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Participation of coloured glass cullet in cementitious materials

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Abstract

In this paper fundamental aspects of the pozzolanic activity of the three most common coloured glass cullet in Greece and of vitrified fly ash were studied. Furthermore, the problem of ASR in mortar systems with high content of finely ground glass cullet was estimated. The chemical behaviour of the added cullet in the cement was determined by XRD, DTA-TG and SEM observations and additionally mechanical tests, metal leaching examination and pore measurements were carried out. Green cullet appeared to be the most pozzolanic material followed by the flint glass. None of studied materials have shown any expansion, due to the deleterious ASR reaction. The potential utilisation of coloured glass cullet in various cementitious products is very encouraging especially for decorative and architectural applications.

Keywords: Cullet; Vitrified fly ash; Pozzolanic activity; ASR; Cementitious products

1. Introduction

Glass cullet represents a major component of the municipal solid waste material, relatively easy to separate from the general solid waste and due to its physical and chemical properties, it seems to be a prime candidate for recycling. It must be noticed that a great proportion of cullet does not fulfil the requirements of the glass industries for production, while the use of large amounts of recycled cullet changes the input of the glass melting process from a well-defined batch to raw materials with varying redox conditions, which all affects the removal of gaseous inclusions [1,2]. It is obvious that, even if it is reached the maximum rate of recycling there still be a great accumulation especially of green cullet. Lately a large section of application appears to be the construction materials area. Bricks and ceramics which contained glass cullet as a binder or flux showed low softening temperature and reduced firing time and consumption of fuel [3]. Moreover, the addition of glass in asphalt enhanced night visibility [4]. Paving stone which contains up to 100% glass aggregates shows great reduction of water absorption and excellent abrasion resistance, due to the high hardness of glass [5]. However, before glass cullet can be used as a component of cementitious materials, the properties and the resulting products have to be studied in order to ensure the suitability of the new material in constructions. A typical pozzolanic material is designated by three characteristics: it contains high silica content, it is amorphous and it has large surface area [6]. The glass cullet satisfies the above requirements, nevertheless, a serious obstacle to its use in concrete is the presence of large quantities of sodium, which connotes a likelihood for the material to undergo the alkali-silica reaction (ASR). Indeed, earlier attempts at using glass as a partial or total substitute of the coarse or fine aggregates have not been successful [7]. Recent studies have shown that the particle size of glass is a crucial factor. In particular, aggregate fineness favours ASR expansion since the ASR reaction is a surface dependent phenomenon. However, there exists a minimum particle size depending on the structure of the glass, where the maximum expansion occurs [8].

An amorphous material with properties similar to glass cullet is the vitrified material mainly derived from the thermal treatment of waste. Vitrification by melting is the most likely stabilization/solidification technology used to convert high-level waste into a disposable solid [9] with a large reduction of the waste volume [10].

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Lignite fly ash can be considered as a waste and it is well known that its mineralogical structure favours its application in the retention of metals during chemical treatment of liquid waste [11]. The vitrification ability of fly ash is based on its chemical composition, which is similar to the system of glass ($CaO–SiO_2–Al_2O_3$) [12] and crystallization can be kept to a minimum by rapid cooling to the glass transformation temperature T_g.

Taking into consideration all the above factors this work has been focused on the use of green, amber and flint glass cullet as a component of cementitious materials either as aggregate, filler or binder. Furthermore, the effect from the addition of a mixture of the above colours was examined since there is no selection at source in Greece. An important property of cullet under evaluation was the ability to enhance the pozzolanic activity. In addition, the particle size effect of the ground material was specified for a particular addition of the waste into the cement. Moreover, the potential expansion of the cement pastes due to the alkali silicate reaction was investigated. In order to evaluate the role of the addition of cullet in cement it was compared with the similar addition of greek fly ash, which is a common substitute of cement.

2. Materials and methods

The glass used in this study was a typical soda-lime glass obtained from recycled containers. Green, amber and flint glass, main colours of Greek market products, were used in order to evaluate the influence of the coloured glass in the cement mixtures. Thus, the necessity of selection during the recycling process of colour glass was estimated. Chemical composition of green, amber, flint glass cullet and fly ashes originated from Ptolemais (Fly ash 1) and Megalopoli (Fly ash 2) Power Plants in Greece, are illustrated in Table 1. It must be taken into consideration that although the chemical analysis of the coloured glasses seems to be similar there are great differences in the structure depending on the role of each element as network former, modifier or intermediate.

