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# Transport phenomena of bubbles in a high viscous fluid

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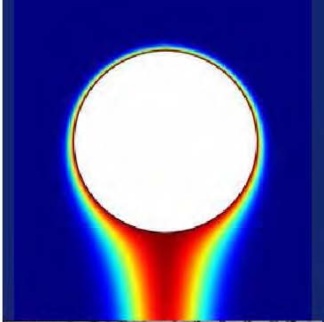

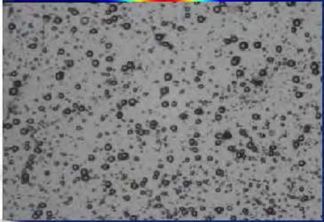

# Industrial context

- Glass melting is a chemical process :

  $SiO_2 + CaCO_3 + Na_2CO_3 \Rightarrow SiO_2 \cdot CaO \cdot Na_2O + CO_2$.

- Large production of $CO_2$ : 0.2 kg of $CO_2$ per kg of glass.
- Low solubility of $CO_2 \Rightarrow$ large quantity of bubbles in molten glass.
- Introduction of “fining” species leads to the bubble removal at high temperature (1450 °C).

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The mass transfer between bubbles and molten glass is essential in glass melting

# Industrial context

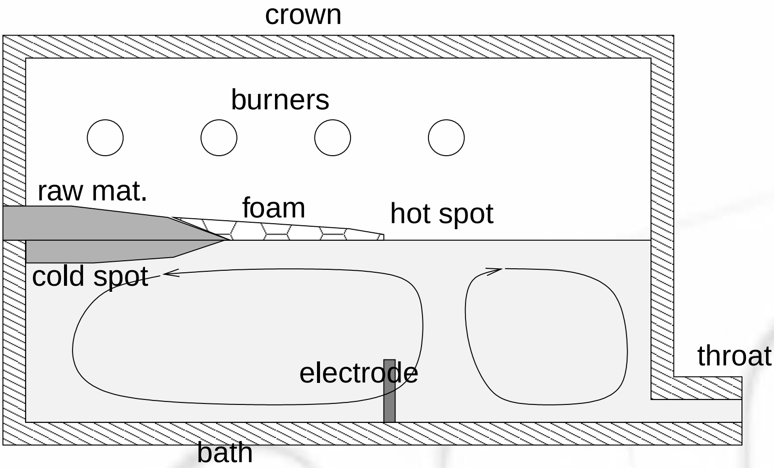
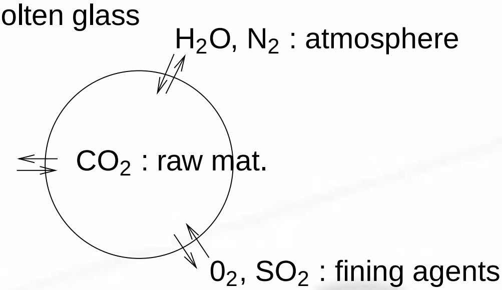


Fig. 1 : *Sketch of furnace.*

# Outline

1. Main features of mass transfer between a bubble and molten glass
2. Experimental study of the shrinkage of $O_2$ bubble
3. Determination of the Sherwood number for $O_2$
4. Modeling of the shrinkage of $O_2$ bubble

# 1. Main features of mass transfer between a bubble and molten glass



molten glass

$H_2O$, $N_2$ : atmosphere

$CO_2$ : raw mat.

$0_2$, $SO_2$ : fining agents

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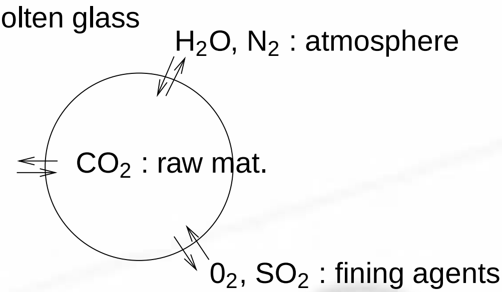
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Mass transfer with a multicomponent bubble.

# 1. Main features of mass transfer between a bubble and molten glass

- At 1500 °C, for a bubble radius of 1 mm, the Reynolds number is $10^{-3}$.
- Due to low diffusion coefficient, the Péclet number is greater than $10^{3}$.

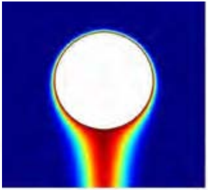

Fig. 2 : *$O_2$ concentration around a rising bubble at $Pe = 10^3$, Comsol, Multiphysics® 3.5.*

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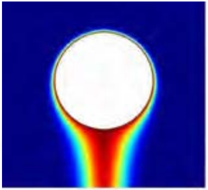

Fig. 2 : *$O_2$ concentration around a rising bubble at* $Pe = 10^3$, *Comsol, Multiphysics® 3.5.*

Mass transfer is mainly driven by advection.

