STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

EXTERNAL REPORT
SCK•CEN-ER-286
15/Kfe/Pub-17

Topical report on tests on vitrified (V)HLW waste in Supercontainer disposal conditions (status 2014)

Topical report for research plan RP.W&D.0061
(O/N references), research programme 2012-2014
Version 1.0

Karine Ferrand

NIRAS/ONDRAF contract CCHO-2009-00940000
SCK•CEN reference CO-90-08-2214-00

October, 2015

SCK•CEN
Boeretang 200
BE-2400 Mol
Belgium

RDW

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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

This report presents the preliminary results of WP8.2 of RP.W&D.0061. This research plan was mainly devoted to the study of the effect of a cement buffer on glass dissolution as foreseen in the Supercontainer Design and was performed by SCK•CEN for NIRAS/ONDRAF as client, in the period 2009-2014. The context, requirements, and objectives of the programme, and the technical content are given in the mentioned research plan. The experiments performed in the period 2009-2011 were described in the SCK•CEN -ER-195 external report [1]. In this report, we briefly describe the experiments for the period 2012-2014.

The experiments planned for 2012-2014 were described in the technical annex (2011-12-08) of the research plan. They included glass leach tests with isolated C-S-H phases but also tests at a high ratio of glass surface area to solution volume (SA/V) to determine the Si saturation level of SON68 and SM513 glasses in synthetic cementitious waters (YCWCa, ECW), and to support the geochemical modeling.

During the technical meetings with NIRAS/ONDRAF, it was decided to postpone the tests with the C-S-H phases to a next programme, and to include extra tests with an International Simplified Glass (ISG) composition.

As these tests are continued in the new research programme for NIRAS/ONDRAF in the period 2015-2020 according to the SCK-15-HLW-03 specification sheet, this report presents the results obtained until 433 days but without any discussion. More interpretation will be given in a topical report including all the raw data, for which the deadline is fixed at 31 December 2016.

1.1 Objective

In the previous static tests in Young and Evolved Cement Water ($pH_{(25°C)}$ = 13.5 and 12.5), the silicon concentrations in solution did not reach a saturation or steady-state with SON68 and SM513 glasses [1]. This means that we do not know the silicon behaviour at high reaction progress, and the possible impact of silicon saturation on the glass dissolution. In the tests performed in 2012-2014, the experiments were performed at a high ratio of glass surface area to solution volume to speed up the silicon concentration increase. This may allow reaching saturation within the experimental timeframe.

In the context of an international collaboration dedicated to a better understanding of the glass dissolution mechanisms, similar tests were carried out with the International Simplified Glass (ISG). They were also conducted at lower pH values using a KOH solution at pH 9 and the synthetic cement water denoted by OCW ('Old Cement Water') at pH 11.7.

1.2 Detailed test matrix

The tested reference glasses were the inactive French AREVA SON68, the SM513 PAMELA and the International Simplified Glass (ISG).

Static leach tests were performed at 30°C and 70°C in Young Cement Water (YCWCa, pH = 13.5) and Evolved Cement Water (ECW, pH = 12.5) at a high ratio of glass surface area to solution volume. Therefore, 12 g of SON68 or SM513 glass powder (125-250 µm size fraction) were added to a PolyPropylene (PP) or PerFluoroAlkoxy (PFA) containers filled with 50 mL of leachant. Four glass monoliths were fixed on a Teflon support. For the ISG, due to the restrictive quantity, only 9 g of glass powder and 2 glass monoliths were used. The ratio of glass surface area to solution volume was 7200 m^{-1} for SON68 and SM513 glasses and 8370 m^{-1} for the ISG. Tests were done in duplicate in a furnace at 30°C and 70°C in a glove box under Ar atmosphere. The experimental conditions are described in Table 1 - Table 3. As continuous magnetic stirring was not possible, the containers were manually stirred a few days before the sampling. After 32, 49, 81, 119, 160, 200, 240, 280 and 433 days, samples of the supernatant were taken for ICP-AES (or MS) and IC analyses. For glass SON68 and SM513,a glass monolith was removed from each container after 80, 160 and 240 days to determine the mass loss and for surface analysis. For the ISG, only one monolith was removed after 200 days.

With the ISG, tests were also conducted in OCW at pH 11.7 and in a KOH solution at the initial pH of 9 at 30°C and 70°C, allowing a better comparison with the tests conducted by other international laboratories on the same glass. For these experiments, 5 g of glass powder (53-125 µm) was placed in a PFA container filled with 100 mL of leachant solution. In this case, only one glass monolith was placed in the container and it will be analyzed at the end of the tests.
In the tests with the KOH solution at the initial pH of 9, no pH adjustment was made during the test (free pH).

Table 1: Experimental conditions for static tests performed at 30°C in YCWCa (pH=13.5) and ECW (pH 12.5) with a high ratio of glass surface area to solution volume.

type of glass	container code	type of container	identification number of the glass monoliths				glass powder in g	leachant	mass in g of the leachant
			1	2	3	4	125 - 250 µm		
SON68	SC/GL/200	PP-50	200	201	202	203	12.000	YCWCa	50.01
	SC/GL/201	PP-50	204	205	206	207	12.001	YCWCa	50.01
	SC/GL/202	PP-50	208	209	210	211	12.001	ECW	49.99
	SC/GL/203	PP-50	212	213	214	215	12.003	ECW	50.00
			1	2	3	4	125 - 250 µm		
SM513	SC/GL/208	PP-50	60	61	62	63	12.001	YCWCa	50.00
	SC/GL/209	PP-50	64	65	66	67	12.004	YCWCa	50.01
	SC/GL/210	PP-50	68	69	70	71	12.005	ECW	50.02
	SC/GL/211	PP-50	72	73	74	75	12.005	ECW	50.00
			1	2	3	4	125 - 250 µm		
ISG	SC/GL/216	PP-50	1		2		9.002	YCWCa	50.02
	SC/GL/217	PP-50	3		4		9.002	YCWCa	49.99
	SC/GL/218	PP-50	5		6		9.003	ECW	50.00
	SC/GL/219	PP-50	7		8		9.003	ECW	50.03
blank	SC/GL/224	HDPE-60						YCWCa	50.01
	SC/GL/226	HDPE-60						ECW	50.01

Table 2: Experimental conditions for static tests performed at 70°C in YCWCa (pH=13.5) and ECW (pH 12.5) with a high ratio of glass surface area to solution volume.

type of glass	container code	type of container	identification number of the glass monoliths				glass powder in g	leachant	mass in g of the leachant
			1	2	3	4	125 - 250 µm		
SON68	**SC/GL/204**	PFA-50	216	217	218	219	12.003	YCWCa	50.01
	SC/GL/205	PFA-50	220	221	222	223	12.001	YCWCa	50.00
	SC/GL/206	PFA-50	224	225	226	227	12.004	ECW	50.00
	SC/GL/207	PFA-50	228	229	230	231	12.002	ECW	50.00
			1	2	3	4	125 - 250 µm		
SM513	**SC/GL/212**	PFA-50	76	77	78	79	12.005	YCWCa	50.01
	SC/GL/213	PFA-50	80	81	82	83	12.003	YCWCa	50.00
	SC/GL/214	PFA-50	84	85	86	87	12.007	ECW	50.01
	SC/GL/215	PFA-50	88	89	90	91	12.004	ECW	50.00
			1	2	3	4	125 - 250 µm		
ISG	**SC/GL/220**	PFA-50	9		10		9.004	YCWCa	50.02
	SC/GL/221	PFA-50	11		12		9.002	YCWCa	49.99
	SC/GL/222	PFA-50	13		14		9.003	ECW	50.02
	SC/GL/223	PFA-50	15		16		9.004	ECW	50.03
blank	**SC/GL/225**	HDPE-60						YCWCa	50.01
	SC/GL/227	HDPE-60						ECW	50.00

Table 3: Experimental conditions for static tests performed at 30 °C and 70°C with ISG in OCW (pH = 11.7) and KOH solution (pH = 9).

type of glass	container code	type of container	Temperature (°C)	identification number of the glass monolith	glass powder in g	leachant	mass in g of the leachant
				1	53 - 125 µm		
ISG	**SC/GL/228**	PFA-180	30	17	5.010	OCW	100.00
	SC/GL/229	PFA-180	30	18	5.010	OCW	100.02
	SC/GL/230	PFA-180	30	19	5.009	KOH	100.02
	SC/GL/231	PFA-180	30	20	5.009	KOH	100.00
				1	53 - 125 µm		
ISG	**SC/GL/232**	PFA-180	70	21	5.008	OCW	100.00
	SC/GL/233	PFA-180	70	22	5.000	OCW	100.02
	SC/GL/234	PFA-180	70	23	5.007	KOH	100.00
	SC/GL/235	PFA-180	70	24	5.000	KOH	100.00
blank	**SC/GL/236**	HDPE-60	30			OCW	50.01
	SC/GL/237	HDPE-60	70			OCW	50.00
	SC/GL/238	HDPE-60	30			KOH	50.01
	SC/GL/239	HDPE-60	70			KOH	46.57

1.3 Detailed method

1.3.1 Glass preparation

The composition of the SON68 and SM513 glasses was presented in Table 3.4 of the SCK•CEN-ER-195 external report [1]. The composition of the ISG glass is given in mol % in Table 4

Table 4: Nominal composition of the International Simplified Glass (ISG) in mol% given by Gin et al. [2].

oxide	mol %
SiO_2	60.2
B_2O_3	16
Na_2O	12.7
Al_2O_3	3.8
CaO	5.7
ZrO_2	1.7

Compared to SON68 and SM513 glasses, this glass contains only six main oxides of a typical borosilicate waste glass. Its composition is similar to the one of CJ4 glass previously studied by Jégou (CEA thesis [3]). The references given with the ISG block were the following:

Glass Annealed Blocks
International Simplified Glass (ISG)
MO-SCI-Corporation
Lot: L12012601-M12042403

The block, with the dimensions of 50 x 50 x 100 mm, was cut in 8 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, and glass powders with size fractions of 53 - 125 µm and 125 - 250 µm were prepared, according to the SCK•CEN work instruction IW.W&D.0032.

For SM513 and SON68, glass powders with a granulometry range between 125 and 250 µm were used. The determination of the specific glass surface area is described in section 3.5 of the SCK•CEN -ER-195 external report [1]. The value for SON68 was equal to 0.03 $m^2.g^{-1}$ and we assume a similar value for SM513 due to the similarity in the glass composition.
The specific glass surface areas of the two size fractions of ISG prepared for the tests described in this report have not yet been determined experimentally, but the following values were provided by CEA:

- ISG 20 - 40 µm (M. Fournier thesis) : 2065 cm²/g (form factor = 2.72)
- ISG 63 - 125 µm (H. Arena thesis) : 720 cm²/g (form factor = 2.97)
- ISG 125 - 250 µm (M. Fournier thesis) : 465 cm²/g (form factor = 3.83)
- CJ4 40 - 63 µm (ancien lot CEA n°3008) : 1140 cm²/g
- CJ4 40 - 63 µm (ancien lot CEA n°6765) : 1260 and 1275 cm²/g (duplicate)
- CJ4 63 - 125 µm (ancien lot CEA n°3008) : 595 cm²/g
- CJ4 63 - 125 µm (ancien lot CEA n°6765) : 595 cm²/g

For the calculation of the normalized mass losses, specific surface areas equal to 0.066 $m^2.g^{-1}$ (average of both values provided for 63 - 125 µm) and 0.046 $m^2.g^{-1}$ were thus used for the 53 - 125 and 125 - 250 µm size fraction, respectively.

