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INNOVATING REUSE OF GLASS CULLET IN CEMENT PRODUCTS

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ABSTRACT.
The current study focused on the utility of glass cullet into cement products, either as partial substitution of cement pastes or as a substitute of mortars' aggregates. When cullet was used into pastes was ground to a size fine enough to activate its pozzolanic behaviour. Additionally, the activation of cullet pastes with NaOH solution has been examined. For comparative reasons complemental samples using Lignite Fly Ash were made. The chemical behaviour between the cement and cullet was determined by XRD and SEM observations. Further measurements of the compressive strength of the pastes and the pozzolanic activity of the cullet were carried out as well as the properties of the fresh mortars. The above tests indicated that the potential utilisation of coloured cullet in various cementitious products is very encouraging especially for decorative applications.

Keywords: Glass Cullet, Cementitious Product, Alkali Activation, Pozzolanic Activity, Glass Aggregates

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INTRODUCTION

Glass cullet is a waste material mainly produced from domestic use. Due to the impurities or mixed colour cullet the largest part of the waste glass cannot be re-melted and utilised as raw material in the glass. Unfortunately the levels of recycling and reuse of waste have been very low and often non-existent in Greece. Regarding cullet, Greece has one of the lowest glass recycling rate in Europe. The EU policy for an improved environment forces for alternative utilisation of cullet as glass industry is shrunk in Greece and the volume of imported glass is increasing. The target for recycling is a minimum recycling of 25% by weight for all packaging materials and the proposed new targets for 2008 is 55% (60% is the target for glass) [1].

The most recent studies of utilization or recycling of glass cullet are mainly based on using it as a component in different manufacturing processes. Some of the applications which have been proposed are as decorative material, glass-asphalt, abrasive element, filtration medium, binder in ceramics and brick etc.[2,3]. The industry of construction materials seems to be one of the most lucrative and applicable due to the fact that have a considerable need for a silicate material therefore, a satisfactory amount of glass cullet could be consumed as a raw material.

Earlier studies in the partial substitution of the coarse or fine aggregates have given unsatisfactory results mainly due to the alkali-silicate reaction (ASR)[4]. It was found that a way to overcome this problem was to ground the waste glass to a size fine enough to activate its pozzolanic behaviour [5].

However, alkali-silica reaction remains an issue for the use of glass cullet in cementitious products mainly due to the conflicted results between the researchers. Soda-lime-silica glasses raises two concerns with respect to expansive ASR: it comprises a reactive form of silica and a potential source of alkalis [6].

Taking into consideration all the above factors this work has been focused on the use of green, amber and white glass cullet as a component of cementitious materials either as aggregate, filler or binder. Earlier studies have shown the ability to enhance the pozzolanic activity [7]. In this article a further evaluation of the pozzolanic activity of the binary system of glass cullet and fly ash was contacted. Furthermore, the compressive strength of pastes with partial substitution of cement by glass cullet or glass cullet and fly ash, fluctuated between 5 and 10%, was measured. Moreover, the alkali-activation of the glass-cement mixtures was studied using NaOH 0.1N the non-evaporable water was measured correlated to the hydration progress. All specimens were examined using X-Ray Diffraction (XRD), Thermal Analysis (TG) and Scanning Electron Microscopy (SEM). The potential alkali-silica reaction of the mortars containing cullet was assessed using the method described in ASTM C1260.

A second series of experiments investigated the potential replacement in either fine aggregates, coarse aggregates or filler aggregates in common plasters. The mechanical strength together with the properties of the fresh mortars was explored.

EXPERIMENTAL DATA

Materials

The three most common cullet colours, green, amber and flint, were used in order to evaluate the influence of the colour of the glass in the cement mixtures.

The chemical composition of the glass is shown in Table 1 and also the chemical analysis of the Fly Ashes.

