Experimental characterization of degraded/molten nuclear fuel at JRC-ITU

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Outline

introduction – context: fuel safety studies

characterization of degraded/molten fuel
  - "real" severe accidents
  - simulated accident conditions
  - spent fuel

summary and perspectives
Safety during irradiation (PIE)

**normal operation**: extended burn-up, HBS, fission gas release, pellet-clad interaction

**off-normal** conditions: fragmentation, LOCA

**severe accidents**: degraded/molten fuel/corium and debris characterization

**post-Fukushima**: sea water corrosion, corium–salt interactions, release source term, spent fuel pool, storage and remediation issues

Safety of spent fuel

extended storage, retrievability

accident conditions

defective fuel rods

↓ ↓ ↓

**TRANSURANUS** code, multi-scale modeling

Rondinella & Wiss, 2010
Back-scattered image showing dense (U-rich) and less dense (Zr-rich) and light (Fe,Ni,Cr-rich) phases in the fully molten rock (1000x)

G12-P9-B fracture surface showing the ferrous crystals in a pore (600x)
SEM micrographs from coarse debris H8-7.2 above upper agglomerate. A wide variety of materials were observed from the debris.

a) BSE image of a dendritic Fe-Ni-Sn phase (Sn from the cladding) in a fused Zircaloy matrix.

b) Fuel remnant with extensive ferrous metal dissolution (attack) along the UO$_2$ grain boundaries.
Microanalysis of degraded fuel

Phebus FPT2
(lower bundle)

Fuel rods, Zircaloy, corium and control rod in the zone below the corium pool

corium is a fully oxidised (U,Zr)O₂ ceramic
[(U,Pu)₀.₅₇Zr₀.₄₀(Fe,Cr,Mo)₀.₀₃]O₂.₀₁

oxidised cladding - ZrO₂
(with ~2-3at%UO₂)

fine thread-like shapes are metallic structural elements
~(Fe,Cr,Mo)₂Zr
Corium Interaction Termochemistry

UO₂ 53 GWd/tU

irradiated fuel: completely dissolved after 25s; irregular attack, small fragments; high porosity

zircaloy, He, 2000°C, 190s

unirradiated: dissolves slowly; uniform attack; low porosity; larger regular fragments
Macroscopic cross-sections

UO$_2$ ~90, MOX ~45 GWd/tU; zircaloy cladding; 2000 °C;
microanalysis and microscopy to characterize structure and composition/distribution of irradiated fuel species
Zircon crystal from Chernobyl “lava”
Pöml, Burakov et al., 2011

$^{235}$U enrichment: in zircon 1.08%; in UO$_x$ inclusions 0.8%

EPMA
Zircon: 3.1–14.6 wt.% UO$_2$ (natural <1.5), Pu traces
UO$_x$: ≈ 0.3 – 0.4 wt.% PuO$_2$, Zr traces
Ex-vessel materials

Hot particle from Chernobyl

metallic Zr particle containing U

U map (EPMA)

Pöml, Burakov et al., 2015
More advanced tools

- Laserflash
- Transmission electron microscopy
- Focused ion beam
- Knudsen cell
- Acoustic microscopy
Obtain data on long-term behaviour to assess SF/wasteform ability to fulfil its expected function in

**Extended Storage**
containment of radionuclides and retrievability ($\geq 100$ y?)
SF evolution: comprehensive understanding of decay damage and He accumulation effects

**Severe accidents**
pools, storage, handling, transport: mechanical load, impact resistance; corrosion, loss of cooling; damaged SF, debris

**Geologic Repository**
acceptable release of long-lived radionuclides over the *geological disposal timescale*
Radionuclides “Source Term”, “Instant Release” with *ad hoc* experiments

Environment and SF properties: effects on matrix corrosion (reduce uncertainties)

Convey experimental data into models and codes (predictions)
Spent fuel leaching in seawater

BWR UO$_2$ 54GWd/t$_{HM}$

U, Pu release in seawater (SW) and deionized water (W)

Cumulative mole released as a function of time. Sequential leaching with total replenishment.

