USE OF GLASS CULLET AS A CEMENT COMPONENT IN CONCRETE

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ABSTRACT. The successful growth of container glass recovery in the UK has lead to the emergence of a green cullet surplus. Alternative routes for using this material are being explored. This paper reports on some of the results from a feasibility study whose aim was to assess the suitability of ground cullet for use as a binder in combination with Portland cement. Cullet from container glass clearly undergoes a pozzolanic reaction when combined with Portland cement. The reaction leads to compressive strengths that either match or exceed those attained by control specimens up to a Portland cement replacement level of 30%. Detrimental expansion due to alkali-silica reaction is reduced. The study concluded that there was potential for using ground cullet as a binder in concrete.

Keywords: Glass, Cullet, Cement component, Strength development, Hydration chemistry, ASR

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INTRODUCTION

Glass cullet recovery has increased relatively steadily in the UK since the introduction of bottle banks in the 1970s. An unexpected side effect of this increase is that, since the mid-1990s a surplus of green cullet has started to arise. The surplus derives from an imbalance in the relatively large quantity of green glass recovered (largely the result of imports of beer and wine) and the smaller quantities of green glass containers produced by the UK glass industry.

Whilst the levels of cullet recovery in the UK are much lower than levels of recovery in other European countries, they are set to rise considerably as action is taken to meet EU directive targets on reducing packaging waste. Such increases will, if alternative uses are not identified, lead to the generation of a considerable 'green glass mountain' which would compromise both the economic viability and the sustainability of cullet recovery in the UK.

Cullet is a hard and relatively strong granular material, which makes it an obvious candidate for use as a construction aggregate. Glass has been used, with some success, as a roadbase material [1] and also as an aggregate in concrete [2, 3]. When used in concrete, however, researchers found that detrimental expansion due to alkali-silica reaction (ASR) was encountered unless pozzolanas or ASR-suppressing admixtures were incorporated in the mix.

The fact that cullet is capable of undergoing ASR means that it contains a reactive form of silica which implies that it will also undergo pozzolanic reactions - reactions with lime to produce cementitious gel products (mainly an amorphous calcium silicate hydrate compound referred to as C-S-H gel). Materials that undergo such reactions are frequently used in combination with Portland cement in concrete, where the material reacts with portlandite ($Ca(OH)_2$, a product of cement hydration reactions. The use of such materials in this way provides economic benefits and, in some cases, enhanced durability properties for certain applications.

There is, in fact, very little difference between a pozzolanic reaction and ASR [4], the key differences between the two reactions which define whether a beneficial or detrimental effect is produced are the timescales involved (rapid for pozzolanic, slower for ASR) and the chemical composition of the resulting gels (a higher calcium / alkali ratio for pozzolanic products) [5].

For a material to undergo pozzolanic reactions effectively it must be finely ground, since a high surface area is required to ensure an adequate rate and degree of reaction. It has been shown that cullet processed in such a way appears to undergo a pozzolanic reaction, at least in terms of strength development [6]. This paper reports on some of the results of a feasibility study carried out into determining the suitability of using ground glass cullet as a cement component in concrete. The main aim of the study was to confirm that the material was pozzolanic in both physical and chemical terms, and to determine the extent to which ASR presented a problem when glass was used in this manner.

MATERIALS AND EXPERIMENTAL METHODS

Whilst finding alternative uses for green cullet is of most importance in the UK, the feasibility study examined the three most common cullet colours (white, amber and green) to allow the findings to be applied in a generic manner to similar problems arising elsewhere in the future.

The Materials

White, green and amber glass cullet samples were obtained from a cullet recycling company. Since they were obtained from actual bottle-bank collection streams, the samples were contaminated with other glass colours to some extent. The bulk oxide analyses of the materials used throughout the study are shown in Table 1. The cullet was washed before being ground in a laboratory ball mill. The resulting powder was passed through a 600μm sieve to ensure no large particles remained. The fineness of the cullets after grinding, measured as the percent mass retained on a 45μm sieve, were 61.5, 21.0 and 44.0% for clear, green and brown cullet respectively. For the purpose of this feasibility study, no attempt was made to tailor particle size distributions, and the powders were used as obtained from the ball mill. The materials were confirmed to be entirely amorphous by powder x-ray diffraction.

