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Aqueous corrosion of lanthanum aluminosilicate glasses: influence of inorganic anions

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Abstract

In order to confine specific long-life actinides, originating from high-level nuclear wastes, lanthanum aluminosilicate glasses are considered. The aqueous corrosion behavior of these glasses is studied under static conditions ($T = 96$ °C, duration between one and six months, glass surface area/leachate volume, $S/V = 0.3$, 50 and 500 cm^{-1}) by means of solution analysis (ICP-MS and spectrophotometry) and solid analysis (X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry). Tests performed at high S/V ratio lead to silicon releases of 10^{-3} $\mathrm{mol\,l^{-1}}$ while lanthanum releases reach $10^{-4.5}$ $\mathrm{mol\,l^{-1}}$. Phosphate anions are found to modify the dissolution, as an amorphous lanthanide phosphate is evidenced at the glass surface after the corrosion experiment. The lanthanide releases decrease in presence of phosphate, but the matrix dissolution process is not reduced. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the case of the separation of long-life actinides (Am, Cm) and storage in specific glass matrix, new glasses compositions must be studied [1–5]. Lanthanum is used to simulate trivalent actinides. Within this framework, lanthanum aluminosilicate glasses can be considered as analogues of aluminosilicate glasses containing transuranium elements (Am, Cm). Lanthanide aluminosilicate glasses have been already studied because of their high mechanical properties [6–17]. However, concerning the chemical durability of these glasses, only a few studies have already been published, giving encouraging results. A high alkaline durability was noted in aluminosilicate glasses containing La_2O_3 and Y_2O_3 [13]. A protective effect of Nd has been noted in studies performed on the aqueous alteration of Nd–Si–Al–O glasses [1–3]. Moreover, the durability towards aqueous alteration of lanthanide borosilicate glasses for plutonium immobilization is 50 times better than the high level waste glasses currently produced [4,5].

Dissolving nitrogen in an oxide glass network modifies various physical and chemical properties [18–23]. Elastic moduli, T_g, hardness and resistance to devitrification increase with increasing nitrogen content. These improvements are due to less polarized Si–N bonds in comparison to the Si–O bonds. If the influence of nitrogen on the chemical durability of glasses is not well known [23], it has been shown that adding nitrogen to aluminosilicate glasses does not affect its alteration

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Table 1
Chemical composition of glasses in mol%

Glasses	Density	Chemical composition (mol%)					Formula
		SiO_2	Al_2O_3	AlN	La_2O_3	Y_2O_3	
LaO	4.0	60.0	20.0		20.0		$Si_{0.6}Al_{0.4}La_{0.4}O_{2.4}$
LaN	4.1	55.0	9.0	18.0	18.0		$Si_{0.6}Al_{0.4}La_{0.4}N_{0.2}O_{2.1}$
YLaO	3.8	60.0	20.0		10.0	10.0	$Si_{0.6}Al_{0.4}La_{0.2}Y_{0.2}O_{2.4}$
YLaN	3.9	55.0	9.0	18.0	9.0	9.0	$Si_{0.6}Al_{0.4}La_{0.2}Y_{0.2}N_{0.2}O_{2.1}$

kinetics and that is a satisfactory alteration tracer for this type of glass [24].

In case of geological repository of vitrified nuclear wastes, alteration mechanisms of borosilicate glasses but also of aluminosilicate glasses might be understood [25–39]. Most of the knowledge of the glass dissolution process comes from borosilicate studies: hydrolysis reactions of the glass network take place, but also recondensation reactions and precipitation of secondary phases. Alteration products are formed at the glass/water interface: an amorphous gel and mineral phases (silicates and rare-earth phosphates). When the medium is dilute, dissolution of glass is congruent; then steady-state concentrations are observed and the glass dissolution rate is decreased. Recent studies have shown that the alteration kinetics are not controlled by the solution chemistry alone. The alteration film has a major role in controlling the reaction, acting as a diffusion barrier. These protective properties seems to depend on the conditions of the film formation [32,36].

The different stages of the glass dissolution can be reached by modifying the S/V ratio. Experiments performed at low S/V ratio (dilute medium) inform about the initial conditions of the dissolution. While experiments performed at high S/V ratio inform about the dissolution at a high reaction progress, in saturation conditions, in particular with respect to Si. Moreover, low S/V conditions favor the formation of an alteration layer, which allow a better analysis on its protective power, while high S/V conditions, on the contrary favor the solution saturation.

Some anions, present in natural groundwaters, form complexes or solid phases with lanthanides and modify the dissolution of glasses. The aqueous geochemistry of the rare-earth elements has been reviewed by Wood [40]. It has been shown that carbonate complexes were predominant in a near-neutral to basic pH [41,42]. The formation of complexes with phosphate ions may also be important [43–47]. Some solid phases such as $Ln(OH)_3$, $LnOHCO_3$, $Ln_2(CO_3)_3$, $LnPO_4$, may be formed, which could control the lanthanide solubility [47–54].

