

International technical evaluation of alteration mechanisms relevant to glass corrosion – SCK•CEN report 2014

Intermediate report for IAEA CRP 1813 on processing technologies for high level waste, formulation of matrices and characterization of waste forms.

Karine Ferrand

IAEA Research Agreement No 17297
SCK•CEN reference CO-90-12-2972-00

September, 2014

SCK•CEN
Boeretang 200
BE-2400 Mol
Belgium

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SCK•CEN
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BE-2400 Mol
Belgium

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Studiecentrum voor Kernenergie
Centre d'étude de l'énergie Nucléaire
Boeretang 200
BE-2400 Mol
Belgium

Phone +32 14 33 21 11
Fax +32 14 31 50 21

<http://www.sckcen.be>

Contact:
Knowledge Centre
library@sckcen.be

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1. Introduction

Vitrification to borosilicate glass is the high-level waste form of choice nearly worldwide. To date, the contributions of physical and chemical processes controlling the long-term glass dissolution rate in geologic disposal remain uncertain, leading to a lack of international consensus on a rate law for glass corrosion. Existing rate laws have overcome uncertainty through conservatism, but a thorough mechanistic understanding of waste form durability in geologic environments would reduce the uncertainty and improve public and regulator confidence. If it is possible to take credit for the true durability of the waste form in repository system evaluations, then it is possible to design the repository with less conservatism and significant cost savings. To gain a fundamental understanding of the dissolution rate law, six nations (USA, Japan, France, Belgium, UK, Germany) have planned collaborative research activities into the mechanisms controlling the long-term corrosion of glass. The collaborating laboratories all conduct fundamental and/or applied research using modern materials science techniques. In order to provide a common benchmark to relate results from different groups using various experimental tools, multi-scale probes, and modeling approaches, it has been decided to formulate a common glass that will be studied by all collaborators. This glass is called the International Simple Glass (ISG). More information about the collaboration can be found in [Gin 2013].

The contribution of four of the participating nations (USA, Japan, France, Belgium) is reported for IAEA CRP1813 on processing technologies for high level waste, formulation of matrices and characterization of waste forms.

This report describes the work carried out by the Belgian Nuclear Research Centre in this collaborative research project. It was performed as part of the programme of the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (NIRAS/ONDRAF) on the geological disposal of high level/long-lived radioactive waste.

2. Background for the Belgian contribution

In Belgium, the *Supercontainer design* with an Ordinary Portland Cement (OPC) buffer with limestone aggregates was selected by the radioactive waste management organisation (ONDRAF/NIRAS) as the reference design for geological disposal of vitrified nuclear waste and Spent Fuel in the Boom Clay formation. More details about this design can be found in [NIROND 2008] and [Wacquier 2009]. The *Supercontainer* will provide a highly alkaline chemical environment allowing the passivation of the surface of the carbon steel overpack and the inhibition of its corrosion. Indeed, it was shown that a pH of 12.5 was high enough to maintain the uniform overpack corrosion at a very low rate due to surface passivation. The most likely corrosion rate is around 0.1-0.2 $\mu\text{m}\cdot\text{y}^{-1}$. A thin layer of oxidation products is expected on the overpack surface [Kursten 2012] which will contribute to the containment of radionuclides and will also have an effect on the retardation of radionuclide release from the waste.

In the *Supercontainer design*, the HLW canisters (C-waste type CSD-V) will be enclosed by a 30 mm thick carbon steel overpack and a concrete buffer about 700 mm thick. As perforation of the overpack is expected to occur at the earliest between 50,000 to 100,000 years but may take place much later than after 100,000 years, glass waste will not be in contact with cementitious pore water during the thermal phase. Nevertheless, after overpack failure that may occur either as a result of localised corrosion (e.g. stress corrosion cracking), or when general corrosion has

reduced the overpack thickness to the point where it is unable to support the stresses exerted by the lithostatic overburden, the high pH of the incoming pore water will cause the start of the waste glass dissolution and the radionuclides migration into the buffer.

Because very few glass alteration studies have been reported in hyperalkaline media [Advocat 1991; Andiambololona 1992; Gin 2001; Mercado-Depierre 2013], a research programme was developed at the Belgian Nuclear Research Centre (SCK•CEN) following a methodology based on mechanism understanding and accurate rate measurements [Poinssot 2012] to assess the rate at which the radionuclides are expected to be released in such an environment.

Generally, glass dissolution undergoes several parallel alteration mechanisms [Grambow 2006; Frugier 2008; Cailleateau 2008; Ojovan 2007; Valle 2010]: interdiffusion between protons and hydronium ions from solution and alkalis within the glass, hydrolysis of Si-O bonds ; in situ condensation of silica species more or less detached from the glassy network and precipitation of secondary crystalline phases, mainly phyllosilicates and rare earth phosphates in the case of SON68 glass at near-neutral pH conditions. Depending on the reaction progress and the leaching conditions, one or more of the previous mechanism will control the global dissolution rate. In a first phase, the dissolution rate is controlled by the rate of hydrolysis of the main glass formers (Si, Al...), whereas the long-term rate (or residual rate) is controlled by the water diffusion through the denser part of the hydrated glass and the precipitation of secondary crystalline phases [Frugier 2008; Gin 2011]. In some cases long term rates resume due to the late and sudden precipitation of zeolites that consume rapidly the element constituting the passivation layer [Ribet 2004; Fournier 2014]. A hyperalkaline medium would accelerate the hydrolysis of the silicate network. It would also dramatically increase the solubility of most of the sparingly soluble elements of the glass like Si, Al, Zr, and allow the precipitation of minerals normally absent in neutral or low alkaline pH like Calcium-Silicate-Hydrates (C-S-H), Calcium-Aluminum-Silicate Hydrates (C-A-S-H) and zeolites. Consequently the different kinetic regimes would be strongly affected in the presence of cementitious waters compared to deionized water [Frugier 2008] or clayey groundwater [Lemmens 2002; Jollivet 2012].

Based on the general knowledge about the glass alteration in aqueous conditions at neutral pH, a set of experiments was performed, allowing to determine the glass alteration rate, and to identify the key mechanisms responsible for the glass alteration in Supercontainer conditions. Most of the tests were performed with the inactive French SON68 glass and the Belgian PAMELA glasses at 30°C or 70°C but a few tests were also done using the less complex ISG glass. The temperature of 30°C is used as the reference long term temperature for the HLW glass under in situ conditions whereas the higher temperature of 70°C is used to accelerate the processes and to reveal the rate determining mechanisms.

The expected evolution of CEM I Ordinary Portland Cement in the Boom Clay host rock has been calculated with a transport-coupled geochemical code [Wang 2009].

Based on classic literature in cement chemistry [Berner 1992, Readon 1992; Bourbon 2003 and Nielsen 2005], the model describes the young cement as a set of hydration phases, more specifically:

- portlandite, $\text{Ca}(\text{OH})_2$
- afwillite $\text{Ca}_3\text{Si}_2\text{O}_4(\text{OH})_6$ or CSH_1.8 ($\text{Ca}_{1.8}\text{SiO}_4 \cdot 6\text{H}_{3,6}$)
- ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
- hydrogarnet, $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$
- hydrotalcite, $\text{Mg}_4\text{Al}_2(\text{OH})_{14} \cdot 3\text{H}_2\text{O}$

- hematite, Fe₂O₃

The high pH of young CEM I cement is due to the presence of K⁺ and Na⁺ in the pore water. In low alkali CEM I, the total alkali content is lower than 0.6 wt %. In charge balancing the system, an equivalent concentration of hydroxyl ions will be produced. Thus a cement pore fluid at the initial stage of hydration has normally a pH higher than 13.

The use of a large amount of cement in the repository changes the geochemical conditions in the repository near field for more or less the entire assessment timeframe, so Boom Clay equilibrium conditions are not expected in the vicinity of the waste. Nevertheless, Boom Clay water species will in-diffuse, while cement species will out-diffuse. This causes a gradual degradation of the concrete phases, and a changing concrete pore water composition in equilibrium with these phases. We thus distinguish three degradation stages with a different cement water composition:

- Stage 1: young cement water (YCWCa); this water still contains the initially dissolved alkalis and has a high pH value of around 13.5
- Stage 2: evolved cement water (ECW); after the leaching out of the dissolved alkalis, this water has a pH value of 12.5, controlled by equilibrium with portlandite
- Stage 3: old cement water (OCW); facilitated by the increasing pore volume of the concrete, pore water is replaced by Boom Clay water, portlandite dissolves and Ca ions diffuse to the host rock. The pore water is in equilibrium with C-S-H phases. The pH drops below 12.

3. Experiments

Glass preparation

The International Simplified Glass (ISG) containing only the six main oxides of a typical borosilicate waste glass is used to perform static leach tests. Its composition in mol% and weight % is indicated in Table 1.

Table 1: Theoretical composition in mol% and weight% of ISG glass.

Oxide	mol %	wt%
SiO ₂	60.2	56.18
B ₂ O ₃	16	6.06
Na ₂ O	12.6	12.17
Al ₂ O ₃	3.8	4.98
CaO	5.7	17.34
ZrO ₂	1.7	3.28

A glass block with the dimensions of 50 x 50 x 100 mm was provided by PNNL with the following references: Glass Annealed Blocks-International Simplified Glass (ISG)-MO-SCI-Corporation-Lot: L12012601-M12042403. The block was cut in eight pieces of around 14 x 14 x 45 mm. From these smaller blocks, glass monoliths of 14 x 14 x 2 mm were cut and polished with SiC papers and cleaned with ethanol. Glass powders with size fractions of 53-125 μm and 125-250 μm were prepared by milling and sieving glass fragments obtained after crushing sample rods with a hammer. Then, the glass powders were cleaned ultrasonically in acetone, in

ethanol, and finally in ultrapure water. The specific surface areas determined by the BET method using Kr were $0.086 \text{ m}^2 \cdot \text{g}^{-1}$ for the 53-125 μm size fraction and $0.046 \text{ m}^2 \cdot \text{g}^{-1}$ for the 125-250 μm size fraction. These values are in agreement with those determined by Arena and Fournier ($0.072 \text{ m}^2 \cdot \text{g}^{-1}$ for glass powder of 63-125 μm and $0.0465 \text{ m}^2 \cdot \text{g}^{-1}$ for the higher size fraction of 125-250 μm).