The glass cullet was ground and separated in the appropriate fraction in order to be used either as coarse or fine aggregate or as filler in cementitious plasters. Furthermore, the two fractions −200 to +90 and −90 μm were selected to be used as a binder into cement pastes. Fly ashes samples have a retained amount of 80% on 56 μm (DIN 4188) and the vitrified fly ash was ground to a fraction <90 μm.

Ordinary Portland cement (OPC) and sand for the pastes were used for the experiments, according to ASTM C778.

X-ray diffraction (XRD) analysis was carried out (Siemens D5000 diffractometer, Cu Kα radiation, Ni Filter) in order to determine the mineralogical composition of the raw materials and the particle shape was observed by scanning electron microscope (Philips XL30 ESEM). Furthermore, the pozzolanic activity was measured according to Chapelle test [13] and the pozzolanic activity rate test which was a similar test to Chapelle showing the development of pozzolanic activity versus time.

2.1. Vitrified fly ash

Samples were prepared after treatment of a liquid waste containing 100 ppm of each of the following

Table 2
Results of physicochemical properties of 14 specimens of vitrified material

	Hardness (kgf/mm^2)	Density (g/cm^3)
1	550	2.4985
2	565	2.4979
3	580	2.5022
4	580	2.5045
5	535	2.4952
6	550	2.4941
7	560	2.4937
8	560	2.4962
9	555	2.5036
10	525	2.4876
11	580	2.5745
12	595	2.5968
13	545	2.5564
14	590	2.5872

Table 1
Chemical composition of glass cullet and fly ashes

% (w/w)	Green cullet	Amber cullet	Flint cullet	Megalopoli fly ash	Ptolemais fly ash
SiO_2	70.50	71.20	70.65	51.26	30.16
Al_2O_3	1.80	1.90	1.75	19.39	14.93
Fe_2O_3	0.45	0.35	0.45	8.44	5.10
CaO	10.15	10.35	10.70	11.82	34.99
MgO	2.75	2.60	2.45	2.27	2.69
SO_3	0.25	0.30	0.45	2.91	6.28
Na_2O	12.95	13.15	13.25	0.53	1.01
K_2O	0.45	0.60	0.55	1.81	0.4
Cr_2O_3	0.25	0.06	–	–	–
Loss of ignition	–	–	–	1.67	3.95

Table 3
Chemical composition of the plasters

	CP	GCPF1	GCPF2	GCPF3	GCPF4
Composition	%	%	%	%	%
Aggregates (2–4 mm)	11	–	11	11	11
Aggregates (1.2–2 mm)	14	14	14	14	14
Aggregates (0.7–1.2 mm)	19	19	8	19	19
Aggregates (0–0.7 mm)	40	40	40	33	33
Cement	9	9	9	9	9
Filler	4	4	4	–	–
Hydrated lime	3	3	3	3	3
Flint glass cullet (2–4 mm)		11			
Flint glass cullet (0.7–1.2 mm)			11		
Flint glass cullet (0–0.7 mm)				7	
Flint glass cullet (filler)				4	11
Chemical additives	0.17	0.17	0.17	0.17	0.17

metals Cu, Zn, Ni, Cd, Fe and Mn with fly ash 1. The resulted retention of metals was 98%, 99%, 85%, 85%, 99%, and 80% respectively. Sodium carbonate was added to the resulted solid samples along with Egyptian sand, so that the appropriate amount of SiO_2 for the production of the glassy material would be achieved. Then heat treatment of the samples at 1450 °C for 2 h was performed.

Measurements of density (ASTM C729-75) and hardness values (Vickers indentation method) of the vitrified ash were carried out (Table 2). The performance of a leaching test was necessary due to the incorporation

