MASTERY OF (U,PU)C CARBIDE FUEL: FROM RAW MATERIALS TO FINAL CHARACTERISTICS

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OUTLINE OF THE PRESENTATION

1 - Mixed carbide: an advanced fuel for fast reactors
   - In comparison to oxide fuels, carbide fuels...
   - The U-PU-C system
   - Carbide fuel specifications
   - Required fuels are...

2 - Mixed carbide fabrication and characterization
   - Reference fabrication process
   - First step of fabrication: carbide synthesis
   - Second step of fabrication: carbide sintering
   - Carbide characterization
   - Alternative fabrication routes
   - Co-converted oxides used as precursors

3 - Manufactured mixed carbides
   - Carbide composition
   - Achievement of different densities
   - Achievement of different open porosities
   - Carbide oxygen content

4 - Conclusions and prospects
   - Conclusions
   - Efforts must now focus on...
MIXED CARBIDE: 
AN ADVANCED FUEL 
FOR FAST REACTORS
IN COMPARISON TO OXIDE FUELS, CARBIDE FUELS...

- present:
  - a higher metal atom density (12.9 g.cm\(^{-3}\) vs 9.8 g.cm\(^{-3}\))
  - a better thermal conductivity (18.8 W.m\(^{-1}\).K\(^{-1}\) vs 2.4 W.m\(^{-1}\).K\(^{-1}\) at 1000K)
  - higher specific power operation and higher breeding ratio
  - a great potential for Fast Reactors

- are less developed (less irradiation experience) and their fabrication poses an additional hazard due to their pyrophoric nature ⇒ fabrication and handling in an inert atmosphere
  - a need for:
    - a demonstration study of feasibility of fabricating a reliable carbide fuel on a laboratory scale
    - an optimization of the fabrication parameters of fuel pellets
Slightly hyperstoichiometric fuels \( C/(U+Pu)>1 \)

Two phases in presence: \((U, Pu)C\) and \((U, Pu)_2\)C\(_3\)

Pu loss by vaporization: Pu(g) and PuO(g), enhanced at high temperatures

A high susceptibility to oxidation and hydrolysis \(\Rightarrow (U, Pu)(C, O), (U, Pu)O_2\) formation
resulting from irradiation feedback:

- A plutonium content of the order of 18%, the mean value for GFR fuel.
- A sintered density of 80 to 85% of theoretical, to partially accommodate the fuel swelling and limit the cladding mechanical interaction to yield decent burnup without breaking.
- A predominant open porosity (Po/Pt > 50%) which promotes the release of fission gases.
- An oxygen content between 500 and 1000 ppm, to limit the degradation of the irradiation behavior of the (U,Pu)C phase.
- A sesquicarbide content \((U,Pu)_2C_3\) between 5 and 10 Vol.% to avoid the presence of a metallic phase with a low melting point, while reducing the risk of clad failure by carburization.
- A minimum metallic impurities content (Na, Si, Cl, F).

❖ A challenging task to meet all these specifications simultaneously!
REQUIRED FUELS ARE...

- globally comparable to those produced and characterized for understanding studies and irradiation programs in the early 1960's (France) and in the 1980-1990's (Japan, Germany, USA). but with a more stringent recommendation for the oxygen content than what used to be specified (tolerance up to 3000 ppm).

- very different in their composition from Indian fuels manufactured from the 1980's:
  - $55\% < [\text{Pu}] < 70\%$ (mixed carbide used as the driver fuel for the Fast Breeder Test Reactor, Indira Gandhi Centre for Atomic Research, India, since 1985)
  - $[O]$ up to 5000-6000 ppm
  - $[M_2C_3]$ up to 20%
MIXED CARBIDE FABRICATION AND CHARACTERIZATION
REFERENCE FABRICATION PROCESS

A two-step procedure in glove boxes under dynamic flow of nitrogen (3 renewals / h), with \([O_2]\) and \([H_2O]\) < 50 ppm each.