Remark: because only one block of glass was available at the beginning of the tests, the quantity of the powder and the number of glass monolith in each series of tests was limited.

Leaching solutions

Four different leaching solutions are used to study ISG alteration in a wide range of pH from 9 to 13.5.

KOH solution

Some tests are performed with a KOH solution at the initial pH of 9. This solution was prepared in a glove box under Ar atmosphere by adding a 0.1 M standard commercial KOH solution (Baker) to degassed milli-Q water. During the tests, pH is not adjusted to this value by adding KOH solution (free pH).

Synthetic cement waters

Most of the tests are conducted with typical synthetic cement waters used in the context of the Supercontainer Design. These waters mentioned before as YCWCa, ECW and OCW simulate the composition and pH in pore waters in equilibrium with hydrated Ordinary Portland Cement at different stages of degradation. The pH measured at room temperature was approximately 13.5 for YCWCa, 12.5 for ECW and 11.7 for OCW.

The cement waters were synthesized in a glove box under Ar atmosphere to prevent carbonation. In a glass bulb-flask of 1L, $\text{Ca}(\text{OH})_2$ was first dissolved with a 1M KOH and/or 1M NaOH solution(s). Then, for YCWCa and OCW, Na_2SO_4 and CaCO_3 was added. Because the Al and Si concentrations in YCWCa and ECW determined by modeling are very low and because phases controlling these concentrations are not known for the OCW, Al and Si components were not added to synthesize the cement waters.

Immediately after the synthesis, the cement waters were placed in PolyEthylene bottles to prevent dissolution of the glass bulb-flask. After two months, the pH and element concentrations were measured to check if the target pH and composition was reached. The composition for most elements was reasonably close to the calculated composition except for Al and Si in OCW as explained previously (Table 2). Due to a higher uncertainty on pH measurement in very alkaline media (± 0.2), the pH of 13.7 was also in agreement with the calculated value.

Table 2: Composition of typical batches of cement waters (YCWCa, ECW, OCW) synthesized at the laboratory. The target concentrations as calculated by equilibration with the hydrated cement phases mentioned in the introduction are given in brackets. The concentrations are given in mg/L.

	Al	Ca	K	Mg	Na	Si	Cl	SO ₄ ²⁻	TIC	pH (30°C)
YCWCa	<0.2 (1.6)	15.7 (28)	12900 (14300)	<0.01 (2x10 ⁻⁶)	3300 (3240)	5.4 (8.4)	<1 (7)	188 (192)	10.8 (3.6)	13.7 (13.5)
ECW	<0.2 (0.1)	520 (612)	9.4 (8)	0.017 (1x10 ⁻⁵)	370 (350)	<0.1 (0.1)	<1 (7)	0.33 (0.7)	<1 (0.1)	12.5 (12.5)
OCW	0.055 (78-250)	26.6 (32-52)	1.1 (8)	<0.01 (2x10 ⁻⁵)	78 (350)	3.7 (22-176)	<1 (7)	1.4 (5)	1 (0.2)	11.7 ~ 12

Static leach tests

Static leach tests are performed at 30°C or 70°C in a glove box under Ar atmosphere with a KOH solution at pH 9 or a synthetic cement water at pH 11.7, 12.5 or 13.5 (pH measured at room temperature). Due to the limited quantity of glass at the beginning of the tests, some tests are conducted using 9 g of glass powder (125-250 µm) and one glass monolith in contact with 50 mL of YCWCa or ECW while others use only 5 g of glass powder (53-125 µm) and 2 glass monoliths in 100 mL of KOH or OCW. The corresponding ratios of surface area to solution volume are equal to 3300 m⁻¹ or 8370 m⁻¹. Experimental conditions are summarized in Table 3 (Annex). For all series of tests, tests were done in duplicate in PolyPropylene containers or PerFluoroAlkoxy containers depending on the temperature either 30°C or 70°C. Containers are manually stirred a few days before each sampling. The aliquot of the solution is analysed by ICP-AES or MS to determine the concentrations of Si, B, Na, Ca, Al and Zr.

4. Results

Evolution of the pH

At both temperatures 30°C and 70°C, in tests carried out at pH 9 (KOH), 11.7 (OCW) and 12.5 (ECW), the evolution of the pH measured at room temperature as a function of time is similar. A slight pH decrease is observed after 200 days in KOH whereas pH decreases immediately in OCW (Figure 1). In OCW, the pH decrease is more important at 70°C where it evolves from 12.6 to 11.4 (Figure 2).

In YCWCa with the high pH of 13.5, pH is constant at 30°C, while a clear decrease is observed from 13.4 to 11.8 at 70°C (Figure 2).

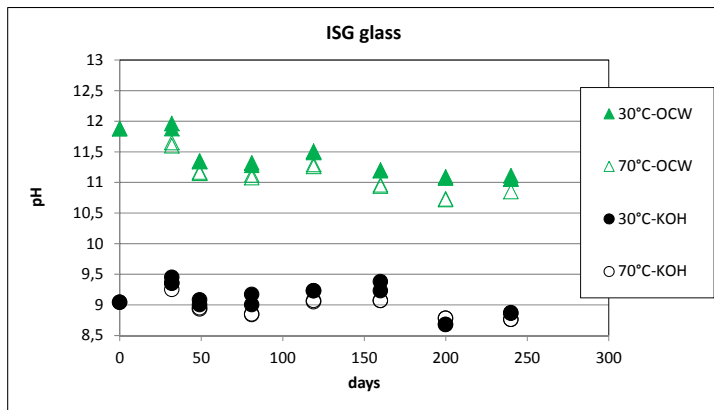


Figure 1: pH evolution in static tests at 30°C and 70°C performed with ISG in a KOH solution at pH 9 or OCW at pH 11.7.

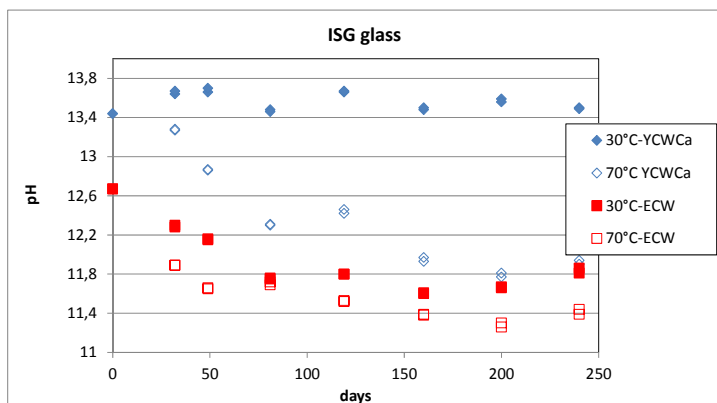
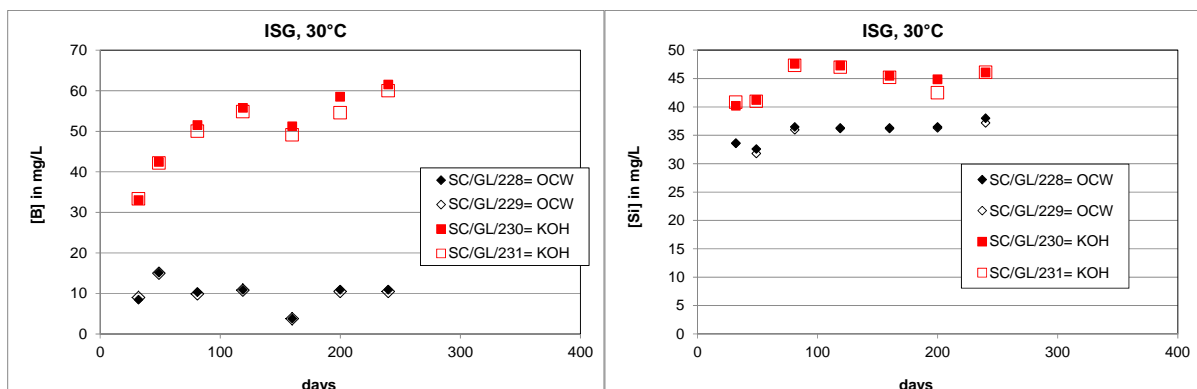


Figure 2: pH evolution in static tests at 30°C and 70°C performed with ISG in YCWCa at pH 13.5 or ECW at pH 12.5.

Evolution of the element concentrations in KOH at pH 9 and OCW at pH 11.7

As shown in Figure 3, at 30°C and pH 9 in KOH, the boron concentration is increasing and a concentration around 60 mg/L is reached after 220 days whereas at pH 11.7 in OCW, a steady-state boron concentration of 10 mg/L is reached very quickly after the beginning of the test. At both pH values, Si concentration is constant with a steady-state value of 35 mg/L slightly lower at pH 9 than that of 45 mg/L at pH 11.7. Al concentration is also constant at pH 9 and very low. In OCW, Al concentrations are higher around 2 mg/L, and seem to decrease after 200 days but it still has to be confirmed. Ca concentration is constant around 5 mg/L at pH 9, while after 200 days a decrease from 20-25 to 5-10 mg/L is observed at pH 11.7.