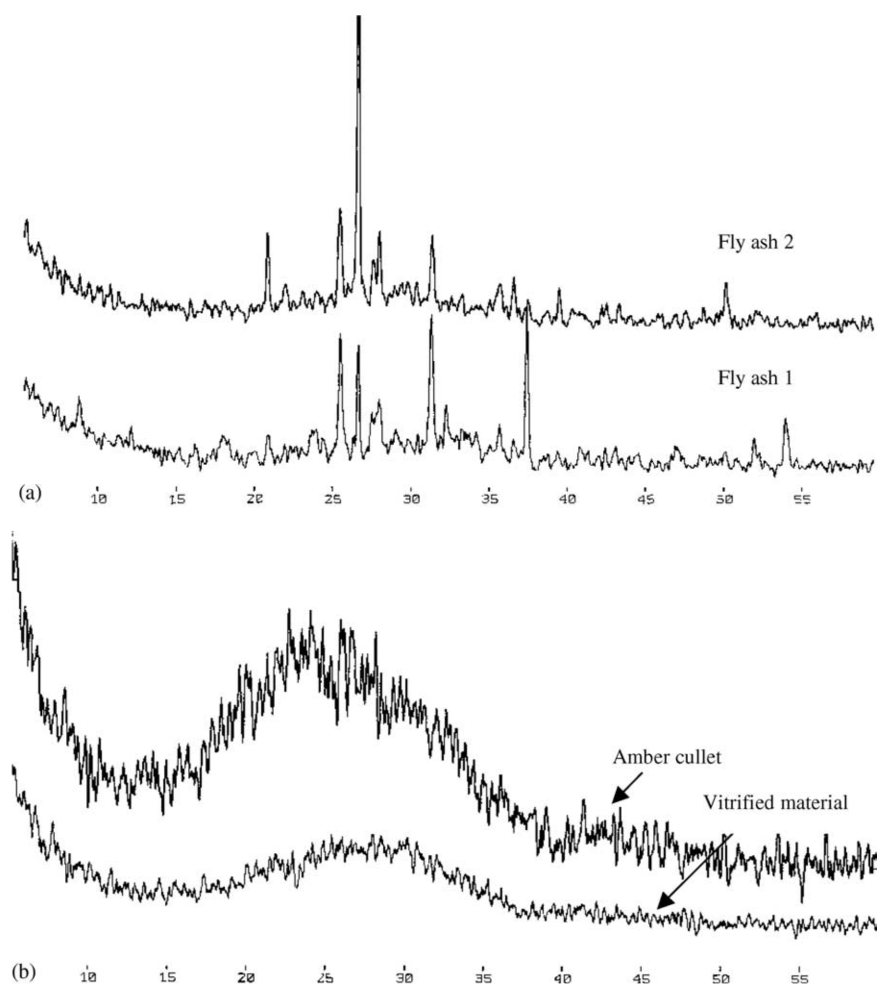


Fig. 1. (a) X-ray spectrums of the fly ash 1 and fly ash 2. (b) X-ray spectrum of ground amber glass and vitrified fly ash.

Table 4
Reacted $Ca(OH)_2$

	g $Ca(OH)_2$ reacted/g of sample
Green	0.3011
Amber	0.3346
Flint	0.2907
Vitrified	0.2672
Fly ash 1	0.3817

of toxic metal in its structure and was carried out according to DIN 38414 S4.

The produced material was further examined by the aforementioned analyses as the raw materials.

2.2. Cement pastes

In order to determine the influence of the glass colour in the cement pastes, mortar mixtures were prepared by replacing 25% of cement content with green, amber and flint glass in accordance with EN 196 Part I. Moreover, specimens of equal replacement of 8.5% of each green, amber and flint cullet and also comparative cement specimens with 25% fly ashes were composed.

Compressing strength measurements of cement paste containing ground cullet, vitrified material and fly ashes were carried out at ages of 2, 7 and 28 days. The cement pastes were examined with XRD, DTA-TG and

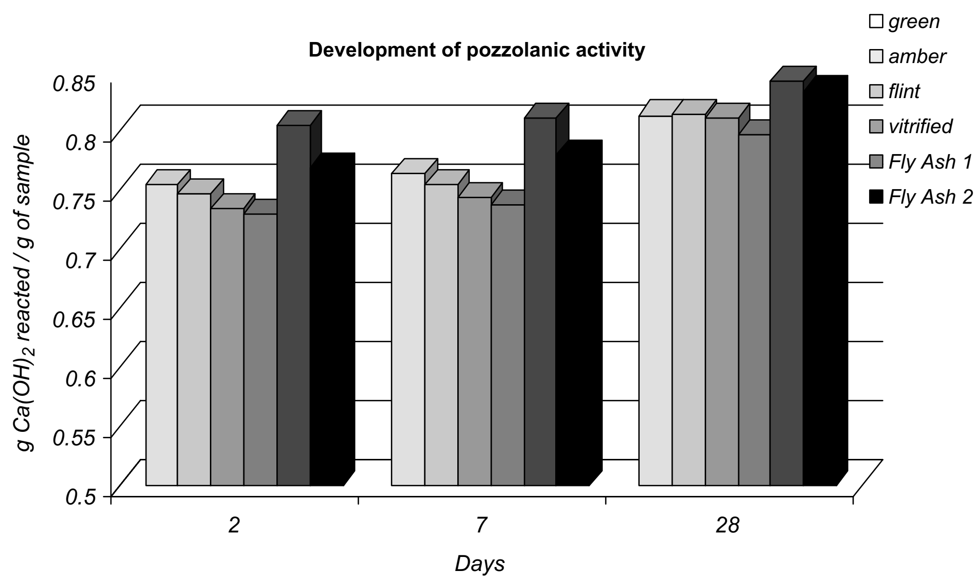


Fig. 2. Results of the pozzolanic activity rate test.

