Static Leaching and Alteration Mechanisms of Zirconium Alkali Resistant Glasses Containing Heavy Metals

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Authors' contributions

Article Information

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ABSTRACT

The aim of this study is to understand mechanisms that occur during leaching of alkali-resistant zirconium-containing glasses in acid and alkaline solutions. For this, we have developed 5 glass compositions: two alkali-resistant model glasses type CEMFIL, V1 (with zirconium and without heavy metals) and V2 (with zirconium and heavy metals), then three glasses of fly ashes V3

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(without zirconium and with heavy metals), V4 (with 30 % of V3, zirconium and heavy metals) and V5 (with 60% of V3, zirconium and heavy metals). V4 and V5 are obtained using V3 as raw material and supplementing with SiO_2, ZrO_2 and Na_2O to give them alkali-resistant properties. Glasses leaching in acidic and basic medium led to an important basification from the first times of alteration at pH = 4 when a basification decrease is observed for solutions initially at pH = 13. Normalized elementary mass losses results showed that, glass alteration is higher for low-calcium glasses (V1 and V2) and V4 and V5 glasses have the lowest elemental mass losses at pH = 4 and 13. SIMS profiles made on glass alteration films permitted to observe behaviour of H, Na, Ca, Si and Zr elements after 28 days at pH = 4 and 13 and understand the different dissolution mechanisms involved. SIMS profiles showed that a hydrated film develops on glass surface characterized by hydrogen enrichment and sodium depletion irrespective of the glass. These glasses are also characterized by a surface enrichment of zirconium (except V3 which does not contain zirconium) whatever the pH. Hydrated film thickness confirm that V1, V2 and V3 glasses are more altered than V4 and V5 glasses. These results are confirmed by ICP-AES leachate analysis.

1. INTRODUCTION

Glasses have been used for the confinement of hazardous elements such as heavy metals and nuclear waste. Many studies on alteration of these glasses have been conducted to predict their chemical durability [1]. In contact aqueous solutions, glass gets degraded by ion exchange, hydration of the glass network, re-condensation, precipitation and secondary phase formation [2, 3]. During alteration, four mechanisms (ion exchange, hydrolysis, condensation, precipitation) generally occur [4] : Molecules of water and its dissociated species OH-and H+ diffuse within the glass structure, exchange with alkalis or with alkaline earths (interdiffusion), and hydrolyze the silicate network (dissoulution) [5,6,7]. These two reactions are strongly coupled [8] and lead to a hydrated glass with a modified, hydrated and dealkalinized structure. Otherwise, the condensation of detached silica species, leads to the formation of an amorphous and hydrated residual layer on the glass surface also called "gel" [9,10,11,12]. Also, it is very common to observe secondary minerals precipitation on the gel surface [13]. During the dissolution of silicate glasses, four different types of altered films can be encountered [14]: a hydrated protective alteration layer having a composition identical to glass, a protective film rich in network-forming elements, a multi-layer protective film: either a double layer rich in network formers, or a multilayer consisting of insoluble oxides and hydroxides, a non-protective layer due to its low content of network-forming elements and its high concentration of OH-. Mechanisms of glass alteration are still the subject of much discussion within the scientific community, and no consensus has yet been reached on formation of

the passivation layer on glass surface [15,16,17,18]. Vernaz and al. [19] studied the leaching behaviour of French reference glass R7T7 and showed that alteration layer can be compared to a gel because its porosity reaches 30% by volume and its specific surface is 66 m^2/g. Most heavy elements appear to be concentrated in this layer and the gel has been considered a potential secondary containment material. Gin and al. [20] and Collin and al. [21] conducted studies under saturated Si conditions and under slightly alkaline pH conditions. They characterized the material passivation. In these conditions, B, Na and Ca are leached out. Zr and Al are not released in the solution and no exchange is observed between Si of the solution and Si of the network. This confirms that network formers are not completely hydrolysed and partially re-condense after dissolution to form a porous gel layer [22]. Thus, best chemical durability of a glass is obtained when a large amount of forming elements (Si, Al, Zr, Ti) is added with a smallest possible amount of modifying elements (Na, Mg, K, Ca) [23]. On the one hand, addition of heavy elements oxides such as TiO_2 from 10 mol% [24] or ZrO_2 from 4.6 mol% [25] in silicate glass compositions improves their chemical durability. On the other hand, alkaline oxides such as Na_2O disrupt the Si-O-Si forming bonds by substituting for Si and by introducing unbridged oxygen sites (Si-O-Na+) [26]. Glass corrosion occurs through H+ or H_3O+ protons diffusion of glass [27] and the counter diffusion of alkaline cations. Perret et al. studied the impact of Ca on the durability of alkali-resistant glasses and showed that addition of calcium below 17 mol% reduces the mobility of other ions and thus improves its resistance whereas above of this value thermodynamic

stability drops sharply [23]. Chemical durability of a glass during leaching is therefore highly dependent on its chemical composition. The aim of this work is to study the effect of zirconium on the composition of altered films formed on the surface of alkali-resistant glasses containing heavy metals after leaching in acidic and basic solutions.

2. MATERIALS AND METHODS

2.1 Glass Synthesis

All glasses were synthesized at the CNRS/CEMHTI laboratory in Orleans (France).

We developed 5 glass compositions including: two alkali-resistant model glasses type CEMFIL V1 (with zirconium and without heavy metals) and V2 (with zirconium and with heavy metals), three glasses of fly ashes V3 (without zirconium), V4 (30% of V3) and V5 (60% of V3). V4 and V5 glasses are obtained using V3 as raw material and supplementing with SiO_2, ZrO_2 and Na_2O to give them superior alkali-resistant properties.

V1 glass: it has a composition similar to that of CEMFIL glass with a high content of CaO (5% instead of 1.5% for CEMFIL). This glass represents the basic composition.

V2 glass: It is obtained by introducing into V1 glass heavy metals present in the fly ashes such as Pb, Zn, Cd and Cr.

V3 glass: This is the composition of Frugier's PFTS1 glass [17]. This fly ash glass is doped with heavy metals.

V4 glass: V4 glass contains 30% of V3 glass (PFTS1) supplemented with SiO_2, Na_2O and ZrO_2 to obtain a alkali-resistant glass composition close to V1 glass. The forming oxides SiO_2 and Al_2O_3 represent 61% by weight in V1 glass so only 46.3% of SiO_2 will be necessary to approach the composition of V1 glass. It is the same for alkali and alkaline earth (Na_2O, K_2O, CaO, MgO) which represent 23% by weight in V1 glass, 12.7% by weight of Na_2O will be sufficient to approach this composition. And finally, we add 16% of ZrO_2.

V5 glass : V5 glass is obtained in the same way as V4 glass but with 60% of V3 glass (PFTS1). To get closer to alkali-resistant composition of V1 glass, we added 21.6% SiO_2, 2.41% Na_2O and 16% ZrO_2. All glasses are prepared under the same conditions from a mixture of precursors in powder form: SiO_2, Na_2CO_3, K_2CO_3, $CaCO_3$, MgO, Al_2O_3, ZrO_2 and for pollutants Cr_2O_3, CdO, ZnO, $PbCO_3$. The melting takes place in a Joule effect furnace rocking at 1550 °C for 1 hour under air with manual stirring followed by refining for about one hour. Homogenized liquid is poured onto a square steel plate 8cm long. The glass thus obtained is annealed at 550ºC for 8 hours in a conventional muffle annealing furnace and is then naturally cooled in the oven at room temperature. The glass squares thus obtained are cut with a diamond saw so as to obtain cubes of 1cm * 1cm of sides and 1cm thick. Composition of glasses after fusion is shown in Table 1.

