Use of glass waste as an activator in the preparation of alkali-activated slag. Mechanical strength and paste characterisation

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ABSTRACT

The alkaline activation of aluminosilicates yields alkaline cements, eco-efficient alternatives to ordinary Portland cements. Alkaline cements and concretes exhibit highest strength and longest durability when activated with a solution of alkaline silicate hydrates (waterglass). To obtain these alkaline silicates, however, an aqueous solution of the proper proportion of carbonate and silica salts must be heated to temperatures of around 1300 °C. The present paper explores the feasibility of using urban and industrial glass waste as a potential alkaline activator for blast furnace slag (AAS).

AAS pastes were prepared with three activators: waterglass, a $NaOH/Na_2CO_3$ mix and the solutions resulting from dissolving glass waste in $NaOH/Na_2CO_3$. Mechanical, mineralogical (XRD, FTIR) and microstructural (porosimetry, NMR and SEM/EDX) trials were conducted to characterise the pastes obtained.

The findings proved the feasibility of using glass waste to alkali activate slag. Treating glass waste with $NaOH/Na_2CO_3$ (pH = 13.6) favours the partial dissolution of the Si in the glass into its most reactive monomeric form. The solutions resulting from the treatment of glass waste act as alkaline activators, partially dissolving vitreous blast furnace slag. The composition and microstructure of the reaction products identified in the two types of paste were similar. Strength and microstructural development in the pastes activated with glass waste were also comparable to the parameters observed in AAS pastes prepared with conventional activators.

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1. Introduction

Portland cement production is characterised by high energy demands, the consumption of non-renewable prime materials and the emission of greenhouse gases (essentially CO_2) [1,2]. In 1987, the term "sustainable development" was coined to mean the balance between technological development and conservation of the environment. Ever since, in pursuit of such a balance, the cement industry has been seeking ways to minimise the adverse side effects of its activity.

Alkali-activated materials constitute a possible alternative to Portland cement. A.O. Purdon [3], V. Glukhovsky [4,5] and J. Davidovits [6] pioneered research in this area and developed the earliest alkaline cements. Interest in these materials blossomed in the rest of the world beginning in the nineteen nineties [7–21].

Alkaline activation calls for two basic components: preferably amorphous or vitreous aluminosilicates and an alkaline activator. The aluminosilicates may be natural products such as metakaolin or industrial by-products such as blast furnace slag or aluminosiliceous fly ash [17].

The alkaline solutions able to interact with aluminosilicates to generate such new binders include: alkaline metal or alkaline-earth hydroxides (ROH, $R(OH)_2$), weak acid salts (R_2CO_3, R_2S, RF), strong acid salts (Na_2SO_4, $CaSO_4 \cdot 2H_2O$) and $R_2O(n)SiO_2$-type siliceous salts,

where R is an alkaline ion such as Na, K or Li. From the standpoint of end product strength and other properties, the most effective of these activators are NaOH, Na_2CO_3 and sodium silicate hydrates [22,23]. And of these, the solutions that induce the best mechanical behaviour in alkali-activated materials are waterglass-based [12,24–26].

The cements obtained by alkali-activating aluminosilicates are characterised by high mechanical strength [5], low heat of hydration [6] and high impermeability [27], as well as resistance to high and low temperatures [28,29] and sulphate, sea spray and acid attack [27,30–32].

A number of materials, including silica fume, pozzolans, rice husk ash [33] and others can be used as a supplementary source of silica in alkali-activated systems. Certain types of waste or industrial by-products can also be valorised to minimise the adverse (energy demand and CO_2 emissions) effect of the industrial production of sodium silicate, also known as waterglass, which calls for heating an aqueous solution of the proper proportion of carbonate and silica salts calls to around 1300 °C [34,35].

The present study aimed to evaluate the feasibility of using glass waste as a source of silica to replace waterglass in the alkaline activation of blast furnace slag. Urban glass waste is an amorphous material with a chemical composition based essentially on SiO_2 (65–75%), CaO (6–12%), Na_2O (12–15%), Al_2O_3 (0.5–5%) and Fe_2O_3 (0.1–3%) [36–38].

