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Durability of Alkali-Resistant Glass Fibers Reinforced Cement Composite: Microstructural Observations of Degradation

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RESEARCH ARTICLE

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Abstract

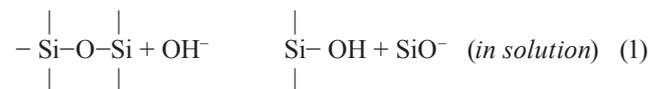
Usually, glass fibers in concrete permit the increase of the flexural strength. But the fibers in contact with cement are quickly degraded by alkali reactions due to the presence of portlandite. This article presents the results of investigations carried out to study the influence of curing conditions on the durability of alkali-resistant glass fibers in a cement matrix. Test results showed that alkali resistant fibers treated with zirconium oxide, present the same degradation phenomenon. The used cement nature has a large influence on the protection of the fibers. In addition, the degradation is weakened when silica fumes are added, owing to the pozzolanic effect that decreases the portlandite quantity. In spite of those different ameliorations, the use of such materials in humid environment is proving to be risky. The used techniques to study those phenomena are SEM equipped with energy dispersive spectrometer (EDX) to observe the attack microstructures of the fibers and X-ray diffraction to quantify the portlandite and other phase development.

Keywords

glass fiber; cement matrix; durability; curing conditions

1 Introduction

The use of fibres to strengthen materials which are much weaker in tension than in compression goes back to ancient times. Now, fibres of various kinds are used to reinforce a number of different materials, such as epoxies, plastics, ceramics and concrete [1, 2]. Glass fibers have particularly high an ultimate tensile strength and a very high Young's modulus, compared to other organic or inorganic fibers [3]. As a solution, they are a material of choice for improving the cracking resistance and the toughness of many composite products [4]. However, the studies on the Glass Fiber Reinforced Cement (GFRC) showed the low durability of the fibers in the cement matrix [5–7]. The fiber degradation is due to the portlandite ($\text{Ca}(\text{OH})_2$) produced during the hydration and the setting of the cement. This lime keeps the high pH of interstitial solution in the pores of cementitious matrix (pH of about 12.6). This alkaline environment leads to a rapid deterioration process which involves strength and weight losses, and a reduction in the filament diameter [8]. This process can be attributed to breaking of the Si–O–Si bonds in the glass network, by the hydroxyl ions (OH^-) which are highly concentrated in the alkaline pore solution as shown in Eq. (1):



In fact, portlandite increases the alkalinity of the matrix and develops large crystals. In addition, the glass fibre degradation is also caused by the deposition and growth of the portlandite ($\text{Ca}(\text{OH})_2$). This portlandite fills spaces between and around the glass fibre filaments, thus cementing them together and reducing their flexibility. This causes excessive bonding and local concentration of stresses under load at the surface of fibres, resulting in embrittlement of GFRC [9]. Both phenomena weaken the fibers [8]. Alkali resistant glass fibers, called CemFil, have been developed using zirconium oxide (ZrO_2) additives that inhibit the cement matrix attacks. However, they are still sensitive to a humid environment: a decreasing of the flexural strength is observed [10, 11].

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Several techniques are used to protect fibers. One of these is to protect the fibers by using a cement at low basicity [12–16]. Some authors used a cement at low alkalinity such as the sulphoaluminate cement (LASC) [17]. For this cement matrix no $\text{Ca}(\text{OH})_2$ crystals are detected by SEM observation and XRD analysis. The pH value of the pore solution for cement matrix of LASC is 10. Another technique can be also used by densifying the interface between fibers and matrix with polymers (PVA, AC or VAC) to prevent the lime diffusion into fibers [18, 19]. Other techniques consist in limiting the alkali-silica reaction by reducing the amount of portlandite into the matrix under pozzolanic effect. For instance, fly ashes, silica fumes or granulated blast furnace slag could be added to conventional concrete in order to substitute a part of the cement. [20–24].

