La modélisation Monte-Carlo cinétique :
un outil pour comprendre la corrosion des verres

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Nuclear waste confinement glasses

Among more than 30 oxides:
- Silica 45%
- Boron oxide 14%
- Alkali oxide 14%
- Earth-alkali oxide 5%
- Alumina 4%
- Zirconia 2%
- Fission products 12%
- Minor Actinides 1%

Long term geological storage

Need for understanding and modeling the dissolution mechanisms for safety assessment
Biosolubility of insulation and reinforcement fibers

Lung clearance mechanisms

- short fibers (< 20 \( \mu m \))
  - transport by macrophages

- long fibers (> 20 \( \mu m \))
  - dissolution in extracellular fluid (pH 7)
  - breaking after partial dissolution in macrophage phagolysosomes (pH 4.5)

Fibers with high alumina content

Is there a threshold for biosolubility?

Nguea et al., Arch. Toxicol. 79, 487 (2005)

Work guidelines

- to associate Monte-Carlo simulations and experiments on the same glasses

- to study series of glasses with simplified composition
  
  - influence of oxides more soluble than silica
    - $(100-2x)\text{SiO}_2 - x\text{B}_2\text{O}_3 - x\text{Na}_2\text{O}$
    - $(64-x)\text{SiO}_2 - x\text{Al}_2\text{O}_3 - 36\text{Na}_2\text{O} / \text{CaO}$
  
  - influence of oxides less soluble than silica
    - $(61-x)\text{SiO}_2 - x\text{ZrO}_2 - 17\text{B}_2\text{O}_3 - 18\text{Na}_2\text{O} - 4\text{CaO}$

- effect of substituting earth-alkali for alkali
  - $62\text{SiO}_2 - 2\text{ZrO}_2 - 17\text{B}_2\text{O}_3 - (19-x)\text{Na}_2\text{O} - x\text{CaO}$

- to use controlled corrosion conditions
  
  - Calibrated powders + monoliths
  
  - Initial dissolution (low SA/V) and saturation regime (high SA/V)
  
  - Fixed temperature and pH: $T = 90^\circ\text{C}$, pH 7 and 8 / $T = 37^\circ\text{C}$, pH 4.5
The simulated "glass"

\( \beta \)-cristobalit structure

Mapped on a cube

Simulation of samples of \( 10^8 \) sites in a few hours to a few days
The local environment of cations is preserved
Reactivity model

- All the reactions take place at the solid-water interface

- Soluble cations (boron, alkali, earth-alkali, Al in acidic medium) are dissolved immediately and never condense again

- Si dissolution probability depends on Si neighboring:
  \[ P_{\text{diss}} = f \cdot w_n \text{ with } f = 1 \ (\text{Si}), \ f > 1 \ (\text{B, Ca}) \ ou \ f < 1 \ (\text{Zr}) \]

- Si condensation probability is proportional to the concentration in solution:
  \[ P_{\text{cond}} = w_c \cdot c_{\text{Si}} \]

- Insoluble cations (Zr, RN) are only dissolved as colloidal particles
choix de la composition
choix des paramètres
choix des conditions
- dynamique : $c_{\text{flux}}$
- statique : $S/V$, $c_{\text{init}}$

construction du « verre »

dissolution à la surface
condensation à la surface
connectivité des pores*

$t = t + 1$

Stockage des données
- cinétique $c(t)$
- morphologie

* Algorithme de Hoschen-Kopelman
Initial dissolution regime (far from saturation)

\[ R = 0.30 \]

\[ t = 0 \]

\[ t = 1000 \]

\[ t = 2000 \]

\[ t = 3000 \]

\[ t = 4000 \]

\[ t = 5000 \]

\[ \frac{S}{S_0} \]

\[ 0 \]

\[ 50 \]

\[ 100 \]

\[ 0 \]

\[ 5 \times 10^3 \]

\[ 1 \times 10^4 \]

\[ 1.5 \times 10^4 \]

GDR Verres, Marcoule, 12 mai 2011

PMC (CNRS - Ecole Polytechnique)
Effect of composition on the initial dissolution rate $(t = 5000)$