The aqueous chemistry of lanthanide in glass/water systems was investigated [55–58]. It was found that 98% of the lanthanide released from the glass were retained in the alteration products on the glass surface and the retention was enhanced by the presence of phosphate in the solution. Recently, a protective effect of phosphate has been revealed at low S/V and in acidic medium, while at high S/V and in basic medium, on the contrary, phosphate have been found to increase the glass dissolution process. Moreover, calcium and rare-earth phosphate are found to be accumulated at the outer part of the alteration layer [36].

This paper is focussed on the dissolution of lanthanide aluminosilicate glasses in the presence of inorganic anions, which are present in groundwaters: sulfate, carbonate and phosphate. The glasses studied are labeled LaO, LaN, YLaO, YLaN. Their compositions are given in Table 1. For all these glasses, a high chemical durability has been previously shown, towards aqueous alteration in deionized water [59,60]. Static tests ($S/V = 0.3$ cm^{-1}, $T = 96$ °C) and Soxhlet tests were performed during one month. In this work, leaching tests have been performed under static conditions in presence of carbonate, sulfate and phosphate anions, with a low S/V and then with a high S/V ratios.

2. Experimental

2.1. Synthesis

Synthesis of glasses in the system Y–La–Al–Si–O–N glasses has been described previously [59]. Glasses are homogeneous (EDX analysis). Monoliths samples are prepared by hot pressing in a graphite vessel at 850 °C for 30 min. Monoliths (diameter 2 cm, thickness 0.4 cm) are polished in different stages (6 μm—SiC powder and 1 μm—C diamond powder). Glass powders are crushed (<75 μm and 75–150 μm) and then rinsed three times in water and then three times in acetone. Specific area has not been measured.

2.2. Corrosion tests

The corrosion experiments are performed in a Teflon recipient (savillex). Each leaching test is duplicated (except for the $S/V = 0.3$ cm^{-1} tests). Experiments are performed using glass surface area (S) (assuming equal to geometrical surface) to solution volume (V) ratios of 0.3 cm^{-1} (using monoliths), 50 and 500 cm^{-1} (using powders). Duration of the experiment is 1, 3 or 6 months. The temperature is chosen to be 96 °C (in order to accelerate the kinetics). It should be observed that teflon being permeable, there will be an equilibrium with atmospheric CO_2 within hours. When the temperature is increased, the system takes up CO_2 and cause the pH to decrease. When the system is cooled to room temperature, pH is measured at 25 °C but the inorganic carbon is still from 96 °C. Temperature corrected pH measurements would have been more appropriate. In fact, the absence of CO_2 partial pressure control is an experimental limitation which prevent any discussion about lanthanum solubility as well as about pH variations.

In the case of tests using glass powders, a glass quantity of 2 g is used with a volume of leachant (deionized water) of 5 ml and 20 ml respectively. Water is also charged with some inorganic anions: carbonate, phosphate and sulfate using 5×10^{-3} mol l^{-1} solutions of $NaHCO_3$ ($pK_1 = 6.3$ and $pK_2 = 10.3$), Na_2HPO_4 ($pK_1 = 2.1, pK_2 = 7.2$ and $pK_3 = 12.4$) and Na_2SO_4 salts respectively. In these cases, the initial pH was adjusted to 8, by adding KOH or HNO_3.

2.3. Analyses of leachates

After cooling, the pH of the leachate is measured with a combination glass electrode. The leachate is filtered (0.45 μm), acidified with Normatom nitric acid (65%) to pH about 2, and kept in a polypropylene vial. It may be noted that this filtration is not sufficient to remove colloids from the solution. Solutions should have been ultrafiltrated to remove the colloidal part. The solution is analyzed in order to detect La, Y and Al by ICP-MS. Each analysis is repeated three times and the relative error of the measurement is about 1–2%. The relative error introduced by diluting the leachate is below 10%. Spectrophotometry analysis is used to determine silicon concentration in the leachate, according to the molybdate blue method. Relative errors on aqueous concentration were estimated less than 10%. Ion Chromatography is used to determine ammonium concentration in the leachate. Ammonium is formed by the hydrolysis of the Si–N bonds. Relative errors on aqueous concentration are estimated less than 10%.

For high S/V experiments, results presented are the average of two leaching tests. Normalized releases are calculated from the relation

$$N_i = \frac{[i]V}{f_i S}, \text{in g/m}^2,$$

where $[i]$ is the ith element concentration (mg/l), f_i is the weight percent of the ith element, V is the leachate volume, S is the glass surface area (geometrical area).

The normalized mass loss is usually calculated for mobile elements (boron, alkaline) in order to known the glass quantity altered. For the others elements, it is an estimation of the retention power of the alteration products.

