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WASHOUT BEHAVIOUR OF CHROMIA-DOPED UO_2 AND GADOLINIA FUELS IN LWR ENVIRONMENTS

C. DELAFOY – M. ZEMEK

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  - Washout behaviour
    - Experimental means
    - PWR and BWR conditions
- **Conclusions**

Introduction

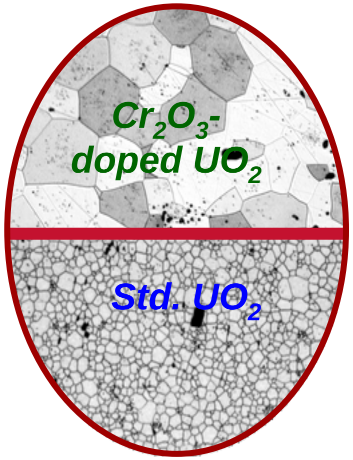
General Background

- Action lines continuously reviewed to maintain nuclear power generation more economical and competitive
  - **Long term ➨ Upgraded operating practices:**
    - Power uprate / High burn-up / extended fuel cycles
    - Improvement in nuclear plant availability and flexibility
      - Load-follow
      - Extended low power operations
      - Fast return to power
  - **Short term ➨ Fuel reliability and robustness**
    - Substantial lever for improving plant availability

» **Double challenge in the development of advanced fuel materials**

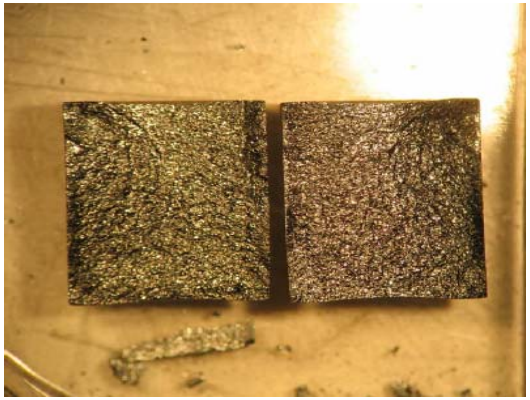
AREVA Cr_2O_3-Doped Fuel Development

- Fuel development initiated by AREVA in 1990 with **the aim** to **provide a fuel product for:**
  - **Better uranium utilization**
  - **Higher reliability and robustness**
- AREVA optimized Cr_2O_3-doped UO_2 fuel **key advantages:**
  - **Better Fuel Utilization**
    - High density fuel giving an **increase of the U^{235} mass** per fuel assembly
  - **Improved PCI Performance**
    - Very high adaptability in terms of power level variation (ramp rate)
    - Bring **additional margins** in **fuel maneuverability**
  - **Increased Operational Margins**
    - **Enhanced fission gas retention inducing lower internal pressure in fuel rods at end of life**
      - Enable to **operate** the fuel assemblies up to high burnup levels**,** for reactor **power uprate, fuel stack length optimization**
      - **Improved back-end fuel cycle conditions**

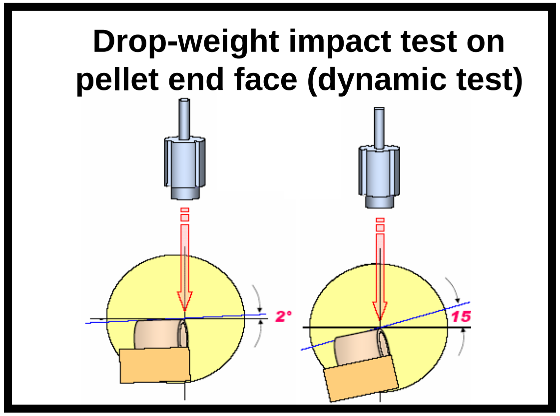


AREVA Cr_2O_3-Doped Fuel Development (Cont.)

- AREVA optimized Cr_2O_3-doped UO_2 fuel **key advantages:**
  - **Improved Reliability**
    - Higher **resistance to chipping** (missing pellet surface)



Fracture of Cr_2O_3-doped pellet generates few particles



Chipping mass loss ratio :

$$\frac{Cr_2O_3\text{ - doped fuel}}{Std.\,UO_2\text{ fuel}} = 0.60$$

- **Enhanced wash-out behavior** for **lower activity release** in case of defective rods

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Focus on Washout Fuel Consequences

- Failed fuel degradation after the occurrence of primary defects can affect nuclear reactor operation:
  - High **release of fission products** to **primary coolant**
  - **Fuel washout** due to direct contact of fuel pellet with the coolant
    - Tramp uranium results in increasing background activity level
- Previous experiments and observations reveal:
  - **UO_2 fuel readily oxidized** (high oxygen diffusion rate)
  - **Oxidation process controlled by surface reaction** (grain boundaries)

