Development of a process for producing zirconium-rich alkali-resistant glasses containing heavy metals present in fly ashes from municipal solids waste incineration.

ABSTRACT: The objective of this study is to develop a process for producing alkali-resistant zirconium-containing glasses for use as a heavy metal retention matrix contained in fly ashes. 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 (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 SiO₂, ZrO₂ and Na₂O to give them alkali-resistant properties. Differential thermal analysis show a glass transition temperature Tg of 656 °C for V1, 616 °C for V2, 615 °C for V3, 641 °C for V4 and 664 °C for V5. Extremely small peaks of alumina can be observed on the V1, V2 and V3 glasses and peaks of ZrO₂ only on the V5 glass. Surface analysis of glasses show that they are essentially homogeneous although we note the presence of some heterogeneities: V1 and V2 contain small crystals of ZrO2, V3 has a slight crystallization of Fe chromite spinel (CrO₄) and V5 contains large crystals rich in zirconium. This study has shown that all glasses are totally amorphous. Also, alkali-resistant fly ashes glasses V4 and V5 are the most resistant to leaching and the least attacked in alkaline medium than CEMFIL type glasses V1, V2 and V3.

Keywords : Glass, alkali-resistant, heavy metal, fly ash, zirconium.

1. INTRODUCTION

The first alkali-resistant glasses were developed in 1967 by Majumdar [1]. They have been developed for use as reinforcement in cementglass matrices [2] to improve their chemical durability in alkaline medium [3]. Because of their alkali-resistant nature, glasses containing zirconium are used to produce glass fibers [4]. The first fiberglass, developed by Pilkington in the 1970s and known as "CEMFIL", is a satisfactory compromise between fiber drawing performance and cost characteristics. Numerous leaching studies of zirconium-containing glasses available in the literature have revealed the formation of a protective layer on the surface of direct corrosion of the glass framework [3]. All the studies carried out on ZrO2-rich glasses showed a clear improvement of the chemical and mechanical durability in basic medium as soon as one adds 4.6% in mass of ZrO₂ [5]. Thus, a study on CEM-FIL (18.1% ZrO₂) and NEG (21.2% ZrO₂) glasses in basic medium at PH = 13, has demonstrated that the addition of ZrO₂ significantly improves the corrosion resistance and chemical durability that has increased by more than 30% compared to initial glasses [6]. Also, the glasses deteriorate much more slowly in the presence of zirconium and their degree of deterioration increases significantly with the low zirconium content

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whereas at higher zirconium contents ([ZrO₂]> 10%), it decreases to become inferior to that of reference glass without zirconium [7, 8]. The variation in the amount of ZrO₂ in zirconium-rich glasses also influences the crystallization: the glasses having an amount of ZrO₂ greater than 12,28 % by mass crystallize completely [4]. Otherwise, the incineration of municipal solids waste is a source of emission produces nonhazardous waste classified (clinker) as well as residues of purification of fumes (fly ashes). Fly ashes contain the most heavily loaded fraction of heavy metals (Cd, Cr, Zn, Pb ...) which requires special management [9]. Also, the conversion of fly ashes into stable glasses through vitrification is perfectly controlled and allows the retention of heavy metals in the vitreous matrix [10, 11, 12]. During the leaching of these vitrifiates, the destruction of the vitreous network is the main phenomenon responsible for the release of heavy metals and the protective layers that form on the surface of the vitrifiates play a determining role in the retention of these heavy metals. Thus, the presence in the composition of glasses of poorly soluble elements such as zirconium makes the vitreous network more solid, slows the kinetics of alteration of the glasses [13] and improves their durability [14, 15] by the formation of a zirconiumrich alteration layer that acts as a heavy metal retention barrier [16, 17]. The purpose of this study is to develop and characterize alkali-resistant zirconium-rich glasses that could serve as a matrix for the retention of heavy metals from residues of purification of fumes (fly ashes) coming from municipal solids waste incineration.

2. MATERIALS AND METHODS

2.1 Composition of alkali-resitant glasses

We have developed 5 glass compositions including: two alkali-resistant model glasses type CEMFIL V1 (with zirconium and without heavy metals) and V2 (with zirconium and heavy metals), three alkali-resistant glasses of fly ashes V3 (without zirconium and with heavy metal), V4 (30 % of V3 with zirconium and heavy metals) and V5 (60 % of V3 with zirconium and heavy metals). V4 and V5 glasses are obtained using V3 as raw material and supplementing with SiO₂, ZrO₂ and Na₂O to give them superior alkali-resistant properties.