Our study aims at analyzing the fibers evolution into the cement matrix, under different storage conditions and with or without silica fume addition. The fibers are observed by scanning electron microscopy (SEM) and the content of portlandite is determined by X-ray diffraction using the integrated method (semi-quantitative measurements of “step to step”).

2 Experimental

2.1. Materials

2.1.1. Matrix materials

The used cement is CEM II/B-V (32.5R) from Ciment Lafarge Ltd (France), conformed to EN 196-1 [25]. The chemical composition according to the manufacturer is given in Table 1. The sand used is a siliceous fraction that does not exceed 500 μm in size (see Fig. 1). Silica fume (a byproduct of the semiconductor industry brought from Bretagne area in France) added for a series so as to reduce the amount of portlandite by pozzolanic effect, it replaces cement (Table 4). To ameliorate the fresh mixture workability, the superplasticiser Sikament FF86, conformed to NF EN 934-2 [26], is used. Its physical and chemical characteristics are given in Table 2.

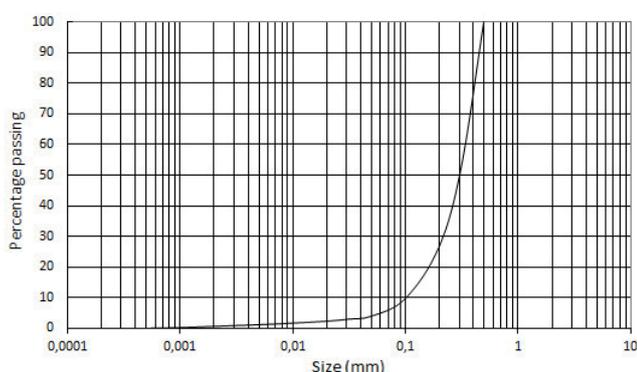


Fig. 1 Particle size distribution of sand

Table 1 Chemical composition (mass %) of the cements and of the silica fumes.

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Cl^-	Insolubles	Loss on ignition
Cement	25.05	8.6	3.5	55.4	0.9	1	0.15	2.7	0.022	11.8	2.2
Silica fume	97.64		0.1	0.14	0.15	0.39	0.14				

Table 2 Physical and chemical characteristics of the superplasticiser Sikament FF86

	Aqueous solution
Density	1.23
pH	7–11
Cl^- (weight %)	< 0.1
Na_2O equivalent (weight %)	< 6.0

2.1.2. Glass fibers AR

The studied glass fibers are alkali resistant fibers, CemFil, from Saint Gobain Vetrotex manufacturer. The fibers (12 mm length) have a high content of zirconium oxide ZrO_2 (16.6 mass %), that should protect the fibers from the alkaline attacks of the cement matrix. The major physical and mechanical properties, given by the manufacturer, are displayed in Table 3.

Table 3 Physical and mechanical properties of the AR fibers

Density	2.68 g/cm^3
Tensile strength: virgin filament	3000 MPa
Tensile modulus	73000 MPa
Elongation at break	4.30%
Coefficient of linear thermal expansion (between 20 and 100°C)	$5.10 \cdot 10^{-6}$ m/m/K
Flammability	773 °C

2.2. Sample preparation and tests

Three series of mortars have been prepared. The formulation parameters of the different glass fiber reinforced matrix are shown Table 4. The low silica fume addition is conditioned by the use of CEM II/B 32.5 cement that contains 24 % of fly ash.

Table 4 Compositions of the used mortar series

Constituents (weight % and ratios)	CEM II/B-V (32.5R)		
	1 (Reference)	2	3
Cement/Sand	1	1	1
Water/Cement	0.35	0.35	0.35
CemFil fibers	0	2	2
Silica fumes	0	0	3
Superplasticizer	0	0	2

Mortar samples ($4 \times 4 \times 16 \text{ cm}^3$) have been prepared and demoulded after 24 hours. They were cured in a moist room (20 °C and 95 % relative humidity) during 7 days and then during 1 year in different environments: in a moist room (20°C, 95 % relative humidity) and at ambient air. The sample formulations and curing condition are given Table 5.