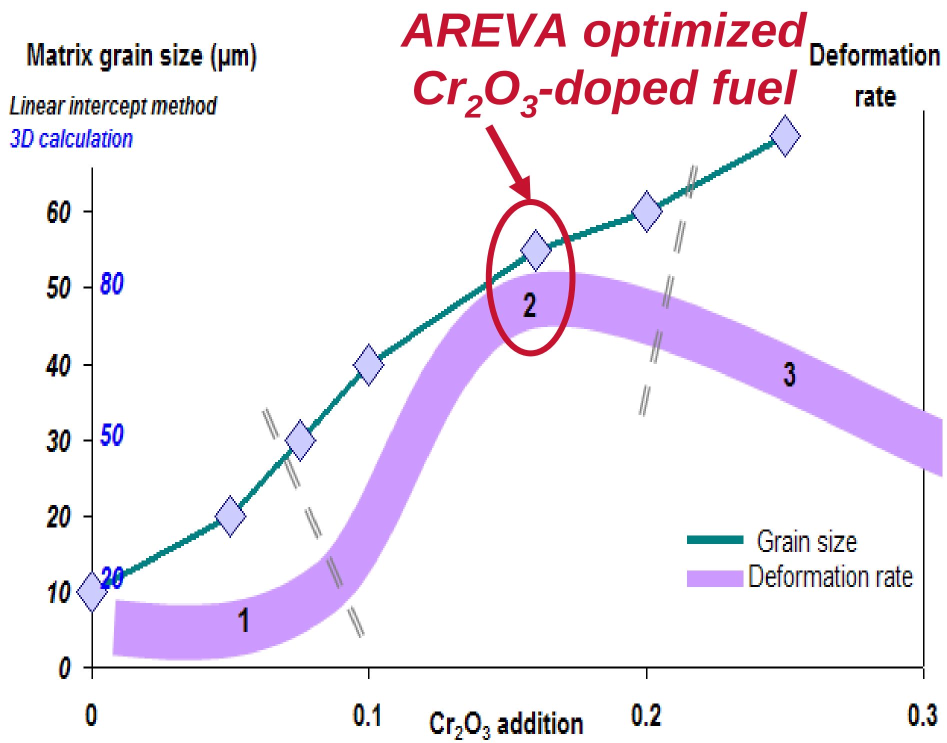
Fuel pellet characteristics may have a crucial impact on its dissolution tendency

Assessment of AREVA Cr_2O_3-Doped Fuel Behaviour in a Defective Fuel Rod

Fuel Specimens

Fuel Specimens
AREVA Optimized Chromia-Doped UO_2

- **General features:** large grain (FGR target), viscoplastic (PCI target) microstructure with the right amount of Cr_2O_3



Maximum of improvement with a nominal Cr_2O_3 addition of 0.16 wt.%

- Homogeneous crystalline structure
  - **Large grain size of 50-60 µm**
  - No large Cr_2O_3-free particles in fuel matrix
- Enhanced densification of fuel matrix
  - **High density 96 % TD easily achievable**

Fuel Specimens
AREVA Optimized Chromia-Doped (U-Gd)O_2

- Development process launched on the model of Cr_2O_3-doped UO_2 fuel
- Fundamental and basic studies:
  - To assess the influence of Cr_2O_3 doping on (U-Gd)O_2 properties
  - To optimize the Cr_2O_3 doping level for maximum of improvements
- (U-Gd)O_2 **densification behaviour** can be significantly **enhanced**
  - Low doping amount: < 0.075 wt% ➡ hardly no effect
  - High doping amount: >0.3 wt% ➡ solarization effect
- (U-Gd)O_2 **phase structure** only modified when Cr_2O_3 in excess to its solubility limit into the fuel matrix:

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<tr>
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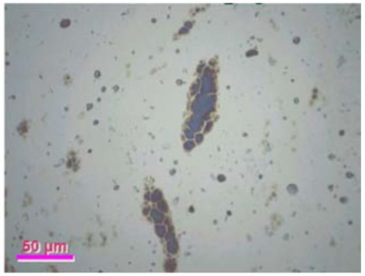
<td>
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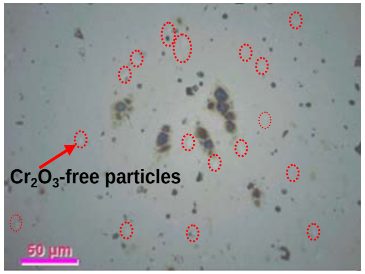
<td>
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<tr>
<td>Un-doped (U-Gd)O_2 fuel</td>
<td>Chromia doped (U-Gd)O_2 fuel
0.16 wt%</td>
<td>Chromia doped (U-Gd)O_2 fuel
1 wt%</td>
</tr>
</table>