CEMFIL glass with a high content of CaO (5%

V1 glass: it has a composition similar to that of 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. This will permit to follow their evolution within the glass (leaching in solution or maintenance within the matrix). The heavy metals are introduced by addition to the glass V1 and not by substitution because the effect of the increase of deterioration due to the presence of zirconium is clearer when this element is replaced with silicon than when it is added. The introduction of elements by addition makes it possible, among other things, to keep the same matrix.

V3 glass: This is the composition of Frugier's PFTS1 glass [18]. This fly ash glass is doped with heavy metals.

V4 glass : V4 glass contains 30 % of V3 glass (PFTS1) supplemented with SiO₂, Na₂O and ZrO₂ to obtain a alkali-resistant glass composition close to V1 glass. The forming oxides SiO₂ and Al₂O₃ represent 61 % by weight in V1 glass, so only 46.3 % of SiO₂ will be necessary to approach the composition of V1 glass. It is the same for alkali and alkaline earth (Na₂O, K₂O, CaO, MgO) which represent 23 % by weight in V1 glass, 12.7 % by weight of Na₂O will be sufficient to approach this composition. And finally, we add 16 % of ZrO₂. The mass percentage of pollutants is then 4.96 %.

V5 glass : V5 glass is obtained in the same way as V4 glass but with 60 % of V3 glass (PFTS1). To get closer to the alkali-resistant composition of V1 glass, we added 21.6 % SiO₂, 2.41 % Na₂O and 16% ZrO₂. The mass percentage of pollutants is then 9.92%.

2.2 Synthesis of alkali-resistant glasses

The alkali-resistant model glasses V1 and V2 and the fly ashes glasses V3, V4 and V5 are prepared under the same conditions from a mixture of precursors in powder form: SiO₂, Na₂CO₃, K₂CO₃, CaCO₃, MgO, Al₂O₃, ZrO₂ and for pollutants Cr₂O₃, CdO, ZnO, PbCO₃. The vitrifiats are prepared in a platinum crucible with a capacity of approximately 300 g by melting the mixture of oxides and carbonates. 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 1 hour. The homogenized liquid is poured onto a square steel plate 8cm long. The glass thus obtained is annealed at 550 °C for 8 hours in a conventional muffle annealing furnace and is then naturally cooled in the oven at room temperature. This annealing operation is very important because it eliminates the residual stress which is a privileged environment for corrosion. The glass squares thus obtained are cut with a diamond saw so as to obtain cubes of 1cm * 1cm of sides and 1cm thick. These glass cubes are then polished with SiC paper underwater from 600 up to 4000 grade and then with diamond up to 1 micron. The glass cubes are then rinsed with water and acetone under ultrasound then dried in an oven at 90 ° C.

2.3 Analytical methods

Chemical composition analyzes: 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 the charges, the samples are metalized with carbon before mounting them on the sample holder. Using a microscope video display system, a bombardment is made perpendicular to the surface to probe the different phases of the glass. For our study, the analyzed surface is 1 µm² and the depth of penetration is around 3-4 µm.

Differential thermal analyzes, structural analyzes as well as the observation of the surface of the glasses were carried out at the CNRS/CEMHTI laboratory in Orléans (France).

Differential thermal analyzes: they allowed to determine the glass transition temperatures of the 5 glasses (V1, V2, V3, V4, V5) using a SETARYS SETSYS 2400 analyzer evolution with a heating rate of 5 °C /min. This device is composed of a sealed enclosure that allows the control of the sample atmosphere, a temperature control oven, a microbalance, a thermocouple in opposition to measure the temperature. 40 to 60 mg is placed in an aluminium crucible while another empty crucible is used as reference. Analyzes are carried out in a temperature range from 0 to 1600 °C under an inert controlled

atmosphere (argon).