$R = 0.15$

$R = 0.20$

$R = 0.25$

$R = 0.30$

$R = 0.35$

$R = \frac{B}{(Si+B)} \%$

$dissolution rate (a.u)$
Variation of the initial dissolution rate with glass composition

\[(100-2x) \text{SiO}_2 - x \text{B}_2\text{O}_3 - x \text{Na}_2\text{O}\]

Percolation of the boron sublattice

\[R_B < p_c\]
- Si limited congruent dissolution

\[R_B > p_c\]
- Selective dissolution

percolation threshold on diamond lattice
- site: \(p_c = 0.42\)
- bond: \(p_c = 0.39\)
Saturation regime

1) \( w_1 = w_2 = w_3 \)

formation of a swelling foam

Saturation regime

2) $w_1 > w_2 > w_3$

formation of a passivating layer

Long term corrosion kinetics

\((100-2x) \text{SiO}_2 - x \text{B}_2\text{O}_3 - x \text{Na}_2\text{O}\)  

\(T = 90^\circ \text{C}\)  
\(\text{pH} 8.5\)  
\(100 \mu\text{m}\)  
\(\text{SA/V}=1 \text{ cm}^{-1}\)

\(R_B = 0.22\)

\(R_B = 0.30\)

\(R_B = 0.37\)

\(R_B = 0.43\)


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Variation of the final degree of corrosion with glass composition

The degree of corrosion results from a competition between:
- the formation of the porous structure, whose thickness increases with $R$
- the restructuring due to Si dissolution-condensation kinetics

Si: chemical equilibrium ($c \approx c^* \approx 150$ mg/L)
B and Na: controlled by the formation of the passivating barrier

**Influence of insoluble oxides: replacing SiO₂ by ZrO₂**

(61-x) SiO₂ - x ZrO₂ - 17 B₂O₃ - 18 Na₂O - 4 CaO

90°C, pH 7, 30 µm, SA/V = 15 cm⁻¹

The corrosion is slowed down, but the final degree of corrosion is higher.

Why do the glasses with a low dissolution rate undergo a high degree of corrosion?

The Monte-Carlo answer: gel restructuring!

- Without insoluble oxides: the restructuring induces a corrosion blocking

  - The pore network gets non-percolating and the corrosion stops

- With insoluble oxides: the restructuring is slowed or inhibited owing to the strengthening of the glass network.

  - The pore network remains percolating and the corrosion goes on

shrinkage densification and porosity closure

no shrinkage, no densification
**The gel restructuring at the atomic scale** (\(^{29}\text{Si NMR}\))

Pristine glass:
- broad line, \(T_1 \approx 5000\text{s}\)

100% corroded glass:

<table>
<thead>
<tr>
<th></th>
<th>(Q^1)</th>
<th>(Q^2)</th>
<th>(Q^3)</th>
<th>(Q^4)</th>
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</thead>
<tbody>
<tr>
<td>ppm</td>
<td>-80</td>
<td>-90</td>
<td>-100</td>
<td>-110</td>
</tr>
<tr>
<td>Exp</td>
<td>-</td>
<td>-</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td>(T_1)</td>
<td>-</td>
<td>-</td>
<td>30s</td>
<td>70s</td>
</tr>
<tr>
<td>MC</td>
<td>2%</td>
<td>7%</td>
<td>20%</td>
<td>71%</td>
</tr>
</tbody>
</table>
The gel restructuring at the mesoscopic scale (SAXS)

Porod law: \( I(q) \sim \Sigma q^{-4} \)

Pristine glass: \( \Sigma = 0.43 \text{ m}^2/\text{g} \) \( h < 3 \) network scattering \( h = D_F \)

Corroded glass: \( \Sigma = 108 \text{ m}^2/\text{g} \) \( 3 < h \leq 4 \) surface scattering \( h = 6 - D_S \)
Glass restructuring as studied by SAXS

SAXS measurements after $\tau_K/4$, $\tau_K/2$, $\tau_K$, $2\tau_K$, 40 days and long term corrosion

