Effect of groundwater on the dissolution rate of the simulated nuclear waste glass SON68 under gamma irradiation

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Abstract

The leaching behaviour of the inactive reference of the R7T7 glass is investigated here in a synthetic clayey groundwater solution, focusing on the effect of gamma irradiation on this residual alteration rate, under static conditions, at 90°C. Results don’t underlie any significant effect of gamma irradiation on the residual alteration rate up to 5kGy/h, compared to experiments performed out of irradiation in groundwater or in pure water. Moreover, the evolution of boron releases in groundwater versus time is similar whatever the dose rate. These observations are consistent with SEM characterizations.

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Glass ; clayey groundwater ; irradiation ; gamma ; dose rate ; leaching

1. Introduction

In France, borosilicate glass, known as R7T7 glass, has been used to confine high level radioactive waste remaining after reprocessing of spent nuclear fuel, for disposal in a geological repository. The French reference site currently being examined and qualified is a Callovian–Oxfordian argillite layer in the northeast sector of the...
Paris basin [1]. In these conditions, the glass alteration by groundwater is the most probable process by which radionuclides can be released from the matrix. The SON68 glass (inactive surrogate of R7T7 glass) alteration has been extensively investigated since the beginning of the 1980s, leading to determine the key mechanisms and the kinetics of borosilicate glass dissolution [2-6]: first interdiffusion, then glass network hydrolysis and finally, after a rate drop, a residual rate regime in which glass dissolution results from the formation of secondary aluminosilicate crystalline phases such as phyllosilicates and the interdiffusion of water and solvated ions through the “passivating reactive interphase” PRI. The influence of groundwater on the kinetics of the SON68 glass alteration has been investigated more recently [7]. This study shows that the groundwater delays the rate drop and induces dissolution rates higher than in pure water. This effect would be due to the presence of magnesium, which precipitates in secondary phases with silicon while the other elements found in groundwater have no significant effects on the glass kinetics.

However, it must be kept in mind that under disposal conditions, glass packages and the surrounding environment, including the groundwater, will be subjected to irradiation. Thus, the impact of irradiation on the elemental releases from the glass matrix must be considered. Radiation could modify the glass leachability through structural damage to the matrix [8-10], and/or changes in solution chemistry via radiolysis [11]. In addition, depending on the initial system, it could induce the formation of new species which could react with the glass or altered products like the formation of oxalates, formiates from carbonates [11-12]. These changes could modify leaching mechanisms and/or rates, by for example enhancing the formation of new phases, during the residual rate. In this study, we thus focus on the effects of gamma radiation on the SON68 glass (R7T7-inactive glass) residual rate in groundwater conditions.

2. Experimental

2.1. Description of experiments

Leach tests have been conducted with SON68 glass, the inactive surrogate of R7T7-type nuclear glass, whose composition is detailed in table 1, with a volumic mass of 2.68 g.cm$^{-3}$ measured by hydrostatic weighing.

Table 1 : SON68 glass composition in oxide weight percents

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO$_2$</th>
<th>B$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>ZnO</th>
<th>ZrO$_2$</th>
<th>Li$_2$O</th>
<th>MoO$_3$</th>
<th>Nd$_2$O$_3$</th>
<th>Cs$_2$O</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt fraction (%)</td>
<td>47.51</td>
<td>14.89</td>
<td>10.93</td>
<td>4.92</td>
<td>4.14</td>
<td>2.42</td>
<td>2.2</td>
<td>2.1</td>
<td>1.66</td>
<td>1.59</td>
<td>1.13</td>
<td>6.51</td>
</tr>
</tbody>
</table>

Gamma irradiations have been performed at the underwater gamma irradiation facility BRIGITTE (Big Installation under Gamma Irradiation for Tailoring and Testing Experiments, SCK-CEN, Mol, Belgium) with $^{60}$Co sources [13]. Two different gamma dose rates have been chosen, taking into account the total electronic dose rate evolution of the R7T7 glass versus time: one very high dose rate (5 kGy.h$^{-1}$) in order to exacerbate radiation effects and one realistic dose rate (0.05 kGy.h$^{-1}$) relating to water arrival [1].

