In-depth distributions of elements in leached layers on two HLW waste glasses after burial in clay; step-scan by SIMS

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Abstract

Two glasses developed as potential radioactive high-level waste (HLW) forms were investigated with respect to long-term corrosion resistance in geological environment. Loaded with simulated reactor waste, including fission products, the SON68 and SM513 HLW glasses were leached for 5 years, buried in Boom Clay at 85°C. The results were evaluated by quantitative secondary ion mass spectrometry (SIMS), using a step-scan technique yielding the in-depth concentration profiles of more than 20 relevant elements in successive sub-surface transformed layers to depths of the order of 500 μm. The observed elemental kinetics provided experimentally convincing evidence of a predominantly selective-substitutional leaching mode in both glasses. The rate of corrosion and element depletion in SON68 (a Cogéma type glass) was found to be by ca 20–40% slower than in SM513 (Pamela-type). In the reacted layers of both glasses, 'mobile' elements (e.g., Li, Cs, B) were practically eliminated, but also Si was significantly depleted, while more 'inert' elements (e.g., Al, Zr, Cr) remained essentially preserved in the residual network of the 'gel'. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Radioactive waste management in several countries is considering reprocessing of the spent reactor fuel, and the subsequent vitrification of especially the high level-waste (HLW) [1,2]. The development of optimal vitreous waste forms for long-term disposal in different geological environments requires careful study of the rates of corrosion (leach-abilities) in glasses of different compositions. Particularly, the knowledge is desired of the mobilities of different elements (vitrified waste as well as original glass network constituents) during the interaction of the waste form with the leaching environment.

During recent years, a convenient and rewarding method for a quantitative study of such leaching parameters has become available in secondary ion mass spectrometry (SIMS) [3,4]. The technique has been specially modified to allow the study of elements, even

at very low concentrations, in insulating materials such as glasses, ceramics and biological mineralized tissues [5]. In leached HLW glasses, the distribution of practically all relevant elements throughout and beneath the corrosion layers can be charted rapidly and quantitatively.

The chief application of SIMS to waste form dissolution is the recording of elemental in-depth concentration profiles from the surface, through interacted sub-surface layers, into the unaffected bulk [3,5]. Usually hitherto, the corroded layers after long-term leaching have extended to some 0.1–10 μm in depth; such profiles were recorded by SIMS in ca 10–60 min, employing 'head-on' ion bombardment of the specimen surface, gradually sputtering off successive sub-surface layers under simultaneous elemental analysis of the emitted secondary ions. However, for HLW glasses reacted with Boom Clay (which is the candidate host rock studied in Belgium) the affected layers are often found to extend into considerably greater depths, of the order of 10^2–10^3 μm. The recording of a 'head-on' type profile in such a case would require several hours, or even days, of sputtering. Another problem typically encountered in specimens leached in Boom Clay is that

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the relatively thick corroded layers tend to 'peel' off from their substrate, and the residual small islets of reaction products may be difficult to localize by the sputtering beam. Consequently, a 'step-scan' mode of profiling [5] has lately been adopted for glasses leached by long-term burial in Boom Clay. A section is cut at 30° to specimen surface through a microscopically identified residual portion of the corroded layer. The focused primary ion beam is directed to successive points on the section, at step distances of the order of 5–20 μm. At each point the dwelling time of the bombardment may be adjusted so as to yield optimal counting statistics for the secondary ions even of very dilute elements. This 'step-scan' mode of profiling may therefore be considered as more sensitive than the 'head-on' mode, while the depth resolution remains adequate for relatively deep corrosion layers. Another advantage of the step-scan mode is the direct and precise determination of the depth scale even throughout the leached-out, porous, layer in the glass (β-zone, see Section 3). The depth scale assessment in head-on profiling requires empirical or semi-arbitrary assessment concerning the enhancement of the rate of sputter erosion due to porosity [3,5].

In the present paper, the potentialities of SIMS step-scan elemental profiling are demonstrated and used to supply new, confidently based, information on the dissolution mechanisms in two types of HLW glasses leached by long-term burial in Boom clay within the CERBERUS in situ test [6].

2. Experimental details

2.1. Test material

The HLW glasses selected for this study were SON68 (Cogéma type) and SM513 (Pamela type). For their compositions, see the 'c_{bulk}' columns in Table 2. Both types have been frequently discussed from different points of view as prospective matrices for waste immobilization. The present specimens for SIMS profiling has been exposed during 5 years to Boom Clay at 85°C within the Belgian CERBERUS burial project [6–8].