Table 1. Chemical composition of the glass cullets and Portland cement used in the study

COMPONENT	GLASS CULLET, % mass			PC
	White	Green	Amber	
CaO	6.43	10.26	10	64.9
Al_2O	2.41	2.81	3.2	5
SiO2	70.39	72.05	70.01	21.1
K_2O	0.23	0.52	0.82	0.6
Na_2O	16.66	14.31	15.35	0.3
Fe_2O_3	0.32	0	0	2.7
MnO	0.04	0.04	0.04	0.1
MgO	2.59	0.9	1.46	1.6
TiO_2	0.08	0.11	0.11	0.2
Cl^-	0.02	0	0	0.03
SO_3^-	0.19	0.07	0.06	3.3

Compressive Strength Measurements

Compressive strength measurements were taken at ages of 2, 7, 28 days on specimens prepared, cured and tested in accordance with BS 196 Part 2 [7]. Specimens were prepared containing white, amber and green glass cullets at Portland cement replacements of 10, 20, 30 and 40% by mass.

Mineralogical Analysis

Cement pastes containing ground cullet were prepared for analysis using powder x-ray diffraction and thermogravimetry. Hydration reactions were stopped at an age of 28 days by first grinding the specimens with acetone before drying under vacuum at a temperature of 40°C.

Thermogravimetry was carried out with platinum crucibles containing 10mg samples in a nitrogen atmosphere. A temperature regime of ambient to 1000°C was used at a rate of 2°C/minute.

Powder x-ray diffraction was carried out using a Philips diffractometer with a Cu-kα radiation source and a single crystal graphite monochromator. An angular range of 3-90°2θ in 0.05°2θ increments was used throughout.

Rietvelt refinement was conducted on the diffraction traces, enabling an estimate of the mineralogical composition of each blend to be obtained. The computer programs X-FIT and KOALARIET were used [8-13]. The non-crystalline materials in the hydrated pastes in the form of cullet as well as calcium silicate hydrate (CSH) gel produced during reaction, could not be quantified using Rietveld refinement. However, determining the quantity of Portlandite present from thermogravimetry measurements allowed this phase to be used as a 'pre-existing' internal standard, allowing quantification of the total amorphous content of each sample.

Fracture surfaces of hydrated paste specimens were also studied under the scanning electron microscope (SEM).

Alkali-Silica Reaction

The propensity for mortars containing glass cullet to undergo alkali-silica reaction was assessed using the method described in ASTM C 1260 - 94 [14], with the exception that the same mortar mixes as used for strength development measurements were used, to allow more meaningful comparison.

RESULTS AND DISCUSSION

Introduction

In cases where very little difference was displayed by different colours of cullet, the results obtained from just one colour are shown.

The Pozzolanic Reaction of Ground Cullet from a Chemical Perspective

The compressive strengths of mortar prisms containing PC replacements of green cullet are shown in Figure 1. It is apparent that by 28 days, the compressive strengths obtained for replacements of up to 30% are similar to, or exceed, the compressive strength of the control. The compressive strength results certainly suggest that the cullet is undergoing a pozzolanic reaction. This is further reinforced by examining the calcium hydroxide content of the pastes measured using thermogravimetry (Figure 2). These results have been expressed as a percentage of the original Portland cement content of the paste, since this allows more meaningful comparison of portlandite levels. The following equation was used for these calculations:

$$\text{Adjusted portlandite content} = \frac{\text{Mass of portlandite in sample (mg)} \times 100}{\text{Mass of sample residue at 1000°C (mg)} \times \text{PC content of PC / cullet blend (\%)}}$$

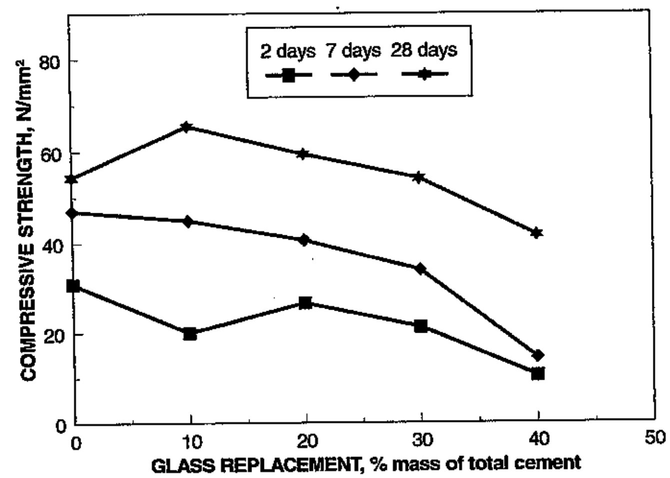

Figure 1. Compressive strengths of mortar prisms containing green glass cullet.