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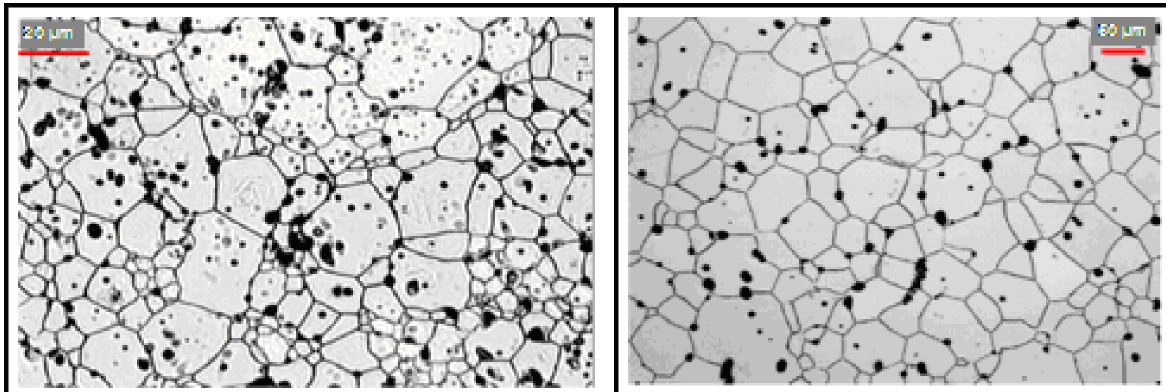
Fuel Specimens
AREVA Optimized Chromia-Doped (U-Gd)O_2 (Cont.)

- (U-Gd)O_2 **polycrystalline structure**:
  - **Large grains > 40 µm from 0.16 wt% doping amounts**



Standard (U-Gd)O_2 pellets	Chromia-doped (U-Gd)O_2 pellets

- (U-Gd)O_2 fuel **thermal conductivity**:
  - Laser flash method up to 1500°C
  - **No impact of Cr_2O_3-doping** in comparison to non-doped (U-Gd)O_2 fuel

Fuel Specimens
AREVA Optimized Chromia-Doped $(U\text{-}Gd)O_2$ (Cont.)

- $(U\text{-}Gd)O_2$ **fuel viscoplasticity**:
  - Creep testing at high temperatures (1500°C) and compression stresses [30-60 MPa]
  - In comparison to non-doped $(U\text{-}Gd)O_2$ fuel:
    - **Cr_2O_3 doping enhances** distinctly the **fuel plastic behaviour: improvement factor up to 10**
    - Positive effect attributed to the grain size enlargement allowing compensation of the fuel matrix hardening due to solid solution formation

» **Optimum Cr_2O_3 level of 0.16 wt% for $(U\text{-}Gd)O_2$ doping as for UO_2 resulting in a large grain and viscoplastic fuel matrix without detrimental effects on thermal characteristics**

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Assessment of AREVA Cr_2O_3-Doped Fuel Behaviour in a Defective Fuel Rod

Oxidation Behaviour

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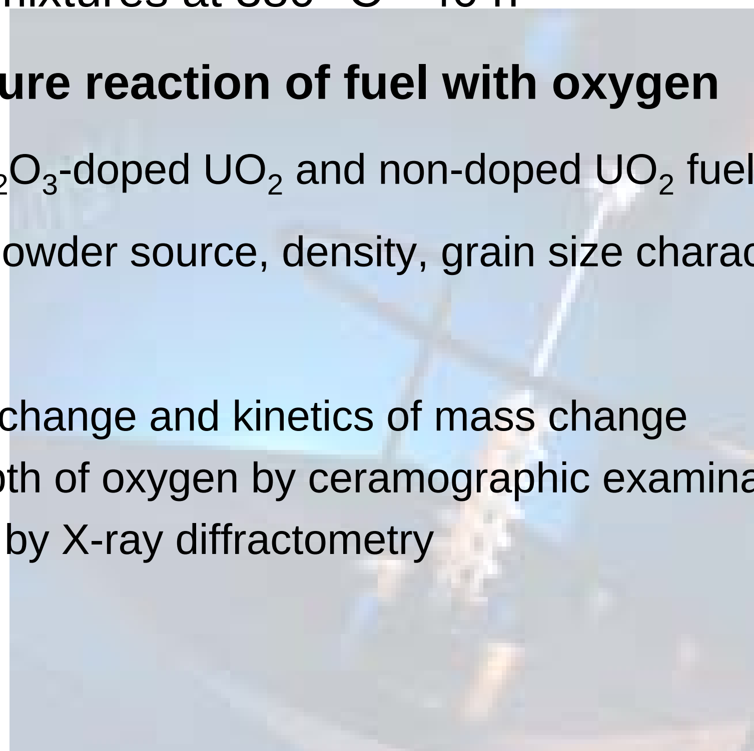
Fuel Oxidation Behaviour Experimental Means

- Test program to characterize:
  - The oxidation behaviour of fuel pellets by thermogravimetry tests under Ar/O_2 gas mixtures at 380 °C - 40 h

    ⇘ Pure reaction of fuel with oxygen

    - Comparison Cr_2O_3-doped UO_2 and non-doped UO_2 fuel pellets
    - Variants: UO_2 powder source, density, grain size characteristics
  - Follow-up:
    - Absolute mass change and kinetics of mass change
    - Penetration depth of oxygen by ceramographic examinations
    - Phase analysis by X-ray diffractometry



