Phénomènes de transfert dans les liquides réactifs à haute viscosité. Application au procédé d’élaboration du verre

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I started at **Saint-Gobain Recherche (SGR)** in 2000 to study the physics of glass melting.

I am currently working in the Joined lab **Surface du Verre et Interface**.

Treat topics at the crossroad between industry and research:

- Take an applied subject to transform an academic subject.
- In the team **Heterogeneous and Reactive Materials**

The main purposes:

- Improve the basic knowledge in
  - Glass melting
  - Building materials

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- I will speak only about of soda-lime silica glasses.
Glass melting is a chemical process:

\[
\text{sand (70\%)} \quad \text{limestone (15\%)} \quad \text{soda ash (15\%)} \Rightarrow \text{silicate}
\]

\[
\text{SiO}_2 + \text{CaCO}_3 + \text{Na}_2\text{CO}_3 \Rightarrow \text{SiO}_2 \cdot \text{CaO} \cdot \text{Na}_2\text{O} + \text{CO}_2(g). \quad (1)
\]
Glass melting
Glass melting

Solid creation

CO2 release

Foam creation

Glass melting

Bubbles
transport phenomena

natural convection in glass furnaces

mass transfer between bubbles and molten glass

glass foam stability
Natural convection in glass furnaces

1. Origins
2. Horizontal convection
3. Synthesis
4. Perspectives
Natural convection in glass furnaces

1 Origins

Figure 1: Sketch of the glass furnace.
Natural convection in glass furnaces

1 Origins

Figure 1: Sketch of the glass furnace.

hot spot
1550-1600 °C

cold spot
1150-1200 °C

1150 °C
Natural convection in glass furnaces

1 Origins

- Natural convection drives
  - heat transfer;
  - glass homogenization;
  - spreading of the residence time distribution.
Natural convection in glass furnaces

1 Origins

Figure 2: Residence time distribution for a “float” furnace.
Natural convection in glass furnaces

2 Horizontal convection

- Heat and mass transfer are important to know for the glass furnace designers.

Find the control parameters of the heat and mass transfer in glass furnaces

- Work achieved in collaboration with J.-M. Flesselles (Glass melting Dept., SGR).
Natural convection in glass furnaces

2 Horizontal convection

- Larger than height.
- Wider than height.
- Heating from above.
Natural convection in glass furnaces

2 Horizontal convection

- Temperature applied on one horizontal boundary.
- Closed system.

Figure 3: Rectangular cavity with kinematic and heat boundary conditions.
Natural convection in glass furnaces

2 Horizontal convection

- Configuration studied in geophysics
  - Overturning of oceans due to the heating of the Sun.
- Convection appears without threshold.
- Three dimensionless numbers have to be taken into account

\[
\text{Pr} = \frac{\nu}{\kappa} \quad (2a)
\]
\[
A = \frac{H}{L} \quad (2b)
\]
\[
\text{Ra} = \frac{g \beta \Delta T H^3}{\nu \kappa} \quad (2c)
\]
Natural convection in glass furnaces

2 Horizontal convection

- Configuration studied in geophysics
  - Overturning of oceans due to the heating of the Sun.
- Convection appears without threshold.
- Three dimensionless numbers have to be taken into account

\[
Pr = \frac{\nu}{\kappa} \sim 100 - 10^3 \tag{2a}
\]

\[
A = \frac{H}{L} \sim 0.1 - 0.05 \tag{2b}
\]

\[
Ra = \frac{g \beta \Delta T H^3}{\nu \kappa} \sim 10^4 - 10^7 \tag{2c}
\]

- The Prandtl number is irrelevant when \( Pr \gg 1 \):
  - Only two parameters : \( A \) and \( Ra \).
Natural convection in glass furnaces

2 Horizontal convection

Figure 4: Isotherms and streamlines in the cavity of $A = 1/5$.

- Two regimes are observed:
  - Conductive regime;
  - Convective regime.
Natural convection in glass furnaces

2 Horizontal convection

- What is the control parameter when $A$ and $Ra$ change?
- What are the laws of heat and mass transfer in the two regimes?
Natural convection in glass furnaces

2 Horizontal convection

- What is the control parameter when $A$ and $Ra$ change?
- What are the laws of heat and mass transfer in the two regimes?

- From the scale analysis, we show$^1$: $Ra\,A^2$ is the only parameter.

\[
Ra\,A^2 = \frac{H^2/\kappa}{L/U}, \quad (3)
\]

\[
U = Ra\frac{\kappa}{L}. \quad (4)
\]

Natural convection in glass furnaces

2 Horizontal convection

$$\text{Pe} A^2 = \frac{\pi \sqrt{3}}{432} \text{Ra} A^2 \approx 1.26 \cdot 10^{-3} \text{Ra} A^2$$

$$\text{Pe} A^2 = 4.6 \cdot 10^{-1} (\text{Ra} A^2)^{2/5}$$

Figure 5: Pe $A^2$ vs. Ra $A^2$ where Pe = $\frac{|u|_{\text{max}} L}{\kappa}$.