2.4. Analysis of solid corrosion products

2.4.1. X-ray photoelectron spectroscopy

The exciting X-ray source is a non-monochromatic AlK_α (1486.6 eV). Pressure in the sample chamber is kept less than 2×10^{-10} mbar. Surface and thickness analyzed are about 1 cm$^2 \times 20$ Å. The Si_{2s}, Al_{2p}, $La_{3d5/2}$, Y_{3d} and O_{1s} percents are calculated after correction by the ionization cross-sections.

2.4.2. Rutherford backscattering spectrometry

The solid is analyzed by Rutherford backscattering spectrometry (RBS). This technique is used to analyze the repartition of heavy elements at the surface (the thickness analyzed is between 2 and 5 μm) [61]. RBS experiment has been performed on the Van de Graaff accelerator at INSTN (CEA, Saclay). Helium-4 ions of an incident energy of 1.8 MeV are backscattered from the sample at an angle of 150°. Backscattered ions are collected with a surface barrier detector. The diameter of the incident beam is 0.5 mm^2. The beam current is 5 nA and a charge of 10 μC has been integrated. Simulation of the spectrum are performed with the RUMP software package [62].

3. Results

3.1. Corrosion of an YLaN and YLaO glasses at low S/V ratio (0.3 cm^{-1})

Leaching experiments have been performed on YLaN and YLaO glasses at $S/V = 0.3$ cm^{-1}, in pure water during one to six months. Some experiments in water charged with phosphate, carbonate or sulfate anions, have been performed on a YLaN glass during three months.

3.1.1. Solution analysis

In pure water, the silicon release (Table 2) is about $10^{-4.4}$ mol l^{-1}. The aluminum release is lower at about 10^{-5} mol l^{-1}. Lanthanum and yttrium releases are well below at about 10^{-7} mol l^{-1}, except in the three-month experiment where the releases reach about 10^{-5} mol l^{-1}. Nitrogen release increases from 10^{-5} to 10^{-4} mol l^{-1} between one and six months. No significant difference is noted concerning elemental releases, between the YLaO

Table 2
Silicon, ammonium, aluminum, lanthanum and yttrium releases in the leachates ($S/V = 0.3$ cm^{-1})

Glasses	Duration (month)	Anions	pH	Log[M]					NL[M] g m^{-2}			
				Si	Al	La	Y	N	Si	Al	La × 10^{-2}	N
YLaN	1	Pure water	7.3	−4.2	−4.9	−6.9	−7.2	−4.8	0.3	0.1	0.2	0.3
	3	–	6.8	−4.4	−5.5	−5.0	−5.4	−4.5	0.2	0.03	19	0.6
	6	–	7.8	−4.4	−4.5	−7.8	−7.4	−3.8	0.2	0.3	0.03	2.9
YLaO	1	–	8.4	−4.6	−5.0	−7.6	−4.5		0.1	0.08	0.03	
	3	–	7.5	−4.3	−5.2	−5.2	−5.7		0.3	0.06	11	
	6	–	7.2	−4.5	−4.8	−6.8	−6.6		0.2	0.15	0.3	
YLaN	3	CO_3^{2-}	10.2	−3.7	−4.7	−6.2	−6.8	[a]	1.2	0.17	1.2	[a]
	3	SO_4^{2-}	8.7	−4.5	−4.8	−6.6	−7.6	[a]	0.2	0.15	0.4	[a]
	3	PO_4^{3-}	8.4	−3.5	−4.4	−7.1	−7.6	[a]	2.0	0.36	0.1	[a]

[a] Below the detection limits due to the presence of large sodium concentrations.

and the YLaN experiments. Since nitrogen can be considered as a tracer of the glass corrosion, normalized nitrogen losses are given. They increase from 0.3 to 2.9 g/m^2 between one and six months of alteration with pure water.

Concerning the influence of the anions, an increase in the silicon release is noted in the presence of phosphate and carbonate anions (Table 2). In the case of carbonate test, it might be due to the pH largely higher than in the case of the pure water test. In the case of phosphate, a pH effect can not explain the increase of the silicon release. The modification of the alteration layer, as seen later, is more probably involved.

Unfortunately, the nitrogen concentrations in presence of anions are lacking, because of the proximity of a very important sodium peak by ionic chromatography. Measurements are below the detection limits and experiments should be performed for duration longer than three months with lower sodium concentrations. The nitrogen releases, since it is the only reliable tracer, would have allowed some conclusions about the influence of anions on the dissolution rate of these glasses.

The anions concentrations after interaction with glass have not been reported, but very small changes were expected (below 1%) so no information could be extracted from these measurements.

3.1.2. Solid analysis

The X-ray photoelectron spectrum of an YLaN glass is reported in Fig. 1(a). The O_{1s} photoelectron line is located at 531.5 ± 0.1 eV. The Al_{2p} photoelectron line is at 74.1 ± 0.2 eV. The La_{4d} doublet is located around 105.8 ± 0.2 and 102.5 ± 0.2 eV. The Si_{2p} photoelectron line overlaps with the $La_{4d5/2}$ one at 102.5 eV. The Si_{2s} photoelectron line is at 153.2 eV. The N_{1s} photoelectron line is located at 398.0 eV, covered with the Y_{3s} signal. The $La_{3d5/2}$ core photoelectron line is located at 835.6 ± 0.3 eV. A $La_{3d5/2}$ satellite is about 3.5 eV towards higher binding energy due to the charge transfer between the oxygen O_{2p} and the lanthanum La_{4f} [63].