2.2. Analyzing procedure

A modified version of a Cameca 3F/4F secondary ion micro-analyzer [5,9] was employed. SIMS step-scan type in-depth profiling was performed on glass sections cut at 30° angle to the leached surfaces. 20–24 elements were recorded simultaneously as selective and quantifiable mass spectra, under the following analytical conditions:

- *Primary ions*: 0^-; beam current ca 200 nA, accelerating voltage 12 kV; probe diameter 50 μm, raster 75 μm, step length 25 μm.

- *Secondary ions*: Positive. Sampling time per mass number in each spectral cycle: 1 s. Analyzed area: 30 μm diameter.
- *Chief assets (approximated figures)*: In-depth resolution ca 10 μm. Limits of quantitative detection (depending on element) ca 10^{-2}–10^2 ppm.

3. Results

3.1. In-depth concentration profiles; characteristic sub-surface zones

For each of the two glasses several sets of profiles were recorded. The elemental ion currents of the mass spectra were quantified to the respective mole concentrations according to an earlier described [4,5] procedure. Figs. 1 and 2 typify the in-depth distributions of concentrations as obtained, respectively, for SON68 and SM513. For each set of profiles, normalization was made on the semi-arbitrary assumption of Al as an element nearly 'inert' to leaching. The acceptability of such premises has been discussed in earlier work [5,6].

The figures exhibit the characteristic features of the 'selective' leaching behavior [4,10]. In the reacted glasses successive sub-surface layers may be distinguished; in recent publications [1,5,6,10], these are conveniently alluded to as 'precipitation zones' α and 'depletion zones' β. The α_1 and α_2 sub-zones are usually understood [1,4] as produced by reactions between the leached-out constituents and the outside fluid. Of the three depletion sub-zones, β_0 ('main depletion layer'), β_1 ('gradient layer') and β_2 ('diffusion layer'), β_0 (sometimes also referred to as 'gel') is of particular significance in the evaluation of elemental leaching kinetics. It constitutes a residue of the near-surface portion of the original specimen, selectively depleted in 'mobile' elements such as boron and the alkalis. The loss of such elements, and of elements of intermediate leachability, is partially compensated by an influx of hydrogen and other abundant components of the leachant. Of the other two, more moderately depleted sub-layers, β_1 contains the main reaction front of the glass in interaction with the leachant, and β_2 is chiefly characterized by initial substitutions of mobile elements by hydrogen.

