Ablation of PICA-like Materials
Surface or Volume phenomenon?

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Lunar return: CEV with a PICA TPS
Stardust (PICA TPS)

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Introduction and Objective

“The time to study and fully understand the limits of PICA is NOW”

Introduction:

– The ablation of the char layer in ablative material is usually described in term of recession velocity. This “surface” description is valid for dense materials.
– However, the recession of the average surface in porous materials may not recede uniformly but matrix and fibers may progressively vanish in depth inside the structure: “volume ablation”.
– PICA-like materials are porous and may undergo volume ablation with two important consequences:
  • The material weakens in volume and is possibly subject to mechanical erosion (Spallation)
  • The ablation enthalpy distributed in volume modifies the thermal response

Objectives of this presentation:

– Model and understand ablation using a porous medium model
– Estimate whether volume ablation is an important phenomenon or not
– Decide if an elaborated model taking into account a volume ablation fully coupled with pyrolysis have to be developed (many years of development). If it is the case, a first model will be presented.
1. Modeling of the structure of PICA-like materials

2. Modeling of the Ablation of porous materials
   - Microscopic model
   - Numerical Simulation at microscopic scale
   - Homogenization $\rightarrow$ macroscopic behavior

3. Application to Stardust Reentry Conditions
   - Macroscopic model including blowing effects
   - Volume or Surface Ablation?

4. Possible ablation model for a volumetric coupling with Pyrolysis

5. Conclusion & Next steps
1. Modeling of the structure of PICA-like materials

Structure of “PICA-like” materials

- **Preform**:  
  - Random arrangement of carbon fibers  
  - High porosity

- **Matrix**:  
  - Phenolic resin  
  - Low mass fraction

- **Material type**:  
  - Ablator  
  - Low density

M. Stackpoole et al., AIAA 2008-1202 (Reno 2008)
1. Modeling of the structure of PICA-like materials

Fibrous preform: fiber size / orientation / porosity (statistical)

- Random drawing of non-overlapping cylinders (Monte-Carlo algorithm)
- Cylinders more or less parallel to the surface (Bias on azimuthal angle)
- Choice of a Length/Radius ratio (around 50 for PICA-like materials)

Totally Random

Complementary Azimuthal angle: +/- 15°

Interesting result: limit porosity = 0.85 for totally random structures / 0.9 for parallel
1. Modeling of the structure of PICA-like materials

Matrix

- **Before pyrolysis: different possibilities**
  - Thin layer of matrix surrounding the fibers
  - “Fluffy” matrix occupying the pores of the fibrous structure
- **After pyrolysis: matrix structure is modified**
  - Due to an important mass loss during pyrolysis
  - Resulting structure varies with experimental conditions
- **Models:**

  - Thin matrix layer around the fibers
  - Virgin fluffy matrix homogeneous at fiber scale
Objective:
- Estimate whether volume ablation is an important phenomenon or not using a simple model
  - In order to decide if an elaborated model taking into account a volume ablation fully coupled with pyrolysis have to be developed

Main Hypothesis:
- If volume ablation occurs, it occurs mainly in the char layer
  - Ablation model loosely coupled with pyrolysis

Approach:
- Multiscale modeling: microscopic scale (fibers) \(\rightarrow\) macroscopic scale (composite)
- Numerical models to provide guidelines and accurate results
- Simplified analytical models to provide understanding
- Application of the models to flight conditions (includes a loosely coupling with pyrolysis)
2. Ablation model for porous media

Reaction/Transport & Recession model in a carbon felt

- **Idea**: Use a simplified model to try and understand the Ablation of porous media
- **Hypotheses**:
  - Simplified structure: carbon fibers randomly oriented
  - Simple chemistry (C sublimated or oxidized by O\(_2\))
- **Starting point**: differential recession of a heterogeneous surface \( S \) by gasification

\[
\frac{\partial S}{\partial t} + \mathbf{v} \cdot \nabla S = 0
\]

\[
\mathbf{v} = \Omega \cdot J \cdot \mathbf{n}
\]

\[
J = k_f C
\]

\[
\frac{\partial C}{\partial t} + \nabla \cdot (-D \nabla C) + \mathbf{v}_g \cdot \nabla C = 0
\]

**N.B.**: oxidation notations BUT sublimation is mathematically equivalent
2. Ablation model for porous media

Reaction/Diffusion: Simulation (1/2): diffusion $\ll$ reaction ($D/L \ll k_f$)

Hypotheses:
- Isothermal
- No pyrolysis gas

Simulation tool
2. Ablation model for porous media

Reaction/Diffusion: Simulation (2/2): diffusion >> reaction (D/L >> k_f)