Structural analyzes: They were performed by X-ray diffraction (XRD) using a Brucker D8 advance diffractometer. It includes an X-ray source which is a vacuum tube provided with a device for selecting a single wavelength and an electromagnetic detector which measures the X-ray intensity in the direction. The wavelength λ is thus fixed and one follows the variations of diffracted energy as a function of the angle 20. The sample is in the form of a flat glass plate. The resolution depth is 2-3 µm and only crystallites with concentrations greater than 1% can be analyzed.

Surface composition analyzes: They were carried out using an XL40 ESEM TMP scanning electron microscope (SEM). It consists of a secondary vacuum chamber where an electron beam is shaped by electromagnetic lenses to excite the object to be studied. The electron beam is focused on the surface of the sample as a spot, shifted line by line so as to scan a rectangular surface. The electron source is a tungsten filament traversed by a heating current at T = 2700 °C. Its resolution is of the order of 5 nm. It can analyze samples whose size can vary up to 150 mm with a magnification between 15-200.000 times their real size.

Superficial hydration: the superficial hydration of the synthesized glasses was observed using the Elastic Recoil Detection Analysis (ERDA) method at Saclay's Atomic Energy Center (CEA). The beam used consists of He⁺ ions with energy of 3.1 MeV. This technique consists of sending to the sample a monocinetic beam of ions of mass M1 heavier than the element to be assayed with mass M2. Backscattered incident ions are not detected, but light atoms of the target projected forward. The different profiles obtained by ERDA give the number of hydrogen atoms detected as a function of their energy.

3. RESULTS AND DISCUSSION

3.1 Synthesized glasses

Fig. 1 makes it possible to highlight the colour of

of the glasses as well as their transparency or their opacity. V1 glass is colourless and transparent. V2 glass, which is dark green, shows some heterogeneities. The difference of colour between V1 and V2 is certainly due to the presence of heavy metals in V2. V3 glass is a black and opaque glass. V4 glass is transparent green with some heterogeneities. V5 glass, which is also green in color, has areas that are lighter than the matrix on the entire surface of the glass. This phenomenon may be due either to a phase demixation which occurs when one of the compounds has reached its solubility limit or at the beginning of crystallization [19].

3.2 Chemical composition of alkali-resistant glasses

The experimental chemical weight composition of the different glasses, determined by electron microprobe, is listed in Table 1. These results are in agreement with the theoretical percentages (Table 1) although there is a small difference between the two compositions. The difference between theoretical and experimental percentages is not significant given the uncertainty of the method which is 1 to 2%.

3.3 Glass transition temperature of alkaliresistant glasses

Evolution of the glass transition temperature (Tg) as a function of the glasses is shown in Fig. 2. These analyze show a glass transition temperature (Tg) around 656 °C for V1 glass and 616 °C for the V2 glass. For V3 glass, a transition temperature Tg at 615 °C and an exothermic peak of crystallization around 756 °C are observed. This crystalline growth is significant over a restricted temperature range, between 725 and 825 °C. This exothermic peak may be due to the fact that V3 glass is likely to present a slight crystallization of spinels under the slow cooling conditions [12]. The V4 and V5 glasses respectively have transition temperatures of 641 °C and 664 °C. A small exothermic phenomenon is also observed at 1073 °C for V4 glass and at 1024 °C for V5 glass.