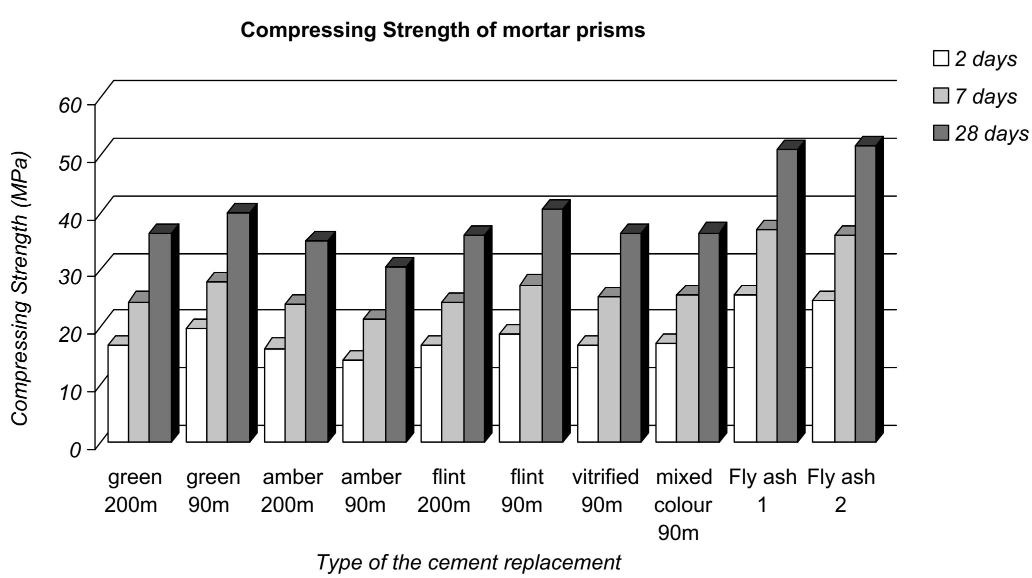
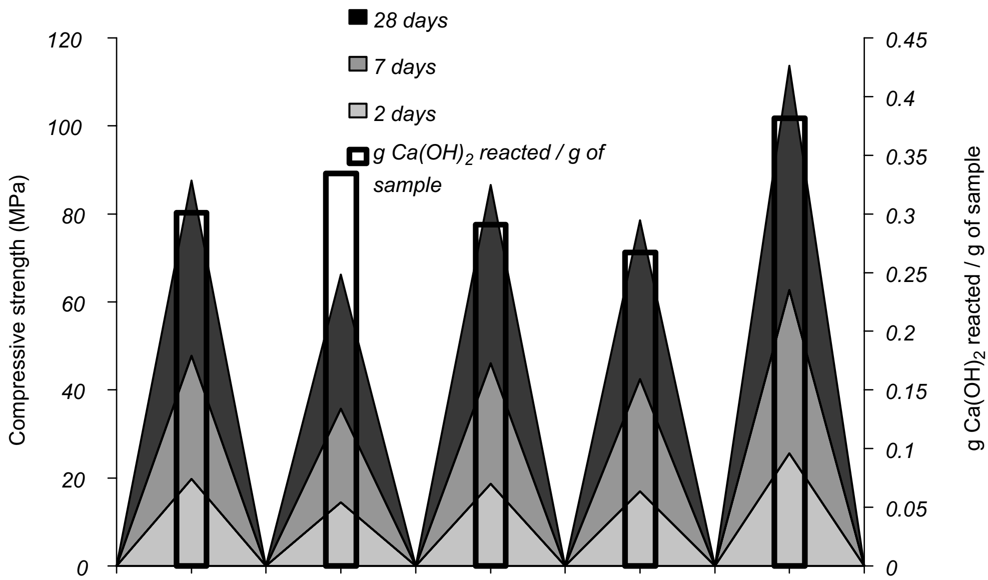


Fig. 3. Compressive strength of mortar prisms.



