Dissolution of plasma treated non-radioactive surrogate cemented concentrates and ion exchange resins in KOH solution at 40 °C

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Abstract. In Belgium, plasma incineration is a possible option to (re-)condition low and intermediate level short-lived waste streams in order to obtain end products which can fulfill the criteria developed for a near surface disposal facility. In this study, the chemical durability of plasma treated non-radioactive surrogate cemented concentrates and ion exchange resins (or plasma slags) was investigated by performing MCC-1 leach tests in a KOH solution at pH 13.5 and 40 °C. Results showed that initial dissolution rates of plasma slags were similar to that of SON68-I glass, and final dissolution rates around one order of magnitude lower. SEM analysis revealed the presence of alteration layers rich in K, Ca and Fe, which probably act as diffusion barriers and, associated with the increase of Si and Al concentration in solution, lead to the decrease of the plasma slag dissolution rates.

1. Introduction

Thermal techniques are frequently used for the treatment or conditioning of radioactive waste as significant volume and hazard reductions can be obtained. Vitrification is the most commonly used thermal treatment for reprocessing solutions, but the conventional vitrification installations are not suitable for all waste streams. For these more problematic waste streams, worldwide, different alternative thermal techniques are under development. A problematic waste stream particularly relevant for Belgium concerns cemented low and intermediate level short lived waste showing alkali silica gel formation. A few years ago, the formation of such alkali silica gels was observed on cemented concentrates and on some drums containing cemented resins from nuclear installations [1]. Gel formation might compromise the stability of the immobilization matrix and its swelling could affect the mechanical integrity of the engineered barrier system of the disposal. Therefore, a R&D programme was developed which defines four scenarios for the management of these drums. One of these scenarios considers the full reconditioning by a thermal treatment. Plasma incineration was selected, because it is believed to be a versatile technique for the (re-) conditioning of both unconditioned and conditioned waste streams. In the past, such a technique was successfully used to vitrify PuO_2 simulant and CeO_2 in an amorphous calcium iron aluminosilicate component of a product slag with simultaneous destruction of the organic and polymer waste fractions [2]. The end products should be disposable, this means that their compliance with the conformity criteria developed for the disposal system (near surface disposal) should be proven. One of these waste acceptance criteria is chemical durability. In the

framework of the EC THERAMIN project, this chemical durability was tested on a series of test samples, to demonstrate the potential of the technique for this type of waste. As samples, surrogate non-radioactive concentrates and resins were made, cemented and reprocessed using the plasma torch technique. The methodology for the preparation of such surrogate waste forms, described in detail in [3], was based on assumptions on the plasma torch operational parameters and the available information on the cementation campaigns for the real waste. In this paper, we investigate the dissolution of six different plasma treated non-radioactive surrogate waste forms in a KOH solution at pH 13.5 and 40 °C in order to assess their chemical durability in disposal conditions dominated by the presence of high pH cement.

2. Plasma treated surrogate waste forms

Surrogate non-radioactive concentrates and resins were made, cemented and reprocessed at the Phoenix Solutions Hutchinson Test Facility using a plasma torch power of 1200 kW. The plasma treated surrogate waste forms, or plasma slags, originating from concentrates are referred to as Simuli samples (from 1 to 4) and those from resins as R1 IRN 77 and R2 IRN 78. Their composition, determined by X-Ray Fluorescence (XRF), is indicated in Table 1. Plasma slags were composed of 38 – 50 wt % SiO_2, 12 – 30 wt % Fe_2O_3, 21 – 28 wt% CaO and 5 – 15 wt% Al_2O_3. For some plasma slags, low contents in sodium, magnesium and zinc oxides were also detected (< 2.2 wt%).

Table 1. Plasma slags composition (in wt. %) from XRF.

	SiO_2	Fe_2O_3	CaO	Al_2O_3	NaO	MgO	ZnO
Simuli 1	41.1	21.9	23.6	7.6	1.9		
Simuli 2	40.1	30.5	20.7	5.0			1.5
Simuli 3	49.5	14.0	25.6	6.0	2.1		1.1
Simuli 4	50.0	15.4	25.1	6.5			1.0
R1 IRN 77	38.2	19.0	22.7	14.7		1.7	1.0
R2 IRN 78	45.6	11.8	27.9	9.0		2.2	