2.2 Experimental Leaching Protocole

In order to understand which mechanisms are responsible for glass alteration (dissolution and / or gel formation), all leaching experiments were carried out in static mode on monolith in a closed, unstirred and non-renewed environment. This involves placing glass monoliths in an altering solution in a rigid Teflon beaker, in order to put all surfaces of sample in contact with the solution. We chose this experimental protocol because it allows to promote development of a film or alteration gel on glass surface in order to compare leachate and solid analysis under the same alteration conditions. To avoid problems with external contamination of solution, Teflon baskets and beakers were cleaned before each leaching experiment with 1N nitric acid and then rinsed 5 times with deionized water. Leaching experiments were carried out at 90ºC for all glasses (V1, V2, V3, V4 and V5) at all leaching times, i.e 6 hours, 12 hours, 1, 7, 14, 21 and 28 days with HCl and NH_3 leaching solutions. Glass samples of 1cm × 1cm were immersed firstly in a slightly acidic solution of HCl (pH=4) and secondly in a basic solution of NH_3 (pH=13) for 28 days at 90ºC. pH of starting leaching solution is measured at room temperature. After each leaching experiment, pH of the leachates is measured after Teflon containers removed from oven have been cooled to room temperature. All leaching experiments were carried out at 90ºC at pH = 4 and pH = 13 at S / V = 0.3. Solutions have not been buffered, so pH evolved freely over time. The slightly acidic pH, pH = 4, was chosen to simulate attack of acid rain and alteration in basic medium at pH = 13 was chosen to model attack in cementitious matrices. HCl and NH_3 solutions were chosen so as to avoid a contribution of ions already present in

glasses as well as for their low complexing nature. The glass area / volume ratio of sintering solution (S / V) was fixed at 0.3 for all leaching duration. The choice of a low S / V ratio makes it possible, while remaining far from the saturation conditions, to favor the formation of an alteration film and thus to follow alteration kinetics. After pH measurement, all leachates were acidified with nitric acid HNO_3 1N to avoid colloids formation and then stored in the refrigerator for analysis by ICP-AES.

2.3 Analytical Methods

Leachate analyzes: Leachates were analyzed by atomic emission spectrometry ICP-AES in LISA laboratory (Interuniversity Laboratory of Atmospheric Sciences) at Paris VII University. The ICP-AES spectrometer used is Optima 3000 XL type. It allows to dose major and minor elements. In order not to dose too large quantities to avoid any saturation effect of the spectrometer, we have carried out a dilution in this following way: 100 µl of leachate are taken and completed up to 10 ml with a 1% solution of 1N HNO_3. These diluted solutions are then placed on the automatic dispensers of ICP-AES spectrometer alongside 5 standard solutions and a natural water white. Once the calibration is completed, the liquid sample to be analyzed is taken by a peristaltic pump. The liquid is then brought into fogger to be aerosolized. Aerosols produced are then driven under argon flow to the torch where plasma will excite and ionize the atoms present. By de-energizing, atoms emit photons with characteristic wavelength whose emission intensity line is proportional to concentration of the elements in sample. The emitted photons arrive in the optical system and then on a detector which is itself connected to a computer system where software will analyze emission lines for different elements.

Glass composition: Chemical composition of the various glasses was determined by a micro-analyzer with an ion probe or electron microprobe of brand CAMECA SX50 with a potential difference of about 10 kV at Paris VI University. To evacuate charges, samples are metalized with carbon before mounting them on the sample holder. Using a microscope video display system, a bombardment is made perpendicular to surface to probe the different phases of glass.

Glass surface analyzes: Secondary Ion Mass Spectrometry (SIMS) has been used to characterize the morphology of "gel" layer on glass surfaces. SIMS analyzes were carried out using a CAMECA IMS-4f device at Bellevue CNRS in Meudon town to establish profiles of element concentrations as a function of time and depth in the first two or three atomic layers. Before any analysis, the target sample is metallized with fine gold. The primary ion beam used is cesium radiation (Cs+) with energy equal to 5 keV. This radiation makes it possible to detect negative secondary ions (O, C). Elements such as Si, Na, Ca, Zr, although they are better detected in positive secondary ions, still have good sensitivity in negative secondary ions because their proportion within material is important. For our study, area swept by the beam is 150 × 150 µm². Detection limit is of the order of 1-10 ppm. Lateral resolution is 1 µm and resolution in depth is 1 nm.

3. RESULTS AND DISCUSSION

3.1 Leachate Chemical Characterization

Evolution of leachate pH: In general, all glasses studied have similar behaviours as a function of pH whatever alteration duration. The leachate pH increases in initially acidic medium (Fig. 1) whereas it decreases in initially basic medium (Fig. 2). For slightly acidic solutions initially of pH = 4, a significant drift of pH is observed from the first leaching times. Indeed, there is a basification of the solution with a pH increase of 1 to 3 units up to 1 day of leaching and can reach nearly 5 units for the longest time for all glasses. This phenomenon of basification of acidic solutions has also been observed and studied by many authors [26, 28]. In fact, when a glass is brought into contact with an aqueous solution, it diffuses into glass and ion exchange takes place between hydrogen and mobile ions of the vitreous network: this process causes an increase of leaching solution pH and dissolution of the network [14,29]. Ion exchange and network dissolution processes can take place at the same time but in general one of the processes predominates as a function of leachate pH. Thus, leachate drifts at pH = 4 can be explained by the fact that when leachate pH <9, then ion exchange is the mechanism which controls reaction and release of alkalis and / or alkaline-earths. It causes an increase of pH due to accumulation of residual OH- ions in the solution, followed by stabilization due to the saturation effect of the medium [30]. For solutions initially pH = 13, evolution of pH over time is less significant than for solutions initially

