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Dissolution of lanthanide alumino-silicate oxynitride glasses

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Abstract

The aqueous corrosion behavior of lanthanide aluminosilicate glasses has been studied under static conditions ($T = 96°C$, duration = 1 and 3 months, glass surface area/leachate volume, $S/V = 0.3$ cm^{-1}) by means of solution and solid analyses. It was found that these glasses exhibit a high chemical durability. The influence of yttrium, magnesium and nitrogen, which are supposed to improve the mechanical properties, on the chemical durability, has been investigated. After a one-month experiment, lanthanum and yttrium releases were found to be about 10^{-7} mol l^{-1}, while silicon and aluminum releases were about 10^{-5} mol l^{-1}. Yttrium seems to improve the chemical durability. The presence of nitrogen does not seem to modify the glass constituents releases, but seems to improve the surface state of the altered glass. XPS experiments reveal that lanthanum and yttrium are more concentrated near the surface (20–30 Å) of the glass after the leaching test. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Glass dissolution has been the subject of extensive research, because borosilicate glasses are used as confinement matrices for nuclear waste [1–9] and because groundwater is the main dissemination factor of radionucleides. It is known that an ionic exchange takes place between mobile ions such as alkaline ions and H^+, and that water molecules diffuse into the glass, react with Si–O–Si and Si–O–M, forming Si–OH silanol groups. Network hydrolysis reactions lead to the formation of an altered surface layer on the glass. Modeling of waste glass corrosion shows that the dissolution might be controlled by this hydrous gel [3] or by the activity of H_4SiO_4 [1]. The SiO_2 gel layer is enriched in insoluble elements (transition metals, actinides, rare-earths...). This gel is supposed to be formed either by in situ recombination of insoluble elements or by precipitation of solubility limiting phases. It may become a diffusion barrier against corrosion. In the field of radioactive waste vitrification, research is developing on specific conditioning of long life actinides such as (^{243}Am, ^{237}Np, ^{239}Pu) [10,11]. Assuming that rare-earth elements can be used to simulate actinides, a lanthanide aluminosilicate glass, La–Al–Si–O, could be considered as a potential specific matrix of immobilization of some long life trivalent actinides, such as ^{243}Am.

Lanthanide aluminosilicate glasses are known for their interesting mechanical properties. They are hard materials, with high elastic moduli, very durable in alkali medium [12–16]. Moreover they exhibit high glass transformation temperature ($T_g = 900°C$). The unusual properties of these glasses are not clearly understood and their structure, not well known yet, is probably highly disordered [17–21]. Although they do not contain any classical network modifiers, such as alkaline or alkaline earth ions, lanthanum and yttrium could be considered as trivalent modifier ions, with at least a six-fold coordination. The majority of the aluminum ions are tetrahedrally coordinated, but five- and six-fold coordinations are also found [14,15]. Yttrium and magnesium are known to improve the mechanical properties of the lanthanide aluminosilicate glass [18].

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Besides, the O substitution for N strengthens the glass structure and improves the physical properties of the glass, such as elastic moduli, fracture toughness and hardness [22–25]. It also increases the glass transformation temperature. However it is not yet known whether or not the chemical durability is improved by the incorporation of nitrogen [24,25].

This paper is focussed on the dissolution behavior of lanthanide aluminosilicate oxynitride glasses. Solution analyses and surface analyses are combined in order to understand the dissolution of lanthanide aluminosilicate glass and to evaluate the influence of the substitution of lanthanum for yttrium and magnesium, and of oxygen for nitrogen. The glass studied are labeled LaO, LaN, YLaO, YLaN, YMgLaO and YMgLaN. Their compositions are given in Table 1. The LaO glass is described by the formula: $La_{0.4}Al_{0.4}Si_{0.6}O_{2.4}$ and its homologous oxynitride LaN by the formula $La_{0.4}Al_{0.4}Si_{0.6}O_{2.1}N_{0.2}$. Half of the lanthanum was then substituted for yttrium or for yttrium and magnesium. Leaching tests have been performed in static conditions. Solutions were analyzed using inductively coupled plasma – mass spectrometry (ICP-MS) for La, Y and Al and spectrophotometry for Si. Solid analyses were performed using SEM–EDX (scanning electronic microscopy coupled with an X-ray microanalysis device), and Infrared spectroscopy. For the outer surface analysis (20–30 Å), X-ray photoelectron spectroscopy (XPS) was used.

2. Experimental

2.1. Synthesis of glasses

Oxides (SiO_2, Al_2O_3, La_2O_3, Y_2O_3, $MgSiO_3$) and aluminum nitride powders were mixed together and melted in a molybdenum crucible by induction heating under nitrogen atmosphere at 1400°C for 30 min. Further hot-pressing was performed in a graphite vessel at 850°C for 30 min. The exact nitrogen content was measured by chemical analysis according to a modified Kjeldahl method [26].

The amorphous character was confirmed by X-ray diffraction. Monoliths (diameter 2 cm, thickness 0.4 cm) were polished in different stages (SiC and C diamond at 6 and 1 μm).