**Ongoing:**

leaching of TMI-2 debris, spent fuel in different cooling media (collaboration with CRIEPI)
Impact load tests on spent fuel rods

hammer impacting on a ~74 GWd/t PWR rod (high speed camera sequence)

simulated impact accident during spent fuel rods transport

PWR and BWR rods tested: 19 – 74 GWd/t

fuel release: < 2 g/break collected, i.e. < 1 fuel pellet

D. Papaioannou et al., 2009
SPAR III Tecdoc, 2014
Fracture surfaces

PWR 43 GWd/t corresponding fractures (a,b)

PWR 19 GWd/t

BWR 53 GWd/t

D. Papaioannou et al., 2009
SPAR III Tecdoc, 2014

different angles (a-a, b-b)
Perspectives

- Significant amount of knowledge on fuel behaviour during severe accidents exists from international projects. E.g. on mechanisms, kinetics, thermodynamics, T, oxygen potentials, key compounds, phases, specific interactions and transitions.

- New programmes (internationally and in JRC-ITU) to extend the experimental data base for modeling and fill R&D gaps (e.g. on spent fuel safety, storage, remediation).

- Advanced techniques are available to improve the outcome of experimental characterization.

- Integrated approaches allow to optimize use of resources (less money and time than in the past)
  → international programmes
  → experimental/theoretical approach
  → possible application to Fukushima-daiichi decommissioning
Major findings

• Corium molten pool forms in a predictable geometry. Composition ~\((U,Zr)O_2\). Rapid cool-down leaves corium as a single, deformed cubic phase, slower cooling results in formation of separate U-rich & Zr-rich oxides

• Ag-Zr and Ni- (or Fe)-Zr interactions can create liquefied cladding already by 1200°C (well below \(UO_2\) melting) which can rapidly attack the fuel

• Irradiated fuel undergoes a more rapid degradation than non-irradiated fuel, because
  - it is mechanically weak (pre-existing cracks)
  - fg release & precipitation into bubbles → very high porosity: 'foaming' at very high T
  - increased surface area for attack by corium

• Cs release <100%, some Cs remains in the overheated fuel and even in the melt pool

• Cs condenses on cooler surfaces (<700°C), but easily revolatilises (> 500°C) in steam (also inert atmospheres) probably as \(CsOH\) - regardless of the deposit composition

They allow obtaining the following types of information

• mechanistic: mechanisms, rate
• thermodynamic: temperature, oxygen potentials
• conditions: key compounds, phases, specific interactions & transitions T (eg.\(T_m\))
Studies on fuel safety during irradiation

- Full understanding of fuel (high burnup structure, composition, irradiation history, additives,…) and cladding properties is essential to assess/predict their behaviour

- Perspective: improve fuel rod response under accident conditions.

Key aspects determining fuel rod safety:
- thermal transport
- fission gas (release) behaviour
- fuel-cladding interaction
- cladding behaviour

Fuel restructuring and heterogeneity due to non-uniform and non-homogeneous conditions during irradiation, e.g. fission density, burnup temperature.

Rondinella & Wiss, 2010
Safety of nuclear fuel cycle at JRC-ITU

Conventional, Advanced Nuclear Fuels and Cycles

- samples synthesis, materials science studies
  PIE: safety during irradiation, (severe) accidents
  LWR, extended burn-up
  sustainable fuels: (V)HTR, FR, MSR

- Back-end: Partitioning & Transmutation, storage, disposal

- Post-Fukushima studies: sea water corrosion,
corium – salt interactions, source term, severe accident analysis, cooling pool/storage issues

Predictive tools: TRANSURANUS, multi-scale fundamental approach

use “real” and simulated corium and damaged fuel for investigating properties/behaviour in view of removal, storage, treatment, disposal of damaged fuel at Fukushima-daiichi
Nuclear fuel studies at JRC-ITU

