POTENTIAL POZZOLANICITY OF GLASS CULLET FINES AND AGGREGATES

Rachida IDIR[a,b,c], Martin CYR[a], Arezki TAGNIT-HAMOU[b]
[a]Université de Toulouse; UPS, INSA; LMDC (Laboratoire Matériaux et Durabilité des Constructions);
135, avenue de Rangueil; F-31 077 TOULOUSE cedex 4, France.
[b]Département de génie civil, Université de Sherbrooke, Laboratoire Matériaux Cimentaires Alternatifs,
2500 boul. Université, Sherbrooke (Québec), J1K 2R1, Canada
[c]Laboratoire Eco-Matériaux, Centre d'Etudes Techniques de l'Equipement,
Direction Régionale et Interdépartementale de l'Équipement et de l'Aménagement Ile-de-France,
319 avenue Georges Clemenceau, BP 505, 77015 MELUN Cedex, France

1. INTRODUCTION

The glass used in cement-based materials can lead to two types of behaviors 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 [SHA 00, SHA 06] but the results are quite dispersed and difficult to generalize. 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 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 [CAR 08, CYR 09]. Results of the literature showed that the pozzolanic activity of the glass depended on several parameters and that each type of glass should be studied to evaluate its activity [SHA 00, BY 04, SHA 06].

This paper deals with the use of mixed glass cullet of different colors in replacement of cement which represents an alternative to existing recycling ways. 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.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The glass (G) used in this study was bottle soda-lime silica glass of mixed colours. It was composed of 40, 33, 20 and 1% of colourless, brown, green and blue glasses, respectively. The material also contained around 6% of impurities. Different sizes of glass particles noted Gx (X denotes the specific surface of the glass) were obtained after grading, washing, drying, crushing and sieving the raw material. **Table 1** give the chemical composition and the fineness of the classes used in this study. It can be seen that the chemical compositions of all classes are 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 [AFN 01] (**Table 1).** The sand used for the pozzolanic study was a non-reactive quartz sand in accordance with standard EN 196-1 [AFN 06].

2.2. Sample preparation and test methods

The pozzolanic activity of the different size classes of glass was tested through compressive strength measurements on standardized mortars. Four types of mortars were prepared according to standard EN 196-1 [12]. After demoulding, the prismatic samples (4x4x16 cm) were cured in water at 20°C until the age of test (1, 7, 28, 90 and 210 days).
Lime consumption was determined by thermogravimetric analysis (TG) on pastes stored at 20°C and composed of 65% of glass (coarse G_2 or fines G_{540}) and 35% of $Ca(OH)_2$ by weight. 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

Chemical composition (% by mass)	**Cement**	**Glass**				
		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 ** (m^2/kg)	440	2.2	4.5	18	200	540
Particle size ranges (µm)	-	1250-2500	630-1250	160-315	<80	<41
Mean diameters (µm)	-	1875	940	237	23	8
Specific gravity (g/cm^3)	3.15	2.40	2.41	2.41	2.43	2.48

* Gx: x is the specific surface of the glass
** Blaine for cement, G_{200} and G_{540}; calculated from the particle size distribution for G_2, G_4 and G_{18}

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

	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

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

elementary compositions were measured using energy dispersive X-ray spectroscopy (EDX, 15 kV and 10 nA) and X-ray fluorescence (XRF).

3. RESULTS

Figure 1 presents the compressive strength of mortars containing the different size classes of glass (all numerical values are grouped into Annex 1). As can be seen, the strengths depend on the fineness and glass content. The highest strengths are obtained for the smallest particles (G_{540}), with values sometimes exceeding those of the reference without glass, regardless of the replacement rate used (up to 40%). Nevertheless, except for glass G_{540} the general trend is that the replacement of the cement by glass leads to a decrease of the compressive strength, principally due to a cement dilution effect.

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

$$\sigma = K_b\left(\frac{C}{W+V} - 0,5\right) \qquad \text{(Equation 1)}$$

where σ is the compressive strength of mortar, C and W are respectively 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.

Figures 2 show the relative strengths (strength ratio of mortar with and without glass particles) of all glass-mortars up to 210d, versus the specific surface area of glass. The inert straight lines were calculated using Bolomey's law (**equation 1**).