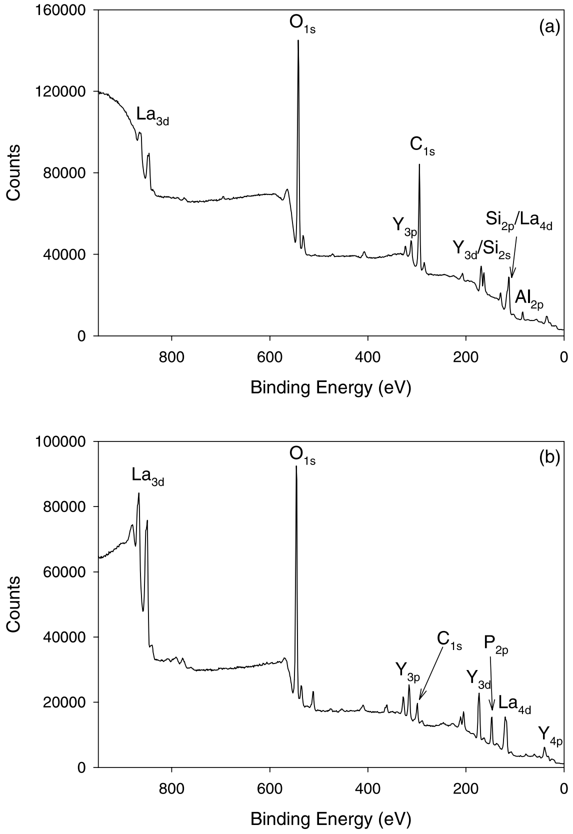

Fig. 1. X-ray photoelectron spectra of an YLaN glass before (a) and after (b) a three-month leaching test ($S/V = 0.3$ cm^{-1}) in phosphate charged water.

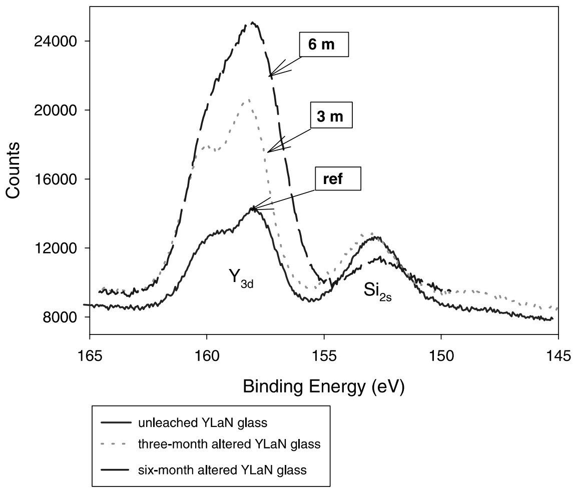

Fig. 2. X-ray photoelectron spectra (Y_{3d}–Si_{2s} zone) of an YLaN glass before and after a three-month and six-month leaching test ($S/V = 0.3$ cm^{-1}) in pure water.

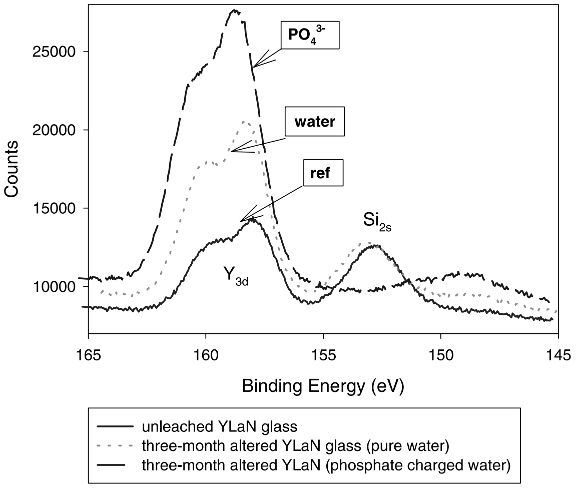

Fig. 3. X-ray photoelectron spectra (Y_{3d}–Si_{2s} zone) of an YLaN glass before and after a three-month leaching test ($S/V = 0.3$ cm^{-1}) in phosphate charged water.

The spin–orbit splitting between the $La_{3d5/2}$ and $La_{3d3/2}$ is about 17 eV.

The Y_{3d} photoelectron line position is noted at 158.3 and 160.0 eV due to the $Y_{3d5/2}$ and $Y_{3d3/2}$ states respectively.