1.3.2 *Cement water*

The synthetic cementitious waters used in the experiments were the Young Cement Water (YCWCa), Evolved Cement Water (ECW) and Old Cement Water (OCW) with $pH_{(25°C)}$ of 13.5, 12.5 and 11.7, respectively. The preparation of these waters was described in section 3.2 of the SCK•CEN -ER-195 external report [1].

1.3.3 *KOH solution*

With the ISG, some tests were also performed using a KOH solution at the initial pH of 9.
This solution was prepared in the 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 was not adjusted to this value (free pH).

1.3.4 *Containers*

For tests conducted at 30°C with 50 mL of leachant solution, PolyPropylene (PP) containers were used whereas at the higher temperature of 70°C, Teflon PerfluoroAlkoxy (PFA) containers were chosen. PFA containers with a volume of 180 ml were used at both temperatures for tests with 100 mL of leachant solution.

1.3.5 *Calibration*

The periodic calibration of the balances was realized according to SCK•CEN procedure PO.BSU.0603.N.
Standardisation of pH electrodes was realized according to the SCK•CEN guideline IW.W&D.0044: "Potentiometrische pH bepaling: onderhoud en standaardisatie".
The furnace temperature was controlled according to procedure IW.W&D.0047.

1.3.6 *Sampling method*

For the sampling, the containers were removed from the oven at 30°C or 70°C and one mL of the supernatant was transferred into a previously weighed plastic bottle. Then, the pH of this sample was measured in the glove box at room temperature. To finish, the containers were firmly closed and placed back in the oven. The aliquots of solution were taken out of the glove box; for each sample the mass was noted (accuracy 0.005 g) and 2 mL of Milli-Q water was added. The mass after dilution (accuracy 0.005 g) was noted to calculate the dilution factor. Then, the diluted sample was ultrafiltered (YM10). In these samples, the concentrations of Si, B, Na, Mg, Ca, Li, Mg, Cs, K, Al, Mo, Fe , Zr, SO_4^{2-} and Cl^- were determined for SON68 and SM513 glasses, whereas for ISG only Si, B, Na, Ca, Al and Zr were measured. The analyses were performed by ICP-AES (or ICP-MS) and IC.
After 80, 160 and 240 days, a glass monolith was removed from the solution, it was rinsed with Milli-Q water and dried at room temperature in the glove box. After drying, it was removed from the glove box and weighed to determine the mass loss.

As these tests are not stopped yet and continue in the programme 2015-2020, one glass monolith is still present in each container.

1.4 Results

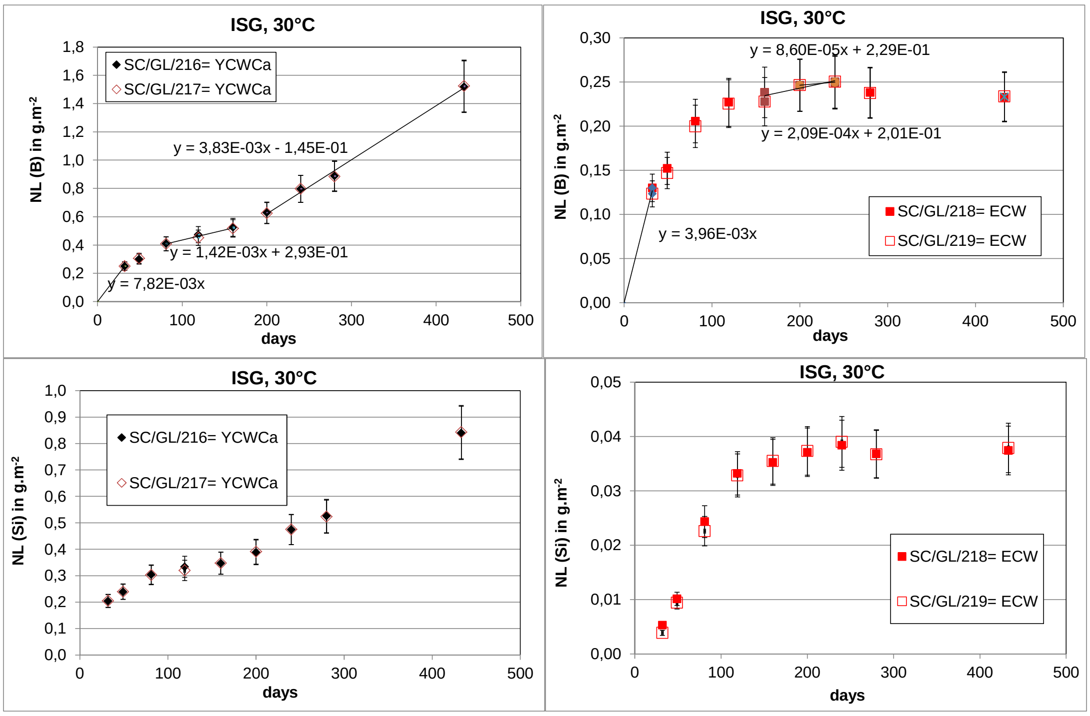
1.4.1 Estimation of dissolution rates

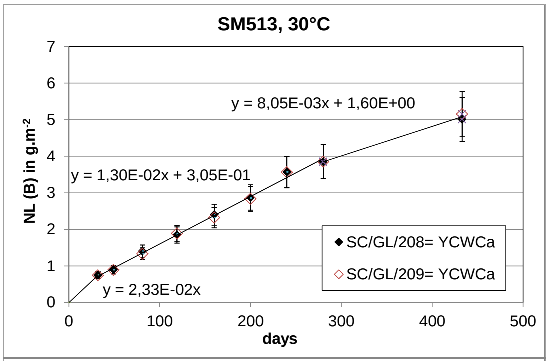
1.4.1.1 Tests at 30°C in YCWCa and ECW

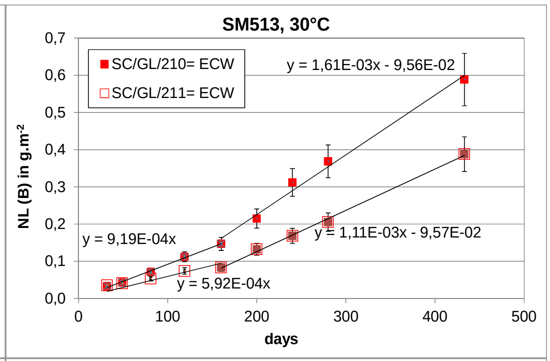
1.4.1.1.1 Normalised mass Losses

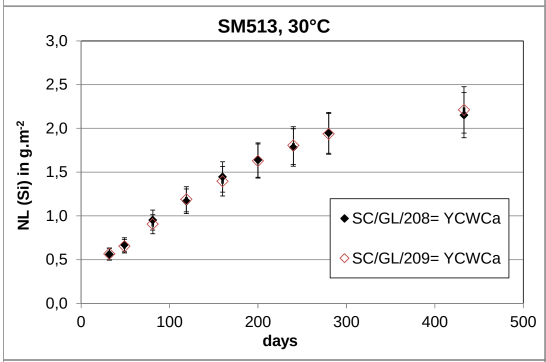
The normalized mass losses (NL) calculated from the Si, B and Li concentrations in solution as a function of time are shown in Figure 1. The calculation takes into account the volume decrease due to the periodic sampling of solution aliquots and to evaporation.

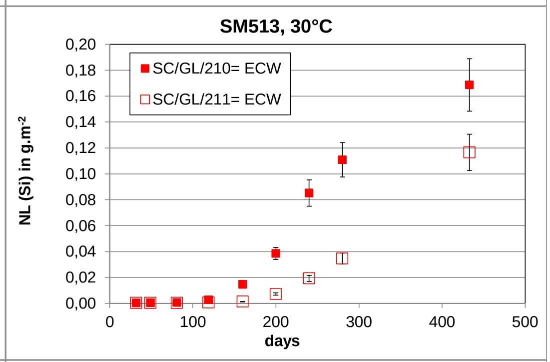
Remarks :
- As indicated in Table 4, ISG contains no Li_2O in its composition.
- For SON68 glass in ECW, NL(Li) is shown only after 160 days, because for a shorter time, Li concentration was lower than the detection limit.

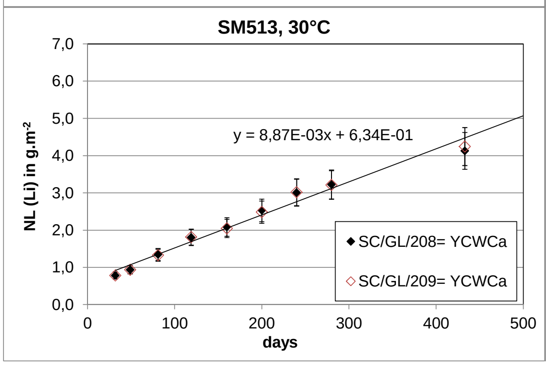


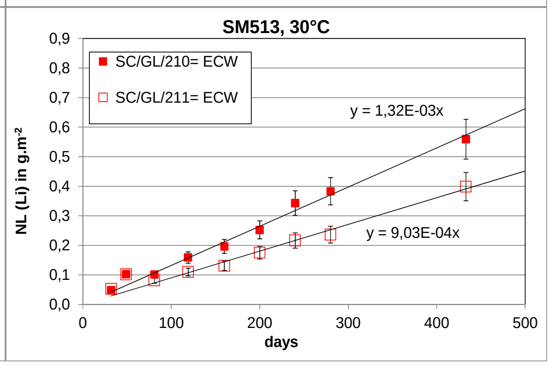

SM513, 30°C
NL (B) in g.m-2
days
y = 8,05E-03x + 1,60E+00
y = 1,30E-02x + 3,05E-01
y = 2,33E-02x
SC/GL/208= YCWCa
SC/GL/209= YCWCa


SM513, 30°C
NL (B) in g.m-2
days
SC/GL/210= ECW
SC/GL/211= ECW
y = 1,61E-03x - 9,56E-02
y = 9,19E-04x
y = 1,11E-03x - 9,57E-02
y = 5,92E-04x


SM513, 30°C
NL (Si) in g.m-2
days
SC/GL/208= YCWCa
SC/GL/209= YCWCa


SM513, 30°C
NL (Si) in g.m-2
days
SC/GL/210= ECW
SC/GL/211= ECW


SM513, 30°C
NL (Li) in g.m-2
days
y = 8,87E-03x + 6,34E-01
SC/GL/208= YCWCa
SC/GL/209= YCWCa


SM513, 30°C
NL (Li) in g.m-2
days
SC/GL/210= ECW
SC/GL/211= ECW
y = 1,32E-03x
y = 9,03E-04x

