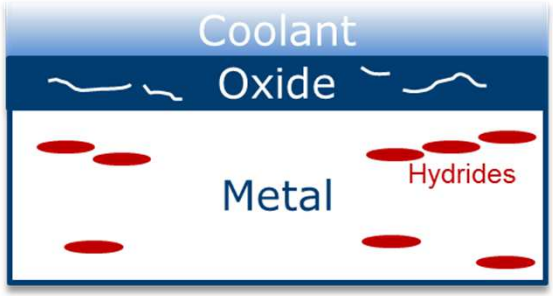
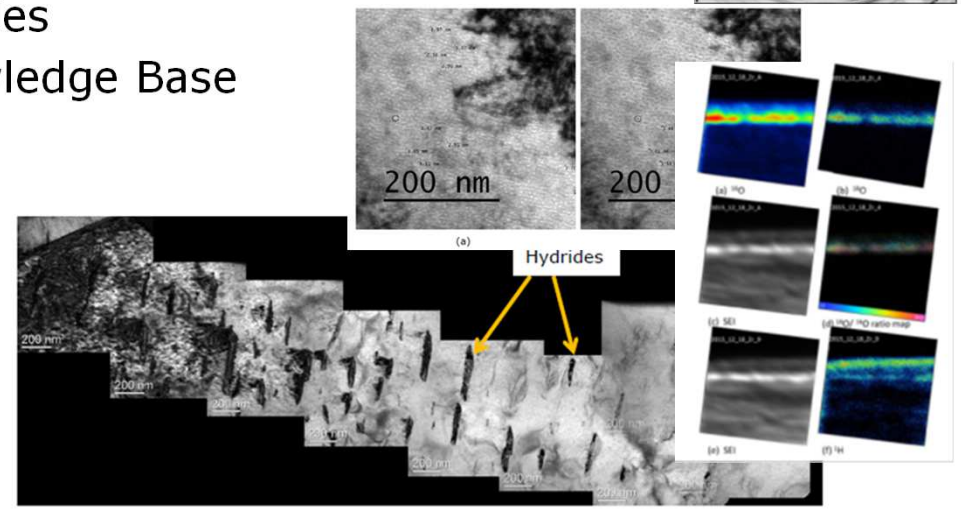
- **Zircaloy Corrosion**
  - Using advanced techniques to develop a mechanistic understanding of oxidation (corrosion) and hydrogen gettering:
    - Synchrotron X-Ray Diffraction (SXRD) Studies at the European Synchrotron Radiation Facility (ESRF)
    - NanoSIMS studies on oxidation profiles and hydrogen distribution
    - Microstructural Studies on active and inactive samples
    - Advanced EELS/TEM of Gas Bubbles
    - Development of a Gettering Knowledge Base
    - Model development





Fontevraud 8 - Contribution of Materials Investigations and Operating Experience to LWRs' Safety, Performance and Reliability

Study Of Zircaloy Corrosion To Develop Mechanistic Understanding

S. Ortner*, H. Swan, A. Laferrere, C. English, J. Hyde, P. Styman (National Nuclear Laboratory)[1] - UK, K. Jurkschat (University of Oxford)[2] - UK, H. Hulme, A. Pantelli, M. Gass, V. Allen (AMEC)[3] - UK, P. Frankel (University of Manchester)[4] – UK.

[1] NNL, 168 Harwell Science Campus, Didcot, Oxfordshire, OX11 0QT, UK.
[2] Department of Materials, University Of Oxford, Parks Road, Oxford OX1 3PH, UK.
[3] AMEC, Walton House, Birchwood Park, Risley, WA3 6GA, UK.
[4] Manchester Materials Science Centre, University of Manchester, Grosvenor Street , Manchester M1 7HS, UK.

