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Pozzolanic properties of fine and coarse color-mixed glass cullet

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ABSTRACT

Mixed glasses of different colors are economically difficult to reuse for the fabrication of new glass products but their use in cement-based materials is a promising way to recycle this material. This paper deals with the pozzolanic activity of mixed glass cullet, by evaluating the pozzolanic behavior of a large range of glass particle sizes, from less than 40 μm (540 m^2/kg) up to 2.5 mm (2.2 m^2/kg). Five different classes of glass are assessed separately, in terms of compressive strength tests on mortars, consumption of lime (TG), morphology (SEM) and composition of hydrates (EDX and X-ray fluorescence). The results show that the pozzolanic activity increases with glass fineness and that, compared to a reference material without glass, equivalent or superior compressive strength can be obtained when using up to 40% of glass of 540 m^2/kg fineness. A transition fineness around 30 m^2/kg (140 μm) is highlighted, for which the pozzolanic activity becomes substantial. However, a slight but significant pozzolanic activity is detected for coarse particles (>1 mm), as confirmed by the consumption of $Ca(OH)_2$, the formation of C–S–H-like hydrates and an increase of 10% (5 MPa) in the compressive strength compared to an inert admixture. The chronology of the reaction (pozzolanic and alkali-reactive) for coarse glass particles is discussed.

1. Introduction

The use of mixed glass cullet of different colors in cement-based materials represents an alternative to other recycling routes such as abrasives, glass wool or water filtration media. This application remains promising mainly because of the difficulty of recycling this material for the fabrication of new glass products. However, the glass used in cement-based materials can lead to two types of behavior having antagonistic effects: alkali–silica reaction, which causes damage in concretes, and pozzolanic reaction, which is beneficial for concrete properties.

The alkali–silica reaction (ASR) is usually associated with coarse particles containing amorphous silica. The destruction of the silica network releases silica that combines with alkali (and calcium) to form N,K–(C)–S–H gels causing expansion of the concrete. Different studies have shown the effect of glass particle size on the expansion of mortars and concretes [1–4] but the results are quite dispersed and difficult to generalize. The minimum sizes leading to deleterious expansions vary from around 150 μm to more than 1 mm, depending on the type (e.g. color) of glass, type of concrete and experimental conditions used for the tests (temperature, immersion, etc.).

The pozzolanic activity is usually related to fine particles also composed of amorphous silica. As for ASR, the silica network is attacked by hydroxide ions but the silica released combines with calcium from Portlandite (and a certain amount of alkalis that might be present in the pore solution) to form C–(N,K)–S–H which improve concrete properties.

A few papers [5,6] have reported that most alkali-reactive aggregates can show pozzolanic activity when they are ground to a few tenths of a micrometer or smaller, supporting the idea that the pozzolanic reaction only concerns fine materials (crushed or natural). In the case of glass, it has been shown that fine particles have pozzolanic properties [1–4,7–10], sometimes higher than for other pozzolans. Shao et al. [1] obtained higher strength on 30% glass concrete (<38 μm) compared to fly ash concrete, but much lower strength than that obtained with silica fume. The work of Shi et al. [2] confirmed this result, since mortars containing 20% of glass of fineness higher than 264 m^2/kg led to better mechanical performance than fly ash mortars at all the ages studied.

The pozzolanic activity of glass could depend on several formulation parameters: use as sand or cement replacement, color of glass, fineness, glass content, etc.

The use of glass as sand replacement usually gives better results than for cement replacement [3], as already shown for other types of pozzolans. Some authors studied the effect of glass color (amber or brown, green and white) on the compressive strength of mortars and concretes. While Park et al. [7] and Sobolev et al. [8] found no significant difference in the performance of glasses, Karamberi and Moutsatsou [9] and Dhir et al. [10] showed that green and white glass led to higher 28 days-activity indices than amber glass.

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The effect of glass fineness was assessed by Shao et al. [1], Sobolev et al. [8] and Shayan and Xu [4]. When using 30% of glass as cement replacement, Shao et al. [1] showed that particles smaller than 38 μm and times of 90 days were necessary to obtain a strength equivalent to that of a mixture containing only cement. In the work of Shi et al. [2], at least 467 m^2/kg and 28 days were needed for 20% glass-mortars to reach the same result. At 28 days, Shayan and Xu [3] obtained lower strength compared to the reference, even for very fine glass (800 m^2/kg). The maximum relative strength was 0.87 for 10% replacement. These results were attributed to a late development of the pozzolanic activity. Results from the literature tend to show that each kind of glass should be assessed in order to evaluate its reactivity.

This paper deals with the use of mixed glass cullet of different colors in cement-based materials. The main objective is to evaluate the pozzolanic activity of a large range of glass particle sizes, from less than 40 μm (540 m^2/kg) up to 2.5 mm (2.2 m^2/kg). Since studies in the literature are usually limited to small particles, coarser particles are used to determine the size up to which it is possible to detect a pozzolanic activity. Five different classes are assessed separately, in terms of compressive strength tests on mortars, consumption of lime, morphology and composition of hydrates. Attention is also paid to the risk of ASR that can occur in mortars.

2. Experimental procedures

2.1. Materials

The glass (G) used in this study was bottle soda–lime silica glass of mixed colors, coming from the group Unical (Canada). It was composed of 40%, 33%, 20% and 1% of colorless, brown, green and blue glasses, respectively. This composition was the mean value of three samples of 10 kg mixed glass cullet. The material also contained around 6% of impurities composed of plastic, metal and paper. Different sizes of glass particles, denoted G_x (where x is the specific surface of the glass), were obtained after grading, washing, drying, crushing and sieving the raw material. Table 1 gives the chemical compositions and the finenesses of the classes used for the pozzolanic study. It can be seen that the chemical compositions of all classes were similar, confirming the homogeneity of the material. The mean density was 2.5 g/cm^3.

The cement used was a Portland cement CEM I 52.5R according to EN 197-1 [11], with a specific gravity of 3.15 g/cm^3 and a Blaine specific surface of 440 m^2/kg. Its chemical composition is given in Table 1. This cement was composed of 56% C_3S, 26% C_2S, 12% C_3A and 6% C_4AF. The sand used for the pozzolanic study was a non-reactive quartz sand in accordance with standard EN 196-1 [12]. A coarse quartz powder (Q_{Ref}) having a mean diameter of 215 μm and a specific surface (Blaine) of 23 m^2/kg was used to quantify the effect of cement dilution in the mortars.

2.2. Sample preparation and test methods

The pozzolanic activity of the different size classes of glass was tested through compressive strength measurements on mortars. The mortars were composed of three parts of sand and one part of binder (cement and glass). The water-binder ratio was 0.5. Four types of mixtures were made, with increasing proportions of glass used as cement replacement: 0%, 10%, 20%, 30% and 40% of glass of classes G_2 (1250–2500 μm), G_4 (630–1250 μm), G_{18} (160–315 μm), G_{200} (<80 μm) and G_{540} (<41 μm) (total of 21 mortars). Mortars were prepared according to standard EN 196-1 [12]. After casting, the prismatic samples (4 × 4 × 16 cm) were cured in water at 20 °C until the age of test (1, 7, 28, 90 and 210 days). Each compressive strength result was the mean value of 6–9 individual tests.