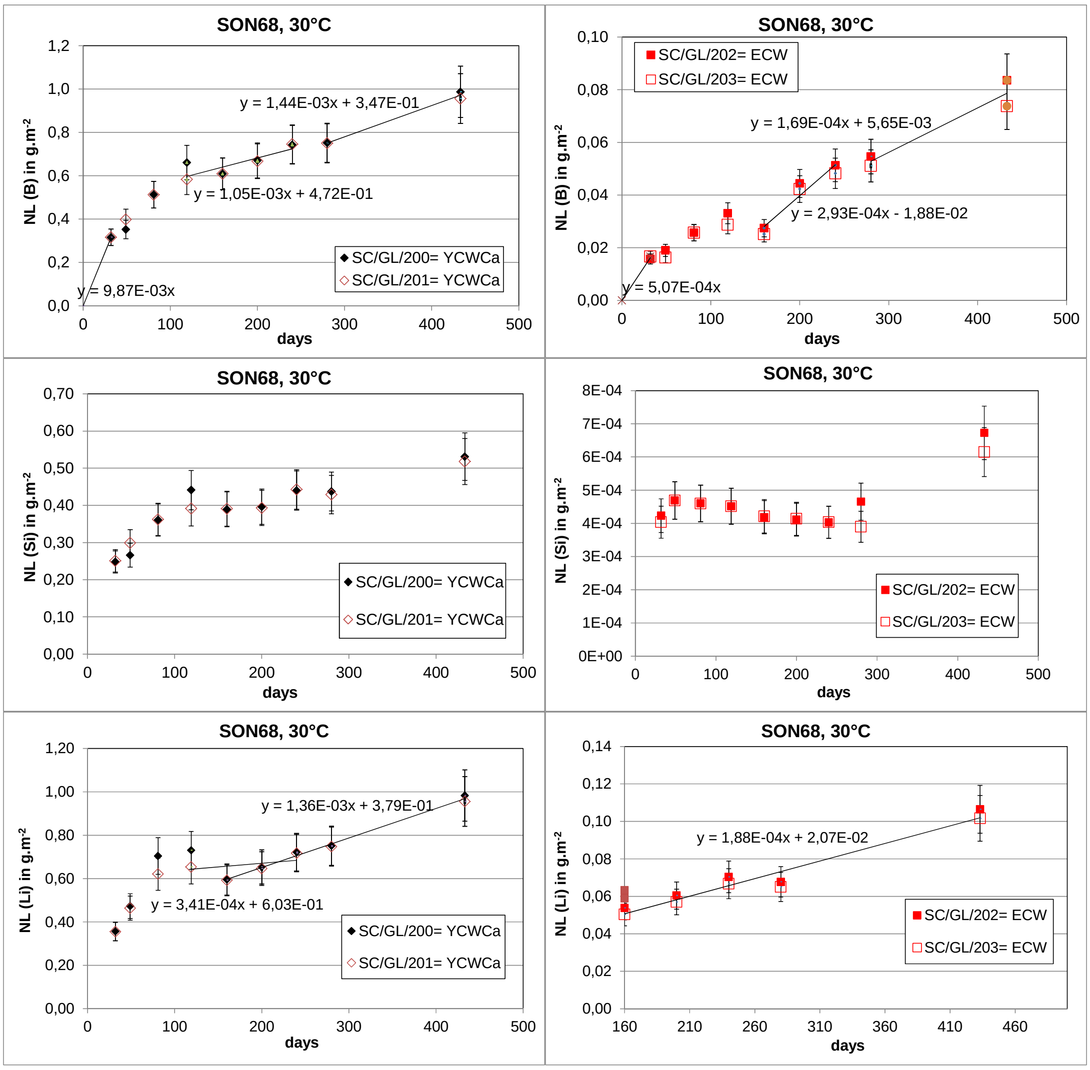


Figure 1 : Evolution of NL(Si), NL(Li), NL(B) in tests with SON68, SM513 and ISG at 30°C in YCWCa (pH = 13.5) and ECW (pH = 12.5).

For ISG altered at pH 13.5, after 200 days, glass alteration resumption occurs. The dissolution rate determined between 200 and 433 days is about three times higher than that between 81 and 160 days ((3.83 ± 0.46) x 10^{-3} versus (1.42 ± 0.17) x 10^{-3} $g.m^{-2}.d^{-1}$). NL(Si) has the same trend as NL(B) and after 433 days, around 44% of the silicon is precipitated in secondary phases.
At pH 12.5, after 200 days, a very low residual rate of (8.6 ± 1.03) x 10^{-5} $g.m^{-2}.d^{-1}$ is reached. No alteration resumption is observed after 433 days.

For SM513 glass, only a slight dissolution rate drop is observed ((2.33 ± 0.28) x 10^{-2} $g.m^{-2}.d^{-1}$ between 0 and 32 days versus (8.05 ± 0.87) x 10^{-3} $g.m^{-2}.d^{-1}$ between 280 and 433 days). More than 50 % of Si is included in secondary phases.
The results of the alteration test in ECW (pH 12.5) are not very reproducible: large discrepancies are observed in the determination of the element concentrations in both containers. However, after 160 days, an increase of the glass dissolution rate by a factor 1.8 is observed in both containers ((1.11 ± 0.13) x 10^{-3} - (1.61 ± 0.19) x 10^{-3} $g.m^{-2}.d^{-1}$ versus (5.92 ± 0.71) x 10^{-4} – (9.19 ± 1.10) x 10^{-4} $g.m^{-2}.d^{-1}$). We can notice that more than 119 days are necessary before detecting silicon in solution (kind of retardation time as for cement hydration).

For SON68 altered at the high pH of 13.5, the dissolution rate was decreased by a factor 10 but after 433 days, it seems that an alteration resumption occurs (has to be confirmed).
At pH 12.5, a low rate based on NL(B) around (1.69 ± 0.20) x 10^{-4} – (2.93 ± 0.35) x 10^{-4} $g.m^{-2}.d^{-1}$ is determined but a plateau is not reached. NL(Si) was very low and constant. The last value is, however, higher.
In both cementitious waters at pH 13.5 and 12.5, Li is a good dissolution indicator for SM513 and SON68 glass alteration.

Table 5: summarizes the glass dissolution rates at 30°C in YCWCa and ECW expressed in $g.m^{-2}.d^{-1}$ and determined from NL(B). They are lower in ECW than in YCWCa probably due to the lower pH. The possible alteration resumption (AR) occurring for SON68 in YCWCa and SM513 in ECW will be verified with future analyses.
For all glasses, the same order of magnitude for dissolution rate is observed at pH 13.5 whereas at pH 12.5, dissolution rates are very different.

Table 5: Glass dissolution rates ($g.m^{-2}.d^{-1}$) at 30°C in YCWCa and ECW.

Glass	YCWCa (pH 13.5)	ECW (pH 12.5)
ISG	(3.83 ± 0.46) x 10^{-3}	(8.6 ± 1.03) x 10^{-5} (constant)
SON68	(1.44 ± 0.17) x 10^{-3} (AR?)	(2.93 ± 0.24) x 10^{-4}
SM513	(8.05 ± 0.97) x 10^{-3}	(1.61 ± 0.19) x 10^{-3} (AR?)

The rates obtained in YCWCa can be compared to those from dynamic rates. They are 29 - 54 times lower for SON68 but only 5 times lower for SM513. Similar rates were obtained in dynamic tests at pH 13.5 and 30°C for SM513 and SON68 whereas a different behavior is observed in these static tests. This may suggest that despite a similar composition, different secondary phases are formed.

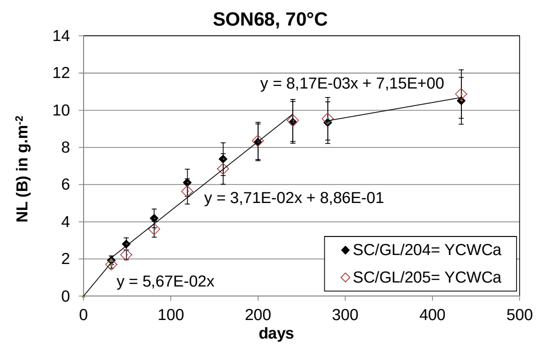
1.4.1.1.2 Mass Losses

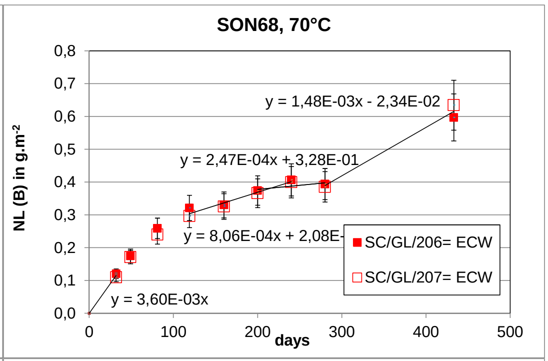
In tests with SM513 and SON68, a glass monolith was removed after 81, 160 and 242 days but in most cases, the final weight was higher than the initial weight. Consequently, the calculation of a mass loss dissolution rate makes no sense. The samples can possibly be used for surface analyses, though. For ISG, one of both monoliths was collected after a duration of 200 days.

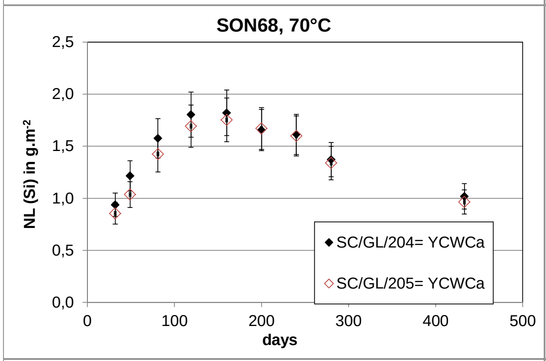
1.4.1.2 Tests at 70°C in YCWCa and ECW

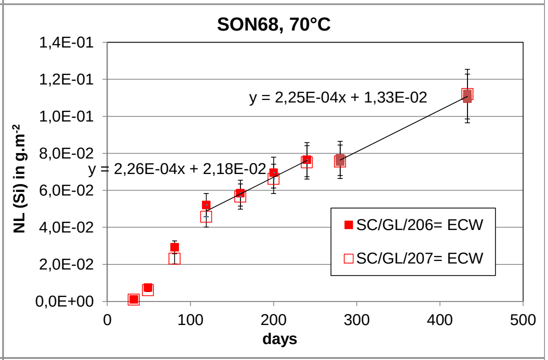
1.4.1.2.1 Normalized mass losses

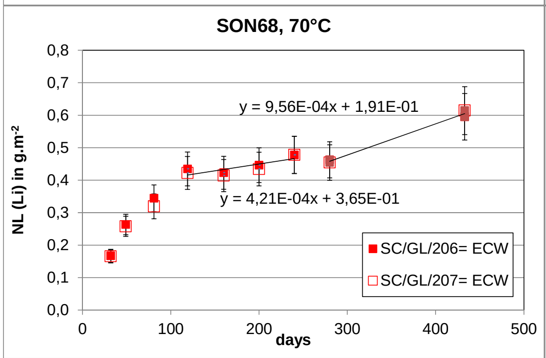
The evolution of the normalized mass losses calculated from the Si, B and Li concentrations in solution and taken into account the volume decrease are presented in Figure 2.