at pH = 4 for all glasses. Indeed, there is a slight drop in pH less than 1 unit. The slight drop in leachates pH of initially basic solutions at pH = 13 is more difficult to explain. It may be thought that consumption of OH- ions may be due to hydrolysis of bridging bonds or equilibrium of solution with the secondary products which precipitate or condense on the glass surface since we are in a closed environment [31]. At long times, the pH evolution of leachates seems to tend towards an asymptote certainly due to a saturation of the medium.
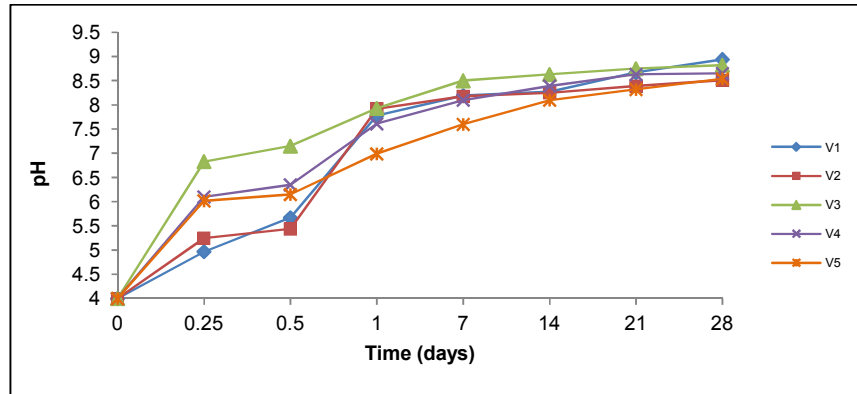
Fig. 1. pH evolution of leaching solutions initially at pH = 4 and containing V1, V2, V3, V4 and V5 glasses at 90 °C as a function of time
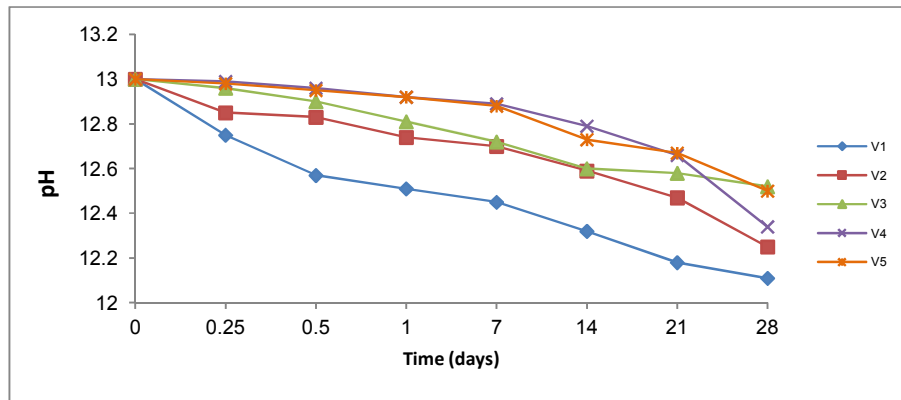
Fig. 2. pH evolution of leaching solutions initially at pH = 13 and containing V1, V2, V3, V4 and V5 glasses at 90°C as a function of time
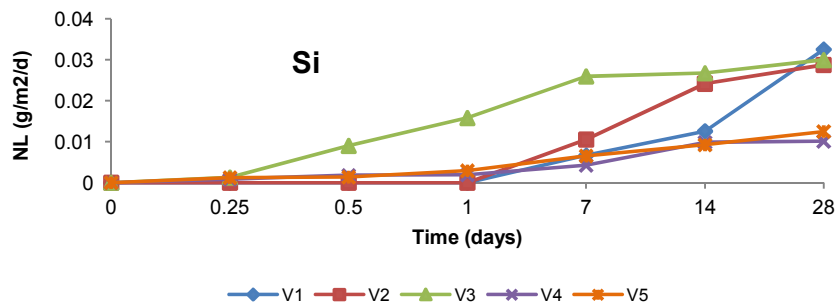
Fig. 3. Normalized mass losses of Si during pH=4 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time

Table 1. Composition of glasses (% weight)

% in weight	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	ZrO_2	TiO_2	Fe_2O_3	Cr_2O_3	CdO	ZnO	PbO	P_2O_5	LiO
V1	60,50	14,92	1,88	4,91	0,91	1,08	15,80	—	—	—	—	—	—	—	—
V2	58,10	14,20	1,78	4,55	0,95	1	15,36	—	—	1,04	1,05	0,99	0,98	—	—
V3	34,63	1,93	0,39	31,61	2,20	13,20	—	2,20	2	1,52	2,04	1,90	3,78	1,59	1, 01
V4	53,86	12,08	0,51	8,40	0,76	4,14	15,20	0,62	0,69	0,39	0,68	0,64	1,20	0,46	0,37
V5	42,93	3,22	0,21	19,20	2,07	9,20	13,55	1	1	0,65	1,70	1	2,87	0,75	0,65

3.2 Normalized Mass Losses (NL)

It characterizes the mass loss of each element per unit area. To better understand the effect of dissolution on glasses, we compared the glasses together by representing on the same graph, the evolution of the elementary normalized mass losses, between 6 hours and 28 days for major forming elements (Si, Zr) and network modifiers (Na, Ca). Silicon and zirconium are the main glass forming elements except for V3 which does not contain zirconium. Thus, to study their behaviour during alteration is equivalent to follow the dissolution network: these are the markers of dissolution of glass network. Studied glasses contain significant quantities of network modifiers (from 16.68% to 26.75% by elemental mass according to the glass) belonging to alkaline and alkaline-earth groups. The alkalis, being easily leachable, can be considered as markers of the effective dissolution of glass.

In acidic medium at pH = 4: As regards the network formers, Si and Zr, it can be seen in Fig. 3 and Fig. 4 that it is the V3 glass that loses the most silicon and V4 and V5 dissolution glasses are much lower than for V1, V2 and V3 glasses.

On the one hand, dissolution of V2, V3, V4 and V5 glasses is rapid in the early stages of alteration and then tends towards an asymptote when time increases. These glasses seem to reach a saturation state of silica. This tendency towards a steady state can be explained by equilibration of the solution with the solid by dissolution mechanisms followed by precipitation or condensation [32]. Only V1 and V2 glasses let zirconium pass in solution. No significant change in Zr normalized mass loss over time was observed for these two glasses. It is between 0.01 and 0.015 g /m^2. Zirconium is below the detection limit for V4 and V5 glasses. It is therefore kept in the glass or in the altered film for V4 and V5 glasses. The evolution of normalized mass losses of network modifying elements Na and Ca can be observed in Fig. 5 and Fig. 6. By following the evolution of Na and Ca mass losses, one can notice that these elements are more leached in V1 and V2 glasses. A rapid dissolution occurs at the very beginning of alteration, then the steady state is very quickly reached for V3, V4 and V5 glasses compared to V1 and V2 glasses. In summary, it can be said that V4 and V5 glasses have the lowest normalized mass losses at pH = 4.
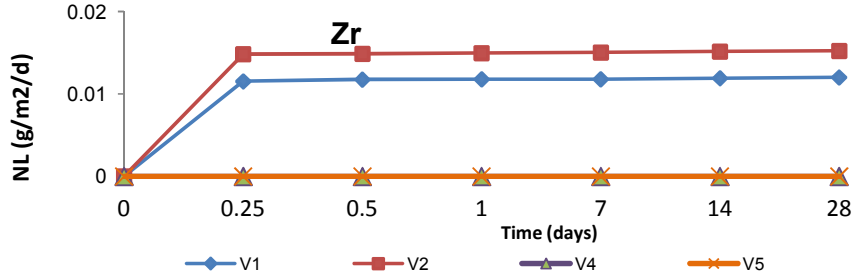

Fig. 4. Normalized mass losses of Zr during pH=4 leaching of V1, V2, V3, V4 and V5 glasses at 90 °C as a function of time
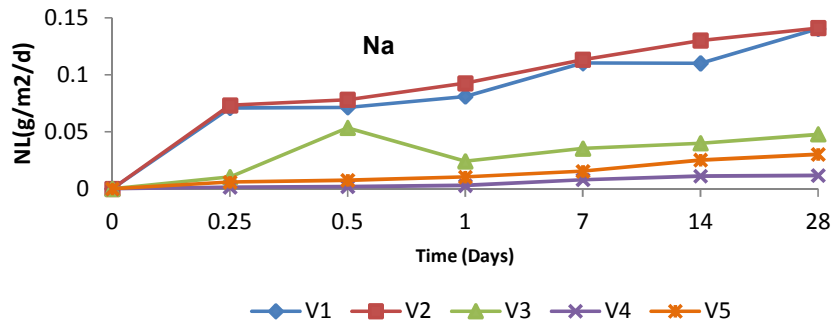