APT Work

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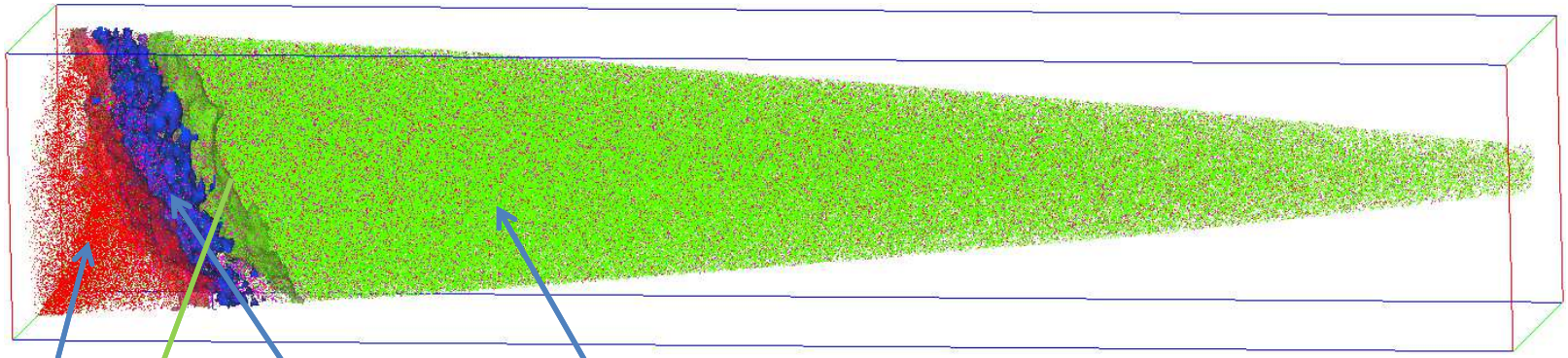
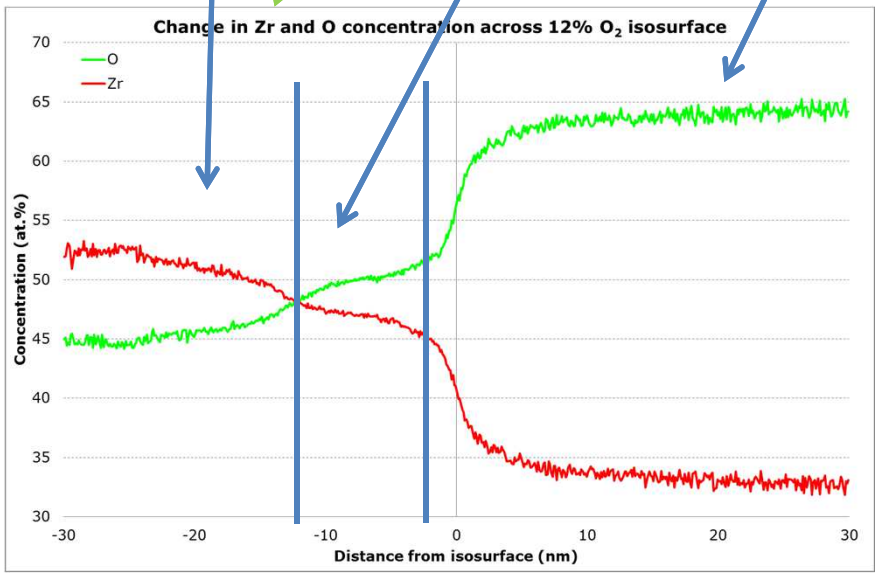


Metal Sub-Oxide Oxide



Element	Whole Sample	Oxide	Sub-oxide	Metal
Zr	35	31	46	51
O	61	64	50	45
Nb	1	1	0.3	0.1
Sn	0.5	0.4	0.7	0.6
Fe	0.03	0.03	0.03	0.01
H	2	2	2	2
O:Zr ratio	**1.7**	**2.0**	**1.1**	**0.9**