Table 1: Chemical composition of cullet and fly ashes

%(w/w)	Green cullet	Amber cullet	Flint cullet	Fly ash 1	Fly ash 2
SiO_2	69.40-71.60	70.20-72.20	69.30-72.00	51.26	30.16
Al_2O_3	1.40-2.20	1.70-2.10	1.30-2.20	19.39	14.93
Fe_2O_3	0.20-0.70	0.20-0.50	0.30-0.60	8.44	5.10
CaO	9.60-10.70	9.50-11.20	9.70-11.70	11.82	34.99
MgO	2.40-3.10	2.30-2.90	1.70-3.20	2.27	2.69
SO_3	0.10-0.40	0.10-0.50	0.30-0.60	2.91	6.28
Na_2O	11.90-14.00	12.30-14.00	11.70-14.80	0.53	1.01
K_2O	0.30-0.60	0.40-0.80	0.40-0.70	1.81	0.4
Na_2O+ K_2O	12.2-14.6	12.7-14.8	12.1-15.5	2.34	1.41
Cr_2O_3	0.20-0.30	0.01-0.10	-	-	-
Loss of ignition	-	-	-	1.67	3.95

Fly Ashes (Class C) originated from Megalopoli and Ptolemais area in Greece, where used as comparative materials or as constitute of a ternary system of glass cullet-fly ash-cement.
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,–90μm were selected to be used as a binder into cement pastes. Fly ashes samples have a retained amount of 80% on 56μm (DIN 4188).
Ordinary Portland Cement (OPC) and sand for the pastes were used for the experiments, according to ASTM C778.
The alkali activator that has been used was NaOH 1N.

Pozzolanic activity

The pozzolanicity of glass cullet as well as of fly ashes and mixtures of fly ash and cullet was estimated according to the Chapelle Methodology [7]. All the sediments of the above test were examined using X-Ray Diffraction (Siemens D5000 diffractometer, Cu Ka radiation, Ni Filter) and Thermal Analysis TG (Mettler TGA/SDTA851^e).

Mix Proportions of cement pastes

Former studies [8,9] have shown that for 25% substitution of cement, green and flint glass exhibit the better performance than amber glass. In order to estimate the degree of substitution of cement by cullet glass-cement pastes were prepared in accordance with EN 196 Part I with glass fluctuate from 5% to 10% by volume. The ratio binder to water was determined to 3/1 arisen from the workability of the fresh pastes defined by the table flow tests (EN 1015-3). Furthermore, specimens with 5% glass cullet and 5% fly ash were prepared in order to examine the potential promote of pozzolanic activity due to the presence of a highly reactive material.
The hydration of the pastes was studied using X-ray Diffraction Analysis, Thermal Analysis and Scanning Electron Microscopy (Philips XL30 ESEM). Furthermore, mechanical strength and the non-evaporable water were estimated following a procedure similar to that described by Y.M. Zhang et al [10].

Alkali Silica Reaction

The high alkali content in the cement pastes necessitated for the expansion examination due to alkali-Silica Reaction. The potential alkali-silica reaction of the mortars containing cullet was assessed according to ASTM C1260. Specimens have been prepared with 25% substitution of cement by cullet of each colour. The used aggregates were accorded to the ASTM C778 and are not prone to alkali-silica reaction.

Mix Proportions of Plasters

A common masonry plaster was prepared using white cement and flint, green or amber glass cullet as a partial replacement for both aggregate and filler. The proportions are being presented at Table 2.
The properties under examination, except from the mechanical strength measurements, were the properties of the fresh plasters. In particular, retained water (EN 1015-8), air content (1015-7), specific weight (EN1015-6) and table flow tests (EN 1015-3) were estimated.

Alkali-Activated Glass-Cement Pastes

The stimulating effect of NaOH on the activity of fly ash, and other pozzolans as well, has been observed by many other researchers [11,12]. In the present study 1 N NaOH was used in order to study this phenomenon. The same proportions such as for the non activated samples were kept. Mechanical Strength and non-evaporable water tests were performed and also all specimens were examined using XRD and TG analysis.

RESULTS AND DISCUSSION

It is known from former study [9] that the two greek Fly Ashes performed better pozzolanicity according to the Chapelle test. In order to evaluate the interaction between the fly ashes and the three glass cullet mixtures consisted of equal quantities of glass cullet and fly ash were subjected to the aforementioned test. The results shown that flint cullet is corporated better with Ptolemais fly ash and green cullet with Megalopolis fly ash.