Leach tests under gamma irradiation have been carried out in 12 mL unitary titanium container covered by a passivating TiO$_2$ in order to ensure as less interaction as possible between the species generated by water radiolysis and the experimental setup. One unitary container corresponds to one duration for one leaching experiment at a given dose rate.

To reach residual rate regime, tests have been carried out at 90°C with a high glass-surface-area-to-solution-volume ratio (100 cm$^{-1}$). The specific area of glass has been determined for a glass powder size fraction between 63 and 125 µm to be 0.0495 ± 0.0049m$^2$.g$^{-1}$ (Kr adsorption, BET method). The glass mass in each container is 2.0 g, and the volume of groundwater added is 10 mL. The composition of the groundwater used for these
leaching tests is indicated in table 2. The samples have all been sealed for irradiation after being bubbled with argon gas for 1 hour and then adjusted the pH of the groundwater to 6.05 at 25°C by CO₂ bubbling. In this condition, the residual rate regime is reached after 120 days [14]: thus, we have realized samplings from 120 days to 811 days of leaching.

Table 2 : Initial chemical composition of groundwater (mg.L⁻¹) and pH measured at 90°C

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Si</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
<th>pH 90°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>897.00</td>
<td>37.50</td>
<td>60.80</td>
<td>401.00</td>
<td>14.90</td>
<td>23.60</td>
<td>1453.00</td>
<td>961.00</td>
<td>610</td>
<td>6.01</td>
</tr>
</tbody>
</table>

These experiments are compared to unirradiated control samples, which means leach tests conducted in titanium containers: one experiment performed in groundwater and one experiment performed in initial pure water.

Finally, containers with only groundwater have also been placed for 365 days at 90°C, at 5 and 0.05kGy.h⁻¹ and without irradiation, in order to follow the ageing of the groundwater in these conditions.

2.2. Post-irradiation analysis

For each container (i.e. each “sampling”), both solution and solid analyses have been performed after container opening by milling. The leachate pH has been measured at room temperature. The leachate has been directly taken in the container and has been separated into two fractions: soluble ions and/or ions retained on a colloidal fraction have been measured on a fraction filtered at 0.45 µm. Soluble ions have been measured on a fraction previously ultrafiltered at 10000 Daltons. Then, both fractions have been acidified with nitric acid at pH ~ 0.5.

H₂O₂ concentrations have been determined by chemiluminescence on a Turner design 20/20 device (using the standard additions method). The associated analytical uncertainty was ± 10%.

The cation analyses have been performed with an ICP-AES Jobin Yvon JY66 system. The analytical uncertainty is ±3% for concentrations above 10 mg.L⁻¹, ±5% between 1 and 10 mg.L⁻¹ and ±20% for concentrations below 1 mg.L⁻¹. Anions have been analyzed with a Metrosep A Supp 16 ionic chromatography. The analytical uncertainty was ±10%.

The glass alteration is monitored by the boron release evolution versus time. Thus, boron releases are expressed in terms of boron normalized mass losses (NL₅ in g.m⁻²) and have been calculated as follows:

\[ NL₅ = \frac{C_B \times V}{S \times x_B} \]  

Where \( C_B \) is the boron concentration in solution (g.L⁻¹), \( x_B \) its mass fraction in the glass, \( S \) the glass surface area (m²) and \( V \) the volume of solution (L). The absolute uncertainty on the NL₅ calculation has been estimated to be around 10%, by using the spreadsheet method suggested by Eurachem guide [15].

The altered glass powder samples taken after each leaching duration tests have been dried for 1 day at 90 °C. Altered layer have been observed after platinum metallization by scanning electron microscopy (SEM). These analyses have been carried out on raw grains by using a Zeiss Supra 55. This FEG-SEM is equipped with a Silicon Drift Detector X-max, cooled by Peltier effect (Oxford Instruments). The accelerating voltage is 15 kV.