2.2. Corrosion tests

Static corrosion experiments were performed using glass surface area (S) (assumed equal to geometrical area) to solution volume (V) ratios of $0.3\ cm^{-1}$. Duration of the experiments was 1 and 3 months. The temperature was chosen to be 96°C (in order to avoid boiling and to accelerate the kinetics). Glass monoliths (2 cm in diameter and 0.4 cm in thickness) were used with a volume of leachant (deionized water) of 20 ml. The corrosion experiments were performed in a Teflon container (Savillex, Poly Labo), placed in a controlled-temperature oven at 96°C. After reaction, the glass was rinsed with deionized water. Each leaching test was duplicated. The CO_2 partial pressure has not been controlled. Vessels are closed but not sealed, so that contamination with atmospheric CO_2 is very likely, which can lead to modification of the measured pH. Besides, this contamination could introduce some carbonate ions which play a decisive role in lanthanum and yttrium solubilities. The pH was not buffered and was then very sensitive to perturbations. These experimental limitations will prevent a complete discussion about lanthanum solubility.

2.3. Analysis of leachates

After cooling, the pH of the leachate was measured with a combined glass electrode. Temperature corrected pH measurements would have been more appropriate.

The leachate was filtered (0.45 μm), acidified with 20 μl of Normatom (Prolabo) nitric acid (65%), and kept in a polypropylen container. The solution was analyzed in order to detect La, Y and Al by ICP-MS, with a PQ 2+ – Thermo Optek instrument. Each analysis was repeated three times and the relative error of the measurement was about 1–2%. The relative error introduced by diluting the leachate was below 10%. Spectrophotometry analysis was used to determine silicon concentration in the leachate, according to the molybdate blue method (Spectroquant silicium 14794, Merck). Relative errors on aqueous concentration were estimated less

Table 1
Chemical composition of glasses in mol (%)

Chemical composition (% mol)	SiO_2	Al_2O_3	AlN	La_2O_3	Y_2O_3	MgO	Density
LaO	60.0	20.0		20.0			4.0
LaN	55.0	9.0	18.0	18.0			4.1
YLaO	60.0	20.0		10.0	10.0		3.8
YLaN	55.0	9.0	18.0	9.0	9.0		3.9
YMgLaO	57.1	19.0		9.5	4.8	9.5	3.6
YMgLaN	52.1	8.7	17.4	8.7	4.4	8.7	3.7

than 10%. Solutions have not been ultrafiltrated, as they should have been, to separate the colloid part from the solution.

2.4. Analysis of the altered layer

2.4.1. Scanning electron microscopy coupled with an EDS analysis

The surface layer was analyzed using a Cambridge stereoscan 120 scanning electron microscope (SEM) equipped with a Kevex energy dispersive X-ray spectrometer (EDX). This experiment gives information both on the morphology and on the chemical composition (probed volume 1 μm^3). Samples were observed after coating by a conducting carbon film (thickness about 300 Å) to avoid charging effects.

2.4.2. X-ray photoelectron spectroscopy

The apparatus used for XPS measurement was a VG Escalab Mark II. The exciting X-ray source was a non-monochromatic Al K_α (1486.6 eV). Pressure in the sample chamber was kept less than 2×10^{-10} mbar. Surface and thickness analyzed were about $1\ cm^2 \times 20$ Å. The intensity ratios of the photoelectron lines O_{1s}/Si_{2s}, Al_{2p}/Si_{2s}, La_{3d}/Si_{2s} and Y_{3d}/Si_{2s}, were calculated after correction by the ionization cross-sections. As our aim was to follow the evolution of these ratios produced by leaching, no attempt was made to derive quantitatively the exact elemental ratios from XPS measurements.

2.4.3. Reflection infrared spectroscopy

Infrared spectra of the samples were measured using a Fourier transform infrared spectrophotometer (FTIR Model Nicolet 550). Reflection spectra were collected with specular reflectance accessories. The angle of incidence was fixed at 41°. The IR reflection spectra were collected from 400 to 4000 cm^{-1}. All spectra are sums of 128 scans with a resolution of 4 cm^{-1}.

3. Results

3.1. Leachate analyses

Results of leachates analyses are given in Table 2. As previously stated, each leaching experiment was duplicated. The pH values indicated are those measured at the end of the experiment (after cooling). Indeed, there was a pH increase from the initial value 5.5 (Milli-Q water) to 6.2–8.6 at the end of the experiment. This pH increase indicates some leaching of the glasses. Nevertheless, the partial pressure of CO_2 has not been controlled and equilibration with atmospheric CO_2 may induce pH variations. So pH measurements are not perfectly reliable. The [Si], [Al], [La], [Y] and [Mg] concentrations are given in mol l^{-1}.

Normalized releases have been calculated from the relation $N_i = [i]V/f_iS$, in g/m^2, where $[i]$ is the i element concentration (mg/l), f_i the weight fraction of the i element, V the leachate volume, S the glass surface area (geometrical area).

The results obtained for duplicated tests are somewhat scattered. The discrepancies observed can be due to different surface roughness of samples. It could also be explained by the fact that a simple 0.45 μm filtration has been used. Ultrafiltration would have been necessary to separate colloids from the solution part, which are very likely formed with lanthanides, silica and alumina. Moreover, the absence of control of the pCO_2 may have induced possible errors on pH measurements and on lanthanide concentrations. However, some trends can be drawn, which are discussed in part 4.