Lime consumption was determined by thermogravimetric analysis (TG) on pastes composed of 65% of glass (coarse G_2 or fines G_{540}) and 35% of $Ca(OH)_2$ by weight. The pastes were prepared by hand mixing the required amounts of solids with deionized water at 20 °C for 2 min. After mixing, they were cast into small polyethylene bottles. All specimens were sealed to prevent moisture exchange and carbonation. The pastes were cured at 20 °C until analyzed. The thermogravimetric analyses were made on powders obtained after crushing and sieving the hardened pastes at a diameter of less than 80 μm. These tests were carried out at temperatures ranging between 40 and 1000 °C, at a heating rate of 10 °C/min.

The analysis of new-formed hydrates according to glass particle sizes was performed on suspensions containing $Ca(OH)_2$ or C_3S, glass (coarse G_2 or fines G_{540}) and a solution of 1 mol/l KOH (Table 2). These suspensions were prepared in small stainless steel reactors and kept in a thermostatic bath maintained at 60 °C until the analysis. Precipitates were separated by filtration from the solution and then dried at 20 °C in a vacuum freeze dryer. The morphology of hydrates was determined by scanning electron microscopy (SEM – JEOL JSM 6380 LV). Their elementary compositions were measured using energy dispersive X-ray spectroscopy (EDX, 15 kV and 10 nA) and X-ray fluorescence (XRF).

Table 1
Chemical and physical characteristics of cement and glass cullet.

Chemical composition (% by mass)	Cement	Classes of glass[a]				
		G_2	G_4	G_{18}	G_{200}	G_{540}
SiO_2	19.8	69.4	69.3	69.4	69.4	68.9
Al_2O_3	5.6	2.0	2.1	2.1	2.1	2.1
Fe_2O_3	2.5	0.2	0.2	0.3	0.4	0.3
CaO	63.6	12.5	12.6	12.4	12.5	12.3
MgO	1.8	1.1	1.1	1.1	1.1	1.0
SO_3	3.1	0.2	0.2	0.2	0.2	0.2
Na_2O	0.1	13.7	13.6	13.7	13.2	13.6
K_2O	0.7	0.6	0.6	0.6	0.6	0.6
Loss on ignition	1.7	0.3	0.3	0.3	0.6	1.0
Physical characteristics						
Specific surface[b] (m^2/kg)	440	2.2	4.5	18	200	540
Particle size ranges (μm)	–	1250–2500	630–1250	160–315	>81	<41
Mean diameters (μm)	–	1875	940	237.5	23.5	7.8
Specific gravity (g/cm^3)	3.15	2.40	2.41	2.41	2.43	2.48

[a] G_x: x is the specific surface of the glass.

[b] Blaine for cement, G_{200} and G_{540}; calculated from the particle size distribution for G_2, G_4 and G_{18}.

Table 2
Mixture proportions for the analysis of new-formed hydrates in diluted systems ($Ca(OH)_2$ and C_3S) containing glass.

	Suspension $Ca(OH)_2$–glass		Suspension C_3S–glass	
Binder	$Ca(OH)_2$	6.0 g	C_3S	5.0 g
Glass	G_2 or G_{540}	3.0 g	G_2 or G_{540}	2.7 g
Solution	KOH 1 mol/l	50.0 g	KOH 1 mol/l	50.0 g

3. Results

Fig. 1 presents the compressive strength of mortars containing the different size classes of glass (mean relative interval of confidence: 2%; e.g. 65 ± 1.3 MPa). As can be seen, the strengths depend on the fineness and glass content. Higher strengths are obtained for the smaller particles (G_{540}), with values sometimes exceeding those of the reference without glass, regardless of the replacement rate used (up to 40%). Nevertheless, the general trend is for the replacement of the cement by glass to lead to a decrease of the compressive strength, principally due to a cement dilution effect.

The dilution curves were obtained by two methods: experiments and calculation. The dilution effect was assessed by using a coarse and chemically inert addition for the replacement of cement. A coarse quartz powder (Q_{Ref}) was used to quantify the dilution of cement in the mortars [13,14]. Q_{Ref} had a mean diameter of

