Annual Meeting of Hot Laboratories & Remote Handling

# HOTLAB 2016

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# Application of Material Properties Data to Strategy / Problems facing Decommissioning in Fukushima Dai-ichi NPPs.

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# Examination of degraded fuel and fission product samples and their application to optimising decommissioning techniques.

1. Introduction
2. TMI-2 investigation (OECD –NEA project)
3. Phébus PF- an IRSN–lead project
4. Chernobyl
5. Revaporisation
6. Small scale tests
7. Discussion & Conclusions

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# Examination of degraded fuel and fission product samples and their application to optimising decommissioning techniques.

## 1. Introduction

a) Renewed interest in severe accident (SA) research, especially following Fukushima

b) Thus application of the research findings on degraded fuel and debris to the decommissioning techniques become of immediate relevance.

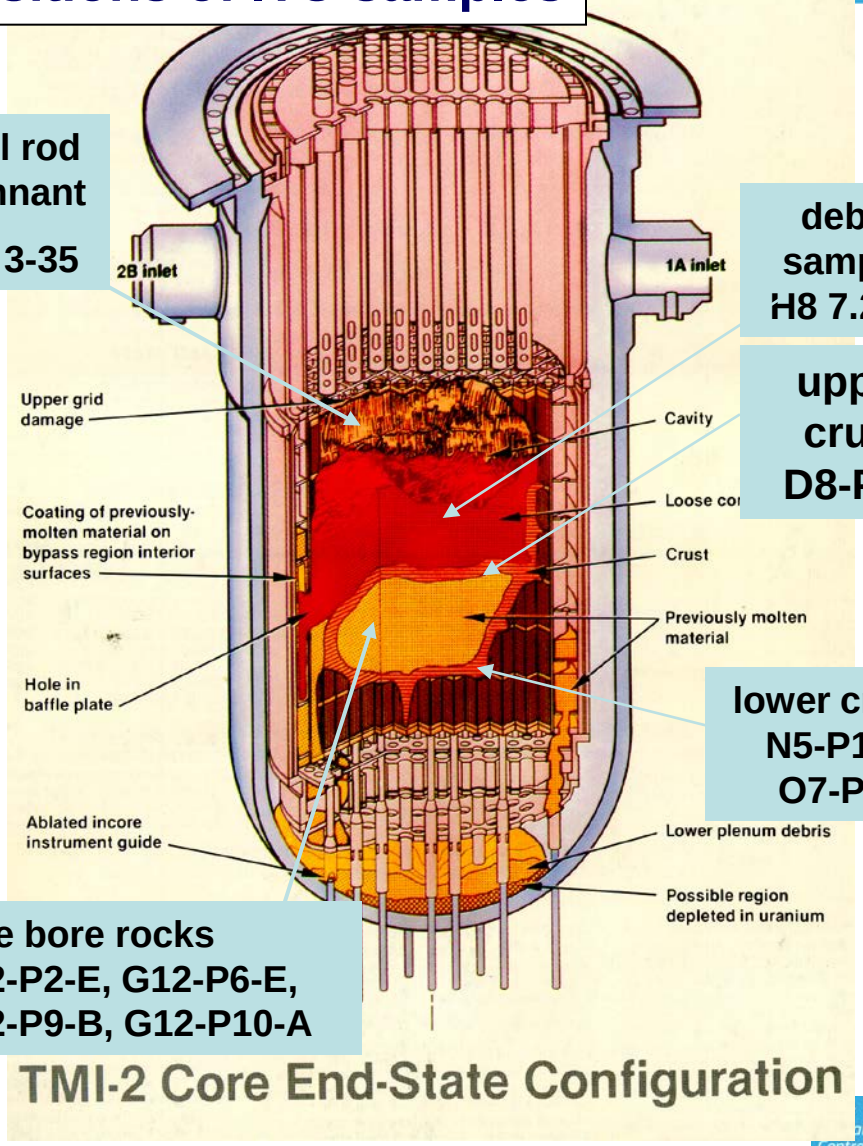
c) Review data from previous major incidents such as Chernobyl (1986) and TMI-2(1974): these can bring much experience on the longer term effects of waste accumulations, as can remediation of old sites (eg. Sellafield, Semipalatinsk polygon)

d) ITU-Karlsruhe is involved is SA and fuel debris research with European partners via Framework Programmes (eg.SARNET1, 2 and NUGENIA) as well as previous projects (eg Phebus PF, TMI-2).

e) Results are important for directing future SA research (identifying phenomena & indicating priorities: experimental, modelling/TD calculations (re-evaluating PIRTs)

# 2. TMI-2 Sample Analysis –OECD –NEA project

## Positions of ITU samples




fuel rod remnant
C7 3-35

debris samples
H8 7.2-7.9

upper crust
D8-P2,3

lower crust
N5-P1-E
O7-P4

core bore rocks
G12-P2-E, G12-P6-E,
G12-P9-B, G12-P10-A

## Objectives of the examination:

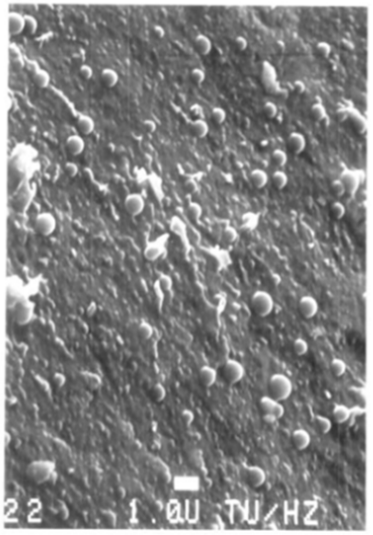
- characterize corium (& other phases)
- determine temperature levels and prevailing oxygen potential conditions
→ degradation reactions

**Conditions during accident**

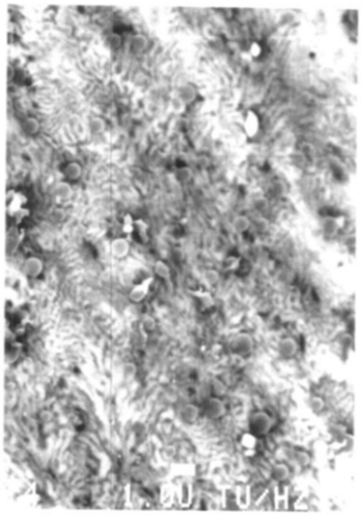
- Tmax: core edge: T < 800C
  agglomerate: T ~ 1500C (steel Tm)
  molten core: T = 2000-2500C
  (up to 2850C ?)
- Cool-down. core edge: transient T rise; slight degradation
  agglomerate: more rapid & variable
  molten core: slow (2-54 h)

# 2.1 TMI-2 Core bore rock –mainly oxidic

**G12-P9-E Fracture Surface -SEM**
**a) & b) dense (U-rich) phases and lighter (Zr-rich) oxide phases**
**c) Many fine metallic Ag precipitates on the surface.**
**Fe-rich oxide phases also present.**



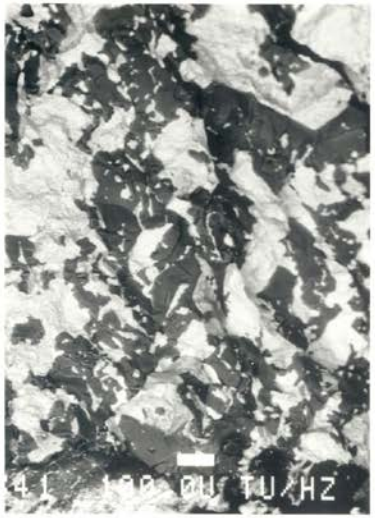

SEI



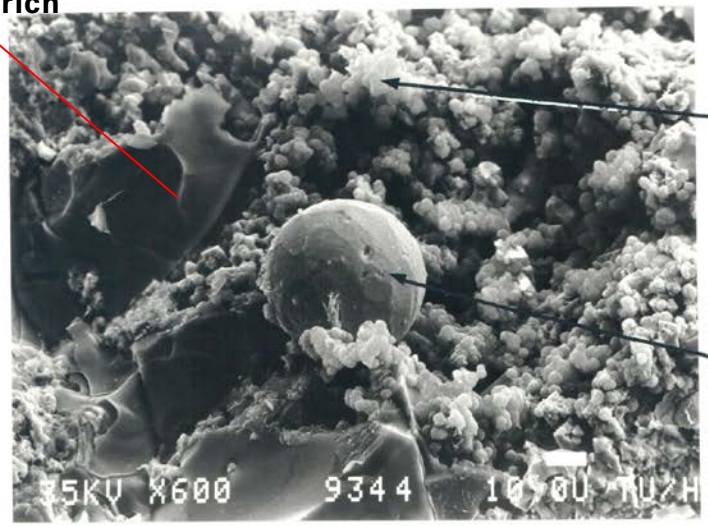
BEI

**Note the very fine eutectic structure with lamellae <1µm wide - suggesting cooling times of up 50 h for central corium.**