It can be seen from **Figures 2**, at least for up to 30% of glass, that the relative strengths were higher than the inert curves (except for 1d), 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 1d, there was a limited effect of fineness, since almost all sizes led to relative strength similar to the dilu-

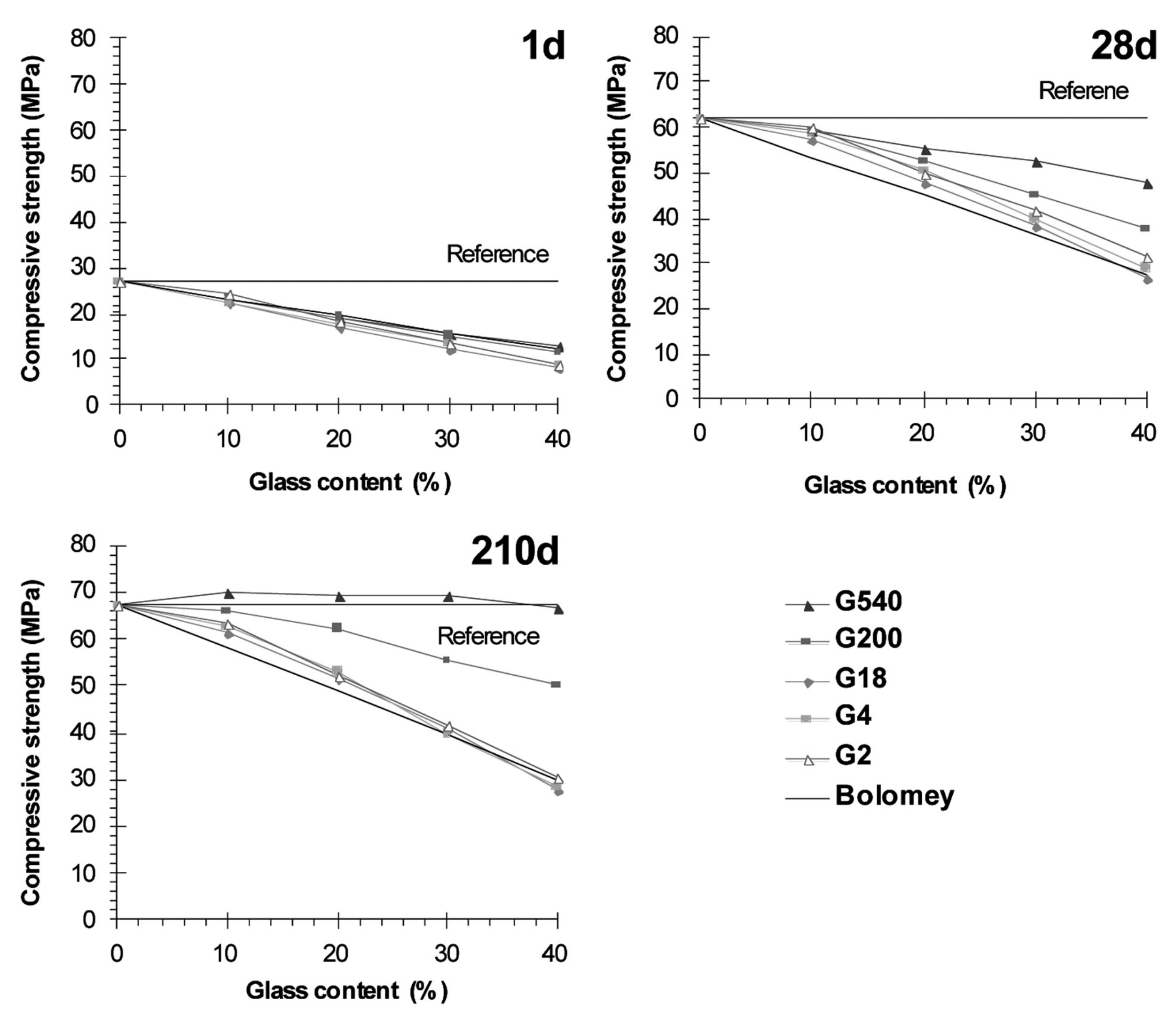

Figure 1: Compressive strength of mortars cured at 20°C and containing up to 40% of glass of different finenesses. Comparison with the dilution curves given by Bolomey's law

tion curve. Only the finer class began to detach from other curves at later ages (90 and 210d). 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, 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.
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. 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. [SHA 00] and Shi et al. [SHI 05].