Domains

- Thermodynamics (vapor pressure, $C_p$, melting point)
- Thermal transport
- Fission products, gases, minor actinides: phase distribution, matter transport
- Radiation damage: mechanisms and effects
- Fuel restructuring: microstructure – macroscopic properties evolution, corrosion, creep

Scope (fuels)

LWR advanced reactors

HTR

high burnup

U, Th MOX

non-oxides

minor actinides

cladding/coating

normal/off-normal operation

extreme conditions

storage and waste disposal

multidisciplinary approach

analytical/modeling tools

Experimental tools

- samples synthesis (MA lab)
- optical, acoustic microscopy; SEM, FIB, EPMA, SIMS; TEM-SEM; XRD
- th. conductivity: laserflash, POLARIS
- high T laser-heating (melting, vaporization, conductivity, high-P)
- high T effusion, revaporization, annealing, KüFA (HTR)
- non destructive PIE: rod profilometry, radiography, outer oxide layer, $\gamma$-spectrometry
- clad: $H_2$-hydrides, creep, burst indentation, impact-fracture
- fission gas release, density
- chemical analysis, laser ablation separation (aqueous, pyro-)
- leaching, electrochemistry
Acoustic microscopy

Acoustic waves are generated by a piezoelectric transducer

**Acoustic waves** propagate in:

1. **Cylinder of high purity silica**
2. **Coupling liquid**
3. **Sample**

Reflected echo is recorded by the same transducer
Acoustic microscopy

Excitation Signal

Acoustic sensor

Stepper motor

Sample holder

Micrometric screws

Acquisition HF Signal processing

Post Process
FIB system standard (commercial) configuration. Hot cell installation requires adaptation work: where possible, sensitive parts (mainly electronics) are separated and installed outside the cell.
Hot cell installation – Pb cell
Infrastructure, facilities and equipment

- Solid State NMR
- Hot cells (24)
- Transmission electron microscopy
- MINOR Actinide laboratory
- Integrated surface analytical laboratory
- Large geometry secondary ion mass spectrometry (SIMS)
- Laserflash (thermophysics & thermodynamics labs)
Impact load tests on spent fuel rods

hammer impacting on a ~74 GWd/t PWR rod (high speed camera sequence)

simulated impact accident during spent fuel rods transport

PWR and BWR rods tested: 19 – 74 GWd/t

fuel release < 2 g/break i.e. less than the mass of a single fuel pellet

Papaioannou et al., 2009

GNS-AREVA collaboration
Phebus FPT3 revaparisation tests: Cs-activity from vertical line deposits in steam & mixtures to 1000 °C

Effect of a) heat-up rate & b) reducing atmosphere
Spent fuel leaching in seawater

BWR UO$_2$ 54GWd/tHM; no cladding

Comparison of U, Cs release in Japanese seawater* (SW) and deionized water (W)

Fraction of inventory in the aqueous phase as a function of time

Sequential leaching with total replenishment

*ongoing post-leaching analysis

*collaboration with CRIEPI
PIE of degraded Phebus bundle; FPT2 (reducing conditions)

ITU tasks: bundle sectioning (14x2cm discs) - analysis to establish composition, main interactions - examination of filters to assess release
Compared to unirradiated, irradiated UO$_2$ and MOX show considerable attack. Unirradiated UO$_2$ and MOX show “regular” attack & dendrite formation.

Cracks in fuel during testing (HBU UO$_2$ – full fragmentation)
Fission gas release & bubbling (irradiated MOX). Extended cracking & inherent stresses at high burn-up increases the rate of break-up and dissolution.

