

REACTION BETWEEN CEMENT AND ARTIFICIAL GLASS IN CONCRETE

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SYNOPSIS

This paper reviews the literature concerning the embedding of glass in concrete and the use of artificial glasses or aggregates in concrete and the available information on chemical reactions between such glasses and alkalis in cementitious products.

A case study of the use of an artificial glass aggregate for the fabrication of non-structural precast concrete cladding is considered in detail.

Some preliminary laboratory experiments are reported on the use of artificial glasses with cements and the effectiveness of certain pozzolans in combating deleterious expansive reactivity.

SAMEVATTING

Hierdie referaat gee 'n oorsig oor literatuur wat betrekking het op die inlê van glas in beton en die gebruik van kunsglassoorte of kunsglasaggregate in beton en die beskikbare inligting oor chemiese reaksies tussen sulke glassoorte en alkalië in sementprodukte.

'n Gevallestudie oor die gebruik van 'n kunsglasaggregaat vir die vervaardiging van nie-strukturele voorgegiete betonbekleding word in besonderhede behandel.

Verslag word gelewer oor sommige preliminêre laboratoriumeksperimente oor die gebruik van kunsglassoorte met sement en die doeltreffendheid van sekere possolane om skadelike uitsetreaktiwiteit te bekamp.

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1. INTRODUCTION

Silicon is, after oxygen, the most abundant element in the earth's crust and the chemistry of traditional heavy construction materials (such as clay bricks and tiles, cement and concrete) is essentially silicate chemistry. The silicates, although owning a common origin in the stable tetrahedral SiO_4 group vary greatly in their properties from well-ordered holocrystalline compounds (eg β -Ca₂SiO₄ Larnite) to isotropic apparently amorphous glasses.

Artificial glasses are manufactured from readily available and relatively cheap raw materials using simple manufacturing processes and at reasonable energy costs. The resultant materials have technically desirable properties particularly in terms of stability and chemical inertness and through suitable processing to provide a cellular structure, can achieve a good thermal insulation performance.

Silicate materials constitute the major proportion of aggregates used for Portland cement concrete which is one of the most versatile and widely used construction materials. Glassy aggregates, glass and glass components are frequently used in association with cement and concrete, although a number of cases of undesirable chemical interactions have been reported.

This paper is based on an account of a practical problem with the use of an artificial glass aggregate and reviews the available literature on the subject of glass-cement reactivity. The implications for precautions against deleterious reactions are considered.

2. CASE STUDY

In 1967-68 a small industrial building was erected in North East London. The building was a windowless structure approximately 5×5 m in plan and about 10 m high and housed electrical machinery.

Although the area was semi-industrial the particular site was in a sensitive location adjacent to a school and beside a small park and therefore the external appearance of the building was given a special architectural treatment intended to be a white sparkling surface with protruding mullions (or ribs) to give shadow modelling.

The structure itself was of reinforced concrete frame construction with cavity walls of clay brick inner leaf and precast concrete cladding panels attached with non-ferrous fixings. The cladding panels consisted of a number of different shapes including flat panels (approximately 1 m wide by 2,5 m high), chevron units at the corners, rib units, and channel sections at one side at the top of the structure where the frame was exposed.

The concrete units were manufactured from white Portland cement with a pale-pink (oyster) artificial glass aggregate and were up to 150 mm thick. The design cover to embedded steel was only 12 - 13 mm and so galvanised steel was used for the reinforcement.

It was originally intended to expose the coarse aggregate of the panels using a surface retarder applied to the moulds. However, it was not found possible to obtain a satisfactory finish by this method and an alternative grit-blasting system was eventually used.

Once initial problems with fixing the cladding units had been overcome the building gave satisfactory service except that the white appearance was gradually lost due to dirt deposition from the rather grimy atmosphere.

In October 1978 however a section of concrete fell from the top of the structure and a preliminary survey found that extensive cracking and distortion had occurred to the cladding units.

3. SITE INSPECTION

Inspection revealed that numerous cracks were present in the precast concrete units. Within the mullion/rib units these cracks tended to be more or less vertical and the same general direction applied to the chevron corner units. With the flat panels the cracks had a random orientation and this was particularly pronounced towards the top of the structure where the cracks had an appearance of 'map cracking' (Figures 1 and 2).



FIGURE 1: Top section of mullion/rib units of Case Study structure, showing cracking and distortion of precast concrete elements.



side. These sections were examined using conventional petrographic techniques.

The aggregate appeared to be angular fragments of a vesicular glass set in a pale-coloured cement matrix. The glass aggregate particles contained rounded and eroded remnants of quartz grains apparently crystals which had not fused completely in the melt.

Numerous cracks were present in the aggregate particles sometimes sub-parallel to the edges, sometimes linking voids and sometimes traversing the aggregate to continue into the cement paste. In many instances the cracks and voids were seen to contain isotropic gel or a microcrystalline birefringent material, apparently secondary reaction products (Figure 3).

The gel showed typical shrinkage phenomena with often a gap between the gel and the edges of the crack or void and more or less regularly spaced fissures within the material.

Cracks in the cement matrix typically propagated from positions of stress concentration such as corners of angular aggregate and some cracks could be followed from aggregate to aggregate.

Towards the original outside edges of the concrete carbonation of the cement paste had occurred with carbonation extending along the edges of the cracks.

A curious feature of certain portions of the sections was the presence of highly-birefringent curly crystals, associated with gel-containing cracks and voids with many of the crystals extending out of the plane of the section and curling over the edges of cracks to lie over the adjacent aggregate or cement paste where they had been flattened on to the surface when the cover-glass was cemented into position. Although no undue delay had occurred during the preparation of these sections, no particular precautions had been taken to avoid atmospheric moisture or carbon dioxide and it appeared likely that the curly crystals were a carbonation product.

5. DIAGNOSIS

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The macro appearance of the distorted and cracked concrete, the overall increase in dimensions of the precast units, the presence of gelatinous reaction product associated with a glassy aggregate and the characteristic expansion cracks observed in the aggregate and cement matrix were diagnosed as typical of deleterious alkali-aggregate reactivity¹.