Scanning Electron Microscopy (SEM) and elemental mappings showed that Simuli 1, Simuli 3, Simuli 4 and R2 IRN 78 samples were amorphous, contrary to Simuli 2 and R1 IRN 77 in which crystalline phases, i.e. bright and light grey dendrites, were observed (Figure 1). By combining Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) analysis these phases were identified as magnetite (Fe_3O_4) and clinopyroxene ($CaAl_{0.7}Fe_{0.2}Mg_{0.6}Si_{1.5}O_6$). The fractions of amorphous and crystalline phases were quantified by mixing the milled samples with about 9% ZnO, which served as internal reference. The Simuli 2 and R1 IRN 77 samples were partially amorphous (48.7% and 42.7%, respectively) and contained magnetite (13.9% and 2.1%, respectively) and clinopyroxene (36.7% and 48.3%, respectively). For R1 IRN 77 other diffraction peaks that might be attributed to plagioclase (6.6%) were also detected. SEM images also evidenced the presence of many pores, with a size up to 50 µm, in these two plasma slags.
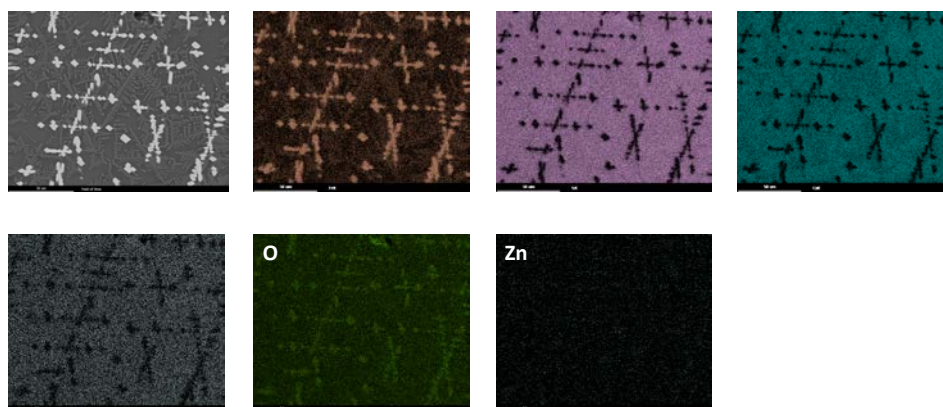
Figure 1. SEM image and elemental mappings for the Simuli 2 sample.

3. Dissolution methodology

Plasma slag dissolution experiments based on the MCC-1 static Leach Test Method [4] were carried out in a KOH solution at $pH_{(25\,°C)}$ 13.5 ± 0.2 and at 40 ± 0.1 °C. In a glove box under an argon atmosphere the plasma slags, cut into rectangular coupons of 5 x 10 x 2 mm (width x length x thickness) and inserted into a Teflon® sample holder in a vertical position, were placed in a 25 mL Teflon® container. Then, 17 mL of the leaching solution was added to reach the low sample surface area to solution volume ratio of 10 m^{-1}, which guarantees that the concentration of rate controlling elements remains below the saturation concentration, and that the dissolution rate remains relatively high, allowing the relative durability of the different slags to be distinguished. Similar tests were performed with the French inactive reference nuclear glass SON68, but without U and Th in its composition (denoted as SON68-I), which is thus used as a reference material. At the end of each leaching test, i.e. after 1, 2, 4, 7, 14, 28, 56 and 182 days, 5 mL of solution was collected using a syringe and filtered on a 0.20 µm membrane. An aliquot of solution was used for pH measurement, and 1 mL was diluted with 2 mL of ultrapure water, ultrafiltered at 6000 RPM for 20 minutes, and diluted with 2% ultrapure HNO_3 to determine the elemental concentrations by ICP-AES (Thermoscientific Iris Intrepid II dualview). The normalized mass loss (NL in g m^{-2}) from the Si and Al released from the sample to the solution was calculated according to Equation (1):

$$NL(i) = \frac{(C_i.V)}{(f_i\,SA)} \tag{1}$$

Where C_i is the concentration of the element i in the aliquot of solution in g m^{-3} (or mg L^{-1}), V is the total volume of solution in m^3, f_i is the weight percentage of element i in the unaltered sample, SA is the total surface area of the exposed sample in m^2.

Tests with a duration of 28 days were done in triplicate, and blank tests, i.e. containers with only the leaching solution, were also carried out.

4. Alteration layer analysis methodology

The plasma slags altered for 182 days were removed from the solution, rinsed with ultrapure water, left to dry at room temperature in the glove box prior to be analyzed by XRD, and then embedded in epoxy resin for SEM analysis.