Table 5 Samples compositions and curing conditions

Samples	Fiber rates (mass %)	Silica fumes (weight %)	Storage conditions
FSH2	2	-	Moist room
FCA2	2	-	Ambient air
FSH3	2	3	Moist room
FCA3	2	3	Ambient air

The phase composition of each sample was determined by X-ray diffraction (XRD) using a Philips PW3710 type (Cu-K α radiation) and the microstructure was examined using a scanning electron microscope SEM (JOEL JSM-6301F) coupled with EDX microanalysis.

3 Results and discussion

3.1. Quantitative analysis of Portlandite in cement matrix

According to some authors [9, 10] the presence of portlandite between fibers would be one of the causes of their degradation. The calcium hydroxide is formed into the spaces between fibres as shown in Figure 2. Two modes of attack on the glass fibres are evident: hydroxylation and notching by Ca(OH)₂ crystals. The surface of fibres becomes generally hydroxylated due to the high pH of the matrix, but notching attack is concentrated at points where a fibre is in good contact with Ca(OH)₂ crystals, leading to their impingement on and into fibres [27]. The content of portlandite was determined using X-ray diffraction.

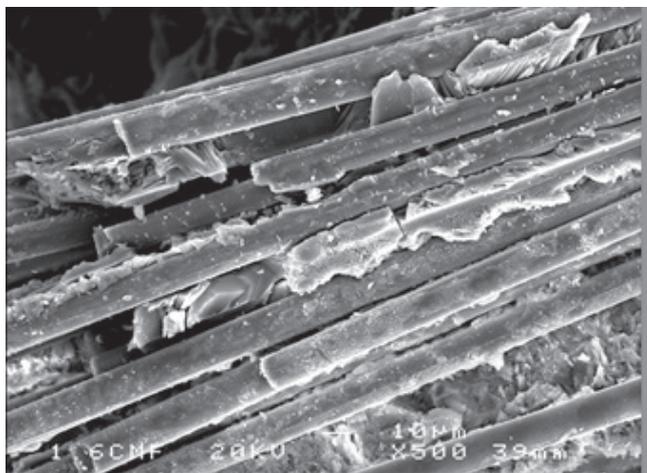


Fig. 2 Filling of the spaces between the filaments by calcium hydroxide. Note surface corrosion and notching by Ca(OH)₂

The X-ray diffraction (λ K α Cu, Ni filter), step-to-step) has been performed on 4 samples: FSH2 and FSH3 cured in moist room, FCA2 and FCA3 cured at ambient air. The X-ray patterns are given in Fig. 3. The peak intensity of the calcium hydroxide (portlandite) on the diffraction pattern is measured by the integrated method (semi-quantitative measurements of “step to step”); results are reported in Table 6. It is also mentioned the peak intensity of the calcium carbonate (calcite) in order to assume the carbonation of the samples.

Table 6 X-ray diffraction peaks intensity of the calcium hydroxide and the Calcite