The case did, however, present one unusual feature and that is that white Portland cement is in the UK a low-alkali cement and as such might have been expected to have been immune from the problem of alkali-silica reactivity. Indeed,



FIGURE 3 : Thin-section of glass-aggregate concrete, showing eroded quartz crystals, cracks, voids and alkalisilicate gel in an aggregate particle. (Partially crossed polars, X50).



The crack width was greatest where restraint was least and One unit had been partially removed and it could be seen at the top of the structure crack widths up to 2 mm were that the galvanised steel reinforcement was in excellent condition. The non-ferrous fixings were also uncorroded. measured.

Mastic seals at the joints between the cladding units showed signs of movement with extrusion of the mastic and in some places where the concrete units had touched spalls had occurred.

Some of the mullion/rib cladding units had bowed by about 6 mm and the overall height of the mullions had increased by about 10 mm.

Where cladding panels had been restrained by adjacent units considerable bowing had occurred. One measured bow was of 25 mm in a panel 2,5 m high.

Within and around many cracks a white exudation or stain was observed. This had a similar appearance to carbonated lime. No rust stains or signs of corrosion of reinforcement were observed.

At the upper part of the structure the concrete frame was exposed although still clad with glass-aggregate precast concrete units. The horizontal frame members were clad with an inverted channel-section unit with a flat panel covering the soffit of the beams. Tears and gaps in the mastic jointing at the junction between the cladding units showed that the arms of the channel units had apparently moved apart.



FIGURE 2 : Map-cracking of glass-aggregate precast concrete panel

4. LABORATORY EXAMINATION OF SAMPLES

(a) Macro appearance. Visual examination of pieces of concrete taken from the structure showed that the aggregates consisted of a graded pinkish glass which included numerous bubbles within the material. The cladding panels had coarse glass aggregate (approx 20 mm) exposed at the surface, the mullion/rib units had a maximum aggregate size of about 5 - 6 mm. The cement matrix was typical of white Portland cement.

The outer surfaces of the samples had darkened and stained due to exposure to the polluted atmosphere and on breaking open the concrete it could be seen that the dirt staining extended into the cracks for several millimetres.

Extensive random cracking (map-cracking) was present on all surfaces and this was most easily seen on the reverse side of the units which had been protected from the weather and where the original moulded face could be observed.

(b) Thin-section examinations. Large-area thin-sections, 30 1m thick, were prepared from a portion of a claddingpanel containing coarse aggregate and a piece taken from a mullion/rib unit from the top of the structure on the NE

reclaimed rubber solution was normally used to coat such tiles, but that in this case the coating had been omitted.

It has been said that this case includes the only example of personal injury caused by alkali-silica reactivity viz a broken leg due to slipping on silica gel on the bathroom floor⁹.

The Denver Art Museum, Colorado, USA designed by James Sudler Associates¹⁰ is a 6-storey concrete structure completely clad with 76 x 152 mm glass tiles. The tiles are of opaque glass of shallow pyramidal shapes with a keyed back to provide a good bond with the cement mortar used to fix the tiles to the concrete. The facetted, reflective tiling is intended to provide visual interest to the large surfaces and to be not easily soiled.

The accidental inclusion of glass in concrete as a contaminant of aggregate has been the cause of occasional problems of poor durability. In Canada, glass particles in the 3 - 6 mm range caused pop-outs in the surface of concrete under floor-tiles¹¹. The origin of the pop-outs was identified as a clear artificial glass (RI = 1,51) and the cement was found to be of moderate alkali content (0,65 - 0,70 per cent equivalent Na₂O).

Bottle glass contamination of river gravel used to construct a concrete road running up a valley has been identified as the cause of distress and cracking of the concrete¹². In this instance the damage only occurred downstream of a picnic area and it was assumed that the glass was derived

from beer bottles discarded into the gravel pit by visitors.

A not dissimilar problem is the case of spalling from the soffit of a cast in-situ reinforced concrete floor slab of a factory building in Scotland¹³. Each spall was associated with a glass shard at its origin but no glass was detected within the body of the concrete. Enquiries revealed that the shuttering and reinforcement had been made ready prior to the Hogmanay holiday and the concrete poured after the return to work. It was presumed that revellers had hurled bottles into the formwork, thus causing the glass to be present only as occasional fragments at the bottom of the slab.

Cracking and pop-out development in 2 - 4 year old roads and concrete pavements in Germany were found to be due to the presence of glass fragments in the concrete¹⁴. Examination of the aggregate sources confirmed that glass contamination was continuing. Long-term laboratory experiments with concrete prisms (100 x 100 x 500 mm) cement content 300 kg/m³ and 500 g assorted glass replacing aggregate in each prism found expansion after outdoor storage to be 0,1 per cent at 1 year, 0,9 per cent at 2 years, 2,0 per cent at 3 years, 4,0 per cent at 5 years and 5,3 per cent at 10 years. Colourless window glass was found to be more affected by alkali and cement effluent solutions than coloured glasses. A number of glass fragments were analysed for composition and, these results are reproduced in Table 1. It can be seen that all the glasses are soda-lime silicate glasses with varying percentages of alumina and potassia present. The colourless glasses appeared to be of

TABLE 1 : Results of chemical analyses of glass fragments¹⁴

	Percentage composition of various types of glass								
			Colourless				Mean of		
Compound	Green bottle	Green	Brown	(1)	(2)	(3)	(4)	glasses 2, 3 and 4	
SiO2	63,4	65,4	72,3	71,5	69,6	67,0	69,4	68,7	
Al_2O_3	8,6	5,1	0,3	0,5	0,6	1,2	0,6	0,8	
Fe ₂ O ₃	1,6	1,4	0,2	0,1	0,1	0,0	0,1	0,1	
CaO	12,2	8,6	5,5	8,7	5,9	6,5	5,8	6,1	
MgO	0,8	2,7	0,2	0,6	0,1	0,1	0,0	· 0,1	
MnO	-	0,6	0,1	0,2	-	-	0,0	-	
Na ₂ O	10,0	15,5	19,9	17,7	22,2	24,0	21,9	22,7	
K₂O	2,1	0,9	1,2	0,7	1,2	1,3	2,0	1,5	

Glass units set in precast concrete surrounds are a familiar elsewhere in Europe the use of white Portland cement has sight in city pavements where they provide light to basebeen specifically recommended as a method of avoiding ment areas. These units have been used for very many years deleterious alkali reactions². and, except for impact damage, suffer little deterioration. There has, however, been one published report of alkali-This latter aspect prompted a further exploration of the glass interaction in Chicago⁵ where the expansion produced use or association of glass with Portland cement and the by the reaction caused the rectangular panel to bow into a occurrence of damage caused through adverse reactions. pillow shape. Petrographic examination of the failed concrete showed typical expansion cracking due to alkalisilica reactivity with the glazing units showing spalling 6. A REVIEW OF THE USE OF GLASS parallel to the edges and internal traverse fractures mostly WITH CEMENT in the border zones.