Plasma slags were scanned using a Bruker D8 advance apparatus with the following settings: spinning (15 min^{-1}), radial soller slit 2.5°, automatic divergence slit, 2θ range 10 – 90°, step size 0.03°, CuKα LFF X-ray tube operated at 40 kV and 40 mA, and a position-sensitive X´Celerator detector. The

resulting XRD patterns were evaluated with the aid of the X´Pert High Score Plus software and the PDF-2 Mineral Database.

SEM analysis of the cross sections coated with a 3 nm C layer was performed on a JEOL JSM 6610 with an accelerating voltage of 15 keV and a work distance of 10 mm. The microscope was coupled with an Energy Dispersive Electron Spectroscopy detector providing semi-quantitative analysis.

5. Results and discussion

5.1. Solution analysis

The mean pH of the aliquots of solution collected over the test period, measured at room temperature, was approximatively pH 13.5; it was similar to the mean pH of the blank solutions indicating that the plasma slag dissolution did not significantly affect the pH of the system.

Figure 2 shows the Si, Al and Ca concentrations as a function of time for the Simuli 2, R1 IRN 77 and SON68-I samples. The concentrations measured for the other plasma slags, not presented here, were in the same range of values as those of the Simuli 2 and R1 IRN 77 samples. The silicon concentration increased from $1 - 2$ mg L^{-1} up to $20 - 31$ mg L^{-1} except for the SON68-I sample for which a higher Si concentration of 56 mg L^{-1} was measured. The aluminium concentration increased from $0.4 - 1$ mg L^{-1} up to $5 - 18$ mg L^{-1}. The calcium concentration increased up to $6 - 13$ mg L^{-1}, and then slightly decreased down to $5 - 6$ mg L^{-1}. Very low iron concentrations (< 1 mg L^{-1}) were measured and the K concentration was the same as in the blank solutions.
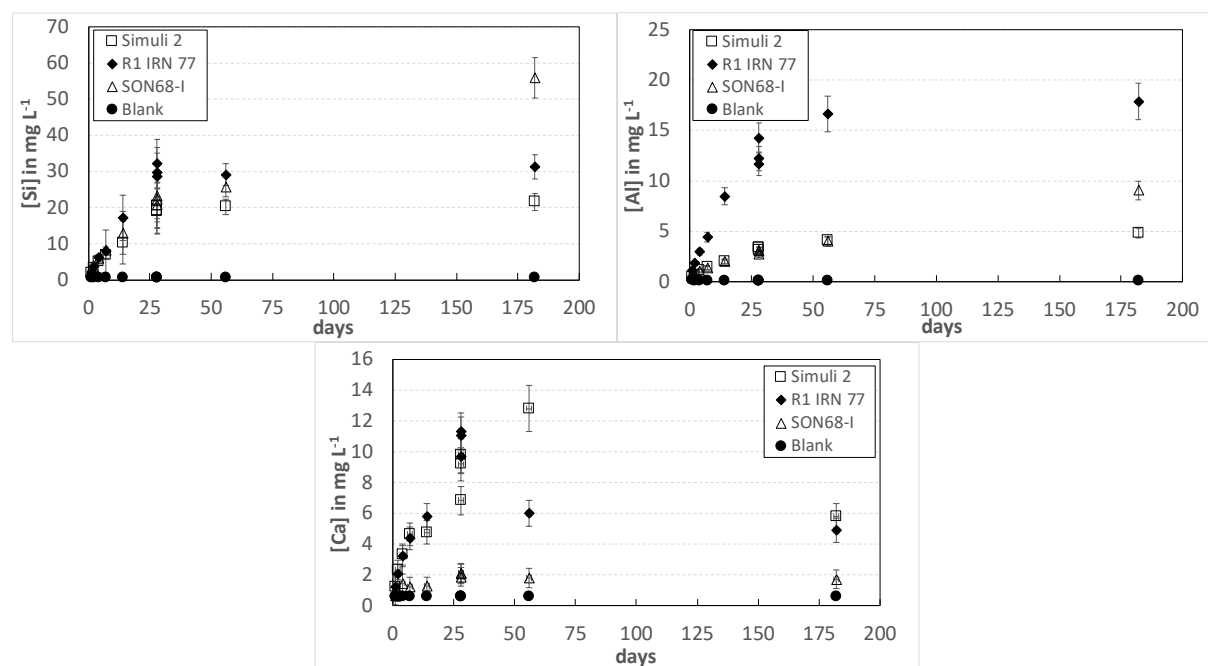

Figure 2. Si, Al and Ca concentrations (mg L^{-1}) as a function of time for the Simuli 2, R1 IRN 77, SON68-I samples and a blank test (leach tests in KOH solution at pH$_{(25\,°C)}$ 13.5 ± 0.2 and at 40 ± 0.1 °C).