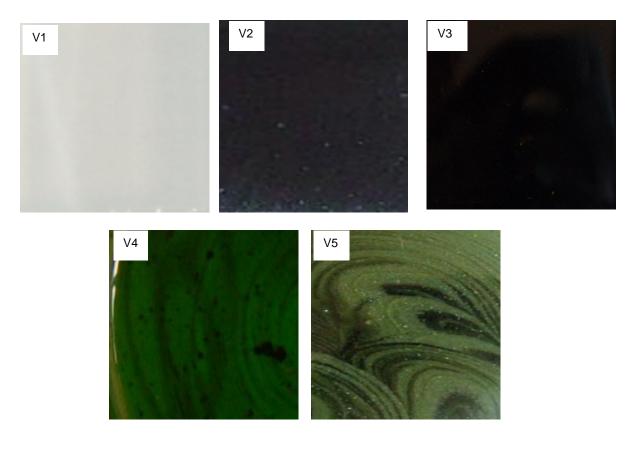


Fig.1: Photographs of alkali-resistant glasses V1, V2, V3, V4 and V5

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Table 1 : Theoretical (Th.) and experimental (Ex.) ponderal chemical composition of synthesized alkali-resistant glasses											
	\ \	V1	V2		V3		V4		V5		
% in weight	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	
SiO ₂	60,00	60,50	57,7	58,1	35,1	34,63	53,99	53,86	42,72	42,93	
Al ₂ O ₃	1,00	1,08	0,96	1	13,5	13,2	3,93	4,14	8,28	9,2	
K ₂ O	2,00	1,88	1,92	1,78	0,41	0,39	0,48	0,51	0,3	0,21	
CaO	5,00	4,91	4,82	4,55	30	31,61	8,55	8,4	19	19,2	
PbO	0,00	0,00	0,96	0,98	4,01	3,78	1,14	1,2	2,4	2,87	
CdO	0,00	0,00	0,96	1,05	2,26	2,04	0,65	0,68	1,36	1,7	
Cr ₂ O ₃	0,00	0,00	0,96	1,04	1,33	1,52	0,37	0,39	0,7	0,65	
Na ₂ O	15,00	14,92	14,42	14,2	1,9	1,93	12,43	12,08	3,18	3,22	
MgO	1,00	0,91	0,96	0,95	2,54	2,20	0,72	0,76	1,52	2,07	
ZrO ₂	16,00	15,80	15,38	15,36	0	0,00	15,19	15,20	15,08	13,55	
ZnO	0,00	0,00	0,96	0,99	2,14	1,90	0,61	0,64	1,28	1	
Fe ₂ O ₃	0,00	0,00	0,00	0,00	2,33	2	0,66	0,69	1,38	1	
TiO ₂	0,00	0,00	0,00	0,00	2,02	2,2	0,59	0,62	1,26	1	
P_2O_5	0,00	0,00	0,00	0,00	1,53	1,59	0,44	0,46	0,98	0,75	
LiO	0,00	0,00	0,00	0,00	0,93	1,01	0,25	0,37	0,56	0,65	

Obtaining the V2 glass by adding the heavy metals to the composition of V1 glass leads to a sharp decrease in the glass transition temperature Tg from 650 °C to 616 °C. When comparing V3, V4 (made with 30% V3) and V5 (made with 60% V3) glasses, it is found that the glass transition temperature increases when you go from V3 glass (Tg = 615 °C) to V4 glass (641 °C) then to V5 glass (664 °C). The glass transition temperature is a physical quantity that depends on the organization of the atoms within the glass network (density of the recoveries of the covalent bonds, length and

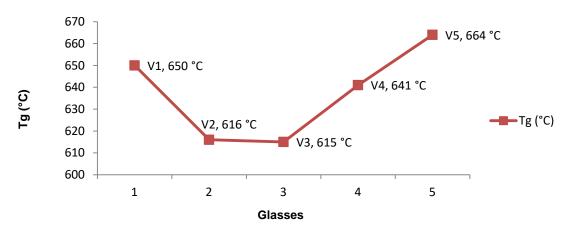


Fig. 2: Evolution of alkali-resistant glass transition temperatures

number of bonds between cation and oxygen anion). It therefore depends on the free volume existing between the structural entities. Thus, a low glass transition temperature Tg can be attributed to the decondensation of the glassy network and high Tg reflects a strengthening of the glassy network.

3.4 Structural analysis of alkali-resistant glasses

The diffractograms of V1, V2 V3, V4 and V5 glasses are given in Fig. 3. The diffractograms of V1 and V2 glasses have approximately the same shape. Indeed, one can notice a strong fluorescence and the absence of discrete and fine lines of diffraction on the spectra of these glasses. In fact, large visible bumps are created by disordered line distributions in these materials. These kinds of poorly formed or very wide diffraction lines are characteristic of low crystallinity of materials. V1 and V2 glasses are totally amorphous. On the diffractograms of V3, V4, and V5 glasses, the presence of extremely small peaks (red lines in Fig. 3) characteristic of the corundum or alumina of formula α -Al₂O₃ can be observed. The diffractogram of V5 glass reveals additional peaks (blue lines) attributed to baddeleyite (ZrO₂). The shape of the diffractograms shows that V3, V4 and V5 glasses are predominantly amorphous.