3. Results and discussion

The table 3 details the concentrations and the pH measured for the groundwater samples in ageing and for the glass leaching samples in groundwater at 5, 0.05 kGy.h⁻¹ and without radiation, for the last sampling. The pH
values measured on irradiated and non-irradiated groundwater in ageing are similar, which lead to three affirmations. First, this traduces the good airtightness of the sealed containers because the presence of air would induce a decrease in the pH by HNO₃ formation [16-17]. Second, this pH stability under irradiation shows that the carbonated species from groundwater, which play an important part in the groundwater pH value, have not been quantitatively transformed in oxalate ions [12], that would have induced an increase in the pH according to JCHESS calculations [18]. Moreover, no oxalate have been detected in our system. Third, ion concentrations remain stable over time, even under irradiation. In conclusion, these results indicate the good stability of groundwater under irradiation in our systems.

Concerning the glass leach tests in the groundwater medium, we have noted that both tests performed in groundwater lead to pH values around 0.5 pH unit lower than observed for leaching tests in pure water. This difference can be explained by the formation of magnesium silicates phases as sepiolite in presence of groundwater [7]. We can also note that pH values measured on leach tests performed in groundwater under irradiation are similar to these measured on their control sample out of irradiation, traducing the good airtightness of the systems during experiment.

Table 3: Elemental concentrations (mg.L⁻¹) and pH measured at 25°C: a- in the containers with only groundwater after 365 days of ageing at 90°C under irradiation and -b- on the last sampling of the leaching tests in groundwater under irradiation. For both cases, comparison with the corresponding control samples out of irradiation.

<table>
<thead>
<tr>
<th>Dose rate</th>
<th>H₂O₂ (mol.L⁻¹)</th>
<th>B</th>
<th>Li</th>
<th>Ca</th>
<th>Na</th>
<th>Si (mg.L⁻¹)</th>
<th>Sr</th>
<th>Mg</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>pH 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-----</td>
<td>--</td>
<td>--</td>
<td>446</td>
<td>1028</td>
<td>29.6</td>
<td>17.7</td>
<td>70.3</td>
<td>1682</td>
<td>1082</td>
<td>6.01</td>
</tr>
<tr>
<td>0.05</td>
<td>Not measured</td>
<td>--</td>
<td>--</td>
<td>452</td>
<td>1046</td>
<td>27.4</td>
<td>18.0</td>
<td>71.8</td>
<td>1735</td>
<td>1109</td>
<td>5.95</td>
</tr>
<tr>
<td>5</td>
<td>Not measured</td>
<td>--</td>
<td>--</td>
<td>448</td>
<td>1026</td>
<td>29.2</td>
<td>17.9</td>
<td>70.8</td>
<td>1749</td>
<td>1109</td>
<td>6.02</td>
</tr>
<tr>
<td>0.05</td>
<td>(3.4±0.3)×10⁻⁶</td>
<td>307</td>
<td>91.6</td>
<td>35.8</td>
<td>1494</td>
<td>78.0</td>
<td>1.47</td>
<td>&lt;0.1</td>
<td>1670</td>
<td>987</td>
<td>8.81</td>
</tr>
<tr>
<td>5</td>
<td>(2.9 ± 0.3)×10⁻⁵</td>
<td>354</td>
<td>92.9</td>
<td>24.8</td>
<td>1415</td>
<td>90.2</td>
<td>0.87</td>
<td>&lt;0.1</td>
<td>1747</td>
<td>1006</td>
<td>8.93</td>
</tr>
</tbody>
</table>

Regarding the concentrations evolution observed from the glass leaching tests, firstly we note that hydrogen peroxide concentrations measured on irradiated systems are one and two orders of magnitude higher than expected in pure water without glass[14], from CHEMSIMUL calculations [19], and that these H₂O₂ concentrations seem to increase with the dose rate. A similar increase has ever been seen on leached glasses in initially pure water [14] and may be attributed to a modification of the glass or the alteration layer, involving transfers from solid to water under irradiation. Secondly, we can notice an important decrease in calcium concentrations for both tests: this decrease can arise from the precipitation of aragonite because it has ever been observed experimentally with X-ray diffraction under similar conditions [20]. Moreover, a total consumption of magnesium has been observed from the first sampling (120 days of leaching) for both tests (0.05 and 5 kGy/h) and also for the control experiment. According to the literature, the effect of groundwater on the glass alteration rate becomes negligible when Mg is consumed [7], thus in our case, for all the durations studied.