Effect of Radiation on Materials

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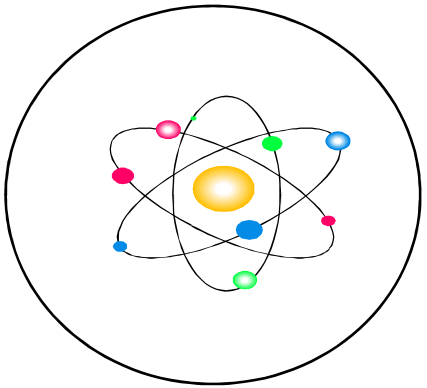
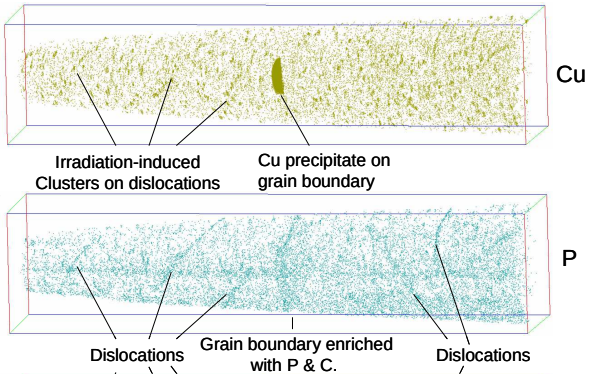
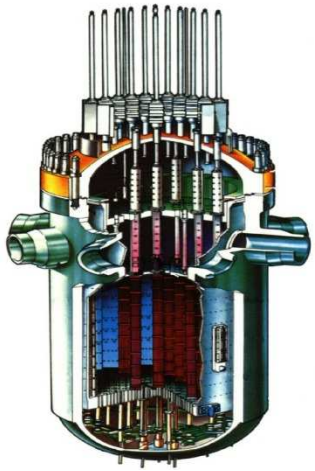
- Radiation damage limits life of many structural components
- Radiation damage effects are complex and not easy to predict
  - Mechanistic understanding, underpinned by microstructural data is essential
  - Mechanistic understanding is directly linked to plant integrity
- Research programmes play a central part in ensuring safe operation of Nuclear Power Plants (& plant life extension)

During service solute atoms in the steel cluster. This affects the integrity of the RPV.







Atomistic Processes

Microstructural Development

Applications

RPV Embrittlement

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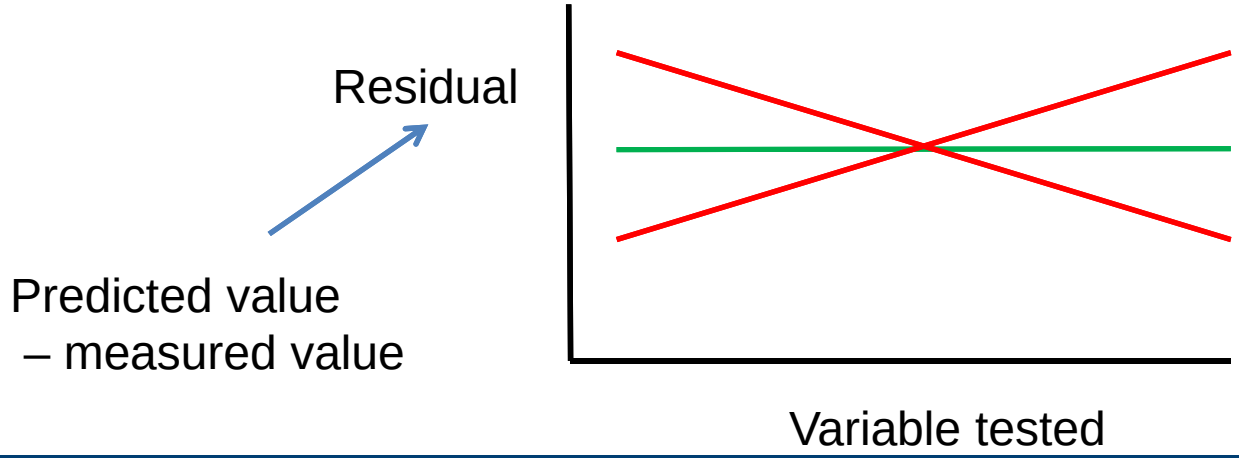
- For PLEX we desire accurate predictions of the embrittlement of RPV steels (allows for reduced margins)
- Many factors can influence the level of embrittlement
  - fluence, flux, product form, composition, temperature, yield stress.
- Not all are currently incorporated into existing models
- To predict embrittlement we currently use empirical models ('Embrittlement Trend Curves' ETCs) calibrated to existing surveillance data
- A good model should show no bias towards variables