Table 2
Solution analysis results ([Si] were measured with spectrophotometry, [Mg] by electrophoresis, [Y], [La] and [Al] were measured with ICP-MS)

Solution analysis results			[Si]		[Al]		[La]		[Y]		[Mg]
Glasses	Duration (months)	pH final	mol l^{-1} $\times 10^{-5}$	g/m^2	mol l^{-1} $\times 10^{-5}$	g/m^2	mol l^{-1} $\times 10^{-7}$	g/m^2 $\times 10^{-3}$	mol l^{-1} $\times 10^{-7}$	g/m^2 $\times 10^{-3}$	mol l^{-1} $\times 10^{-5}$
LaO 1	1	7.7	10.0	0.67	2.6	0.26	2.5	2.5			
LaO 2	1	8.3	13.5	0.92	6.3	0.63	0.2	0.2			
LaN 1	1	8.3	5.3	0.35	4.4	0.46	1.4	1.5			
LaN 2	1	8.3	12.1	0.81	9.2	0.95	1.2	1.3			
YLaO 1	1	8.3	2.1	0.13	1.1	0.10	0.1	0.2	0.2	0.4	
YLaO 2	1	8.6	2.1	0.13	0.7	0.07	0.3	0.5	0.4	0.7	
YLaN 1	1	7.4	2.8	0.17	0.7	0.07	1.1	2.2	0.4	0.7	
YLaN 2	1	7.3	9.3	0.56	1.5	0.14	1.2	2.4	0.7	1.2	
YMgLaO 1	1	6.2	4.3	0.25	0.2	0.01	27.1	46.0	3.4	11.9	1.5
YMgLaO 2	1	6.2	4.6	0.27	0.3	0.03	122.0	207.0	29.4	105.2	1.2
YMgLaN 1	1	8.0	2.1	0.12	1.1	0.10	2.9	5.2	1.4	5.0	0.7
YMgLaN 2	1	8.0	2.8	0.16	1.5	0.13	0.4	0.7	0.2	0.9	1.1
YLaO 3	3	7.5	4.5	0.28	0.6	0.06	61.1	113.8	19.1	35.6	
YLaN 3	3	6.8	3.5	0.21	0.3	0.03	103.6	189.7	41.5	76.1	

3.2. Analysis of the altered layer

Relative mass losses are very low: about 3×10^{-5} ($\Delta m/m$) (the weight loss is about 100 μg for a total weight of 4 g; the weight loss precision is about ±20 μg).

3.2.1. Microscopy observations

Observation of the glass surface by SEM (Fig. 1) reveals that the corrosion is not at an advanced stage and is not homogeneous. In the case of the LaO glasses, large pits are observed (50 μm in diameter). A concentric zone is observed around the pits.

In the case of YLaO glasses, pits are in greater number and they are smaller. The altered zone seems to extend all over the surface as a very thin white layer.

For YMgLaO glasses, there are almost no pits and no layer observed. But very small fibrous precipitates are covering the glass surface.

The altered surface of LaN and YLaN oxynitride glasses seems to be less pitted than that of their homologous oxide.

EDX analysis (Table 3) reveals that circular altered zones observed in the LaO/LaN glasses are La/Si enriched. The white layer observed in the YLaO/YLaN glass presents La/Si, Al/Si and more especially Y/Si ratios higher than those of the unaltered glass. The fibrous precipitate observed in a YMgLaO corroded glass seems to have a higher Al/Si ratio than the unleached one. It should be mentioned that EDX analysis is not perfectly suitable to investigate an alteration layer which is probably very thin, compared with the probe volume analyzed which is about 1 μm^3.

Perpendicular sections, observed with TEM or SEM would be necessary to investigate in more detail the alteration layer.

3.2.2. XPS investigations

XPS analyses have been performed on LaO, LaN and YLaO glasses before and after the leaching experiment. The energy reference is the C_{1s} photoelectron line at 284.6 eV.

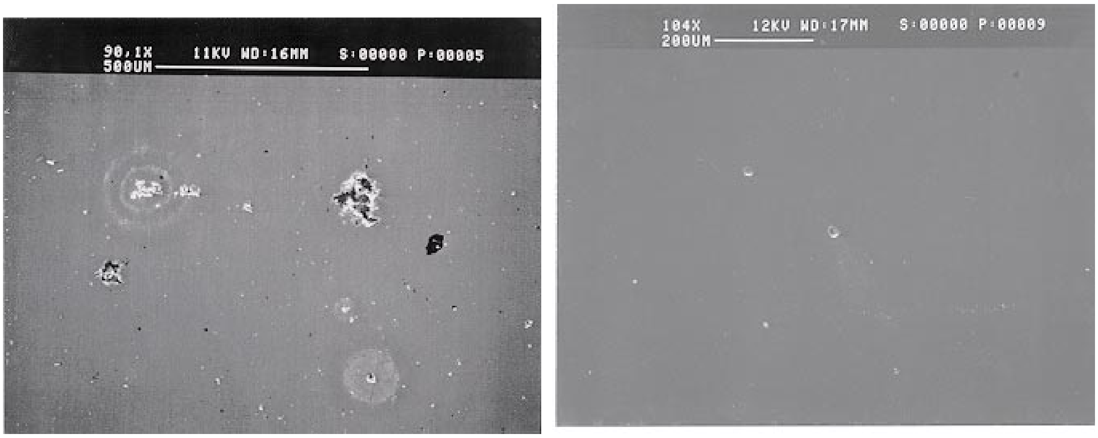
3.2.2.1. Unaltered glasses. The O_{1s} photoelectron line is located at 531.3 ± 0.2 eV. The Al_{2p} photoelectron line is at 74.1 ± 0.2 eV. The Si_{2p} photoelectron line overlaps with the La_{4d} doublet, around 105.8 ± 0.2 eV and 102.5 ± 0.2 eV. The Si_{2s} photoelectron line at 153.2 eV is then more appropriate to analyze silicon. The N_{1s} photoelectron line is located at 398.0 eV for a LaN glass, but is covered with the Y_{3s} signal in a YLaN glass. The $La_{3d5/2}$ core photoelectron line in glasses is located at 835.6 ± 0.3 eV. The $La_{3d5/2}$ satellite is about 3.5 eV away from the higher binding energy side of the core level towards higher binding energy. It has been attributed to the charge transfer between the oxygen O_{2p} and the lanthanum La_{4f} [27]. The spin-orbit splitting between the $La_{3d5/2}$ and $La_{3d3/2}$ is about 17 eV. The Y_{3d} photoelectron line position in glasses is noted at 158.3 and 160.0 eV due to the $Y_{3d3/2}$ and $Y_{3d5/2}$ states, respectively. This splitting is due to the spin-orbit coupling.