Natural convection in glass furnaces

2 Horizontal convection

\[ \langle \text{Nu} \rangle = 0.245 (Ra A^2)^{1/5} \]

\[ \langle \text{Nu} \rangle = 1.8 \cdot 10^{-4} (Ra A^2)^{1.4} \]

Figure 6: \( \langle \text{Nu} \rangle \) vs. \( Ra A^2 \) where \( \langle \text{Nu} \rangle = \sqrt{A \int_0^{1/A} \left( \frac{\partial \theta}{\partial y} \right)^2 (x) dx} \).

---

3 Synthesis

- Only, one parameter: $Ra A^2$.
- Two regimes with very well established scaling laws.
- The glass furnaces are in the convective regime.
- The typical velocity is given by

$$u_0 \sim \left( \frac{\beta \Delta Tg}{\nu} \right)^{2/5} \kappa^{3/5} L^{1/5}. \quad (5)$$

- Since $\kappa \sim \beta_R^{-1}$:
  - Strong influence of the infrared absorption of glass.
- $H$ is irrelevant to describe the heat and mass transfer.
Natural convection in glass furnaces
4 Perspectives, applied works

- Find a link between the residence time distribution and the control parameter of the flow, $Ra A^2$:
  - Important to predict the period of transition between two glasses.
- Develop the same study for electric furnaces:
  - Energy source in the bulk (Coll. with S. Adjoua, SGR).
Natural convection in glass furnaces

4 Perspectives, fundamental works

- Stability of horizontal convection:
  - The flow becomes unsteady when $Ra$ increases.

- E. Uguz (Ph. D. student of Univ. of Florida) has developed a spectral solver:
  - Collaboration with G. Labrosse (Univ. d’Orsay) and R. Narayanan (Univ. of Florida).
  - Determination of the stability diagram $Ra$ vs. $A$. 
Natural convection in glass furnaces

4 Perspectives, fundamental works

Unsteady flow in the cavity
Natural convection in glass furnaces

4 Perspectives, fundamental works

Figure 7: Critical Rayleigh number versus $A$ for $Pr = 10^3$ and $Pr = 7$. 
Natural convection in glass furnaces
4 Perspectives, fundamental works

- Siggers et al.\(^3\) established using a variational method that the heat flux (Nusselt number) behaves as \(Ra^{1/3}\).
- However, the numerical simulations give always a trend as \(Ra^{1/5}\)?

\[^3\text{J. H. Siggers et al. } J. \text{ Fluid Mech.}, 517:55-70, 2004.\]
Mass transfer around a bubble

1. Main features
2. Experiment with O₂ bubbles
3. Sherwood number determination
4. Experiment vs. numerical
5. Synthesis
6. Perspectives
Mass transfer around a bubble

1 Main features

- **molten glass**
- **CO$_2$: raw mat.**
- **H$_2$O, N$_2$: atmosphere**
- **0$_2$, SO$_2$: fining agents**
Mass transfer around a bubble

1 Main features

molten glass

\[ \text{H}_2\text{O, N}_2: \text{atmosphere} \]

\[ \text{CO}_2: \text{raw mat.} \]

\[ \text{O}_2, \text{SO}_2: \text{fining agents} \]

Mass transfer with a multicompomponent bubble.
Mass transfer around a bubble

1 Main features

- At 1500 °C, for a bubble radius of 1 mm, \( \text{Re} = \frac{V T^2 a}{\nu} \approx 10^{-3} \).
- Due to low diffusion coefficient, \( \text{Pe} = \frac{V T^2 a}{D} > 10^3 \).

Figure 8: \( \text{O}_2 \) concentration around a rising bubble at \( \text{Pe} = 10^3 \).
Mass transfer around a bubble

1 Main features

- At 1500 °C, for a bubble radius of 1 mm, \( \text{Re} = \frac{V_T^2 a}{\nu} \approx 10^{-3} \).
- Due to low diffusion coefficient, \( \text{Pe} = \frac{V_T^2 a}{D} > 10^3 \).

Figure 8: \( O_2 \) concentration around a rising bubble at \( \text{Pe} = 10^3 \).

Mass transfer is mainly driven by advection.
Mass transfer around a bubble

2 Experiment with \( \text{O}_2 \) bubbles

Figure 9: Sketch of the laboratory furnace.

- To increase the residence time of a bubble, it is trapped and transferred with a silica tube (“Shuttle method”)\(^4\).
- The bubble size is determined by a counting of pixels.


Figure 10: Snapshots of the bubble in the experiment (O. Mario & E. Grignon, SGR).
Two glasses were studied based on the same composition (flat glass).