4. DISCUSSION

Results of expansion measurements on mortar prisms made with 20% of glass of different classes can be found in a complementary study [IDI 09]. These results show that a critical threshold of grain size under which no expansion occurred. Only coarse particle size classes (class G_2 > 1.25mm) led to significant expansion of mortar prisms. 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

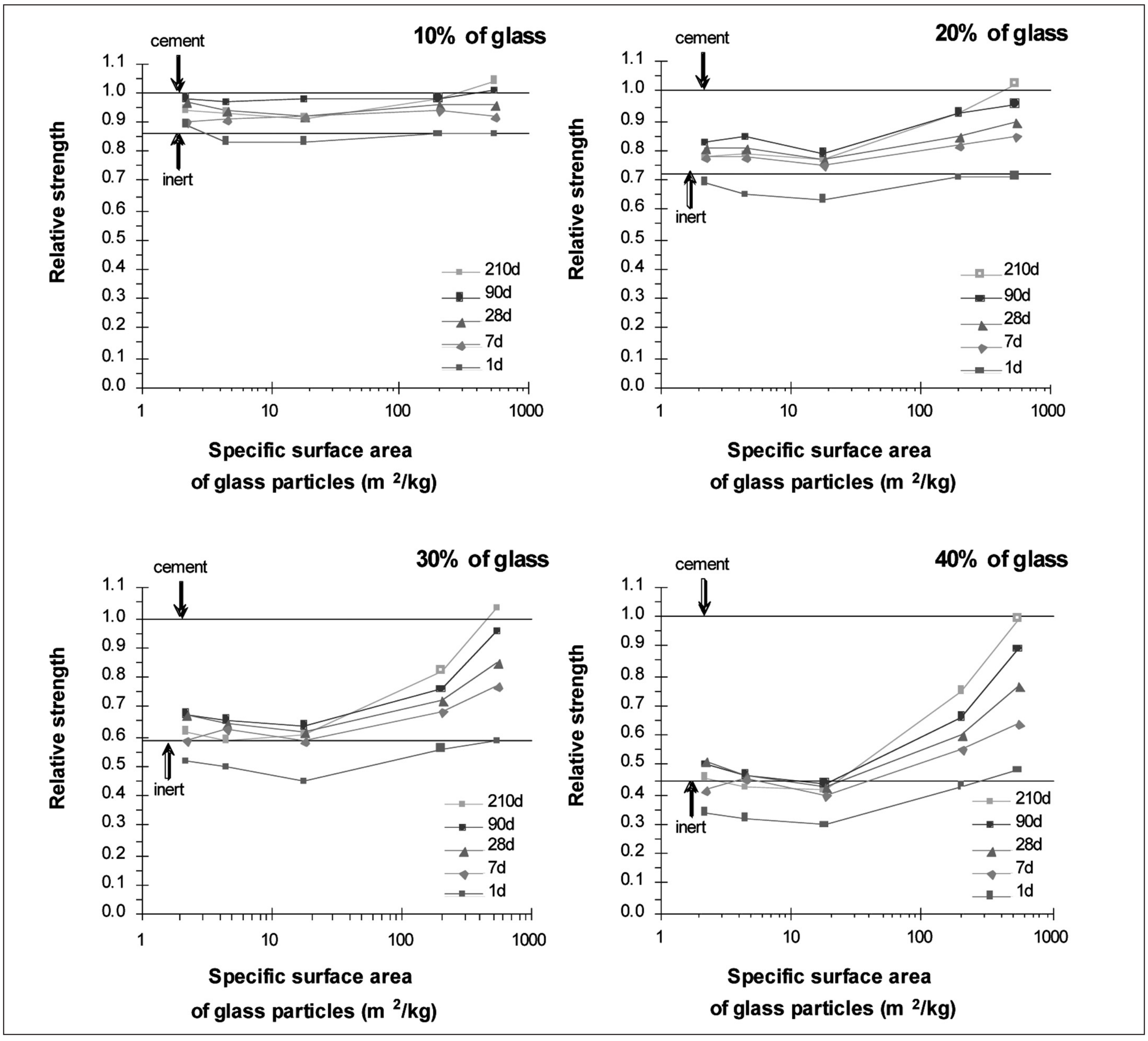

Figure 2: Relative strength (%) of mortars according to glass fineness. Comparison with the theoretical relative strength of mortars containing an inert admixture

and microscopic observations of the samples containing glass of particle sizes down to 315 µm.