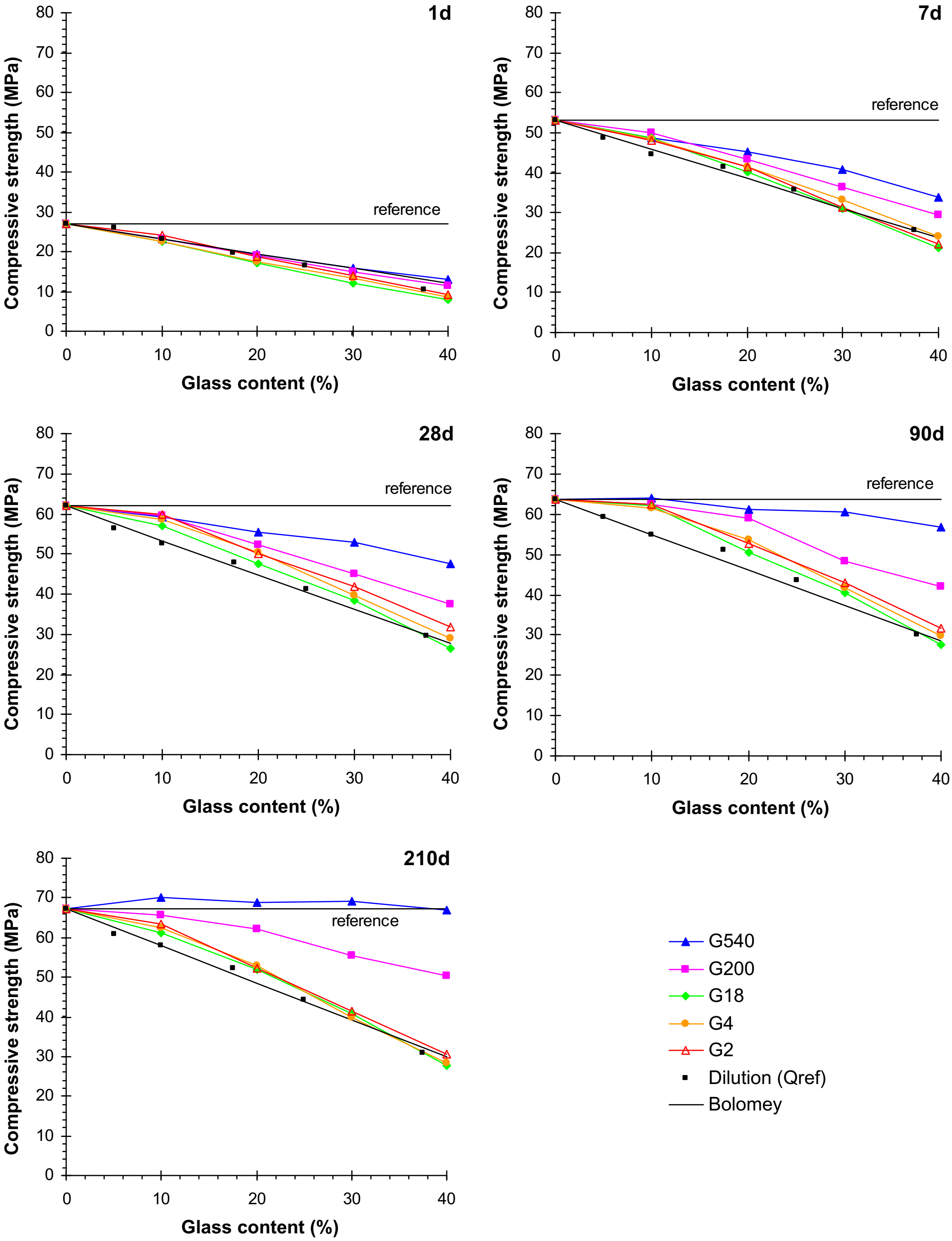

Fig. 1. Compressive strength of mortars cured at 20 °C and containing up to 40% of glass of different finenesses. Comparison with the dilution curves given by Bolomey's law and by using an inert admixture (Q_{Ref}).

215 µm, and a specific surface SS (Blaine) of 23 m^2/kg. These characteristics meant that this powder had very little influence on cement hydration, whatever the cement replacement rate used [13]. The use of a coarse and chemically inert addition allowed us to assume that the physical (e.g. germination) and the chemical (e.g. pozzolanic) effects could be neglected.

The calculation of the dilution curves was made with Bolomey's law (Eq. (1)), by considering only the effective quantity of cement used in the mortars (for instance 10% of glass implied that only 90% of cement contributed to the development of strength).

$$\sigma = K_b\left(\frac{C}{W+V} - 0.5\right) \tag{1}$$

where σ is the compressive strength of mortar, C and W are the masses of cement (without taking glass into account) and water, respectively, V is the volume of air void (taken here as 10% of the water content), and K_b is a coefficient that takes the characteristics of cement and aggregate into account. This coefficient was calculated at each hydration time by using the compressive strength of the reference without glass.

Figs. 2 and 3 show the relative strengths (strength ratio of mortar with and without glass particles) of all glass-mortars up to 210 days, versus the specific surface of glass (Fig. 2) and versus time (Fig. 3). The inert straight lines were calculated using Bolomey's law (Eq. (1)).

3.1. Effect of glass content and fineness

It can be seen from Figs. 2 and 3 that, at least for up to 30% of glass, the relative strengths were higher than the inert curves (except for 1 day), meaning that there was a non-negligible activity of glass particles of all sizes, including the coarser ones.

For glass content of 10% and hydration times longer than 1 day, there was a limited effect of fineness, since almost all sizes led to comparable relative strength, higher than the inert curve (Fig. 2). Only the finer class began to detach from other curves at later ages (90 and 210 days). This means that the cement can be replaced by glass of any size without affecting the activity and the relative strength too much, which stays over 0.9 in all cases.

At 20%, 30% and 40% of glass, a gradual change of behavior was observed (Fig. 2), related to the size effect, which became more significant with the increase of glass content.

1. The relative strength of mortars with coarse particles (G_2, G_4 and G_{18}) moved toward the inert curve as the glass content increased: 20% glass was still better than inert but 40% glass behaved at best like an inert material. This means that, for a glass content of 40%, the strengths of classes G_2, G_4 and G_{18} were only due to the cement, without any perceptible effect of glass activity.

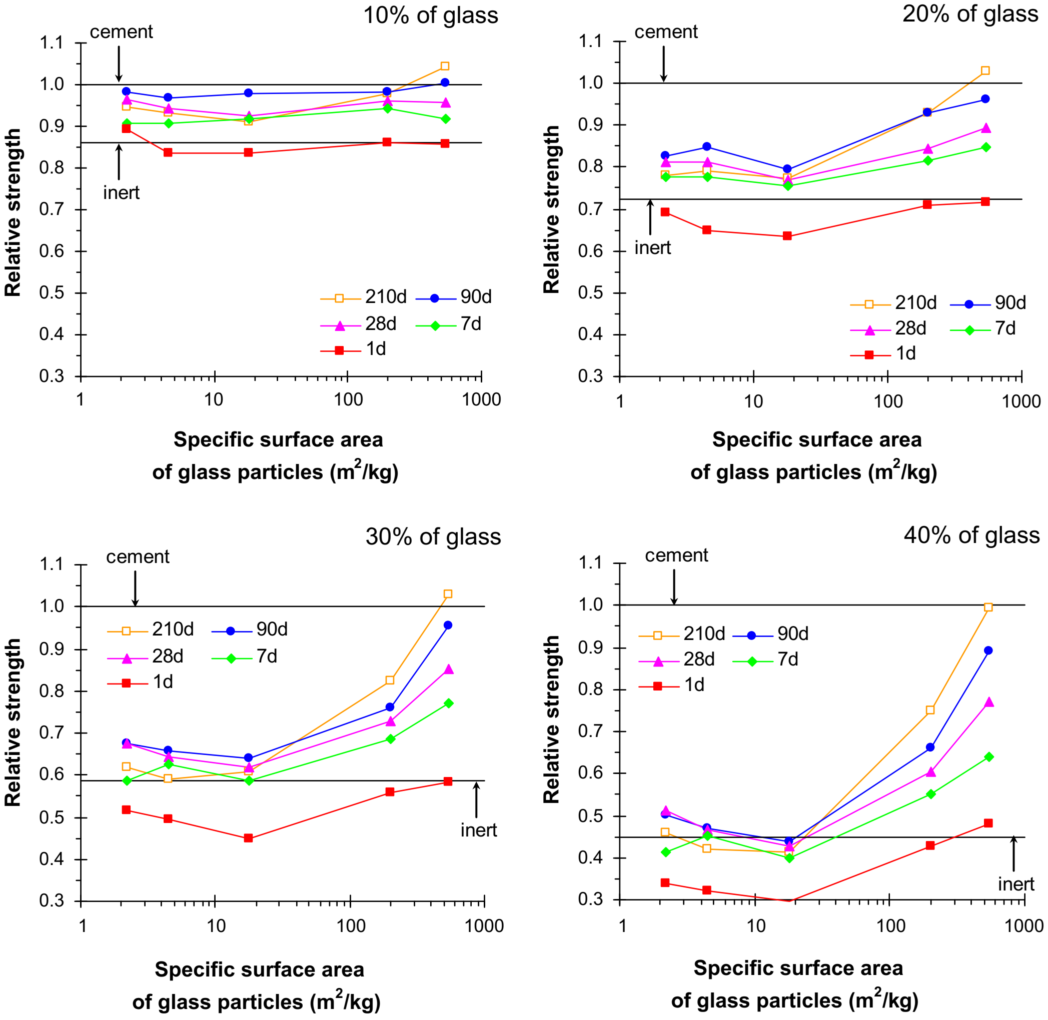

Fig. 2. Relative strength (%) of mortars according to glass fineness. Comparison with the theoretical relative strength of mortars containing an inert admixture.