Green	Amber	Flint	Vitrified	Fly ash 1
0.3011	0.3346	0.2907	0.2672	0.3817
g $Ca(OH)_2$ reacted / g of samp le				

Fig. 4. Comparative results of compressive strength and pozzolanic activity tests.

observed by SEM. Also mercury intrusion measurements were performed.

The potential alkali-silica reaction of the mortars containing cullet was assessed according to ASTM C1260.

2.3. Plasters

Common plasters were produced by substituting fine, coarse aggregates or filler for flint glass cullet. The compositions of the plasters are illustrated in Table 3. Retained water (EN 1015-8), air content (1015-7), specific weight (EN1015-6) and table flow tests (EN 1015-3) were estimated.

3. Results and discussion

Fig. 1(a) and (b) illustrate the XRD patterns of amber glass, vitrified material and fly ashes and verify the differences of the materials. The three coloured glasses showed similar XRD patterns and amber glass is selected to be compared to the vitrified material owing to their similar coloration. Measurements of density and hardness values verify that the vitrified product has relevant properties to glass. Fly ashes presented a crystalline formation and amorphous phase. In addition, SEM observations revealed that the ground glass exhibited angular shapes while fly ashes consisted mainly of spherical particles. The high angularity of

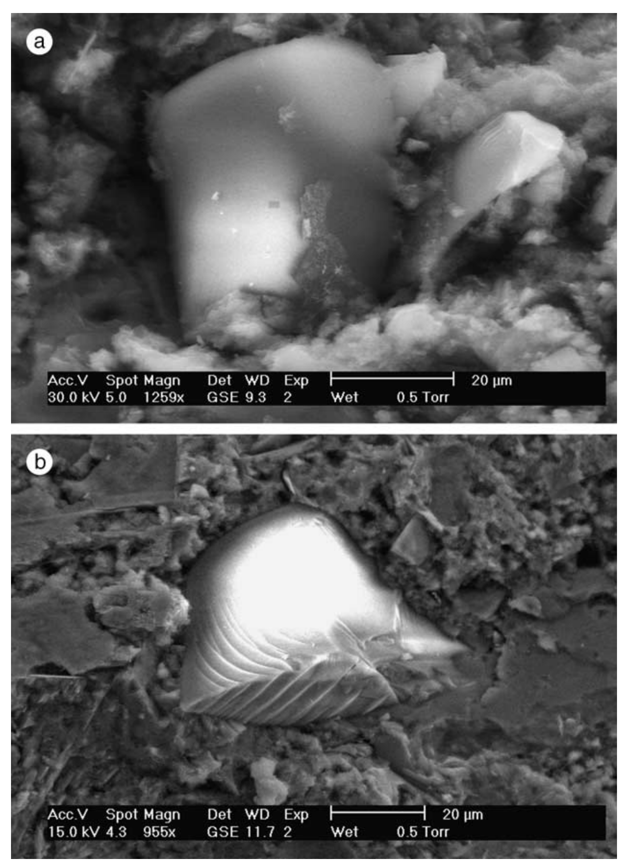


Fig. 5. SEM observation of cement paste with (a) green cullet and (b) amber cullet.

cullet provided more mechanical interlocking which leads to the reduction of plaster's workability.

3.1. Pozzolanic activity and compressive strength development

Table 4 presents g $Ca(OH)_2$/g testing material during the pozzolanic reaction (Chapelle test). Both green and amber cullet performed better pozzolanicity than flint cullet and vitrified material. Probably, the basic coloration elements may react with the $Ca(OH)_2$ without giving hydration products which contribute to the development of the strength of the cementitious materials. However, higher pozzolanic activity might be due to its different structure which may lead to the development of different hydration products and its finer granulometry. For the examination of the development of the mechanical strength an additional test of the pozzolanic activity rate was carried out. The results are shown in Fig. 2. Flint cullet exhibited higher pozzolanicity at the late days and succeed to reach the pozzolanicity of green and amber glasses.

In Fig. 3, are presented the compressive strength development of the cement pastes containing ground coloured glass and fly ash. In opposition to the pozzolanic activity tests, green and flint glass perform better results than the amber glass and the vitrified material (Fig. 4). The result is further reinforced by SEM observations of the cement pastes at 28 days. The green glass particle, as Fig. 5(a) demonstrates, has reacted with cement, producing C–S–H gels as EDX analysis verified. On the other hand, the glass particle of the amber glass, as it is shown in Fig. 5(b), appeared inactive. Strange as it may seem, amber glass cullet performed better behaviour at 200 μm fraction of glass cullet than 90 μm. It is apparent that the development of the pozzolanic activity is influenced not only by the particle size of cullet but also by its chemical structure. The strength development of the amber cullet is unsatisfied, nevertheless, its use in a mixed colour batch it is not impossible. However, further investigation is required since the results do not follow linear combination.