Only, the iron content changes:
- Glass 1: 0.03 wt % of iron;
- Glass 2: 0.11 wt % of iron.

No sulfate $\Rightarrow$ very low concentration of SO$_2$. 
Mass transfer around a bubble

2 Experiment with O\textsubscript{2} bubbles

Figure 11: Bubble size vs. $t$ with glasses at low and high iron content obtained at $T = 1400$ °C.
Mass transfer around a bubble

2 Experiment with $O_2$ bubbles

![Graph showing bubble size vs. time for two glasses at low and high iron content obtained at $T = 1400 \, ^\circ C$.]

Figure 11: Bubble size vs. $t$ with glasses at low and high iron content obtained at $T = 1400 \, ^\circ C$.

Need to explain the effect of the iron content.
Mass transfer around a bubble

3 Sherwood number determination

- Sherwood number for $O_2$ ⇒ solve the equation:

$$\frac{DC_{O_2}}{Dt} = D_{O_2} \nabla^2 C_{O_2} + \dot{r}_{O_2}. \quad (6)$$

- Assumptions:
  - The flow around the bubble is in the Stokes regime.
  - Interface between the bubble and glass is fully mobile\(^5\).
  - Oxidation-reduction reaction of iron oxide is in chemical equilibrium.
  - Diffusion of iron is assumed very low.

$$\dot{r}_{O_2} = -\frac{C_{Fe} K_{Fe}}{16 C_{O_2}^{3/4} (K_{Fe} + C_{O_2}^{1/4})^2} \frac{DC_{O_2}}{Dt}. \quad (7)$$

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Mass transfer around a bubble

3 Sherwood number determination

Figure 12: Sherwood number versus Péclet number at $T = 1500$ °C.

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Mass transfer around a bubble

4 Experiment vs. numerical

Figure 13: Bubble size vs. time for the two glasses, at $T = 1400 \, ^\circ \text{C}$. Comparison between experimental and numerical results.

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5 Synthesis

- Effect of the iron content established.
- Determination of the modified Péclet number taking into account the iron content.
- The scaling law of $O_2$ bubble resorption has been done$^8$.

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Mass transfer around a bubble
6 Perspectives, applied works

- Describe a bubble population:
  - Bubble consumption of gas $\Rightarrow$ chemical equilibrium of the glass.
  - Two ways:
    - Development of a population balance equation and solve it.

- Determine the bubble flux toward the free surface of the glass bath:
  - Important to know to determine the foam layer.
Glass foam stability

1. Motivations
2. Bubble drainage on the free surface
3. Synthesis
4. Perspectives
Glass foam stability

1 Motivations
Glass foam stability

1 Motivations

Primary foam

Secondary foam
1 Motivations

- Foam is a thermal screen:
  - Reduction of 60% of radiative fluxes:
    - Increase of fuel consumption.
  - Reduction of temperature in the bath.
  - Increase of temperature in combustion space:
    - Wear of the crown;
    - Rising of pollutant emissions.

- What are the main phenomena leading the glass foam stability?
  - Chemistry?
  - Heat transfer?
Glass foam stability

1 Motivations

■ Mesoscopic studies:
  ● Bubble drainage on a free surface:
      with F. Rouyer, Lab. Navier, Ecoles des Ponts et Chausées).
    ▶ Numerical method (coll. with A. Sellier, LadHyX);
  ● Stability of vertical film:
    ▶ Numerical method;
      with F. Rouyer).
Glass foam stability

1 Motivations

- Mesoscopic studies:
  - Bubble drainage on a free surface:
    - Numerical method (coll. with A. Sellier, LadHyX);
  - Stability of vertical film:
    - Numerical method;
Glass foam stability

2 Bubble drainage on the free surface

Rising of a bubble
Glass foam stability

2 Bubble drainage on the free surface

\[ a^3 \Delta \rho g \sim a \gamma \rightarrow Bo = \frac{\Delta \rho g (2a)^2}{\gamma}, \text{ Nombre de Bond.} \quad (8) \]

Figure 14: Force balance for a bubble close to a free surface.
Glass foam stability

2 Bubble drainage on the free surface

\[ U \sim \frac{\rho g(2a)^2}{\mu}, \tau = \frac{\mu}{\rho g2a}. \]  (9)

Figure 15: Film drainage with free shear interfaces.
Glass foam stability

2 Bubble drainage on the free surface

Figure 16: Experimental set-up to study the bubble drainage on molten glass (H. Kočárková).
Glass foam stability

2 Bubble drainage on the free surface

- Experimental set-up has been duplicated at room temperature.
- Four liquids have been studied:
  - Two glasses (high temperature):
    - classical flat glass;
    - glass rich in Al$_2$O$_3$.
  - Two oils (room temperature, exp. achieved by S. Metallaoui, Master 1):
    - Castor oil;
    - UCON™ oil.
Glass foam stability

2 Bubble drainage on the free surface

Figure 17: Film thickness versus time for the four liquids.
Glass foam stability

2 Bubble drainage on the free surface

- Since the molten glass is a high viscous fluid:
  - Reynolds number $\ll 1$.
  - Stokes equations can be used to describe the motion of fluid.