Glass set in a cement matrix has been used by several artists Glass is commonly used in contact with cement in as a medium for expression and 'stained glass' windows construction and has been so for very many years. There utilising this principle have been developed to a spectacular are in the UK numerous old security walls topped with standard by the monks of Buckfast Abbey, Devonshire broken-glass set in cement mortar as a scaling deterrent. under the direction of Dom Charles Norris, OSB. These Such use of broken glass is not permitted in new work windows consist of cleaved chunks of coloured glass located (even burglars have rights nowadays) but some of the walls in a cement mortar surround and strengthened by concrete in city centres which were built in the early decades of this mullions and transoms. The best known example of this century still have the glass firmly fixed. work is the great East Window depicting Christ at the Eucharist (1966) in the Chapel of the Blessed Sacrament at Glass bottles have occasionally been used as decorative the Abbey of Buckfast itself⁶ but other smaller windows features in concrete walls. Probably the most famous include those of St Paul the Apostle, Tintagel (1968) example of this use is the moat wall around the garden also designed by Dom Charles Norris and again made at belonging to Sir Gordon Russell, (former Director of the Buckfast Abbey⁷.

Design Council) at Chipping Camden, Gloucestershire³ ⁴ where glass wine-bottles have been set horizontally to give a 'bulls-eye' feature finish. Another well known wall containing glass is at the public house 'The Royal Standard of Old England' at Forty Green, Buckinghamshire, where glass bottles and even a glass beer-mug have been set in cement mortar into brick walls.

Glass aggregate, usually green in colour and partially opalescent due to occluded bubbles, is also commonly used as a decorative covering within the box-kerb type of grave in cemeteries in the UK. In this use it is not normally in contact with cement but except for the colour it does appear to be very similar to the aggregate present in the Case Study concrete.

Glass bricks are used in the walls of buildings to allow light to enter whilst yet still providing security. Nowadays they have a rather utilitarian image although in the 1920's

One case of cracking and spalling of bathroom tiles has and 1930's they were often used to provide a decorative been reported from Australia*. The tiles, 408 x 204 facade to industrial buildings. Glass bricks are set in cement x 6 mm with ribbed backs, were of various colours and the mortar with apparently no adverse effects although someglass included numerous small bubbles within it (presumtimes carbonated lime runs, originating from the mortar, ably providing the opalescent effect). The tiles had been set form on the glass surfaces. These 'stains' can be very firmly in 1:1:3 cement : lime : sand mortar. After 8 months the adherent presumably due to etching of the glass by the glass tiles exhibited an extensive network of very fine alkaline solution. cracks with incrustations and occasional dribbled smears of sticky exudate which hardened to a white crust. Analysis A similar etching problem has occasionally been reported of the exudate showed it to be essentially sodium silicate. where windows of new concrete office buildings have been Tests on crushed new tiles by the Rapid Chemical Test set forward in the window reveal to give a 'flush' appear-(ASTM C 289) showed Sc/Rc ratios between 8,2 and 13,6. ance to the facade. The absence of a moulding or drip at Laboratory experiments with tiles set in 1:1:1 cement : the window head has allowed rainwater running down the lime : sand mortar were able to reproduce the effect and it surface of the building to run directly over the glazing with was shown that coating the back of the tiles with bitumen consequent etching and staining of the glass. This has was a satisfactory preventive measure. It was reported that mostly been a problem with tinted, solar-control glasses.

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The sculptor William Mitchell, one of the pioneers of concrete as a sculptural medium, has included glass in a number of his works. The group of statuary 'The Corn King and the Spring Queen' (1964) in the grounds of the Cement and Concrete Association at Wexham Springs, Buckinghamshire, includes coloured glass pieces set in concrete (some of which are now exhibiting a whitish exudation at the periphery) and also large pieces of 'oyster' glass aggregate set in a black-pigmented concrete - in fact the same glass aggregate as was used in the concrete of the structure discussed in the Case Study.

Glass tiles have been used both internally and externally as decorative, easily cleaned and durable surfacings. In this use opaque or opalescent glass is used so that the method of fixing is obscured.

A particular effort to utilise waste glass-rich residues from refuse incinerators has been sponsored by the US Bureau of Mines⁴⁴.⁴⁵. In one investigation the incinerator residue had average composition SiO₂ 66,9 per cent, Al_2O_3 3,9 per cent, Fe_2O_3 O,9 per cent, B_2O_3 1,5 per cent, Na₂O 11,4 per cent, K₂O 1,0 per cent, CaO 8,2 per cent, MgO 2,1 per cent, S 0,2 per cent and LOI 2,6 per cent. The residue pulverised to less than 75 um (78 per cent m/m) was pelletised with clay (20 per cent) and sodium silicate (Na₂O : SiO₂ of 1 : 3,22) (2 per cent) and then fired at 850 °C for 15 minutes. The resultant aggregate had a good pore structure and steam cured concrete of density 1660 kg/m³ made from the material had an average 28-day compressive strength of 17,6 N/mm². Aggregate tested for potential alkali reactivity by the method of ASTM C289 found Sc = 307 millimoles/litre and Rc = 553 millimoles/ litre and was classified as innocuous. Measurements of linear expansion at 38 °C showed expansion at 6 months to be 0.025 per cent.

