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## The effect of Ordinary Portland Cement on nuclear waste glass dissolution

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### Abstract

To evaluate the durability of the glass matrix and to identify the key mechanisms responsible for glass alteration in the cementitious environment imposed by the *Supercontainer design*, glass leach tests were conducted at 30°C under Ar atmosphere in suspensions of Ordinary Portland Cement and synthetic young cement water with the high pH of 13.5. The cement appears to trigger the glass dissolution by consumption of glass matrix components leading to a fast glass dissolution at a constant rate with the formation of a porous gel layer on the glass. The key mechanism driving the long-term glass dissolution is secondary phase formation with Si and Al from the glass matrix. The two main reactions are the reaction of Si released by the glass with portlandite, leading to the formation of Calcium Silicate Hydrate (C-S-H) phases, and the further conversion of C-S-H phases with Al from the glass to form Calcium Aluminum Silicate Hydroxide (C-A-S-H) phases. After consumption of the portlandite, the glass alteration rate is expected to decrease.

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**Keywords:** Supercontainer design, Ordinary Portland Cement, glass dissolution, hyperalkaline pH, pozzolanic reaction

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## 1. Introduction

The *Supercontainer design* is the current Belgian reference design for geological disposal of High-Level Waste and Spent Fuel (Bel et al., 2006). The glass canisters will be enclosed by a carbon steel overpack and a concrete buffer made of Ordinary Portland Cement (OPC) providing a highly alkaline chemical environment. After local perforation of the overpack, the high pH of the infiltrating water may have an impact on the lifetime of the vitrified waste. Very few glass alteration studies have been reported for hyperalkaline media (Andriambololona *et al.*, 1992; Gin and Mestre, 2001). Hence, a research program was started at the Belgian Nuclear Research Centre (SCK•CEN), financed by ONDRAF/NIRAS, to evaluate the durability of the glass matrix and to identify the key mechanisms responsible for glass alteration in such a cementitious environment. This paper presents the results of static leach tests performed at 30°C with simulated reference nuclear waste glasses SON68 and SM539 in a synthetic young cement water (YCWCa) of pH 13.5 in presence of hardened OPC. This water simulates the composition and pH in the pore water in equilibrium with hydrated OPC at the first stage of degradation (Wang, 2009). This stage may last for a long time depending on processes that are difficult to quantify, especially the clogging of the concrete pores by precipitation of Ca-carbonates.

## 2. Experimental

Static leach tests were performed at 30°C ± 1°C in a glove box under Ar atmosphere in presence of OPC. The tested reference glasses were the inactive AREVA SON68 glass and the SM539 HE 540-12 PAMELA glass. Their composition is given in Table 1. frugierlass powder (7.5 g of a 125-250 µm size fraction) were mixed with 2.14, 7.5 or 22.5 g of cement powder (400-500 µm) in a PolyPropylene container filled with 100 mL of YCWCa at pH of 13.5 (Table 2). With a BET specific surface area of 0.031 m<sup>2</sup>.g<sup>-1</sup> for SON68 and 0.030 m<sup>2</sup>.g<sup>-1</sup> for SM539 glass, the ratio of glass surface to leachant volume is equal to 2250 m<sup>-1</sup>. The determination of the glass dissolution rate was based on the mass loss of four glass monoliths mounted on the floating magnetic stirrer avoiding thus the cementation by direct contact with the concrete powder. For each series, four different containers were used and blank tests without glass were also carried out. Solution samples were taken at regular time intervals, which were different for the various containers. Each sample was ultrafiltered and element concentrations were determined by ICP-AES. Solid analyses such as X-ray diffraction and High Resolution Transmission Electron Microscopy were conducted to study the composition and the morphology of the altered glass. Geochemical modelling using the PHREEQC code with the CEMDATA07 database (Jacques, 2009) was performed to fit the experimental data obtained with SON68 glass.

Table 1: SON68 and SM539 glass compositions in weight %.