RPV Embrittlement

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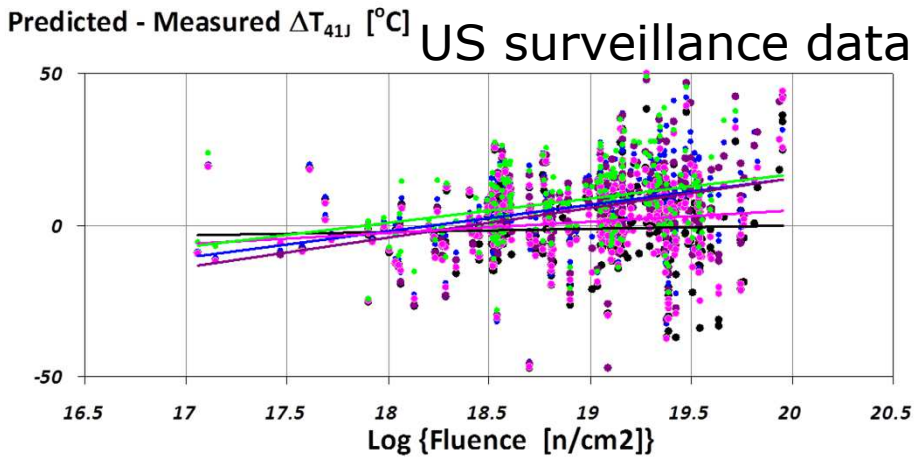
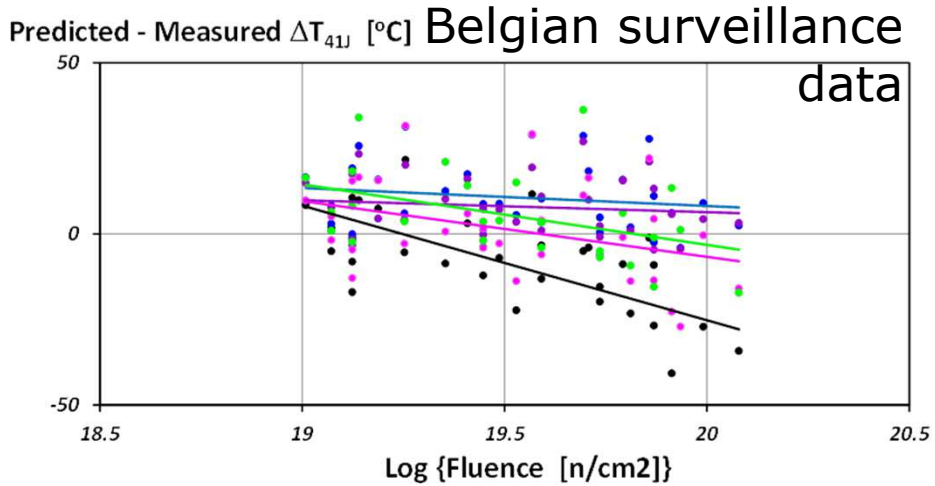
- A number of ETCs are in use, but they exhibit national effects





WR-C(5) Rev 1 **RR/UCSB** **E900-02**
EDF 900MW **JEAC4201-2007**

Cu<0.07, Ni<1.00, f<$4 \times 10^{12} ncm^{-2}s^{-1}$

"What would be the best DDR to use for a pressure vessel built in the UK, according to a French/US design of reactor, using a beltline forging produced in Japan, operated according to UK procedures?"