Table 2: Plasters Composition

Plasters Composition (% w/w)		Flint Cullet			Green Cullet			Amber Cullet		
Composition Code		GCFC	GCFF	GCFFi	GCGC	GCGF	GCGFi	GCAC	GCAF	GCAFi
Aggregates	0.7-1.4mm	-	11	11	-	11	11	-	11	11
	0-0.7mm	57.5	-	57.5	57.5	-	57.5	57.5	-	57.5
Cement		9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
Filler		13	13	-	13	13	-	13	13	-
Lime		9	9	9	9	9	9	9	9	9
Chemical Additives		0.145	0.145	0.145	0.145	0.145	0.145	0.145	0.145	0.145
Cullet 0.7-1,4mm		11	-	-	11	-	-	11	-	-
Cullet 0-0.7mm		-	57.5	-	-	57.5	-	-	57.5	-
Cullet		-	-	13	-	-	13	-	-	13

The results of the compressive strength are illustrated at the Figure 1. It is obvious that the two greek fly ashes performed better behaviour that the glass cullet. Nevertheless, fly ash and grounded glass cullet seems to interact providing promotion of the pozzolanic reaction. Furthermore, following the results from the Chapelle test, Ptolemais fly ash performed higher compressive strength in mixtures containing flint cullet than green or amber cullet. Likewise, Megalopolis fly ash seems to interact better with green cullet.
Unexpected were the outcomes from the alkali activation. All samples developed lower compressive strength than the non-activated samples. One explanation might be the very week alkali solution.