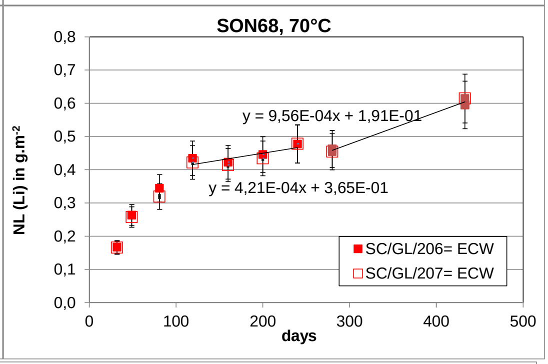

SON68, 70°C
y = 8,17E-03x + 7,15E+00
y = 3,71E-02x + 8,86E-01
y = 5,67E-02x
SC/GL/204= YCWCa
SC/GL/205= YCWCa
NL (B) in g.m-2
days

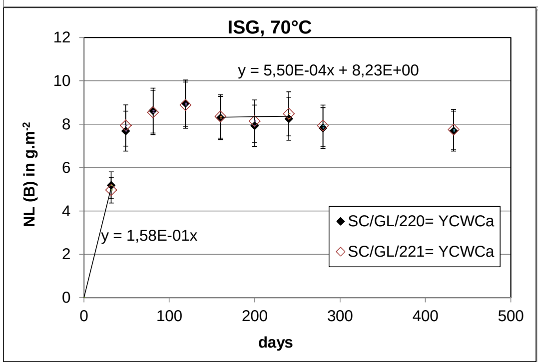

SON68, 70°C
y = 1,48E-03x - 2,34E-02
y = 2,47E-04x + 3,28E-01
y = 8,06E-04x + 2,08E-
y = 3,60E-03x
SC/GL/206= ECW
SC/GL/207= ECW
NL (B) in g.m-2
days

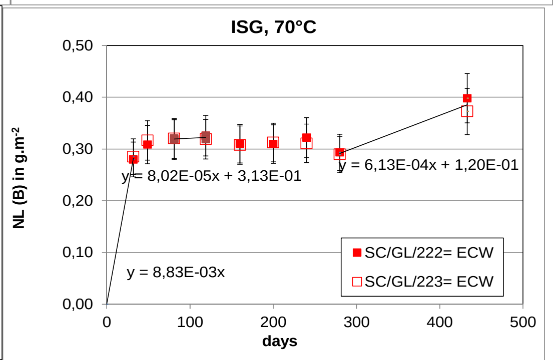

SON68, 70°C
SC/GL/204= YCWCa
SC/GL/205= YCWCa
NL (Si) in g.m-2
days

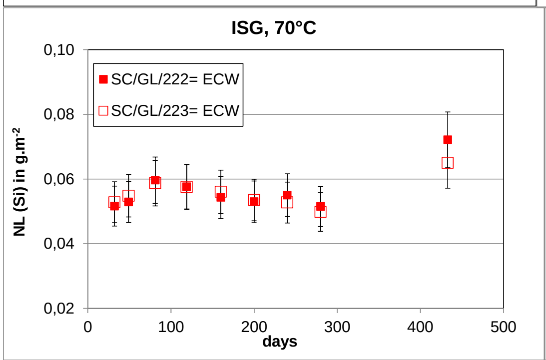

SON68, 70°C
y = 2,25E-04x + 1,33E-02
y = 2,26E-04x + 2,18E-02
SC/GL/206= ECW
SC/GL/207= ECW
NL (Si) in g.m-2
days

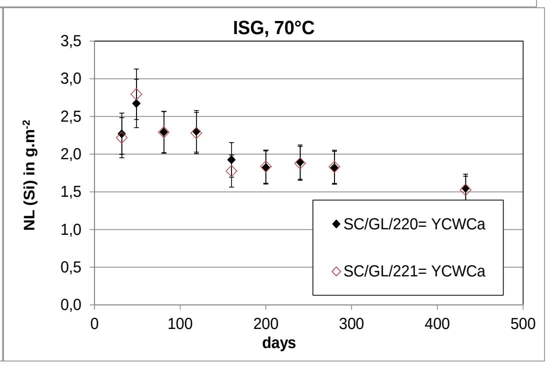

SON68, 70°C
y = 9,56E-04x + 1,91E-01
y = 4,21E-04x + 3,65E-01
SC/GL/206= ECW
SC/GL/207= ECW
NL (Li) in g.m-2
days


SON68, 70°C
y = 9,56E-04x + 1,91E-01
y = 4,21E-04x + 3,65E-01
SC/GL/206= ECW
SC/GL/207= ECW
NL (Li) in g.m-2
days


ISG, 70°C
y = 5,50E-04x + 8,23E+00
y = 1,58E-01x
SC/GL/220= YCWCa
SC/GL/221= YCWCa
NL (B) in g.m-2
days


ISG, 70°C
y = 8,02E-05x + 3,13E-01
y = 6,13E-04x + 1,20E-01
y = 8,83E-03x
SC/GL/222= ECW
SC/GL/223= ECW
NL (B) in g.m-2
days


ISG, 70°C
SC/GL/222= ECW
SC/GL/223= ECW
NL (Si) in g.m-2
days


ISG, 70°C
SC/GL/220= YCWCa
SC/GL/221= YCWCa
NL (Si) in g.m-2
days

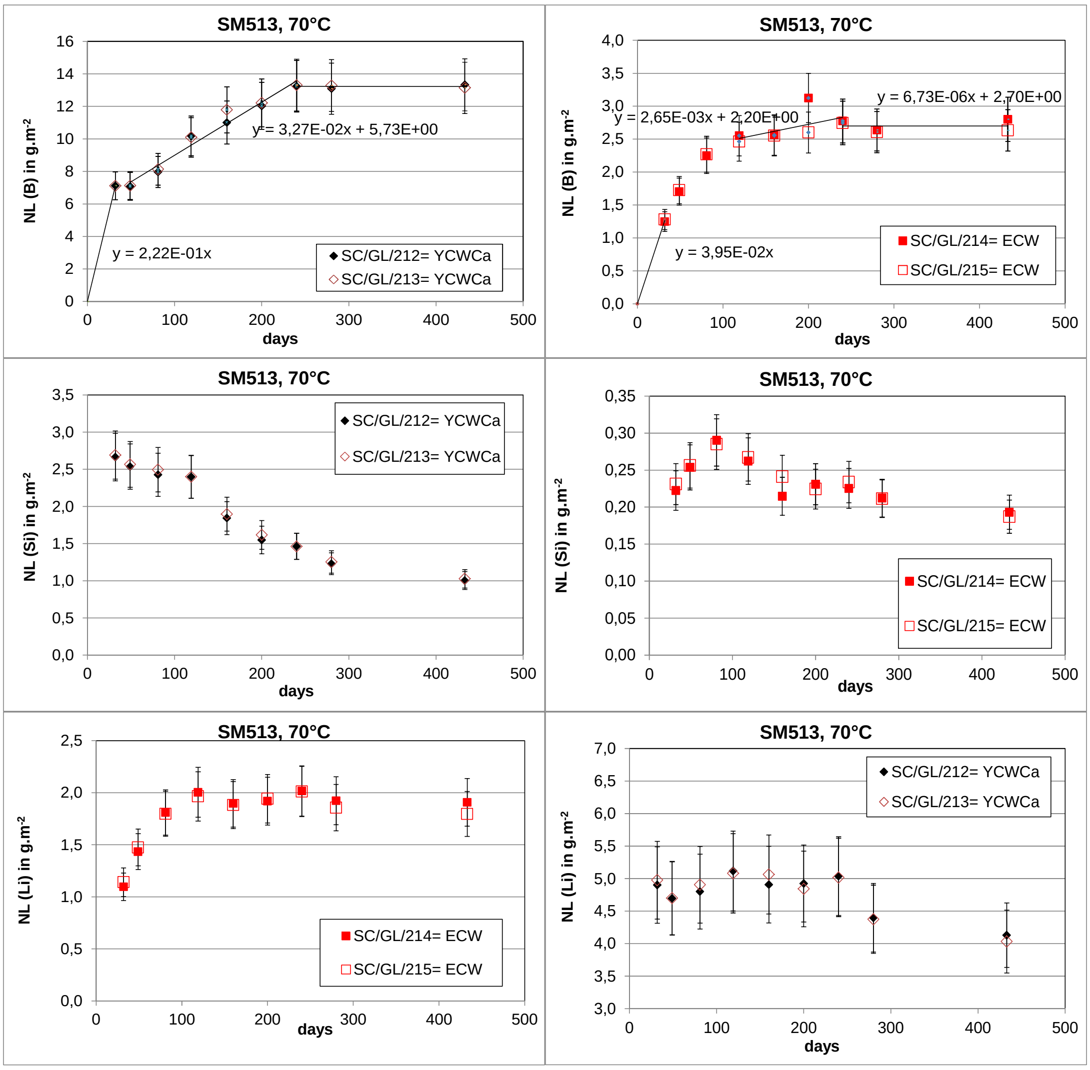


Figure 2 : Evolution of NL(Si), NL(Li), NL(B) in tests with SON68, SM513 and ISG at 70°C in YCWCa (pH = 13.5) and in ECW (pH = 12.5).

For SON68 altered at pH 13.5 and 70°C, a low rate drop is observed; the dissolution rate determined between 280 and 433 days is about 7 times lower than the value obtained between 0 and 32 days ((8.17 ± 0.98) x 10^{-3} $g.m^{-2}.d^{-1}$ versus (5.67 ± 0.68) x 10^{-2} $g.m^{-2}.d^{-1}$). At pH 12.5 and 70°C, a low rate of (2.47 ± 0.29) x 10^{-4} $g.m^{-2}.d^{-1}$ is reached after 200 - 280 days, and then the rate increases by a factor 6.

At 70°C for SON68 alteration in YCWCa, Li is not a good dissolution indicator. We can estimate that 50% of Li is retained in secondary phases (sorption or Li-containing phase).

For ISG altered at pH 13.5, a very low and constant rate of (8.02 ± 0.96) x 10^{-5} $g.m^{-2}.d^{-1}$ is reached after about 100 days. It is also the case at pH 12.5 but it seems to increase after (has to be confirmed).

For SM513 alteration at pH 13.5, the linear regression to determine the long term rate leads to a negative slope. This rate is however several orders of magnitude lower than the one calculated between 0 and 32 days ((2.2 ± 0.26) x 10^{-1} $g.m^{-2}.d^{-1}$). At pH 12.5, a very low long term rate of (6.73 ± 0.81) x 10^{-6} $g.m^{-2}.d^{-1}$ is observed; a plateau seems to be reached. Table 6 gives the long term glass dissolution rates in $g.m^{-2}.d^{-1}$ determined from NL(B) in tests performed at 70°C with YCWCa and ECW.

Table 6: Glass dissolution rates ($g.m^{-2}.d^{-1}$) in tests at 70°C with YCWCa and ECW.

Glass	YCWCa (pH 13.5)	ECW (pH 12.5)
ISG	(5.50 ± 0.66) x 10^{-4} (plateau)	(6.13 ± 0.73) x 10^{-4} (AR?)
SON68	(8.17 ± 0.98) x 10^{-3} (AR?)	(1.48 ± 0.18) x 10^{-3} (AR?)
SM513	not determined	(6.73 ± 0.81) x 10^{-6}

The rates obtained for SON68 in YCWCa can be compared to those from dynamic rates; they are 5 - 10 times lower.

1.4.1.2.2 Mass Losses

A glass monolith of SM513 and SON68 was removed after 81, 160 and 242 days, but as in the test at 30°C, the final weight was higher than the initial weight in most cases. Consequently, the calculation of a mass loss dissolution rate has not been performed.. The samples can possibly be used for surface analyses, though.
For ISG, one of both monoliths was collected after a duration of 200 days.

1.4.1.3 Static tests performed with ISG in OCW and a KOH solution at 30°C and 70°C

1.4.1.3.1 Normalized mass losses

The normalized mass losses calculated from the Si and B in solution as a function of time are given in Figure 3. The calculation takes into account the volume decrease.