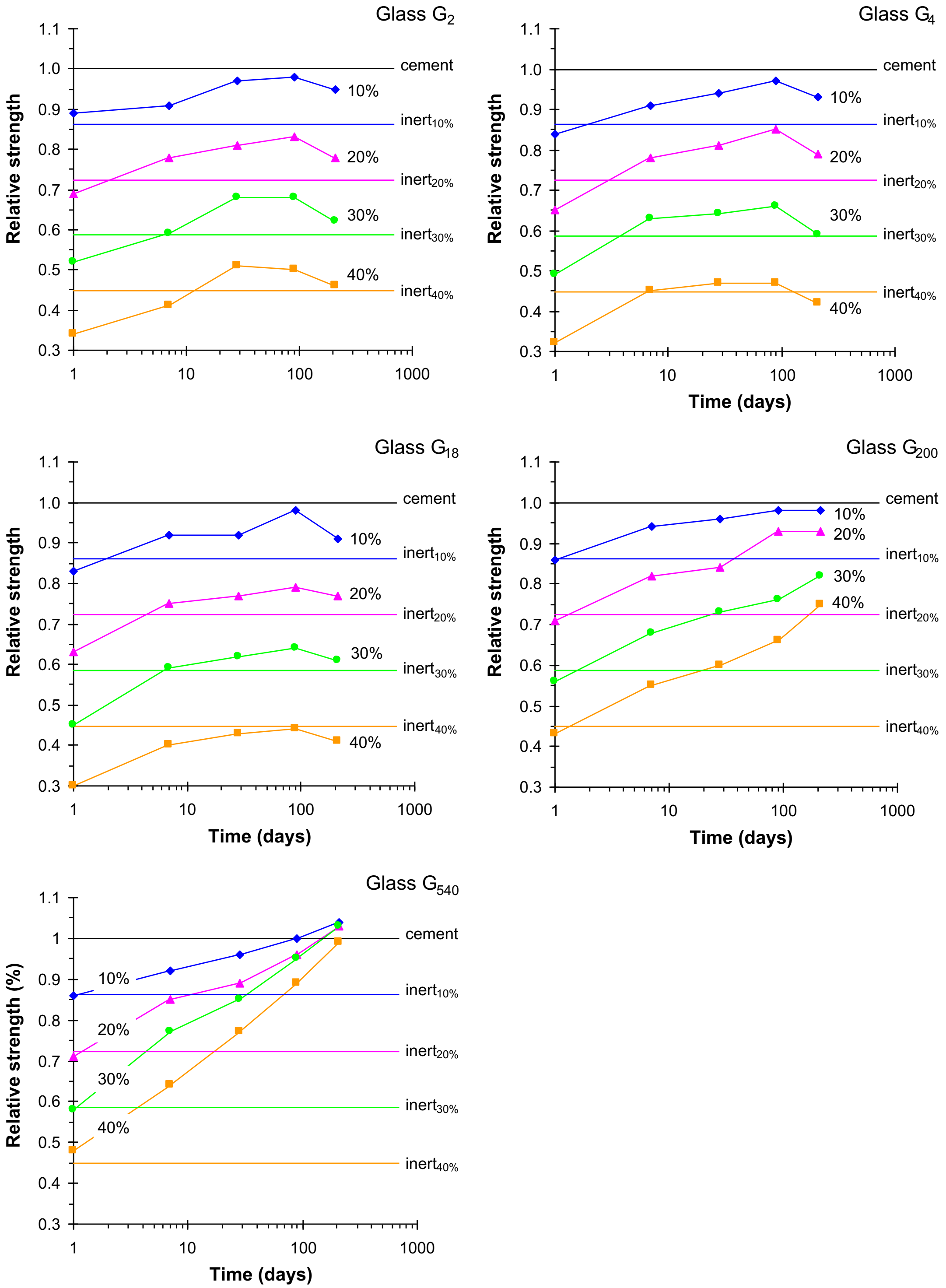

Fig. 3. Relative strength (%) of mortars versus time. Comparison with the theoretical relative strength of mortars containing an inert admixture.

2. A significant pozzolanic activity seemed to develop over time for the two finer classes (G_{200} and G_{540}), highlighted by the increase in relative strength with hydration time (Figs. 2 and 3). At 210 days, the relative strength remained around 1 for G_{540}-mortars containing up to 40% of glass. These results are in agreement with those presented by Shao et al. [1] and Shi et al. [2].
3. The packing efficiency of the grain structure might also affect the strength.

3.2. 1-Day behavior

The behavior at 1 day was different since, for all glass contents, the relative strengths were at best at the level of the inert curves (Fig. 2).

The coarser classes even led to poorer performance compared to mixtures containing the same amount of cement, but without glass. This effect, which was amplified with increasing glass content, could be due to a retarding effect on cement hydration caused

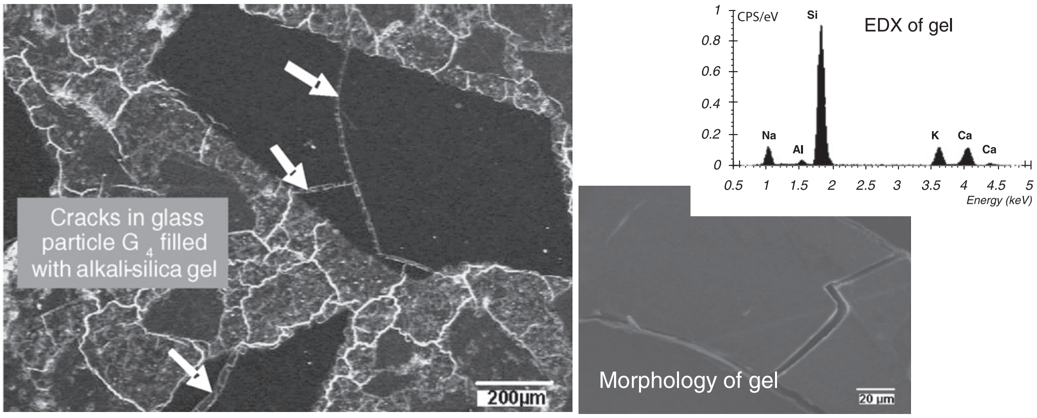

Fig. 4. Broken glass particle (class G_4) filled by ASR gel, in a mortar cured at 60 °C.

by minor elements leached from glass particles in the first hours after casting, and thus affecting the strength development at young age. Glass contained a few elements such as phosphorous (P) and zinc (Zn) which were present in small quantities (200 and 20 ppm, respectively) but are known as retarders of cement hydration [15–18]. According to Arliguie et al. [15], an amorphous hydrate layer is formed around an anhydrous cement grain, slowing down the diffusion between the pore solution and the cement and thus perturbing its hydration.