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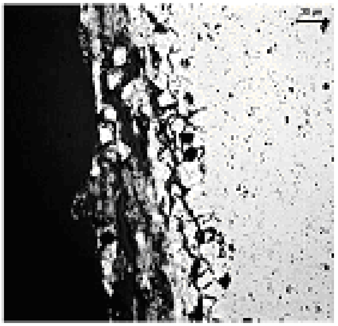
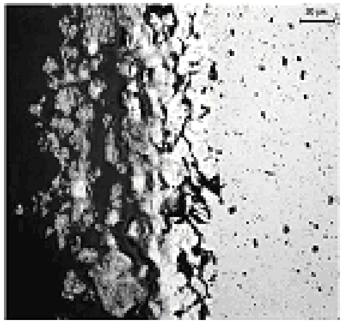
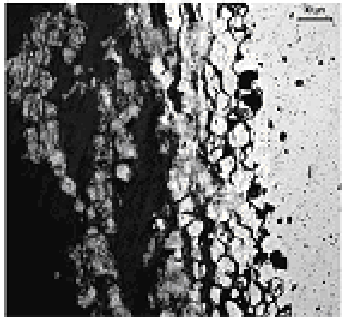
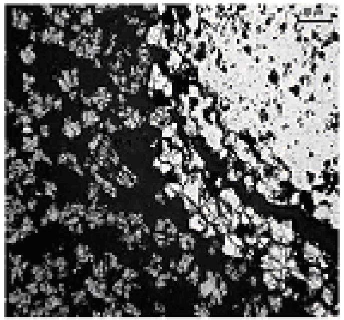
Fuel Oxidation Behaviour
Investigation of Pure Reaction with Oxygen

- Non-doped UO_2 samples - Ar+O_2 mixtures – 0.01 < O_2% < 1


0.01 % O_2


0.05 % O_2


0.1 % O_2


1 % O_2

Intergranular oxidation mode

- Consequent matrix volume increase: oxidizing-induced stresses leading to crack propagation and to strip deeper grain layers
- Significant attack from 0.1% O_2
- Pellet pulverization after 20h testing under Ar+1% O_2

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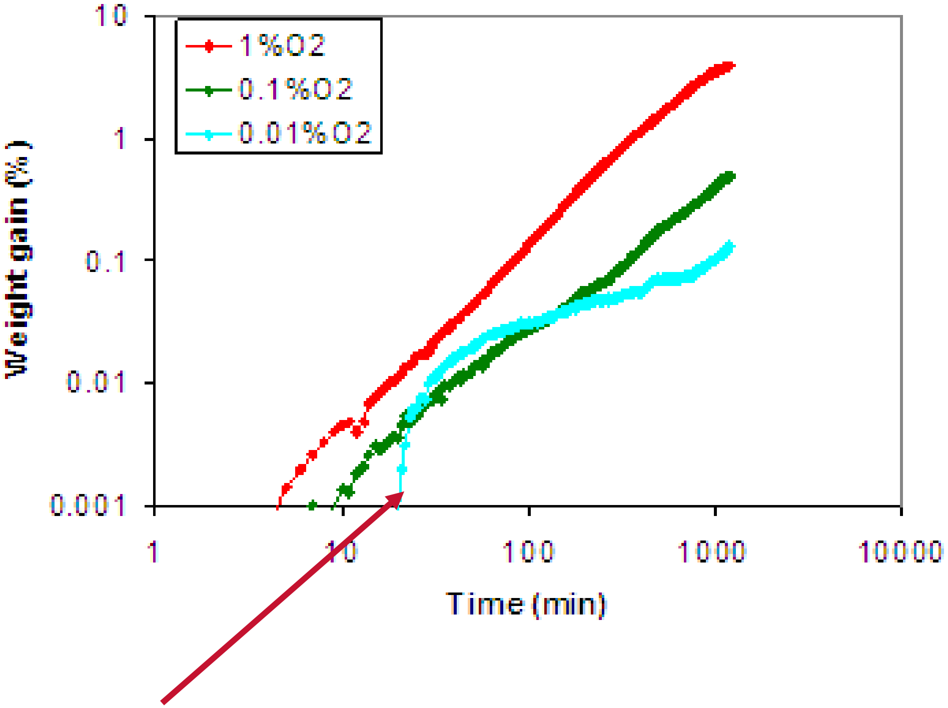
Fuel Oxidation Behaviour
Investigation of Pure Reaction with Oxygen (Cont.)

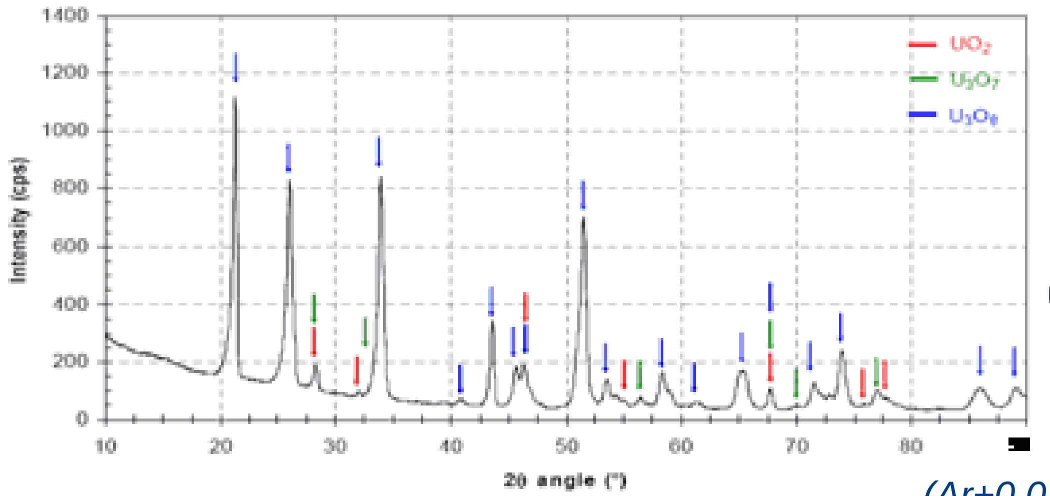
- Oxidation kinetics varies according to [O_2] in Ar