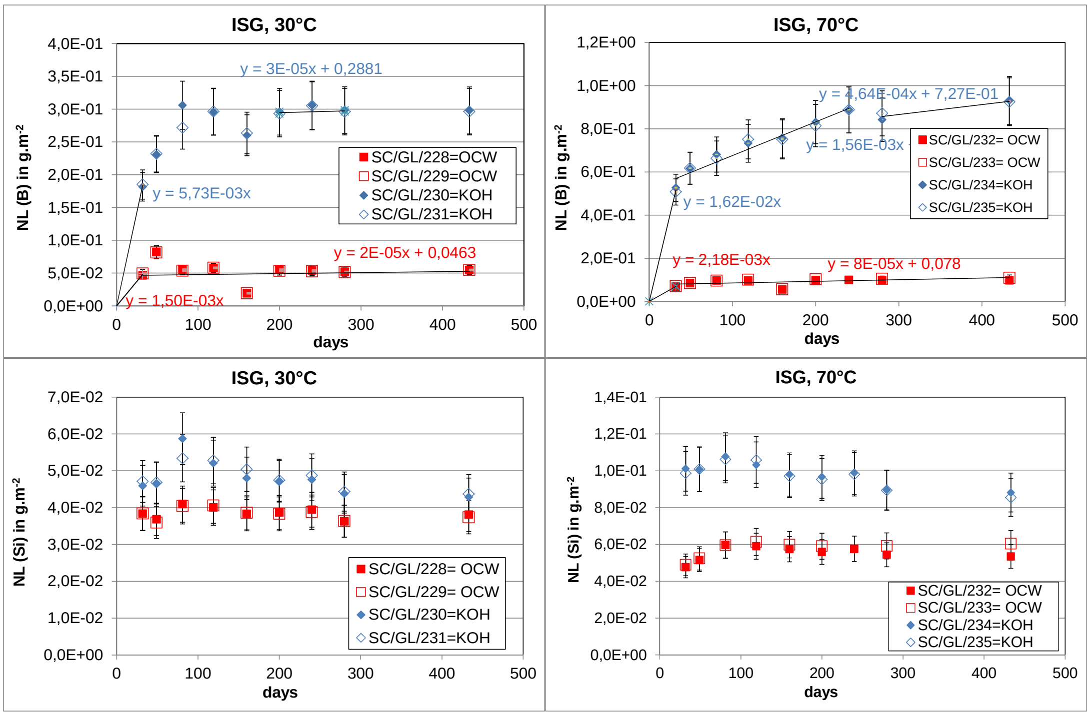


Figure 3 : Evolution of NL(Si), NL(Li), NL(B) in tests with ISG at 30°C and 70°C in KOH (pH = 9) and OCW (pH = 11.7).

At 30°C, a constant NL(B) is reached faster and at a lower value in tests performed with a KOH solution at the initial pH of 9 than in tests with OCW despite of the higher pH of 11.7. Low residual rates are determined in both series of tests.
At 70°C, low long term rates are found, a plateau is reached in OCW but not yet in KOH.

1.4.2 Solution analyses

1.4.2.1 Static tests at 30°C in YCWCa and in ECW

1.4.2.1.1 pH measurement

Figure 4 shows the pH evolution in tests at 30°C in YCWCa and ECW. At 30°C, for all glasses, pH is quite constant at the reference pH of 13.5. In ECW with the pH of 12.5, pH is quite constant at the reference value for SON68 whereas for ISG and SM513, pH firstly decreases from 12.7 to 11.6 and then increases again. This pH decrease appears to be faster for ISG than for SM513.

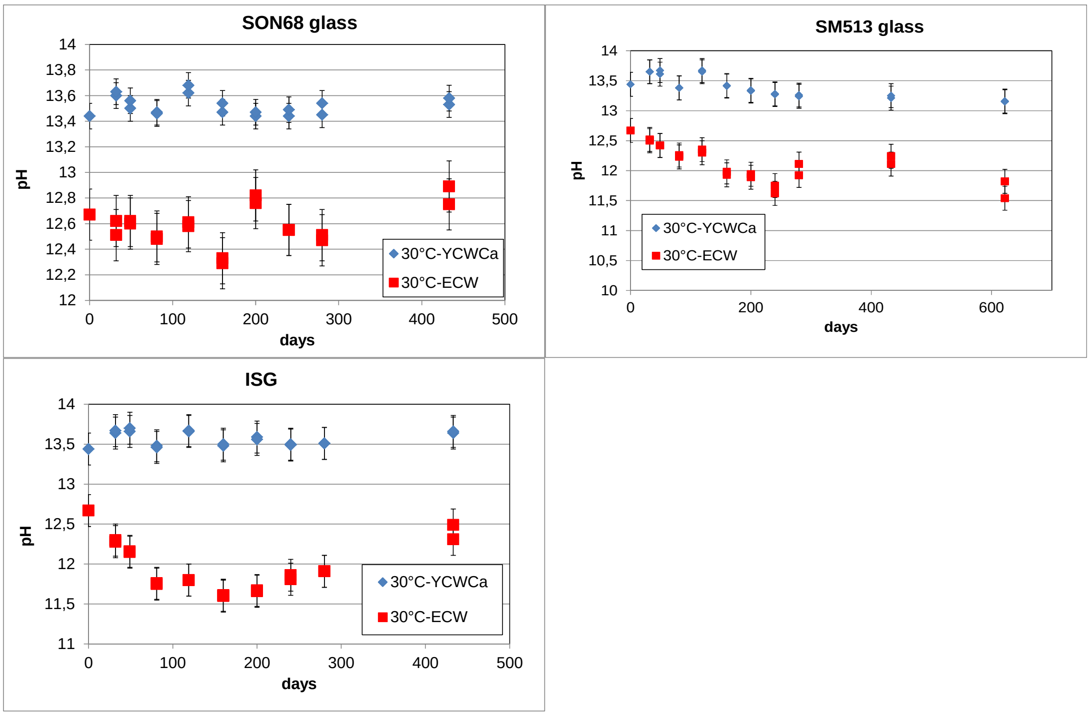


Figure 4: pH as a function of time in static tests performed with SM513, SON68 and ISG glasses at 30°C in YCWCa (pH = 13.5) and ECW (pH = 12.5).

1.4.2.1.2 Concentrations in the leachates

The evolutions of the element concentrations in the solution in tests conducted at 30°C in YCWCa and ECW are shown in Figure 5.