7. LABORATORY STUDIES OF ALKALI-GLASS REACTIVITY

Early in the laboratory investigation of deleterious alkalisilica reactions in concrete it was realised that a standard reactive aggregate was needed to enable consistent experimental results to be obtained. The US Bureau of Reclamation proposed the use of Pyrex glass (lump cullet 7740) in about 1945 and since then a great deal of research into alkali-silica reactivity has used Pyrex glass as a reactive aggregate. It is believed that the person who first thought of using Pyrex glass was Omar J Glantz who at that time was supervisor of the Bureau's Cement testing laboratory at Denver, Colorado46.

The pioneer UK studies of alkali-aggregate reactivity by FE Jones and RD Tarleton⁴⁷ made considerable use of Pyrex glass as a reactive aggregate and most British work has followed their example, although more recently the naturally-occurring Beltane opal rock has been preferred 48.

As with other highly-reactive aggregates Pyrex glass when used as a replacement in inert aggregate exhibits a pessimum proportion for maximum expansivity. The pessimum proportion depends on the particular experimental conditions and reported values vary from 20 per cent⁴⁹ to 10 per cent. Similarly, aggregate size has an effect on maximum expansion and the reported pessimum sizes for Pyrex glass are 0,15 - 0,24 mm with Portland cement of 0,71 per cent Na₂O equivalent⁵⁰ and 0,30 - 0,42 mm in 1 : 0,75 cement : sand mortar bars of $w/c = 0,4^{51}$. It was also found that the extent of gel diffusion and cracking depended on aggregate particle size and it was therefore deduced that the reaction between the alkaline pore fluid and the aggregate was essentially a surface phenomenon.

It has been shown that the reactivity of Pyrex glass with cement can be reduced by a suitable period of thermal treatment at elevated temperature eg 1100 - 1 200 °C⁵² or 1 200 °C⁵³ although curiously other work has shown that heat treatment at 630 °C for 2 hours facilitates leaching of Pyrex-type glasses by water⁵⁴.

In this connection it is instructive to note that glasses in general when used as aggregate in mortar bars for linear expansion measurements have a pessimum value for silica content and it has been found that glasses of about 50 per cent SiO, are more reactive than crystalline substances of the same silica content and also more reactive than both glasses and crystalline substances of 95 per cent SiO, content⁵⁵. With siliceous crystalline aggregates, however, it has been found that the strength of the cement-aggregate bond is proportional to the silica content of the aggregate⁵⁶.

Silicate glasses show varying resistance to attack by alkaline solutions and the results obtained depend on the particular test method. Table 2 shows the comparative depth of attack of alkali solution (pH = 12) at 80 $^{\circ}$ C as measured by an optical interference technique on polished glass surfaces.

 TABLE 2
 : Comparative resistance of commercial
glasses towards alkali solutions and their percentage composition (D Hubbard & G F Rynders, 1948, quoted in reference 54)

	Rate of attack by alkali solutions least attacked \rightarrow most attacked						
	Percentage composition of various types of glass						
Compound	Flint glass	Barium crown glass	Chemical Pyrex	Borosilicate crown glass			
SiO₂	45,6	49,7	81,0	66,4			
B₂O₃	-	3,6	13,0	12,4			
Na ₂ O	3,6	0,4	3,6	8,4			
K ₂ O	5,2	7,7	0,2	11,8			
BaO	-	30,8	-	-			
РЬО	45,1	-	-	-			
ZnO	-	7,2	-	0,5			
As ₂ O ₃	0,5	0,2	0,002	0,5			
Sb ₂ O ₃	-	0,4	-	-			
R ₂ O ₃		-	2,2	-			

two distinct types, one high silica, high lime and low potassia, and the other type with higher soda, lower silica and lime, slightly higher alumina and significantly increased potassia.

Vast amounts of glass waste require disposal each year in the developed Nations and a number of attempts have been made to utilise this waste as a construction material. Thus in the UK approximately 9 per cent of domestic refuse is glass, equivalent to 1,8 M tonnes per annum 15 and in the USA some 10 - 12 M tonnes of glass waste (7 per cent of all refuse) accumulates each year¹⁶. Incinerator residues (after ferrous metal separation) may contain glass as the major fraction.

Direct use of glass waste, or glass-rich incinerator residues, as replacement for aggregate in concrete has been the aim of several research projects and the use of refuse glass as a sharp aggregate for concrete is the subject of a German patent 17. There is also a French patent which cites the utilisation of ground refuse, including glass, as a building aggregate 18.

Substitution of 35 per cent by weight of aggregate by refuse glass, was found to be practicable for masonry block manufacture¹⁶. The compressive strength was reduced by 20 - 30 per cent compared with control blocks but linear shrinkage was only 0,034 per cent. Alkali reactivity tests (storage at 25 °C and 100 per cent RH) showed no deterioration in compressive strength and expansion was 0,05 per cent at 6 months. It was considered that overall the aggregate combination could be considered non-reactive despite the continuing small upward trend for linear expansion. Other experiments utilising glass waste for terrazzo tiles are also mentioned.

Another study of the use of waste glass as coarse aggregate for concrete¹⁹ utilised both crushed glass (20 mm) and incinerator residue (44 per cent glass, 29 per cent ferrous metal. 1 per cent non-ferrous metal, remainder nonmetallics and ash). Concretes made with these materials and both high alkali (1,13 per cent Na₂O equivalent) and low alkali (0,58 per cent Na₂O equivalent) cements gave excessive expansions, although there appeared to be a critical condition associated with maximum values for alkali equivalent and cement content below which concretes performed satisfactorily (up to 1 year). Replacement of 25 - 30 per cent of cement with fly-ash pozzolana effectively controlled expansion but aggregate dilution with inert gravel did not completely suppress alkali reactivity. It was found that the amount of expansion associated with the onset of surface cracking varied with the mix proportions of the concrete, a value of 0,03 per cent expansion at 1 year was taken as distinguishing satisfactory from unsatisfactory performance.

Russian work using window glass aggregate has confirmed the effectiveness of pozzolana (in this case Gliezh-burnt

clay) in combatting excessive expansion²⁰ and pulverised beer-bottle glass has itself been found to be an effective pozzolan^{21, 22, 23}

A further investigation of the use of incinerator residues as an aggregate for concrete²⁴ includes both the glasscontaining coarse material (up to 50 per cent glass with sand, slag ash and some metallic components) with the fly-ash collected from the plants' electroprecipitator. Tests indicated that the potential problem of alkali reactivity could be controlled by suitable mix design.