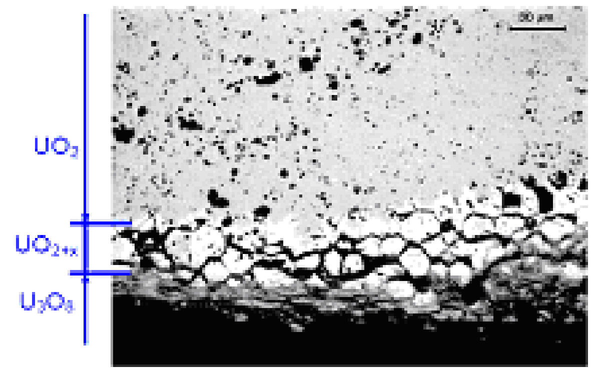


Induction period: oxidation governed by surface processes mainly

Fuel Oxidation Behaviour
Investigation of Pure Reaction with Oxygen (Cont.)

- Oxidation phase identification





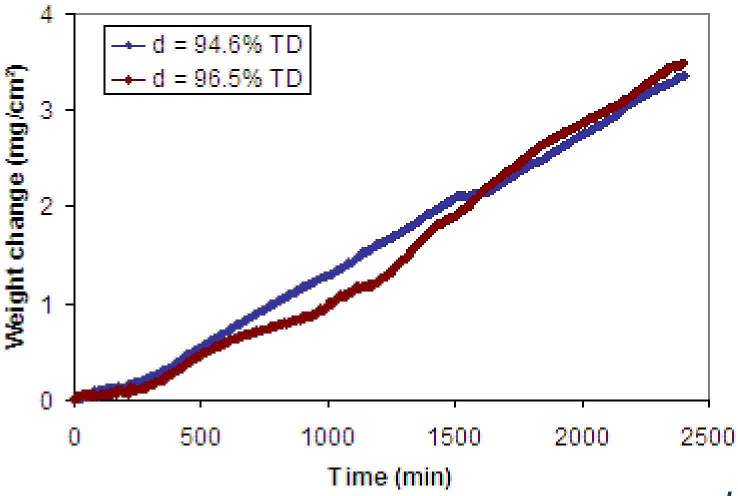
(Ar+0.01% O_2 – 380 °C)

Two-step reaction process: $UO_2 \rightarrow U_4O_9/U_3O_7 \rightarrow U_3O_8$

Formation of intermediate U_4O_9/U_3O_7 compound corresponds to initial non-linear oxidation before intergranular cracks formation

Fuel Oxidation Behaviour
Influence of Pellet Characteristics

- UO_2-source powder and pellet density (94.5 to 96.5 % TD) play no fundamental role in the UO_2 fuel oxidation:



UO_2 samples
(Ar+0.01% O_2 – 380 °C)

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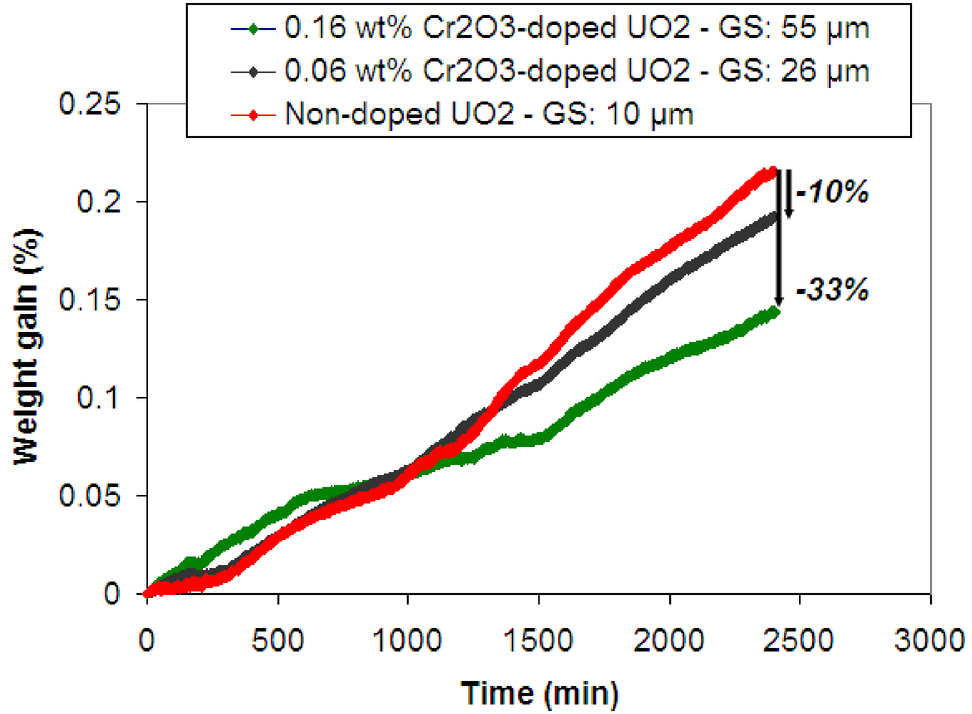
Fuel Oxidation Behaviour
Influence of Pellet Characteristics (Cont.)