Carbide storage in specific sealed containers.

Some limitations:
- many process steps
- plutonium (and also americium) volatilization
- carbide reactivity with oxygen...
First step of fabrication: carbide synthesis

\[
(1-x)UO_2 + xPuO_2 + (3+y)C \rightarrow (U_{1-x},Pu_x)C + (U_{1-y},Pu_y)_2C_3 + 2CO
\]

Theoretical weight loss \(\sim 18.5\%\) (CO gas release, no plutonium vaporization)
Experimental weight losses around 20\% (slight amount of CO\(_2\) gas, plutonium vaporization)

- oxygen content
- T : Pu loss
- carbide crude density (and occluded CO)

Carboreduction at \(\sim 1620^\circ\text{C}\)
**SECOND STEP OF FABRICATION: CARBIDE SINTERING**

<table>
<thead>
<tr>
<th><strong>Crushing/milling</strong></th>
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<tr>
<td>manual crushing</td>
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<td>25min 25Hz</td>
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<th><strong>Pelletizing</strong></th>
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<tr>
<td>StZn addition (lubricant)</td>
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<tr>
<td>Pore former addition</td>
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<tr>
<td>Ø ~5mm</td>
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<tr>
<td>P <del>500MPa (F</del>10kN)</td>
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<tr>
<th><strong>Sintering</strong></th>
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<tr>
<td>60°C.h⁻¹ / 600°C / 2 h</td>
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<tr>
<td>200°C.h⁻¹ / 1750°C / 5 h</td>
</tr>
<tr>
<td>200°C.h⁻¹ / 20°C Ar-5%H₂</td>
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Green pellet density ~ 65% of theoretical (Dth = 13.61 g.cm⁻³)
sintered density ~ 91% of theoretical, with a fraction of open porosity ~ 3%,
(Po/Pf ~ 33%) without pore former

Pore formers used: StZn (Zn(C₁₈H₃₅O₂)₂), StCa (Ca(C₁₈H₃₅O₂)₂) and AZB (C₂H₄O₂N₄), up to 3 wt%
Determination of the sintered density by Archimedes’ method using bromobenzen as a medium.

Composition analysis after synthesis (before and after milling) as well as after sintering on powder specimens.

Determination of the oxygen content by the inert gas fusion principle using a LECO TC600 analyzer.

Oxygen can be:
✓ adsorbed at the surface,
✓ present as “surface oxide layer”,
✓ present as (U,Pu)O₂ precipitate,
✓ in solution of the type (U,Pu)(C,O).

Phase identification by X-Ray Diffraction on a Siemens D5000 X-ray diffractometer.

Mixture of the fuel powder with epoxy resin mounted on a sample holder.
Ceramographic examination after mechanical polishing of resin mounted specimens.

Fast oxidation kinetics of the surface samples...

Just after preparation, 1 day after preparation, after 48 h under vacuum, which can be limited by a specific preparation.
Use of new oxide precursors
whose synthesis is based on the co-conversion of actinides

- to simplify the manufacturing process by reducing the number of process steps (removal of the co-blending step)
- to avoid the additional oxygen contamination of the final product
- to limit the radiation exposure to the operators

**potential starting materials**, instead of $\text{UO}_2$ and $\text{PuO}_2$:

- $(\text{U,Pu})\text{O}_2$
- precursors obtained by direct incorporation of carbon graphite or a carbon molecule in the structure of the mixed oxalate
Carboreduction at 1520°C for:

- co-grinded (COB) and co-converted oxides (COP)
- two plutonium contents: 11% and ∼45%

A lower plutonium volatilization when (U,Pu)O₂ is used as starting powder, rather than co-grinded UO₂ and PuO₂
MANUFACTURED MIXED CARBIDES
Various amounts of oxygen after carboreduction, especially after milling: oxygen pickup from 800 to more than 10000 ppm, reduced by sintering