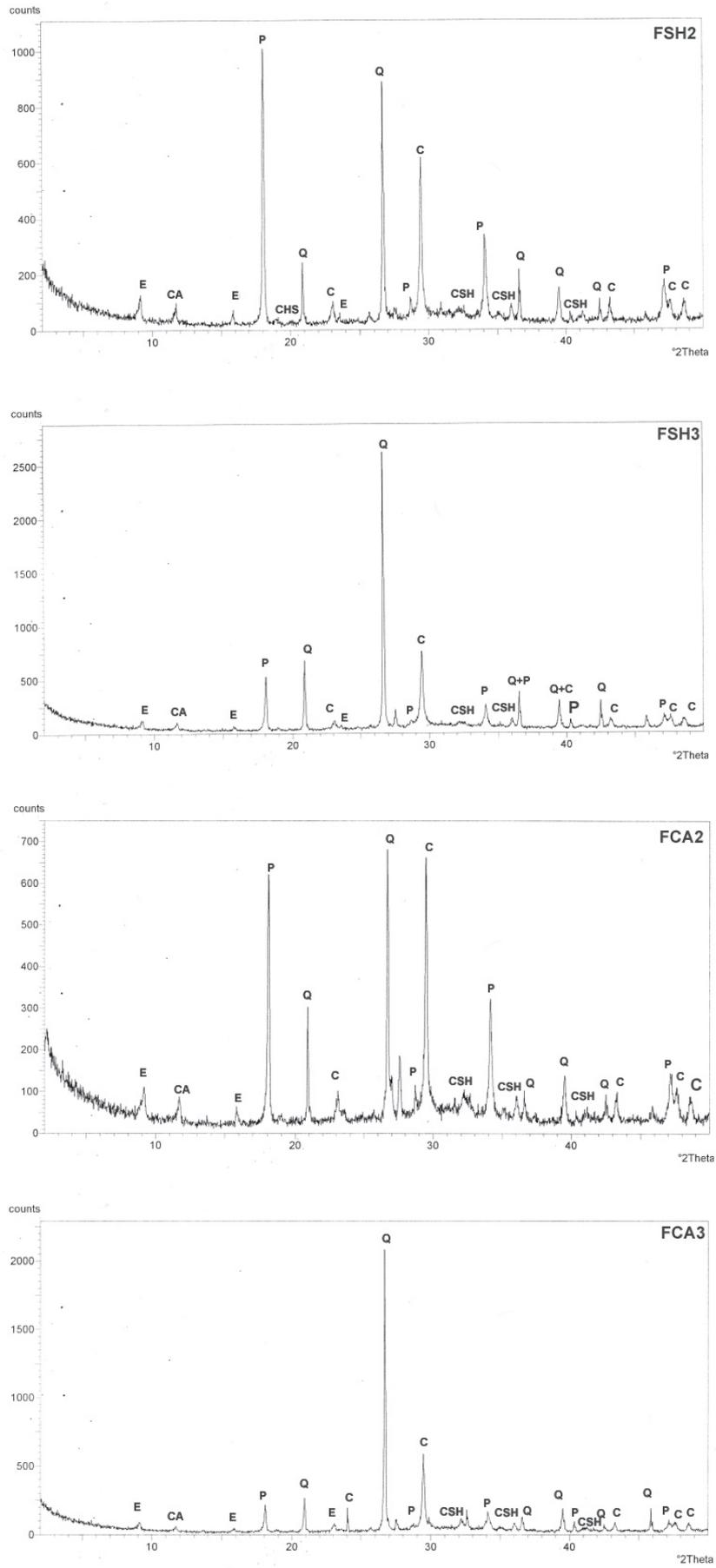
	2 θ	d(Å)	Formulations			
			FSH2	FSH3	FCA2	FCA3
Calcium hydroxide [Ca(OH) ₂]	18.08	4.90	995	504	603	171
	34.1	2.62	305	202	291	146
	47.13	1.93	125	103	114	62
Calcite [CaCO ₃]	23.11	3.84	65	87	70	48
	29.45	3.02	542	728	639	517
	47.62	1.90	67	95	69	61

The intensity of the portlandite peaks is lower for the FCA samples, cured at ambient air, than for the FSH samples, cured in moist room. The development of the portlandite crystals in FSH samples can be explained by the presence of water in the pores of the samples. The water permits the Ca⁺⁺ ions diffusion towards the matrix and then the growth of the portlandite the solution in the paste is always saturated with Ca⁺⁺ ions and the voids are simply the free place for crystallization not only of portlandite but also of ettringite [28–30]. Portlandite peaks are weaker in the samples containing silica fume. That confirms a reaction between portlandite and silica, and thus the expected pozzolanic effect. The carbonation phenomenon is observed in all samples, regardless of the curing conditions, but is limited when samples are cured in moist room. When the relative humidity increases, the fraction of pores filled with water also increases and obstructs the diffusion of CO₂ gas which is approximately 10,000 times smaller in liquid phase than in gaseous phase (in order of 10⁻¹² m²/s, against 10⁻⁸ m²/s) [31].