3.2. Reacted depths and element concentrations from the SIMS profiles

In Table 1 is listed the effective thickness of the depletion layers, mean of observation from three sets of profiles for each glass. These SIMS results are compared to reacted depths in the same specimens as observed by electron probe (EPMA) imaging of the glass cross-sections [8] and as calculated from parallel mass loss measurements. The density assessment for this calculation
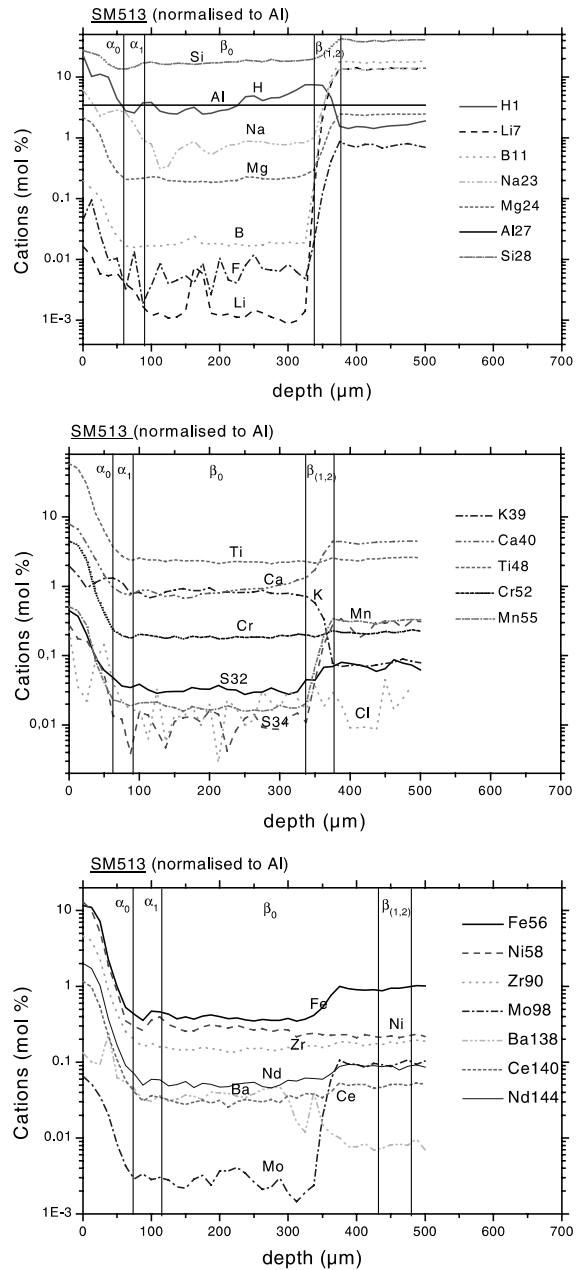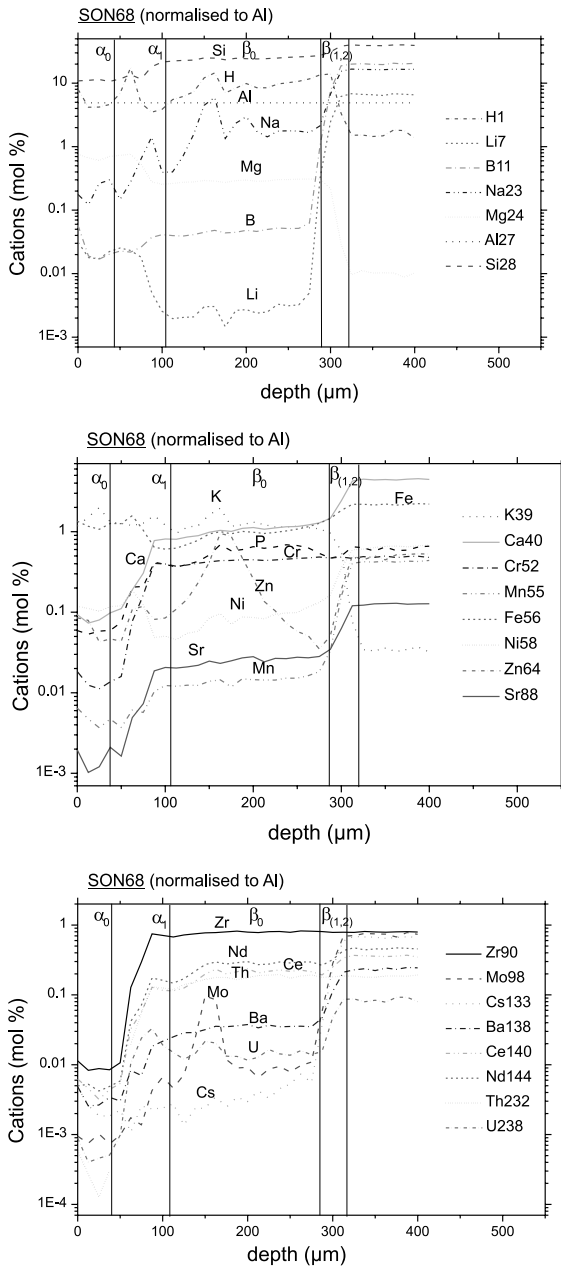
Fig. 1. In-depth profiles (quantitative SIMS) of element concentrations through leached layers on SON68 glass after 5 year burial in Boom Clay at 85°C.

Fig. 2. In-depth profiles (quantitative SIMS) of element concentrations through leached layers on SM513 glass after 5 years' burial in Boom Clay at 85°C.

was based on the chemical composition of the gel (see $c_{\beta 0}$ column in Table 2), and could be approximated to ca 50% of the bulk density for SON68, ca 40% for SM513.

Table 2 presents the concentrations after exposure (each a mean from three profiles) in the major depletion layer β_0, as well as the fractional extent of the concentrations after 5 years' leaching related to those in

Table 1
Leached depths (layers $\beta_0 + \beta_1$, μm) in two HLW glasses after 5 years' burial in Boom Clay at 85°C

From:	SIMS	(EPMA[8])	(Weight loss[8])
SON68	250 ± 15	(220)	(300)
SM513	320 ± 20	(350)	(400)

Table 2
Concentrations of elements (mol% related to sum of cations in bulk glass) in unleached material and in major depletion layers (β_0) of two HLW glasses after 5 years burial in Boom Clay at 85°C