Only the finer particles counteracted the delay in strength development (Fig. 2), probably because of a germination effect of very fine glass particles, which acted as nuclei for cement hydrates and thus enhanced short-term hydration. This physical effect has already been reported by several authors [13,19–20]. Lawrence et al. [13] showed that the heterogeneous nucleation effect became insignificant for specific areas lower than 50–100 m^2/kg, explaining why classes G_2, G_4 and G_{18} were unable to compensate for the retarding effect.

3.3. Development of strength at later ages

Fig. 3 shows that relative strength usually increased with time, especially for the finer size classes (G_{200}, G_{540}), which is a sign that there was still significant pozzolanic activity at later ages.

In contrast, the relative strength of the three coarser classes (G_2, G_4 and G_{18}) reached a plateau or even decreased after 90 days. This is related to the fact that the strength of the reference mortar continued to increase while those of mortars with G_2, G_4 and G_{18} did not (they reached an asymptotic strength). These results might be explained by different mechanisms, the main one probably being a negative effect due to ASR near the coarser particles. Accelerated tests [21] showed that coarse particles could produce ASR and that glass particles could be broken by tensile stress created by ASR gels formed near or inside the particles (Fig. 4). The possible slight pozzolanic effect developed by these particles (see Section 4) was probably over at that time and could not counteract the negative effect of ASR.

4. Discussion

4.1. Quantification of the pozzolanic activity

The pozzolanic effect of glass particles can be quantified from the difference between the strengths of mortars with glass and with Q_{Ref} ($\sigma_{dilution}$). Fig. 5a presents the increase in strength $\Delta\sigma$ at 210 days, according to the specific surface of glass particles for 10–40% of glass in mortars. It can be seen that the increase in strength depends on the fineness and amount of glass. As already stated, lower finenesses presented a pozzolanic effect that could not be neglected (up to 8 MPa at 90 days), although it decreased with the increase in glass content. For higher finenesses, $\Delta\sigma$ reached 37 MPa (40% of G_{540}), which shows the significant pozzolanic effect of fine glass particles.

The simplest approach for taking the fineness and amount of glass into consideration simultaneously is to use the total surface of contact S_{tot} (per unit mass of cement) of the glass in the mortar:

$$\begin{aligned} S_{tot} &= \frac{S_S \cdot G}{C} = \frac{S_S \cdot pC_{0\%}}{(100\% - p)C_{0\%}} \\ &= S_S \frac{p}{100\% - p} \; [\text{in m}^2 \text{ of glass/kg of cement}] \qquad (2) \end{aligned}$$

where $C_{0\%}$ is the mass of cement in admixture-free mixture, G and C are the masses of glass and cement respectively in the mixtures with glass, S_S is the specific surface area (m^2/kg) of the glass and p is the replacement rate.

Fig. 5b presents the increase in strength at 210 days due to glass as a function of the glass total surface area S_{tot} in mortars. It is seen that the values of $\Delta\sigma$ can be reasonably described by a single trend curve, especially for higher values of S_{tot}, where almost all points lie on a straight line (i.e. exponential evolution). This mode of representation brings out a threshold value of S_{tot} above which significant increases in $\Delta\sigma$ are observed.

Fig. 6 gives the trend curves obtained for all hydration times (2, 7, 28, 90 and 210 days). It can be seen that the initial plateau increases with time, except for 210 days (see previous discussion in the result section). The slope also increases with time, denoting a higher pozzolanic activity at later ages. The threshold for S_{tot} is around 20 m^2/kg at 210 days. The use of this threshold value and Eq. (2) allows us to calculate the specific surface for which the pozzolanic effect becomes substantial. In the case of 40% of glass, a minimum specific surface of 30 m^2/kg is calculated, corresponding to a maximum size of 140 µm. This means that, above that size, only slight increases of strength due to the pozzolanic effect will be obtained. However, it does not mean that coarser particles are not chemically active, as discussed in the following section.

4.2. Activity of coarse and fine glass particles

Glass can present two main types of behavior in cement-based materials: alkali–silica reaction and pozzolanic reaction.

The deleterious alkali–silica reactivity, usually associated with coarse particles, is related to the formation of gels mainly composed of silica and alkalis (Na and K) with small amounts of calcium (which tend to increase with time). Results of expansion

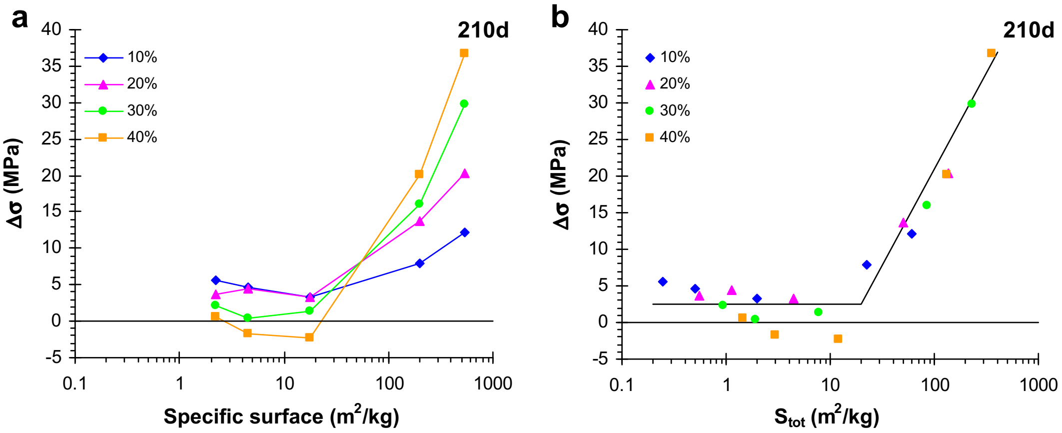

Fig. 5. Increase in compressive strength $\Delta\sigma$ due to glass at 210 days, as a function of the glass: (a) specific surface and (b) total surface area S_{tot} in mortars.

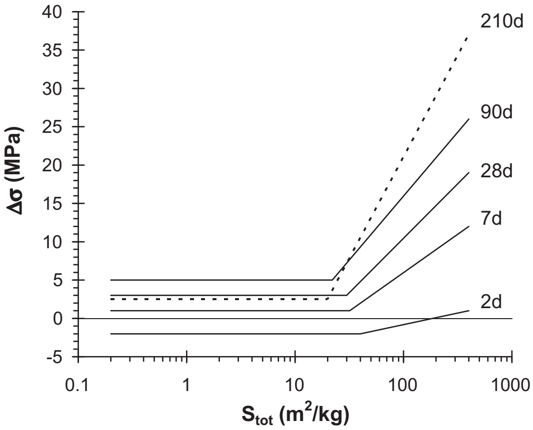

Fig. 6. Increase in compressive strength $\Delta\sigma$ (trend curves) due to glass up to 210 days, as a function of the glass total surface area S_{tot} in mortars.

measurements on mortar prisms made with 20% of glass of different classes can be found in a complementary study [21,22]. These results show that a critical threshold of grain size around 0.9–1 mm (class G_4) was observed, under which no expansion occurred. Only coarse particle size classes (class $G_2 > 1.25$ mm) led to significant expansion of mortar prisms. Particle sizes under that threshold had no effect on length variations [21].