Further investigation of the porosity of the cement pastes indicated a micro porous product. In Table 5, are illustrated the results from the porosity measurements of the flint glass. During the hydration of the material there was a shift to the minor pores, due to the appearance of hydrated products corresponding to the decrease of the porosity. Flint, green and amber cullet cement specimens showed similar behaviour to the common cement pastes.

In order to verify the presence of hydrated phases with respect to the reduction of $Ca(OH)_2$ the sediments of the above tests were examined using XRD and DTA-TG analysis and the results are shown in Figs. 6 and 7. The endothermic peak at 90–200 °C referred to calcium silicate hydrates, calcium aluminate hydrates and sulphoaluminate hydrates. The endothermic peak at 400–500 °C can be attributed to the decomposition of $Ca(OH)_2$, while the endothermic peak at 620–750 °C is corresponding to the decomposition of $CaCO_3$. As the hydration proceeds the intensity of the $Ca(OH)_2$ peak was decreased while the hydrated products were simultaneous increased. Due to the carbonation of $Ca(OH)_2$, $CaCO_3$ was present in all the samples. Furthermore, the hydration products are mainly amorphous which connotes their easy attack by atmospheric CO_2. The XRD patterns indicate the presence of calcium silicate hydrates and calcium aluminate hydrates. Especially the vitrified material showed important amounts of calcium aluminate hydrates.

It is obvious that pozzolanic reaction of the glass have occurred at the later ages, thus the presence of glass cullet has no influence on the early hydration reactions of the Portland cement.

Table 5
Porosity measurements

	Total cum. vol. (mm^3/g)	Spec. surf. area (m^2/g)	Pore radius aver. (μm)	Bulk den. (g/cm^3)	Corr. bulk den. (g/cm^3)	Total sample por. (%)
7 days	73.64	3.66	0.11	2.14	2.54	15.75
28 days	59.25	3.72	0.07	2.20	2.53	13.03

Pore size distribution	50–10 μm	10–5 μm	5–1 μm	1–0.5 μm	0.5–0.1 μm	0.1–0.05 μm	0.05–0.01 μm	0.01–0.005 μm	0.005–0.001 μm	0.001–0.0000 μm
Spec. vol. (mm^3/g)										
7 days	0.68	1.02	2.05	4.68	34.21	49.76	70.22	73.1	73.64	73.64
28 days	0	0.12	0.61	1.02	12.35	34.47	55.58	58.64	59.25	59.25
Rel. vol. (mm^3/g)										
7 days	0.68	0.34	1.03	2.63	29.53	15.55	20.46	2.88	0.54	0
28 days	0	0.12	0.49	0.41	11.33	22.12	21.11	3.06	0.61	0