The sharp texture of waste glass can provide a useful anti-skid surfacing for flooring. Terrazzo tiles made with glass waste aggregate^{25, 26} showed up to 15 per cent improvement in skid resistance over conventional aggregates when tested dry and over 60 per cent improvement in the wet. Prototype tiles had performed satisfactorily during 2 years use. It was also found that ball-milling waste glass with insoluble pigments could be used to provide enhanced coloration of concrete products. Test specimens of 35 per cent glass waste in cement when stored under water at 20 ^oC showed 25 per cent reduction in compressive strength after 18 months, but when 3 per cent polyvinyl acetate was included in the mix the originally lower strength improved by 40 per cent after 18 months waterstorage.

Glass suitably processed to form hollow shapes suitable for light weight concrete aggregate is a patented idea²⁷ and provision of a roughened surface texture has also been patented²⁸. Waste glass bound into a suitable size and shape with cement is another method which has been proposed for the manufacture of aggregate for concrete²⁹. Devitrification of glass and use for highway surfacing^{30, 31} and road marking³² are other patented applications.

Glass waste bound with water-glass and fired at 950 -1100 °C has been proposed for roadmarking material³³ and use of a similar mixture for both dense and lightweight aggregate manufacture has been reported from Japan³⁴. High-silica industrial wastes bound with either water-glass or aluminium phosphate, pelleted and heated at 400 °C are included in a Japanese patent for lightweight concrete aggregate³⁵.

Waste-glass and clay/shale mixtures pelleted with a suitable expansion agent and fired in a furnace have been used to prepare lightweight aggregates suitable for construction purposes^{36, 37, 38, 39, 40} and incorporation of calcined bauxite has been used to give improved skid resistance for road use41. A pelleted foamed-glass aggregate (Balolit) of this type was in commercial production in Switzerland in 1965 and for some years thereafter, but is no longer on the market⁴². Balolit was made as pellets 2 - 20 mm diameter with a closed-pore structure and relative density 1,25 - 1,80 and was particularly used in lightweight insulation screeds. Evidence of slight alkali reactivity and expansivity of a similar lightweight aggregate has been noted 43.



TABLE 5 : Composition of glass and comparison of linear expansion obtained in mortar bar test s⁵⁰

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Table 3 compares the alkali resistance of chemical glassware towards 5 per cent sodium hydroxide solution at 95 °C. Table 4 illustrates the results obtained in the treatment of glass powder samples with N/50 NaOH solution for 4 hours at 25 °C after which the sodium extracted was determined.

An interesting feature of these tables is that Glass A of Table 4 is clearly Pyrex borosilicate glass and this showed least sodium oxide extracted whereas in Tables 2 and 3 the borosilicate glasses show the poorest resistance to alkali attack.

A number of commercial glass compositions were tested as 6 per cent replacement in an inert aggregate (Ottawa sand) to determine the linear expansions produced in the mortar bar expansion test58. The glass compositions and alkali expansivity are given in Table 5. These tests show that except for the fused silica the Pyrex glass gave the highest expansion.

A series of expansion bar tests at 38 $^{\rm O}{\rm C}$ and 100 per cent RH using binary glasses (Na₂O - SiO₂ in the range 50 - 100 per cent SiO₂) as 6 per cent replacement in Ottawa Sand and low alkali (0,17 per cent Na₂0 equivalent) and high alkali (1,15 per cent Na₂0 equivalent) cements showed that maximum expansions occurred with glasses of 75 - 85 per cent SiO₂ with low alkali cement and 80 - 90 per cent SiO₂ with the high alkali cement⁵⁹. Expansions were

TABLE 3 : Comparative resistance of commercial glasses to 5% NaOH solution at 95 °C and their percentage compositions (Corning⁵⁷)

	Attack by alkali solution least attacked → most atta Percentage composition of various types of glass					
Compound	Soda-lime glass	Vycor glass	Pyrex borosilica glass			
 SiO2	72,0	96,0	80,0			
Al_2O_3	2,0	0,5	2,0			
Na2O	1	-	4,0			
K ₂ O	5 ^{15,0}	-	0,5			
B ₂ O ₃	-	3,0	13,0			
CaO	1		-			
MgO	آ ^{11,0}	-	-			

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greater and the pessimum peaks better defined with the low alkali cement. With K₂O - SiO₂ glasses maximum expansions were obtained in the range 70 - 90 per cent SiO₂ with both low and high alkali cements. PbO - SiO₂ and Li₂O - SiO₂ glasses did not cause expansion with either cement. The expansion produced by the $Na_2O - SiO_2$ glasses was found to be suppressed by the addition of pozzolan (ground opal).

Experiments with high alumina cement and gypsum plaster showed that the soda-silica glasses caused large expansions (approximately 2,5 and 0,55 per cent respectively) with maxima in the region of 60 - 80 and 60 - 85 per cent SiO₂ for the two binders.

Thus it appears that such glasses supply both the silica and the alkali for the expansive alkali-silica reaction. The binder acts simply as a medium for the transport of water. Since pozzolana was still able to combat the deleterious expansion it also appears that the action of such highly reactive siliceous material must be with the hydroxyl ions in the pore fluid rather than combination with the alkali metal ions which are already present within the aggregate.

In fact the attack by alkaline solutions on both amorphous silica and Pyrex glass is highly dependent upon pH. Below a pH of about 9 the effects are very small but at pH values above about 10 the rate of attack increases very rapidly (see Figures 4 and 5). This may be particularly significant where

TABLE 4 : Comparative resistance of glasses of different composition towards N/50 NaOH solution at 25 $^{\circ}$ C (W C Taylor & R D Smith, 1936, quoted in reference 54)

	lea	Na ₂ O e st extra	xtracted cted	lbyN/ → mo	50 NaC ost extr	DH racted
	Percentage composition of specific glass samples					
Compound	A	В	С	D	Е	F
SiO2	81	35	72	63	73	60
R ₂ O ₃	2	-	1	1	1	3
Na ₂ O	4	-	13	7	17	8
K ₂ O	-	7	-	7	-	-
B ₂ O ₃	13	-	-	-	-	29
CaO	-	-	9	-	5	-
MgO	-	-	5	-	3	-
РЬО	-	58	-	22	-	

(iii) Glass 'marble' aggregate concrete (BRE). This section had been prepared from a sample of concrete supplied by Dr John Newman of Imperial College, London who had used glass balls (spherical aggregate) in a mortar matrix as a model for studying the forces present at the aggregate-cement interface⁵⁴. The exposure history of the sample was not known but it was thought to have been stored indoors in a dry atmosphere since casting.