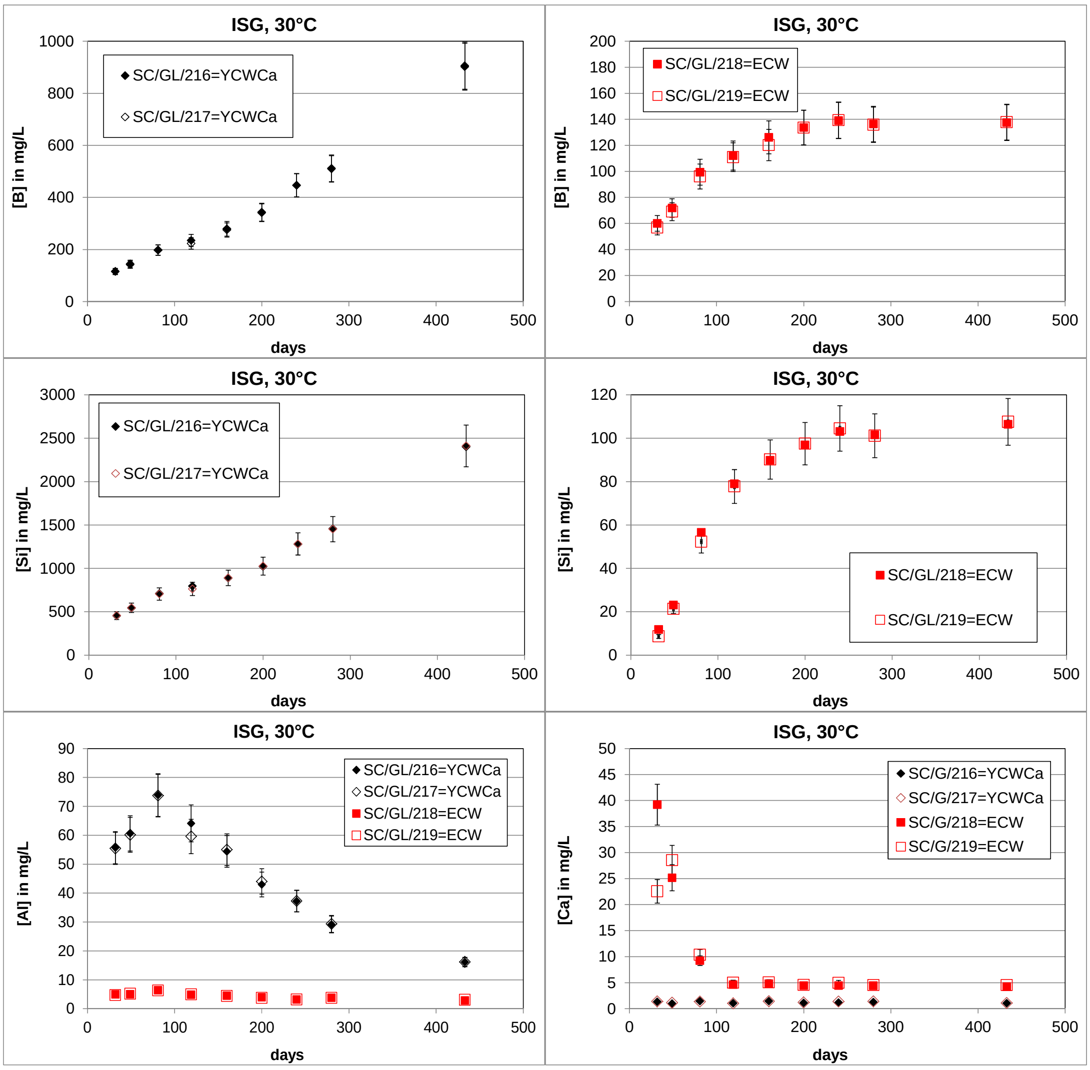
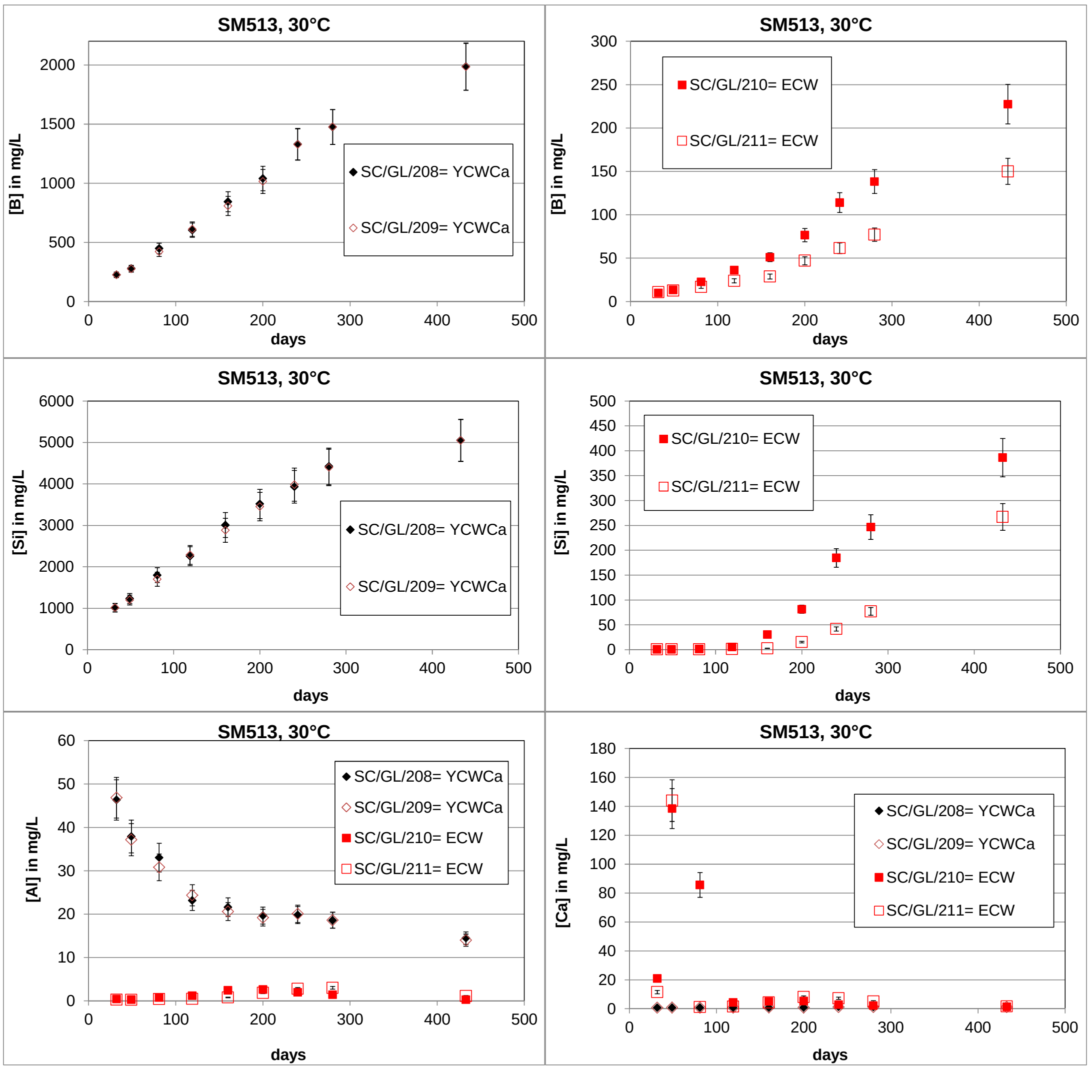
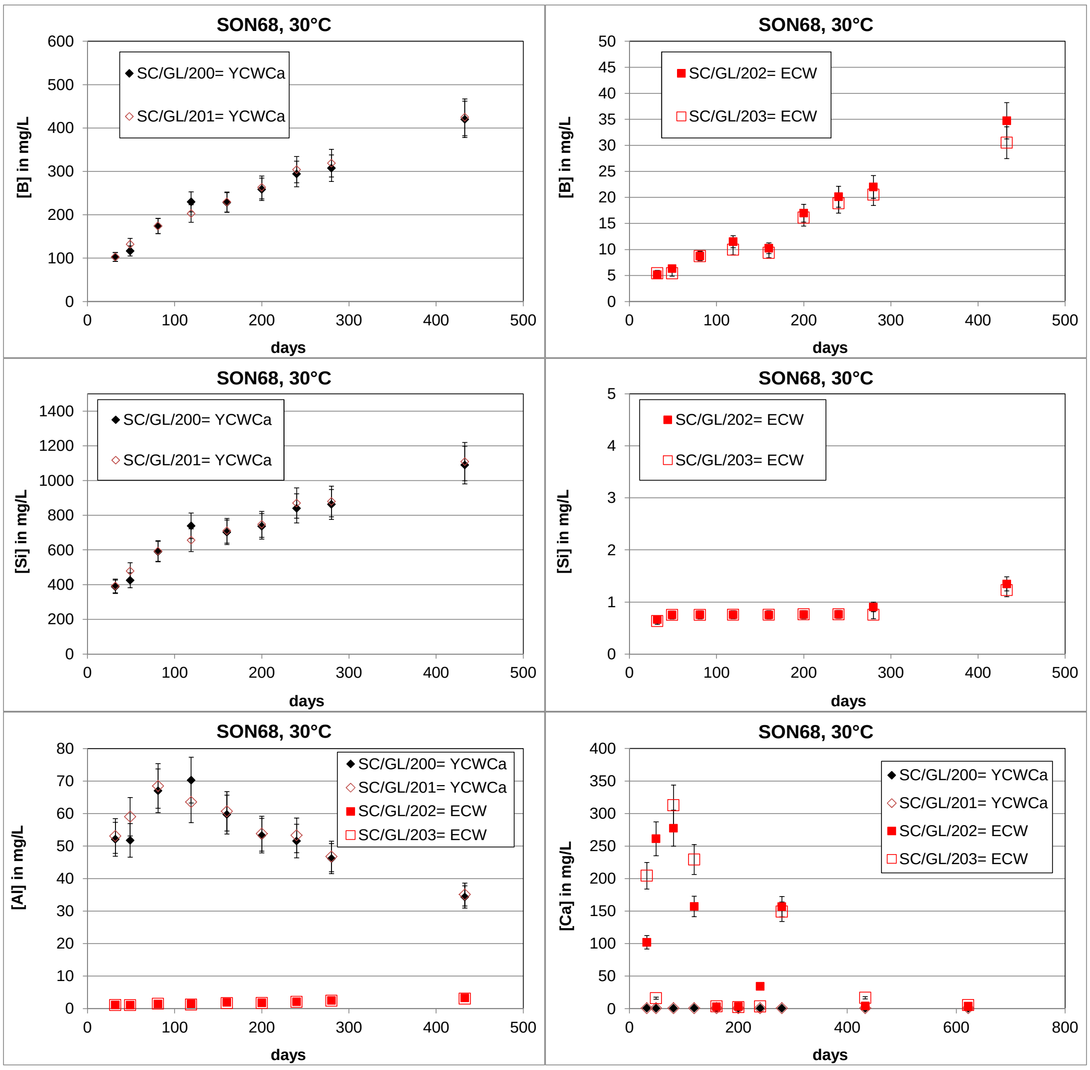

ISG, 30°C
[B] in mg/L
days
SC/GL/216=YCWCa
SC/GL/217=YCWCa
SC/GL/218=ECW
SC/GL/219=ECW
[Si] in mg/L
[Al] in mg/L
[Ca] in mg/L
SC/G/216=YCWCa
SC/G/217=YCWCa
SC/G/218=ECW
SC/G/219=ECW

Figure 5


SM513, 30°C
[B] in mg/L
days
SC/GL/208= YCWCa
SC/GL/209= YCWCa
SM513, 30°C
[B] in mg/L
days
SC/GL/210= ECW
SC/GL/211= ECW
SM513, 30°C
[Si] in mg/L
days
SC/GL/208= YCWCa
SC/GL/209= YCWCa
SM513, 30°C
[Si] in mg/L
days
SC/GL/210= ECW
SC/GL/211= ECW
SM513, 30°C
[Al] in mg/L
days
SC/GL/208= YCWCa
SC/GL/209= YCWCa
SC/GL/210= ECW
SC/GL/211= ECW
SM513, 30°C
[Ca] in mg/L
days
SC/GL/208= YCWCa
SC/GL/209= YCWCa
SC/GL/210= ECW
SC/GL/211= ECW


SON68, 30°C
[B] in mg/L
days
SC/GL/200= YCWCa
SC/GL/201= YCWCa
SON68, 30°C
[B] in mg/L
days
SC/GL/202= ECW
SC/GL/203= ECW
SON68, 30°C
[Si] in mg/L
days
SC/GL/200= YCWCa
SC/GL/201= YCWCa
SON68, 30°C
[Si] in mg/L
days
SC/GL/202= ECW
SC/GL/203= ECW
SON68, 30°C
[Al] in mg/L
days
SC/GL/200= YCWCa
SC/GL/201= YCWCa
SC/GL/202= ECW
SC/GL/203= ECW
SON68, 30°C
[Ca] in mg/L
days
SC/GL/200= YCWCa
SC/GL/201= YCWCa
SC/GL/202= ECW
SC/GL/203= ECW

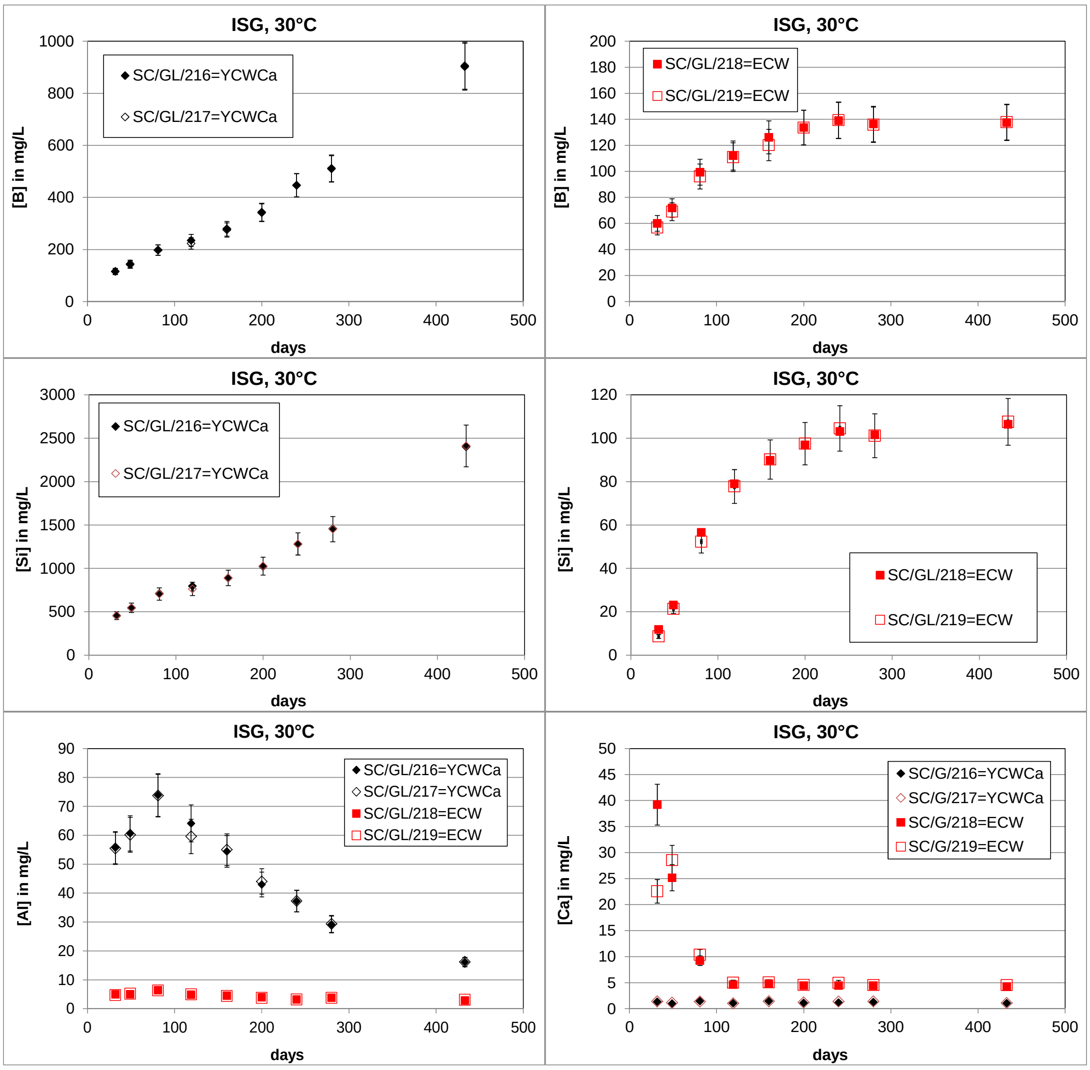


Figure 5: B, Si, Ca and Al concentrations as a function of time in tests performed with SM513, SON18 and ISG at 30°C in YCWCa (pH = 13.5) and ECW (pH = 12.5).