a) Secondary Electron Image **60x mag**



b) Back-scattered Electron Image **60x mag**




c) Silver Sphere Precipitate **600x mag**

# 2.2 TMI-2 Agglomerate - metallic and oxidic phases

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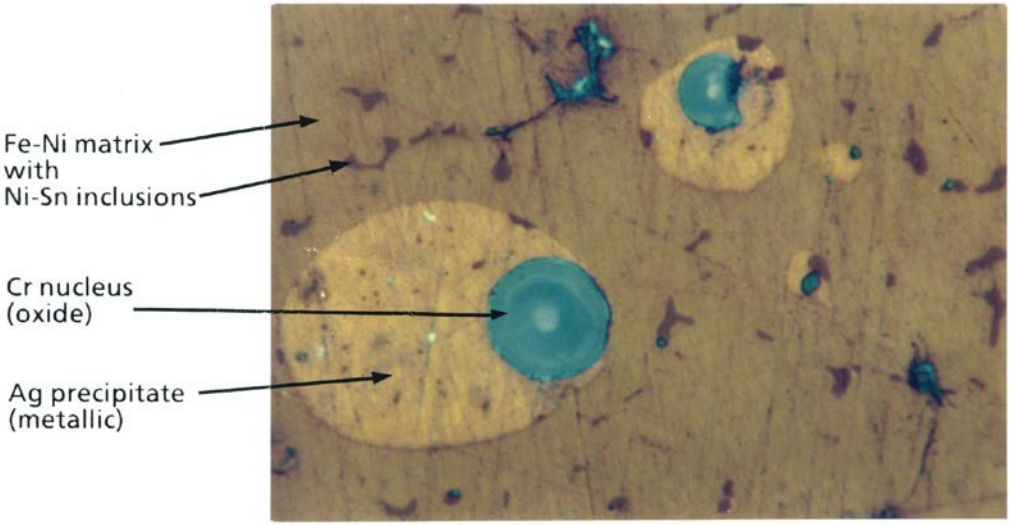
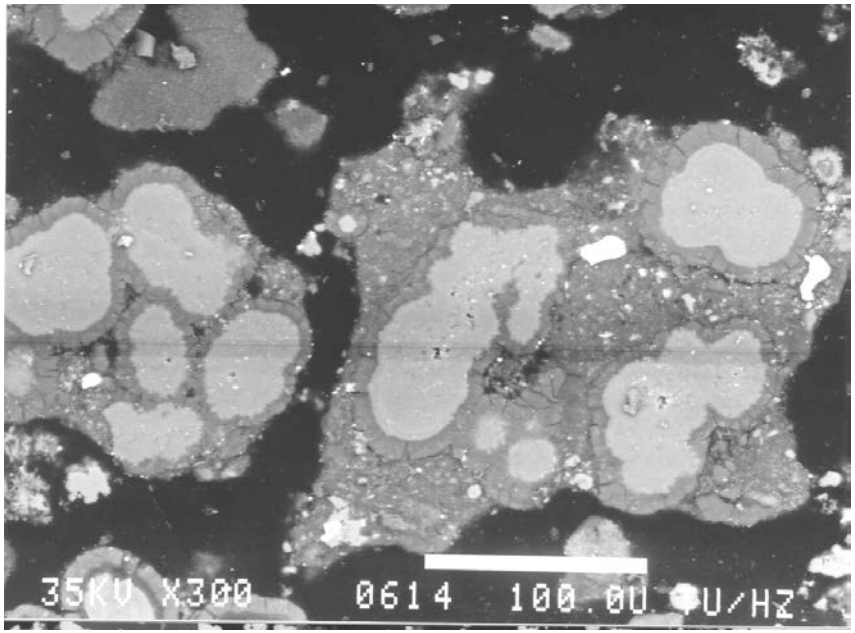
## Examples of partially oxidised materials




b) Interference Micrograph (1033x)




**Agglomerate N5-P1-E (1033x).**
**(CuO vapour coating)**
**ceramic & metallic phases from a control rod**
**ρ ~6.7 g/cm³ (steel ρ= 7.93 g/cm³)**
**Stainless steel control rod cladding with Ag precipitates that contain Cr oxide nuclei.**

**Agglomerate crust O7-P4-EA**

**Fe-Ni nodules with pure Fe metallic core (lighter centres) surrounded by Fe-Ni oxide crust (darker zones) due to preferential oxidation (BSE-1000x)**

# 2.3 TMI-2 summary of findings

1) Core bore rock were fully oxidic U,$ZrO_2$ with Fe-rich (with Cr, Ni) phases.

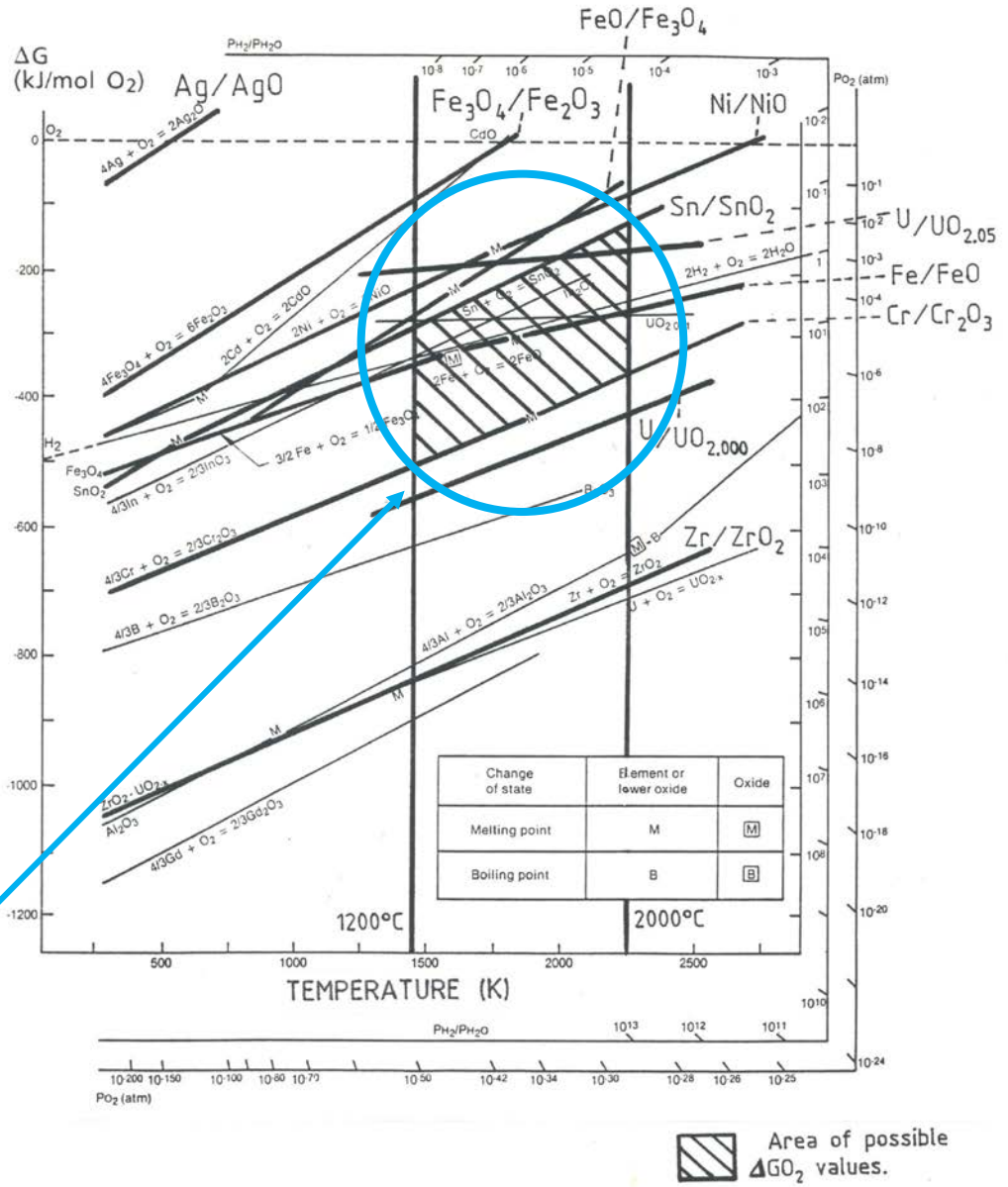
2) $Al_2O_3$ also seen from burnable ($Gd_2O_3$) poison rods.

3) Slightly superstoichiometric

4) Oxygen potential at temperatures of 1200C to 2000C were estimated at -150kJ/mol to -510kJ/mol $O_2$.

5) Core centre probably cooled down judging by lamellae in 40-50 hours.