Oxide	SON68	SM539	Oxide	SON68	SM539	Oxide	SON68	SM539
SiO <sub>2</sub>	45.48	35.27	Fe <sub>2</sub> O <sub>3</sub>	2.91	0.45	Cs <sub>2</sub> O	1.42	-
B <sub>2</sub> O <sub>3</sub>	14.02	25.57	ZrO <sub>2</sub>	2.65	0.05	Nd <sub>2</sub> O <sub>3</sub>	1.59	0.02
Na <sub>2</sub> O	9.86	8.77	ZnO	2.5	-	NiO	0.74	0.01
Al <sub>2</sub> O <sub>3</sub>	4.91	20.24	Li <sub>2</sub> O	1.98	3.49	other	6.2	1.61
CaO	4.04	5.04	MoO <sub>3</sub>	1.7	0.02			

Table 2: Composition of the synthetic young cement water (YCWCa) in mg.L<sup>-1</sup>.

Al	Ca	K	Mg	Na	Si	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	TIC
<0.2	15.7	12900	<0.01	3300	5.4	<1	188	10.8

### 3. Results

As shown in Figure 1, the mass loss dissolution rate clearly depends on the amount of cement added. When 2.14 g of cement are mixed with SON68 glass, the dissolution rate is  $0.005 \text{ g.m}^{-2}.\text{d}^{-1}$ , this is close to the long-term NL(Li) rate of  $0.0062 \text{ g.m}^{-2}.\text{d}^{-1}$  measured in YCWCa in absence of cement suggesting that after reaction of the most reactive cement components, the glass dissolution rate falls back to the long-term rate of the system without cement. For tests with SM539 glass, a dissolution rate ten times higher is determined *i.e.*  $0.053 \text{ g.m}^{-2}.\text{d}^{-1}$ . With 7.5 g of cement, for both glasses, the dissolution rates are higher than with 2.14 g of cement, and are equal to  $0.040 \text{ g.m}^{-2}.\text{d}^{-1}$  for SON68 and  $0.27 \text{ g.m}^{-2}.\text{d}^{-1}$  for SM539. These rates are similar to those obtained in dynamic leach tests with YCWCa without cement meaning that the presence of cement triggers the glass dissolution rate to the maximum rate ( $0.061 \text{ g.m}^{-2}.\text{d}^{-1}$  for SON68 and  $0.39 \text{ g.m}^{-2}.\text{d}^{-1}$  for SM539). Due to a conglomeration effect limiting the accessibility to the reactive sites, the maximum dissolution rate is not observed for tests with the highest quantity of cement (22.5 g). This phenomenon was observed also by Utton et al.(2013).

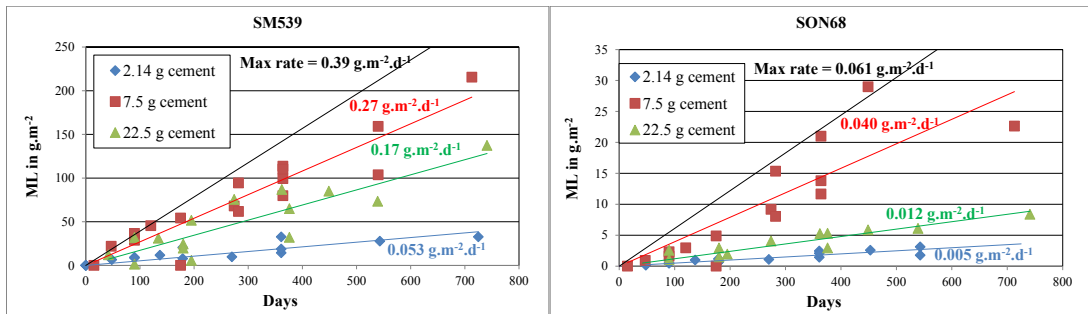
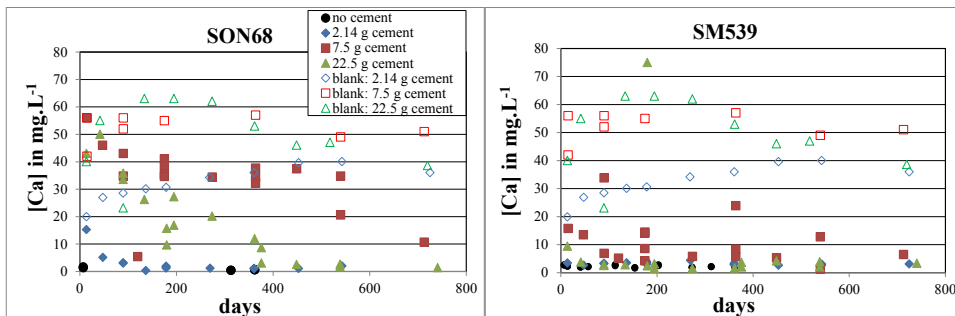