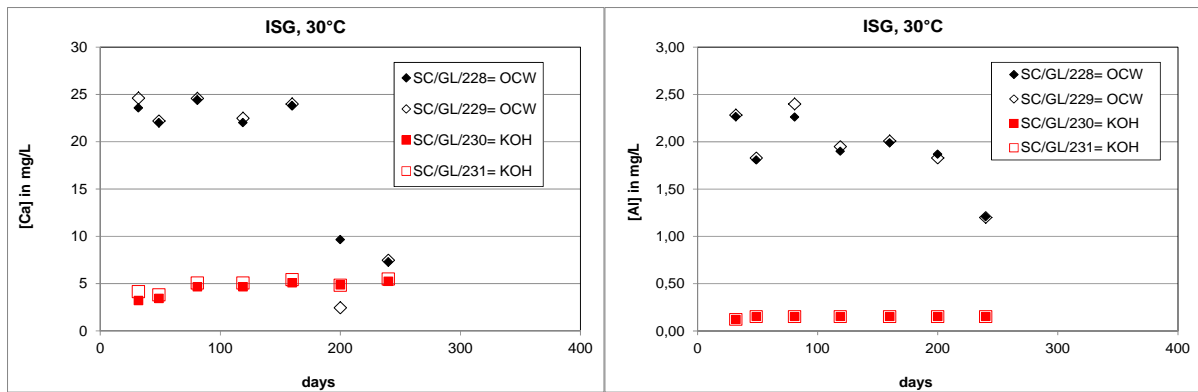


Figure: B, Si, Ca and Al concentrations in static tests performed at 30°C with ISG glass in KOH at pH 9 and OCW at pH 11.7.

At 70°C, as expected the higher temperature leads to a faster release of the elements into the solution (Figure 4). In KOH at pH 9, boron concentration increases to 200 mg/L whereas in OCW, a constant concentration of 20 mg/L is reached very quickly after the start of the experiment. In both solutions of alteration, a steady-state Si concentration is reached: 100 mg/L in KOH and 60 mg/L in OCW. As observed at 30°C, Al concentration is very low at pH 9 and it decreases slightly after 200 days in OCW. Ca concentration increases slightly until 6 mg/L at pH 9 compared to the higher pH of 11.7 where it decreases until a constant value of 10 mg/L.

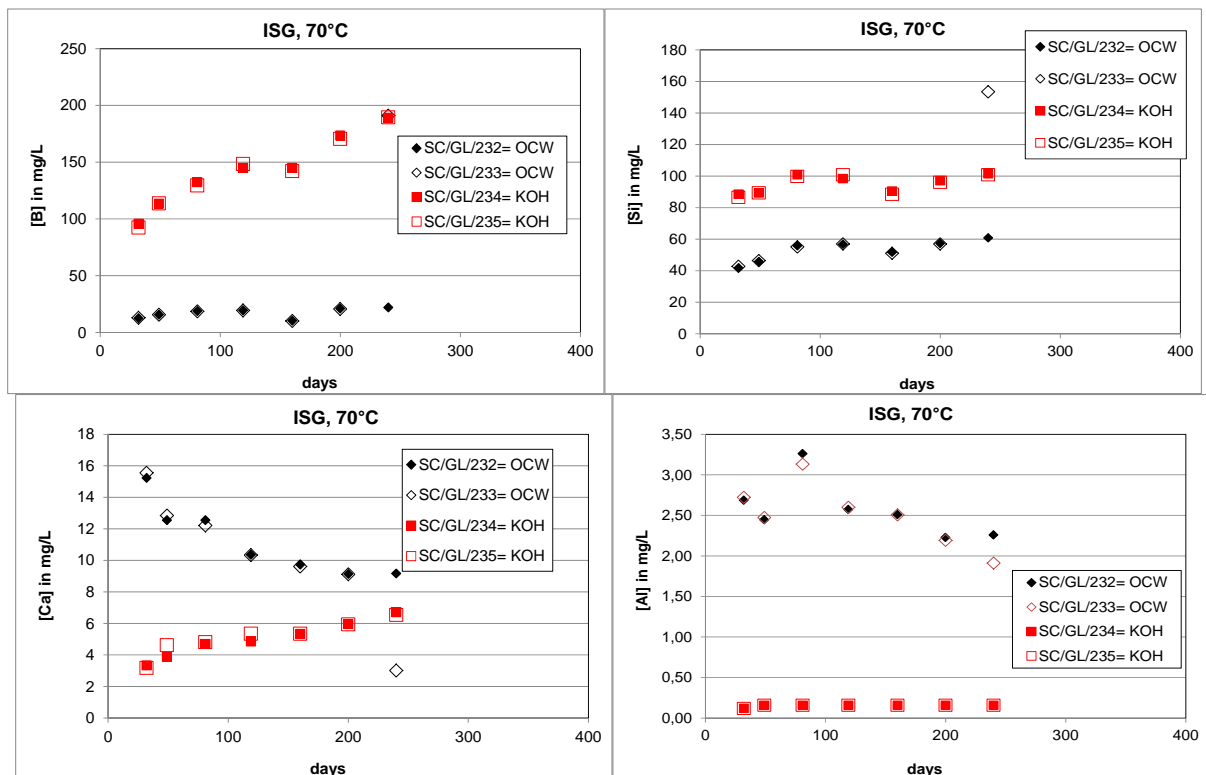


Figure 4: B, Si, Ca and Al concentrations in static tests performed at 70°C with ISG glass in KOH at pH 9 and OCW at pH 11.7.

Evolution of the element concentrations in YCWCa at pH 13.5 and ECW at pH 12.5

Si, B, Ca and Al concentrations determined in static tests performed at 30°C in YCWCa at pH 13.5 and ECW at pH 12.5 are presented in Figure 5. At 30°C in YCWCa, Si concentration increases until a high Si concentration of 1300 mg/L whereas in ECW, a steady-state

concentration around 100 mg/L is reached. Similarly, B concentration increases to 400 mg/L in YCWCa and seems to be constant in ECW.

For Al, the concentration increases to 70 mg/L at the beginning of the test and then decreases indicating Al-secondary phase precipitation. In ECW, Al concentration is low and quite constant since the start of the test. Ca concentration shows an immediate decrease at the high pH of 13.5 compared to the progressive decrease to 5 mg/L at pH 12.5 until reaching steady-state Si concentrations suggesting in both solutions the control of the Si concentration in solution by a secondary phase.

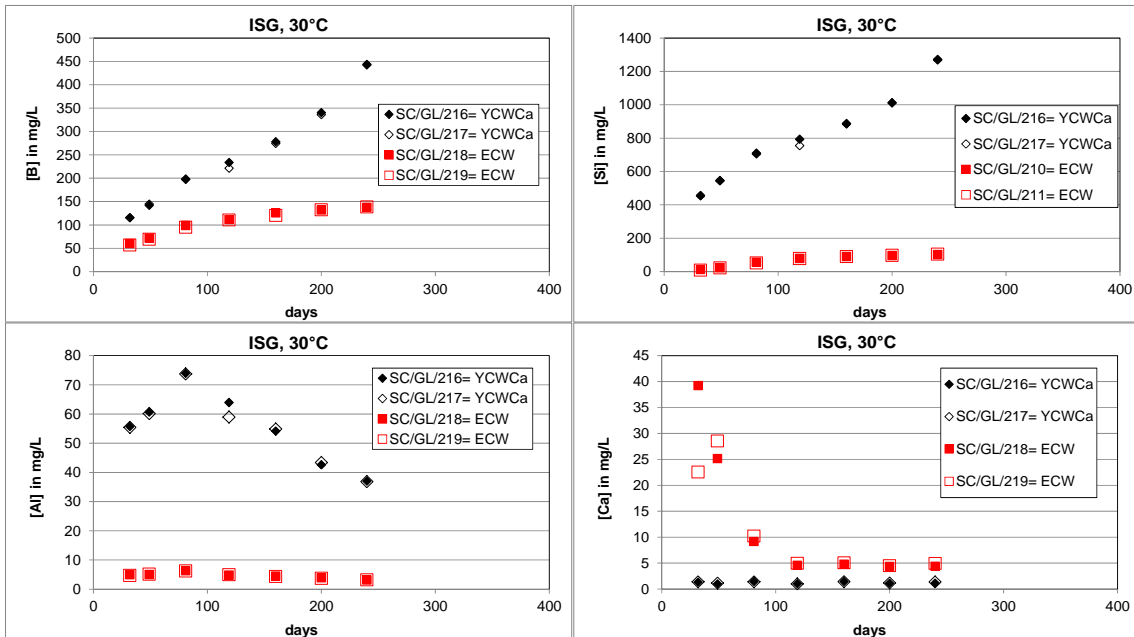
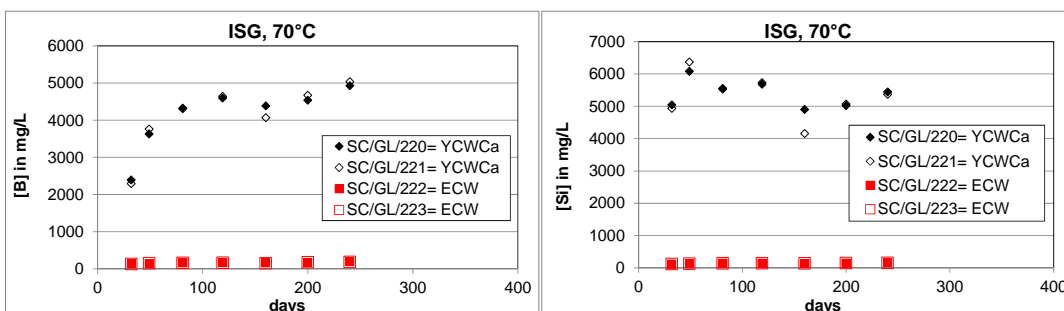


Figure 5: B, Si, Ca and Al concentrations in static tests performed at 30°C with ISG glass in YCWCa at pH 13.5 and ECW at pH 12.5.

At 70°C, in YCWCa, very high Si concentrations between 5000 and 6000 mg/L are measured, while, a steady-state concentration 30-40 times lower is observed at the lower pH of 12.5 (Figure 6). B concentration increases until the high value of 5000 mg/L after 240 days at pH 13.5 whereas a steady-state concentration around 200 mg/L is reached at pH 12.5. Al decreases at both pH values to very low values of 1-2 mg/L due to precipitation of secondary phases, occurring however faster at pH 12.5. Ca concentration decreases at both pH values to very low values suggesting the control of Ca in solution by a secondary phase.