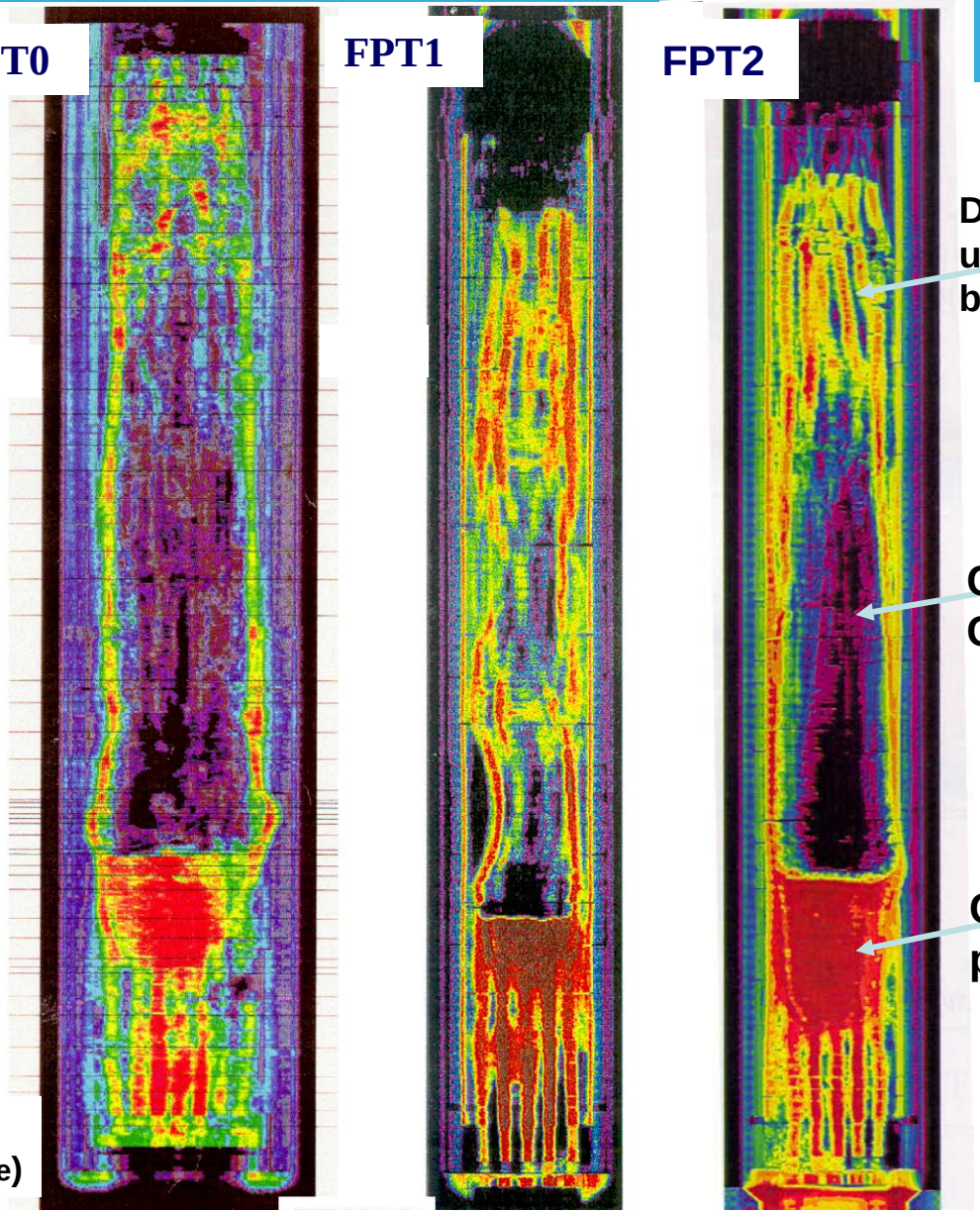
6) Agglomerates were mixed cladding/fuel/structural materials debris in partially oxidic & metallic form
(Fe-Ni-Sn metal, (Fe,Ni)-Zr-U oxides, partially oxidised Ni,Fe nodules, metallic Ag nodules)




**Range of oxygen potential observed in core bore rocks & agglomerate zones**

# 3.1 Phebus PF






**Reproducible degradation geometry**

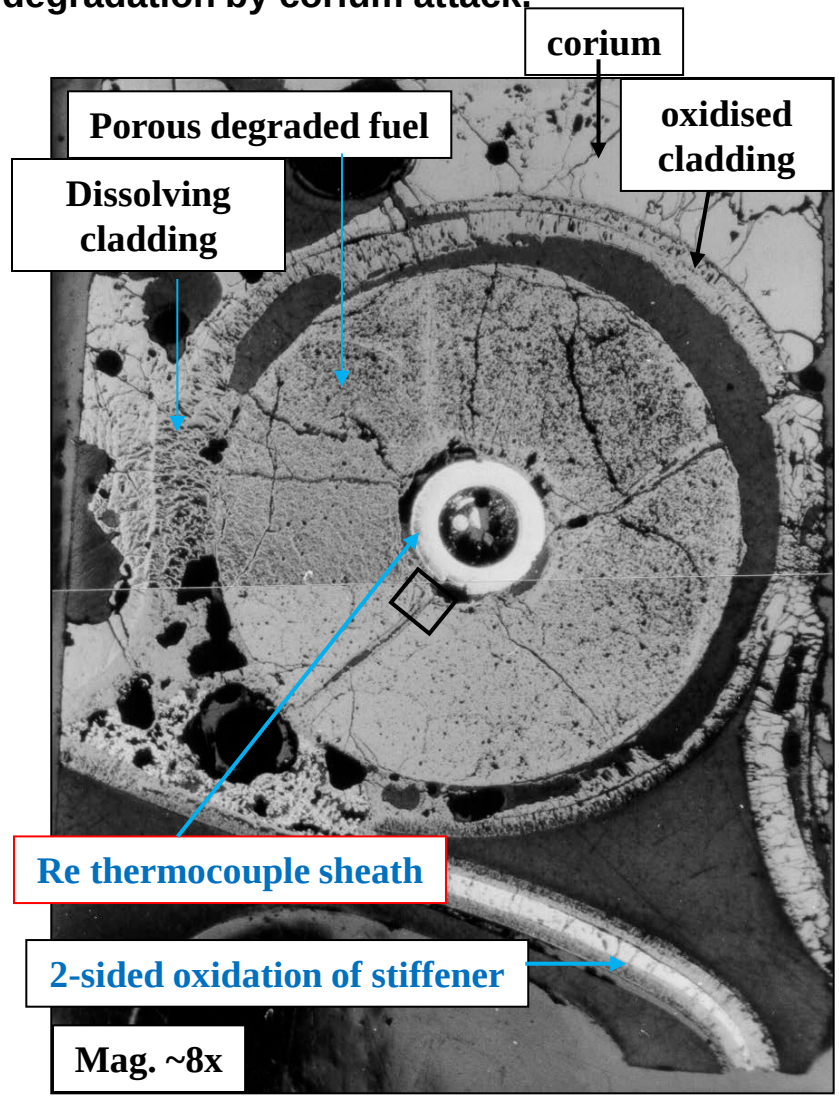
(IRSN Cadarache)

False colour tomography of FPT bundles with dense molten pools (red) at quarter-height & central cavities (black) above (IRSN).

# 3.2 Phebus PF

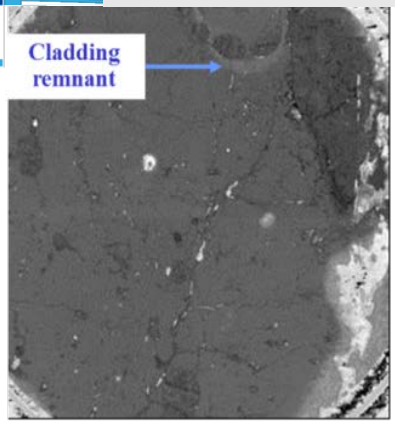
## Phebus FPT0 - Corium Pool edge

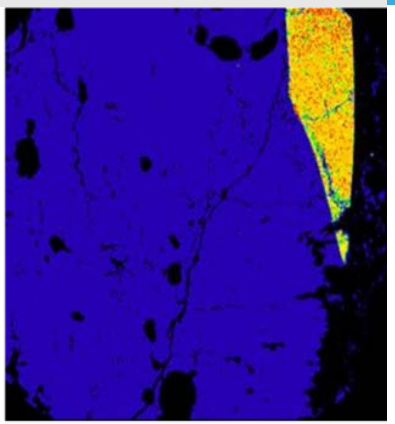
Cladding of outer fuel rod undergoing degradation by corium attack.