3.5 Superficial hydration of alkali-resistant glasses

The ERDA spectra relating to the surface hydration of V1, V2, V3, V4 and V5 glasses are represented in Fig.4. The height of the peaks which

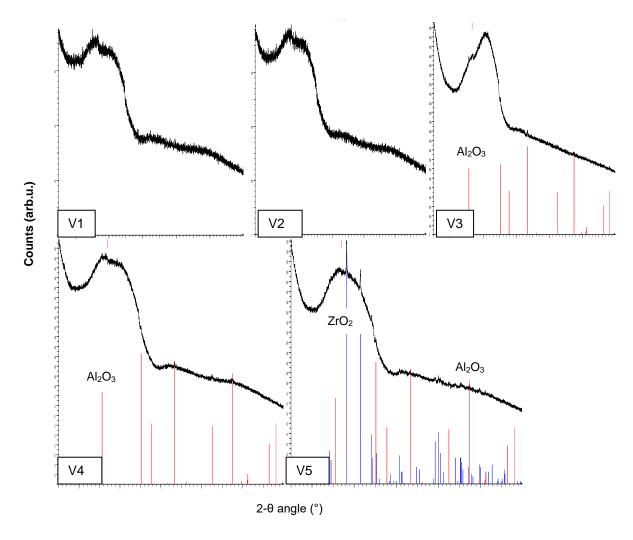


Fig. 3: XRD spectra of alkali-resistant glasses V1, V2, V3, V4 and V5

corresponds to the surface hydrogen is proportional to concentration whereas the width of the peaks that corresponds to the hydrogen at depth varies depending on the hydrated depth (deep hydration = signal to the lower channels). It is clear that increase in the peak height corresponding to the signal of the surface hydrogen as well as the broadening of the hydrogen signal at depth strongly depends on the composition of the glasses: V3 <V5 <V4 <V2 < V1. This is probably related to the hygroscopic nature of certain components of the glasses (SiO₂, ZrO₂ ...) which are responsible for a slight hydration by contact with the ambient atmosphere. Indeed, V1, V2 and V4 glasses contain more SiO₂ and ZrO₂ than V5 and V3 glasses.

3.6 Surface composition of alkali-resistant unaltered glasses

Observation of the polished surfaces of raw glasses with the scanning electron microscope as well as the analysis allowed us to highlight that there are heterogeneities on the glasses (Fig.5):

V1 and V2 glasses: These are essentially homogeneous glasses with polyhedral crystals of a few microns. Analysis shows that they are ZrO_2 crystals. It is certainly unfused zirconium oxide (Baddeleyite). These crystals are in minority.

V3 glass: This glass includes metallic crystals rich in iron and chromium. These crystals are few and randomly distributed throughout the glass. It could be dominant chromium iron spinels ($FeCrO_4$).

V4 glass: The analysis of V4 glass does not show heterogeneities on the surface.

V5 glass: This glass has areas lighter than the matrix. It also includes isolated crystals of large size (200 μ m) and rich in zirconium. These crystals consist of ZrO₂ (63%), O (29%), Si (4%) and Ca (2.5%).

3.7 Alkali-resistance of altered glasses

Fig.5 shows SEM images of the surface morphologies of V1, V2, V3, V4 and V5 glasses after 28 days of treatment in aggressive alkaline solution (pH=13) at 90 $^{\circ}$ C.

V1 glass altered at pH = 13 develops on its surface an irregular alteration layer. We note the presence of some precipitates isolated or organized in clusters. Dealkalization (between 4 and 5 % of Na instead of 12.54 % in the unaltered glass) and relative enrichment of Zr (between 17 and 18 % instead of 12.25 % in the unaltered glass) in the alteration layer as well as calcium enriched precipitates are observed.

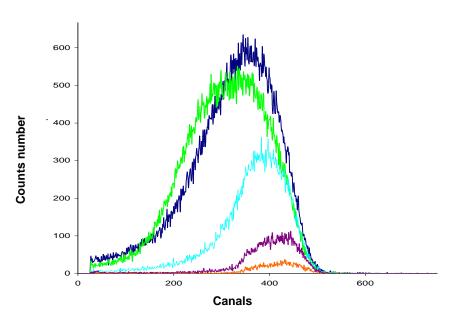


Fig. 4: ERDA spectra of V1, V2, V3, V4 and V5 glasses

V2 glass has a heterogeneous alteration layer including crystals. The unaltered glass-film interface has cracks that progress inside the film, certainly due to the roughness of the glass. The chemical microanalysis of these precipitates shows 3 significant characteristic peaks of Si, Ca and Zr. The chemical composition of the alteration layer and the precipitates reveals a dealkalization (between 3 and 5 % of Na instead of 10.54 % in the unaltered glass) and an enrichment in Zr (between 14 and 15 % instead of 11.37 % in the unaltered glass) of both the alteration layer and the precipitates are actually enriched in Ca (11.28 % instead of 3.25 % in the reference glass).