# 1. Main features of mass transfer between a bubble and molten glass

- Iron is the major transition metal present in glass :
  - Naturally present in mineral elements used as raw materials ;
  - Added to change the optical properties of glass.
  - Iron content : [0.01; 5] wt %.
- Iron undergoes the following oxidation-reduction reaction :

$$\mathrm{Fe}^{3+} + \frac{1}{2}\mathrm{O}^{2-} \rightleftharpoons \mathrm{Fe}^{2+} + \frac{1}{4}\mathrm{O}_2. \qquad (1)$$

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The transport of $O_2$ is also controlled by iron.

# 2. Experimental study of the shrinkage of $O_2$ bubble

## Experimental set-up

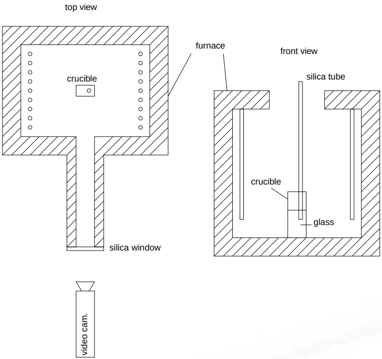

Fig. 3 : *Sketch of the laboratory furnace.*

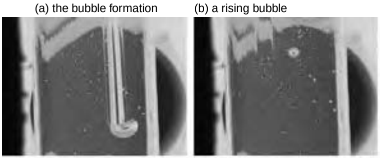
(a) the bubble formation (b) a rising bubble

Fig. 4 : *Photographs of the bubble in the experiment.*

- To increase the residence time of a bubble, it is trapped and transfered with a silica tube (“Shuttle method”)[1].
- The bubble size is determined by a counting of pixels.

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[1] J. Kloužek, and L. Němec (2003) *Ceramics* **47**, 155-161.

# 2. Experimental study of the shrinkage of $O_2$ bubble

## Studied glasses

- Two glasses are 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 ⇒ very low concentration of $SO_2$.

# 2. Experimental study of the shrinkage of $O_2$ bubble

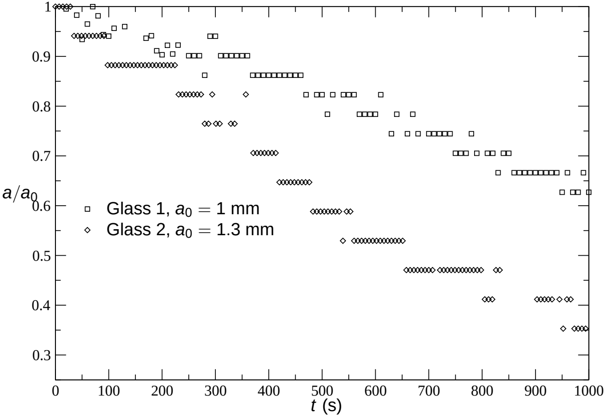

Fig. 5 : *Bubble size vs. t with glasses at low and high iron content obtained at* $T = 1400\ ^\circ C$.

# 3. Determination of the Sherwood number for $O_2$

## Present model

- Sherwood number for $0_2 \Rightarrow$ solve the advection/diffusion/reaction equation :

$$\frac{DC_{\mathrm{O}_2}}{Dt} = \mathcal{D}_{\mathrm{O}_2}\nabla^2 C_{\mathrm{O}_2} + \dot{r}_{\mathrm{O}_2}. \qquad (2)$$

- Assumptions :
  - The flow around the bubble is in the Stokes regime.
  - Interface between the bubble and glass is fully mobile[2].
  - Oxidation-reduction reaction of iron oxide is in chemical equilibrium.
  - Diffusion of iron is assumed very low.

$$\dot{r}_{\mathrm{O}_2} = -\frac{C_{\mathrm{Fe}}K_{\mathrm{Fe}}}{16C_{O_2}^{3/4}(K_{\mathrm{Fe}} + C_{O_2}^{1/4})^2}\frac{DC_{\mathrm{O}_2}}{Dt}. \qquad (3)$$

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[2] E. J. Hornyak & M. C. Weinberg (1984) *J. Am. Ceram. Soc.* **67**, C244-C246.