**Hard thermocouple materials present**

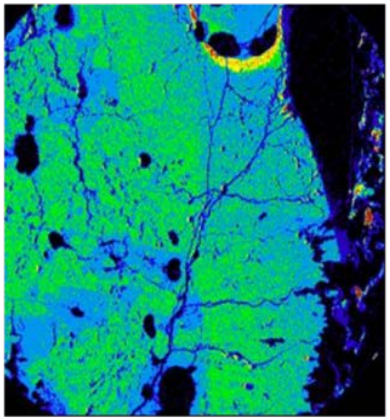
## Phebus FPT2- Corium Pool

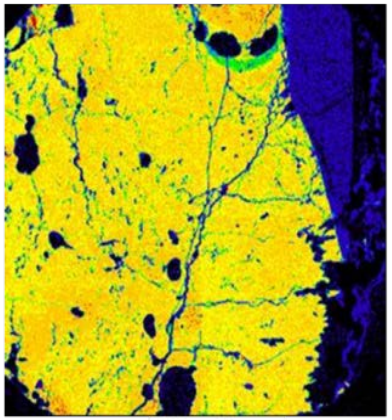


Absorbed current (AEI)

Thorium





Zirconium

Uranium

Large area mapping of disc 4 of Phébus FPT2 upper corium pool. Mappings show the Zr,U oxidic corium varies with position.

**Remnants of structure eg cladding can be hidden within the relatively uniform corium.**

# 3.3 Phebus PF

## Phebus FPT0- PIE of Corium Pool

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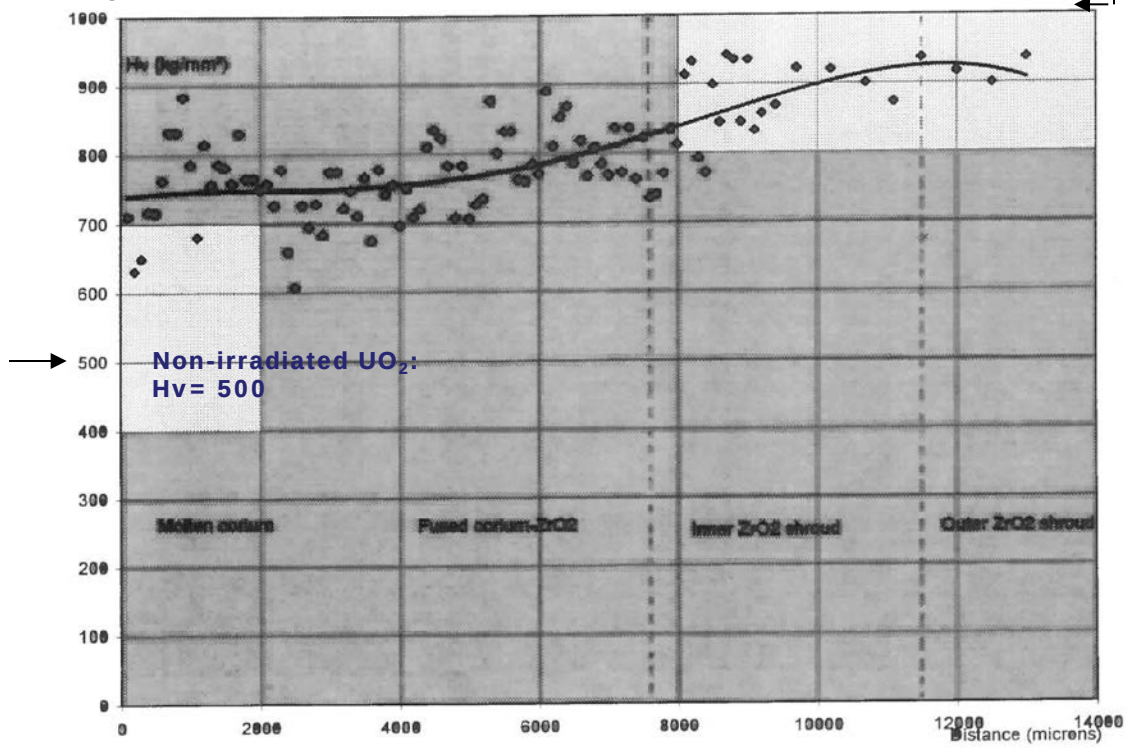
### Vickers Hardness Measurements (Hv) of corium / $ZrO_2$ shroud interface

Kg / mm²

$ZrO_2$: Hv= 1000

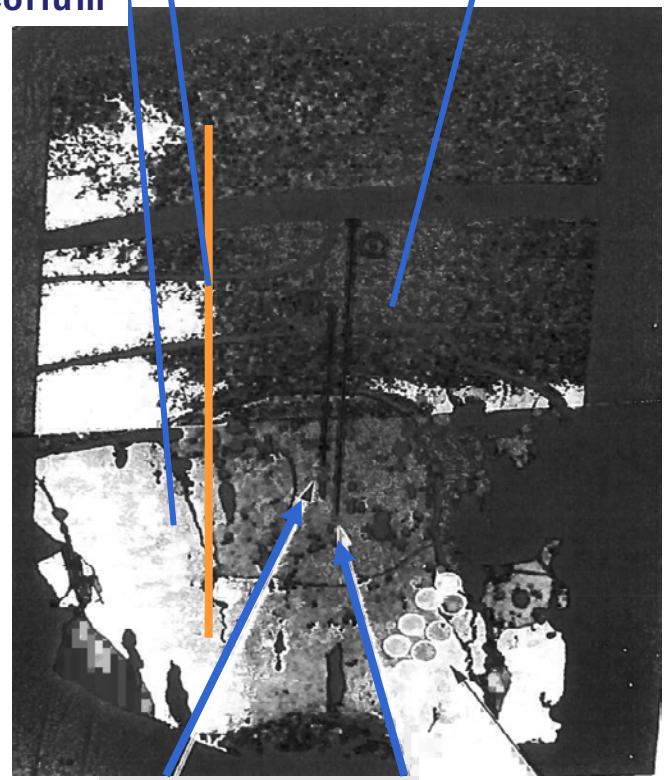
Weight: 100g,
Loading time: 10s




Hardness profile

$ZrO_2$ shroud

Corium

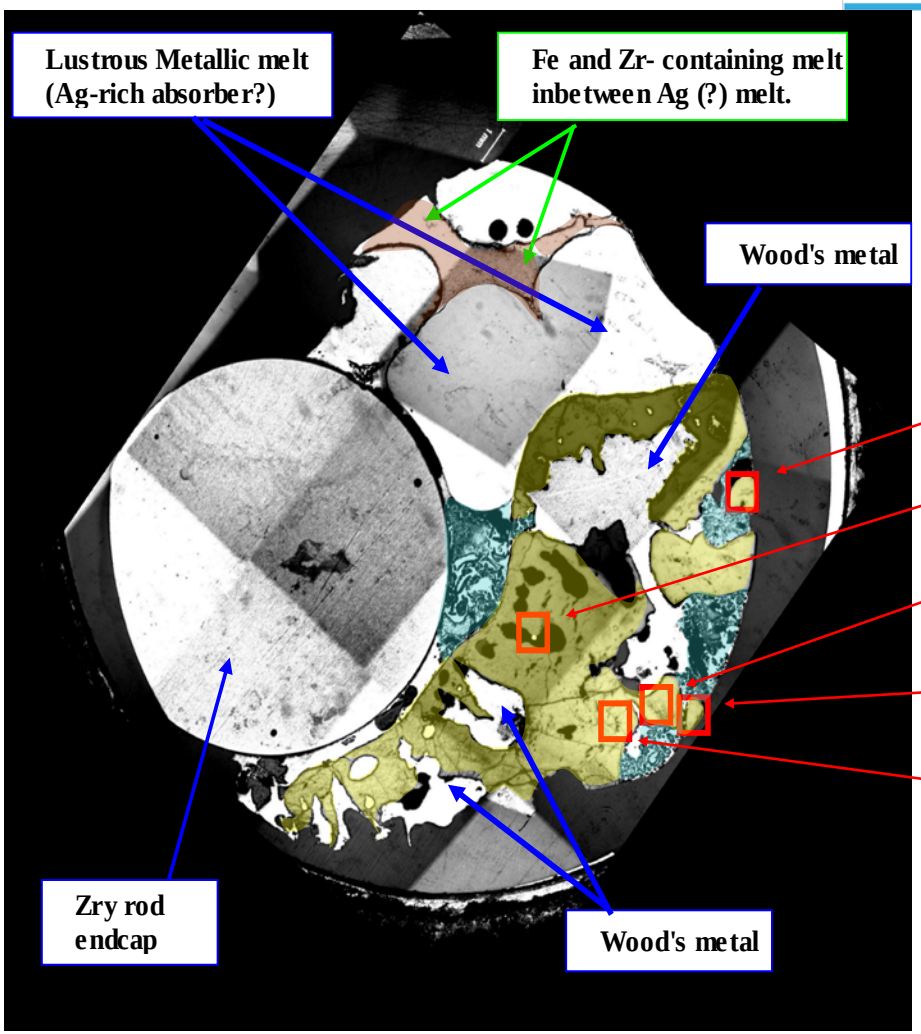


EMPA linescans

a slow hardness transition due to interdiffusion between mixed $(U,Zr)0_2$ corium & $ZrO_2$ shroud