RPV Embrittlement

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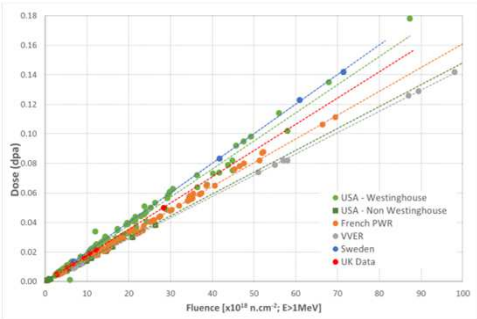
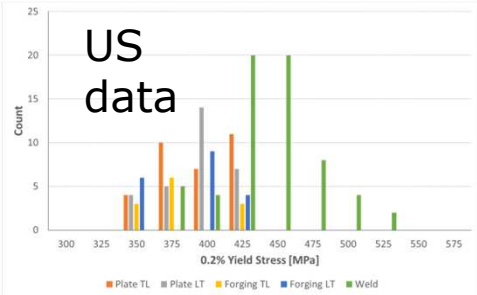
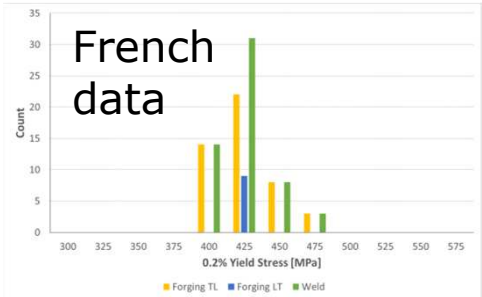
- Investigated possible sources of scatter (dpa and initial yield stress)
- Clear nation to nation variations in both dpa and initial yield stress
- Dpa does not result in any trends in residuals in low Cu data
- Initial yield stress effects complex and probably incorporated into composition terms







NUGENIA - AGE 60+

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- Applicability of ageing related data bases and methodologies for ensuring safe operation of LWR beyond 60 years
- 4 partners, AREVA, CIEMAT, MTA EK, UJV Rez a. s

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- 5 work packages:
  - WP1: Expansion and utilisation of MnMoNi RPV steel embrittlement database.
  - WP2: Scoping and population of VVER RPV steel embrittlement database.
  - WP3: Scoping and population of low alloy steel thermal ageing database relevant to reactor operation.
  - WP4: Raising awareness and scoping an acceptable database on RPV internal degradation.
  - WP5: Raising awareness and scoping an acceptable database on concrete ageing.

RPV Research - Ringhals

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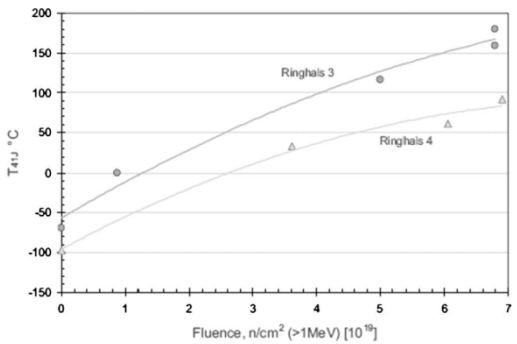
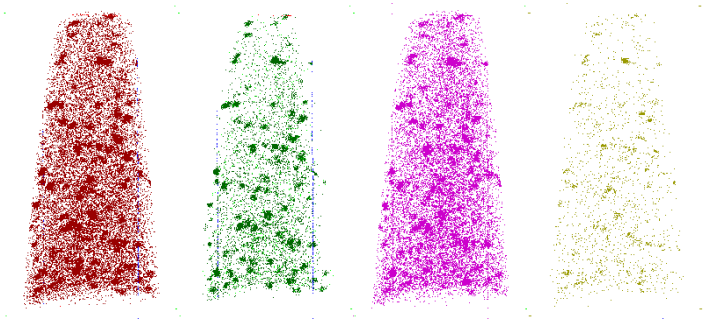
- Knowledge on the effect of irradiation on higher Ni materials is relatively limited
- Need to improve the mechanistic understanding of embrittlement in these materials
- Ringhals R3 welds are low in Cu (0.07 wt.%) but high in Ni (1.5 wt.%)
  - High Ni gives better start-of-life properties
  - Shifts in DBTT were higher than expected
- Shifts in DBTT seen in R3 are due to a high number density of 3 – 4 nm diameter Ni-Mn-Si-Cu clusters.





- Post irradiation annealing has been performed to investigate the formation of these clusters.