One of the most prominent properties of glass, in addition to its transparency, is its high resistance to chemical attack. That notwithstanding, some interaction always takes place between glass and

chemical substances. Glass is attacked by both acid and alkaline solutions, although the mechanisms and degree of corrosion differ [39]. Glass is highly soluble at alkaline pH values [40–42]. At values of 9 to 10.7, the solubility of amorphous silica rises due to the formation of silicate ions, along with a monomer in equilibrium with the solid phase. At values higher than 10.7, the amorphous silica in the solid phase dissolves to form a soluble silicate. High temperatures also favour glass solubility [42,43].

Prior studies determined the solubility of different types of glass waste in highly alkaline media [35–37]. This waste has been found to dissolve most effectively (highest amounts of dissolved SiO_2 and Al_2O_3) when a 50/50 Molar solution of $NaOH/Na_2CO_3$ is heated at 80 °C for 6 h [44]. The question that must now be addressed is whether the solutions resulting from the treatment of glass waste can replace traditional waterglass in the preparation of alkaline cements. Consequently, the primary objective of the present research was to explore the feasibility of using urban and industrial glass waste as a potential alkaline activator for blast furnace slag.

2. Experimental

2.1. Materials

Table 1 gives the chemical composition of the Spanish vitreous blast furnace slag and the glass waste used in this study. The vitreous phase accounted for 99% of the slag content (modified McMaster method) [45] and specific surface of this material was 325 m^2/kg (EN 196–6). XRD and FTIR characterisation confirmed the amorphous nature of both types of waste.

The following activating solutions, all at a constant 5% Na_2O by slag mass, were used:

- 50% mix of NaOH and Na_2CO_3 in molar (Panreac analytical grade 98% sodium hydroxide and 99.8% sodium carbonate), yielding a solution with a pH of 13.6.
- Commercial waterglass (Merck, 27% SiO_2; 8% Na_2O and 65% H_2O by weight) with a SiO_2/Na_2O ratio of 1.2.
- 50% (wt) $NaOH/Na_2CO_3$ solutions with different amounts of dissolved glass waste (from 1 to 25 g per 100 mL of solution).

The last group was prepared by adding 1, 10, 15, 20 and 25 g of glass waste (with a particle size of under 45 μm) to the sodium hydroxide/sodium carbonate solution, stirring at 80 ± 2 °C for 6 h and subsequent filtering, as described in [34]. The ions dissolved in the filtered solutions were analysed by ICP-AES on a VARIAN 725-ES inductively coupled plasma atomic emission spectrometer. Table 2 lists the weight of oxides dissolving out of the glass and into the activating solution (g/100 mL).

2.2. Paste preparation and trials conducted

Paste specimens measuring $1 \times 1 \times 6$ cm were prepared to the compositions given in Table 3. The liquid/solid ratio was 0.4 or 0.44, depending on the type of activator, to ensure that plasticity was as recommended in European standard EN 196–3 in all cases. The pastes were chamber-cured (99% relative humidity, 20 ± 2 °C) for 1, 2, 7 or 28 days and the prismatic specimens tested for mechanical strength.

Table 1
Chemical composition of slag and glass (wt.%).

wt.%	CaO	SiO$_2$	Al$_2$O$_3$	MgO	Fe$_2$O$_3$	S^{2-}	SO$_3$	Na$_2$O	K$_2$O	[1]L.O.I
Slag	41.00	35.54	13.65	4.11	0.39	1.91	0.06	0.01	–	2.72
Glass waste	11.75	70.71	2.05	1.17	0.52	–	–	11.71	1.08	0.83

[1] L.O.I = Lost on ignition.

Table 2
SiO$_2$, Al$_2$O$_3$, CaO and MgO (g) from the glass waste dissolved after treatment in 100 ml of 50% (wt) NaOH/Na$_2$CO$_3$.