	SON68			SM513		
	c_{bulk}	$c_{\beta0}$	Rating	c_{bulk}	$c_{\beta0}$	Rating
Li	6.85	0.002	→→→	13.1	0.002	→→→
Na	11.45	1.6	→→	13.75	0.6	→→→
K	(0.04)	1.0	<<	(0.06)	0.8	<<
Cs	0.45	0.002	→→→	0.04	0.001	→→→
Mg	(0.01)	0.3	<	2.40	0.2	→→→
Ca	3.75	0.85	→→	3.80	0.7	→→
Sr	0.165	0.03	→→			
Ba	0.20	0.03	→→	0.03	0.04	<
Zn	1.60	1.1	*			
B	20.7	0.05	→→→	17.6	0.02	→→→
Al	5.0	5.0	* * *!	3.3	3.3	* * *!
Si	39.2	23.6	→ !	40.9	16.4	→ !
P	0.2	≅0.2	* * *			
Ti				2.65	2.3	**
Zr	1.15	1.15	* * *	0.305	0.25	**
Cr	0.345	0.3	**	0.165	0.15	**
Mo				0.09	0.002	→→→
Mn				0.353	0.015	→→
Fe	1.90	0.55	→→	0.98	0.4	→
Ni	0.285	0.06	→→	0.265	0.25	**
Ce	0.30	0.2	→	0.050	0.03	→
Nd	0.5	0.3	→	0.075	0.04	→
Th	0.12	0.1	**			
U	0.095	0.04	→			
		Σ: 36.5%			Σ: 25.5%	
H	≅1	≅10	<<	≅1.5	≅6	<<
F				1.85	0.01	→→→
S				0.265	0.015	→→

Element ratings: 'Inert' (∗ ∗ ∗); 'Mobile' (→→→); 'Influx' (<<<).

unleached glass. All concentrations in the gel are expressed in mole percent of the sum of cations in pre-burial glass.

4. Discussion

From Figs. 1 and 2 as well as Tables 1 and 2 it may be seen that the two HLW glasses, although somewhat different in elemental compositions, exhibit essentially similar long-term leaching tendencies in interaction with Boom Clay at 85°C.

In regard of the depth of the corroding attack, the present results for both glasses agree satisfactorily with those computed from earlier weight loss measurements [6,11] when related to the same temperature. Corrosion is found to extend somewhat deeper (by some 25%) in SM513 than in SON68. Analogously (see Table 2) the total amount of cations leached from SM513 is greater than that from SON68, and the loss of the main network element (Si) from the Pamela-type glass is correspondingly greater than from the Cogéma glass. Thus al-

though the leachabilities of the two HLW glasses are seen to be of the same order of magnitude, SON68 shows better resistance to corrosion in Boom Clay environment than does SM513.

The time dependence of the extent of corrosion of HLW glasses in Boom Clay has been studied particularly by weight-loss measurements [6–8]. Leaching was performed under laboratory conditions for exposures up to 2 years, and in geological burial between 2 and 7.5 years. The results for SON68 and SM513, with the weight-loss figures recalculated (via density of gel) to respective thickness of corroded layers ($\beta_0 + \beta_1$) are illustrated in Fig. 3.

For SON68 the leached depth was found to grow initially about proportionally to root of exposure time ($\sim t^{1/2}$), which implied a diffusion-steered substitutional mode of leaching. At longer duration (beyond ca 1 year), however, an accelerated process suggested itself, the rate of attack gradually tending to a linear time dependence ($\sim t^1$), which rather indicates a congruent leaching mechanism [7]. Corresponding weight-loss results for SM513 are available only from the long-term burial
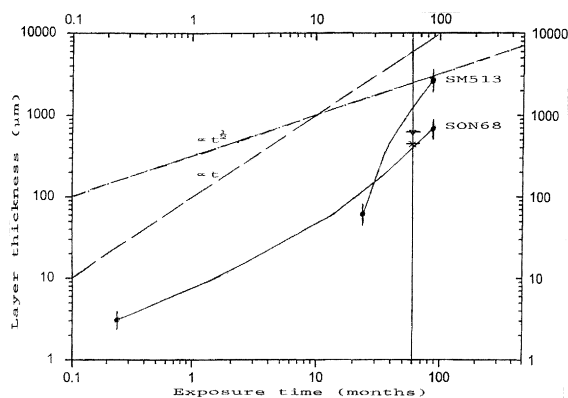
Fig. 3. Reacted depths of two HLW glasses corroded in contact with Boom Clay, as function of exposure time. Whole drawn curves: earlier work at 90°C; computed from weight-loss measurements [6]. Points at 60 months' exposure: from weight-loss work [8] at 85°C, extrapolated to 90°C; ($\times$) SON68; (∇) SM513.

studies. Although the present results (including their indications of difference in performance between the two glasses) show acceptable agreement with the weight-loss data as well as with earlier SIMS data, some anomalies could be suspected in the behavior of SM513 at extended duration of burial in clay: the extent of attack appeared to increase very fast with time (about $\sim t^4$). As an explanation it has been suggested [11] that the SM513 glass in interaction with Boom Clay exhibits secondary phase formation, which might affect the interpretation of the weight loss results. SIMS and EPMA studies have tended to corroborate such a hypothesis.