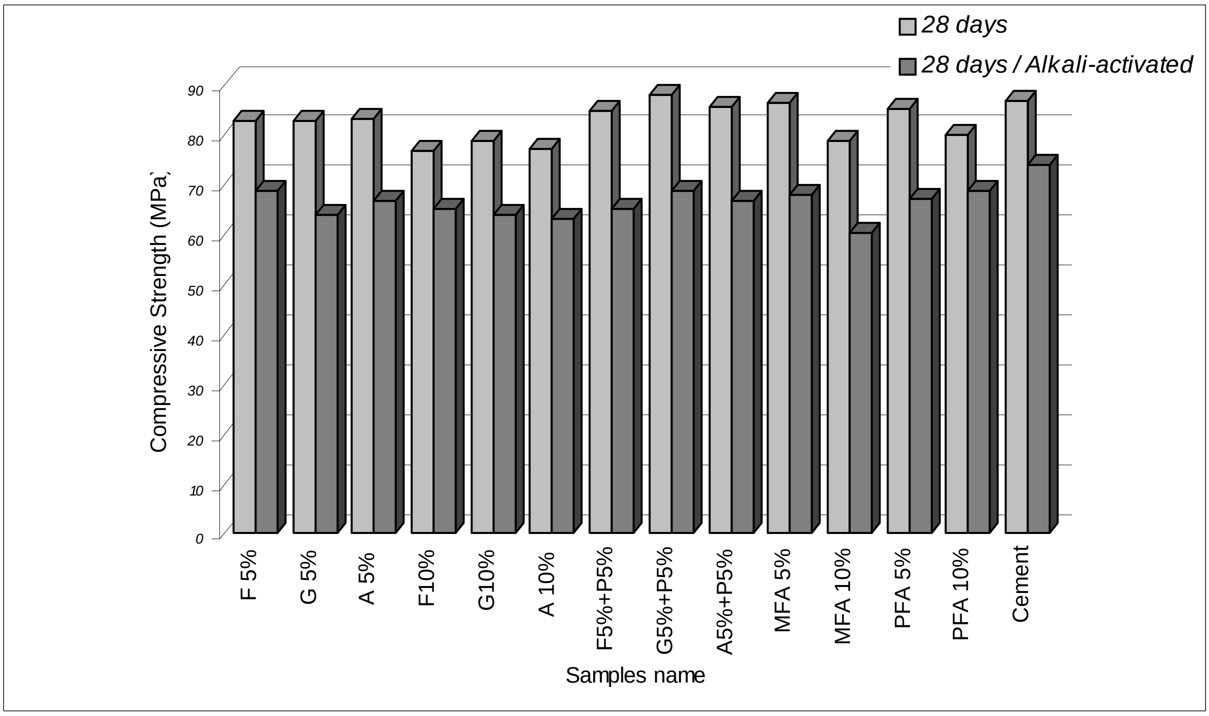

Figure1: Compressive Strength of the Samples

It must be mentioned that the alkali-activated samples shown better flexural strength than the non activated samples.
The DTG curves of the pastes at 28 days are demonstrated in the following Figure 2. Moreover, at Figure 3 the XRD spectrums of the glass-cement paste containing green glass cullet are illustrated. At the DTG curves the presence of the hydrated products at 90-200^{o}C is obvious. The endothermic peak at 400-500^{o}C can be attributed to the decomposition of $Ca(OH)_2$, while the endothermic peak at 620-750^{o}C is corresponding to the decomposition of $CaCO_3$. Moreover, XRD pattern shows production of Calcium aluminate hydrate and ettringite. Moreover, the consumption of $Ca(OH)_2$ during the days is presented. It must be mentioned that both fly ashes showed similar behaviour during the tests, although their differences in chemical and mineralogical composition.

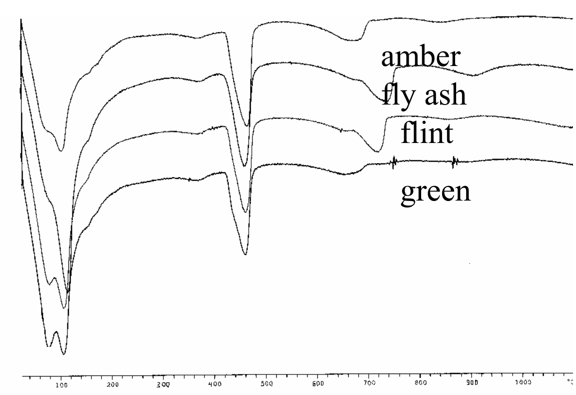

Figure 2: DTG curves of the glass-cement pastes at 28 days

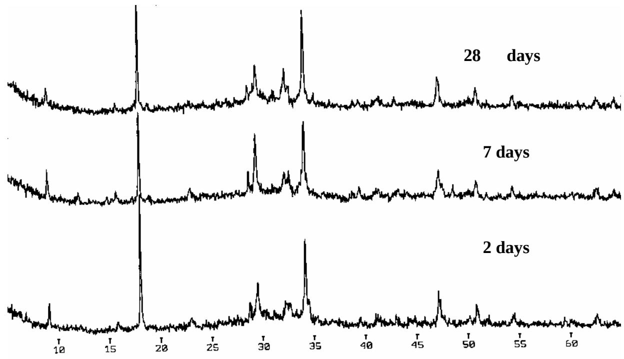

Figure 3: XRD patern of a glass-cement paste containing green cullet at 2, 7, 28 days

Table 3 shows the non-evaporable water content of glass-cement pastes. It can be seen that the non-evaporable water of alkali-activated pastes is lower in comparison to the non-activated samples for the same replacements. The non-evaporable water is increasing when the glass contain is increased but is decreasing at the presence of fly ash. In order to explain the above observation further examination of the samples is needed and the below results must be combined with the CH content of the cementitious pastes.

The application of the glass cullet in the cementitious plasters significantly improved their compressive strength,especially when it used as a filler, without any notable affection to the properties of the fresh mortars. One negative factor was that the workability of the fresh glass-cement plaster was decreased. This phenomenon might be owed to the angular shape of the glass particles, which favours the creation of interlocks and consequently decrease the workability of the produced plasters.

The resulted properties of the glass-cement plasters are illustrated in the table 4.

Table 3: Non-evaporable water of non activated and alkali activated pastes at 28 days

Non-evaporable water (%)	Non Activated	Alkali activated
Sample name	28 days	28 days
Green 5% (G5%)	18.85	18.46
Amber 5% (A5%)	19.12	18.97
Flint 5% (F 5%)	20.78	18.52
Green 10% (G10%)	22.36	19.04
Amber 10% (A10%)	22.36	22.63
Flint 10% (F 10%)	22.14	19.63
Green 5% Megalopolis Fly Ash 5% (G5%+M5%)	22.32	16.82
Amber 5% Megalopolis Fly Ash 5% (A5%+M5%)	22.22	16.15
Flint 5% Megalopolis Fly Ash 5% (F5%+M5%)	22.31	16.59