Fig. 5. Normalized mass losses of Na during pH=4 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time
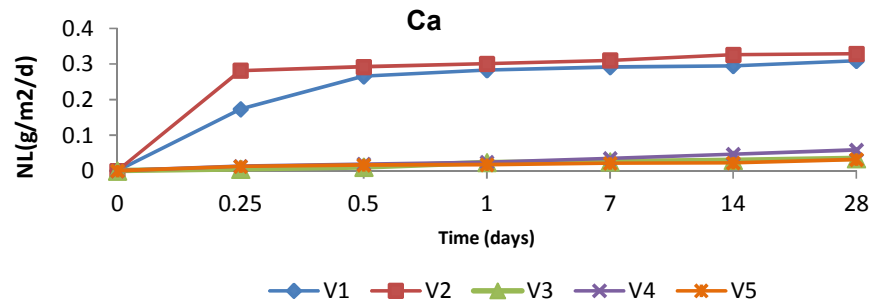
Fig. 6. Normalized mass losses of Ca during pH=4 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time
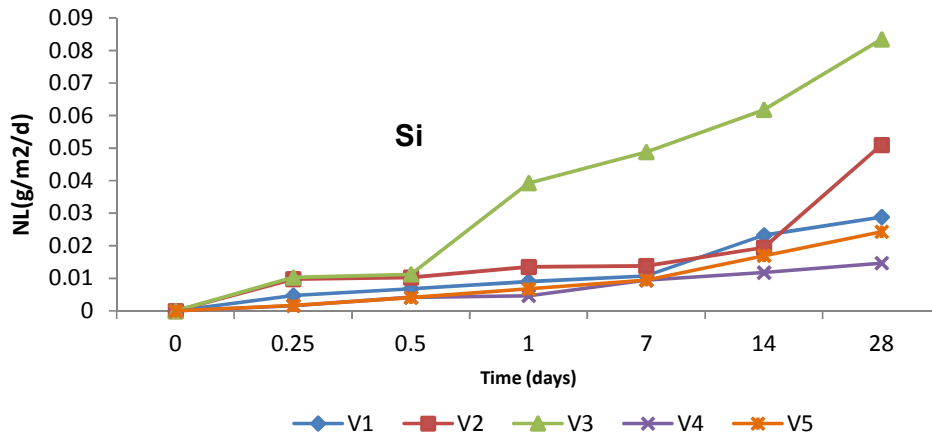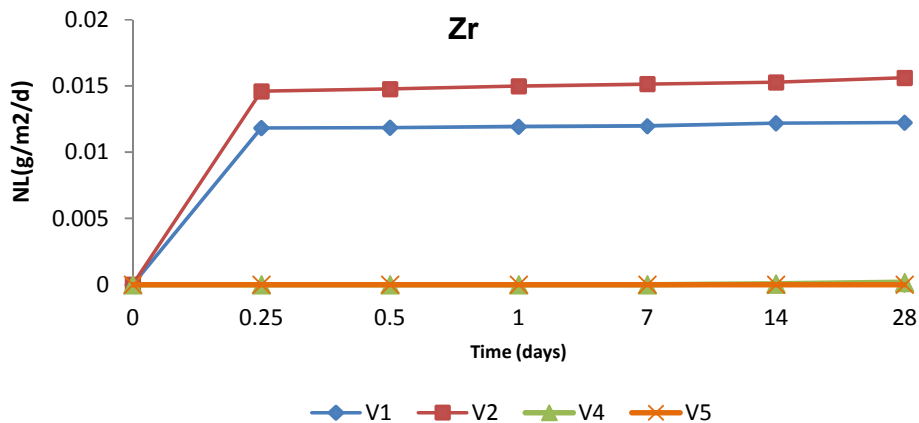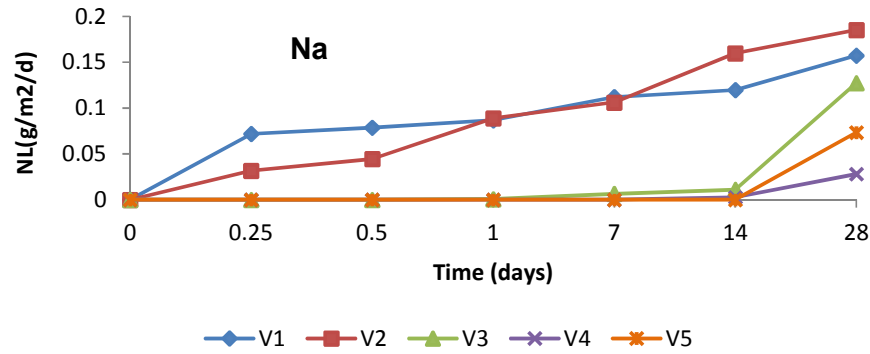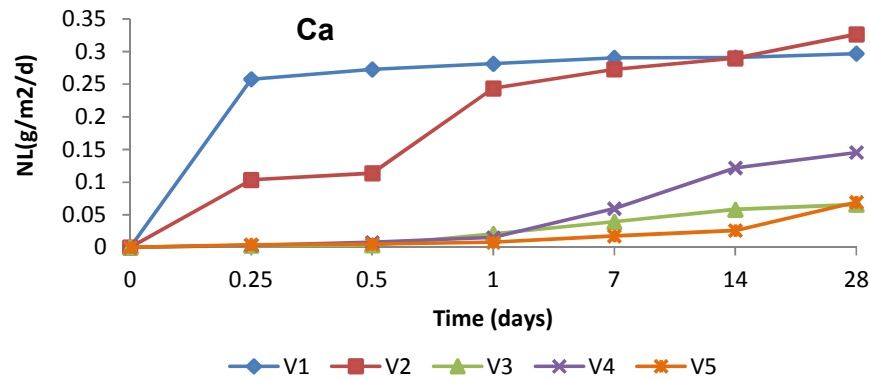

Fig. 7. Normalized mass losses of Si during pH=13 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time

Fig. 8. Normalized mass losses of Zr during pH=13 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time

Fig. 9. Normalized mass losses of Na during pH=13 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time

Fig. 10. Normalized mass losses of Ca during pH=13 leaching of V1, V2, V3, V4 and V5 glasses at 90°C as a function of time
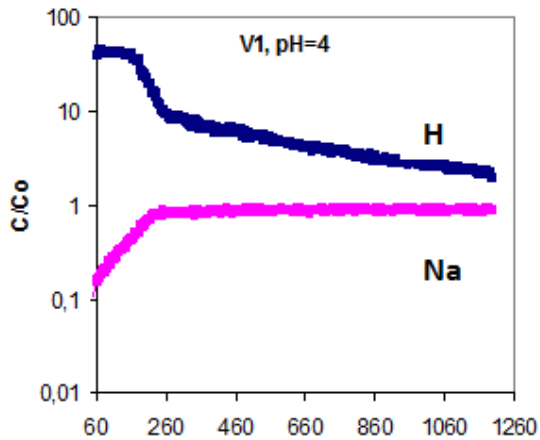
Fig. 11-a. Deep profiles of Na, and H elements on V1 surface glass altered at pH = 4 for 28 days
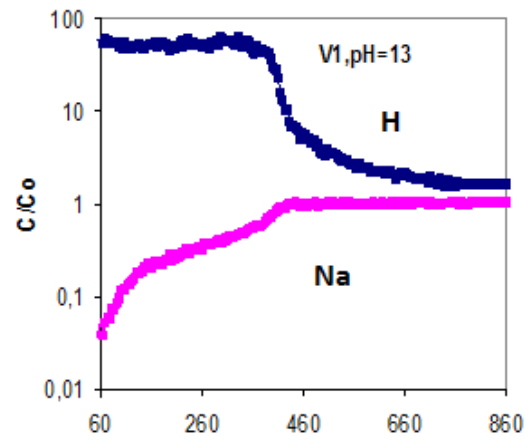
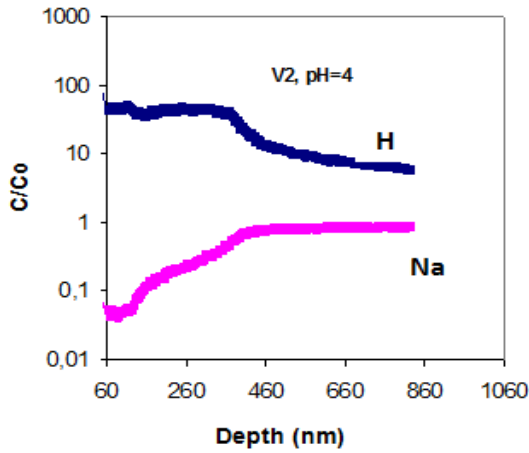**Fig. 11-b. Deep profiles of Na, and H elements on V1 surface glass altered at pH = 13 for 28 days**