Research Centre

# 3.4 Phébus FPT2 - Phase  Map of Disc 1 – beneath the corium pool




**LEGEND**

Corium

Mixed Debris areas

Fe-Ze melt

**Corium U/Zr ratios**

Zone 8: U/Zr = 1.179

Zone 17: U/Zr = 1.233

Zone 4: U/Zr = 1.016

Zone 3: U/Zr = 0.845

Zone 18: U/Zr = 0.856

Mean U/Zr = 1.026

Two corium flows of slightly differing compositions - at different times ?

central zone

Edge zones (Zr-richer)

**North-west is metallic melt**
**South-east is mainly corium**

**Bottom of bundle is very heterogeneous with sturdy supporting structures & solidified debris / corium**

# 3.5 Phébus PF: Comparison of EMPA corium analyses of FPT1 & FPT2 (at different heights)

| | Bundle Zone | Formula | U/Zr ratio | O/M |
|---|---|---|---|---|
| Disc 4 | Pool | $[(U,Pu)_{0.517}Th_{0.042}Zr_{0.416}(Fe,Cr,Mo)_{0.021}Nd_{0.003}]O_{2.22}$ | 1.44 | 2.22 |
| Disc 2 | Below pool | $[(U,Pu)_{0.57}Zr_{0.40}(Fe,Cr,Mo)_{0.03}]O_{2.01}$ | 1.44 | 2.010 |
| Disc 1 | Base of column | $(U_{0.49}Zr_{0.48}Fe_{0.017}Cr_{0.008})O_{2.01}$ | 1.03 | 2.001 |

EMPA analysis of FPT1 corium pool $(U_{0.52}Zr_{0.44}Fe_{0.03}Cr_{0.01})O_{2+x}$ U/Zr (at) = 1.18

1) Coria is usually close to stoichiometry: ~2.01 (O content in FPT2 corium seems too high)

2) The U/Zr ratio varies with height. More Zr at the bottom than the pool. Local variations can be bigger.

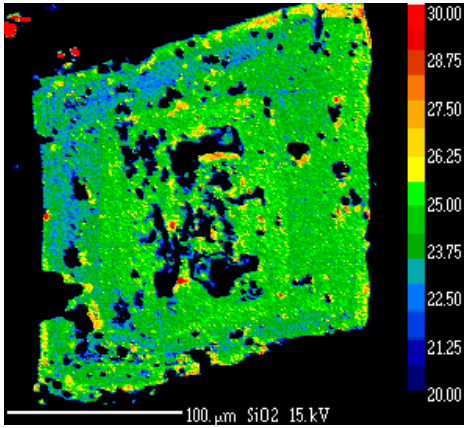
3) Corium at the bottom (eg Disc 1) has not accumulated Th (from shroud) or Pu from irradiated fuel.

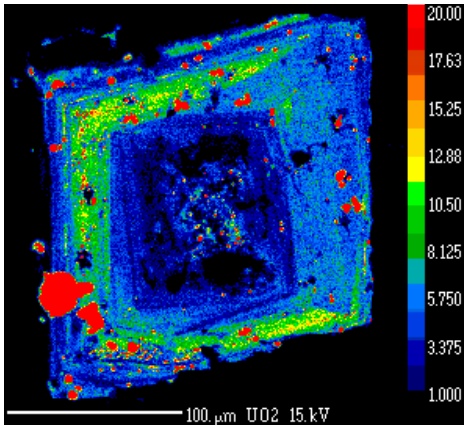
4) 3% structural materials in coria: Fe, Cr & traces of Ni & Ag (Ag found as large separate masses or as fine precipitates dispersed in fuel).

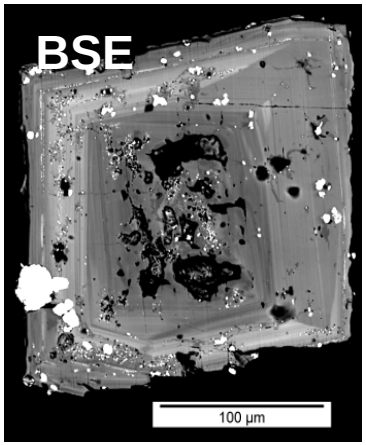
5) FPT1 & FPT2 coria have comparable U/Zr ratios 1.18 and 1.44 resp.

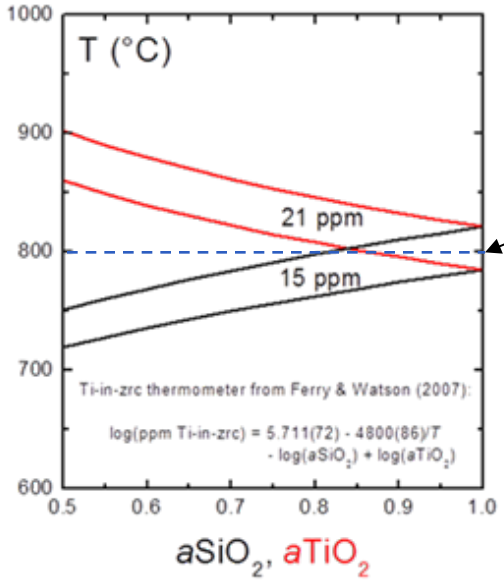
The quantitative analysis of corium pool enables
1) Determination of large parts of fissile inventory
2) Assessment of potential criticality issues & activity levels.
3) Corium at bottom more oriented to lower melting materials.

# 4.1 Chernobyl lava samples from reactor unit 2 at ITU



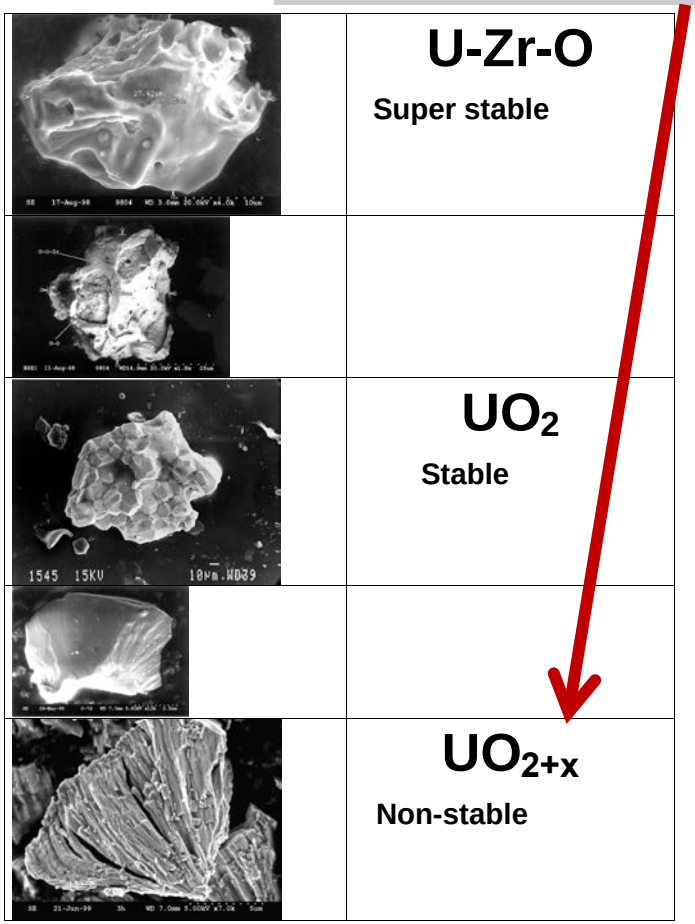

**Ferry & Watson Ti in Zr thermometer [Contributions to Mineralogy and Petrology, 154, p429-437 (2007)].**

**The graph shows the correlation of the solidification or crystallization temperature for [$SiO_2$] levels of 15ppm and [$TiO_2$] levels of 21 ppm.**
**The likely lava crystallization temperature is ~800° C.**

**Position of sample + crystallisation temperature indicates flow characteristics (eg lava viscosity). It can verify models of lava flow in Severe Accident codes particularly ex-vessel (MCCI) conditions with higher Si contents**

# 4.2 STCU project # 4207 (proposal) Experimental study of the fuel particles (FP) destruction rate, & dependence on the matrix characteristics (oxidation degree) & update of Database

Chernobyl «Hot particles» (HP) classification and Database indicates there is a longer term, small (μm) particle release as aerosol.