In Fig. 2 are reported the X-ray photoelectron spectra (Y_{3d}–Si_{2s} zone) of an YLaN glass, three- and six-month altered in pure water. The glass surface is progressively enriched with yttrium. In Table 3 are reported the intensities of the photoelectron lines in YLaN and YLaO glasses, corrected by ionization cross-sections. The Al_{2p} and Si_{2s} lines intensities decrease as a function of time, while the O_{1s}, La_{3d} and Y_{3d} lines intensities increase. The glass is continuously dissolved and lanthanides, very few soluble are recombined at the glass surface.

In Figs. 1(b) and 3 are reported the X-ray photoelectron spectra of an YLaN glass altered in a phosphate charged water (survey spectrum and Y_{3d}–Si_{2s} zone). In presence of phosphate anion, the silicon and aluminum photoelectron lines are below the detection limits (Table 3), while phosphorus is observed (133.4 eV) at the glass surface (Fig. 1(b)). The yttrium retention at the glass surface seems to be enhanced (Fig. 3). The P concentrations in solution should have been indicated to obtain an accurate phosphorous balance. Nevertheless, the formation of a lanthanide phosphate layer, with a 150 nm thickness, as observed later in RBS analysis, needs less than 1% of the P initially present in the solution. In the case of a leaching test in a carbonate or sulfate charged water, the glass surface composition contains less silicon than in the case of pure water (Table 3).

Table 3
Intensities (%) of the photoelectron lines before and after the alteration process in YLaN and YLaO glasses ($S/V = 0.3$ cm^{-1})

Glasses	Duration (month)	Anion	Al_{2p} (%)	Si_{2s} (%)	O_{1s} (%)	Y_{3d} (%)	$La_{3d5/2}$ (%)	P_{2p} (%)
YLaO	Unleached		8.8	17.3	68.1	3.3	2.4	
	1	Pure water	6.5	11.8	71.5	5.7	4.4	
	3	–	6.6	9.4	73.3	5.7	5.0	
	6	–	6.2	8.7	72.1	7.2	5.7	
YLaN	Unleached		10.1	18.5	64.8	4.0	2.5	
	3	Pure water	7.6	12.5	70.8	5.8	3.2	
	6	–	4.5	8.7	72.8	9.2	4.7	
YLaN	3 m	CO_3^{2-}	6.8	4.4	75.4	8.5	4.8	
	3	SO_4^{2}	6.3	3.2	76.6	7.4	6.3	
	3	PO_4^{3-}	0	0	69.8	7.7	7.1	15.3

The analysis of the altered glass surfaces by X-ray photoelectron spectroscopy (XPS) reveals that phosphate anion seems to increase the yttrium and lanthanum retention at the glass surface, likely because of the formation of lanthanide phosphate at the glass surface. The influence of the anions carbonate and sulfate on the glass alteration process is not obvious.

An RBS experiment is performed using a millibeam (0.5 mm^2) of helium-4 ions [61]. The RBS spectrum of a reference YLaN glass (Fig. 4(a)) consists of several steps which characterize yttrium, lanthanum, silicon/aluminum, and oxygen respectively. A carbon deposition on the reference YLaN glass is used to allow charge conduction, while copper is used for the altered glass (for best quality of the scanning electronic microscopy). The spectrum of the YLaN corroded glass in presence of phosphate, is very different from the reference one (Fig. 4(b)). Yttrium and lanthanum steps are overlapped with a sharp peak, revealing an yttrium and lanthanum enrichment at the glass surface. A new peak is observed, which characterizes the presence of phosphorus at the glass surface. The simulation of this spectrum (code RUMP), suggests that the altered glass surface is constituted of a layer of lanthanum and yttrium phosphate, the thickness of which is about 150 nm. In presence of carbonate or sulfate, the RBS experiment has not been done since XPS experiment reveal the absence of these anions from the glass surface. Combination of XPS and RBS results show that, in presence of phosphate anions, an altered layer of about 150 nm is formed, constituted of an amorphous (from an X-ray diffraction analysis) lanthanum and yttrium phosphate. This layer may have a protective role in the glass alteration but, probably, less effective compared with a layer formed in a pure water medium.

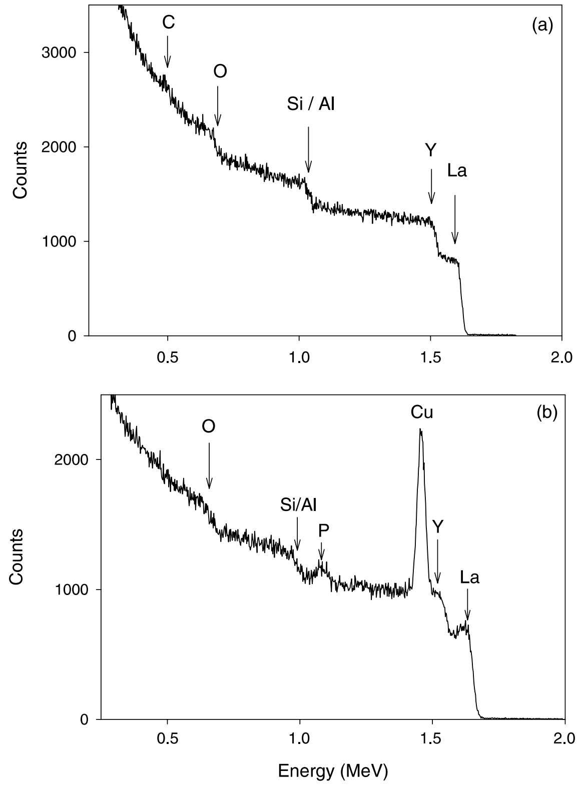

Fig. 4. Rutherford backscattering spectra of an YLaN glass (a) before and (b) after the three-month leaching test in phosphate charged water.