The evolution of the boron normalized mass losses (NL₆₇) versus time is presented in figure 1 for the control system in pure water (no irradiation) and for the experiments performed in the groundwater medium. First, control sample results in pure water underline the dispersion of data due to experimental protocol (use of unitary titanium containers). Then, in groundwater, we observe that the NL₆₇ are slightly higher than in pure water: this is probably due to the formation of magnesium silicates phases during the first 120 leaching days, and leading to a thicker alteration layer, according to the gel thickness measured from the SEM analyses (figure 2). However,
these magnesium phases, like balls [7], have not been observed on our samples. This absence can be explained by
the high surface area compared to the low content in Mg in the solution and thus, the low probability to find them
on the solid surface.

![Graph showing normalized boron mass losses versus time for different systems studied under irradiation and control samples in groundwater and pure water.](image)

Figure 1: on the left: Normalized boron mass losses versus time for the different systems studied under irradiation and for the control samples in groundwater and pure water. In the table 5, on the right: Residual rates calculated for each system studied from normalized boron mass losses.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Dose rate (kGy.h⁻¹)</th>
<th>Vr(B) g.m².j⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>5 kGy/h</td>
<td>(4.3 ± 1.4) 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>0.05 kGy/h</td>
<td>(3.0 ±1.7) 10⁻⁴</td>
</tr>
<tr>
<td>Control sample</td>
<td>Control sample</td>
<td>(1.5± 0.8) 10⁻⁴</td>
</tr>
<tr>
<td>Pure water</td>
<td>Control sample</td>
<td>(5.6 ± 1.4) 10⁻⁴</td>
</tr>
</tbody>
</table>

However, the NLₐB evolution versus time (figure 1) does not display a significant difference between irradiated and no irradiated systems. But, for each system studied, the residual rate values, calculated from a linear regression on the NLₐB between 120 (included) and 811 days (table 5, figure 1) seem to indicate a little dose rate effect for glass leachings performed in groundwater. Nevertheless, we must notice that the residual rate calculated from data for the control test in pure water includes the residual rate values calculated in presence of groundwater. In conclusion, the gamma irradiation up to 5kGy/h and the associated radiolytic species have no significant effects on the residual rate alteration of the SON68 glass in groundwater and in a closed system.

![SEM image of the surface of a grain leached for 9 months in groundwater under 5 kGy/h (b) and the corresponding control sample (a).](image)

Figure 2: SEM image of the surface of a grain leached for 9 months in groundwater under 5 kGy/h (b) and the corresponding control sample (a)
4. Conclusion

The influence of groundwater on the residual rate regime of the SON68 glass has been investigated under gamma irradiation up to 5kGy/h for 811 days. Out of irradiation, groundwater effect is negligible on the residual rate regime: this is consistent with the observation of a total consumption of magnesium from the first sampling at 120 days. Concerning irradiated samples, the groundwater appear to remain stable over time. Then, concerning the leach tests, the alteration data show that radiolytic species and/or potential defects formed in the glass or its alteration layer under irradiation have non significant effects on the residual glass alteration rate. The residual rates measured are similar for each dose rate studied and similar to the residual rate measured from glass leached in pure water out of irradiation. Finally, in a closed system, gamma dose rate up to 5 kGy/h appears to have a negligible effect once the magnesium is consumed. In prospect, it would be interesting to focus on the potential effect of magnesium on the glass alteration under irradiation by renewing the groundwater solution during the leaching.

References