However, in that case, the absence of expansion was not sufficient to prove the non-existence of ASR, since it did not mean that there was no trace of ASR gels in the mortars. Indeed, signs of ASR were detected in macroscopic and microscopic observations of the samples. Exudations on the mortar surface were found in mixtures containing glass of particle sizes down to 315 µm. SEM observations confirmed the presence of typical ASR gels for these mixtures [21].

Class G_{18} (160–315 µm) was in a transition zone of fineness: no ASR gels were detected, but it must be said that these gels are more difficult to detect when particles are small since gels are diffused in the paste. So ASR cannot be excluded for finer glass particles but pozzolanic hydrates (i.e. higher calcium content than ASR gels) probably have a greater importance. The existence of two concomitant reactions cannot be excluded, but the effects of the pozzolanic reaction exceed those of ASR in the case of fine glass particles.

Pozzolanic activity is generally associated with fine amorphous particles which react with Portlandite to form C–S–H having low Ca/Si ratios (<1.4). These C–S–H are able to trap significant amounts of alkalis compared to the classic C–S–H (Ca/Si ~ 1.7) produced by the hydration of the cement. In fact, in the presence of high alkali concentration, these low Ca/Si C–S–H tend to have a composition near C–(N,K)–S–H, with (N + K)/S up to 0.2.

On the one hand, it seemed evident from the compressive strength results that finer classes (G_{200}, G_{540}) had a chemical activity leading to significant increases of strength with time. On the other hand, small increases in strength were also measured for coarser classes (Figs. 2 and 3). In the latter case, the increase in strength could not be due to a physical effect such as heterogeneous germination, since the particles were too large (SSB <50–100 m²/kg) [13]. Thus it can be supposed that a chemical activity (e.g. pozzolanic reaction) of coarse particles cannot be neglected.

This assumption was assessed by studying new-formed hydrates according to the glass particle sizes. Thermal analysis, X-ray fluorescence and electronic microscopy (SEM) coupled with EDX were used.

Fig. 7 gives the evolution of the consumption of $Ca(OH)_2$ by G_2 and G_{540} over several months (pastes of $Ca(OH)_2$ and glass). The curves show that glass G_{540} has a higher lime consumption than glass G_2, which seems reasonable considering the significant differences of fineness of the two classes. After 290 days, all $Ca(OH)_2$ has reacted with G_{540}, confirming the significant pozzolanic activity of this class. However, the reactivity of class G_2 cannot be neglected, since 15% of lime has been consumed at that time.

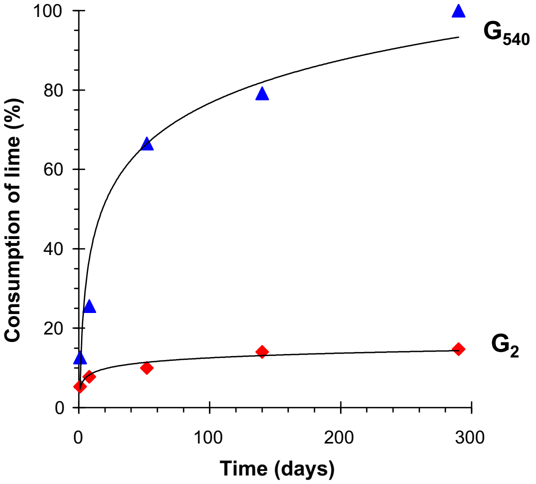

Fig. 7. Lime consumption (in%) of pastes containing 65% of glass and 35% of $Ca(OH)_2$, calculated from TG measurements.

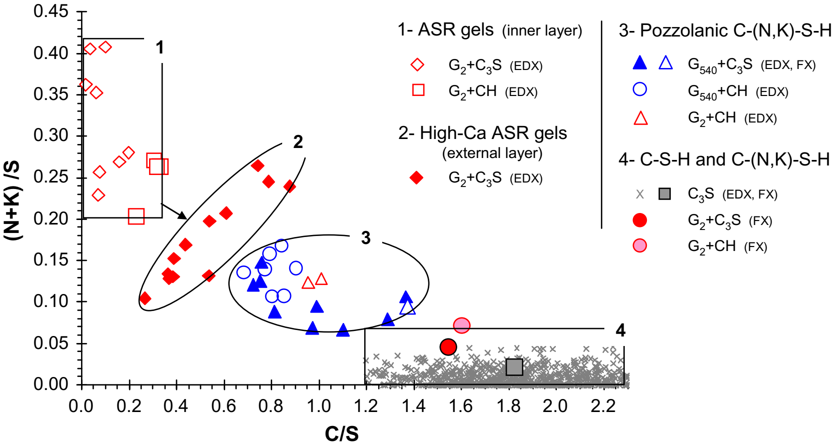

Fig. 8. Composition of new-formed hydrates produced by the reaction of glasses G_2 and G_{540} in C_3S–KOH solution (154 days at 60 °C) and $Ca(OH)_2$–KOH solution (129 days at 60 °C).