MEB analysis is not reported because no alteration products could be observed. TEM analysis would have been very useful in such studies to provide more data on the nature of the glass alteration products, as analyses performed by TEM and EDS on glass cross sections by Gin et al. [36], which shows the formation of an outer alteration layer, rich in P, rare-earth and Ca.

3.2. Corrosion of glasses LaO/LaN and YLaO/YLaN at high S/V ratio (50 and 500 cm^{-1})

3.2.1. Solution analyses

3.2.1.1. Deionized water. Leaching experiments are performed on glass powders of different compositions, with S/V ratios of 50 and 500 cm^{-1}. The solution results are reported in Table 4.

The final measured pH depends on the glass composition (Table 4). The yttrium for lanthanum substitution and the nitrogen for oxygen substitution lead to an increase of the final pH. The final pH is about 6 in an LaO glass and about 9 in an YLaN glass. The nitrogen release, under the ammonia form, explains the higher pH values measured in the case of oxynitride glasses.

At $S/V = 50$ cm^{-1}, silicon releases are about $10^{-3.7}$ mol l^{-1} and are not pH dependant. Aluminum release increases when the pH increases. Lanthanum and yttrium releases are about 10^{-5} mol l^{-1}, showing a quite high total lanthanides release (colloid part and solution part).

Increasing the S/V ratio (from 50 to about 500 cm^{-1}) increases of the silicon release to $10^{-3.1}$ mol l^{-1}. The lanthanum release also increases to $10^{-4.5}$ mol l^{-1}, as the yttrium one.

Besides, important nitrogen releases are observed: $10^{-3.8}$ mol l^{-1} for LaN glass at $S/V = 50$ cm^{-1}, and $10^{-3.5}$ mol l^{-1} for $S/V = 500$ m^{-1}. Higher releases are observed for YLaN compositions ($10^{-3.1}$ and $10^{-2.8}$ mol l^{-1} for $S/V = 50$ and 500 cm^{-1}). But it should not be concluded that YLaN compositions are less durable, since nitrogen may have been lost during preliminary washing steps. It may be added that more reliable nitrogen measurements should be done on glasses which have not been washed in water.

Table 4
Silicon, aluminum, lanthanum, yttrium and ammonium releases after a three-month leaching test ($S/V = 50$ and 500 $\mathrm{cm^{-1}}$)

S/V		50 $\mathrm{cm^{-1}}$					500 $\mathrm{cm^{-1}}$				
Glasses	Anions	pH (25 °C)	log [Si]	log [Al]	log [La] (log [Y])	log [N]	pH (25 °C)	log [Si]	log [Al]	log [La] (log [Y])	log [N]
LaO	Pure water	6.4	−3.7	−4.9	−5.5		5.9	−3.3	−5.8	−4.5	
YLaO	–	6.9	−3.8	−4.8	−5.0 (−5.2)		7.6	−2.9	−3.6	−4.4 (−4.5)	
LaN	–	7.3	−3.8	−4.8	−5.5	−3.8	6.9	−3.4	−4.5	−5.2	−3.5
YLaN	–	9.0	−3.7	−3.6	−6.8 (−6.8)	−3.1	8.5	−3.1	−3.4	−4.6 (−4.7)	−2.8
LaO	CO_3^{2-}	9.9	−2.8	−2.9	−5.4		10.2	−2.8	−3.0	−4.5	
	SO_4^{2-}	7.3	−3.6	−4.4	−4.6		6.1	−3.2	−5.5	−4.3	
	PO_4^{3-}	9.5	−3.1	−3.1	−6.9		9.5	−2.7	−3.0	−5.5	
YLaO	CO_3^{2-}	10.1	−3.5	−3.6	−6.6 (−6.4)		10.5	−2.8	−3.2	−4.8 (−5.1)	
	SO_4^{2-}	7.5	−3.9	−4.6	−6.6 (−7.0)		6.8	−3.6	−4.9	−4.9 (−5.5)	
	PO_4^{3-}	9.5	−2.5	−3.0	−8.3 (−8.2)		9.6	−4.9	−3.0	−5.5 (−5.7)	
LaN	CO_3^{2-}	10.0	−2.8	−2.7	−6.1	−3.5	10.1	−2.8	−3.0	−4.8	−3.5
	SO_4^{2-}	8.3	−3.8	−3.7	−6.5	−3.9	8.7	−3.3	−3.9	−4.5	−3.2
	PO_4^{3-}	9.2	−3.0	−3.1	−6.8	−3.7	10.0	−2.6	−2.9	−5.4	−3.1
YLaN	CO_3^{2-}	10.2	−3.4	−3.3	−6.6 (−6.4)	−3.0	10	−3.2	−2.6	−4.9 (−4.7)	−2.8
	SO_4^{2-}	9.3	−3.8		−8.7 (−8.5)	−3.1	9.4	−3.3	−3.6	−6.0 (−6.0)	−2.6
	PO_4^{3-}	9.2	−3.2	−3.3	−6.6 (−6.5)	−3.1					