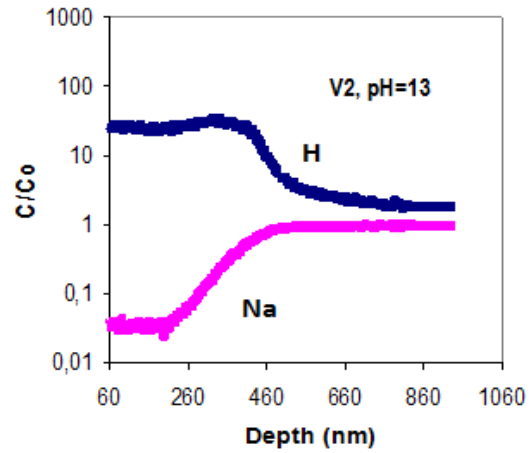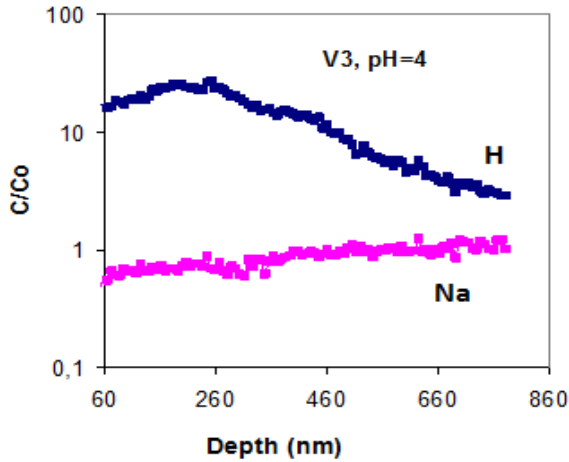**Fig. 12-a. Deep profiles of Na, and H elements on V2 surface glass altered at pH = 4 for 28 days**

Fig. 12-b. Deep profiles of Na, and H elements on V2 surface glass altered at pH = 13 for 28 days

Fig. 13-a. Deep profiles of Na, and H elements on V3 surface glass altered at pH = 4 for 28 days
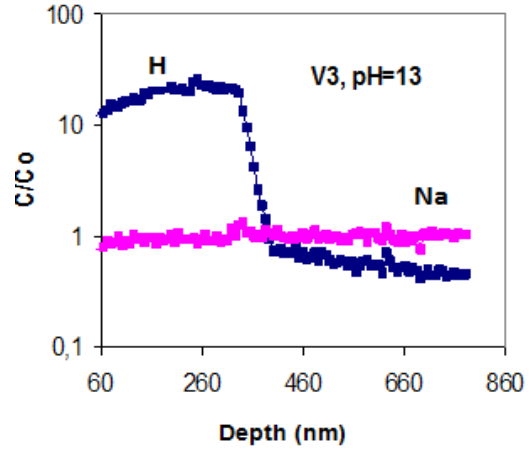
Fig. 13-b. Deep profiles of Na, and H elements on V3 surface glass altered at pH = 13 for 28 days
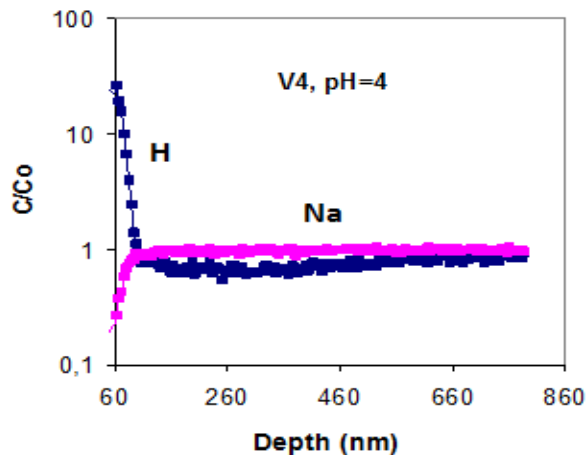

Fig. 14-a. Deep profiles of Na, and H elements on V4 surface glass altered at pH = 4 for 28 days
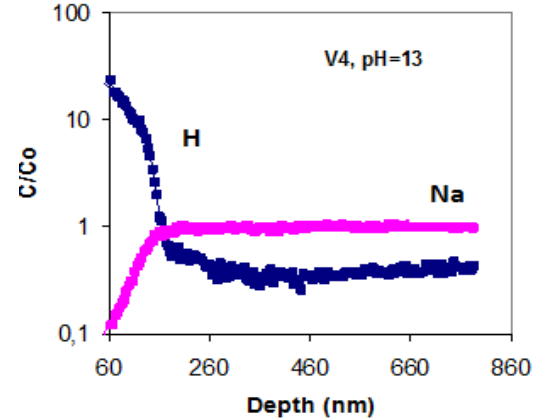
Fig. 14-b. Deep profiles of Na, and H elements on V4 surface glass altered at pH = 13 for 28 days
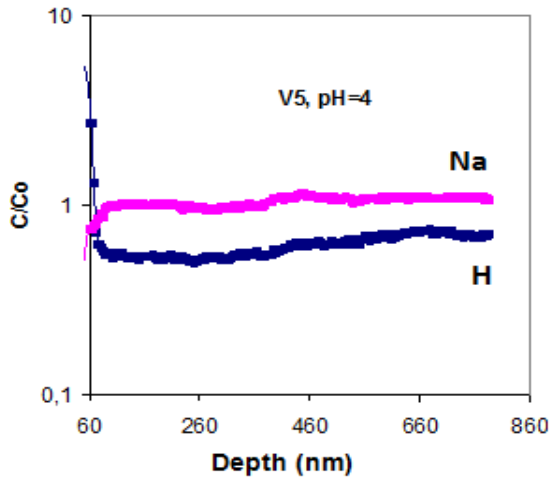
Fig. 15-a. Deep profiles of Na, and H elements on V5 surface glass altered at pH = 4 for 28 days
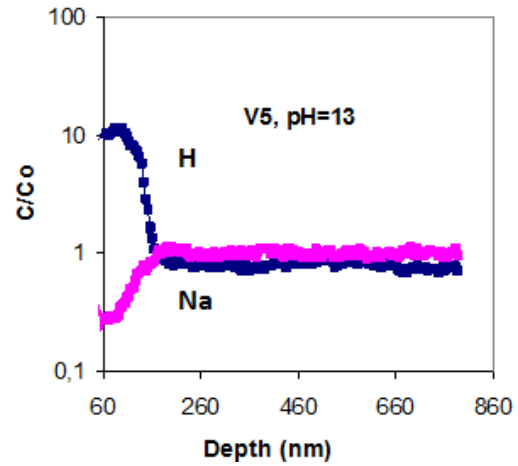
Fig. 15-b. Deep profiles of Na, and H elements on V5 surface glass altered at pH = 13 for 28 days