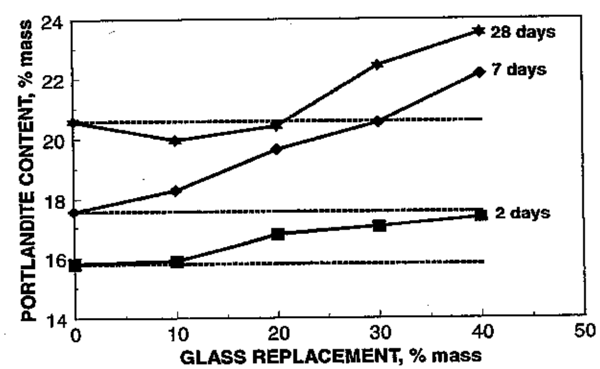

Figure 2. Portlandite contents of pastes containing white cullet. Results are expressed as a percentage of the original Portland cement content. Dotted lines represent levels of portlandite expected for an entirely inert replacement material.

In the situation in which an entirely inert material is used as the cement replacement this type of plot should comprise three entirely horizontal lines, indicating that no portlandite has reacted. However, if a pozzolanic material is present, it would be expected that portlandite levels would be lower than the control. In this case the results seem, at least initially, unusual. As time passes a drop in portlandite is observed at lower cullet replacement levels (10-20%).

However, at higher glass replacements there is a distinct increase in portlandite. This seems unusual until the composition of the cullet is considered - it is rich in sodium and it is likely that these sodium ions will be incorporated in the C-S-H gel formed during hydration [15]. Since the sodium will substitute for calcium, more calcium ions will be available for the formation of portlandite.

The full range of crystalline hydration products identified and quantified in the pastes are presented in another publication [16], although it is worth pointing out that, apart from portlandite, all of the hydration products were those which would normally be formed in hydrating Portland cement paste, and all crystalline hydration products were present in the expected quantities.

Since C-S-H gel is largely viewed as contributing most to the compressive strength of a hardened cement-based material, it was attempted to estimate how much of this substance was formed. Using total water content measurements made using thermogravimetry and then subtracting the quantities of water associated with the crystalline hydration products an estimate of the gel-bound water can be obtained. This is shown in Figure 3, and it should be noted that these results are *not* expressed as a percentage of the original Portland cement content.

It would appear that as hydration proceeds, relatively large quantities of C-S-H gel are formed in the pastes containing glass cullet - so much so that the gel-bound water levels in the glass pastes are almost the same as in the control. However, some caution is required when interpreting these results, since the amount of water associated with the gel will vary with changing composition. Since it is likely that the gel contains varying quantities of sodium ions, the gel-bound water values cannot be directly related to the total amount of gel.

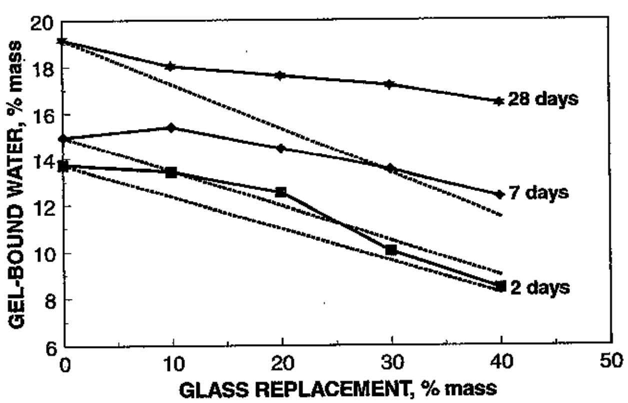

Figure 3. Estimated gel-bound water in pastes containing white cullet. Dotted lines represent levels of gel-bound water expected for an entirely inert replacement material.

The formation of C-S-H gel is also apparent when the pastes are examined under the SEM. Figure 4 is an SEM micrograph showing a particle of cullet in a cement paste matrix. There is clearly a layer of C-S-H gel on the particle's surface, although it is clearly uncertain whether

the gel is derived from the reaction of the cullet or has simply precipitated on the surface. Marks can be seen on the particle surface which may be pits etched into the glass as it reacts. However, it is also possible that these pits were, in fact, air bubbles in the glass.