Fig. 1: Mass losses ( $\text{g.m}^{-2}$ ) versus time in static tests with SON68 and SM539 glasses at  $30^\circ\text{C}$  and pH 13.5 in presence of cement.

An inverse correlation between Ca and Si concentrations was observed (Fig. 2). Indeed, the Si concentration increases when Ca decreases suggesting the conversion of portlandite into C-S-H phases. By plotting the glass dissolution rate measured by the increase in the Li concentration in solution as a function of the Ca concentration in solution, after a threshold value of  $0.4\text{mM}$  (initial calcium concentration in Table 2), a proportionality was observed which is consistent with the proposed reaction of Ca from the cement with Si from the glass (Ferrand et al., 2013).



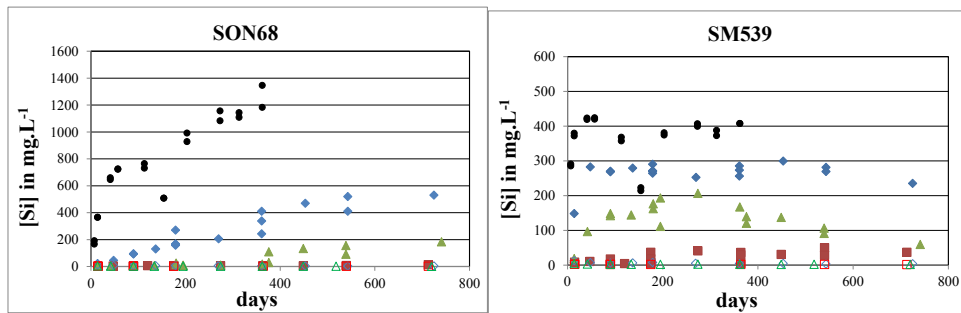


Fig. 2: Ca and Si concentrations versus time in static tests with SON68 and SM539 glasses at 30°C and pH 13.5 in presence of cement.

XRD analysis performed on altered glass/cement mixtures after 364 and 713 days revealed the disappearance of the portlandite peaks. It disappeared faster for SM539 than for SON68, this glass dissolving faster. A decrease of the CS peaks was also observed, due to the further transformation of the remaining unreacted clinker phases into amorphous C-S-H phases during the leach tests. For SM539, tobermorite ( $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) peak appeared and C-A-S-H peaks attributed to *katoite* ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ) increased, suggesting that C-S-H phase was transformed into C-A-S-H phase by reaction with Al leached from the SM539 glass.

HRTEM on SON68 glass powder altered with cement for 713 days showed a homogeneous microstructure mainly made of an amorphous porous gel. Pores with a mean size of 10 nm were distributed uniformly and were connected, as shown in Figure 3. Consequently, water molecules can diffuse as rapidly as in the bulk solution and the alteration layer should be thus little protective (Bunker, 1994). This is in agreement with the high and constant glass alteration rate observed. EDX analysis showed that the gel layer was enriched in Ca and K and depleted in Si and Al, compared to the pristine glass. A Si retention factor of 40 % was determined whereas it ranges between 80 and 90% for protective gel layers (Gin and Mestre, 2001). This confirms that the gel layer formed on SON68 glass altered in YCWCa at pH 13.5 is non protective.