Element concentrations determined in each series of tests are presented in Table 4 (Annex).



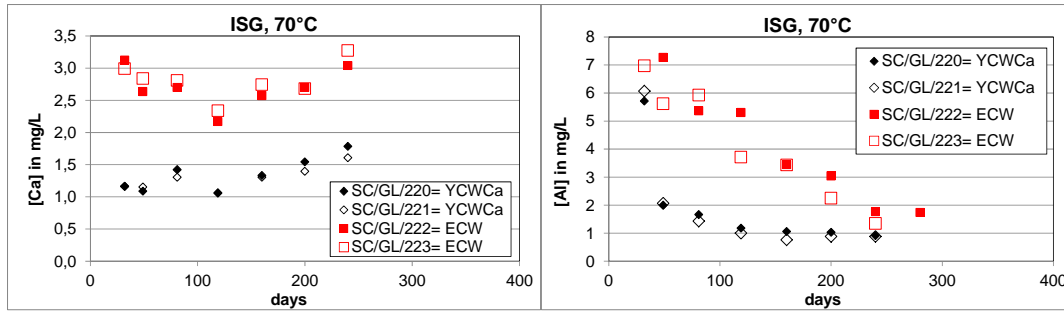


Figure 6: B, Si, Ca and Al concentrations in static tests performed at 70°C with ISG glass in YCWCa at pH 13.5 and ECW at pH 12.5.

Boron Normalized Mass losses in KOH at pH 9 and OCW at pH 11.7

Figure 7 presents the boron normalized mass losses for tests performed at 30°C or 70°C in KOH at pH 9 and OCW at pH 11.7.

In KOH, the long term rate is equal to $10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ which is 130 times lower than the forward rate of dissolution determined for SON68 in dynamic tests at the same pH.

In OCW, the rate is very low around $10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$, which is close to that of $5.10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ determined for SON68. We observe that the rate in OCW which contains Ca is lower than in KOH without Ca suggesting a positive effect of Ca on glass dissolution as it was already observed for SON68 and PAMELA glasses in dynamic tests [Ferrand 2013]. Indeed, in these tests, the dissolution rates in YCWCa containing Ca were lower than in KOH at the same pH.

As expected, rates obtained at 70°C are higher than at 30°C. At pH 9, the rate of $1.4 \times 10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$ is 14 times higher than at 30°C ($10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$) and at pH 11.7, only a factor 4 is observed ($4 \times 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ vs $10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$). This rate at 70°C in OCW is quite close to the value of $1.4 \times 10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ found for SON68 altered in the same leachant.

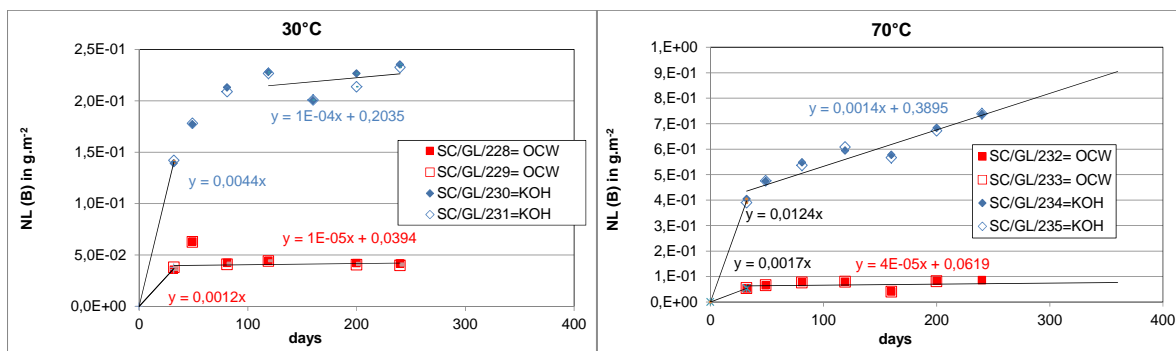


Figure 7: NL(B) for tests performed with ISG glass in KOH at pH 9 and OCW at pH 11.7.

Boron Normalized Mass losses in YCWCa at pH13.5 and ECW at pH12.5

Figures 8 and 9 show the boron normalized mass losses for tests performed at 30°C or 70°C in YCWCa at pH 13.5 and ECW at pH 12.5.

At 30°C, a rate of $2.3 \times 10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$ is obtained for ISG dissolution in YCWCa at pH 13.5 which is quite similar to that of $8.5 \times 10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$ for SON68 glass. As expected at the lower pH of 12.5, a lower rate of $2 \times 10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ is determined, which is 10 times lower than for SON68 glass.

At 70°C, at both pH values 13.5 and 12.5, glass dissolution rates are constant and lower than at 30°C. They are equal to $5 \times 10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ in YCWCa and $6 \times 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ in ECW, respectively.

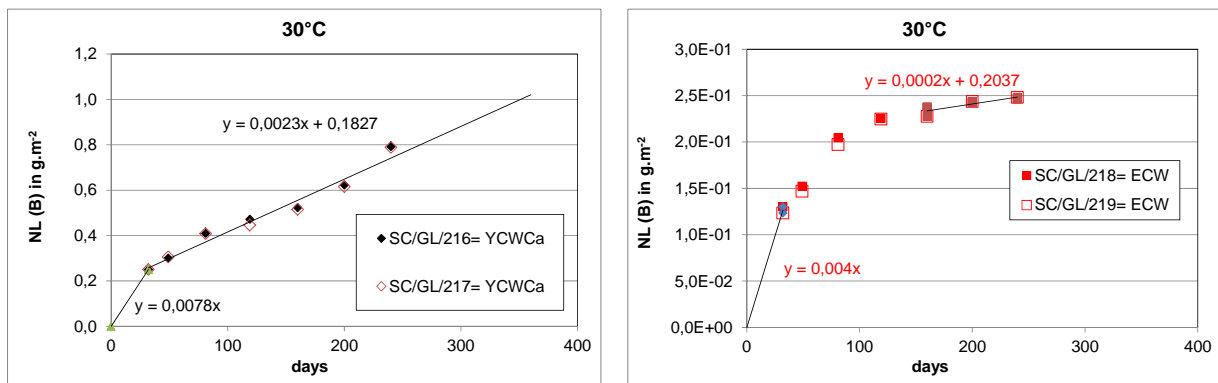


Figure 8: NL(B) in static tests carried out at 30°C in YCWCa (pH 13.5) and ECW (pH12.5).

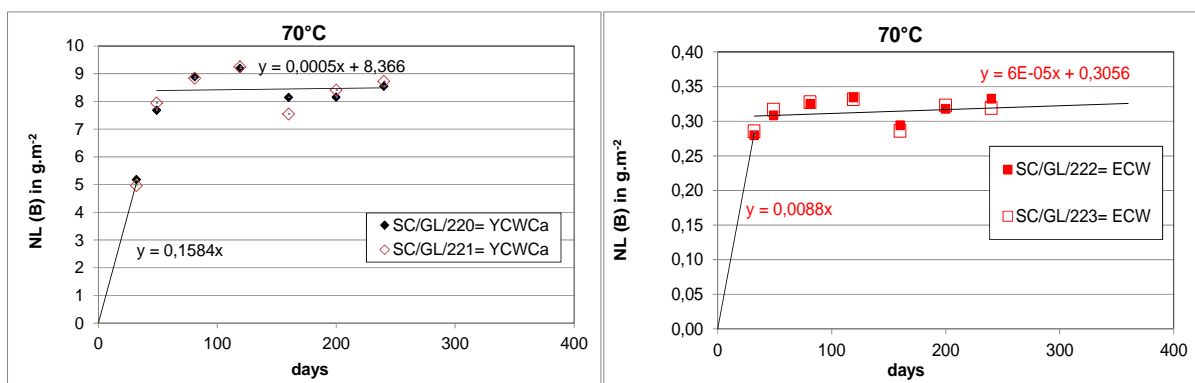


Figure 9: NL(B) in static tests carried out at 70°C in YCWCa (pH 13.5) and ECW (pH12.5).

Comparison between ISG and SON68 alteration in synthetic cementitious waters at 30°C and 70°C

Even if tests with ISG glass are not yet finished, they can be already compared to those performed with SON68 glass. Figures 10-12 give the evolution of the Si, B, Al and Ca for both glasses SON68 and ISG altered in the synthetic cementitious waters at 30°C and 70°C. Tables 5-7 (Annex) indicate the concentrations of these elements in tests with SON68 glass.

In YCWCa at pH 13.5:

At 30°C in YCWCa, ISG glass evolves like SON68 glass (Figure 10). For both glasses, Si and B concentrations increase until high values of 1200 mg/L and 400 mg/L, respectively. The evolution of the Al and Ca concentration is also the same. In the first days, Al concentration increases to 70 mg/L and then decreases suggesting Al precipitation. [Gin 2001] has also observed a threshold Al concentration around this value for zeolite precipitation. An immediate Ca decrease from 16 to 0.5-1.5 mg/L is observed suggesting Ca precipitation since the beginning of the test.

At 70°C, a very high constant Si concentration of about 5500 mg/L is reached for ISG compared to the increasing concentration until 4000 mg/L for SON68 (constant value confirmed after 612 days but not shown here). As a low dissolution rate of $6 \times 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ is observed for ISG compared to the value of $9 \times 10^{-2} \text{ g.m}^{-2}.\text{d}^{-1}$ for SON68, this may suggest for this glass an affinity effect at this high pH. As for Si, B concentration seems quite constant around 5500 mg/L

whereas it is increasing to 4000 mg/L for SON68, an alteration resumption occurring after 100 days. Al evolution is similar, first an increase to higher values however for SON68 and then a decrease to values around 2 mg/L, suggesting the precipitation of different Al-bearing phase. In the case of SON68, the alteration resumption is correlated to this Al decrease after 100 days. The fast depletion of Ca observed for both glasses suggests also Ca integration in secondary phase.