Two phases identified by XRD, and in some cases (U,Pu)O₂

Lattice parameters in agreement with those reported in the literature:

$$4,950 \, \text{Å} \leq a \leq 4,970 \, \text{Å}$$ for fcc (U,Pu)C

$$8,092 \, \text{Å} \leq a \leq 8,102 \, \text{Å}$$ for cc (U,Pu)₂C₃

No significant differences between post carboreduction and post sintering patterns, and 6 months after the sample preparation.
ACHIEVEMENT OF DIFFERENT DENSITIES: FROM GREEN TO SINTERED PELLETS

P~500 MPa

⇒ decrease of the green density as the oxygen content in the raw carbide powder increases

⇒ increase of the sintered density as the green density increases

⇒ Importance of the oxygen content in the raw carbide
Decrease of the sintered density with increasing additive amounts

A homogeneous distribution of the porosity and some macropores

An amount of 1 to 1.5 wt% of pore former is suitable to reach the specified sintered density
**Estimation of the sintered density** as a function of the green pellet density, the sintered pellet density without additive and the pore former amount.

\[ D_s = \frac{D_{oc}}{\frac{D_g}{(100-P_p)+1}} \]

- **Ds**: sintered density without pore former
- **Dg**: green density
- **Pp**: weight percentage of pore former

After Y. Honda et al., *Ceram. Bull.*, **60** [12], 1296-1299 (1981) for UO₂ pellets
A decrease in the open porosity with increasing sintered density

A fraction of open porosity \( \frac{P_o}{P_t} \geq 70\% \) for sintered densities lower than 85\% of theoretical

\( \Downarrow \) in agreement with the recommendations (Po/Pt > 50\%)

CEA - DEN

MINOS Workshop - December 5-7, 2012, CEA - INSTN Saclay, France
A wide range of oxygen content measured in sintered pellets

An oxygen content lower than 3000 ppm for a fraction of open porosity $\frac{Po}{Pt} \geq 40\%$

A lower reachable oxygen content of 1000 ppm, the upper limit of the recommendations
CONCLUSIONS AND PROSPECTS
Hyperstoichiometric mixed uranium-plutonium carbides (mono(xy)carbide, and sesquicarbide as a secondary phase) can be produced by conventional carbothermic reduction and sintering ⇒ suitable procedures.

Some Pu loss is unavoidable during carboreduction, but it can be limited.

Raw carbides can present various amounts of oxygen, which may affect the green density and hence the sintered density.

The use of organic pore formers allows:
- an adjustment of the sintered density,
- the fabrication of mixed carbides with an open-pore microstructure.

Sintered carbides with a high open porosity exhibit a lower oxygen content.

Achievement of a carbide fuel within the specified limits is possible, except for the oxygen content ([O] < 1000 ppm):
- D ~ 80 %DT, Po/Pt ~ 70%, [O] ~ 2000 ppm when 1.5 wt% StZn is added.
EFFORTS MUST NOW FOCUS ON...

- The robustness of the fabrication process: perhaps more complex phenomena at a larger scale?

- The development of control methods (X-ray diffraction) and fine characterization techniques (Optical and Scanning Electron Microscopies, Electron Probe Micro-Analyzer) to guarantee the stability of carbides before and during the analysis.

- The achievement of specified densities by adapting the sintering cycle (duration and/or temperature) instead of using pore formers.

- The carbide synthesis from innovative precursors in order to reduce the volatilization of plutonium.

- The mastery of the carbide reactivity with oxygen (kinetic and thermodynamic approaches of the U-Pu-C-O system), but also with moisture and nitrogen, in order to define optimal manufacturing conditions.
THANK YOU FOR YOUR ATTENTION

WITH THANKS TO THE TEAM OF THE LABORATORY
FOR THE STUDY & EXPERIMENTAL FABRICATION OF ADVANCED FUELS