Without Zr: fast restructuring
With Zr: slow restructuring

Evolution of the surface area of the porous network in $^{0}$Zr

**SAXS**

\[ \Sigma = \frac{l(q) \ q^4}{2\pi \ d \ b^2 \ \Delta \rho^2} \]

**MC simulations**

\[ \Sigma = \frac{S(k) \ k^4}{2\pi \ d \ a} \]

\( k = q \ a \quad a = 0.32 \text{ nm} \)

<table>
<thead>
<tr>
<th>Time</th>
<th>( \Sigma ) (m$^2$/g)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>202</td>
<td>2.5</td>
</tr>
<tr>
<td>39 days</td>
<td>84</td>
<td>3.6</td>
</tr>
<tr>
<td>125 days</td>
<td>69</td>
<td>4.2</td>
</tr>
</tbody>
</table>

BET

\[ 2.2 \text{ m}^2/\text{g} \]

<table>
<thead>
<tr>
<th>Time</th>
<th>( \Sigma ) (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 \times 10^5 steps</td>
<td>140</td>
</tr>
<tr>
<td>3 \times 10^6 steps</td>
<td>71</td>
</tr>
<tr>
<td>10^7 steps</td>
<td>49</td>
</tr>
</tbody>
</table>
The porosity closure tested by ToF-SIMS after solvent exchange with a K\(^+\) labeled solution

The porosity closes at long time in the glass without ZrO\(_2\), not in the others

The porosity closure tested by small angle neutron scattering with index matching

- H$_2$O
- Glass
- H$_2$O-D$_2$O mixture
- Partial matching
- Perfect matching (~ 65 % D$_2$O): Signal extinction
- Close porosity
- No extinction
Small angle neutron scattering with index matching

The porosity closes at long time in glass 0Zr

It remains open in glasses 4Zr and 8 Zr

Principales conclusions

1. L'augmentation de la vitesse de dissolution avec la proportion de cations solubles (B, Al) est due à l'augmentation de la surface active en relation avec des effets de percolation.

2. Dans certaines conditions, il se forme une couche passivante qui conduit à un (quasi) blocage de la corrosion. Cette passivation est due à la restructuration de la couche poreuse altérée, qui entraîne retrait, densification et fermeture de la porosité.

3. La présence d'oxydes insolubles ralentit l'altération, mais elle ralentit aussi la restructuration, ce qui conduit à une augmentation du degré de corrosion.
Aurélien Ledieu
PhD 2004
Philippe Barboux
Bernard Sapoval
Frédéric Angeli
Mehdi Arab
Stéphane Gin
Patrick Jollivet
Yves Minet
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Olivier Spalla
Jacques Jestin

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PMC, CNRS - Polytechnique
LCLT, CEA Marcoule
LIONS, CNRS - CEA Saclay (SAXS)
LLB, CNRS - CEA Saclay (SANS)

GDR Verres, Marcoule, 12 mai 2011

PMCCNRS - Ecole Polytechnique
Implicit hypotheses

✓ Si first order kinetics:

\[
\frac{dN_{Si}}{dt} = \sum_{i \in S} \{P_{diss}(i) - w_c \times c_{Si}\} \rightarrow c^*_{Si} = \frac{\langle P_{diss}(i) \rangle_{i \in S}}{w_c}
\]

✓ Diffusion in solution is very fast

✓ Solid-state diffusion is neglected
Porosity closure tested by solvent exchange

methylene blue permeation

ToF-SIMS
K\(^+\) labeled solution

spatially resolved mass spectroscopy
analysis beam

abrasion beam

Corroded glass

**Main conclusions**

1. The increase of the dissolution rate with the proportion of soluble network forming cations is mainly due to the increase of the glass-water interface area in relation with percolation properties.

2. In certain conditions, a passivating layer is formed, which causes a corrosion blocking after saturation of the solution with respect of silica.

3. The passivation is due to the restructuring of the porous surface layer which leads to sample shrinkage, densification of the layer and closure of the porosity.

4. The presence of insoluble oxides slows down the kinetics, but increases the degree of corrosion by inhibiting the porous layer restructuring.

5. The glasses with a high dissolution rate undergo fast restructuring and corrode slightly; the glasses with a low dissolution rate undergo slow restructuring and corrode deeply.