- **Cr_2O_3-doping distinctively enhances the resistance of fuel pellets against oxidation:**
  - Limited improvement when increasing the fuel density
  - **More decisive effect due to fuel matrix grain size**



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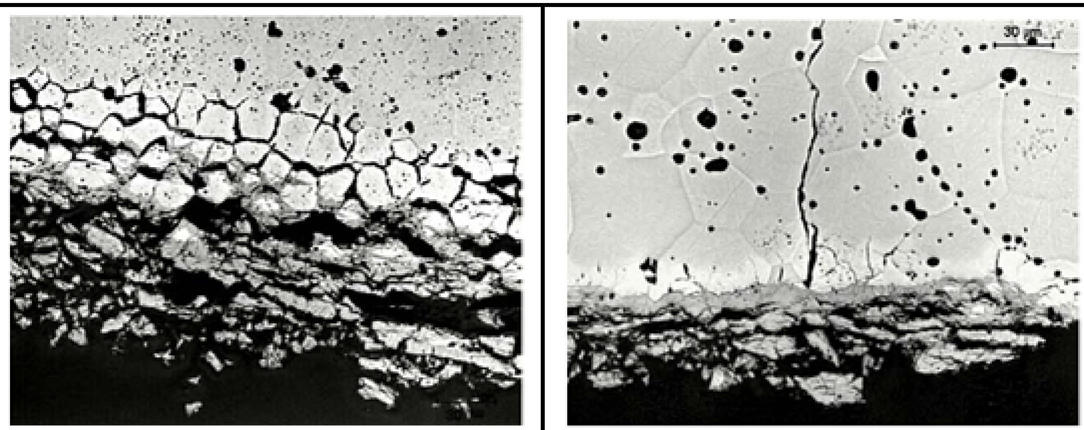
Fuel Oxidation Behaviour
Influence of Pellet Characteristics (Cont.)

- Oxidation mode for Cr_2O_3-doped fuel pellets:



Standard UO_2 pellets	Chromia-doped UO_2 pellets

Ar+0.01% O_2 at 380 °C

No intergranular cracks formed in Cr_2O_3-doped samples:

- **Oxidation surface mode**
- **Oxidized layers offer a protection against oxygen diffusion and decelerate the oxidation rate**
- **Attacked layer thinner by a factor up to 2.5 compared to non-doped UO_2**

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Assessment of AREVA Cr_2O_3-Doped Fuel Behaviour in a Defective Fuel Rod

Corrosion Behaviour

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Fuel Corrosion Behaviour
Experimental Means

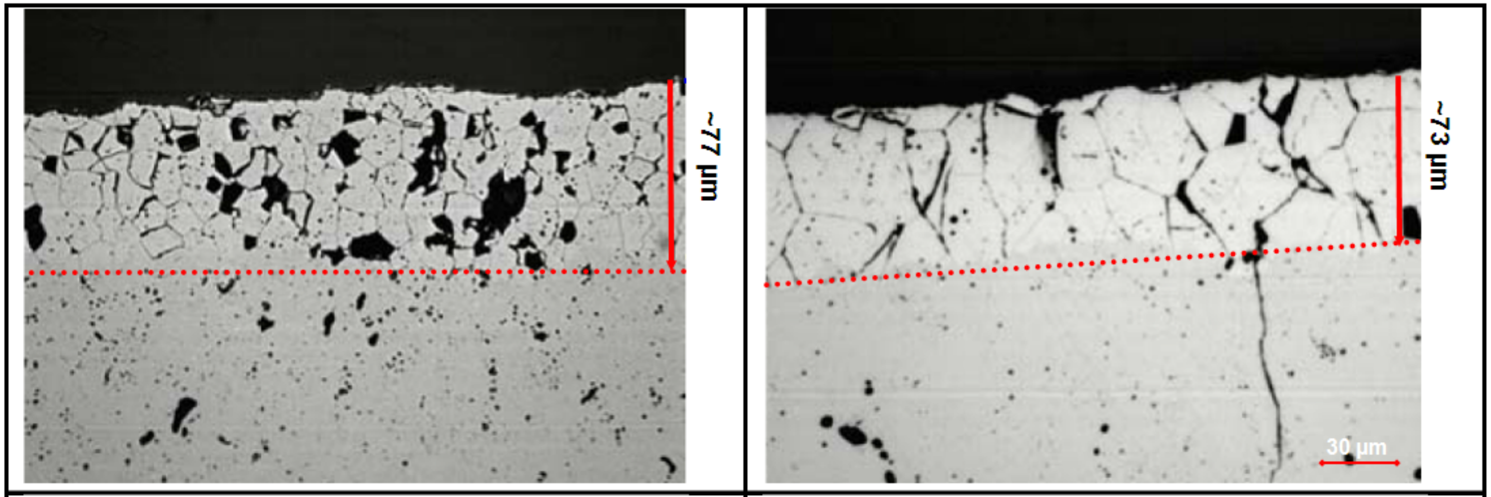
- Test program to characterize:
  - **The corrosion behaviour of fuel pellets by autoclave leaching tests:**
    - **Simulation of in-reactor environments**