Glass waste	SiO$_2$	Al$_2$O$_3$	CaO	MgO
	(g/100 ml)	(g/100 ml)	(g/100 ml)	(g/100 ml)
1 g	0.42	0.05	1.2 E^{-03}	1.5 E^{-05}
10 g	2.82	0.13	5.3 E^{-04}	3.0 E^{-05}
15 g	3.34	0.16	6.1 E^{-04}	4.3 E^{-05}
20 g	4.49	0.19	6.9 E^{-04}	7.2 E^{-05}
25 g	4.54	0.25	8.2 E^{-04}	2.0 E^{-04}

The total porosity and pore size distribution were determined on pastes AAS N/C-25, AAS N/C and AAS WG at all ages. All other characterisation trials were conducted on the same pastes, but only on the 7-day specimens. After the mechanical tests, the pastes were immersed in acetone/ethanol to detain the hydration/activation process. The tests conducted on these pastes were Hg intrusion porosimetry, FTIR, XRD, ^{29}Si and ^{27}Al MAS NMR and BSEM/EDX.

Mechanical strength tests were conducted on an Ibertest Autotest 200/10 hydraulic press as specified in European standard EN 196–1 at a rate of 2400 N/s ± 200 N/s to failure. Total porosity and pore size distribution were found with Hg intrusion porosimetry on a Micromeretics Autopore IV 9500 analyser able to exert pressure of up to 32 000 Psi ($\approx$220 608 MPa, equivalent to a pore size as small as 0.0067 μm). The FTIR spectra were obtained by analysing KBr pellets containing 1.0 mg of sample in 300 mg of KBr on an ATIMATTSON Genesis Series FTIR-TM spectrometer. The spectra were recorded after running 64 scans in the 4000–400 cm^{-1} range. The XRD patterns for the samples were recorded on a Bruker AXS D8 Advance diffractometer fitted with a Lynxeye super speed RX detector, a 2.2-kW Cu anode and no monochromator. The scanning range, from 5 to 60°, was covered in a 24-minute period. The instrument was set at 40 kW and 30 mA and the sample was not rotated during scanning. The ^{29}Si and ^{27}Al solid state nuclear magnetic resonance (MAS NMR) spectra were obtained with a Bruker MSL 400 spectrometer operating at 79.49 and 104.26 MHz. All the spectra were packed into a 4-mm zirconium MAS rotor and spun at 10 000 Hz. For the ^{27}Al spectra, the relaxation time applied was 5 s and 360 acquisitions were obtained per scan. For the ^{29}Si spectra, the values were 10 s and 1200 acquisitions. After the spectra were recorded, the curves were deconvoluted with Dmfit software, which fits the theoretical to the experimental curves. The 7-day samples were embedded in an epoxy resin and subsequently cut, polished and carbon-coated for back-scattered electron microscopic examination on a JOEL JSM 5400 scanning electron microscope fitted with a solid state back-scattered detector. Microanalyses were conducted using LINK-ISIS energy dispersive X-ray (EDX) techniques.

Table 3
Pastes prepared and activation conditions.

Sample name	Activator type	L/S	Glass content	SiO$_2$/Na$_2$O	pH
[*]AAS N/C	NaOH/Na$_2$CO$_3$	0.4	–	0	13.60
[**]AAS WG	Waterglass	0.44	–	1.2	13.76
[***]AAS N/C-1	NaOH/Na$_2$CO$_3$	0.4	1 g	0.08	13.79
AAS N/C-10	NaOH/Na$_2$CO$_3$	0.4	10 g	0.54	13.70
AAS N/C-15	NaOH/Na$_2$CO$_3$	0.4	15 g	0.63	13.63
AAS N/C-20	NaOH/Na$_2$CO$_3$	0.4	20 g	0.85	13.60
AAS N/C-25	NaOH/Na$_2$CO$_3$	0.4	25 g	0.86	13.48

[*] AAS N/C = slag alkali activated with NaOH/Na$_2$CO$_3$.
[**] AAS WG = slag alkali activated with waterglass.
[***] AAS N/C-(1-25) = slag alkali activated with NaOH/Na$_2$CO$_3$ and from 1 to 25 g of glass waste.