3.2.2.2. Altered glasses. The XPS spectrum of the altered glass is slightly modified. An analysis of the intensities of the main photoelectron lines (Table 4) reveals that there is an increase of the O_{1s}/Si_{2s} ratio from 2.0–3.1 to 3.8–6.5. The evolution of the Al_{2p}/Si_{2s} ratio is not very clear. It seems that this ratio increases in the case of yttrium containing glasses. The La_{3d}/Si_{2s} ratio increases from 0.17–0.13 to 0.40–0.35 for LaO/LaN glasses and from 0.06–0.07 to 0.19–0.24 for YLaO/YLaN glasses. The Y_{3d}/Si_{2s} ratio increases also from 0.30–0.37 to 0.82–1.33. The same tendency could be observed in the Y_{3d}–Si_{2s} region and in the La_{4d}–Si_{2p} region (Fig. 2). In the first region, (Si_{2s}–Y_{3d}), there is an increase of the yttrium signal (Y_{3d}) compared with that of silicon (Si_{2s}). In the second region (Si_{2p}–La_{4d}), the Si_{2p} signal overlaps with the La_{4d} doublet [28]. Nevertheless, it can be observed that the silicon signal (Si_{2p}) is decreased compared with that of lanthanum (La_{4d} doublet), after the leaching experiment. The evolution of the N_{1s} photoelectron line during alteration can be observed on a LaN sample. The N_{1s}/Si_{2s} ratio almost does not change before (0.13) and after alteration (0.15). This indicates that nitrogen does not seem to be preferentially released nor retained in the alteration process. The great width of the N_{1s} signal (about 4 eV) does not allow a conclusion to be made about the oxidation state of nitrogen at the interface.

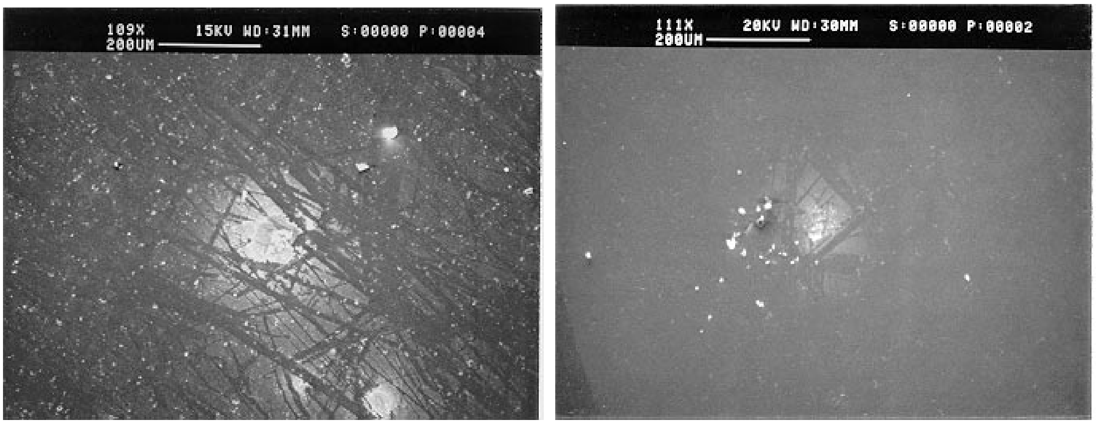
3.2.3. Infrared investigations

The FT-IR reflection spectra of glasses are presented in Fig. 3 and Table 5. The spectra of glasses exhibit two broad signals at about 930 and 440 cm^{-1} while a small shoulder is noted at 675 cm^{-1}, results already observed in Ref. [15,16]. The 930 cm^{-1} band is due to the stretching vibrations of SiO_4 tetrahedra, while the 440 cm^{-1} is due to bending vibrations of SiOSi and SiOAl linkages. The absorption band at 675 cm^{-1} has been attributed to the stretching vibration of AlO bonds with aluminum in fourfold coordination [16]. It is known that the absorption bands of the Q_n units with $n=4$, 3, 2, 1 and 0 are centered around 1200, 1100, 900 and 850 cm^{-1}, respectively [16]. The low value of the stretching vibration of SiO_4 could indicate a Q_n distribution (where Q_n design a silica tetrahedron with n bridging oxygen), centered around Q_2. The nitrogen incorporation induced the formation of Si–N linkages, which are observed by a low-frequency shift of the Si–O stretching vibration [29].