# 3. Determination of the Sherwood number for $O_2$

## Present model

- Four dimensionless numbers are involved :

$$Pe = \frac{2aV_T}{\mathcal{D}_{\mathrm{O}_2}}, \qquad (4)$$

$$Sa = \frac{C^{\infty}_{\mathrm{O}_2}}{C^{S}_{\mathrm{O}_2}}. \qquad (5)$$

$$N_{\mathrm{Fe}} = \frac{C^{\infty}_{\mathrm{Fe}^{2+}}(1-\mathcal{R}^{\infty})Sa^{1/4}}{16C^{S}_{\mathrm{O}_2}}, \qquad (6)$$

$$\mathcal{R}^{\infty} = \frac{C^{\infty}_{\mathrm{Fe}^{2+}}}{C^{\infty}_{\mathrm{Fe}^{2+}} + C^{\infty}_{\mathrm{Fe}^{3+}}}. \qquad (7)$$

- The problem is solved by two methods :
  - Boundary layer theory for large Péclet number.
  - A full numerical method developed in Comsol, Multiphysics® 3.5.

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[3] F. Pigeonneau (2009) *Chem. Eng. Sci.*, **64**(13), 3120-3129.

# 3. Determination of the Sherwood number for $O_2$

## Effect of iron content

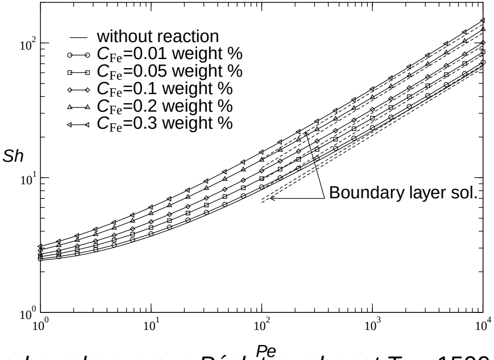

Fig. 6 : *Sherwood number versus Péclet number at T* $= 1500\ ^\circ C$, $\mathcal{R}^\infty = 0.2$.

# 3. Determination of the Sherwood number for $O_2$

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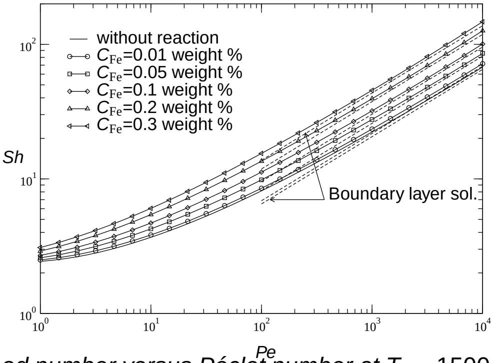

Fig. 6 : *Sherwood number versus Péclet number at T* $= 1500\,^\circ C$, $\mathcal{R}^\infty = 0.2$.

Enhancement of mass transfer coefficient due to the chemical reaction for all values of *Pe*.

# 4. Modeling of the shrinkage of $O_2$ bubble

- The bubble size changes due to the mass transfer of various species :

$$
\begin{aligned}
\frac{dn_i}{dt} &= 2\pi a Sh_i \mathcal{D}_i (C_i^{\infty} - C_i^S), && (8) \\
C_i^S &= L_i P_i^{\beta_i}, && (9) \\
\frac{3RT\sum_{i=1}^{N_g} n_i}{4\pi a^3} &= P_0 + \rho g (H - z) + \frac{2\sigma}{a}, && (10) \\
\frac{dz}{dt} &= V_T. && (11)
\end{aligned}
$$

- Equation system solved by a fourth-order Runge-Kutta method.

# 4. Modeling of the shrinkage of $O_2$ bubble

## Comparison of various Sherwood numbers

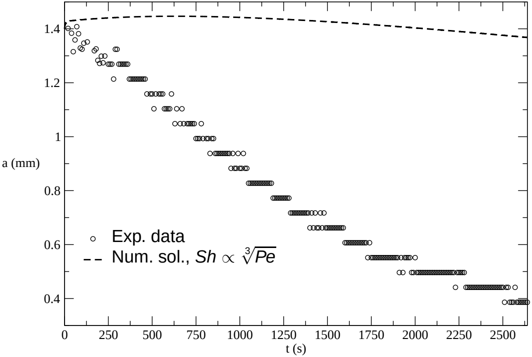

Fig. 7 : *a versus time obtained for the glass 1 (low iron content) at* $T = 1400\ ^\circ C$.