- Stokes equations have two important properties:
  - Linear equations $\Rightarrow$ fundamental solutions are known.
  - Existence of a reciprocity relationship (Principle of Lorentz reciprocity).

Integral formulation of Stokes equations solved by a Boundary Element Method\(^9\)

Glass foam stability

2 Bubble drainage on the free surface

Figure 18: Shapes of a bubble near the free surface.

Comparison with the previous work of Princen\textsuperscript{10}.

Glass foam stability

2 Bubble drainage on the free surface

Figure 18: Shapes of a bubble near the free surface.

Comparison with the previous work of Princen\textsuperscript{10}.

Glass foam stability

2 Bubble drainage on the free surface

Figure 18: Shapes of a bubble near the free surface. Comparison with the previous work of Princen\textsuperscript{10}.

Glass foam stability
2 Bubble drainage on the free surface

Figure 19: Film thickness at the top of the bubble. For $Bo = 0$, the Bart’s solution is used$^{11}$.

Glass foam stability

2 Bubble drainage on the free surface

- Strong influence of the bubble deformation:
  - drainage controlled by the pressure due to the buoyancy force on the cap.

- Assuming a pure extensional flow:

\[
\frac{1}{h} \frac{dh}{dt} = -\frac{4\pi}{9S_{cap}}. \tag{10}
\]

Figure 20: Bubble shape obtained by the static equilibrium, $Bo = 1$. 
Glass foam stability

2 Bubble drainage on the free surface\textsuperscript{12}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure21}
\caption{$\tau_d^{-1} = -\frac{1}{h}\frac{dh}{dt}$ versus $\text{Bo}$ for the four liquids.}
\end{figure}

Glass foam stability

3 Synthesis

- Effect of the bubble size established.
- UCON™ oil and Castor oil are liquid models to represent molten glass.
- Observation of the “daughter bubbles” due to the rupture of the large bubbles in molten glass:
  - When a dynamical viscosity lesser than 10 Pa·s.
- On the vertical film:
  - Stability has been observed on molten glass experiment due to Na₂O evaporation¹³.

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Glass foam stability
4 Perspectives, applied works

- A foam is formed by a large quantity of bubbles:
  - Can foam stability be explained with the stability on one bubble?
  - Need to develop new experiments and new theoretical models:
    - Glass foam aging should be investigated;
    - Heat transfer has to take into account.

- Development of new products based on glass foam.
Glass foam stability
4 Perspectives, fundamental works

- Fundamental aspect of hydrodynamic interaction of a bubble with a free surface:
  - Behavior of hydrodynamic force when $B_0$ is small but not equal to zero?
    - Extension of the work of Berdan and Leal\textsuperscript{14}.

- Development of 3D solver based on the B.E.M. to describe the bubble dynamics (M. Guémas):
  - Study the mixing induced by the rising of bubbles;
  - Rheology of bubbly flows.

- Experimental work on vertical film of molten glass:
  - Extension for various glass natures (work in progress, J.-C. Guillard, Master 2).
  - Frankel experiment: Film thickness vs. pulling-out velocity.

\textsuperscript{14}C. Berdan & L. G. Leal \textit{J. Colloid Interface Sci.}, 87:62-80, 1982.
Glass is a reactive media where the measures are difficult to do:

- Difficult to develop theoretical models.
- A lot of things stay to do.

The general method is to try a simpler model to obtain a maximum of results to comeback after an original media.

Connections with other science domains:

- Geophysics (oceanographies, vulcanology, mantle convection) ⇒ close collaboration with M. Toplis (Obs. Midi-Pyrénées).
- Metallurgy.
Figure 22: Daughter bubbles observed for molten glass with a dynamical viscosity lesser than 10 Pa·s.
Figure 23: Bubble shape for $\hat{\mu} = 5$ and $Bo = 1$. 
Thanks to thermodynamics, it is possible to find the ion and gas concentrations:

- Constant equilibrium + equilibrium between a liquid phase and “gas” phase.

Iron content play a role at low temperature:

- A larger consumption of sulfate;
- Glass is more reduced.
Figure 24: Concentration of $\text{SO}_4^{2-}$ vs $T$ with three iron contents.
Figure 25: $a$ vs $t$ with three iron contents.
Figure 26: $a$ vs $t$ with two redox, $\mathcal{R} = C_{\text{Fe}^{2+}}/C_{\text{tot}}$. 