In purely selective-substitutional mode of leaching, 'mobile' elements (among which, in the Boom Clay environment, are predominantly boron and the alkali metals) are avidly removed by the leachant, while 'network forming' elements, such as Si or Al, remain preserved in the residual network of the gel [1]. Such behavior has been frequently observed for HLW glasses leached in other burial environments [4,10]. Here, however, it is evident that at prolonged exposure to Boom Clay not only the 'mobile' elements are lost, but even the main network component of both glasses, Si, becomes clearly impoverished. This seems likely to cause a gradual transition from purely selective to a congruent mode of leaching. A long-term extrapolated prediction of the progress of corrosion should therefore probably be based on a linear proportionality to exposure time, rather than a $t^{1/2}$ relationship. On the other hand, the gradual cooling of the repository, and the corresponding decrease in the rate of the dissolution reaction, should also be taken into account in such a prediction.

When comparing the behavior of the two glasses, it appears (in qualitative agreement with earlier experience

[2,4,6]) that increasing content of Al up to a point tends to enhance resistance to leaching, whereas greater concentrations of alkalis accelerate dissolution. The qualitative difference in performance between SON68 and SM513 might conceivably also be influenced by the presence of F and S in the latter, possibly contributing to the formation of unstable surface phases.

As for the different elemental tendencies in leaching, Table 2 shows a distinct category of mobile, fast-leaching, elements ($\rightarrow\rightarrow\rightarrow$). Another easily discernible group is that of relatively 'inert' elements ($* * *$), showing good resistance to leaching and essentially preserved in the residual gel network. Other elements may be classified as of intermediate leachabilities. Counted in the first group may be such elements which in the β_0 layer are reduced to 5% or less of their bulk concentrations. According to the Table, this includes Li, Na, Cs, B (in SM513 also Mo, Mn, F and S, not present in the other glass). The inert group, arbitrarily defined as elements preserved in the gel to 80% or more of the original concentration, includes Al, Ti, Zr, Cr and Th, probably also P. Within the group of 'intermediate' elements we note Si, Fe, but also U and the rare elements Nd and Ce. This information on U and the rare earth elements may be an indication for the leaching behaviour of the four- (Np, U) and tri-(Pu, Am) valent actinides in the fully active glass when in contact with the clay.

A particularly significant feature in both glasses, as mentioned above, is that Si belongs to the intermediate group, in distinction to the usual behavior of most HLW glasses in other leaching environments. The sizable leach-out tendency of Si, together with the rapid growth of the corroded layer (by about an order of magnitude faster than in other geological repositories) appears to be distinctive features of glasses buried in clay [4]. Nevertheless, the Boom Clay rock underneath SCK·CEN appears to be a promising host repository for the vitrified high-level waste. Among the advantages one may quote the low diffusive penetrability of clay, along with its homogeneity and plasticity.

It may be noted that Table 2 lists nearly 30 elements, some of them in concentrations as low as in the $10^{-3}\%$ range. Thanks to the sensitivity of the step-scan SIMS mode of profiling, these minor elements could be identified and defined free of confusing analytical scatter.

5. Conclusions

- A SIMS step-scan technique has been used to record elemental in-depth concentration profiles in corroded layers on two HLW glasses, SON68 (Cogéma type) and SM513 (Pamela type). The glasses had been subjected to 5 years' burial in Boom Clay at 85°C. The results of profiling were compatible with earlier long-term leaching studies in clay environment;

however, the introduction of the step-scan mode of analysis allowed improved precision and reproducibility.

- Although in most respects the two glasses displayed qualitatively similar behavior, SON68 showed better resistance to leaching than SM513. The rate of leaching in SM513 is by about 30% faster than that in SON68. In SM513 the residual total of cations in the leached-out gel (β_0 layer) is only ca 25% of that in unleached bulk glass, compared to ca 37% in SON68. In both glasses the major network forming element, silicon, is found to be significantly impoverished in the β_0 layer, in SON68 to about 60%, in SM513 as low as about 40% of the bulk Si concentration.

- Similar to earlier experience, a 'selective-substitutional' mode of leaching is manifested by nearly complete elimination of mobile elements (here particularly B, Li, Cs) from the gel layer, while relatively inert elements remain essentially preserved in the reacted glass. However, the sizable loss of the main network element (Si) suggests that in Boom Clay environment a competing 'congruent' leaching mechanism also becomes operative at extended exposure times. This is corroborative to implications from weight-loss studies of the time dependence of leaching attack on glasses in clay environment.

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