3.2.1.2. *Influence of anions.*

Leaching experiments are performed on glass powders of different compositions, with S/V ratios of 50 and 500 $\mathrm{cm^{-1}}$, using water charged with carbonate, sulfate or phosphate anions.

Our solution results are reported on the Table 4. An important pH increase to 10 is observed in tests performed with carbonate anions. In association with this pH increase, there is an increase of the silicon release (Table 4) from $10^{-3.7}$ $\mathrm{mol\,l^{-1}}$ to about $10^{-3.1}$ $\mathrm{mol\,l^{-1}}$. The aluminum release is increased to $10^{-3.1}$ $\mathrm{mol\,l^{-1}}$. The lanthanum release is unchanged, nor the nitrogen release.

In tests performed with sulfate anions, the final pH values, the silicon, aluminum, lanthanum and nitrogen releases are unchanged.

A pH increase to about 9.5 is noted in tests performed with phosphate anions. The silicon release is increased to about $10^{-2.9}$ $\mathrm{mol\,l^{-1}}$. Lanthanum and yttrium releases are especially lower: about 10^{-7} $\mathrm{mol\,l^{-1}}$. Nitrogen releases are unchanged. In the case of YLaN composition, the influence of phosphate on the lanthanum and yttrium releases is not manifest. The same tendencies are noted for the $S/V = 500$ $\mathrm{cm^{-1}}$ experiment (Table 4).

3.2.2. *Normalized elemental releases*

In the case of leaching tests performed with a S/V of 50 $\mathrm{cm^{-1}}$, normalized silicon releases (Table 5) are in average, about 7×10^{-3} $\mathrm{g\,m^{-2}}$. They are about 2×10^{-3} $\mathrm{g\,m^{-2}}$ for $S/V = 500$ $\mathrm{cm^{-1}}$. Aluminum normalized releases are lower: in average 4×10^{-3} $\mathrm{g\,m^{-2}}$ at $S/\mathrm{V} = 50$ $\mathrm{cm^{-1}}$ and 0.7×10^{-3} $\mathrm{g\,m^{-2}}$ at S/V of 500 $\mathrm{cm^{-1}}$. Lanthanum releases are lower again: 0.5×10^{-3} $\mathrm{g\,m^{-2}}$ and 0.2×10^{-3} $\mathrm{g\,m^{-2}}$ respectively. For nitrogen, normalized releases are about 40×10^{-2} $\mathrm{g\,m^{-3}}$ at $S/V = 50$ $\mathrm{cm^{-1}}$ and 9×10^{-3} $\mathrm{g\,m^{-2}}$ at $S/V = 500$ $\mathrm{cm^{-1}}$.

For $S/V = 50$ $\mathrm{cm^{-1}}$, it is found that carbonate and phosphate anions induce an increase of the silicon releases from 7×10^{-3} $\mathrm{g\,m^{-2}}$ to about 50×10^{-3} $\mathrm{g\,m^{-2}}$. Aluminum releases are also increased to about the same value. Moreover, phosphate anions induce a strong decrease of the lanthanum release from 0.5×10^{-3} $\mathrm{g\,m^{-2}}$ to about 0.01×10^{-3} $\mathrm{g\,m^{-2}}$. Similar results are noted in the case of $S/V = 500$ $\mathrm{cm^{-1}}$. Phosphate anions do not induce a clear modification in the nitrogen releases.

4. Discussion

In low S/V experiments, solution analysis give a limited information concerning the influence of anions, since nitrogen releases, a tracer of the glass corrosion, are lacking (excess of anions $c = 5 \times 10^{-3}$ $\mathrm{mol\,l^{-1}}$). The higher silicon releases observed with carbonate is probably associated to a solubility increase

Table 5
Normalized releases of silicon, aluminum, lanthanum and yttrium releases in the three-month leachates ($S/V = 50$ and 500 cm^{-1}) (measurement uncertainty 20%)