Study case	Pressure (bar)	Temperature (°C)	Water chemistry
BWR	70	290 (water)	70 ppm H_2O_2
	70	360 (steam)	70 ppm H_2O_2
PWR	180	360 (water)	650 ppm B by H_3BO_3, 2 ppm Li by LiOH (pH ~7.4)
	100	400 (steam)	No additives

  - Comparison Cr_2O_3-doped UO_2 / $(U\text{-}Gd)O_2$ and non-doped UO_2 / $(U\text{-}Gd)O_2$ fuel pellets
- Follow-up as for thermogravimetry testing

Fuel Corrosion Behaviour
PWR Conditions *(Water and Steam)*

- No washout achieved due to the low O_2 concentration, but the corrosion process is initiated:
  - Non-doped UO_2 grain boundaries highly weakened
  - U_3O_7 formation as an intermediate step
  - Higher resistance of the Cr-doped fuel outside surface

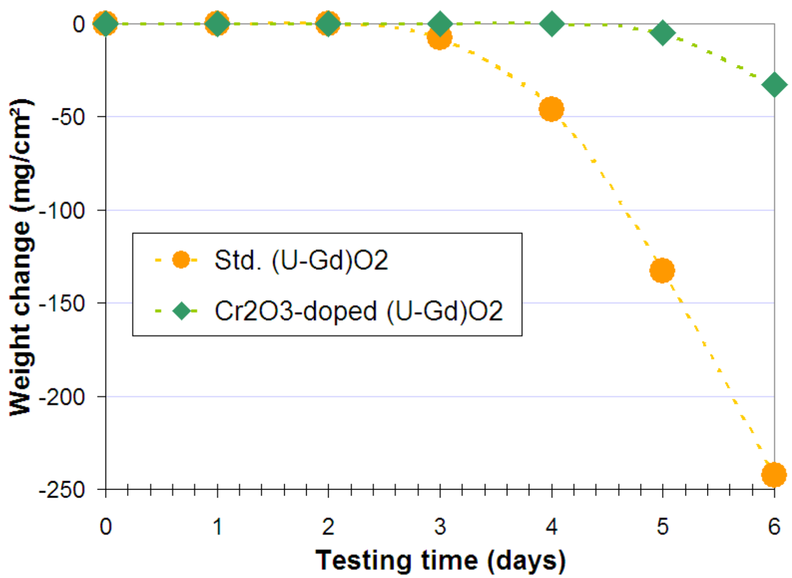


Standard UO_2 pellets	Chromia-doped UO_2 pellets

[water at 360°C, 180 bar, pH 7.4 (650 ppm B – 1.5 ppm Li)]

Fuel Corrosion Behaviour BWR Conditions

- In the most severe conditions investigated (360°C / 70 bars / 70 ppm H_2O_2)
  - Real washout of samples occurs
  - Significant differences revealed between non-doped and doped-samples:
    - **Mass loss reduced by a factor up to 5** for both configurations Cr_2O_3-doped UO_2 vs. non-doped UO_2 and Cr_2O_3-doped $(U\text{-}Gd)O_2$ vs. non-doped $(U\text{-}Gd)O_2$
    - **Mass loss of doped samples is delayed** compared to non-doped samples