•Chemically super stable Fuel Particles (FP) (**U-Zr-O)** formed as a result of the high-temperature melting of the construction materials (zirconium cladding of the fuel elements) and their fusion with $UO_2$. These FPs were formed during the initial explosion on 26.04.86 and were mainly deposited along the narrow western trace of release zone;

•Non-oxidized chemically stable FP (**$UO_2$**) of the first release (26.04.86) formed as a result of the mechanical destruction of the nuclear fuel. These FP were mainly deposited along the narrow western trace of release. The fission products leakage from these FP was minimal, which is confirmed by the fixed radionuclides activity ratios;

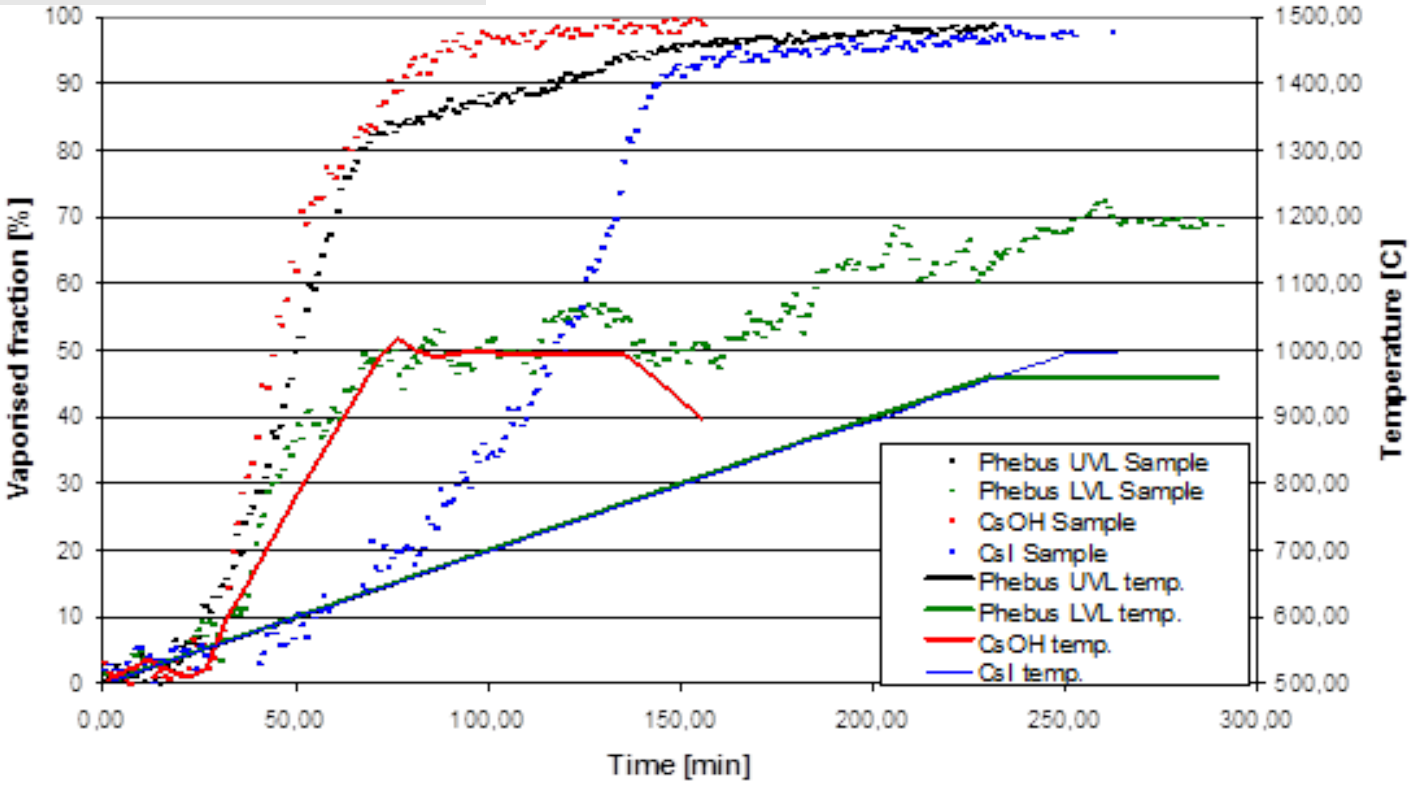
•Chemically non-stable FP (**$UO_{2+x}$**) formed as a result of the nuclear fuel oxidation in the period: 26.04.86-5.05.86. These FPs were mainly deposited at the northern and southern traces of release zone.

One of many publications from Ukrainian Inst. of Radiological Agriculture, Kiev: Kashparov V.A., Lundin S.M., Zvarich S.I., Yoschenko V.I., Levtchuk S.E., Khomutinin Yu.V., Maloshtan I.N., Protsak V.P. Territory contamination with the radionuclides representing the fuel component of Chernobyl fallout //*The Science of The Total Environment*, vol.317, Issues 1-3, 2003, pp. 105-119.

# 5.1 Phebus FPT1 revaporisation tests of Cs-activity from vertical line deposits in steam & mixtures to 1000C

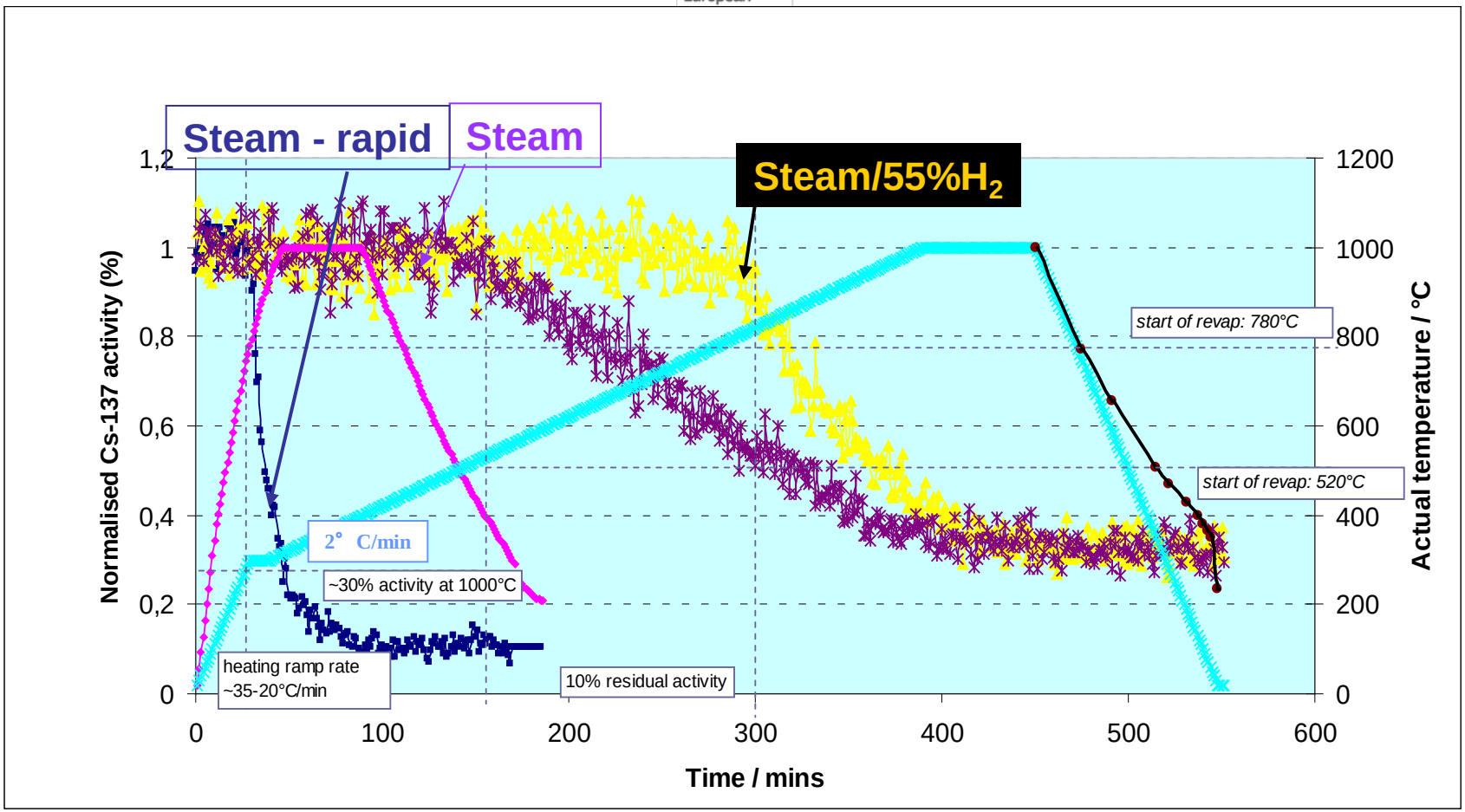
**Cs can revaporise rapidly & quantitatively (as CsOH) under steam >550C. Valuable kinetics information**