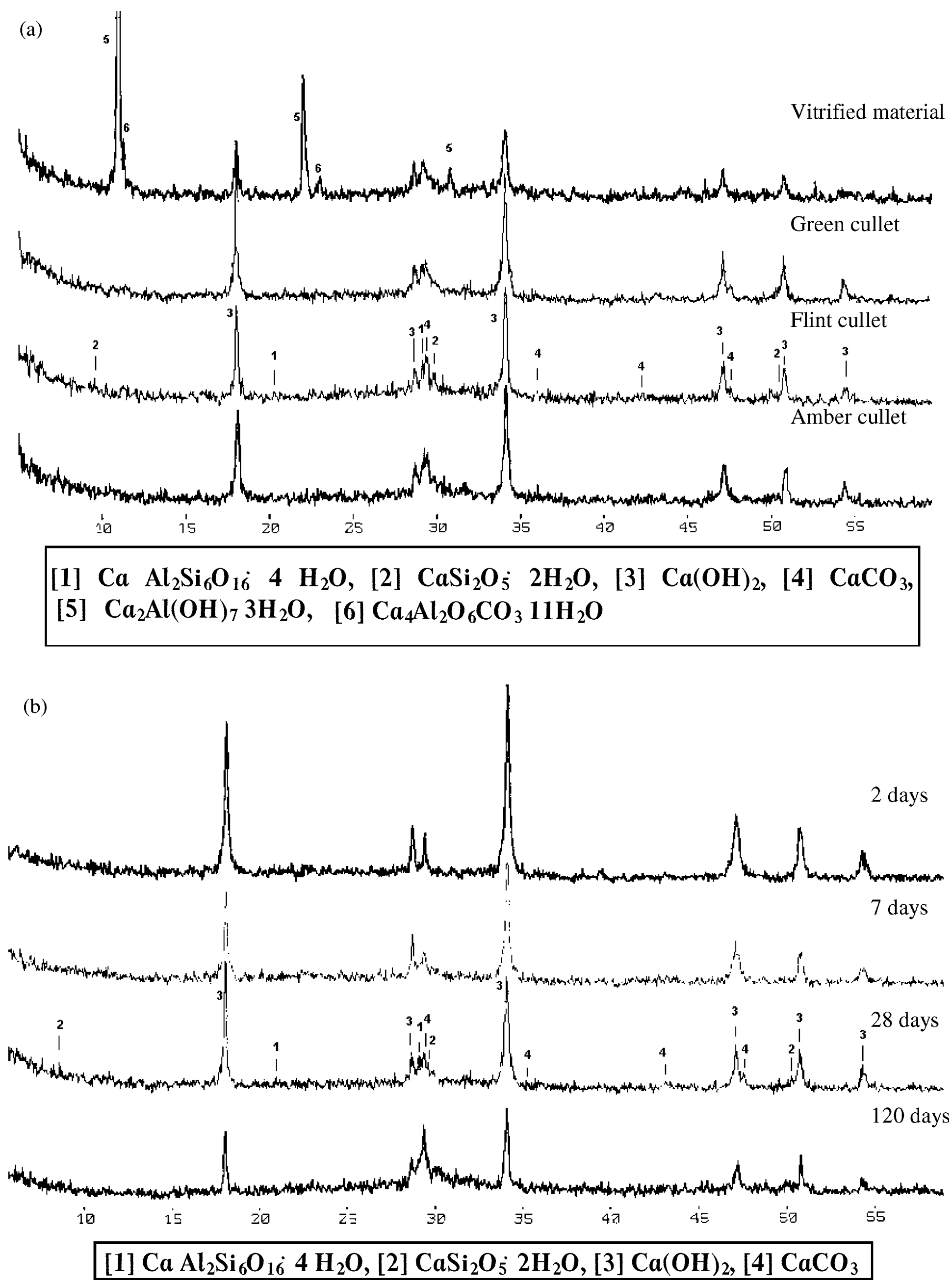


Fig. 6. (a) XRD patterns of the sediments of the pozzolanic activity tests at 28 days. (b) XRD patterns of the sediments of the pozzolanic activity tests of flint glass.

3.2. Alkali-silica reaction

The results of alkali-silica expansion tests of specimens with 25% replacement of cement by 90 μm glass cullet (green, amber, flint) and additionally by 90 μm of vitrified material showed that the mortar prisms performed a slight shrinkage. This outcome provided one more evidence that the finely ground cullet has the effect to lessening expansion of the ASR. The amber cullet performed a larger alteration during the first day probably due to the hydrolysis of the large amount of Fe^{3+} present in the network of the amber glass compared to the Fetotal/Fe^{2+} contained in the green and flint cullet. In an alkaline environment, due to agglomeration and precipitation, the specimens performed initial reduction of their length. It is worth to mention, that an additionally measurement of compressive and flexural strength of the specimens after the end of the alkali-silicate test, revealed impressive outcomes. Except for the specimens with 25% replacement of amber cullet, all others specimens exhibited higher compressive strength than that of the blank specimens. Probably an