At 30°C and pH 13.5, for all glasses, we observe high increasing boron and silicon concentrations (for SM513, until 2000 mg/L and 5000 mg/L; for SON68,until 420 and 1100 mg/L and for ISG, until 900 mg/L and 2500 mg/L).

At pH12.5, for SM513 and SON68, these concentrations are at least 10 times lower and a kind of retardation time before Si release can be observed. It appears to be longer in ECW in which we have a high Ca concentration. In the same water, ISG does not show the same behavior. Indeed, steady-state B and Si concentrations of 140 and 100 mg/L are reached.

In YCWCa, for all glasses, Al concentration peaks and then decreases without reaching a steady-state. In ECW, very low concentrations are measured (mostly below 5 mg/L).

For all glasses, an immediate decrease occurs for Ca in solution until reaching very low values. As initial Ca concentration in ECW is higher than in YCWCa (520 mg/L versus 16 mg/L), it takes more time to reach these values.

1.4.2.2 Static tests at 70°C in YCWCa and ECW

1.4.2.2.1 pH measurement

Figure 6 presents the pH as a function of time in tests at 70°C in YCWCa and ECW. For all glasses, as well in YCWCa as in ECW, a pH decrease is observed. In ECW, it is followed by a pH increase occuring around 200 days. The higher decrease is measured for SM513 reaching a pH value of 10. The minimum values measured for SON68 and ISG are around 11.8 and 11.3, respectively.
At pH 13.5, a fast decrease until 11.8 occurs for ISG whereas for SON68 and SM513, the decrease is slower and until reaching 12.5 - 12.8.

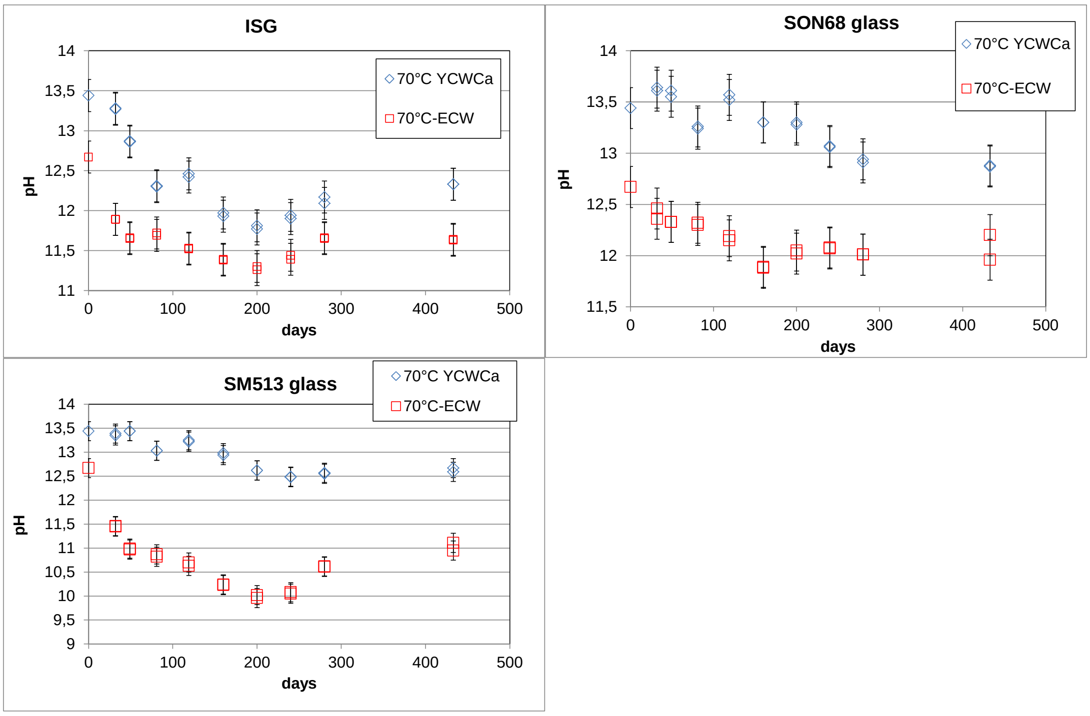
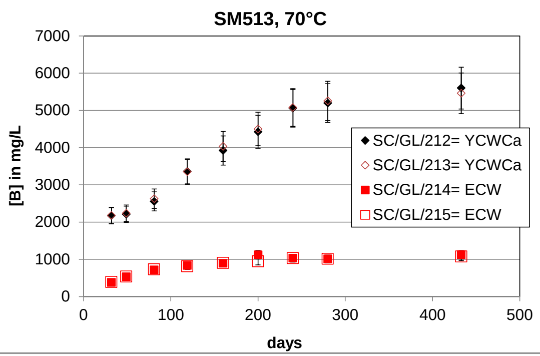
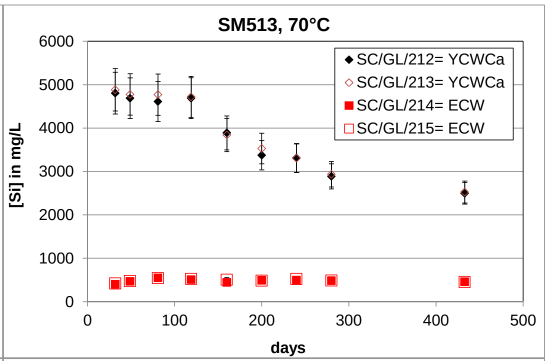


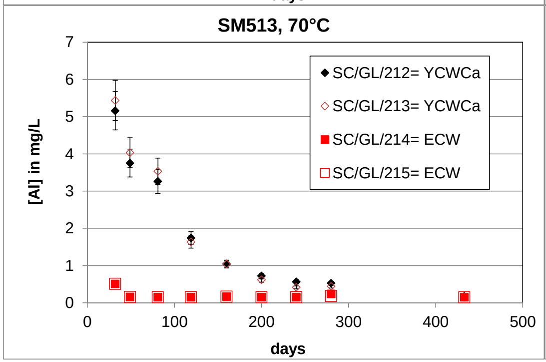
Figure 6: pH as a function of time in static tests performed with SM513, SON68 and ISG glasses at 30°C in YCWCa (pH = 13.5) and ECW (pH = 12.5).

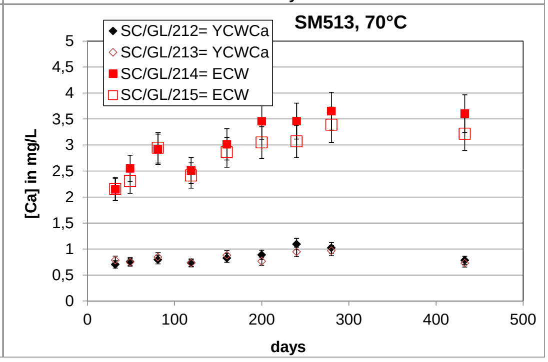
1.4.2.2.2 Concentrations in the leachates

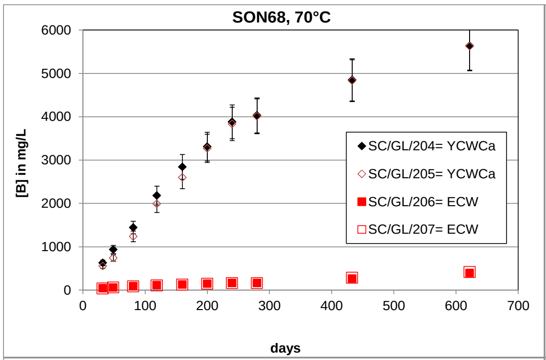
The evolution of the element concentrations in solution in tests conducted at 70°C in YCWCa and ECW is shown in Figure *7*.

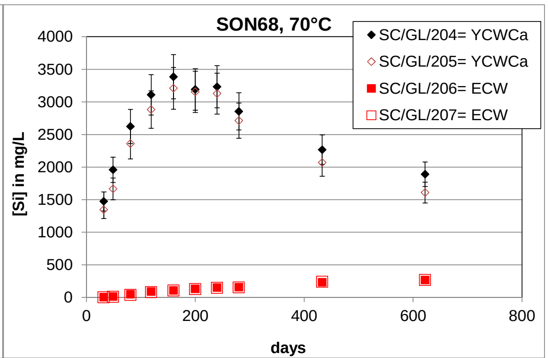

SM513, 70°C
[B] in mg/L
days
SC/GL/212= YCWCa
SC/GL/213= YCWCa
SC/GL/214= ECW
SC/GL/215= ECW

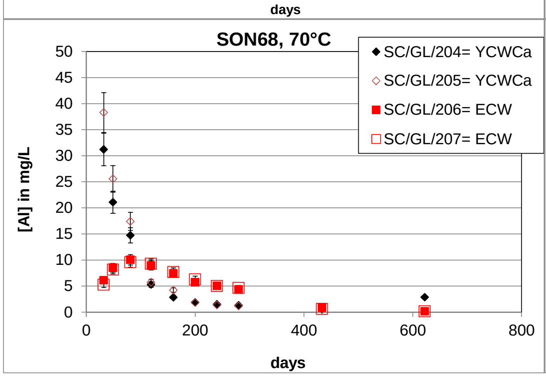

SM513, 70°C
[Si] in mg/L
days
SC/GL/212= YCWCa
SC/GL/213= YCWCa
SC/GL/214= ECW
SC/GL/215= ECW

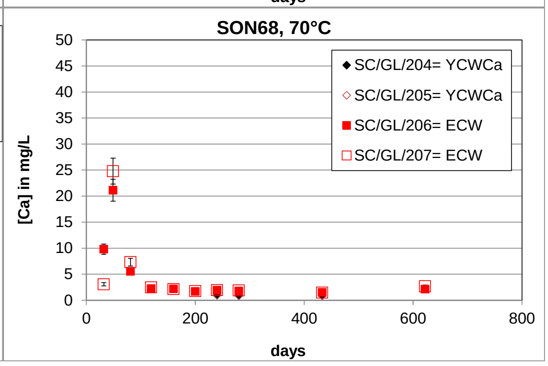

SM513, 70°C
[Al] in mg/L
days
SC/GL/212= YCWCa
SC/GL/213= YCWCa
SC/GL/214= ECW
SC/GL/215= ECW

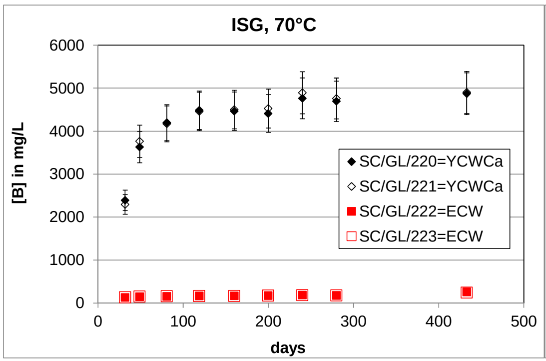

SM513, 70°C
[Ca] in mg/L
days
SC/GL/212= YCWCa
SC/GL/213= YCWCa
SC/GL/214= ECW
SC/GL/215= ECW