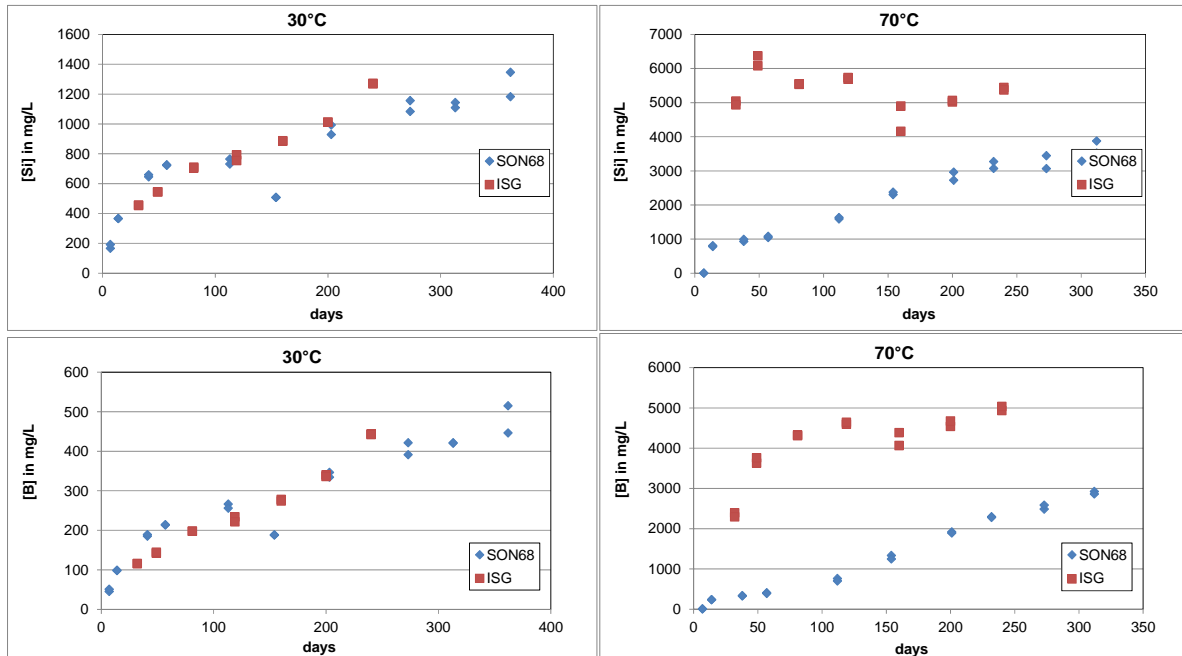


Figure 10: Si, B, Al and Ca concentrations determined in tests with ISG and SON68 altered in YCWCa (pH 13.5) at 30°C and 70°C.

In ECW at pH 12.5:

At 30°C in ECW, a different evolution of the concentrations in solution is observed for both glasses (Figure 11). For SON68 glass, Si stays low until 200 days and then starts to increase until 15 mg/L compared to ISG where this increase occurs very rapidly until reaching 100 mg/L after 240 days. Al concentration reaches quickly 6 mg/L and then, decreases progressively to low values while for SON68, it reaches a similar value only after more than 200 days. An Al decrease for SON68 may also occur later suggesting that the same Al-bearing phase may be formed. Ca concentration presents a very fast decrease for ISG but for both glasses, a complete Ca depletion is observed after 100 days.

At 70°C, in ECW at pH 12.5, a similar steady-state Si concentration (150 mg/L) seems to be reached for both glasses ISG and SON68, suggesting that it may be controlled by the same secondary phase. Ca depletion is observed for both glasses, the values for SON68 are however slightly lower. For ISG glass, Al concentration reaches quickly 8 mg/L and then, decreases progressively to low values while for SON68, a progressive increase to 12 mg/L is first observed, and then a decrease to the low value of 2 mg/L.

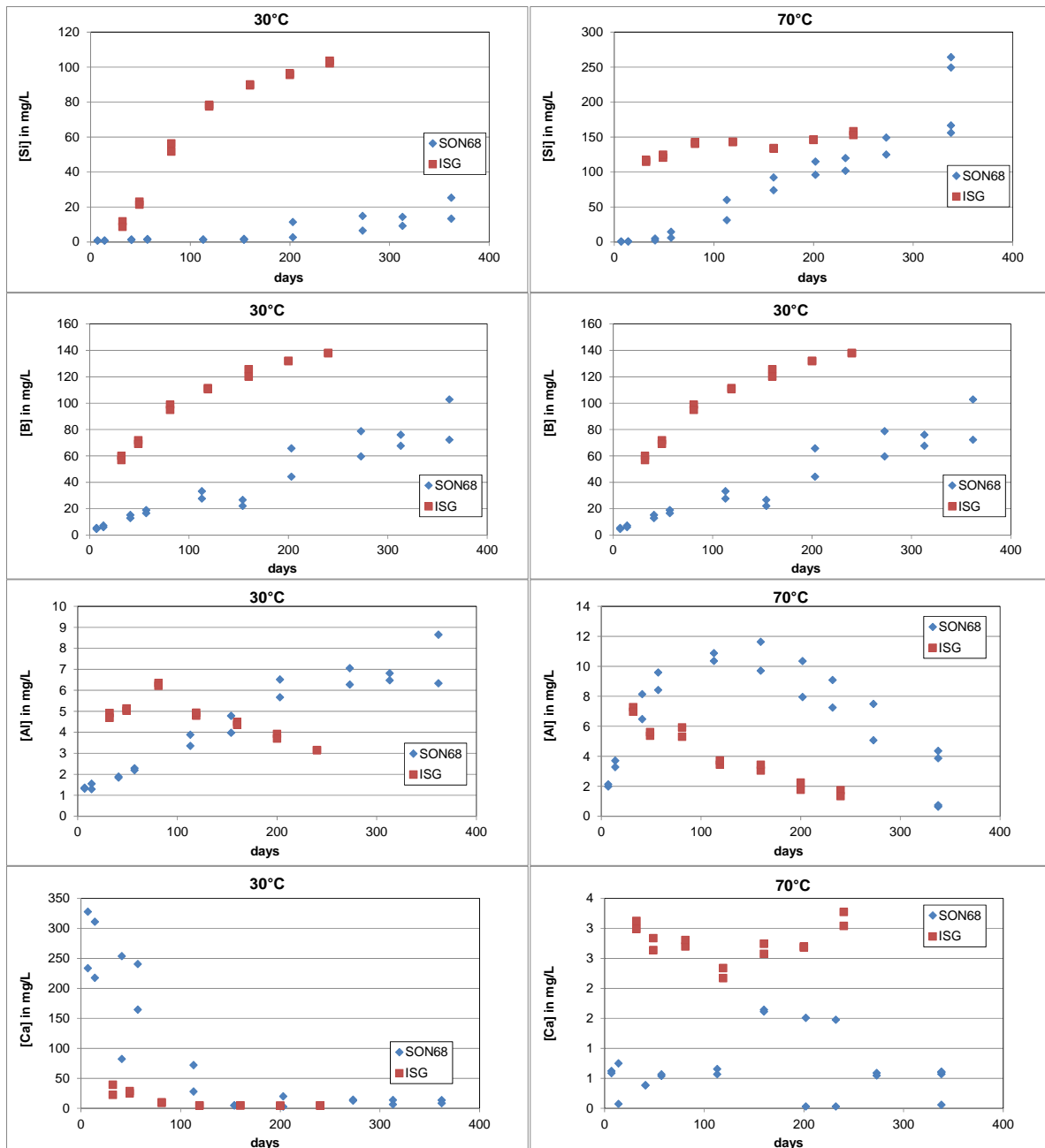


Figure 11: Si, B, Al and Ca concentrations determined in tests with ISG and SON68 altered in ECW (pH 12.5) at 30°C and 70°C.

In OCW at pH 11.7:

In OCW at 30°C, steady-state Si concentrations are quite similar (35 mg/L versus 25 mg/L) for both glasses suggesting that silicon in solution may be controlled by a similar secondary phase. Al concentration is around 2 mg/L and decreases after 200 days. Ca is quite constant for ISG around 20-25 mg/L and decreases to 5-10 mg/L after 200 days whereas for SON68, it decreases progressively from 27 to around 10 mg/L.

In OCW at 70°C, the steady-state Si concentration is two times higher for SON68 than for ISG (120 mg/L versus 60 mg/L) indicating that silicon in solution is probably controlled by a different secondary phase. The Ca concentration decreases faster for SON68 and reaches very

low concentration compared to that for ISG which stays quite constant around 10 mg/L. For the Al concentration, after reaching 2 mg/L, an immediate decrease is observed for SON68, while it is quite constant around 2.5 mg/L and decreases slightly after 150 days for ISG. At 70°C, secondary phases formed are different depending on the leached glass and the kinetic reactions in tests with SON68 are faster than for ISG.