Hypotheses:
- Isothermal
- No pyrolysis gas
2. Ablation model for porous media

Surface or Volume? → depends on experimental conditions

Surface Ablation ($D/L \ll k_f$)

Volume Ablation ($D/L \gg k_f$)
2. Ablation model for porous media

Homogenization and Analytical solution (hyp. : no recession)

- **Volume or surface? → Key information : C, oxidant concentration**
- 1D model to obtain an analytical solution : \( C(z) = f \) (experimental conditions)

\[
q_z(z) - q_z(z + dz) = q_y(z) \\
-D \nabla (C(z) - C(z + dz))S_p = k_f C(z)P_f dz
\]

Mass balance in steady state :

\[
C(z) = C_0 \frac{\cosh\left[\Phi(z/L_s - 1)\right]}{\cosh \Phi}
\]

Thiele number : \( \Phi = \frac{L_s}{\sqrt{D_{eff}/sk_f}} \)

\( S_p/P_f = \varepsilon/s \)

\( s \ (m^2/m^3) : \text{specific surface} \)

Hyp., bulk diffusion between perpendicular fibers : \( D_{eff} = \varepsilon D \)

BUT…
2. Volume Ablation model

Validity domain of the continuous regime hypothesis

- **Knudsen number**: \( Kn = \frac{\bar{\lambda}}{d_p} \) (continuous regime for \( Kn < 0.02 \))
- **Pore size around 50µm \( \rightarrow \) Knudsen regime for mean free path < 1µm

- **Air**: \( \bar{\lambda} = 95 \cdot 10^{-9} \cdot \frac{10^5 \cdot T}{298 \cdot P} \)

**Stardust peak heating (Kn=0.08)**

Reentry conditions: Knudsen regime inside the porous medium

Model still correct in Knudsen regime?
2. Ablation model for porous media

Model still correct in $Kn$ regime but with a modified diffusion coefficient

- **Knudsen effects**: Diffusion coefficient in a capillary (Bosanquet model)
  \[
  \frac{1}{D_{ref}} = \frac{1}{D_B} + \frac{1}{D_K} = \frac{1}{\frac{1}{3} v \lambda} + \frac{1}{\frac{1}{3} v d_\rho} \tag{harmonic average}
  \]

- **Fibers randomly oriented**: tortuosity effects non negligible in $Kn$ regime
  \[
  D_{eff} = \frac{\varepsilon}{\eta} D_{ref}
  \]
  Tortuosity has to be obtained by Monte Carlo simulation inside the porous media (not available yet in the literature for non-overlapping fibers)
2. Ablation model for porous media

Determination of the effective diffusion coefficient $D_{\text{eff}}$

- **Monte Carlo Simulation:**
  - Random Walk rules:
    - $(T,P)$ fixed = $(\lambda,D)$ fixed
    - $\lambda$: Maxwell-Boltzmann distribution
    - constant velocity norm
    - $(D = 1/3 \sqrt{\lambda})$ with 3D random direction drawing

- **Tortuosity as a function of $Kn$ for the fibrous material of this study**

1) Displacement $\vec{\xi}$ of 10000 walkers followed during $\tau$ (chosen for convergence)

2) Einstein relation on diffusion process:

$$D_{ej} = \frac{\left< \xi_j^2 \right>}{2\tau}$$

Illustration: path of a walker in a periodic cell
2. Ablation model for porous media

Parametrical analysis

- Concentration gradient (1D model) as a function of Thiele number

\[
C(z) = C_0 \frac{\cosh[\Phi(z / L_s - 1)]}{\cosh \Phi}
\]

Thiele number
\[
\Phi = \frac{L_s}{\sqrt{D_{\text{eff}} sk_f}}
\]

- Consumption / diffusion velocities for porous media

$L_s$: material depth (m)
$D_{\text{eff}}$: effective diffusivity (m²/s)
$k_f$: fiber reactivity (m/s)
$s$: specific surface (m²/m³)
3. Application to Stardust Reentry Conditions

Model must include blowing effect (pyrolysis gas)

- **Steady state equation including the convective term (continuous regime)**

\[
\frac{\partial^2 C}{\partial z^2} + \frac{1}{L_C} \frac{\partial C}{\partial z} + \frac{1}{L_R^2} C = 0 \quad \text{with} \quad L_C = \frac{D}{v_g} \quad \text{and} \quad L_R = \sqrt{\frac{D_{\text{eff}}}{sk_f}}
\]