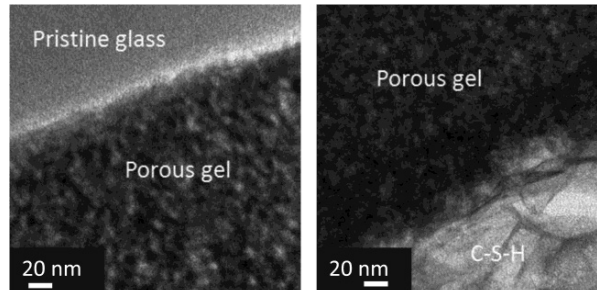


Fig. 3: HRTEM micrographs of SON68 glass powder altered with 7.5 g cement for 713 days.

In geochemical modelling, C-S-H phases were represented as an ideal solid solution with jennite-type and tobermorite-type two end-members (Lothenbach et al, 2008). The considered minerals for fully hydrated cement were portlandite, monocarboaluminate, hydrotalcite, hematite, ettringite, C-S-H tobermorite, C-S-H jennite, and calcite. For glass dissolution, all the oxides were assumed to dissolve congruently and Li was used as dissolution indicator to fit the laboratory measurements. In this study, a regime corresponding to the initial or forward rate  $r_0$  is observed *i.e.* a linear dependence of the concentration with time. Based on the equation proposed by Frugier et al.(2008), it can be expressed by Equation 1, valid for temperatures ranging from 25 to 100°C and pH values from 6 to 14.

$$r_0(T, pH) = k_+ [H^+]^n \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

With  $k_+$ : forward rate constant (= fitting parameter)

$E_a$ : apparent activation energy of initial rate = 76 kJ.mol<sup>-1</sup>

R: ideal gas constant 8.31x10<sup>-3</sup> kJ.mol<sup>-1</sup>.K<sup>-1</sup>

n= -0.32 pH dependence exponent (from dynamic tests in KOH solutions following the method described in Ferrand and Lemmens (2011))

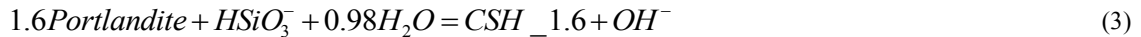
Apart from the forward rate  $r_0$ , the equation that describes the glass dissolution rate also considers the change of the glass surface through a shrinking core model assuming spherical glass particles (Equation 2). Because the leachates are far from saturation with respect to silica, a chemical affinity term was not included. Additionally, as a proportionality between glass dissolution rate and Ca concentration was observed, a factor representing the ratio between the Ca concentration in the solution [ $Ca^{2+}$ ] and the initial Ca concentration as measured in the blanks [ $Ca^{2+}_{blank}$ ] (i.e. 1.4 x 10<sup>-3</sup> M) was also used to fit the data (Equation 2).

$$\frac{dM}{dt} = -r_0 \frac{A_0}{V} \left(\frac{m}{m_0}\right)^{2/3} \frac{[Ca^{2+}]}{[Ca^{2+}_{blank}]} \quad (2)$$

where M (mol) is the amount of glass,  $A_0$  is the initial glass surface area (m<sup>2</sup>), V is the solution volume (L), m and  $m_0$  are the current and initial mass of glass.

Figure 4 presents the resulting geochemical modelling for Li, B, Ca, and Si data in tests with SON68 glass and 7.5 g of cement. The fitted value of parameter  $k_+$  was 1.8x10<sup>7</sup> g.m<sup>-2</sup>.d<sup>-1</sup>. This is lower than the value of 1.2x10<sup>8</sup> g.m<sup>-2</sup>.d<sup>-1</sup> reported in Frugier et al. (2008) for solutions without Ca, suggesting a protective effect as observed by Chave (2011). The presence of Ca would thus decrease the value of  $k_+$  but on the other hand keep glass dissolution rate high due to C-S-H formation. Until 500 days, the presence of portlandite imposes high Ca concentrations and when all portlandite has reacted, Ca is modelled with a C-S-H solid solution. For boron data, a good fit is obtained considering sorption onto cement. Assuming that all cement is accessible, a sorption coefficient  $K_d$  of 14 L.kg<sup>-1</sup> is fitted.