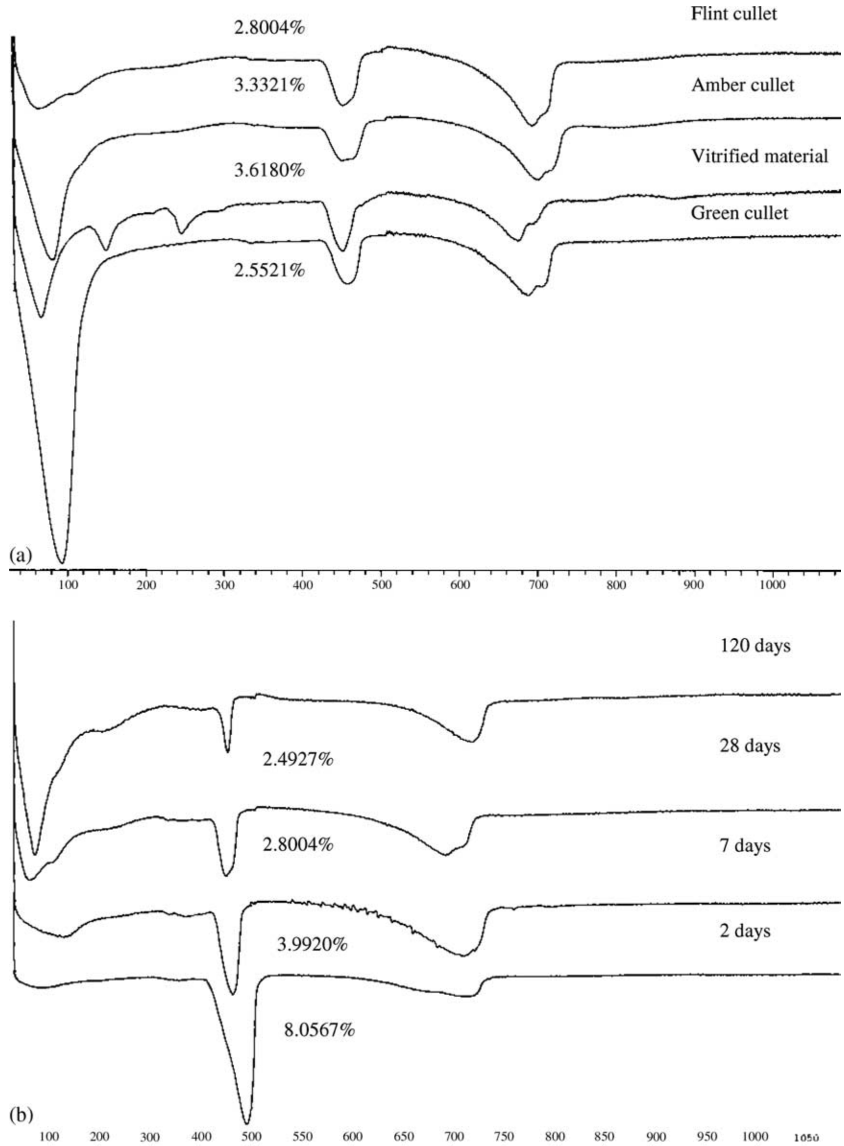


Fig. 7. (a) DTA curves of the sediments of pozzolanic activity tests at 28 days. (b) DTA curves of the sediments of flint glass pozzolanic activity tests.

indication can be that the NaOH solution activated the cement–glass pastes, and especially the vitrified material giving hydration products, while under the alkaline environment of cement hydrates the potential activity by the ground glass could not be achieved.

3.3. Application in cementitious plasters

Aiming to exploit the light weight of the glass cullet, coarse and/or fine aggregates of a common plaster were substituted by flint glass. In Table 6 the technical char-

Table 6
Technical characteristics of fresh mortars

	CP	GCPF1	GCPF2	GCPF3	GCPF4
Request of water (ml)	330	330	330	320	330
Table flow test (cm)	17.1	17.5	16.8	17	17
Retained water (%)	98.2	98.1	98.38	97.41	97.66
Air content (%)	20	18.5	19	19.5	19
Specific weight of the fresh mortar (g/cm^3)	1.74	1.75	1.78	1.77	1.8
Compressive strength 7*d* (MPa)	2.5	2	2.1		2.1
Compressive strength 28*d* (MPa)	3.6	4.4	4.6		4.9

acteristics of the fresh mortar are illustrated. When the ground glass was used as a coarse aggregate in a common plaster there was no alteration in the specific weight. On the contrary, the reduction of the glass particle size had as a consequence a slight increase in the specific weight and the plaster retained fewer amounts of water. The additional compressive strength tests showed significant higher results. In particular, when flint glass cullet was used as filler, the plaster performed 36% higher strength results. Once more, the results at the early days were not encouraging.

4. Conclusions

Coloured glass cullet was tested for potential utilisation as a cement substitute or as aggregate in cementitious materials. It is evident, from the performed tests that green cullet exhibited better results concerning pozzolanic activity and compressing strength development followed by flint glass cullet. Amber cullet showed the worst behaviour, despite the fact that pozzolanic tests demonstrated adequate pozzolanicity. A satisfactory outcome was that finely ground glass cullet was found to cause negligible ASR expansion. Apparently, the use of glass cullet in construction materials seems feasible, taking into consideration the demands of each application area. In addition, further investigation of the vitrified fly ash is necessary, since encouraging results have been achieved in particular by activating in alkaline environment. Especially for the study of vitrified fly ash it must be noticed that incorporating waste into concrete on an appropriately selective base could help to solve some of the problems encountered in waste management.

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