Ringhals Conclusions

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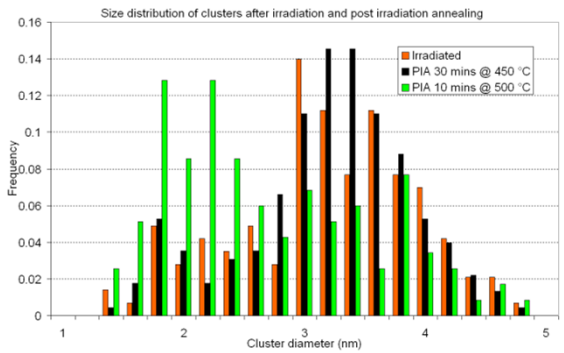
- Post irradiation annealing showed
  - The onset of dissolution of clusters at 450 °C
  - More significant dissolution of clusters at 500 °C



- Dissolution of clusters led by diffusion of Mn
  - Mn couples strongly to point defects
  - Dissolution may be driven by removal of point defects from Ni-Mn-Si clusters
  - Could indicate point defects play a role in Ni-Mn-Si cluster formation

ELSEVIER

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Post-irradiation annealing of Ni–Mn–Si-enriched clusters in a neutron-irradiated RPV steel weld using Atom Probe Tomography

P.D. Styman[a, b], J.M. Hyde[a, b, c], D. Parfitt[d], K. Wilford[d], M.G. Burke[c], C.A. English[a, b, c], P. Efsing[e]

APLUS

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- Development of Standards for the Analysis of **A**tom **P**robe Data to support Improved Mode**l**ling & Mechanistic **U**nderstanding of Radiation Damage in LWR**s**

- 2 partners, University of Rouen, SCK-CEN

- *"The project is quite innovative on scientific terms. It includes 2 EU labs that have high expertise and that lead the development and application of ATP in Europe. That makes the project very credible."*

NUGENIA
NUclear GENeration II & III Association

UK Radiation Embrittlement Forum and IBID

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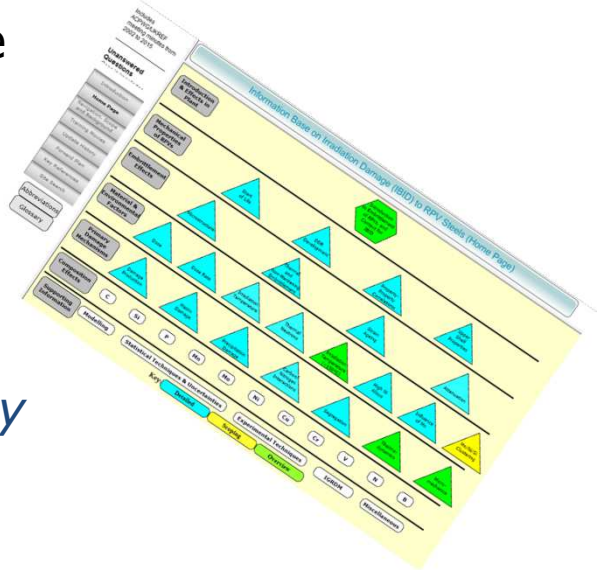
- UKREF has developed from a knowledge capture exercise begun in ~2000 on radiation embrittlement of pressure vessel steels.



- The resultant knowledge base is known as Information Base on Irradiation Damage (IBID). It was formally known as the "*Ageing community project*".

- UKREF intends to exploit broader opportunities / benefits from IBID
  - Facilitate work programmes to aid successor development
  - Enable early identification of materials issues in radiation embrittlement and guide UK response
  - Responding to opportunities associated with new build

UK Radiation Embrittlement Forum and IBID

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- The objectives were to:
  - Develop, manage and maintain a knowledge/expertise system
  - Involve all key UK organisations with an interest in RPV embrittlement (ONR, RR (MoD), EDF, Magnox, NNL)
  - Capture state-of-the-art knowledge incl. expert judgement
  - Ensure product adapted for and available to successors

- Not to be confused with an expert system.