V3 glass altered at pH = 13 is completely opaque. The interface between the unaltered glass and the alteration layer shows some roughness. Precipitation of secondary phases constructed by stacking phyllosilicate-type layers is observed. The chemical analysis of the alteration layer shows that the phyllosilicates-type secondary phases are very enriched in Ca (50 % instead of 22.5 % in the unaltered glass).

Glass V4 seems little attacked. The alteration layer covers the glass surface evenly. No heterogeneity appears on the surface. The homogeneous

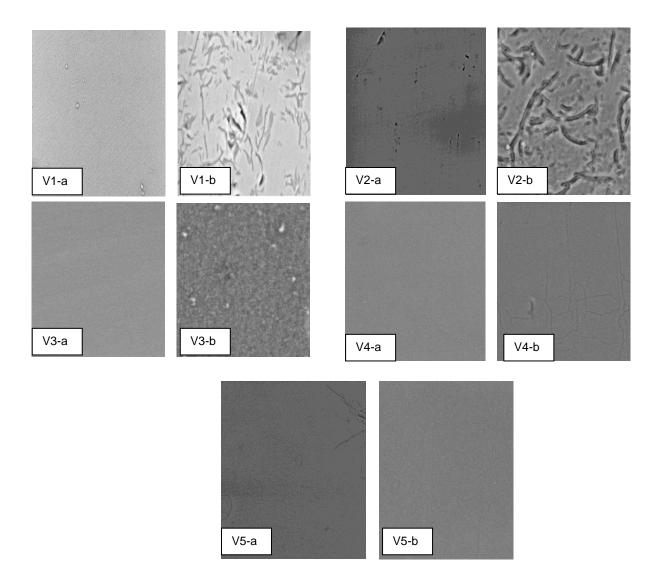


Fig. 5: SEM images (x 700) of V1, V2, V3, V4 and V5 glasses: a) unaltered glasses b) altered glasses after dipping in a alkaline solution of NaOH at pH=13 and 90°C for 28 days.

composition of the layer reveals an enrichment in Zr (18.03% instead of 11.25% in the unaltered glass) and a depletion in Na (5.68% instead of 9.38% in the unaltered glass) and in Si.

The surface of the V5 glass also seems little attacked. However, we note the formation of some phyllosilicates secondary phases and the presence of non-crystalline ZrO_2 crystals from the unaltered glass. The rest of the alteration film appears enriched in Zr (16.91% instead of 10.03% in the unaltered glass) and slightly depleted in Ca (10.93% instead of 13.71% in the unaltered glass).

4. CONCLUSIONS

We have developed 5 glass compositions including two alkali-resistant model glasses type CEMFIL V1 (with zirconium and without heavy metals), V2 (with zirconium and heavy metals), then three glasses of fly ashes V3 (without zirconium and with heavy metals), V4 (30% of V3 with zirconium and heavy metals) and V5 (60% V3 with zirconium and heavy metals). The chemical weight composition of the glasses, determined by electron microscopy is in agreement with the theoretical percentages although there is a slight difference between theoretical and experimental compositions. Differential thermal analyzes show a glass transition temperature Tg around of 600 °C for all glasses. The glasses are totally amorphous even though extremely small peaks of alumina can be observed on the V2 and V3 diffractograms and ZrO2 peaks only on the V5 diffractogram. The analysis of the surface of the they glasses shows that are essentially homogeneous and slightly hydrated. The SEM and electron microprobe analyzes reveal that all the glasses are covered with an alteration layer at pH = 13. These alteration layers are enriched in zirconium (V1, V2, V4 and V5) and depleted in Na. The V4 and V5 glasses have the most enriched zirconium alteration layers and also appear to be the least attacked.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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