5.2. Plasma slag dissolution rates

The Si and Al normalized mass losses as a function of time are presented in Figure 3 with the 95% confidence intervals calculated by error propagation. The slopes of the linear regressions give the sample dissolution rates, with the initial and final dissolution rates determined by connecting the NL values

after 1 day with the origin (0,0) and those after 56 and 182 days, respectively. For all the samples, a maximum dissolution rate was observed after 1 day, followed by a dissolution rate drop that could be due to the increase of the concentration of the glass constituents (Si, Al,…) that are involved in the formation of a protective layer whose morphology depends on the type of sample. Such dissolution behaviour is consistent with results reported for many glass compositions altered under various experimental conditions [5 – 7].
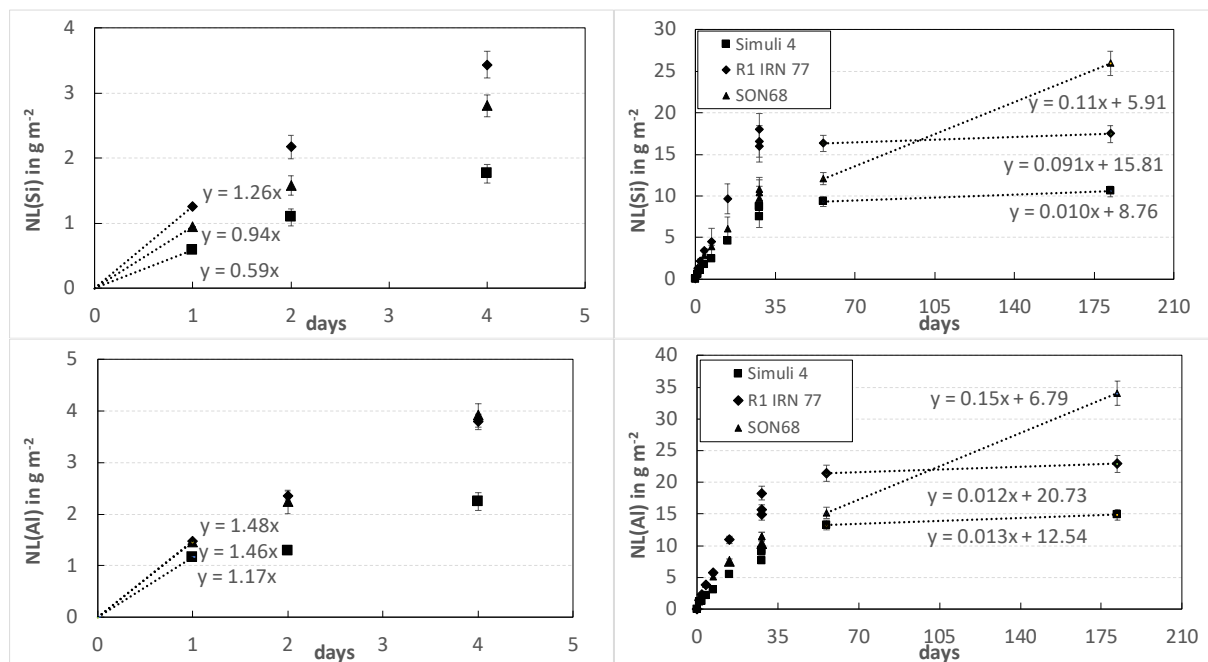

Figure 3. Si and Al normalized mass losses as a function of time for the Simuli 4, R1 IRN 77 and SON68-I samples in leach tests in KOH solution at $pH_{(25\ °C)}$ 13.5 ± 0.2 and at 40 ± 0.1 °C. The graphs on the left hand side show only the data up to 4 days, to focus on the initial dissolution rate; the graphs on the right hand side show all data, to focus on the final dissolution rate.