- **Solution (of the quadratic ODE with one Dirichlet B.C. : C(z=0)=C_0)**

\[
C(z) = C_0 \exp \left[ -\frac{z}{L_C} \left( 1 + \sqrt{1/4 + \left( \frac{L_C}{L_R} \right)^2} \right) \right]
\]

\(L_C > 10L_R \quad \rightarrow \quad \text{Blowing effect negligible (on concentration gradient)}\)

Example: Stardust peak heating

\[L_C / L_R = 0.145 \quad \rightarrow \quad \text{Blowing effect almost negligible}\]
3. Application to Stardust Reentry Conditions
Stardust Peak Heating (stagnation point)

- **model including blowing effects + thermal gradients** (data from FIAT simulations): Concentration in the char layer (FE solution: FlexPDE code)

![Graph showing normalized concentration with volume ablation at 0.5 mm = 50 fiber diameters.](image-url)
3. Application to Stardust Reentry Conditions

Stardust trajectory (stagnation point)

Normalized concentration vs. time (s)

- $C(z=L_s)/C_w$
- $L_s$
- $z: C(z)=10\%C_w$

Normalized concentration vs. depth (m)

- $< 10\% C_0$
- $> 10\% C_0$

Post flight analysis

Stardust trajectory (stagnation point)
4. Volume coupling of Pyrolysis & Ablation
Integration of ablation in the pyrolysis model: first ideas

Mass balance
\[
\frac{\partial \varepsilon \rho_g}{\partial t} + \nabla \cdot (\varepsilon \rho_g \vec{v}_g) = -\frac{\partial \varepsilon_m \rho_m}{\partial t} - \frac{\partial \varepsilon_f \rho_f}{\partial t} + \varepsilon + \varepsilon_m + \varepsilon_f = 0
\]

Momentum balance
\[
\varepsilon \vec{v}_g = -\frac{\vec{K}}{\mu} \cdot \nabla p
\]

Energy balance
\[
(\varepsilon \rho_g c_g + \varepsilon_f c_f \rho_f + \varepsilon_m c_m \rho_m) \frac{\partial T}{\partial t} = \nabla \cdot (k \cdot \nabla T) - \varepsilon_g c_g \vec{v}_g \cdot \nabla T + \delta h_p \frac{\partial \varepsilon_m \rho_m}{\partial t} + \delta h_{abl} \frac{\partial \varepsilon_f \rho_f}{\partial t}
\]

Pyrolysis law
\[
\rho_m = \rho_v - \sum_{i=1}^{n \text{ laws}} (\rho_{v,i} - \rho_{p,i}) \xi_i \quad \text{with} \quad \frac{\partial \xi_i}{\partial t} = (1 - \xi_i)^n_i A_i \exp\left(\frac{-E_{A_i}}{RT}\right)
\]

Ablation law (fibers)
\[
\rho_f = \text{const.} \quad \frac{\partial \varepsilon_f}{\partial t} = ?
\]
4. Volume coupling of Pyrolysis & Ablation

Multiscale modeling of the ablation of the carbon felt

- Ablation: surface phenomenon at microscopic scale, but volumetric at macroscopic scale
  
  - **Mean fiber diameter evolution**

  \[
  \frac{\partial d_f(z,t)}{\partial t} = -\Omega_s 2k_f(T)C(z,t)
  \]

  - **Homogenization**: fiber diameter \(\rightarrow\) mean porosity

  \[
  \varepsilon(z,t) = 1 - (1 - \varepsilon_0) \left( \frac{d_f(z,t)}{d_{f,0}} \right)^2
  \]

  - **Convenient variable for ablation modeling**: \(\varepsilon\)

  \[
  \frac{\partial \varepsilon C(z,t)}{\partial t} - \text{div}(D_{\text{eff}}(T,P)\text{grad}(C(z,t))) = \frac{4k_f(T)C(z,t)}{d_{f,0}} \left[ (1-\varepsilon(z,t))(1-\varepsilon_0) \right]^{0.5}
  \]

  - **Density**:

  \[
  \rho_{\text{material}} = (1 - \varepsilon)\rho_f
  \]
4. Volume coupling of Pyrolysis & Ablation

Illustration of the proposed Ablation law for Stardust Peak Heating thermal conditions

- Simulation of the “oxidation part” of ablation (loosely coupled with pyrolysis) in the carbon felt
4. Volume coupling of Pyrolysis & Ablation
Stardust conditions: pure oxidation from 90s ($T < T_{\text{sublim}}$) to 130s ($T > T_{\text{oxi}}$)

- Simulated in the carbon felt
Overall behavior well predicted by current models (FIAT simulation presented below)