So ASR cannot be excluded for finer glass particles but pozzolanic hydrates 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.

On 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 (**Figure 2**). 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 to 100 m^2/kg) [LAW 03]. Thus it can be supposed that a chemical activity (e.g. pozzolanic reaction) of coarse particles cannot be neglected.

This assumption was verified 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. Measures in time of consumption of $Ca(OH)_2$ by TG 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. 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 1mol/l KOH solution. All these analyses are given in **Figure 3**, as (N+K)/S ratio versus C/S of hydrates.

Different new-formed products could be observed depending on the grain sizes. Thus, it appears that finer particles (G_{540}) led to the formation of only one type of hydrate, similar to pozzolanic C-S-H, both morphologically and in their composition (**Figure 3**). 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, although with slightly different composition (Figure 4) but usually with higher C/S ratio and lower alkali content (XRF analysis).
- Hydrates forming a reaction ring around the grains, which can be regarded as alkali-silica gels containing small amounts of calcium. Their composition (**Figure 3**) and morphology (**Figure 4**) were similar to ASR gels (EDS analysis).
- 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. 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. This mechanism presents similarities with the reaction sequence proposed by HOU et al. [HOU 04] for the formation of ASR products:

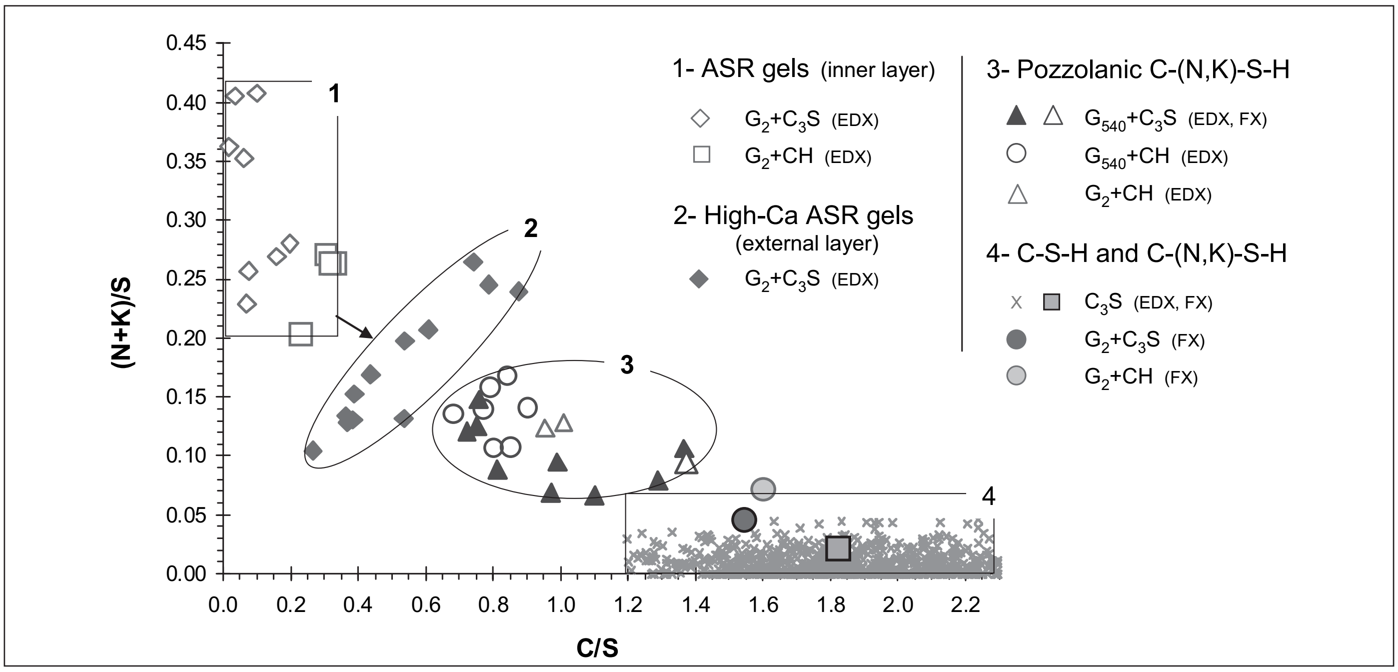

Figure 3: Composition of new-formed hydrates produced by the reaction of glasses G2 and G_{540} in C_3S-KOH solution (154 days at 60°C) and $Ca(OH)_2$-KOH solution (129 days at 60°C).

- 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 (**Figure 3**) following a sequence similar to the pozzolanic reaction.

5. CONCLUSION

This study aimed to evaluate the pozzolanic activity of glass cullet particles as a function of the glass content (10 to 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 and 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.

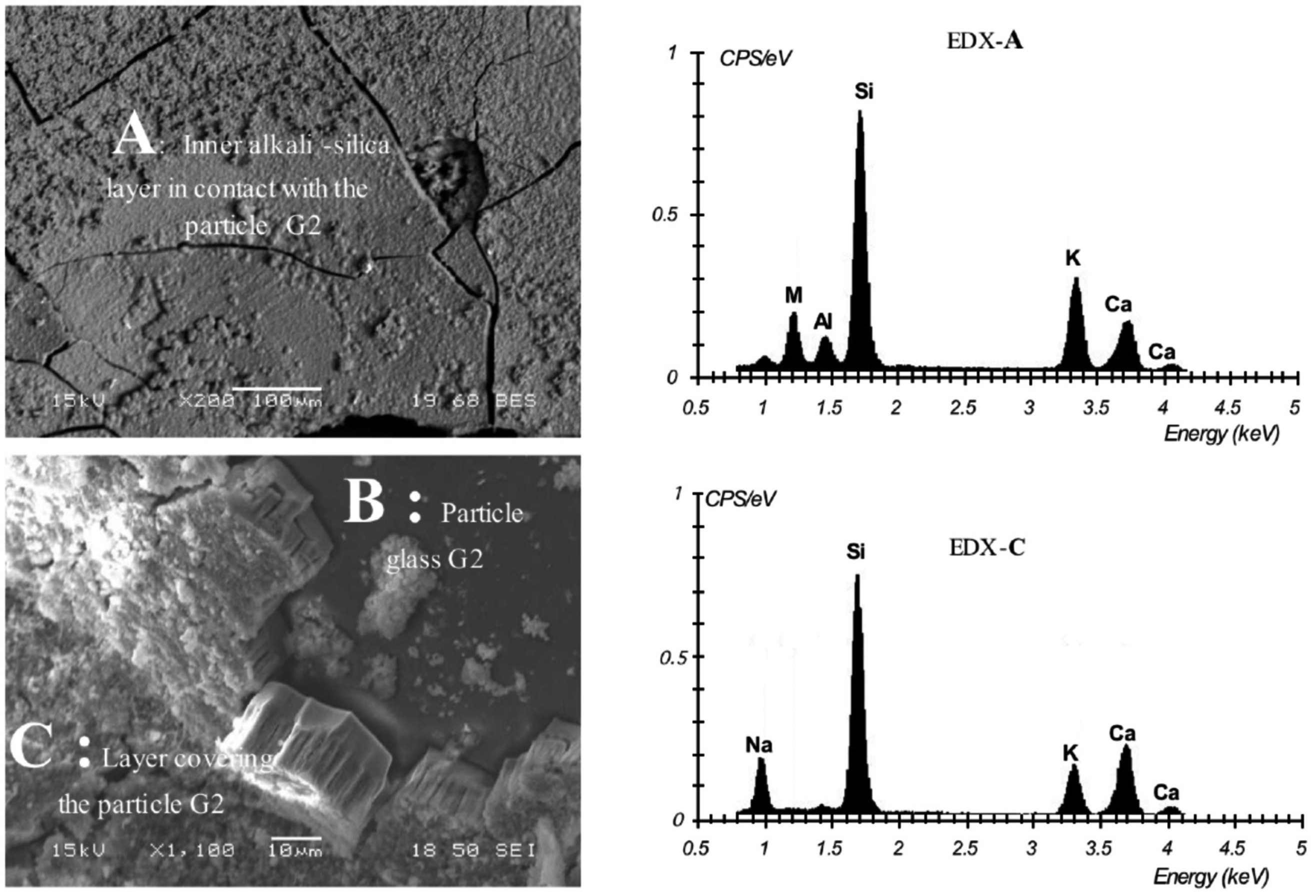

Figure 4: Morphology and qualitative composition of new-formed hydrates produced by the reaction of G_2 in $Ca(OH)_2$ and 1N KOH solution (129 days at 60°C).