The edges of the glass balls showed a rough outline with small cracks and chips apparently due to mechanical damage either during manufacture and handling or when mixed in the concrete. No signs of alkali-silica reaction could be observed and no gel or expansion cracks were present.

However, earlier studies of samples of this concrete using Scanning Electron Microscopy had revealed the presence of curly crystals associated with the glass-cement interface although no analytical data were obtained.

X-Ray diffraction analysis

The samples were pulverised and then mounted in the rotating sample holder of the X-ray diffractometer. Copper K α radiation was employed with 1 degree entrance and exit slits and 0.1 mm beam width. Full-scale deflection was set at 200 counts per second.

The results of the aggregate examinations are shown in Figures 6 to 9 (pages 12 and 13).

(i) Oyster-pink aggregate from Case Study. The diffraction pattern shows α - quartz at 26,65 and 20,9 degrees 2 θ and cristobalite at 22 degrees 2 θ superimposed on a broad flat hump due to the vitreous glass phase.

(ii) Green glass (Minehead). This sample gave virtually no diffraction pattern with only a slight increase in the baseline response due to the glass matrix. Despite the quartz crystals observed by optical microscopy no quartz response was obtained by X-ray diffraction.

(iii) Blue glass aggregate (Minchead). This material gave a broad, shallow hump approximately centred on 24 degrees 2 θ due to the vitreous glass phase and a single quartz peak at 20,9 degrees 2 θ . Normally the 26,65 degree 2 θ peak ('101' or 'hexagon' plane) gives the stronger response for quartz but in this case it is absent from the diffraction pattern. The predominance of the 20,9 degree 2 θ peak ('100' plane) indicates preferential orientation.

(iv) Pyrex glass. The X-ray diffraction pattern shows a rather more prominent hump approximately centred on 21 degrees 2 θ with a small peak due to α - quartz at 26.65 degrees 2 θ .

Chemical analysis of glass

The glass samples were pulverised and analysed for chemical composition. The results expressed as oxide values recalculated to a loss-free condition are presented in Table 6, (page 14).

It was not feasible to analyse samples of the oyster-pink glass removed from the case study concrete because all aggregate particles examined showed evidence of having reacted. However, chemical analysis for alkali metals in a selected sample found Na₂O = 10,30 per cent and K_2O = 0,75 per cent (loss-free values)⁶⁵.

9. DISCUSSION

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The structure of silicate glasses is generally considered to be a three-dimensional network of a random arrangement of SiO, tetrahedra with at least two oxygen atoms of each tetrahedron attached to other silicon atoms. Aluminosilicate glasses include AlO, tetrahedra and borosilicate glasses incorporate both tetrahedral BO₄ units and triangular BO₃ ⁶⁶. Silica surfaces are, in effect, an array of silanol groups (with a density of about six hydroxyl groups per 100 square angstroms surface). The presence of a total of 2 per cent of foreign oxides⁶⁷ increases the affinity for water by a factor of 10.

In solutions of high pH the hydroxyl ions react with the silica network by leaching alkali metal and borate ions etc into solution to leave a silica framework containing pores in the 10 - 40 $^{\circ}$ range⁵⁴. As noted previously the leached alkali can in turn accelerate the attack on the glass.

Qualitatively the expansive reaction associated with the presence of glass in concrete does appear to be somewhat different from that of other highly siliceous aggregates eg opal, chert or chalcedony.

The 'normal' mode of generation of swelling pressure within the concrete appears to be due to the alteration and softening of the aggregate grains by inward diffusion of alkali metal and hydroxyl ions followed by imbibition of water with the development of considerable 'osmotic' pressure and eventual tensile failure and cracking of the surrounding matrix. 'Reaction rims' on the periphery of aggregate grains are commonly observed, with the residues of altered aggregate particles and copious amounts of isotropic alkali silicate gel and gel secondary reaction products.

With glasses the major change visible by optical microscopy appears to be the development of cracks very often subparallel to the outside surface but sometimes traversing the aggregate particles. Gel development is much less prolific and the gel may be more 'sticky' in character and more readily carbonated possibly due to a higher alkali ion content. Where voids are present gel may line these spaces and exhibit shrinkage phenomena similar to those observed with more typical reactive aggregates.

The peculiarities associated with the use of Pyrex glass as a standard reactive aggregate were a principal incentive for the selection of Beltane opal rock as a naturallyoccurring well-defined material which would reflect more closely the behaviour of concrete aggregates. Certainly it does appear that whereas the reaction between Pyrex glass only a limited amount of aqueous phase is in contact with the glass (as with cement pore fluid) since the decomposition of most glasses results in the liberation of alkali and the liberated alkali can then accelerate the further decomposition of the glass⁶¹.

8 FURTHER EXAMINATION OF CASE STUDY AND OTHER GLASS AGGREGATES

Careful re-examination of the cladding panels on the Case Study structure revealed that contaminatory aggregate particles were present amongst the predominating oysterpink exposed-aggregate finish. The contaminants included a few pieces of flint gravel and a number of glass aggregate particles of colours other than pink. The most common alternative colour was of a deep cobalt-blue glass but some pieces of bright green glass were observed together with several pieces which were virtually colourless.

The coloured glass particles were clearly derived from contamination of the aggregate stockpiles at either the suppliers of the aggregate or at the manufacturers of the precast concrete panels.

The blue and green glass particles appeared to be similar to the coloured glass aggregate previously mentioned as being used in cemeteries and so samples of this type of material were procured and thin-sections were prepared from these as well as from a piece of the aggregate taken from the case-study concrete and a piece of the oyster-pink aggregate which had become dislodged from the William Mitchell statue (The Corn King and the Spring Queen) at Wexham Springs.