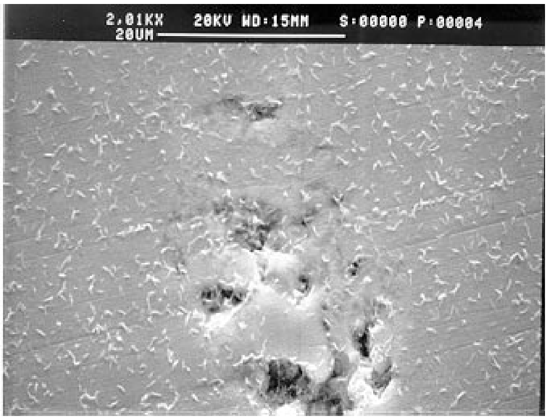
The subtraction of the FT-IR reflection spectra before and after the leaching test is shown in Fig. 4. A very small signal is observed, for a LaO glass, at about



Glass LaO (x100) **Glass LaN** (x100)



Glass YLaO (x100) **Glass YLaN** (x100)



Glass YMgLaO (x2000)

Fig. 1. SEM photographs of glasses surfaces after a static leaching test (one month, $T = 96°C$, $S/V = 0.3\ cm^{-1}$).

1200 cm^{-1}. It reveals a very small decrease of the high frequency part of the Si–O stretching vibrations. The same observation is made concerning a LaN glass before and after a leaching experiment. No information about the evolution of nitrogen at glass/water interface can be obtained by this method.

Table 3
Elemental ratios Al/Si, La/Si and Y/Si measured with an EDX device coupled with an SEM analysis

Ratios	Zone observed							
	LaO/LaN reference	LaO circular altered zone	LaN circular altered zone	YLaO/YLaN reference	YLaO altered layer	YLaN altered layer	YMgLaO reference	YMgLaO fiber zone
Al/Si	0.6	0.6	1.0	0.6	0.6–1.5	0.5–1.7	0.6	1.3
La/Si	0.7	0.8–0.9	0.8	0.4	0.5–1.3	0.5–1.1	0.4	0.3
Y/Si	–	–	–	0.4	0.6–2.6	0.6–1.6	0.2	0.3

Table 4
Intensity ratios of XPS photoelectron lines before and after leaching experiments (only corrected by ionization cross-sections)

Intensity ratios	Glasses								
	LaO reference	LaO 1	LaN reference	LaN 1	YLaO reference	YLaO 1	YLaO 3	YLaN reference	YLaN 3
O_{1s}/Si_{2s}	3.0	5.2	2.8	3.8	3.1	5.3	5.1	2.8	6.5
Al_{2p}/Si_{2s}	0.66	0.66	0.66	0.43	0.61	0.88	0.96	0.67	0.88
La_{3d}/Si_{2s}	0.17	0.40	0.13	0.35	0.06	0.19	0.20	0.07	0.24
Y_{3d}/Si_{2s}	–	–	–	–	0.30	0.85	0.82	0.37	1.33

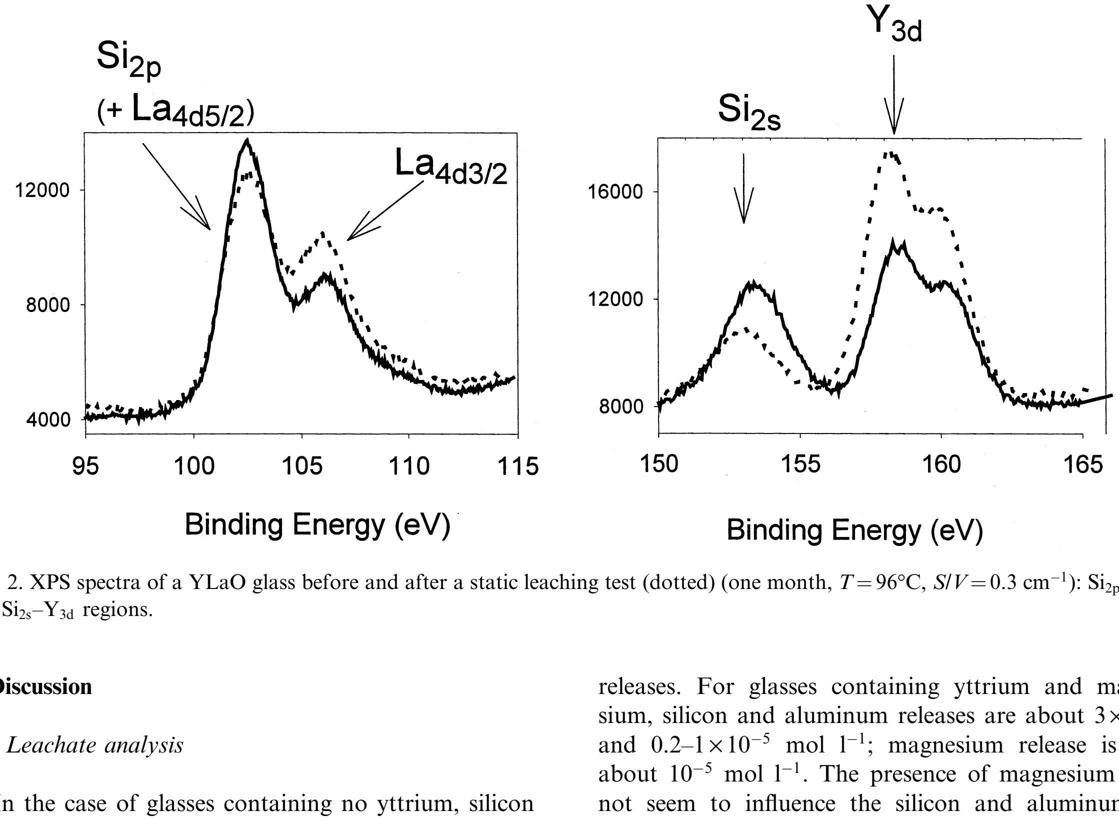


Fig. 2. XPS spectra of a YLaO glass before and after a static leaching test (dotted) (one month, $T = 96°C$, $S/V = 0.3$ cm^{-1}): Si_{2p}–La_{4d} and Si_{2s}–Y_{3d} regions.