S/V		50 cm^{-1}					500 cm^{-1}				
Glasses	Anions	pH (25 °C)	Normalized losses NL 10^{-3} $\mathrm{g\,m^{-2}}$				pH (25 °C)	Normalized losses NL 10^{-3} $\mathrm{g\,m^{-2}}$			
			Si	Al	La (Y)	N		Si	Al	La (Y)	N
LaO	Pure water	6.4	9.0	0.95	0.25		5.9	1.78	0.009	0.20	
YLaO	–	6.9	7.7	1.32	1.64 (1.11)		7.6	4.99	0.70	0.46 (0.30)	
LaN	–	7.3	6.4	0.85	0.17	21	6.9	1.37	0.16	0.017	4
YLaN	–	9.0	7.3	13.5	0.014 (0.015)	72	8.5	2.48	1.9	0.25 (0.23)	14
LaO	CO_3^{2-}	9.9	57.9	62.5	0.20		10.2	6.35	5.3	0.256	
	SO_4^{2-}	7.3	10.75	2.2	1.3		6.1	2.25	0.02	0.298	
	PO_4^{3-}	9.5	31.85	48.5	0.009		9.5	8.55	5.45	0.02	
YLaO	CO_3^{2-}	10.1	11.05	12.0	0.025 (0.042)		10.5	5.10	3.35	0.176 (0.079)	
	SO_4^{2-}	7.5	4.3	1.35	0.03 (0.0095)		6.8	1.55	0.065	0.140 (0.032)	
	PO_4^{3-}	9.5	122.9	55.55	0.0005 (0.0006)		9.6	4.7	4.75	0.06 (0.021)	
LaN	CO_3^{2-}	10.0	69.3	125.6	0.05	43	10.1	5.75	5.35	0.0935	4
	SO_4^{2-}	8.3	5.8	11.2	0.018	17	8.7	1.85	0.75	0.185	8
	PO_4^{3-}	9.2	35.6	45.1	0.0095	27	10.05	9.25	6.35	0.024	10
YLaN	CO_3^{2-}	10.2	15	28.7	0.02 (0.05)	91	10	2.3	12.3	0.139 (0.190)	14
	SO_4^{2-}	9.3	6.3	11.2	0.0002 (0.0004)	72	9.4	1.05	1.35	0.01 (0.0095)	23
	PO_4^{3-}	9.2	22.0	27.23	0.024 (0.035)	72					

with the pH. Nevertheless, in presence of phosphate, higher silicon release is also noted; the formation of a rare-earth phosphate layer is clear and its protective role seems to be less effective than in the case of the alteration layer formed in pure water, as observed by Gin et al. [36]. Experiments at low S/V, performed for duration of at least six months, with lower phosphate concentrations, would allow the nitrogen release measurement and would be very useful to conclude on the protective effect of the alteration layer.

For high S/V experiments, in tests performed with phosphate anions, an increase of the final pH at 9.5, an increase of the silicon and aluminum releases and a decrease of the lanthanum and yttrium releases are observed, while nitrogen releases are not affected. In tests performed with carbonate anions, an increase of the final pH to 10 and an increase of the silicon and aluminum releases are noted. Yttrium, lanthanum and nitrogen releases are not significantly different. Sulfate anions do not seem to modify the glass dissolution process. These experimental conditions do not favor the formation of an alteration layer and the solution chemistry is more likely to dominate the glass dissolution.

In the hypothesis of a thermodynamical control, it may be expected that phosphate solid phases, with very low solubility (about 10^{-10} and 10^{-13} $\mathrm{mol\,l^{-1}}$ at pH 9.5) will control the lanthanide release well below than hydroxycarbonate solid phases (solubility between 10^{-6} and 10^{-8} $\mathrm{mol\,l^{-1}}$). Nevertheless, our experimental limitations (pCO_2 not controlled, pH measurement at 25 °C modified by temperature and CO_2, ultrafiltration not used) prevents any discussion about lanthanide solubility. The thermodynamical control may explain the increase of silicon and aluminum releases as the pH is increased. Nevertheless, the modification of the alteration layer, notably in presence of phosphate may be also an explanation. Nitrogen releases seem to indicate that in these high S/V conditions, the role of the alteration layer is not major. Further experiments on glasses which have not been washed could allow to conclude on the role of the alteration layer.

5. Conclusion

The chemical durability of La–Al–Si–O glasses has been studied by means of static experiments with different S/V ratios, with some inorganic anions, followed by solution and solid analysis (XPS and RBS).

Experiments performed at low S/V ratio with phosphate, reveal an accumulation of phosphor and rare earth on the outer part of the alteration film which seems to be associated with a decrease its protective role compared with the case of an alteration in pure water.

High S/V experiments have shown that silicon releases reach about 10^{-3} mol l^{-1}, while La releases reach about $10^{-4.5}$ mol l^{-1}. It is found that carbonate and sulfate do not significantly influence the glass dissolution process. The presence of phosphate seems to induce the formation of lanthanum phosphate and then a decrease of the La release. The silicon release is increased, probably because both of the less protective alteration layer and of a solubility effect. Nevertheless the role of the alteration layer in these conditions seems to be weak as the nitrogen release is unchanged, whereas nitrogen is a reliable tracer.

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