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THE TRANSPORT AND SETTLING OF PLATINUM-GROUP-METAL PARTICLES IN GLASS MELTS

PRESENTATION BY GUILLAUME BARBA ROSSA

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Short overview of the High-Level-Waste confinement process

- Ensure long-time confinement of High-Level-Waste (HLW) of spent nuclear fuel reprocessing
- Vitrification: atomic-scale incorporation of HLW in a glass melt
- Most recently developed technology used for vitrification
  - Induction-heated cold crucible

*Full scale prototype at CEA*

*Free surface of the melt in the crucible*

*Glass pouring*
Particles encountered in nuclear waste vitrification processes

- Nuclear glass melt
  - Homogeneous borosilicate glass matrix
  - Seeded with small particles (∼10 μm)

- Particles are Platinum-Group-Metals with a much higher density than glass
  - Ruthenium dioxide (RuO₂) needles
  - Palladium (Pd) spheres

 Iso-contours of density from X-ray microtomography (made at ESRF)

SEM

NOVITOM
ADVANCED 3D MICRO-IMAGING
Numerical simulation of the vitrification process in cold crucibles

- Numerical simulation of coupled models
  - Fluid mechanics for stirred glass: Navier-Stokes equations
  - Temperature transport: Energy equation
  - Electromagnetics for induction: Maxwell equations

- But PGM particles have significant effects when their local volume fraction increases (because of settling)
  - Viscosity increase
  - Electrical conductivity increase
  - …

- Need for a supplementary model to compute particles local volume fraction in the melt $C(x, y, z, t)$

Full thermo-hydraulic numerical simulation of the cold crucible
Transport model for particles

- Transport phenomena included in a **one-fluid model**
  - Advection by the flowing suspending fluid

- Hindered settling with Stokes velocity $\tau(C,T)$
  (Michaels & Bolger formula)

- Hydrodynamic diffusion $\kappa(T)$

- Resulting in a single unsteady evolution equation for the particles volume fraction $C$

\[
\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C + \nabla \cdot (\tau \mathbf{g} C) = \nabla \cdot (\kappa \nabla C)
\]
Accounting for temperature-dependent transport properties

- **4 transport parameters**, 2 of them strongly depend on glass viscosity $\eta$

- Maximum packing fraction $C_a$ evaluated from particles’ shape
- Hindering exponent $\beta = 4.65$ computed by Richardson & Zaki
- Settling velocity $\tau$ evaluated from Stokes formula
- Diffusivity $\kappa$ fitted in laboratory experiments

Glass melting processes are non-isothermal and glass viscosity depends on temperature $\eta(T)$

Temperature stratification $T$  \( \alpha \frac{1}{\eta(T)} \)  Change in glass viscosity $\eta(T)$ (VFT)
Laboratory settling experiments with a nuclear waste simulant (1)

- Initially homogeneous nuclear waste simulant seeded with PGM particles
- Heat-treated during prescribed settling time without any stirring ($\mathbf{u} = 0$)

- Crucible vertically sliced after cooling
- Laser Induced Breakdown Spectroscopy (LIBS) to measure vertical concentration profiles $C(z, t)$

Comparison to the transport model (solved numerically)

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C + \nabla \cdot (\tau \hat{g} C) = \nabla \cdot (\kappa \nabla C)$$

*Sliced glass sample in the LIBS apparatus*
Laboratory settling experiments with a nuclear waste simulant (2)

- **Exp. 1**: isothermal case
  - Sample height 2.6cm
  - Uniform temperature 1300°C
  - Ruthenium dioxide particles 0.53%vol (1.5%w)
  - Heating time 16h

- **Exp. 2**: non-isothermal case
  - Sample height 4.5cm
  - Imposed temperature gradient 592°C-1215°C
  - Palladium particles 0.19%vol (0.9%w)
  - Heating time 65h

### Transport parameters used in simulations (at 1300°C)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Particles</th>
<th>$\tau$ ($10^{-7}$ m/s)</th>
<th>$\kappa$ ($10^{-10}$ m$^2$/s)</th>
<th>$C_a$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$RuO_2$</td>
<td>1.3</td>
<td>1.5</td>
<td>8%</td>
<td>4.65</td>
</tr>
<tr>
<td>2</td>
<td>$Pd$</td>
<td>2.9</td>
<td>18</td>
<td>60%</td>
<td>4.65</td>
</tr>
</tbody>
</table>
Structure of the sludge

- Exp. 3: sludge obtained from long-term settling
  - Sample height 4.9cm
  - Uniform temperature 1200°C
  - Both ruthenium dioxide and palladium particles 0.7%vol
  - Heating time 211h

- Intricate percolated network
- Relatively low volume fraction 3.5%vol

\[ \text{RuO}_2 \text{ volume fraction} \]
Conclusion

- Accurate transport model with low computational cost
- Able to account for PGM settling in glass melts, with temperature stratification
- Precise 3d imaging gives an insight into the sludge structure

- Transport model included in 3d simulations of waste vitrification in cold crucibles along with:
  - “Cloud settling” through Rayleigh-Taylor instabilities
  - Percolation model for the electrical conductivity of PGM-laden glass
THANK YOU FOR YOUR ATTENTION
Detailed transport model

\[
\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C + \nabla \cdot \left( \frac{\tau_0}{f_\eta} \hat{g} C \left( 1 - \frac{C}{C_a} \right)^\beta \right) = \nabla \cdot \left( \frac{\kappa_0}{f_\eta} \nabla C \right)
\]

Hindering function

Stokes terminal velocity \( \tau_0 = \frac{d_p^2 (\rho_p - \rho_f) g}{18 \eta_0} \)

Diffusivity \( \kappa_0 = \frac{d_p^2 \alpha}{18 \eta_0} \)

Vogel-Fulcher-Tamman viscosity law \( f_\eta \propto \exp \left( \frac{B}{R(T-T_v)} \right) \)