4. Discussion

4.1. Leachate analysis

In the case of glasses containing no yttrium, silicon and aluminum releases are about 5.3–13.5$\times10^{-5}$ and 2.6–9.2$\times10^{-5}$ mol l^{-1}. When yttrium is contained in the glass, silicon and aluminum releases are about 2.1–9.3$\times10^{-5}$ and 0.7–1.5$\times10^{-5}$ mol l^{-1}. The presence of yttrium seems to slightly decrease silicon and aluminum releases. For glasses containing yttrium and magnesium, silicon and aluminum releases are about 3$\times10^{-5}$ and 0.2–1$\times10^{-5}$ mol l^{-1}; magnesium release is also about 10^{-5} mol l^{-1}. The presence of magnesium does not seem to influence the silicon and aluminum releases.

Comparison between the oxide and oxynitride glasses is not very conclusive. Only one of the LaN glasses has a lower silicon release. The two YMgLaN glasses have a slightly lower silicon release. But it could not be

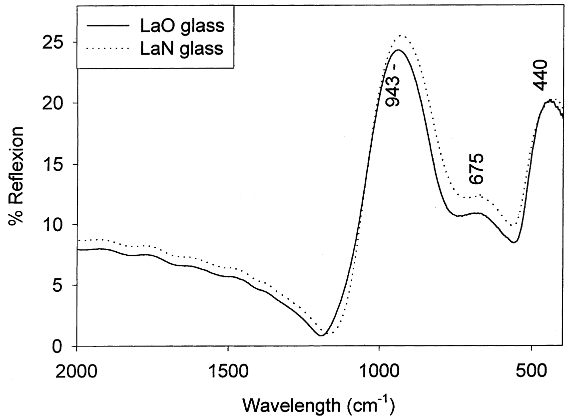


Fig. 3. Infrared spectrum of LaO and LaN glasses before the leaching experiment.

Table 5
Infrared wavelength in glasses (cm^{-1})

Glasses	ν (SiO_4) (cm^{-1})	ν (AlO) in AlO_4 (cm^{-1})	δ(SiOSi)–(SiOAl) (cm^{-1})
LaO	943	690	446
LaN	936	675	440
YLaO	943	680	450
YLaN	932	675	440
YMgLaO	943	685	440
YMgLaN	930	675	425

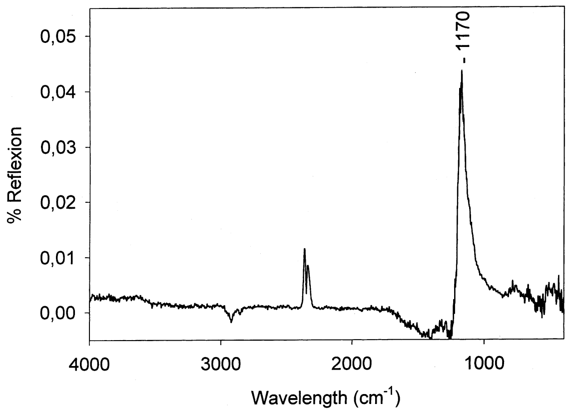


Fig. 4. Subtraction of the infrared spectra of LaO glass before and after the leaching experiment.

concluded from these results that nitrogen modifies silicon or aluminum releases.

Experimental silicon releases are found below the quartz (SiO_2) solubility, which is around 10^{-3} mol l^{-1} at 96°C.

Except in the case of LaN glasses, solutions are depleted in Al relatively to Si (Table 6). The compared releases of Si and Al (ratio of the normalized mass losses) reflect a non-congruent process, which shows that aluminum is retained in the alteration layer compared to Si. This is particularly true for the YMgLaO glasses.

The release of nitrogen has not been followed in this study. It has been shown that nitrogen originally as nitride in similar glasses was released as ammonium in oxidized conditions [30]. Nitrogen was chosen as a corrosion tracer by the authors.

Concerning lanthanum and yttrium releases, they are considerably lower than silicon and aluminum releases, indicating a non-congruent dissolution process (Table 2): $0.1–2.9\times10^{-7}$ mol l^{-1} for [La] and $0.2–1.4\times10^{-7}$ mol l^{-1} for [Y]. The ratios of the normalized mass losses La/Si and Y/Si (Table 6) are about 10^{-3}, except for the YMgLaO glasses and for the three month experiments, indicating an important lanthanum and yttrium retention in the alteration layer, compared with silicon. Oxide glasses containing magnesium exhibit the lowest final pH and the highest lanthanum and yttrium releases: $3\times10^{-7}–1.2\times10^{-5}$ mol l^{-1}. This effect is not yet understood. The existence of a fibrous precipitate has been mentioned, with a higher Al/Si ratio compared with the bulk glass. Moreover, the leachate Al/Si ratio is particularly low (Table 6), which may confirm the presence of aluminum in the alteration layer. A clear characterization of this fibrous precipitate should be performed to elucidate the pH low measured value.

Yttrium and lanthanum releases are influenced by the pH of the leachant. In this case, their releases could be controlled by the solubility of a solid phase such as a hydroxide which is very pH dependent, or a hydroxicarbonate. Nitrogen does not seem to influence yttrium or lanthanum releases, except for the Y–Mg–La glasses.