The thin-sections of the case-study concretes were reexamined and compared with other sections which included glass ie the Scottish spalls¹³ and concrete with glass 'marble' aggregates.

Samples of the pink, blue and green aggregates were analysed to determine the elemental composition and were also examined by X-ray diffraction. Samples of Pyrex glass (Wear Glassworks, Sunderland) and pulverised beerbottle glass (Guinness) were also analysed for comparison.

Thin-section examinations

Coloured glass aggregates (a)

(i) Oyster-pink aggregate from Case Study. This section exhibited the same vesicular isotropic glass appearance reported earlier and although the particular aggregate particle section was one of the pieces exposed at the surface of a panel none the less it included some cracking and gel reaction product.

Higher-magnification examination revealed that the peripheral region of the eroded quartz grains within the aggregate showed what appeared to be an isotropic dissolution zone which was of an RI intermediate between that of the quartz and the bulk of the glass aggregate. This zone sometimes had a comparatively well defined boundary and in many instances could be observed to include finger-like or dendritic outgrowths. Similar dissolution striations or schlieren have been noted for soluble silicates in contact with water⁶². Some quartz grains were so extensively altered that only a skeleton network of acicular crystals remained as an interlocking pattern within the grain boundary. Certain altered quartz crystals included many wedge-shaped twinned crystals apparently of tridymite.

(ii) Oyster-pink aggregate from William Mitchell statue (C & CA). Many more quartz grains appeared to be present in the aggregate of this section compared with the Case Study aggregate although in all other aspects the aggregate appeared to be identical. The same alteration zone was present at the edges of the rounded and eroded quartz crystals.

(iii) Green glass aggregate (Minehead). This section showed the aggregate to have considerably more voids than the oyster-pink material and fewer of the quartz crystals were present. The quartz crystals themselves had a more regular and less eroded appearance.

(iv) Blue glass aggregate (Minehead). This aggregate contained the least number of quartz grains although those present showed similar signs of erosion and alteration to the quartz in the other sections. The voids in this material appeared to be fewer in number but of somewhat larger size.

(b) Concrete Sections

(i) Case Study thin-sections. The original thin-sections were re-examined, and sections prepared by the Cement and Concrete Association and by the Building Research Establishment were also studied.

All sections had the same general appearance. Minor differences appeared to be due to adventitious sampling effects. All the eroded quartz grains showed the same alteration zone at the periphery that was seen in the aggregate sections.

> Three of the four sections included the curly highlybirefringent crystals. These were invariably associated with gel-filled cracks or cavities and appeared most prominent near carbonated areas of cement paste. The crystals had the general characteristics of trona (Na₂CO₃. Na $HCO_{3} \cdot 2H_{2}O)^{63}$.

> (ii) Spallings from soffit of cast in-situ concrete floor (BRE¹³). The glass fragments at the apex of each spall exhibited numerous cracks mostly near the periphery and frequently sub-parallel to the outside surface. Many cracks were empty but a number included gel which mostly showed some birefringence apparently due to carbonation.

> The overall effect of the glass reaction seemed very similar to that reported for the pavement light in Chicago⁵.



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FIGURE 9 : X-ray diffraction pattern for Pyrex glass (W A Gutteridge, C & CA)

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FIGURE 7 : X-ray diffraction pattern for green glass aggregate (Minehead) (W A Gutteridge, C & CA)

and cement is surface area related⁵¹ with Beltane opal rock the reaction is related to the volume proportion of aggregate in the mix and hence independant of particle size⁶⁸.

In terms of oxide composition (Tables 1 to 5) it is not easy to see any pattern which can explain the differences in reactivity and expansivity of the glasses. Where elements such as lead, barium or lithium are present which form insoluble silicates the solubility of silicate glasses is known to be considerably reduced 62. Generally it also appears that those glasses containing a relatively high proportion of boron (except where heavy metals or lithia are also present) are most alkali reactive.

The reactivity (and expansivity) of the borosilicate glasses may in part be due to the greater micro-porosity caused by the presence of foreign groupings in the silicate chain but another factor could also be that despite their transparency borosilicate glasses are known to contain more than one phase. Thermal treatment can encourage phase separation and it has been suggested that this accounts for the increased rate of leaching experienced by Pyrex-type glasses after such heating⁵⁴.

Phase separation and the inclusion of voids are methods used to create opalescent glasses. Such glasses can be particularly alkali reactive and, as illustrated by the Australian wall-tile problem, have been involved in deleterious alkali-silica reactivity. Presumably it is the porosity effect which is responsible for the extreme expansivity of fused silica in mortar-bar tests. On the other hand, materials with a very open structure even if highly siliceous do not appear to give rise to expansion with alkalis. Probably this is due to the high porosity providing space to accommodate pressures generated by any swelling alkali-silicate gel. This would also account for the apparently good performance of the cellular glass lightweight aggregates when used in concretes.

The experiments with binary silicate glasses have demonstrated that an aggregate containing sufficient alkali metal and silica is capable of expansive reaction whether or not a high pH environment is present⁵⁹. Indeed for the most reactive Na₂O - SiO₂ compositions the expansions obtained were greatest with the low-alkali cement. The authors postulated that this might be due to a pessimum relationship between the aggregate composition and the alkali metal jons in the cement pore fluid, a conclusion which appears to be supported by more recent work with Beltane opal rock aggregate⁶⁸.

With more complex glasses if the composition and physical state is such that expansion can occur and providing that sufficient alkali metal oxides and silica are present in the glass it is likely that the reaction will be pH-dependent. It is, therefore, interesting to note that the influence of alkali content of Portland cement on the pH of the aqueous phase and cement-paste may be very small⁵⁸. Thus with a low-alkali cement (Na₂O nil, K₂O 0,29 per cent) and a high-alkali cement (Na₂O 1,10 per cent, $K_2O_0,09$ per cent) it was found that with the low-alkali cement an aqueous extract yielded a pH of 12,52 and the pH of the cement paste was 12,66. Whereas with the high-alkali cement the pH of the aqueous extract was 12,60 and the pH of the cement paste 12.70. Consideration of Figures 4 and 5 shows that both these cements would strongly attack amorphous silica or reactive glasses.