**(Phébus & SARNET)**




**Revaporisation of radiotracer CsI, CsOH deposits and mixed Phébus FPT1 deposits from the upper (UVL) and lower (LVL) parts of the vertical line above the FPT1 bundle.**
**-see rapid volatilisation of FPT1 (Cs-rich deposit) at 550-650C with 95% loss at 1000C; most similar to CsOH deposit.**

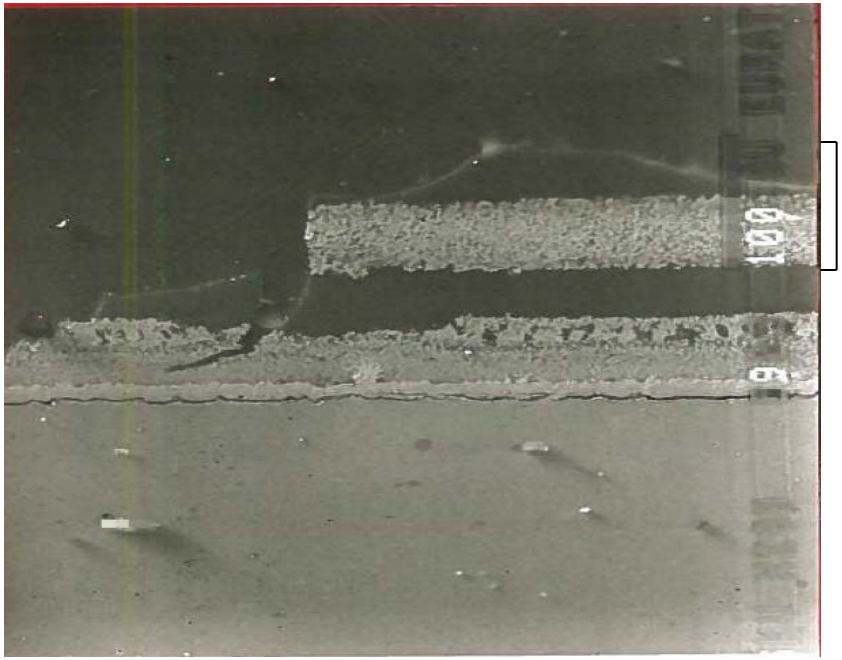
# 5.2 Phebus FPT3 revaporisation tests of Cs-activity from vertical line deposits in steam & mixtures to 1000C




**Effect of a) heat-up rate & b) reducing atmosphere**

**(Cs also very volatile under reducing conditions ($H_2$)).**

# 5.3 Revaporisation testing of thick FPT0 deposits

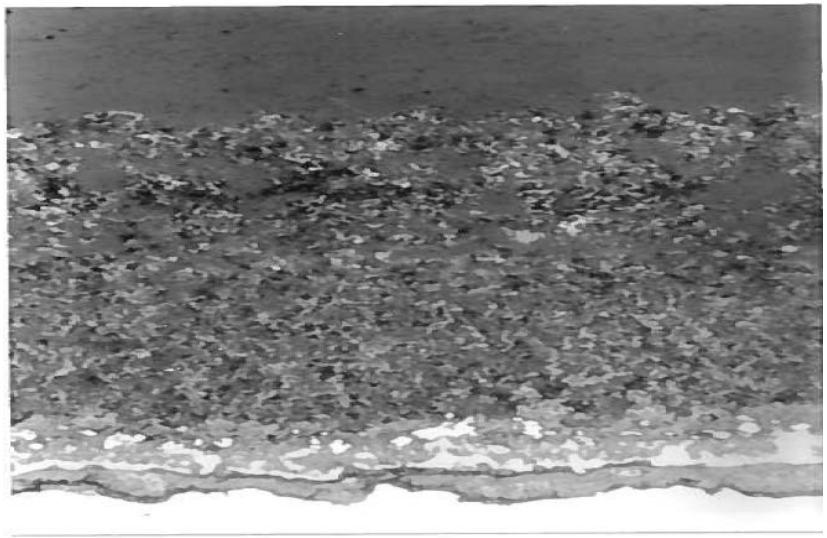


100µm

Deposits on Vertical line of FPT0 (mag. 200x

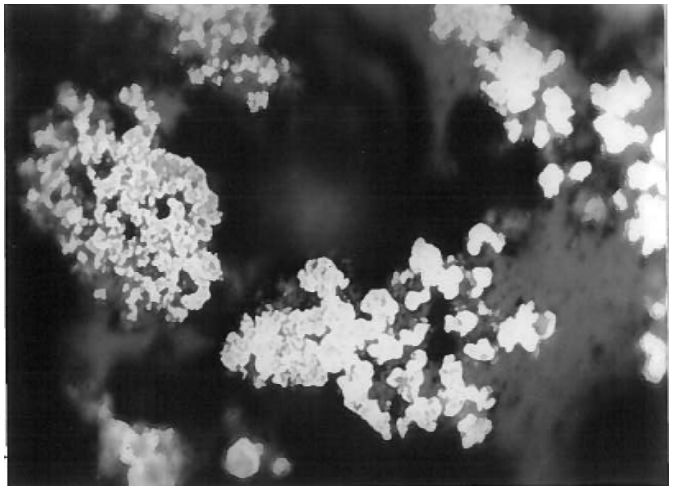
Note the layered deposits, showing different phases of volatilisation of fuel and fission products from the bundle