Fig. 16. Deep profiles of Si element on V1 surface glass altered at pH = 4 for 28 days

Fig. 17. Deep profiles of Si element on V2 surface glass altered at pH = 4 for 28 days
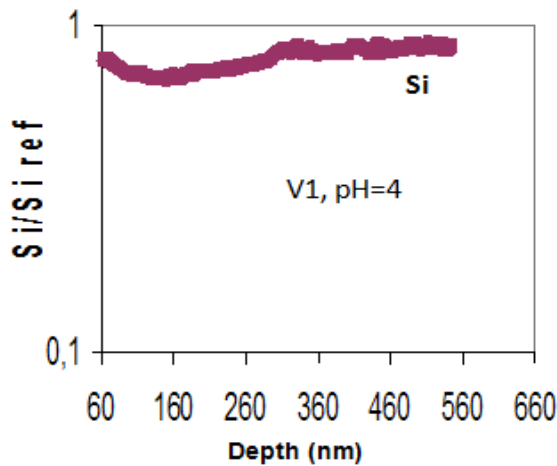

Fig. 18. Deep profiles of Si element on V3 surface glass altered at pH = 4 for 28 days

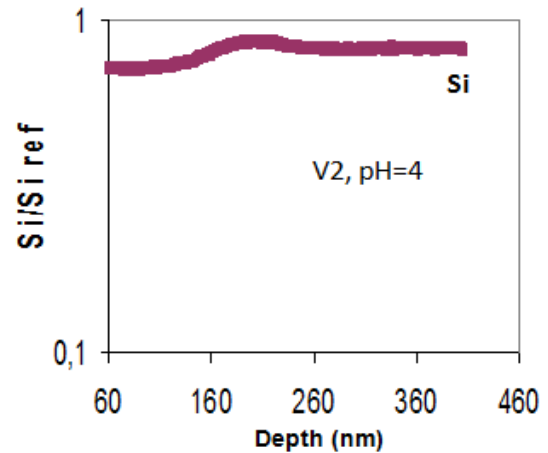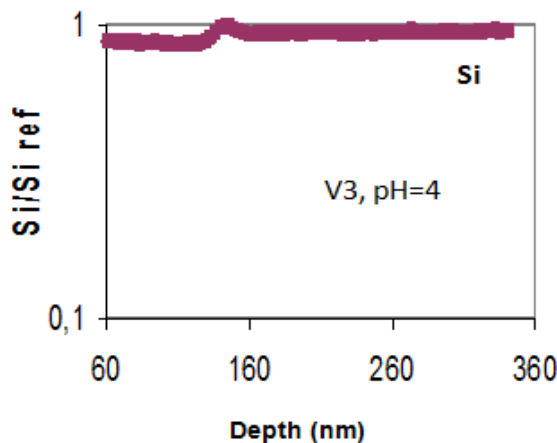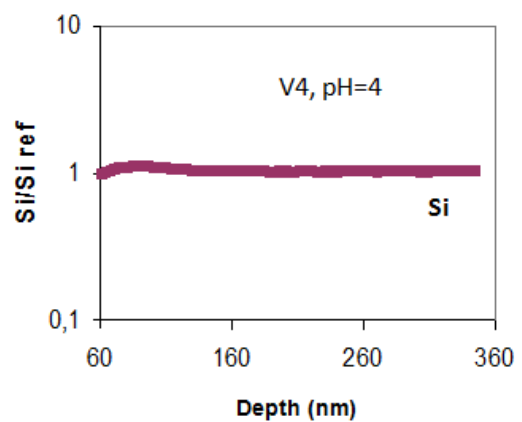**Fig. 19. Deep profiles of Si element on V4 surface glass altered at pH = 4 for 28 days**
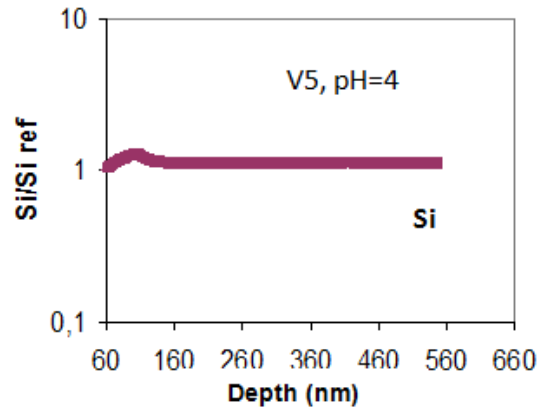
Fig. 20. Deep profiles of Si element on V5 surface glass altered at pH = 4 for 28 days

In basic medium at pH = 13: As regards the network formers, it is noted that release of Si is much higher for V3 glass than for the other glasses (Fig. 7). Indeed, release of Si is very fast at the beginning of alteration and continues to increase with time for the V3 glass. Only V1, V4 and V5 glasses have curves that tend towards an asymptote when time increases. As at pH = 4, the dissolution of silicate network is slower for V4 and V5 glasses and only V1 and V2 glasses release zirconium in solution (Fig. 8). Concerning network modifiers, in general, V4 and V5 glasses have very low concentrations of Na in solution (Fig. 9), generally below the limit detection. V1 and V2 glasses have a rapid release of Na and Ca from the beginning of alteration and then stagnate at long times. V3 and V5 glasses have the least Ca mass losses (Fig.10). As at pH = 4, there are V4 and V5 glasses that have the lowest normalized mass losses at pH = 13. Many studies carried out on leaching of silicate glasses containing zirconium have shown a sharp slowdown in silicon dissolution rate during their alteration [33, 34, 35, 36]. It has been shown that glasses deteriorate much more slowly in presence of zirconium and that alterated degree of glasses significantly increases at low zirconia levels [37, 38]. This is due to the appearance of a fine, zirconium-rich alteration film on surface of glass which, although it does not prevent Si leaching [39], still makes it possible to slow down the corrosion of glass silicate framework or network [30]. This slowing down with the increase of zirconium content can be explained by the fact that Zr-O-Si bonds are much more difficult to dissolve than Si-O-Si bonds. Thus, at low levels of zirconia, the reconstitution of gel is much slower than the dissolution of glass, the blocking then occurs later and glass therefore deteriorates more deeply. When zirconia content increases, it is the slowing down of alteration or dissolution rate of glass that prevails [40]. Thus, glasses rich in Zr are automatically "harder", since proportion of soluble covalent species decreases in favor of poorly soluble covalent species (Si and Zr).
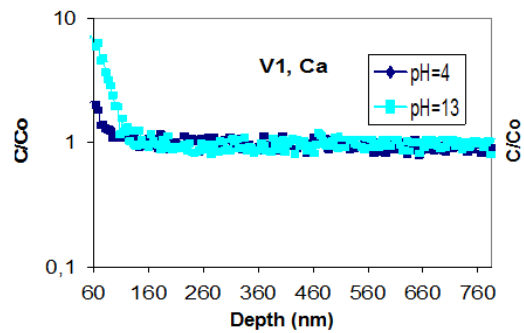