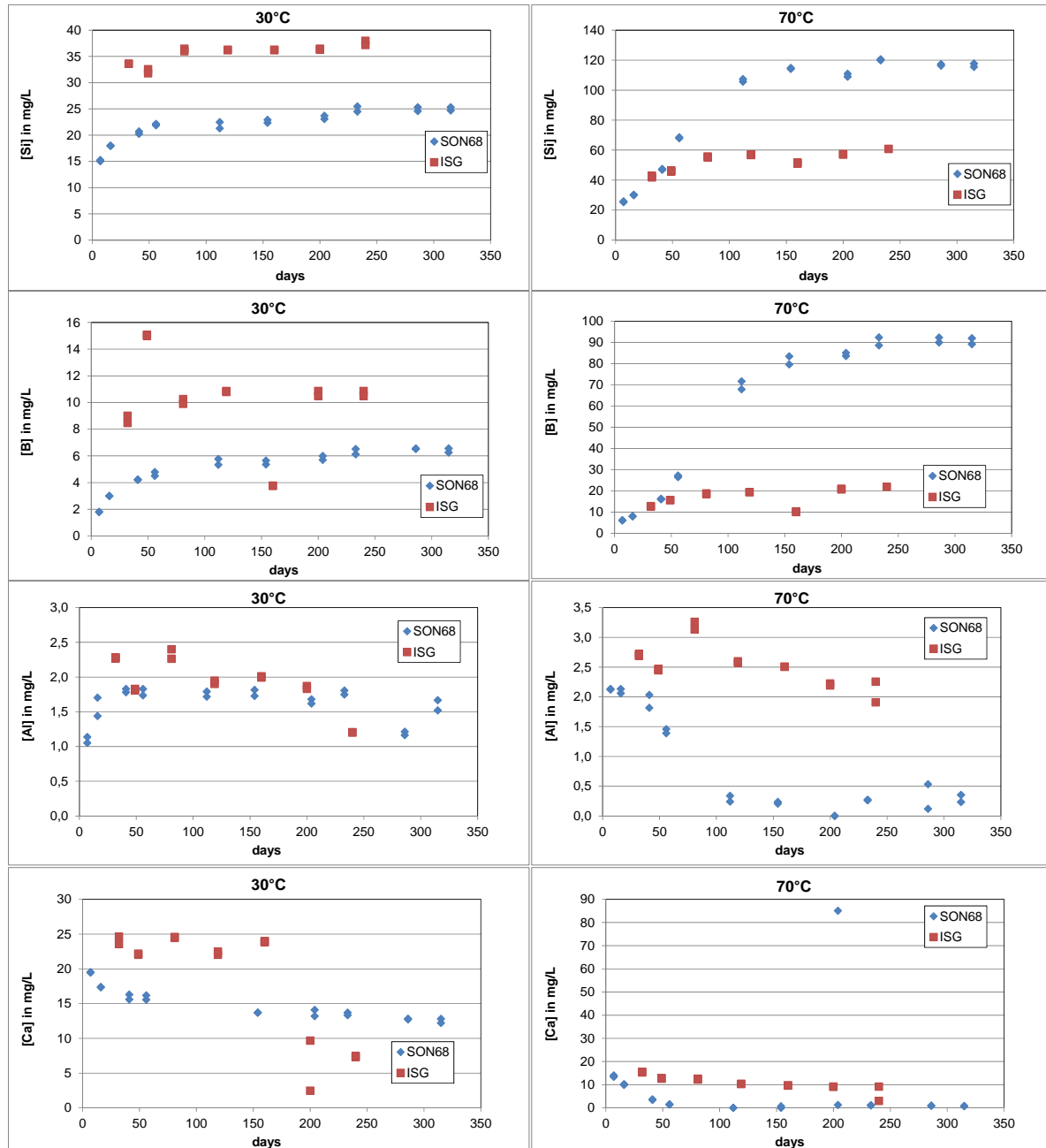


Figure 12: Si, B, Al and Ca concentrations determined in tests with ISG and SON68 altered in OCW (pH 11.7) at 30°C and 70°C.

5. Discussion

ISG dissolution rates increase when pH increases from 11.7 to 13.5. This is in agreement with the fact that hydrolysis of the silica network becomes faster with pH increase [Ojovan 2007].

At 30°C, the glass dissolution rate is equal to $2.3 \times 10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$ for tests in YCWCa at the high pH of 13.5, $2 \times 10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ in ECW at the intermediate pH of 12.5 and $10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ in OCW at the lowest pH of 11.7.

At 70°C, there is no more pH effect on ISG dissolution rate in OCW and ECW because a pH decrease from 12.5 to 11.4 is measured in ECW (4×10^{-5} vs $6 \times 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$). Si concentrations are constant and quite similar around 100-150 mg/L suggesting that Si concentration in solution may be controlled by the same phase. In YCWCa at pH 13.5, a secondary phase with a very high Si solubility (5500 mg/L) is probably formed.

In KOH at pH 9 and 30°C, the ISG dissolution rate appears to be higher than in OCW at pH 11.7. This may be explained by the positive effect of Ca contained in OCW (27 mg/L) compared to the KOH solution without Ca. This effect was also observed in dynamic tests with SON68 glass, where the dissolution rates obtained in YCWCa were lower than in KOH at the same pH [Ferrand 2013]. Similar observations were made for another Si rich glass (CSD-B) in portlandite-saturated water (pH 12.4 at 25°C) compared to KOH solution [Depierre 2011 and 2013]. The favorable Ca effect was ascribed to the formation of passivating C-S-H phases on the glass surface, or to the inclusion of Ca in the altered layer as charge compensator of non-bridging silanol groups. Other studies have also highlighted this protective effect of Ca. Indeed, [Chave 2011] observed this favorable effect on the residual dissolution rate at pH 9 (at 90°C) and this was explained by the condensation of the passivating reactive interphase when Ca participates in its construction. In a study on the alteration of glass in presence of mortars, the incorporation of Ca in the alteration layers was also described by [Andriambololona 1992] and believed to have a protective effect. More recently, [Corkhill 2013] shows that the presence of Ca reduces the dissolution rate of UK HLW glass by one order of magnitude compared to the value obtained in pure water, this was however observed only for a high ratio of surface area to solution volume of 10000 m^{-1} .

At 70°C, this positive Ca effect is also observed with a dissolution rate that is 35 times higher in the KOH solution without Ca. The long term dissolution rate of $1.4 \times 10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$ determined in such a solution (KOH, 70°C) is close to that of $10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$ proposed by [Jégou 1998] on glass 4, which has exactly the same composition as ISG glass, in 0.1 N KOH at 90°C with a SA/V of 80 cm^{-1} .

The effect of temperature is observed, as is shown by the higher rates at 70°C than at 30°C. This is, however, not the case in both very alkaline solutions YCWCa (pH 13.5) and ECW (pH 12.5), in which low rates of $5 \times 10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ and $6 \times 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ are determined at 70°C. The precipitation of secondary phases, with a much higher Si solubility at pH 13.5 (more than 5000 mg/L), leading to an important pH decrease in both solutions may protect the glass surface by forming an effective diffusion barrier.

For ISG glass, an apparent Si saturation is reached in OCW and in ECW at both 30°C and 70°C, whereas in the very alkaline medium YCWCa, it is the case only at the high temperature of 70°C, suggesting that a pseudo-equilibrium can be reached in such media.

In YCWCa at 30°C, the Si concentration increases until the very high concentration of 1200 mg/L. This is comparable to the high Si concentrations observed by Gin during SON68 alteration in KOH at 90°C and pH 11 but in his study, they did not increase further near the end of the experiments [Gin 2001]. At 30°C, reaction kinetics are slower than at 70°C and Si concentration may thus evolve on the long term towards the same constant value of 5500 mg/L observed at

70°C, which suggests an equilibrium with an amorphous silicate which can protect the glass surface.

We observe that the long term dissolution rates decrease by orders of magnitude with respect to the maximum dissolution rate in KOH 0.1N at 90°C ($SA/V = 0.1 \text{ cm}^{-1}$) of about $1.7 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ [Jégou 1998], while the silicon concentrations gradually increased or stabilized. This decrease may be due to the increasing Si concentration, but also to the initial Ca concentration of the cement water.

The dissolution rate suppression was very important in the OCW (30°C, pH 11.5). The resulting rate of $10^{-5} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ is similar to the long term rate of $1.5 \times 10^{-5} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ calculated at near-neutral pH for SON68 glass (from equation given by [Chave 2011]). Similar observations were made by Depierre [Depierre 2013] about CSD-B leaching in a cement water at pH 11.7 (50°C), for which the long term dissolution was also almost the same as in pure water. The fact that in this case, a constant silicon concentration is reached (35 mg/L), suggests that the glass is covered with a protective alteration layer, in pseudo-equilibrium with the solution. The equilibrium Si concentrations are similar to those obtained at pH 9 in clay water at 40°C [Lemmens 2002]. If secondary phases are not observed by SEM, this may be due to the stabilization of the gel by Ca in the old cement water as it was shown for SON68 glass [Ferrand 2013].

In tests with SON68 in KOH at 90°C [Gin 2001], the high silicon concentrations also seemed to have a protective effect. The SON68 dissolution rate decreased by four orders of magnitude relative to the forward rate of dissolution (r_0) in KOH solutions. At pH 11 and 11.5 (measured at 90°C), this effect was however temporary due to secondary phase formation.

In high pH media containing Ca, the incorporation of the Ca in the gel (with limited C-S-H formation) probably also decreases the glass dissolution rate, but once the Ca in solution is consumed in this way, a further decrease of the dissolution rate by this mechanism is not to be expected.

The protective effect of the alteration layer depends on the coverage offered by the layer. Depierre found that high Ca concentrations conditions (tests in the presence of portlandite) lead to relatively little nucleation of C-S-H and the formation of local precipitation with a poor coverage of the surface. Nevertheless, with time, the layer grows and finally covers the whole surface [Depierre 2013].

6. Conclusion

Static leach tests are conducted with ISG glass in contact with synthetic cementitious waters with a pH ranging from 11.7 to 13.5 and with a KOH solution at pH of 9 to estimate the dissolution rates and to determine the key mechanisms of ISG glass alteration in alkaline conditions. The cementitious waters denoted as YCWCa, ECW and OCW with pH values of 13.5, 12.5 and 11.7 at 25°C simulate the pore water in contact with Ordinary Portland Cement at different ages of degradation. The tests were performed at both temperatures 30°C and 70°C, the higher temperature accelerating the reaction kinetics for secondary phase formation.

Both results from ISG and SON68 altered in the same condition are quite similar.. The difference in the kinetic reactions is very small and the main discrepancy is observed for test conducted at 70°C in YCWCa at pH 13.5. A steady-state Si concentration around 5500 mg/L is reached very fast and a low alteration rate of $5 \times 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ is determined, this may suggest an affinity effect at such a high pH.

Surface analyses are necessary to give more information about the alteration layer, the secondary phase formation for a better understanding of the ISG glass dissolution mechanisms.