## Vertical line of FPT0: V110 (stainless steel)

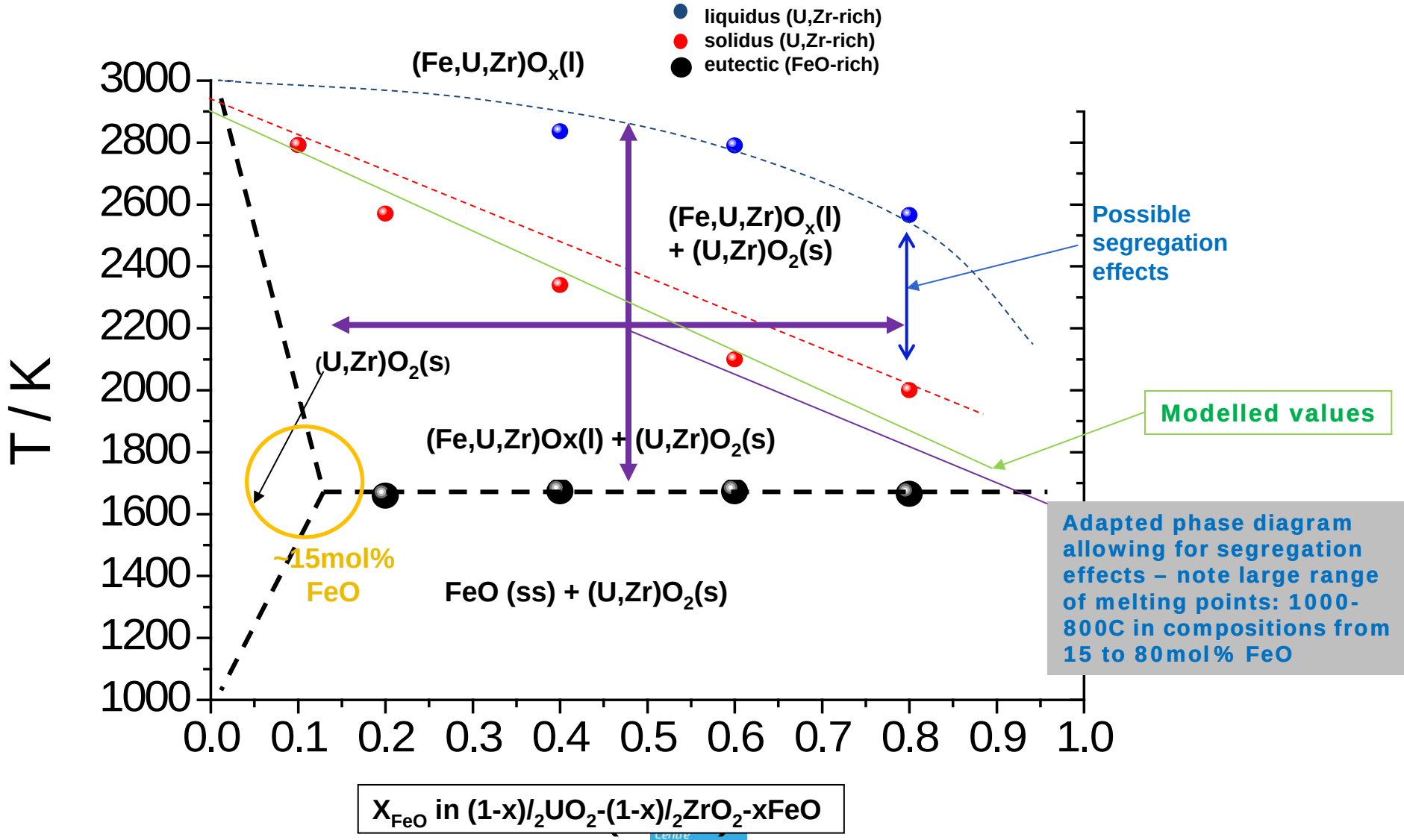


Porous deposits of vertical line: Mag. 1100x

Agglomerated particles from aerosol deposits of vertical line: Mag. 1100x

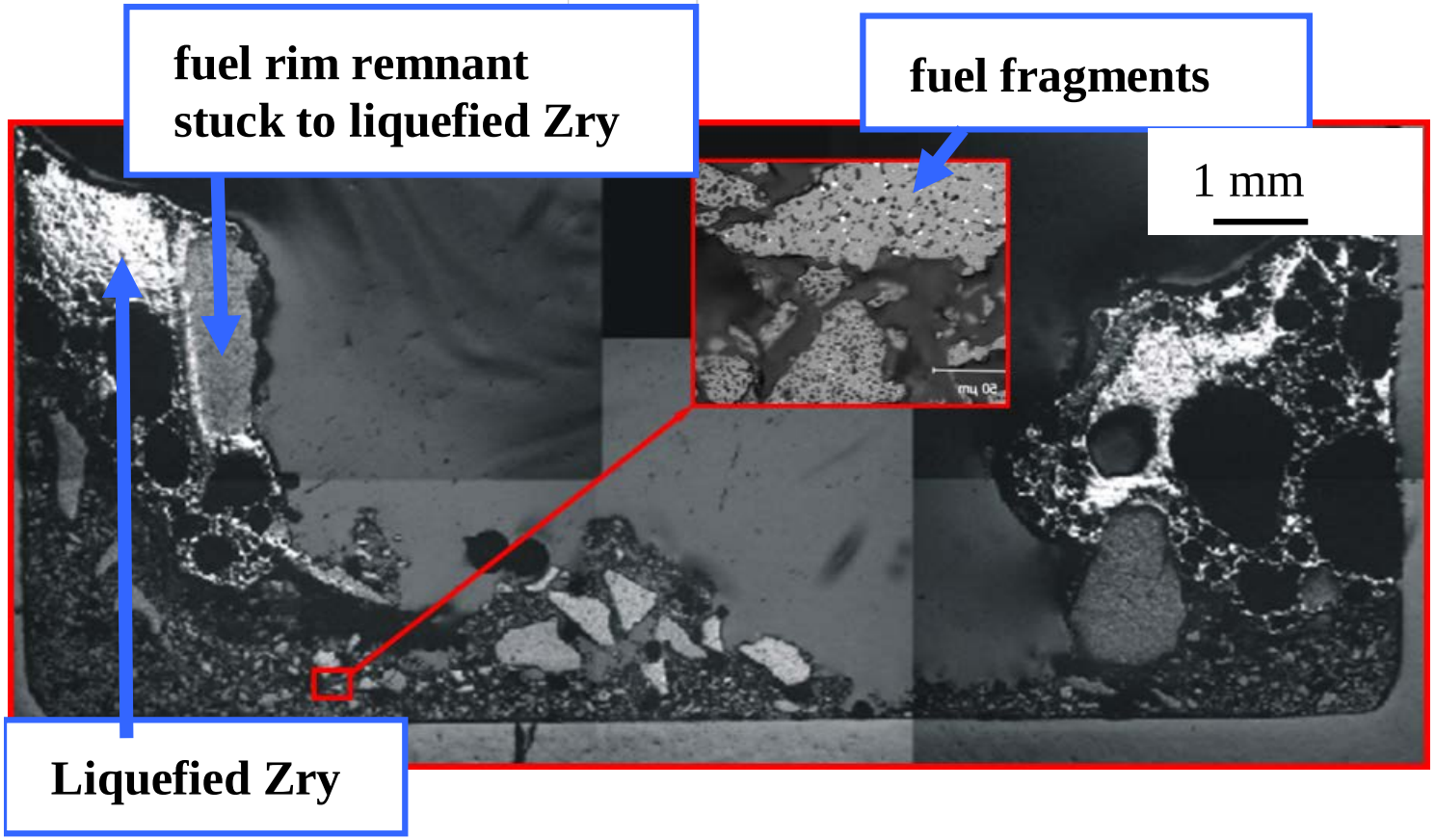


# 6.1 Results from smaller scale tests
## Melting point detn. by laser flash heating: $UO_2$-$ZrO_2$-FeO Phase Diagram



# 6.2 Results from smaller scale tests
# High burn-up $UO_2$/Cladding interactions

## Small $UO_2$ dissolution Tests (COLOSS)




**Cross-section of very high burn-up irradiated $UO_2$ fuel after exposure at 2000° C for 5 mins. in He atmosphere.**
**The fuel has completely fragmented or reacted with the melted cladding**

**Fission gas release causes:**
**1) increased break-up and**
**2) faster mixing of liquidifying irradiated fuel compared to non-irradiated fuel**

# 7. Discussion: Application to optimising decommissioning techniques.

## A) PIE Analysis

1. Bundle degradation results in a cavity and corium pool of a mixed oxidic ceramic: $(U,Zr)O_2$ + structural material oxides that is stoichiometric and stable. Analysis gives
   1) inventory & material distribution
   2) physical properties (eg hardness, density)
   3) oxidation conditions during accident
   4) form (pieces, powder, large masses).

2. a) Chernobyl lava has a more mixed, ex-vessel composition: $(U,Zr)O_2$ + Si, Ca, Na, Mg & Fe oxides; much corium/fuel in powder form.
   b) Super-stoichiometric $(U,Zr)O_{2+x}$ particles appear to be forming micron-sized aerosols (radiation or weathering?).

3. Epoxy resin-embedded fuel observed to produce $H_2$ slowly in 10-20 yr storage.

The debris stability needs to be monitored during decommissioning.

# 7. Discussion 2: Application to optimising decommissioning techniques

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## B) Bundle Cutting

1. Large structures especially at base can be hard and difficult to cut.
2. Hard remnants may be found in corium (eg. Re metal sheath blunting blades; epoxy resin can smear blade and limit cutting).

3. Carotting of large pieces necessary to obtain small samples of interest.

4. $UO_2$ fuel hardness increases steadily with $ZrO_2$ content. Other elements eg B from $B_4C$ could result in extremely hard materials.

5. Cutting is made more difficult by lack of visibility during operation.

# 7. Discussion 3: Application to optimising decommissioning techniques

## C) Fission Product volatility testing

**Considerable advances made in understanding fission product behaviour:**

1) **deposition in bundle or in primary circuit or containment (especially volatiles Cs, I). Deposition can represent considerable activity (potential source term).**

2) **Early condensed species (such as Cs, Te) may be more adherent, but still sensitive to revaporisation (eg. temperature rise by decay heat or steam blast).**

3) **Revaporisation be very high (>95% of total Cs on metal, 65% on porous ceramic surfaces); similar behaviour indicated for Te, Mo, Ru (as volatile oxides).**

# 7. Discussion 4: Application to optimising decommissioning techniques.

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## E) Sampling from primary circuit & containment

**When sectioning/cleaning primary circuit piping & containment areas prior sampling to identify problems is essential; but:**

1. **Sampling likely to dislodge or resuspend thick deposits.**

2. **Potential for FP high release by revaporisation if care is not taken (eg avoid hot air flows or sudden changes of atmosphere).**
   **(steam flows could be also used for removing deposits)**

3. **Underwater sampling: if water is flowing and not filtered before exit this will spread contamination or visibility of sampling area may be clouded by resuspended material.**

4. **Surface swipes or stubbing for analysis will be important (for thick deposits, layering may not be maintained).**

5. **Scratching may be necessary to obtain samples of adherent deposits. Thick sludges can be spooned/scraped out. Crusts may need separate sampling.**

Joint Research Centre

# 7. Discussion 5: Application to optimising decommissioning techniques.

European Commission

## F) Small testing of material properties (CIT, COLOSS, SARNET)

- **Small scale testing can determine corium's physical and mechanical properties & phase diagrams (eg. melting points and melting range). Chernobyl lava's crystallisation properties can be used to verify ex-vessel corium flow models.**

- **Melting points of fuel are not significantly changed with irradiation. However cracking & fission gas release causes very rapid corium mixing & FP release in irradiated fuel.**
- **Thus non-irradiated fuel testing will show the chemistry but will not reproduce the rapid kinetics.**

# Conclusions

1) Research into degraded fuel bundles and debris gives vital understanding into fuel/cladding interaction mechanisms and fission product release.

2) This knowledge of corium & debris composition enable of fissile material distribution and potential criticality risks to be estimated.

3) Determination of many mechanical and physical properties (hardness, density, porosity, viscosity) can be used to assess cutting & handling techniques.

4) Prior single effect testing and analysis of actual samples is essential to assess fission product risks (dispersion & dose rates during operation) as well as the choice of conditioning technique.

5) Necessary to innovate or have several techniques for unexpected problems.