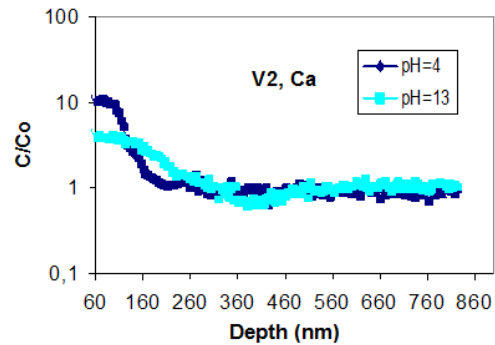**Fig. 21. Deep profiles of Ca element on V1 surface glass altered at pH = 4 and pH=13 for 28 days**

Fig. 22. Deep profiles of Ca element on V2 surface glass altered at pH = 4 and pH=13 for 28 days

Fig. 23. Deep profiles of Ca element on V3 surface glass altered at pH = 4 and pH=13 for 28 days

3.3 Alteration Mechanisms

SIMS allows producing elementary profiles of alteration films of a few tens of thickness. We will present here in depth profiles made on altered glasses V1, V2, V3, V4 and V5 at pH = 4 and pH=13 at 90ºC for 28 days. Only H, Na, Ca, Zr and Si profiles will be presented. To determine which mechanisms are responsible for glass alteration, we will report on one side hydrogen and Na profiles of on the same graph and then, on the other hand Si, Zr and Ca profiles.

Na and H profiles at pH = 4 and pH=13: At pH=4, for V1 (Fig.11-a) and V2 (Fig.12-a) glasses, it is H profile behaves antagonistically to that of Na without cutting. In fact, the penetration depth of hydrogen H increases with the depth of leaching of Na: Na content decreases strongly in alteration film whereas this film is hydrated throughout its thickness. Alteration film is thus

Fig. 24. Deep profiles of Ca element on V4 surface glass altered at pH = 4 and pH=13 for 28 days

Fig. 25. Deep profiles of Ca element on V5 surface glass altered at pH = 4 and pH=13 for 28 days

Fig. 26. Deep profiles of Zr element on V1 surface glass altered at pH = 4 and pH=13 for 28 days

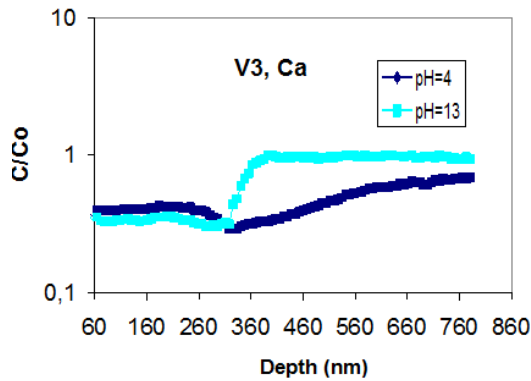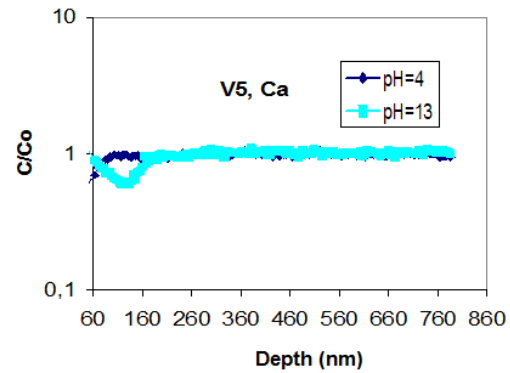**Fig. 27. Deep profiles of Zr element on V2 surface glass altered at pH = 4 and pH=13 for 28 days**
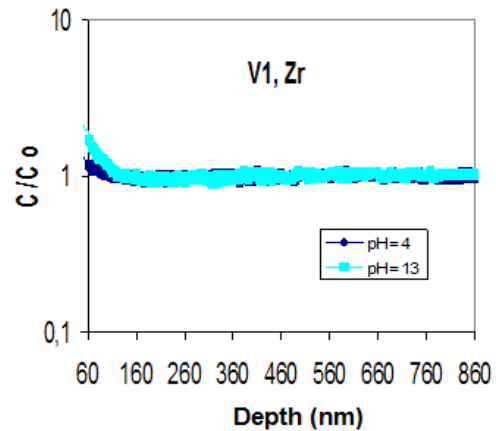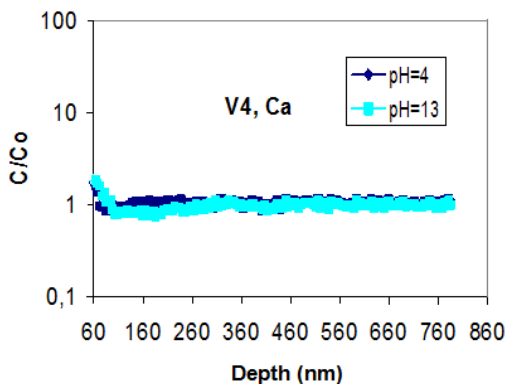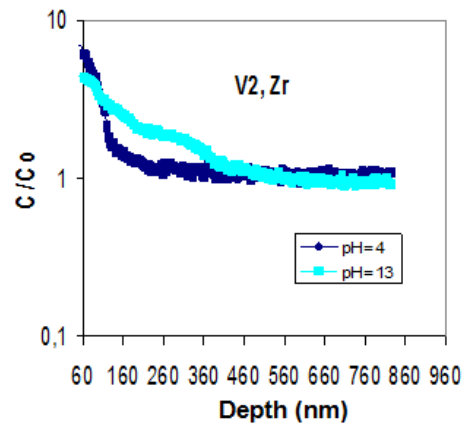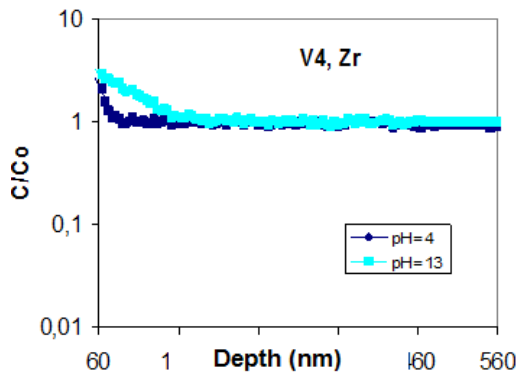
Fig. 28. Deep profiles of Zr element on V4 surface glass altered at pH = 4 and pH=13 for 28 days
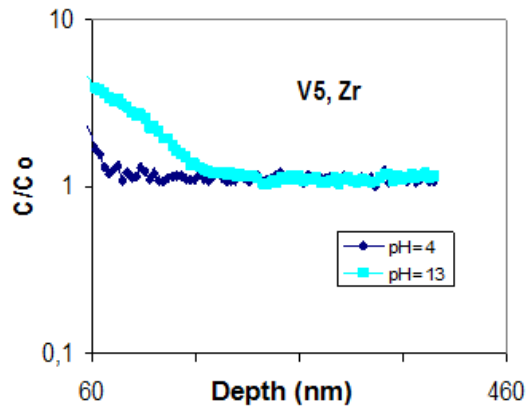