7. Future work

At the end of the test, solid analyses such as SEM, XRD, ToF-SIMS will be conducted on glass monolith and powder.

As it was done for tests conducted with SON68 and PAMELA glasses altered in synthetic cementitious waters, modelling using the PHREEQC geochemical code together with LLNL database can be used to better understand the type of secondary phases that can precipitate in such alkaline media.

If preliminary tests are conclusive, some new tests will be conducted probably at 70°C or even a higher temperature with YWCa to study the evolution of the alteration layer on ISG glass using μ -Raman spectroscopy. Such analysis will be performed at the university of Antwerpen (Belgium).

A few years ago, the glass denoted as CJ4 glass with a similar composition than ISG glass was integrated in the CORALUS project. Pieces of this glass were removed during the dismantling of the tube 4 (90°C, gamma irradiation for 7 years) and were given to CEA (P.Jollivet) and SCK so solid analyses of these samples could be relevant in the context of this international collaboration.

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Annex

Table 3: Experimental conditions of static leach tests with ISG glass.

Container code	Type of container	Temperature (°C)	Number of glass monolith	Quantity of glass (g)	Leachant	Volume of leachant (mL)
				125-250µm		
SC/GL/216	PP-50	30	2	9,002	YCWCa	50,02
SC/GL/217	PP-50	30	2	9,002	YCWCa	49,99
SC/GL/218	PP-50	30	2	9,003	ECW	50,00
SC/GL/219	PP-50	30	2	9,003	ECW	50,03
SC/GL/220	PFA-50	70	2	9,004	YCWCa	50,02
SC/GL/221	PFA-50	70	2	9,002	YCWCa	49,99
SC/GL/222	PFA-50	70	2	9,003	ECW	50,02
SC/GL/223	PFA-50	70	2	9,004	ECW	50,03
				53-125 µm		
SC/GL/228	PFA-180	30	1	5,010	OCW	100,00
SC/GL/229	PFA-180	30	1	5,010	OCW	100,02
SC/GL/230	PFA-180	30	1	5,009	KOH	100,02
SC/GL/231	PFA-180	30	1	5,009	KOH	100,00
SC/GL/232	PFA-180	70	1	5,008	OCW	100,00
SC/GL/233	PFA-180	70	1	5,000	OCW	100,02
SC/GL/234	PFA-180	70	1	5,007	KOH	100,00
SC/GL/235	PFA-180	70	1	5,000	KOH	100,00

Table 4: Si, B, Na, Ca, Al and Zr concentrations in tests performed with ISG glass in YCWCa (pH 13.5), ECW (pH12.5), OCW (pH11.7) and KOH (pH 9).

temperature leachant	main code	tijd d	pH	Si mg/l	B mg/l	Na mg/l	Ca mg/l	Al mg/l	Zr µg/l	TIC mg/l	TOC mg/l
30°C, YCWCa	SC/GL/216	32	13,64	453,39	115,57	3496,73	1,33	55,71	9,48	-	-
		49	13,66	544,28	141,89	3431,34	1,01	60,64	10,50	-	-
		81	13,48	709,93	198,19	3579,24	1,45	73,95	7,69	-	-
		119	13,66	792,76	233,69	3697,56	1,04	63,89	8,11	-	-
		160	13,48	884,46	278,06	3608,82	1,45	54,13	11,24	21	31
		200	13,59	1011,65	340,18	3756,72	1,12	42,60	11,54	-	-
		240	13,50	1271,96	443,71	10205,27	1,15	36,98	15,68	-	-
30°C, YCWCa	SC/GL/217	32	13,67	456,35	115,57	3555,95	1,39	55,41	10,37	-	-
		49	13,70	545,44	144,47	3420,08	1,15	60,15	9,17	-	-
		81	13,46	704,65	197,54	3567,50	1,39	73,71	7,67	-	-
		119	13,67	754,78	221,13	3655,95	1,00	58,97	7,87	-	-
		160	13,50	887,45	274,20	3626,46	1,42	54,84	11,20	23	< 30
		200	13,56	1011,28	336,11	3773,88	1,18	43,34	14,74	-	-
		240	13,49	1267,79	442,25	10319,20	1,36	36,85	20,64	-	-
30°C, ECW	SC/GL/218	32	12,30	11,76	60,02	485,62	39,21	4,92	6,03	-	-
		49	12,15	23,05	71,86	479,04	25,15	5,03	0,30	-	-
		81	11,76	56,29	98,80	508,98	9,16	6,35	2,99	-	-
		119	11,80	78,44	111,38	565,87	4,58	4,79	2,10	-	-
		160	11,61	89,52	125,75	559,88	4,79	4,49	2,99	26	< 30
		200	11,67	95,51	131,74	544,91	4,37	3,92	1,50	-	-
		240	11,86	102,10	137,72	1437,12	4,40	3,14	1,20	-	-
30°C, ECW	SC/GL/219	32	12,28	8,60	56,83	478,13	22,55	4,69	6,01	-	-
		49	12,16	21,32	69,07	477,48	28,53	5,14	0,30	-	-
		81	11,75	51,65	94,90	501,50	10,21	6,22	3,00	-	-
		119	11,80	77,48	110,51	567,57	4,95	4,92	2,10	-	-
		160	11,60	90,09	120,12	561,56	5,05	4,35	3,00	< 20	< 30
		200	11,66	96,40	132,13	552,55	4,50	3,69	1,50	-	-
		240	11,81	103,60	138,14	1441,45	4,92	3,15	1,20	-	-
70°C, YCWCa	SC/GL/220	32	13,28	5042,48	2390,08	6528,99	1,17	5,71	136,99	-	-
		49	12,86	6078,88	3629,18	8014,44	1,09	2,00	145,17	-	-
		81	12,31	5534,50	4324,77	9375,38	1,42	1,66	86,50	-	-
		119	12,46	5685,71	4596,96	9647,57	1,06	1,18	92,24	-	-
		160	11,97	4899,39	4385,26	8891,49	1,33	1,06	104,94	23	22
		200	11,81	5020,36	4536,47	9224,16	1,54	1,03	103,43	-	-
		240	11,94	5443,77	4929,64	10131,46	1,78	0,91	133,07	-	-
70°C, YCWCa	SC/GL/221	32	13,27	4933,11	2292,44	6442,06	1,16	6,06	150,90	-	-
		49	12,87	6370,79	3761,80	8221,35	1,15	2,06	160,79	-	-
		81	12,30	5551,69	4307,87	9343,82	1,30	1,43	103,15	-	-
		119	12,42	5733,71	4641,57	9798,88	1,06	1,00	101,63	-	-
		160	11,93	4156,18	4065,17	8221,35	1,30	0,76	74,63	23	25
		200	11,77	5066,29	4671,91	9374,16	1,40	0,88	116,49	-	-
		240	11,90	5369,66	5035,96	10253,93	1,61	0,88	133,48	-	-
70°C, ECW	SC/GL/222	32	11,89	114,72	129,13	558,57	3,12	7,27	6,01	-	-
		49	11,66	120,37	145,80	564,60	2,64	5,37	0,31	-	-
		81	11,72	142,70	158,21	598,73	2,70	5,30	3,10	-	-
		119	11,53	142,70	167,52	651,46	2,17	3,44	2,17	-	-
		160	11,39	133,40	158,21	586,32	2,57	3,04	3,10	< 20	22
		200	11,30	145,80	176,83	626,65	2,70	1,77	1,55	-	-
		240	11,44	158,21	192,34	1706,22	3,04	1,74	1,24	-	-
70°C, ECW	SC/GL/223	32	11,89	117,28	131,65	559,49	2,99	6,97	5,98	-	-
		49	11,65	124,70	149,64	586,08	2,84	5,61	0,31	-	-
		81	11,69	140,29	158,99	598,55	2,81	5,92	3,12	-	-
		119	11,52	143,40	165,23	654,67	2,34	3,71	2,18	-	-
		160	11,38	134,05	152,76	579,85	2,74	3,43	3,12	23	31
		200	11,26	146,52	177,70	623,49	2,68	2,24	1,56	-	-
		240	11,39	152,76	187,05	1683,43	3,27	1,34	1,25	-	-
30°C, OCW	SC/GL/228	32	11,96	33,58	8,46	120,90	23,58	2,27	6,04	-	-
		49	11,35	32,56	15,08	123,62	22,01	1,81	0,30	-	-
		81	11,32	36,48	10,25	120,60	24,42	2,26	3,02	-	-
		119	11,49	36,18	10,85	132,66	22,01	1,90	2,11	-	-
		160	11,20	36,18	3,77	129,65	23,82	1,99	3,02	49	36
		200	11,09	36,48	10,85	111,56	9,65	1,87	1,51	-	-
		240	11,05	37,99	10,85	331,65	7,30	1,21	1,21	-	-
30°C, OCW	SC/GL/229	32	11,88	33,62	9,01	123,08	24,62	2,28	6,00	-	-
		49	11,34	31,78	14,99	122,92	22,19	1,83	0,30	-	-
		81	11,28	35,98	9,89	119,92	24,58	2,40	3,00	-	-
		119	11,51	36,28	10,79	131,91	22,49	1,95	2,10	-	-
		160	11,19	36,28	3,75	128,91	23,98	2,01	3,00	50	35
		200	11,07	36,28	10,49	110,93	2,46	1,83	1,50	-	-
		240	11,11	37,18	10,49	329,78	7,47	1,20	1,20	-	-
30°C, KOH	SC/GL/230	32	9,45	40,20	33,00	56,70	3,21	0,12	6,00	-	-
		49	9,08	41,21	42,42	78,18	3,42	0,15	4,06	-	-
		81	9,17	47,57	51,51	85,15	4,67	0,15	5,76	-	-
		119	9,23	47,27	55,76	96,97	4,67	0,15	5,00	-	-
		160	9,38	45,45	51,21	100,00	5,09	0,15	4,85	35	30
		200	8,68	44,85	58,48	90,30	4,88	0,15	5,82	-	-
		240	8,87	46,06	61,51	272,72	5,24	0,15	4,18	-	-
30°C, KOH	SC/GL/231	32	9,35	40,81	33,31	55,52	4,14	0,12	6,00	-	-
		49	9,00	40,98	42,18	77,74	3,80	0,15	3,68	-	-
		81	9,00	47,30	50,02	81,65	5,06	0,15	3,01	-	-
		119	9,23	47,00	54,84	96,42	5,06	0,15	4,40	-	-
		160	9,23	45,20	49,11	99,43	5,42	0,15	76,53	30	24
		200	8,68	42,48	54,54	77,74	4,82	0,15	4,55	-	-
		240	8,86	46,10	59,96	299,12	5,48	0,15	3,25	-	-
70°C, OCW	SC/GL/232	32	11,65	41,77	12,53	122,34	15,22	2,69	5,97	-	-
		49	11,17	45,75	15,67	137,88	12,53	2,44	0,31	-	-
		81	11,12	55,78	18,80	141,01	12,53	3,26	3,13	-	-
		119	11,26	56,72	19,43	159,81	10,34	2,57	2,19	-	-
		160	10,96	51,70	10,34	141,01	9,71	2,51	3,13	47	< 30
		200	10,72	57,35	21,00	137,88	9,12	2,22	1,57	-	-
		240	10,85	60,79	21,94	410,50	9,15	2,26	1,25	-	-
70°C, OCW	SC/GL/233	32	11,60	42,77	12,86	125,62	15,55	2,72	5,98	-	-
		49	11,15	46,33	15,65	137,74	12,83	2,47	0,31	-	-
		81	11,08	55,10	18,47	140,87	12,21	3,13	3,13	-	-
		119	11,29	56,97	19,41	162,78	10,33	2,60	2,19	-	-
		160	10,94	51,03	10,02	137,74	9,61	2,50	3,13	39	38
		200	10,73	58,97	20,66	137,74	9,11	2,19	1,57	-	-
		240	11,06	153,39	190,96	1690,43	3,01	1,91	1,25	-	-
70°C, KOH	SC/GL/234	32	9,25	88,50	95,70	156,00	3,33	0,12	6,60	-	-
		49	8,95	89,19	113,46	176,49	3,88	0,16	6,33	-	-
		81	8,84	100,85	132,36	204,85	4,70	0,16	4,73	-	-
		119	9,07	98,33	144,97	245,82	4,85	0,16	4,79	-	-
		160	9,07	90,45	144,97	233,21	5,33	0,16	3,15	39	25
		200	8,78	97,07	173,34	252,12	5,96	0,16	4,60	-	-
		240	8,76	101,48	189,09	743,77	6,71	0,16	2,99	-	-
70°C, KOH	SC/GL/235	32	9,25	86,39	92,32	148,43	3,18	0,12	6,83	-	-
		49	8,95	89,34	113,65	176,79	4,61	0,16	8,27	-	-
		81	8,84	99,76	129,44	198,89	4,80	0,16	6,63	-	-
		119	9,07	100,71	148,38	239,94	5,34	0,16	5,52	-	-
		160	9,07	88,40	142,07	230,46	5,34	0,16	5,37	40	26
		200	8,78	95,97	170,46	252,56	5,94	0,16	5,15	-	-
		240	8,76	100,71	189,42	741,91	6,54	0,16	3,47	-	-