BUT: char zone density overestimated

- Volume ablation could be the cause of the lower density observed
- The fluffy matrix of PICA is likely to play an important role into volume ablation prevention

M. Stackpoole et al., AIAA 2008-1202 (Reno 2008)
Conclusion / Next steps

- Porous media model for the ablation of fibrous materials
  - Importance of Thiele Number (diffusion/reaction competition in porous media)
  - Knudsen regime inside the porous media
  - Volume / Surface phenomenon? \(\Rightarrow\) depends on experimental conditions
  - Stardust conditions:
    - Low effect of blowing on mass transfer inside the porous media
    - Ablation by oxidation in volume for a carbon felt
  - Idea for volume coupling of pyrolysis and ablation at macroscopic scale

- Next steps:
  - Modeling
    - Improve material structure description
    - Sublimation
    - In depth equilibrium chemistry
    - Spallation model (more basic: density threshold)
    - Same approach for heat transfer in porous media (conduction, convection, radiation)
  - Specific experiments to validate the porous media model and the future pyrolysis-ablation coupled model
ANNEXES
Simulation tool: AMA
Brownian Motion simulation technique / Marching Cube front tracking

- Efficient, Robust, No matrix inversion

Original features:
- Sensory Brownian Motion: automatic refinement close to the wall (cf. mesh refinement for Eulerian methods)
- Sticking probability adapted to Brownian Motion (to simulate first order heterogeneous reactions)
# 3 kinds of Experiments

## Improvement & Validation of the models

<table>
<thead>
<tr>
<th>Device</th>
<th>Measured data</th>
<th>Dimension &amp; scale</th>
<th>Time scale</th>
<th>Difficulty</th>
<th>Interest</th>
<th>Other comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM* (Scanning Electron Microscopy)</td>
<td>Architecture (intuitive) resolution: 100 nm</td>
<td>2D surface micro to macro</td>
<td>1 month</td>
<td>Image analysis</td>
<td>Help into architecture modeling at all scales</td>
<td>Relatively low cost for fast preliminary results</td>
</tr>
<tr>
<td>TOMO** (X-ray scanning microtomography)</td>
<td>Architecture (accurate) resolution: 1µm</td>
<td>3D micro</td>
<td>1+ year</td>
<td>- prepare samples - image segmentation</td>
<td>Enable an accurate direct numerical simulation</td>
<td>Key results -&gt; master or PhD student in Bordeaux? +10kEuros</td>
</tr>
<tr>
<td>TGA** (Thermo Gravimetric Analysis) + mass spectrometer</td>
<td>Chemistry Pyrolysis gas analysis Carbon fibers reactivity to these gas</td>
<td>1D micro</td>
<td>1+ year</td>
<td>- data analysis</td>
<td>Understanding of heterogeneous and homogeneous chemistry</td>
<td>- No rush - Data from 1970 - Useful again for porous TPS</td>
</tr>
<tr>
<td>Short ramp IR tests* 0-2500K</td>
<td>Effective conductivity $k=f(T)$</td>
<td>3D macro</td>
<td>6 month</td>
<td>-thermocouple position -data analysis</td>
<td>Useful for radiation analysis</td>
<td>Needed ASAP</td>
</tr>
<tr>
<td>Long steady state IR tests** (+ tangential blowing)</td>
<td>Thermal gradient Density profile Recession</td>
<td>3D micro 2D ortho macro</td>
<td>1-2 years</td>
<td>-thermocouple position -quantify spallation= f(shear stress)</td>
<td>Ablation/pyrolysis coupling Spallation Model validation</td>
<td>Parametrical study on blowing and grad(T)</td>
</tr>
<tr>
<td>Plasma tests**</td>
<td>Idem</td>
<td>3D micro 2D ortho macro</td>
<td>2-3 years</td>
<td>-test conditions -data analysis</td>
<td>Global validation fluid + mater</td>
<td>Parametrical study on P, T, v</td>
</tr>
</tbody>
</table>

* : to be done in priority with available funding / ** : to plan now and begin in 1 year

IPPW6, Atlanta, June 2008

PICA-like materials : Surface or Volume ablation?
ANNEXE. Ablation model for porous media

The effective reactivity of the porous media is not intrinsic

Effective reactivity = reactivity of a flat and homogeneous material (cf graphite) that would lead to the same ablation rate under similar entry conditions

\[ \log_{10} k_{\text{eff}} \]

\[ \log_{10} k_f \]

\[ P = 0.1 \text{ atm} \]

\[ P = 1 \text{ atm} \]

\[ T \approx 2500 \text{K} \]

\[ (D \sim 1/P) \]