Zry dissolution of irradiated fuel: factors such as Zr/UO$_2$ ratio influence the melt viscosity (Zr-U-O or $\alpha$-Zr(O))

Rapid transfer of U (& Pu) into the Zr-rich melt & vice-versa. Minimum 5-10 w% Zr in the U,(Pu)-rich ceramic phase and 7-15 w% of U(+Pu) in the Zr–rich metallic phase. Melt is sub-oxidised U(Pu)-Zr-O system that separates into metallic & ceramic phases on solidification. Element interactions are more pronounced in irradiated fuel.
Investigation of corium formation and properties; fuel attack modes

Fuel
UO$_2$ 53 GWd/tU
non-irradiated UO$_2$
Zircaloy cladding int/ext diam.
8.2 / 9.5 mm
outer oxide thickness 5 - 10 µm
segment height 3 mm

Tests
Hold temperature 2000 °C
Hold times 25, 49, 73, 190 secs

Fuel
UO$_2$ ~90 GWd/tU
non-irradiated UO$_2$
MOX ~45 GWd/tU
non-irradiated MOX
Zircaloy cladding ~9.8 mm ext.
segment height 5 mm

Tests
Hold temperature 2000 °C
Hold times 25, 190, 600 secs, 60mns

Direct electrical heating in graphite crucible - rapid cooldown (oven switch-off) – He atmosphere

Examination: optical microscopy, image analysis, microprobe analysis.

ITU main testing conditions
Irradiated fuel completely dissolved at 25s; unirradiated dissolves slowly. Unirradiated fuel breaks into larger geometric shapes compared to irradiated fuel. Irradiated fuel has irregular surface of attack; unirradiated shows a uniform surface of attack. Irradiated fuel shows very high porosity; unirradiated fuel retains low porosity.

Interaction of cladding with the fuel cladding has 2 phases, fuel highly porous.
EDX mapping picture 3 area 1

Electron Image 1

C

O

Al

Si

Ca

Fe

Zr

U
TMI-2 samples at ITU, after 20 years

Ceramography samples (no polishing)

O7-P4-E (agglomerate)
G12-P6-E (core bore rock)
G12-P9-B, powder
G12-P6-E, fragment
Fuel, corium debris studies

- Source term for radionuclide release.
- Corrosion in seawater and other aqueous media of spent fuel, molten fuel debris.
- Mechanical properties of TMI-2 and other debris to assess retrieval and conditioning options.
- Handling/storage/conditioning of debris; ageing studies.
- Specific aspects of the Fukushima events (BWR, B₄C, ex-vessel interactions,…).
- SAFEST (2014-): JRC leads WP2 on the development of severe accidents research roadmaps.

TMI-2 core bore rock samples, after >25 years
Molten Core Concrete Interaction sample (U, Zr, Ca, Si, Mg, C, O). CEA Cadarache carried out MCCI VULCANO test VBU6: (U,Zr)O$_2$ corium was poured into a silicaceous concrete crucible. Samples provided to ITU and UJV.

ITU carried out EDS, metallographic phase analysis, Laser Ablation-ICP-MS as well as Digestion and chemical analysis by ICP-MS
Fuel, corium debris studies

- Source term for radionuclide release.
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LWR fuel fracturing behaviour

Room temperature impact test, LWR spent fuel rod

Thermal fracturing and source term for release: 920 K, UO$_2$ 160 GWd/t (local)

Papaioannou et al. 2009 (collaboration with GNS, AREVA); CRP SPAR III 2014

Hiernaut et al., 2008
Severe accidents projects (selection)


**Chernobyl.** A real accident with very limited initial data – integral studies made and on-going projects for conditioning waste and slow waste degradation.

**Phebus** FP test. Irradiated fuel bundle degradation and melting (1988-2012). Integral test with good data collection, but still difficulties in interpretation. Led by IRSN (France) and supported by the European Commission. USA, Canada, Japan, Korea and Switzerland also participated.

Five integral tests under different conditions. On-line monitoring of bundle degradation, $fp$ release and subsequent behaviour in the simulated primary circuit and containment.