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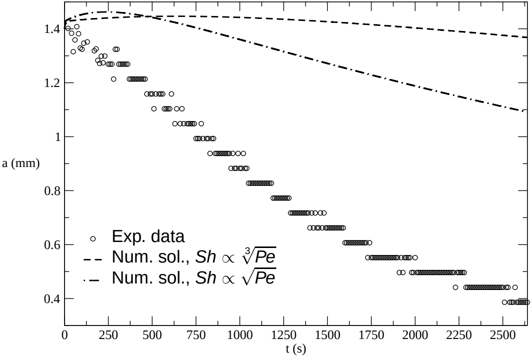

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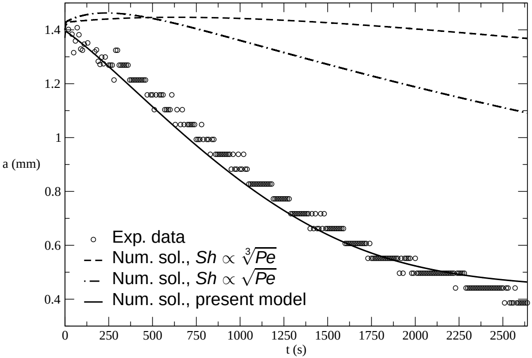

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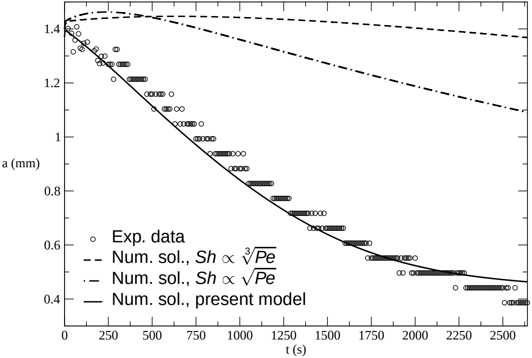

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The relevance of oxidation-reduction reaction of iron is clearly established.

# 4. Modeling of the shrinkage of $O_2$ bubble

## Effect of iron content

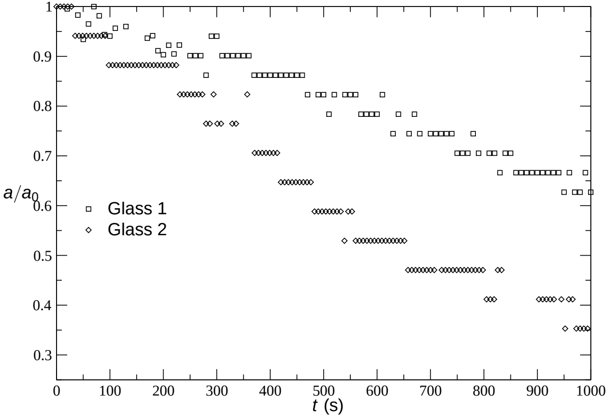
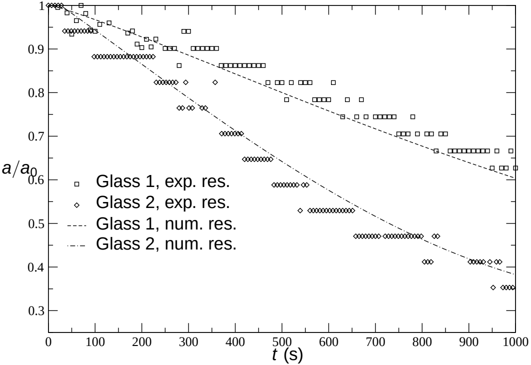


Fig. 8 : *Bubble size vs. time for the two glasses, at $T = 1400\ ^\circ C$.*

# 4. Modeling of the shrinkage of $O_2$ bubble

## Effect of iron content[4]



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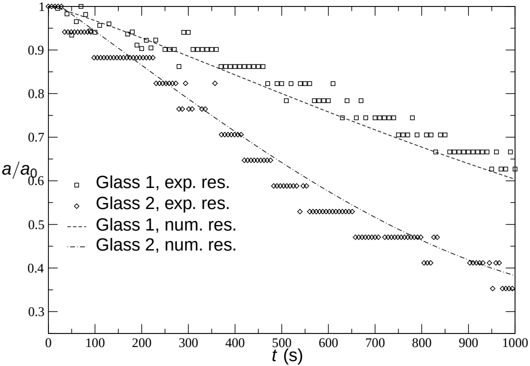

Fig. 8 : *Bubble size vs. time for the two glasses, at* $T = 1400\ ^\circ C$.

Results obtained without data fitting.

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[4] F. Pigeonneau, D. Martin & O. Mario (2010) *Chem. Eng. Sci.*, **65**(10), 3158-3168.

# Conclusion & perspectives

- Determination of a Sherwood number taking into account the redox reaction of iron oxides.
- The experimental results obtained with two iron contents are well reproduced with the proposed model :
  - The larger the reduced iron content, the larger the shrinkage of the $O_2$ bubble.
- Perspectives :
  - Development of numerical model to study mass transfer interaction between molten glass and a large bubble population (bubbly flow model).
  - Bubble motion in a crucible (Level-set model).