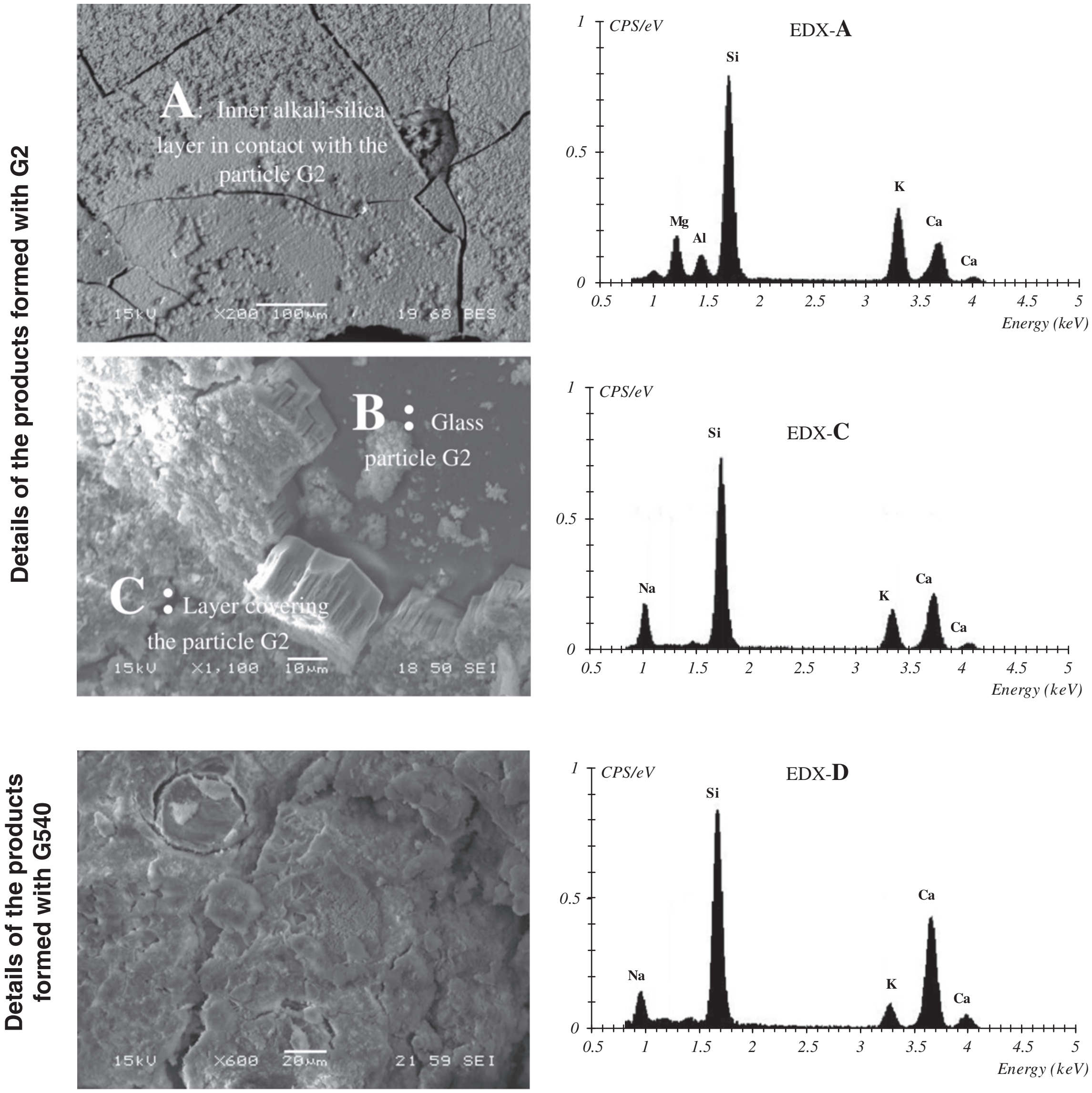

Fig. 9. Morphology and qualitative composition of new-formed hydrates produced by the reaction of G_2 and G_{540} in $Ca(OH)_2$ and 1 N KOH solution (129 days at 60 °C).

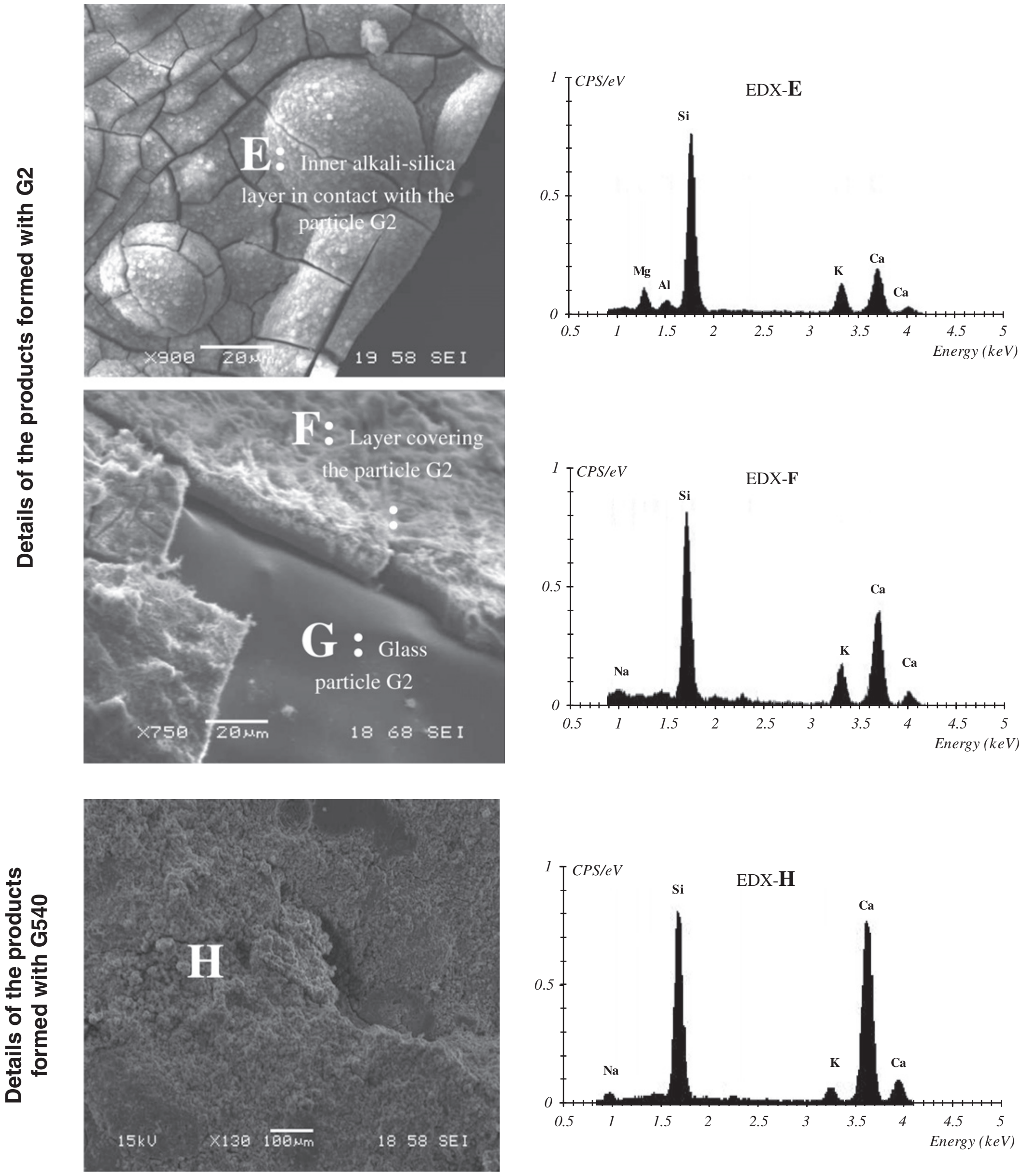

Fig. 10. Morphology and qualitative composition of new-formed hydrates produced by the reaction of G_2 and G_{540} in C_3S and 1 N KOH solution (154 days at 60 °C).

Elementary analyses were made using EDX and XRF on new-formed hydrates from mixtures of $Ca(OH)_2$ or C_3S and glass (G_2 and G_{540}), cured for several weeks in a 1 N KOH solution. All these analyses are given in Fig. 8, as (N + K)/S ratio versus C/S of hydrates.