Table 2 summarizes the initial and final dissolution rates based on NL(Si) and NL(Al) determined for all the samples. In the period 0 – 1 day, the initial dissolution rates based on NL(Si) and NL(Al) were in the range of 0.6 – 1.3 g m^{-2} d^{-1} and 1 – 1.9 g m^{-2} d^{-1}, respectively. Because until 28 days of leaching the uncertainties on the Si concentrations were much higher than those on the Al concentrations, the uncertainties on the dissolution rates calculated from NL(Si) were also much higher meaning that the rates based on NL(Al) were more accurate. Initial dissolution rates were slightly higher for the Simuli 2 and R1 IRN 77 samples, which were the porous plasma slags containing magnetite and clinopyroxene.

The initial dissolution rates based on NL(Si) and NL(Al) for the SON68-I sample were equal to 0.94 g m^{-2} d^{-1} and 1.46 g m^{-2} d^{-1}, respectively. They were similar to those found for the plasma slags suggesting that, under alkaline conditions, the dissolution behaviour of the plasma slags is similar to that of a well performing nuclear glass. The initial dissolution rate based on NL(Al) for the SON68-I sample was close to the maximum dissolution rate of 1.4 g m^{-2} d^{-1} calculated from the equation established by [8] considering the leaching tests data of 19 nuclear glasses at alkaline pH (up to 12). This indicates that the initial dissolution rates established after one day and calculated from the aluminium release can be considered as maximum dissolution rates.

The final dissolution rates of the plasma slags were similar; they were in the range of 0.01 – 0.03 g m^{-2} d^{-1}, except for the R2 IRN 78 sample for which a rate one order of magnitude lower was found (0.004 g m^{-2} d^{-1}). The final plasma slags dissolution rates were around one order of magnitude lower

than those determined for the SON68-I sample indicating thus a better chemical durability under alkaline conditions and at 40 °C for the plasma slags. However, long-term experiments have still to be performed to draw conclusions about the long-term chemical durability.

Table 2. Dissolution rates (g m^{-2} d^{-1}) calculated from NL(Si) and NL(Al) for the plasma slags and SON68-I altered in a KOH solution at pH 13.5 and 40 °C.

Samples	Initial dissolution rate (g m^{-2} d^{-1}) in the period 0 – 1 day		Final dissolution rate (g m^{-2} d^{-1}) in the period 56 – 182 days	
	From NL(Si)	From NL(Al)	From NL(Si)	From NL(Al)
Simuli 1	0.66 ± 0.31	1.04 ± 0.12	0.031 ± 0.020	0.055 ± 0.020
Simuli 2	1.07 ± 0.34	1.94 ± 0.22	0.0052 ± 0.010	0.022 ± 0.020
Simuli 3	0.60 ± 0.27	1.23 ± 0.14	0.015 ± 0.010	0.052 ± 0.010[a]
Simuli 4	0.59 ± 0.27	1.17 ± 0.13	0.010 ± 0.010	0.013 ± 0.020
R1 IRN 77	1.26 ± 0.35	1.48 ± 0.17	0.091 ± 0.020	0.012 ± 0.030
R2 IRN 78	0.75 ± 0.29	1.31 ± 0.15	0.0045 ± 0.010	0.011 ± 0.020

[a] Rate between 28 days and 182 days.

5.3. Alteration layer

At the end of the tests, i.e. after 182 days, alteration products were observed on the surface of the plasma slags. For the amorphous samples, i.e. Simuli 1, Simuli 3, Simuli 4 and R2 IRN 78 SEM images showed an altered layer, comprising four sublayers: a dark porous layer close to the unaltered sample, a less porous grey layer, a second dark porous layer and a very thin outer layer (Figure 4 a and b illustrates the alteration layer observed on the Simuli 4 sample). Elemental analysis of the alteration layer using SEM-EDX indicated that in comparison to the unaltered sample, the alteration layer was depleted in Si, Al and Na, and enriched in Ca, Fe and K. However, in the very thin outer layer in which the highest K content was measured, Fe was only present in a very small quantity.

For the Simuli 2 and R1 IRN 77 samples containing magnetite and clinopyroxene a uniform alteration layer depleted in Si, Al and Na, and enriched in Ca, Fe and K with respect to the dark grey amorphous matrix was observed (Figure 4 c and d shows the alteration layer observed on the R1 IRN 77 sample). Combined with the decrease in Ca concentration and very low Fe concentration in solution, SEM analysis confirmed that, whatever the type of plasma slag, Ca and Fe were retained in the alteration layer. The decrease in K concentration was not observed due to the very high initial concentration in the leaching solution, but K retention in the alteration layer was reported in many studies dealing with glass alteration in YCWCa, a synthetic cementitious water rich in K [9, 10].