The release of rare-earth during the dissolution of a borosilicate glass has been investigated by Rai and Felmy [31] at 25°C, with a pCO_2 control. It was concluded that at pH above 6, neodymium concentrations were controlled by a solubility phenomenon: some form of $Nd(OH)_3$, in $CO_{2(g)}$ deficient environment, or $NdOHCO_3$ in a $CO_{2(g)}$ rich environment (0.00154 atm), more likely “a solid solution of the lanthanides in roughly the proportions present in the glass”.

In the glass dissolution study of Ménard and Advocat [32–34], neodymium concentration was stabilized at about log[Nd] = −7 (for pH comprised between 8.5 and 9). An important retention of rare-earth in the alteration film was observed. They outline the fact that lanthanides released by glass dissolution preferentially form colloids. The true dissolved part is then measured after an ultrafiltration process. It was noted that the kinetics of the glass dissolution were not a dominant factor for the dissolution of rare-earth, and that there was a control of a solid phase which was not a simple one such as a hydroxide or a (hydroxi)-carbonate. They suppose that a

Table 6
Al/Si, La/Si and Y/Si leaching ratios (ratios of the normalized mass losses)

Glasses	Experimental conditions	pH final	Al/Si	La/Si	Y/Si
LaO 1	1 month	7.7	0.4	0.004	
LaO 2	1 month	8.3	0.7	0.0002	
LaN 1	1 month	8.3	1.3	0.004	
LaN 2	1 month	8.3	1.1	0.001	
YLaO 1	1 month	8.3	0.7	0.001	0.003
YLaO 2	1 month	8.6	0.5	0.004	0.005
YLaN 1	1 month	7.4	0.4	0.013	0.004
YLaN 2	1 month	7.3	0.2	0.004	0.002
YMgLaO 1	1 month	6.2	0.04	0.184	0.047
YMgLaO 2	1 month	6.2	0.1	0.766	0.389
YMgLaN 1	1 month	8.0	0.8	0.043	0.041
YMgLaN 2	1 month	8.0	0.8	0.004	0.005
YLaO 3	3 months	7.5	0.2	0.406	0.127
YLaN 3	3 months	6.8	0.1	0.903	0.362

coprecipitation of lanthanides with SiO_2 and Al_2O_3 is possible.

It would be satisfying if experimental concentrations in the leachates could be connected with theoretical solubilities of simple solid phases. Nevertheless, it should not be forgotten that it is probably a purely theoretical view and that solid phases precipitated during the glass dissolution are very unlikely simple phases and more probably mixed phases. Thermodynamic data about lanthanides found in the literature are very unsure and contradictory, even at 25°C. We suppose for our calculation, that Nd^{III} solutions have been equilibrated with atmospheric CO_2 at 25°C, $pCO_2 = 10^{-3.5}$ atm. Thermodynamic data are chosen as follows:

- By analogy with Felmy's work on Am [35], we can suppose that the thermodynamic stable phase is a hydroxycarbonate of Nd. The solubility product $\log K_{sp}$ of −21.6, found by Caroll [36] for $Nd(OH)CO_3$ was chosen.
- Despite the great discrepancy of the literature data, a $\log K_{sp}$ value of 14.96 for $Nd(OH)_3$ has been retained at 25°C [37]. Hydroxide phase is the thermodynamically stable phase supposed to be formed in a CO_2 deficient atmosphere.

Hydrolysis and complexation constants have been chosen in Caroll's work [36]. The solubility of Nd can be calculated as the sum of all $Nd^{(III)}$ species [38,39]. The Table 7 lists the results of the calculated $Nd^{(III)}$ solubility if $Nd(OH)_3$ or $Nd(OH)CO_3$ were the solubility controlling phases.

Our results, after a one month experiment at 96°C, are not contradictory with those of Rai, which reveal that Nd concentrations were controlled by some solid phases such as $Nd(OH)_3$ or $Nd(OH)CO_3$. But it is difficult to make any conclusion as experimental data are too scattered, probably because of some experimental problems:

- the experimental pCO_2 has not been controlled;
- pH measurements are very unreliable (effect of the temperature and CO_2 contamination);
- moreover, a filtration at 0.45 μm has been used while Ménard (39) has noted that most of the rare-earths in a glass leachate were in colloids form and that ultrafiltration would have been necessary to separate the colloids from the solution part.

A serious discussion about La solubility would need new experiments with a perfect pCO_2 control, at 25°C, using ultrafiltration before ICP-MS analysis, and in situ pH measurements to avoid any atmospheric CO_2 contamination.

Two, three months experiment, have been performed on a YLaO and a YLaN glass. Silicon and aluminum releases are about $3.5–4.5 \times 10^{-5}$ and $0.3–0.6 \times 10^{-5}$ mol l^{-1}. Yttrium and lanthanum releases are also about $0.2–1.0 \times 10^{-5}$ mol l^{-1}. The higher lanthanum and yttrium concentrations observed after a three-month experiment (log[La] is roughly equal to −5) could be again explained by the solubility of a hydroxide phase as the pH is a little lower (about 7). Moreover, the colloid formation can explain that the lanthanum and yttrium concentrations

Table 7
Calculated solubility S of Nd^{III} if the hydroxide or the hydroxycarbonate were the solubility controlling phases at 25°C, with a pCO_2 of $10^{-3.5}$ atm

pH	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
$\log S_{Nd(OH)_3}$	−3.1	−4.5	−5.8	−6.6	−7.1	−7.3	−7.0	−6.2	−4.9
$\log S_{Nd(OH)_{CO_3}}$	−3.9	−5.3	−6.6	−7.4	−7.9	−8.1	−7.8	−7.0	−5.7

could have been overestimated in our study, since a filtration at 0.45 μm has only been used.