		Substitution rate of cement				
Classe of glass	Age (days)	0%	10%	20%	30%	40%
G_2	1	26.9 ±0.3	24.1 ±0.3	18.7 ±0.3	13.9 ±0.2	9.1 ±0.2
	7	53.1 ±0.1	48.1 ±1.3	41.3 ±0.6	31.2 ±0.4	22.0 ±0.3
	28	61.9 ±2.3	59.8 ±0.7	50.2 ±0.9	41.8 ±0.2	31.8 ±0.4
	90	63.5 ±1.6	62.5 ±1.0	52.6 ±1.0	43.0 ±0.7	31.8 ±0.6
	210	67.1 ±1.0	63.4 ±1.1	52.3 ±1.0	41.6 ±0.5	30.7 ±0.5
G_4	1	26.9 ±0.3	22.5 ±0.3	17.5 ±0.2	13.3 ±0.3	8.7 ±0.1
	7	53.1 ±0.1	48.3 ±0.0	41.3 ±0.1	33.3 ±0.6	24 ±0.2
	28	61.9 ±2.3	58.5 ±1.4	50.3 ±0.7	39.8 ±0.8	29.0 ±0.6
	90	63.5 ±1.6	61.4 ±1.1	53.8 ±0.7	41.9 ±0.7	29.8 ±0.2
	210	67.1 ±1.0	62.5 ±1.3	53.0 ±1.1	39.0 ±0.5	28.3 ±0.5
G_{18}	1	26.9 ±0.3	22.5 ±0.2	17.1 ±0.2	12.1 ±0.2	8.0 ±0.2
	7	53.1 ±0.1	48.7 ±2.2	40.1 ±0.6	31.1 ±1.1	21.1 ±1.1
	28	61.9 ±2.3	57.2 ±0.9	47.7 ±0.8	38.3 ±0.6	26.4 ±0.7
	90	63.5 ±1.6	62.3 ±1.4	50.4 ±0.9	40.6 ±1.3	27.4 ±0.8
	210	67.1 ±1.0	61.2 ±2.0	51.9 ±1 .1	40.7 ±0.7	27.8 ±0.2
G_{200}	1	26.9 ±0.3	23.2 ±0.2	19.1 ±0.2	15.0 ±0.2	11.5 ±0.2
	7	53.1±0.1	48.7 ±1.5	40.1 ±0.7	31.1 ±2.0	21.2 ±0.7
	28	61.9 ±2.3	57.2 ±1.6	47.7 ±1.3	38.3 ±0.7	26.4 ±1.0
	90	63.5 ±1.6	62.3 ±1.1	50.4 ±0.7	40.6 ±1.2	27.7 ±0.8
	210	67.1 ±1.0	65.7 ±1.4	62.3 ±0.6	55.3 ±1.7	50.2 ±0.5
G_{540}	1	26.9 ±0.3	23.1 ±0.4	19.2 ±0.3	15.7 ±0.2	13.0 ±0.2
	7	53.1 ±0.1	48.7 ±1.1	45.1 ±1.3	40.9 ±0.1	33.9 ±0.3
	28	61.9 ±2.3	59.2 ±1.0	55.3 ±0.6	52.8 ±0.9	47.6 ±0.6
	90	63.5 ±1.6	63.9 ±1.8	61.0 ±1.7	60.7 ±0.8	56.7 ±0.9
	210	67.1 ±1.0	70.0 ±1.4	69.0 ±1.4	69.2 ±1.7	66.8 ±1.3

Annex 1 : Table summarizing the influence of percentage replacement of cement with different classes of glass on the hardening of mortars stored at 20° C

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