Table 5: Si, B, Al and Ca concentrations in tests performed with SON68 in YCWCa at 30°C and 70°C.




30°C, YCWCa					70°C, YCWCa				
SON68					SON68				
time d	Si mg/L	B mg/L	Al mg/L	Ca mg/L	time d	Si mg/L	B mg/L	Al mg/L	Ca mg/L
7	166,61	45,22	22,91	1,64	7	1,15	5,76	0,23	1,15
14	365,99	98,96	49,77	0,73	14	779,11	233,16	82,46	1,36
41	645,77	184,92	75,44	<0,73	38	930,93	333,63	65,65	10,76
57	725,94	213,34	72,30	<0,74	57	1041,70	407,37	50,63	1,16
113	764,64	266,23	58,20	<0,77	112	1588,48	762,00	22,92	1,47
154	507,85	187,88	50,78	<0,73	154	2301,94	1335,25	10,09	1,69
203	992,21	346,39	48,73	<0,59	201	2723,21	1918,35	3,99	1,21
273	1155,93	421,46	44,32	<0,77	232	3069,00	2295,85	2,95	1,18
313	1143,14	420,23	39,97	0,44	273	3065,65	2487,22	1,91	1,16
362	1346,03	515,00	49,16	0,61	312	3520,45	2923,76	2,21	1,73
7	192,13	51,03	25,82	1,35	7	1,15	5,73	0,23	1,15
14	366,08	97,82	46,27	<0,73	14	805,74	237,59	83,16	1,03
41	659,63	189,31	65,96	<0,74	38	992,58	329,03	62,52	1,65
57	722,42	214,38	67,84	<0,73	57	1080,59	389,24	49,96	1,16
113	731,40	255,99	59,12	<0,76	112	1633,86	701,07	32,68	1,49
154	507,63	188,12	50,46	<0,75	154	2377,06	1246,51	10,03	1,39
203	928,66	334,44	46,88	<0,60	201	2959,44	1890,42	4,11	1,21
273	1083,14	391,39	40,96	<0,76	232	3271,11	2277,88	2,91	1,19
313	1108,76	421,68	39,81	0,41	273	3443,58	2582,68	2,12	1,15
362	1182,44	446,37	38,13	0,59	312	3873,24	2860,24	2,44	1,19

Table 6: Si, B, Al and Ca concentrations in tests performed with SON68 in ECW at 30°C and 70°C.

30°C, ECW					70°C, ECW				
SON68					SON68				
time d	Si mg/L	B mg/L	Al mg/L	Ca mg/L	time d	Si mg/L	B mg/L	Al mg/L	Ca mg/L
7	<0,752	5,41	1,36	327,88	7	0,48	8,08	1,97	261,52
14	0,74	7,15	1,55	217,48	14	0,72	18,49	3,70	84,04
41	1,37	15,22	1,88	253,73	41	4,73	54,95	8,14	3,64
57	1,62	18,90	2,29	164,60	57	14,38	69,18	9,58	8,72
113	1,41	33,21	3,88	27,88	113	59,96	105,22	10,87	3,85
154	1,70	26,59	4,78	4,75	160	92,08	120,62	9,71	3,38
203	11,35	65,74	6,51	20,02	202	114,90	141,00	7,95	1,95
273	14,83	78,70	7,05	14,23	232	119,80	148,33	7,25	1,88
313	14,32	75,99	6,81	13,74	273	149,21	166,77	5,06	1,43
362	25,30	102,71	8,65	13,71	338	249,33	266,73	0,64	1,22
7	<0,748	4,49	1,31	233,46	7	0,52	7,46	2,12	270,58
14	<0,748	5,98	1,29	310,96	14	0,55	16,70	3,28	5,96
41	1,10	12,75	1,84	82,14	41	1,99	44,24	6,47	5,94
57	1,29	16,54	2,20	240,57	57	5,87	59,58	8,42	5,60
113	1,24	27,61	3,35	71,96	113	31,07	84,63	10,36	7,34
154	1,16	21,94	3,97	4,92	160	73,94	107,93	11,63	4,20
203	2,58	44,17	5,66	2,88	202	95,90	127,86	10,35	2,04
273	6,42	59,64	6,27	12,78	232	101,64	131,81	9,08	1,90
313	9,16	67,66	6,47	6,47	273	124,77	142,18	7,49	1,83
362	13,26	72,18	6,33	8,46	338	155,93	176,14	3,87	1,36
					338	166,54	194,29	4,35	1,42

Table 7: Si, B, Al and Ca concentrations in tests performed with SON68 in OCW at 30°C and 70°C.

30°C, OCW					70°C, OCW				
SON68					SON68				
time d	Si mg/L	B mg/L	Al mg/L	Ca mg/L	time d	Si mg/L	B mg/L	Al mg/L	Ca mg/L
7	15,02	1,80	1,05	19,53	7	25,29	6,10	2,12	13,95
16	17,93	2,99	1,70	17,33	16	30,13	8,05	2,06	10,20
41	20,22	4,23	1,78	16,30	41	46,86	16,01	1,82	3,39
56	21,86	4,49	1,83	16,17	56	67,84	26,48	1,46	1,40
112	21,30	5,33	1,72	4,91	112	105,60	67,84	0,34	<0,25
154	22,32	5,36	1,73	13,69	154	114,09	79,63	0,24	<0,2
204	23,08	5,69	1,68	14,09	204	110,93	83,56	<0,04	1,22
233	24,47	6,12	1,81	13,69	233	119,87	88,59	0,26	1,02
286	24,57	6,51	1,21	12,73	286	117,35	89,95	0,12	0,86
315	24,70	6,25	1,67	12,79	315	117,70	89,16	0,35	0,74
7	15,25	1,79	1,14	19,44	7	25,75	6,22	2,13	13,32
16	17,98	3,00	1,44	17,38	16	29,90	7,99	2,13	9,89
41	20,69	4,20	1,83	15,59	41	47,40	16,31	2,03	3,63
56	22,13	4,79	1,73	15,55	56	68,53	27,18	1,39	1,48
112	22,47	5,77	1,79	4,65	112	107,33	71,65	0,24	<0,25
154	22,91	5,65	1,81	13,69	154	114,78	83,37	0,21	0,65
204	23,68	5,99	1,62	13,19	204	108,90	85,06	<0,04	85,06
233	25,47	6,51	1,75	13,32	233	120,60	92,35	0,27	1,09
286	25,33	6,56	1,16	12,81	286	116,35	92,30	0,53	0,86
315	25,32	6,55	1,52	12,21	315	115,54	91,91	0,23	0,76

		Date	Approval
Author:	Karine Ferrand	02/12/14	
Verified by:	Liu Sanheng	02/12/14	
QA verification:	Elke Jacops	03/12/2014	
Approved by:	Karel Lemmens	02/12/14	