Fig. 29. Deep profiles of Zr element on V5 surface glass altered at pH = 4 and pH=13 for 28 days

enriched in H and depleted in Na. This overconcentration of hydrogen thus makes it possible to ensure compensation of charges due to the lixiviation of modifying ions of the vitreous network. V3 (Fig.13-a) glass has a behaviour which differs from V1 and V2 glasses under the same alteration conditions. It can be observed that Na is slightly depleted at extreme surface while alteration film is highly hydrated throughout its thickness. Thus, Na and H do not behave antagonistically. The V4 (Fig.14-a) and V5 (Fig.15-a) glasses behave differently than V1, V2 and V3 glasses. Indeed, profiles made are totally opposite and intersect. The maximum hydrogen content is reached at 90 nm of the surface for V4 and 65 nm for V5 glasses. This means that alteration film would be less hydrated in its deepest zone. It therefore appears that Na behaviour differs according to the composition of

glass. This indicates that for V3, V4 and V5 glasses, Na element is not fully leached or participates in surface precipitation of alkaline products [41]. With regard to hydrogen, maximum levels are reached at the extreme surface for all glasses, thus indicating that surface film would be less hydrated than the deeper zone of alteration film. At pH=13, the appearance of Na and H profiles does not differ from that at pH = 4: Na content strongly decreases in alteration films of all glasses except V3. V1 (Fig. 11-b), V2 (Fig.12-b) and V3 (Fig.13-b) glasses are more hydrated than V4 (Fig.14-b) and V5 (Fig.15-b) glasses. But, Na levels in glass surface at pH = 13 are different from those at pH = 4 except for V3. At pH = 13, Na is almost completely leached from surfaces of V1, V2 and V4 glasses while it is retained almost entirely in V3 and partially in V5 glasses. These profiles at pH = 4 and 13 reflect Na modifying cation and hydrogen interdiffusion in solution [26, 27, 42] for V1, V2, V4 and V5 glasses. This overconcentration of hydrogen thus makes it possible to ensure compensation of charges due to the lixiviation of modifying ions of vitreous network. So, the formation of hydrogen bonds of water with relatively immobile species in the glass leads to lowering of water diffusivity [43].

Si profiles at pH = 4 and pH=13: At pH=4, a slight depletion of Si at extreme surface can be observed on V1 (Fig.16), V2 (Fig.17), and V3 (Fig.18) glass profiles, unlike V4 (Fig.19) and V5 (Fig. 20) glasses, which themselves have a slight surface enrichment. Nevertheless, surface contents of all glasses remain close to those in the non-altered glass (C / Co ≈ 1). At pH = 13, one observes the same trend as pH=4.

Ca profiles at pH = 4 and pH=13: Calcium behaviour was studied as a function of depth from the surface of altered glasses for 28 days at pH = 4 and 13. For glasses V1 (Fig. 21), V2 (Fig. 22) and V4 (Fig. 24), whatever the pH, no leaching profile is observed on glass surfaces. On the contrary, we observe an enrichment of Ca on V4 and an over-enrichment on V1 and V2 glass surfaces with sometimes calcium levels almost 10 times higher than in non-altered glass (C / Co≈ 10). A Ca leaching profile is observed on V3 (Fig. 23) surface glass at pH = 4 as well as pH = 13. Nevertheless, calcium levels never fall below 50% of their values in non-altered glass. Calcium is weakly leached on V5 (Fig. 25) glass surface, although it is more pronounced in basic medium. Calcium surface enrichment for V1, V2 and V4 glasses indicates that calcium is retained

Table 2. Enrichment (+) and depletion (-) of elements in alteration films of V1, V2, V3, V4 and V5 glasses altered at pH = 4 and pH=13 for 28 days

Glasses / Elements	V1	V2	V3	V4	V5
Si	– –	– –	-	+	+
Na	-- -- --	-- -- --	--	-- --	-- --
Ca	+ +	+ +	-- -- --	+	--
Zr	+	+ +		+ +	+ +

Table 3. Epaisseurs de la pellicule d'altération (nm)

Verres	pH=4	pH=13
V1	230	415
V2	410	460
V3	500	360
V4	90	150
V5	70	150

in alteration film regardless of pH. But the fact that calcium is not totally leached on the V3 and V5 glass surfaces may mean that calcium participates in precipitation of alkaline earth products on surface. Indeed, calcium silicate hydrates can precipitate and sustain glass dissolution by consuming Si [44].

Zr profiles at pH = 4 and pH=13: Zirconium behaviour was studied as a function of depth from surface of altered glasses for 28 days at pH = 4 and 13. It can be seen that zirconium is held on surface of all glasses (except V3 which does not contain zirconium). This enrichment is much more marked for V2 (Fig. 27), V4 (Fig. 28) and V5 (Fig. 29) glasses with surface Zr concentrations are more than 5 times higher than in healthy glass (C / Co ≥ 5) compared to V1 glass (Fig. 26). It shows that zirconium dioxide slows down corrosion of alkali resistant glasses [45] and improves their chemical resistance [46].

So, surface compositions of the 5 glasses in acidic and basic solutions are summarized in Table 2.

Altered film thickness: The thicknesses of altered films (Table 3) are estimated from hydrogen contents at C / Co = 1/2 considering that abrasion speed is linear. In acidic medium, V2 and V3 glasses have the highest alteration thicknesses, while at pH = 13, there are V1 and V2 glasses which have the highest alteration thicknesses. V4 and V5 glasses have the lowest alteration thicknesses whatever the pH. These alteration thicknesses are higher in basic medium except for V3. The glass alteration rate is a function of the protective layer's transport properties, that is, its thickness and apparent diffusion coefficient. The thickness of the protective layer is function of the interface between the primary solid and the protective layer and a dissolution at the external face of the protective layer [44].

4. CONCLUSION

We developed 5 glass compositions including two alkali-resistant model glasses type CEMFIL V1 (with Zr and without heavy metals), V2 (with Zr and heavy metals) then three glasses of fly ashes V3 (without zirconium), V4 (30% of V3 with zirconium) and V5 (60% V3 with zirconium). Glasses leaching in acidic and basic medium has shown that a basification takes place causing a significant drift of the pH from the first times of alteration at pH = 4 whereas one observes a decrease of basification for solutions initially at pH = 13. In view of normalized elementary mass losses, deterioration degree of glasses is higher for low-calcium glasses (V1 and V2) whereas V4 and V5 glasses have the lowest elemental mass losses at pH = 4 and 13. SIMS profiles of glass alteration films have made it possible to observe H, Na, Ca, Si and Zr elements behaviour at 28 days in pH = 4 and 13 solutions to understand the various mechanisms involved during dissolution. At pH = 4 and 13, SIMS profiles showed that a hydrated film develops on glass surface, characterized by a hydrogen enrichment H and a depletion of sodium Na irrespective of glass, as well as very small variations of Si concentration in surface. These glasses are also characterized by zirconium surface enrichment (except V3 which does not contain zirconium) whatever the pH. These results are in agreement

with ICP leachate analysis results: Zr concentrations are the lowest in solutions for V1 and V2 glasses and are below the detection limit for V4 and V5 glasses, whatever the pH. In addition, comparison of hydrated film thickness reveals a much more pronounced alteration for V1, V2 and V3 glasses than for V4 and V5 glasses. This indicates that it forms rapidly on the surface of glasses during leaching, conditions that slow down corrosion process for V4 and V5 glasses. These results are confirmed by ICP-AES leachate analysis because V4 and V5 glasses have the lowest elementary mass losses in solution whatever the pH. So, V4 and V5 glasses can be goods candidates for cement reinforcement.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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