It now becomes clear that when a susceptible concrete aggregate already contains both alkali metal and silica in requisite proportions, deleteriously expansive alkali-silica reactions can occur no matter what type of Portland cement is used.

This fact has important consequences as regards current recommendations for the avoidance of alkali-silica reactivity which rely upon limitations of the total alkali content (Na, O equivalent) of cement⁶⁹ or total soluble alkali content per cubic metre of concrete⁷ °.

10. CONCLUSIONS

Glasses of a wide range of compositions are capable 1. of reacting expansively with cements.

2. The most reactive glasses have a high boron content and/or alkali metal content or have a relatively porous or phase-separated structure.

3. The reaction between glass and alkalis in concrete is qualitatively different from that of other reactive more porous aggregates (although natural volcanic glassy rocks may be similar) and has a pessimum relationship for particle size, unlike more porous aggregates.

4. Glasses (possibly also other aggregates) which contain both alkali metal oxides and silica in appropriate proportions can give rise to damaging expansions even with low-alkali Portland cements.

5. Neither Pyrex glass nor Beltane opal rock completely model the behaviour of real alkali-susceptible aggregates in concrete. A possible standard expansive aggregate would be fused silica which is a consistent, readily available material.

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	Percentage composition of various samples of glass							
Compound	Oyster-pink glass aggregate (as used in Case Study concrete)	Green glass aggregate (Coalbrookdale)	Green glass aggregate (Minehead)	Blue glass aggregate (Minehead)	Brown beer-bottle glass (Guinness)	Pyrex glass (Corning Ware Glassworks)		
SiO2	73,5	73,1	71,2	72,3	72,7	80,2		
TiO ₂	0,04	0,04	0,04	0,05	0,08	0,03		
Al ₂ O ₃	2,18	1,57	3,00	1,35	1,52	2,33		
Fe ₂ O ₃	0,15	0,15	0,35	0,28	0,35	0,11		
CaO	7,38	9,06	9,27	8,38	10,2	0,08		
MgO	0,57	0,33	0,27	3,08	0,37	0,02		
K ₂ O	1,02	0,29	0,61	0,51	0,45	0,10		
Na ₂ O	12,1	15,0	14,8	13,9	13,9	4,0'		
P_2O_5	0,02	0,02	0,07	0,03	0,01	< 0,0		
Cr ₂ O ₃	< 0,01	0,31	0,38	< 0,01	< 0,01	< 0,0		
CuO	-	-	-	0,27	-	-		
Mn₃O₄	< 0,01	< 0,01		0,02	0,03	< 0,0		
ZrO2	0,01	0,03	-		0,04	0,0		
РьО	0,15	0,01	-	-	< 0,01	< 0,0		
BaO	0,02	0,02	0,02	0,02	0,04	0,0		
B ₂ O ₃	2,05	0,19	0,10	0,02	0,04	12,9		
As ₂ O ₃	c. 0,25	-	-	-	-	-		

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DISCUSSION

Mr D A St John (DSIR, New Zealand) asked whether the type of apparently anomalous result referred to in the keynote address (where reactive aggregate used with a high alkali cement had given unexpectedly low expansion, and in other instances, inexplicably large expansion had occurred) was related to that referred to by Mr Figg.

Mr Figg affirmed this. He added that both low and high alkali cements had similar pH's (12 - 13), and even the lowest alkali cements still had a high alkalinity. In the case of an aggregate that already contained sodium or potassium ions, derived from any source, (it made no difference whether it was a high or low alkali cement, one was only concerned with the hydroxyl ions) and in the extreme case where binary silicate glasses had been used, the greatest expansions had in fact been found with water, so the hydroxyl ions could only have been derived from the water. He suggested that the pH would possibly be increased by the extraction of alkali ions from the binary glass, but felt that aggregates that already contained alkali metal and silica would react whether they were high or low alkali cement, as had been shown in the case study.

Prof J Gillott (University of Calgary, Canada) asked if Mr Figg had found a reason why some of the glasses had apparently not shown the deterioration found in the case study.

Mr Figg replied that he did not know the reason. All the examples he had found of the different types of glass could react in certain circumstances. Ordinary bottle glass was very reactive, in fact the case study glass and bottle glasses had contained 12 to 15 per cent sodium oxide and varying amounts of potassium oxide. They were very high unlike Pyrex (which only had about 4 per cent alkali) and which was in a different group. However, Pyrex was a borosilicate glass so it seemed that glasses which contained borosilicates, or multi-phase glasses (there was some evidence that the borosilicate glasses were multi-phase) and certainly where you have opalescent glasses opalescent either because they were multi-phase or because they contained many voids – became quite reactive. Thus there was a surface area effect, and a phase effect; chemical composition alone did not seem to be the only answer. In the case of glasses which were for example placed on walls, they were in a very porous mortar and Mr Figg assumed that carbonation was faster than any other competitive reaction.

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Dr D Hobbs (C & CA, London, England) added that in the finer sizes of Beltane opal, the pessimum reactive content was not related to size, but above 2 mm particle size there was a size effect on the volume concentration of the pessimum. It appeared that for the finer particle sizes of Beltane opal it was the chemical reaction rate itself which was decided in the dissolution process, and above the 2 mm particles size, it was the rate of diffusion of the hydroxyl ions to the reaction site which controlled the reaction rate. Danish flint which was currently being tested and which contained a relatively high content of opaline type material did in fact show very similar behaviour to Beltane opal.

Dr Dent-Glasser (Aberdeen University, Scotland, Great Britain) agreed that it was a surface-dependent effect. She referred to the experiments on the solution of glasses in ordinary water, where the first step appeared to be the exchange of sodium or potassium ions out of the glass into the water with protons from the water resulting in an increased pH. After that it was very strongly diffusion controlled from the surface and in a dense material such as glass she felt that this would be the rate controlling step. She suggested that this could be an explanation of the reaction Mr Figg had in his experiment with glass bottles in a mortar apart from the porosity of the mortar there simply would not have been enough surface area to react with.

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