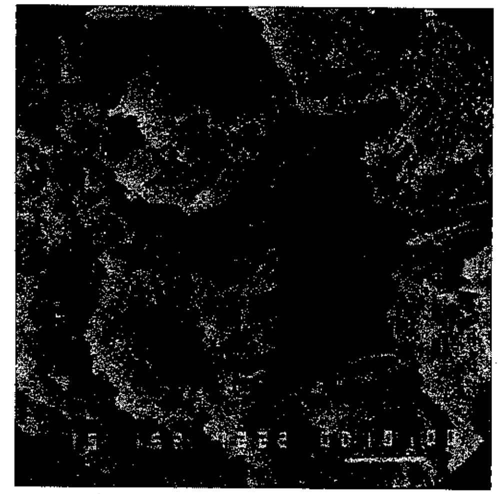

Figure 4. A glass particle in a paste containing green cullet.

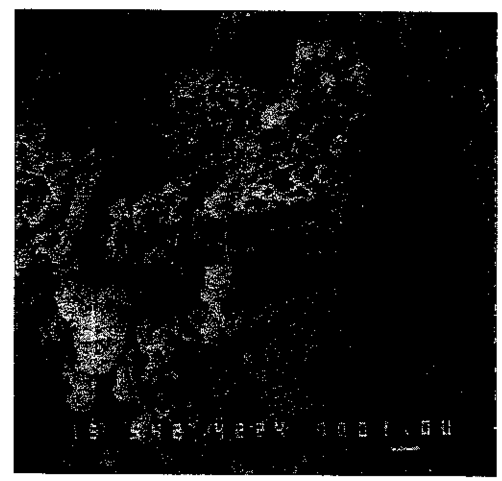

Figure 5. C-S-H gel at the surface of a glass particle.

Alkali-Silica Reaction

The results of alkali-silica reaction expansion measurements made at 16 days on prisms tested to ASTM C 1260. Rather than the glass cullet exacerbating the expansion of the mortar prisms due to ASR, the finely ground material has the effect of lessening expansion. This effect has previously been observed by investigators developing formulations for masonry blocks containing cullet as aggregate [3]. This research has shown that a 'pessimum' particle size exists for which maximum expansion due to ASR is encountered. Below this particle size (around 1200μm) expansion declines. Thus below the pessimum, there is a gradual shift away from the ASR type of reaction towards a pozzolanic reaction.

Differences in the manner in which different colours of cullet perform with respect to ASR have also been observed by other researchers, with green glass performing much more favourably than white glass [3]. Whilst it would appear to also be the case here, it should be remembered that the particle sizes of the various colours of ground cullet were sufficiently different to make direct comparison impossible.

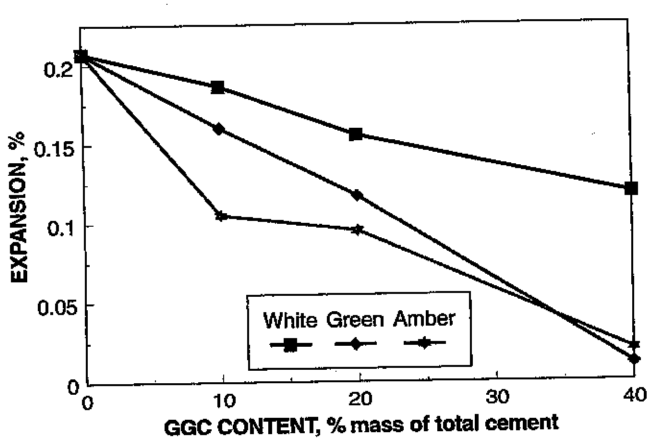

Figure 6. Expansion due to alkali-aggregate reaction at 16 days for prisms containing different coloured ground cullet

CONCLUSIONS

Cullet from container glass clearly undergoes a pozzolanic reaction when combined with Portland cement. The reaction leads to compressive strengths that either match or exceed those attained by control specimens up to a Portland cement replacement of 30%. Detrimental expansion due to alkali-silica reaction is reduced.

It can be concluded that glass cullet in finely ground form has potential for use as a binder in combination with Portland cement. When accelerated methods are used to assess alkali-silica reaction, the expansion behaviour is highly favourable. Due to the promising results obtained during the feasibility study, an underpinning study aimed at developing a technical guidance document for the use of ground cullet in concrete. A key element of this study will be ASR testing in accordance with the recently released British Standard 'real time' test method.

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