However, the calcium carbonate is developed in the beginning near the surface of concrete element as the result of calcium hydroxide transformation. This transformation is accompanied with increase of the content of solid phases that induces a decrease of the cement matrix porosity in the nearsurface. This is mentioned by different authors [32, 34], who have attributed to the precipitation of calcium carbonate reducing porosity.

3.2 Microstructural observations to scanning electron microscope

The SEM observations are displayed in Figure 4 and concern matrixes made of CEM II/B-V 32.5. The first micrograph shows the aspect of the CemFil fiber before mixing: a regular and smooth surface. FSH2 and FSH3 samples, conserved in moist room, present a strong degradation of the fibers, with attack spots observed along the surface. However, spots appear disseminated, the actual degradations are superficial and not homogeneous. It is noted that fibers are less damaged in the FSH3 samples owing to the silica fume additions. The observed degradation is marked either by erosion or notches. The samples cured at ambient air, FCA2 and FCA3 remain intact.



[Q:quartz; P:portlandite; E:ettringite; CA: calcium carboaluminate; C: calcite; CSH: hydrate]

Fig. 3 X-ray diffraction patterns (Cu K α)

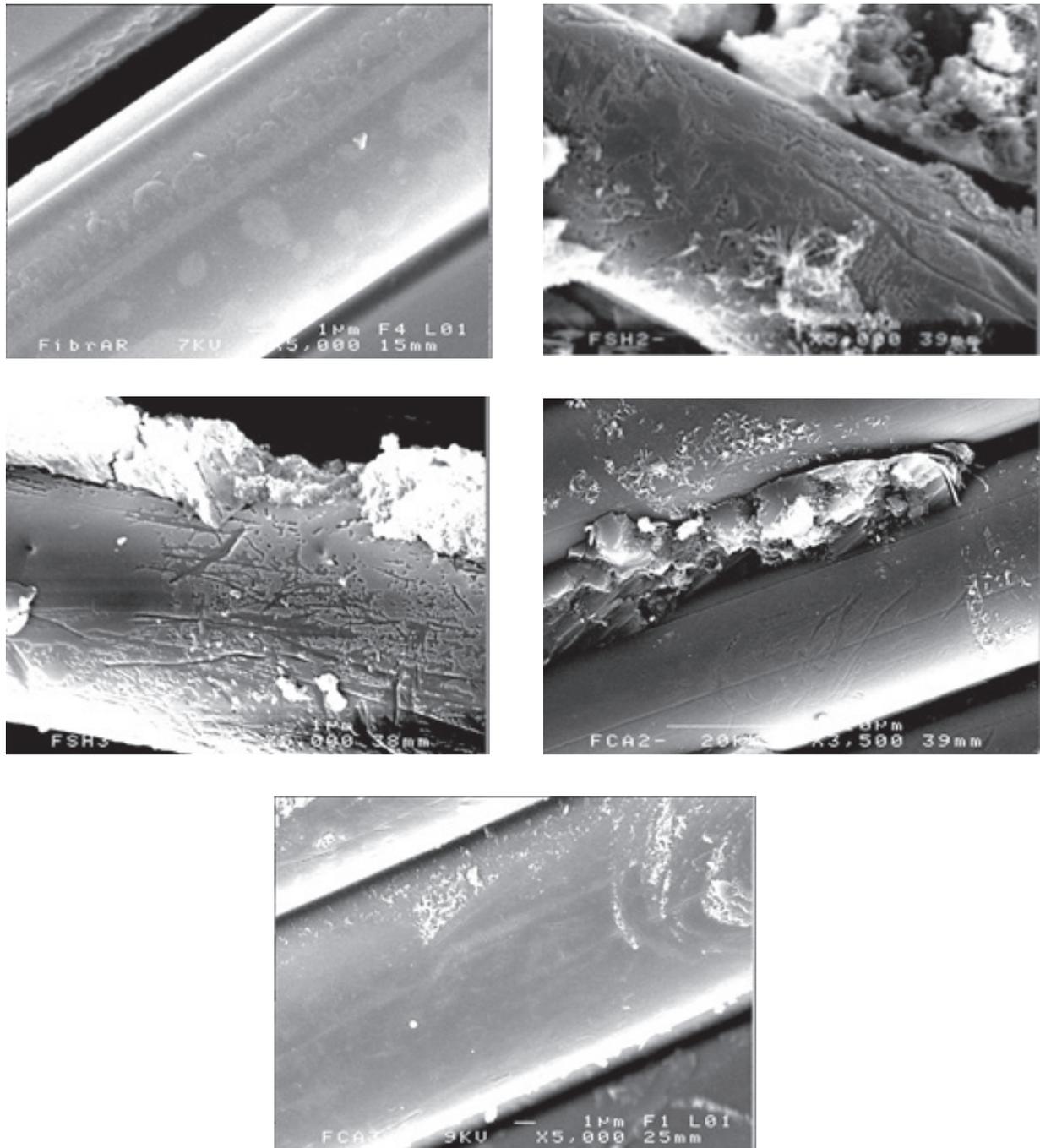


Fig. 4 SEM observations of the CemFil fiber (A.R.) before mixing and of the glass fibers in the CEM II/B 32:5 cement matrix, conserved in different environments

Those observations confirm the results obtained by X-Ray diffraction. First, silica fume additions permit to protect the fibres due to the pozzolanic reaction that transforms portlandite into CSH and thus decreases the matrix alkalinity [34]. Second, the glass fibre appearance remains stable in dry environment: on the one hand, Ca^{++} ion diffusion is braked in this environment and the portlandite cannot develop. On the other hand, the carbonation, developed at the free surface of the samples, reduces the porosity.

In addition, the energy dispersive X-ray (EDX) analysis of the A-R glass fibre surface support the observed results. The localized chemical analysis realized on fibres body different

points (Figs. 5 and 6) shows a degradation of the silicic network of the glass fibre. In the FSH3, which contains the silica fume additions, there is no excessive degradation of the fiber body and the microanalysis shows silica (Si) contents higher than those detected on the fiber of the FSH2 sample. In FCA2 and FCA3 samples, which are conserved at ambient air, the energy dispersive X-ray (EDX) analysis show silica (Si) contents higher than those detected on the fibers of the samples conserved in moist room. This points that the conservation environment at ambient air, of the alkali-resistant glass fibres used in a cement matrix, does not favor the degradation of glass structure.