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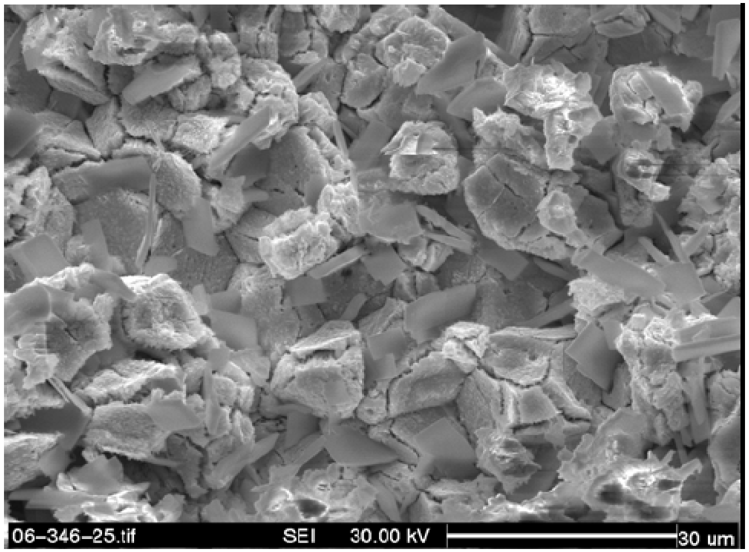
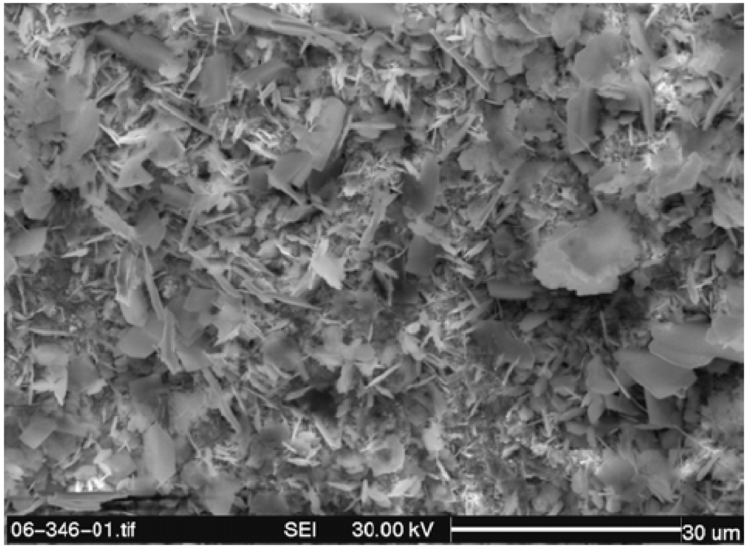
Fuel Corrosion Behaviour BWR Conditions (Cont.)

- Visual inspections on test-samples:





- **UO_2-based samples:** 'cauliflower' structure formed by cracked oxidized grains (volume expansion due to U_3O_8 conversion)
- **Cr_2O_3-doped based samples**: 'partially intact needle-like surface.

» **The outer layer protects the pellet meat from environment**

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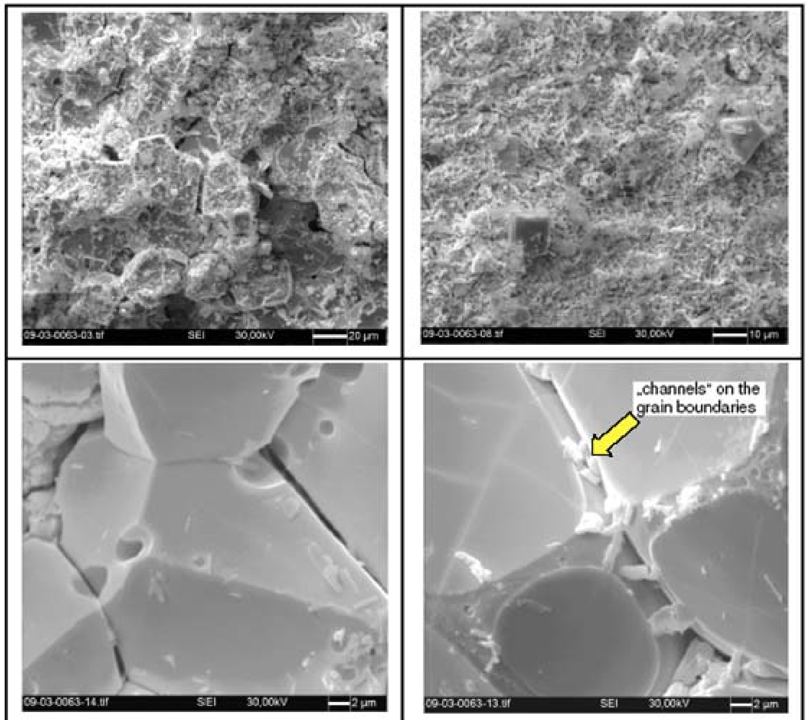
Fuel Corrosion Behaviour BWR Conditions (Cont.)

- Visual inspections on test-samples:



Standard (U-Gd)O_2 pellets	Chromia-doped (U-Gd)O_2 pellets

(top:hydrate regions bottom: leached broken-out areas)

Secondary phase residue on grain boundaries of Cr-doped (U-Gd)O_2 samples which possibly contributes to the better corrosion resistance

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Conclusions

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Conclusions

- The entire testing program demonstrates that **Cr_2O_3-doping enhances** the **corrosion resistance** of the fuel pellets
  - **Improved washout behaviour by a factor of 5** compared to non-doped UO_2 / $(U\text{-}Gd)O_2$ fuel pellets
- The **main driver of improvement is the grain size enlargement** of the fuel matrix
  - The optimum doping amount of **0.16 wt% Cr_2O_3** specified by AREVA for UO_2 and $(U\text{-}Gd)O_2$ fuels is especially efficient to obtain large grains of 50 and 40 µm respectively

»
- **Enhanced operational behaviour** desired to struggle against disintegration of fuel in case of defective rods and combined consequences to LWR primary coolant contaminations
- The **AREVA Cr_2O_3-doped UO_2 and doped $(U\text{-}Gd)O_2$ fuels present high reliability and robustness features**
- Both fuel types are **currently under irradiation** in commercial nuclear plants to meet future more demanding operating requirements

Thank you for your attention!

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