Supported by the solid analyses and by literature (Andriambololona et al,1992; Leemann et al., 2012) two main reactions are proposed to explain why the glass dissolution remains close to the initial rate for 2 years in tests with 7.5 g of cement: the reaction of Si released by the glass with portlandite, leading to the formation of C-S-H phases (Equation 3) and the conversion of C-S-H into C-A-S-H phases like *katoite* (Equation 4).



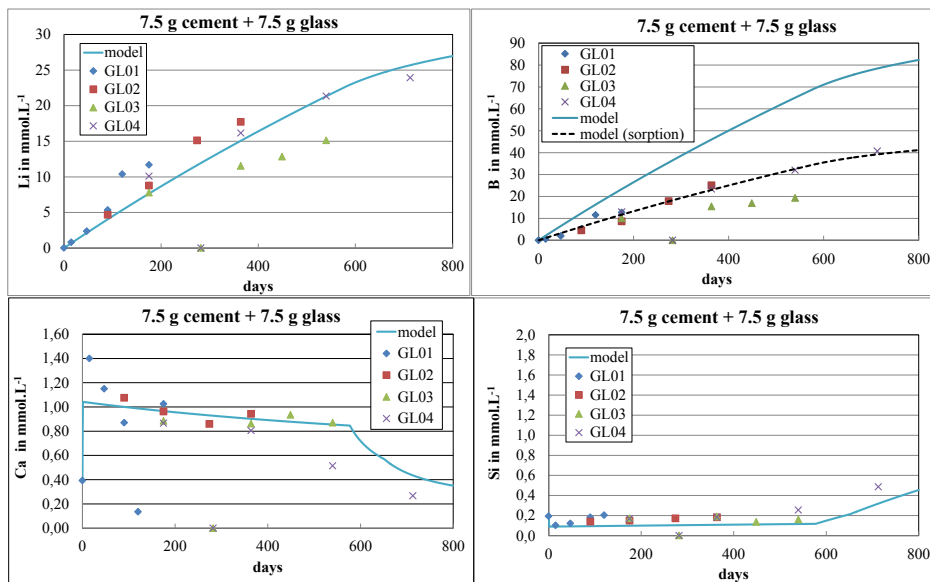


Fig. 4: Measured concentrations and PHREEQC simulations for tests with SON68 glass and 7.5 g cement. GL01-, -02, -03 and -04 indicate the four different test containers.

CSH\_1.6 represents a jennite-type C-S-H phase with a high calcium-to-silica ratio. As long as portlandite is present, it can be converted into C-S-H phases leading to a high glass alteration rate. The conversion of C-S-H into C-A-S-H phases constitutes a second driving force, and is particularly important for the Al-rich glass SM539. This interpretation agrees with the mechanisms suggested by Mercado-Depierre for the effect of Ca on the glass stability: at basic pH and high reaction progress, the leached Si flow is such that the solution is quickly supersaturated with respect to C-S-H. As long as C-S-H precipitate, the activity of Si in solution remains low and the glass dissolves at or near the initial dissolution rate (Mercado-Depierre et al., 2013).

#### 4. Conclusion

The cement acts as a sink for matrix elements of the glass, keeping their concentrations in solution far from saturation and thus the glass dissolution rates high. As long as portlandite is accessible, the rates are similar to the maximum rates in dynamic tests with the cementitious water at pH 13.5 and higher than the rates determined without cement. They are around  $4 \times 10^{-2} \text{ g.m}^{-2}.\text{d}^{-1}$  for SON68 glass and  $3 \times 10^{-1} \text{ g.m}^{-2}.\text{d}^{-1}$  for SM539 glass. A glass dissolution model has been proposed considering the reaction of the silicon released by the glass with the portlandite, forming C-S-H phases. The reaction of glass Al with the C-S-H phases is another parallel driving force for continued glass dissolution. The geochemical model has simulated these effects by using a lower forward rate constant  $k_+$  and a factor considering the Ca concentration in solution.

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