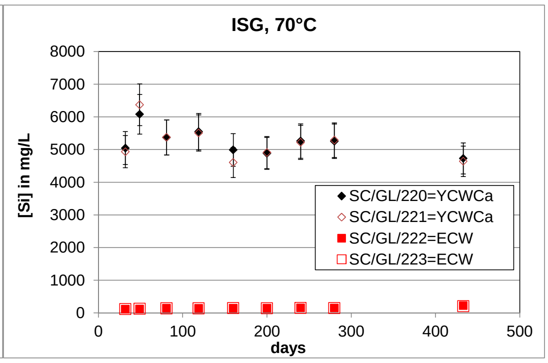

SON68, 70°C
[B] in mg/L
days
SC/GL/204= YCWCa
SC/GL/205= YCWCa
SC/GL/206= ECW
SC/GL/207= ECW


SON68, 70°C
[Si] in mg/L
days
SC/GL/204= YCWCa
SC/GL/205= YCWCa
SC/GL/206= ECW
SC/GL/207= ECW


SON68, 70°C
[Al] in mg/L
days
SC/GL/204= YCWCa
SC/GL/205= YCWCa
SC/GL/206= ECW
SC/GL/207= ECW


SON68, 70°C
[Ca] in mg/L
days
SC/GL/204= YCWCa
SC/GL/205= YCWCa
SC/GL/206= ECW
SC/GL/207= ECW


ISG, 70°C
[B] in mg/L
days
SC/GL/220=YCWCa
SC/GL/221=YCWCa
SC/GL/222=ECW
SC/GL/223=ECW


ISG, 70°C
[Si] in mg/L
days
SC/GL/220=YCWCa
SC/GL/221=YCWCa
SC/GL/222=ECW
SC/GL/223=ECW

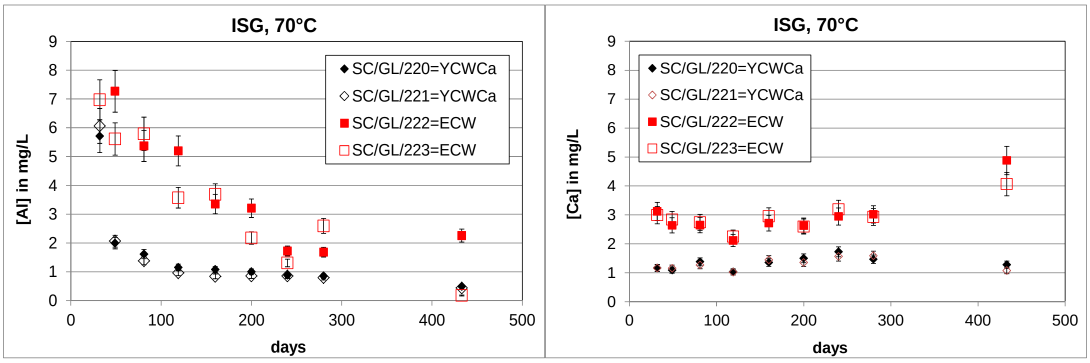


Figure 7: B, Si, Ca and Al concentrations as a function of time in tests with SM513, SON68 and ISG at 70°C in YCWCa (pH = 13.5) and ECW (pH = 12.5).

At pH 13.5, B concentration increases until 5450 mg/L for SM513 and 5000 mg/L for SON68 whithout reaching a steady-state yet. At pH 12.5, a steady-state concentration around 1050 mg/L is observed for SM513 while very low increasing concentrations are measured for SON68. For ISG, a steady-state B concentration is reached at pH13.5 and very low increasing concentrations are determined at pH 12.5 (until 250 mg/L).

For SM513, at pH 13.5, Si concentration is quite constant around 4700 mg/L until 120 days and then it decreases until 2500 mg/L after 433 days. For SON68, it firstly increases until reaching a plateau at 3200 mg/L and then decrease after 240 days. At pH 12.5, it is rather constant around 450 mg/L for SM513 and it increases until 230 mg/L for SON68 .

At pH 13.5, Al concentration firstly peaks to 5 - 7 mg/L for SM513 and ISG compared to the high value of 40 mg/L for SON68 and then decreases. This trend is also observed at pH 12.5 for ISG and SON68 (peaks to 6 - 10 mg/L) but not for SM513 (very low concentrations).

For all glasses, Ca concentration decreases immediately after the beginning of the tests to reach very low values (below 5 mg/L).

1.4.2.3 Static tests performed with ISG in OCW and a KOH solution at 30°C and 70°C

1.4.2.3.1 pH measurement

Figure 8 and Figure 9 present the evolution of the pH and concentrations in the leachates. The same pH evolution is observed at 30°C and 70°C. In KOH, pH is quite constant then a slight decrease occurs after 200 days and pH increases again until reaching a value around 9.8. In OCW, pH decreases until 10.8 - 11 and increases again.

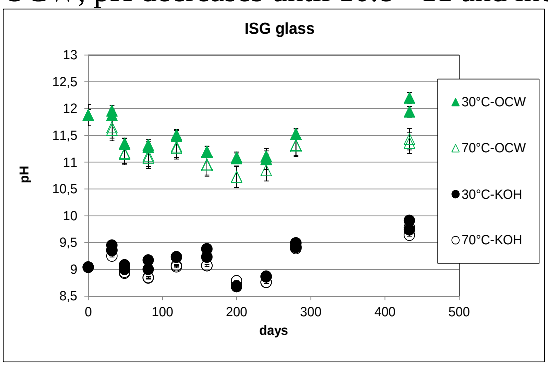


Figure 8: pH as a function of time in tests with ISG at 30°C and 70°C in OCW (pH = 11.7) and KOH (pH = 9).

1.4.2.3.2 Concentrations in the leachates

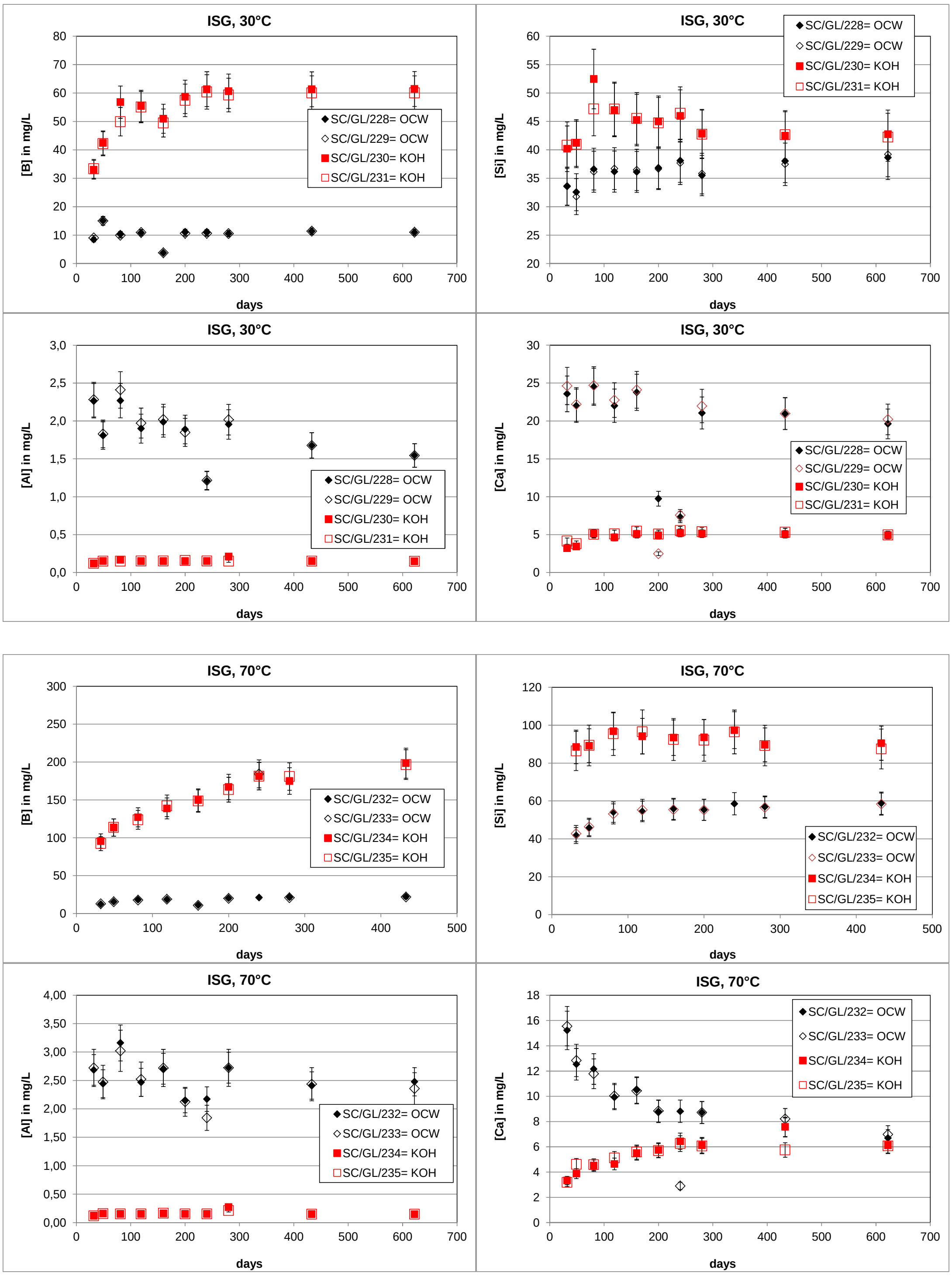


Figure 9: Si, Ca and Al concentrations as a function of time in tests with ISG at 30°C and 70°C in OCW (pH = 11.7) and KOH (pH = 11.7).

Steady-state boron concentrations are reached in both waters KOH and OCW at 30°C, they are equal to 10 mg/L and 60 mg/L, respectively. At 70°C, a constant steady-state concentration is reached at 25 mg/L in OCW meanwhile it increases to 200 mg/L in KOH without reaching a steady-state.

At both temperatures, Si concentrations are quite constant. At 30°C, they are around 45 mg/L in KOH and 35 mg/L in OCW. At 70°C, higher concentrations, around 90 mg/L in KOH and 60 mg/L in OCW, are measured .

At 30°C and 70°C, low Al concentrations are measured, close to 2 - 3 mg/L in OCW and lower than 0.5 mg/L in KOH.
At 30°C in OCW and KOH, Ca concentration stays constant around 20 - 25 mg/L and 5 mg/L, respectively. At the higher temperature of 70°C, in OCW, it decreases to 8 mg/L.

2 Geochemical modeling

To better interpret the dissolution mechanisms of the reference glasses in cementitious waters, a selection of experiments from the period 2009-2012 [1] was simulated by geochemical modeling with PHREEQC. Both tests with and without cement were considered. A first output of the simulations of the tests with cement was published [4]. The simulations of the tests without cement are still in development and will be presented in another report or publication.

3 References

[1] K. Ferrand, Topical report on tests on vitrified (V)HLW waste in Supercontainer disposal conditions (status 2011), External report SCK•CEN-ER-195 (2013).

[2] S. Gin et al, The fate of silicon during glass corrosion under alkaline conditions: A mechanistic and kinetic study with the International Simple Glass, Geochimica et Cosmochimica Acta, Vol. 151, p 68-85, (2015).

[3] C. Jégou, Mise en évidence expérimentale des mécanismes limitant l'altération du verre R7T7 en milieu aqueux. Critique et proposition d'évolution du formalisme cinétique, thèse de l’Université de Montpellier 2, (1998).

[4] K.Ferrand, Liu Sanheng, Karel Lemmens, IJAGS, 1-13, (2013).

		Date	Approval
Author:	Karine Ferrand	19/10/2015	
Verified by:	Karel Lemmens	19/10/2015	
QA verification:	Elke Jacops	25/10/2015	
Approved by:	Elie Valcke	30/11/2015	