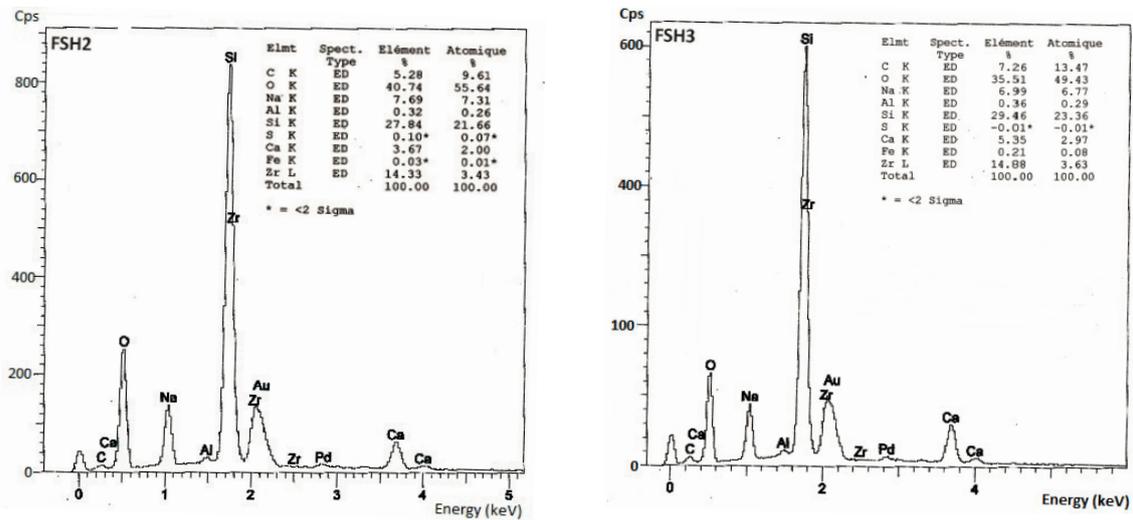


Fig. 5 Spectrometry X-ray analyses of the fibre body of GFRC cured in moist room

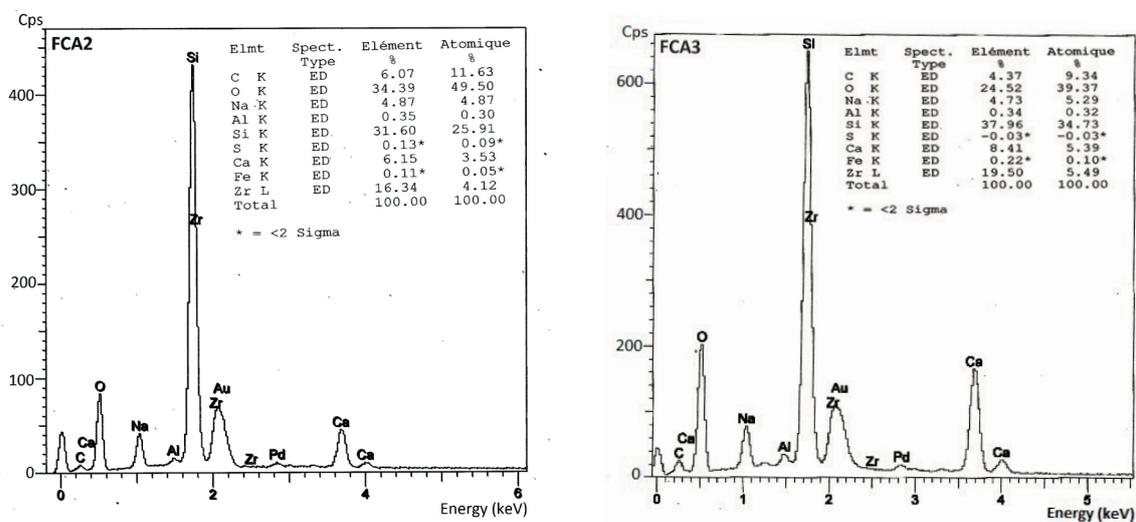


Fig. 6 Spectrometry X-ray analyses of the fibre body of GFRC cured at ambient air

4 Conclusions

This paper has presented the experimental results of a study on the durability of alkali-resistant glass fibers reinforced cement mortar. Based on the results of this study, the following conclusions can be drawn:

If degradations seem to be inevitable, they are reduced by the use of fly ash containing cement (CEM II/B-V). It is also shown that silica fume additives reduce the fiber attack phenomena owing to the pozzolanic effect that transforms portlandite into C-S-H and decreases the porosity. However, using a low alkalinity cement reduces the amount of portlandite ($\text{Ca}(\text{OH})_2$) into the matrix, which results in an impoverishment of hydroxyl ions production, thus decreasing the pH of pore solutions and consequently the environment can be depleted (less basic). On the other hand, Ca^{++} ions that can be combined with silica fume to form the new hydrated calcium silicates are reduced. In addition, the inclusion of a mineral addition such as the silica fume has a slow reaction effect with calcium hydroxide (pozzolanic effect), whereas the kinetics of degradation of glass fibres occur earlier.

Under dry environment or low humidity, like a usual indoor building (case in ambient air), alkali-resistant fibres undergo surface modifications that look like disseminated spots. These degradations do not cast doubt on the structure stability of the glass fibre-reinforced cement.

On the contrary, the use of such materials in a humid environment (in moist room) has to be avoided. The stability of the structure would be endangered in spite of the fiber treatment and the silica fume use in the cement matrix.

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