**Corium Interaction Thermochemistry (CIT).** EC Framework, 8 partners (1997-1999) small scale tests of liquid Zry dissolution of (irradiated) UO$_2$, and modelling

**Core Loss of geometry (CoLoss).** High T interaction with cladding: UO$_2$, MOX

**Revaporisation** testing. EC Framework project, 3 partners single effect tests of (re)volatilisation of fission products under different atmospheres
Objectives of the examination:

- characterize corium (& other phases)
- determine temperature levels and prevailing oxygen potential conditions
  \( \rightarrow \) degradation reactions
TMI-2 and other specimens for Fukushima-related studies

• There are limited core bore & agglomerate samples from TMI-2 available at ITU; some have been retrieved including core bore rock, agglomerate zone and debris

• Samples from other campaigns could be also retrieved

• In the medium term, new degraded/molten fuel samples could be prepared

• Apply available advanced PIE tools in order to examine relevant aspects such as thermo-mechanical properties, elemental/phase distribution, high T behaviour, corrosion/interactions with salt water or molten salts, extended storage effects, …

• Focus on specific conditions of Fukushima-daiichi accident (BWR, prolonged LOCA, MCCI,…)

• Studies on irradiated fuel complemented by thermodynamic measurements on key systems

• A long-term collaboration with CRIEPI is underway; collaboration with JAEA and other Japanese partners in this field is envisaged.
Led by Institut de Protection et Surêté Nucléaire (IPSN); supported by the European Commission. USA, Canada, Japan, Korea, Switzerland also participated.

6 integral tests planned with steam flow being restricted and bundle overheating. Online monitoring of bundle degradation, fission product release and subsequent behaviour in the simulated primary circuit and containment.

- **FPT0**: (base-line test) degradation of a non-irradiated, 20 x 1m fuel rod bundle under a steam atmosphere (restricting steam flow) (Dec ‘93).
- **FPT1**: degradation of 18 irradiated fuel rods (23 GWd/tU mean burn-up)- bundle was degraded under steam (July ‘96).
- **FPT4**: examination of the late stages of an accident with the degradation of a debris bed of irradiated fuel pieces (33 GWd/tU) and oxidised cladding pieces under steam. Here the semi- and non-volatile fission products were particularly investigated (July ‘99).
- **FPT2**: degradation of irradiated fuel bundle (35 GWd/tU) with a period of low steam flow, to see the effect of reducing conditions on bundle degradation interactions (Oct. 2000).
- **FPT3**: degradation of irradiated fuel bundle with B$_4$C absorber present in the reactor (compared to Ag- In- Cd for previous tests) - (2004).
Hot labs at ITU

- 24 hot cells (licensed capacity $10^6$ Ci = $3.7 \times 10^{16}$ Bq)
- Full length individual fuel rods: commercial and advanced reactors, test irradiations
- Shielded SEM, OM, EPMA, SIMS, Laserflash, Knudsen cell, XRD for PIE
- Minor Actinide lab for synthesis of minor actinide fuels and compounds
- Hot labs with glove boxes for scientific studies on unirradiated actinide materials
- Support: radioprotection, ventilation, power, civil engineering, hot cell intervention, decontamination, decommissioning, waste removal, administration, security
- Supporting workshops including manipulators maintenance
Hot cells

big cell layout

caisson for a big cell
Hot cells

chemistry cell layout

Pb-cell layout

materials (samples) transportation: conveyor belt, pneumatic post, transport containers
Matrix dissolution

Seawater

Dissolution rate (mol/m²s)

<table>
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<th></th>
<th>U</th>
<th>Pu</th>
<th>Cs</th>
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<tbody>
<tr>
<td><strong>SW</strong></td>
<td>4.1E-10</td>
<td>1.2E-13</td>
<td>3.7E-05</td>
</tr>
<tr>
<td><strong>DW</strong></td>
<td>2.2E-12</td>
<td>7.2E-13</td>
<td>1.7E-05</td>
</tr>
<tr>
<td><strong>BicW</strong></td>
<td>2.9E-11</td>
<td>2.1E-13</td>
<td>2.3E-05</td>
</tr>
</tbody>
</table>

Higher U corrosion rate in SW
Similar corrosion rate for Pu and IRF