A mono-layer enriched in Ca, Fe, K and Zn was also present on the surface of the SON68-I sample, but Ca and Fe contents were respectively 2 and 3 – 5 times lower than those measured in the alteration layers of the plasma slags. Thanks to the high Ca and Fe content, the alteration layers (mono- or multi-layers) developed on the surface of the plasma slags were thus more protective than the one formed on the SON68-I sample, leading to lower final dissolution rates for the plasma slags. Ca is indeed known to have a protective effect at high pH and high sample surface area to solution volume [11].

XRD analysis conducted on the surface of the Simuli 2 and R2 IRN 78 samples altered for 182 days did not reveal the presence of crystalline phases other than magnetite and clinopyroxene, which were initially present in the samples. Diffraction peaks that might be attributed to magnetite were detected at the surface of the Simuli 3, Simuli 4 and R2 IRN 78 samples whereas no diffraction peaks were observed for SON68-I.
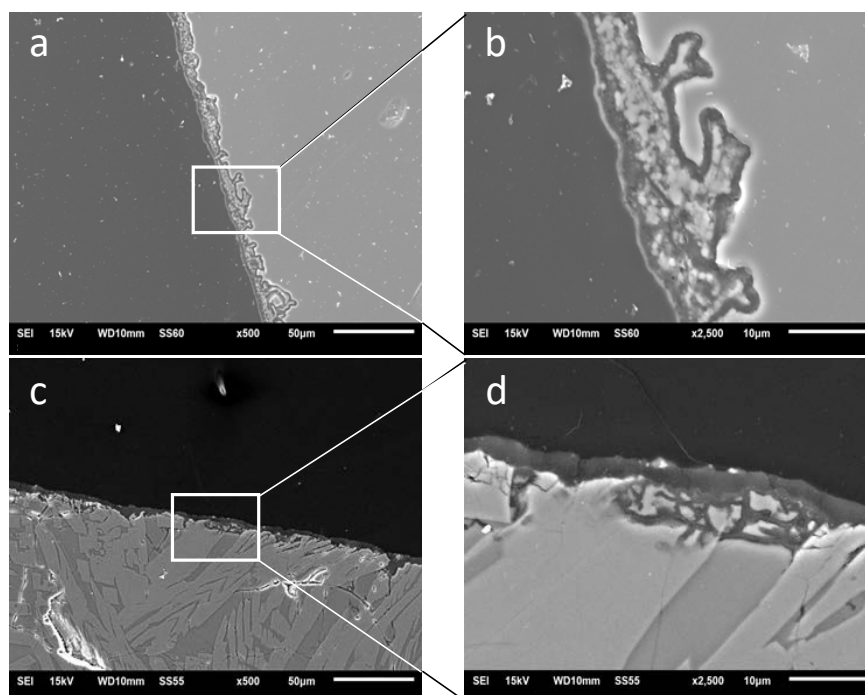
Figure 4. SEM images of the cross sections of the embedded altered samples: a and b) Simuli 4 sample (amorphous plasma slag); c and d) R1 IRN 77 sample (plasma slag containing magnetite and clinopyroxene).

6. Conclusions

The chemical durability of plasma treated non-radioactive surrogate cemented concentrates and ion exchange resins (plasma slags) was investigated by conducting MCC-1 leach tests with a KOH solution at pH 13.5 and at 40 °C. Initial rates calculated from NL(Si) and NL(Al) in the period 0 – 1 day were in the range of 0.6 – 1.3 g m^{-2} d^{-1} and 1 – 1.9 g m^{-2} d^{-1}, and were similar to those of SON68-I glass altered under the same conditions. SEM analysis performed on the samples leached for 182 days showed the presence of a multi-layer for the plasma slags initially amorphous and a mono-layer for those containing crystalline phases. Compared to the unaltered samples, these alteration layers were very rich in Ca, Fe, and also contained K originating from the leaching solution. The formation of such alteration layers combined with the increase of Si and Al concentration in solution leads to a decrease of the dissolution rates by two orders of magnitude. The final plasma slag dissolution rates in the range of 0.01 – 0.03 g m^{-2} d^{-1} were about one order of magnitude lower than those of SON68-I glass, suggesting a better chemical durability. However, this should be confirmed by conducting experiments on a longer term.

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