Table 4: The Technical Characteristics of the Fresh Mortars

Composition Code	GCFC	GCFF	GCFFi	GCGC	GCGF	GCGFi	GCAC	GCAF	GCAFi
Request of water mL	495	505	505	495	505	500	490	510	500
Table flow test cm	17.4	17.2	17.7	17.4	17.4	17.8	17.2	17.5	17.4
Retained water %		86.5	89.82		84.65	88.64		86.06	86.14
Air content %	9.5	13.5	8.6	8.5	11	9	9.4	12	6.6
Specific weight of the fresh mortar g/cm3	1.8	1.65	1.82	1.82	1.71	1.82	1.8	1.67	1.87
Compressive strength 7d (MPa)	0.6	0.7	0.9	0.9	0.9	0.6	0.9	0.6	0.9
Compressive strength 28d (MPa)	2.6	2.5	3.5	2.6	2.9	3.6	2.7	2.4	4.1
Compressive strength 90d (MPa)	2.9	3.6	3.8	2.7	3.8	4	2.7	2.7	4.7
Flexural strength 7d (MPa)	0.3	0.4	0.5	0.5	0.5	0.4	0.5	0.4	0.6
Flexural strength 28d (MPa)	1.1	1.3	1.5	1.1	1.3	1.5	1.1	1.2	1.6
Flexural strength 90d (MPa)	1.1	1.1	1.6	0.9	1.4	1.5	0.9	1.3	1.7

Very encouraging is the fact that non of the examined samples have not shown any expansion due to the alkali-silica reaction.

CONCLUSIONS

The finely ground glass cullet could be utilized as a partial replacement of cement especially for low substitutions. The green and the flint cullet performed better behaviour than the amber glass. More satisfactory were the outcomes from the cullet application as an aggregate or a filler in cementitious plasters, with the only negative factor the reduction of workability of the fresh plaster. Very encouraging was the fact that none of the examined specimens showed any expansion due to the alkali-silica reaction. As a final consumption, the utilization of glass cullet in cementitious materials seems feasible especially for decorative products.

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REFERENCES

[1] The European Commission, Directive 94/62/EC on packaging and packing waste. Brussels 18.10.2002 13272/02, (2001/0291 (COD))

[2] Meyer, C., Egosi, N., Andela, C., Concrete with waste glass as aggregate. Proceedings of the International Symposium Recycling and Reuse of Glass Cullet, Dundee 179-188, March 2001.

[3] Ketov A, Peculiar chemical and technological properties of glass cullet as the raw material for foamed insulation, Proceedings of the International Symposium Recycling and Reuse of Waste Materials, Dundee 695-704, September 2003.

[4] Polley, C., Cramer, S.M., and De la Cruz, R.V. Potential for using waste glass in Portland cement concrete, Journal of Materials in Civil Engineering (1998), Vol. 10, p. 201-211.
[5] Jin, W., Meyer, C., and Baxter, S., "Glascrete"-concrete with glass aggregate, ACI Materials Journal (2000), Vol. 97, p. 208-213.
[6] Dhir R., Dyer T., Tang M., Expansion due to Alkali-Silica Reaction (ASR) of glass cullet used in concrete, Proceedings of the International Symposium Recycling and Reuse of Waste Materials, Dundee 695-704, September 2003.
[7] Largent, R.(1978) "Estimation de l' activite pouzzolanique" Bull. Liaison Labo. P. et Ch., 93, Ref. 2143, p. 61-65.
[8] Moutsatsou, A., Chaniotakis, E., Papageorgiou, D., Karamberi, A.: Treatment and Recycling of Vitrified Fly Ash and Coloured Cullet in Cement Mixtures, International Congress Rec'2002, Geneva, February 2002.
[9] Moutsatsou, A., Chaniotakis, E., Papageorgiou, D., Karamberi, A., Participation of coloured cullet to the hydration and the development of compressive strength of cement, The Sixth International Conference on Concrete Technology for Developing Countries, Amman, Jordan, October 2002.
[10] Zhang, M.Y., Sun, W., Yan, H.D., Hydration of high-volume fly ash cement pastes, Cement and Concrete Composities (2000) Vol. 22, p. 445-452.
[11]Lee, W.K.W., Deventer, J.S.J., The effect of ionic contaminants on the early –age properties of alkali-activated fly ash-based cements, Cement and Concrete Research, (2002) vol. 32, p. 577-584.
[12]Williams