Different new-formed products could be observed depending on the grain sizes. According to elementary analyses (Fig. 8 – N + K/S versus C/S) and SEM observations (Figs. 9 and 10), it seems that finer particles (G_{540}) led to the formation of only one type of hydrate, similar to pozzolanic C–S–H. Coarse particles (G_2) were partially attacked and gave two types of hydrates:

- Hydrates detached from glass grains (precipitate), presenting compositions of C–S–H close to finer particles, but usually with higher C/S ratio and lower alkali content (XRF analysis on the precipitate – Fig. 8).
- Hydrates forming a reaction ring around the grains, which can be regarded as alkali–silica gels containing small amounts of calcium. Their composition (Fig. 8 – EDX) and morphology (Figs. 9 and 10) were similar to ASR gels.

These analyses support the hypothesis given earlier that coarse particles of glass G_2 (1.25–2.5 mm) are able to produce C–S–H hydrates. As illustrated in Fig. 11, and considering the high content of calcium in the solution, it is probable that a precipitation of C–S–H-like hydrates occurred after the superficial dissolution of coarse particles.

This process was probably slowed down by the formation of gel rings around the particles, like those generally observed around alkali-reactive aggregates. The attack of the silica network by hydroxyl ions and alkalis led to the production of (N,K)–S–H gels containing small amounts of calcium, since this element was slowed down by the diffusion process from pore solution to sound grains.

Thus the composition of new-formed products depends on the kinetics of the reaction and on the availability of elements at a given place and a given time. The deficit of alkalis compared to calcium could lead to low (N + K)/S hydrates (high C/S) having compositions near C–S–H, while the inverse case could favor high (N + K)/S ratios, typical of ASR gels.

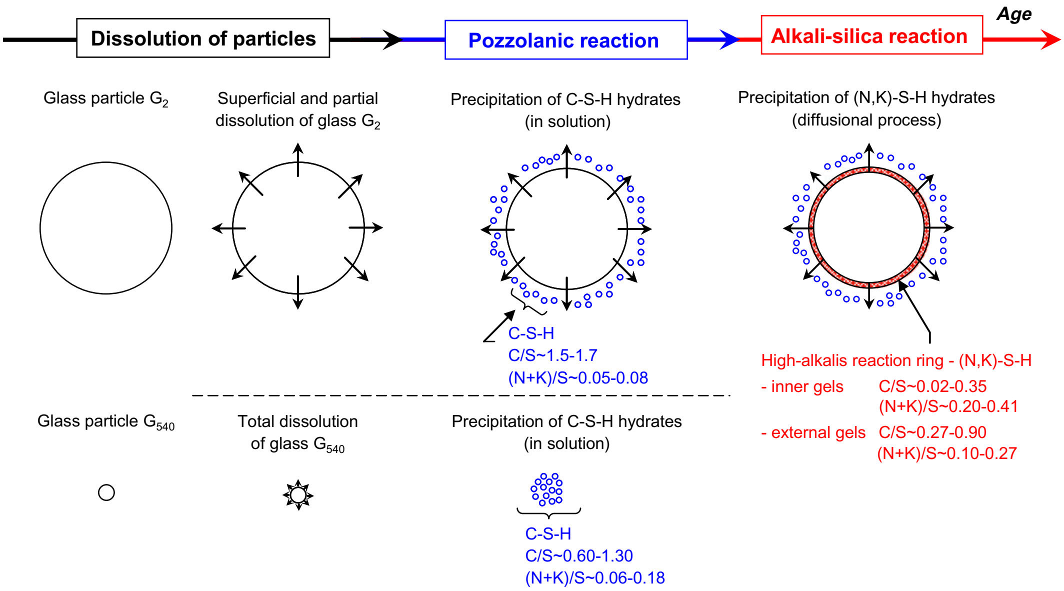

Fig. 11. Successive reactions of coarse and fine glass particles.

This mechanism presents similarities with the reaction sequence proposed by Hou et al. [23] for the formation of ASR products:

- attack of reactive aggregate by OH^-;
- consumption of the released silica due to reaction with Portlandite and thus leading to the formation of C–S–H (until local depletion of Portlandite);
- reaction of silica with primary C–S–H and formation of polymerized Si-rich C–S–H;
- increase of silica concentration in pore solution and gelation to (N,K)–S–H gel.

Up to the last step, this sequence is similar to the pozzolanic reaction.

This double process probably does not take place for finer particles, G_{540}, because of the small size of the glass particles. Thus only one type of hydrates is produced (Fig. 11) following a sequence similar to the pozzolanic reaction.

To sum up, the chronology of the reaction for coarse particles could be the following:

- Development of a pozzolanic-like reaction involving the outer layer of the grain. At the beginning of the reaction, the contact surface of the grains with the aqueous solution favors a rapid dissolution of the silica network.
- Production of hydrate C–(N,K)–S–H (Fig. 8). The presence of calcium near the grain makes possible the precipitation of C–S–H-like hydrates having relatively high C/S ratios ($\geqslant 0.8$), as observed for grains G_2. This production continues until a diffusion process takes place and retards the attack of the silica network.
- Modification of reaction kinetics leading to the production of alkali–silica gels. The diffusion process becomes preponderant due to the formation of a barrier limiting the contact between the grains and the solution. The alkalis penetrating into glass particles react with silica and produce ASR gels containing a small amount of calcium (Fig. 11). According to Stark et al. [24] these gels are responsible for the expansion occurring in cement-based materials. The late arrival of calcium ions (which diffuse slowly compared to alkalis) modifies the composition of the gels (Fig. 8).

5. Conclusion

This study aimed to evaluate the pozzolanic activity of glass cullet particles as a function of the glass content (10–40% of cement replacement) and fineness (from less than 40 µm–540 m^2/kg up to 2.5 mm–2.2 m^2/kg). The following conclusions can be drawn:

- Color-mixed glass cullet presents a pozzolanic activity which increases with the fineness of its particles.
- Compared to the reference without glass, equivalent or superior compressive strength can be obtained when using up to 40% of glass of fineness 540 m^2/kg.
- Strength activity indexes higher than 90% can be obtained:
  - after 7 days of curing for 10% of glass, whatever the fineness of the glass;
  - after 90 days of curing for 20% of glass, only when the specific surface is higher than 200m^2/kg.
- A transition fineness around 30 m^2/kg (140 µm) is highlighted, for which the pozzolanic activity becomes substantial.
- A slight but significant pozzolanic activity is detected for coarse particles (>140 µm), confirmed by:
  - the consumption of $Ca(OH)_2$;
  - the formation of C–S–H-like hydrates;
  - an increase of 10% (5 MPa) in the compressive strength compared to an inert admixture.
    - However, the possible alkali–silica reactivity of these particles should be taken into account, since ASR is detected for specific surfaces lower than 4.5 m^2/kg.
    - The composition of new-formed hydrates depends on the kinetics of the reaction and on the availability of calcium and alkalis at a given place and a given age. The deficit of alkalis compared to calcium could lead to low (N + K)/S hydrates (high C/S) having compositions near C–S–H, while the inverse case could favor high (N + K)/S ratios, typical of ASR gels.

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