- Initial focus was on RPV embrittlement but approach has wider applicability

UK Radiation Embrittlement Forum and IBID

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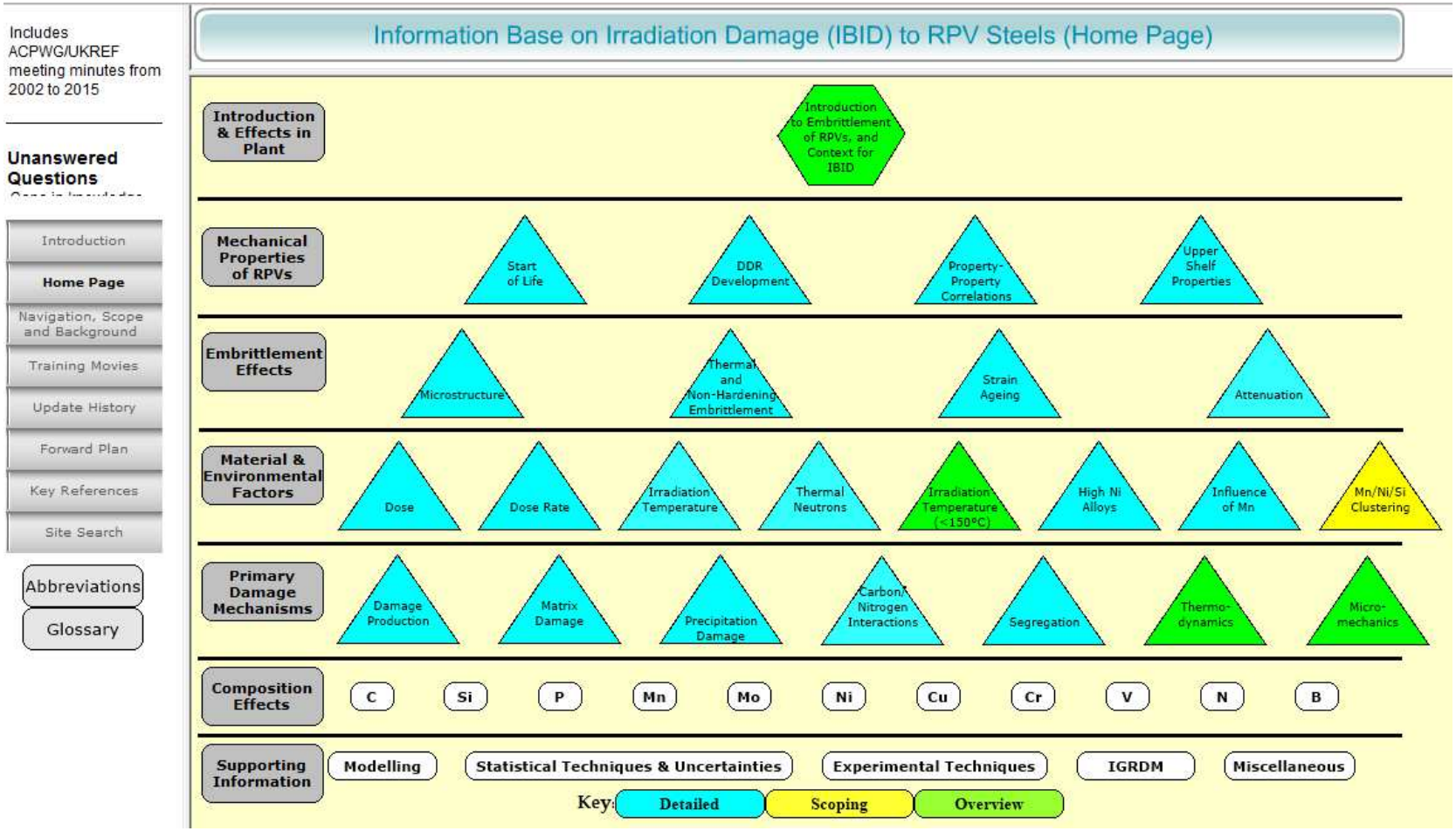
- UKREF formed – coordinated by NNL



Summary

NATIONAL NUCLEAR LABORATORY

- Reactor Chemistry and Corrosion
  - Modelling chemistry (thermodynamics/kinetics) in PWR/AGR/BWR Nuclear reactor systems.
  - Fission product chemistry in PWR severe accidents.
  - Metal and oxide solubilities in PWR primary coolant, corrosion, activity transport modelling.
  - Radiation chemistry: iodine chemistry (PWR faults), PWR and AGR coolant chemistry
- Materials Science and PLEX
  - Effect of irradiation on nuclear materials
  - Using advanced techniques to develop a mechanistic understanding of Zircaloy Corrosion
- Knowledge Management
  - Information Base on Irradiation Damage (IBID)