For glasses containing no yttrium, silicon release is about 0.3–0.9 g/m^2. Aluminum release is about 0.2–0.9 g/m^2. For glasses containing yttrium, silicon release is about 0.1–0.5 g/m^2. Aluminum release is about 0.07–0.14 g/m^2.

It is difficult to compare these glasses with classical nuclear glasses, since their compositions considerably differ. A nuclear glass contains roughly the same proportion of silica (60% mol), but the two other major constituents are B_2O_3 (about 15% mol) and Na_2O (15% mol). While our glasses are composed of SiO_2 (60% mol), Al_2O_3 (20% mol) and La_2O_3 (20% mol). Nevertheless, it can be noted that, in the same conditions, silicon release in a nuclear glass is about 2 g/m^2 [9,40]. As release is a time-dependent process; it can just be concluded that at this moment, these rare-earth glasses seem to have a higher chemical durability compared with that of borosilicate glasses used for nuclear waste treatment. This difference may be due to the absence of boron and alkaline elements in our glasses. The low silicon releases measured could be explained by the presence of lanthanum and yttrium which probably increases the strength of the glass and then reduces the rate of dissolution of silica. Nevertheless, comparing the confining performance of such glasses is hazardous, as they do not contain any soluble tracer. The comparison of the silicon releases is not perfectly reliable as silicon could be retained in the alteration layer. Moreover, nothing can be concluded concerning the long-term dissolution behavior.

Lanthanum and yttrium releases are about $0.2–5.2\times10^{-3}$ and $0.4–5.0\times10^{-3}$ g/m^2, respectively. An important yttrium and lanthanum retention at the surface of the corroded glasses could then be expected. A thickness of 0.03 μm up to 0.2μm glass dissolved could be estimated from silicon analysis of the leachates.

4.2. Solid analysis

The microscopy analysis shows that the altered surfaces of oxynitride glasses seem to be less pitted than that of their oxide homologs. This could be explained by the improvement of the mechanical properties in an oxynitride glass. This analysis seems to give contradictory results to those of solution analysis, since oxynitride glasses exhibit a smaller number of altered zones than oxide glasses, while elemental releases are quite comparable. Clear explanation of this ambiguity has not yet been available.

The EDX analyses of corroded glasses reveal that some secondary phases are locally formed at the glass/water interface. These phases are not clearly identified but may be composed of hydroxides phases such as $La(OH)_3$, $Y(OH)_3$, or mixed hydroxides phases.

The XPS analysis has shown that the glass surface consists of higher La/Si and Y/Si ratios after the alteration process. This fact agrees with solution analysis results, which reveal that silicon and aluminum are more rapidly dissolved than lanthanum and yttrium after a one-month experiment. Nitrogen is still observed at the glass surface of a leached LaN glass, but further experiments are necessary to understand the chemical state of nitrogen in the altered interface. The reflection infrared analysis has shown a shift to low frequencies of the stretching Si–O vibrations. This decrease of the absorbance in the high frequency part of the νSiO, which is generally attributed to the more polymerized structural units, could be explained by an increase of the number of non-bridging oxygen. A very clear decrease of the high frequency part of the absorbance has been observed when the rare-earth percentage was increased in rare-earth aluminosilicate glass [16]. The supposed increase of non-bridging oxygen was attributed to the modifier role of La^{3+} in these glasses. So, the very small decrease of the high frequency part of the absorbance observed in our study could reflect the enrichment of the glass surface in lanthanum. This interpretation is confirmed by some other experiments performed on glasses altered in a Soxhlet device, which have revealed the same behavior with 100 times higher intensity. In these glasses, a alteration layer, clearly enriched in La/Si, has been observed.

Solid analyses confirm an important lanthanum and yttrium retention in the alteration layer but do not provide clear evidence about the mechanisms of formation of this layer. It is not known whether the gel layer is formed by in situ recombination of insoluble elements or by precipitation of a solid phase, when solubility limits have been reached. Some other experiments performed in a Soxhlet device have shown that an altered layer enriched in lanthanum and yttrium, could be formed by an in situ recombination. Another question concerns the protective effect of the gel layer. The low solubility of lanthanides hydroxides phases is probably at the origin of the formation of a layer at the glass–water interface, which may slow down the silicon dissolution. Further experiments will be necessary to characterize the alteration layer and the alteration products.

5. Conclusion

The chemical durability of La–Al–Si–O glasses has been studied by means of static experiments, followed by solution and solid analysis. The experimental procedure is not completely relevant (absence of control of pCO_2, absence of ultrafiltration), which does not allow unambiguous conclusions. However, solution analyses reveal that the silicon releases after one month in static conditions (96°C, S/V 0.3 cm^{-1}) are about 0.1–0.9 g/m^2.

Yttrium and lanthanum releases are 100 times lower. Yttrium seems to improve the aqueous durability of YLaAlSiO glasses. The effect of nitrogen and of magnesium on the corrosion behavior have not been evidenced with solution analysis. The solid analyses (SEM/EDX) reveal that the alteration process is not homogenous and that areas enriched in yttrium, lanthanum or aluminum are formed. The morphology of the altered surface oxynitride glasses is more homogeneous than for an oxide glass, which may be due to improved mechanical properties. XPS analysis of the corroded glass confirms that Y/Si and La/Si ratios are increased. The releases of lanthanum and yttrium are delayed with respect to the glass dissolution. Nevertheless, further experiments are needed to understand the kinetics of the releases and whether lanthanides are retained or precipitated in the surface reaction layer.

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