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Review article

Alternative prime materials for developing new cements: Alkaline activation of alkali aluminosilicate glasses

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ABSTRACT

This study explored the use of alkali aluminosilicate glass obtained by melting and quenching common clay, feldspar and fluxing oxides as a possible starting material for alkaline activation. The glass was synthesized at two different temperatures (1250 and 1400 °C), using Na_2O (8 wt%) as a fluxing oxide. The effect of including small amounts of calcium in the starting mix (5.6 wt% of CaO) was likewise studied. The alkaline activation of such glasses yielded cements with high compressive strength (65 MPa after 20 h at 85 °C). The presence of calcium in the vitreous network favored the formation of a very compact cementitious matrix. TEM-EDX analyses showed that the gel forming in these systems was compositionally (and presumably structurally) non-uniform, with some local high-calcium, high Si/Al ratio (CASH-type gel) areas co-existing with low calcium and low Si/Al ratio clusters (NASH-type gel).

Contents

1. Introduction

The enormous promise of alkaline cements as a sustainable alternative for ordinary Portland cement (OPC) has given rise to thousands of articles on these materials. One of the main advantages of these binders is that their use in place of OPC would entail a drastic reduction of anthropogenic carbon dioxide emissions. However, a few limitations have to be overcome before such new eco-cements will be industrially applicable [1–3].

Portland cement is the construction material par excellence not only for its high strength and durability, but also because the prime materials needed in its manufacture (primarily limestone) are fairly abundant and available practically all over the Earth's crust. Moreover, its excellent price/quality ratio has made it one of the materials most widely consumed worldwide. The inference of the foregoing is that one of the important factors to bear in mind when evaluating the possible use of an OPC alternative is the availability, abundance and cost of the prime materials required for its manufacture.

Aluminosilicate-based (low CaO content) alkaline cements are generally made with type F fly ash or metakaolin. High-CaO

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alkaline cements, in turn, have traditionally been prepared with blast furnace slag. While fly ash and blast furnace slag have yielded promising results [4–8], the geographic limitations on the availability of these two industrial by-products generates shipping needs, thereby raising production costs [3]. Moreover, the industrial processes that generate these two types of waste are carbon-based and consequently, tend to be replaced by more eco-efficient procedures that lower both the demand for natural resources and CO_2 emissions [3]. In other words, the long-term supply of fly ash and blast furnace slag is not guaranteed. Metakaolin is a natural aluminosilicate, but perceptibly more costly than the limestone used to manufacture portland cement, besides, the water demand required by this material to reach a good workability is high, which generally turns into higher porosities.

A possible solution to these supply problems may lie in the use of common clay and other natural aluminosilicates such as feldspar, materials found in abundance all over the world. Nonetheless, the studies conducted to date show that such materials generally exhibit only limited reactivity, even after heating [9–12]. In this regard, one of the properties of blast furnace slag, fly ash and metakaolin known to favor their reactivity under the experimental conditions governing alkaline activation is their disorderly structure [9,13]. Taking this into account, it would seem reasonably feasible to obtain glass or essentially vitreous materials with initially optimal compositions from natural aluminosilicates such as common clay or feldspar and fluxing oxides, thereby solving the low reactivity problems posed by these materials.

The use of glass has very recently begun to arouse interest in both the cement industry and the scientific community [14–18]. The common denominator of the aforementioned lines of research is the use of glass whose main constituents are silicon and calcium, i.e., similar in composition to blast furnace slag (synthetic slag), to produce either supplementary cementitious materials (SCM) [14,15] or starting materials for alkaline activation [16,17]. Recently, the alkali activation of synthetic aluminosilicate glasses produced with laboratory reagents was likewise addressed [19].

The possible use of aluminosilicate glass obtained from natural aluminosilicates as the sole starting material for alkaline activation has not yet been covered. The area holds great promise since it might open the door to the satisfactory use of common clay and feldspar (prime materials commonly used in glass manufacture), solving the problem of the limited supply of prime materials for alkaline cement production.

In light of the foregoing, the present study aimed to explore the possibility of using aluminosilicate glass synthesized from natural aluminosilicates as the starting material for manufacturing alkaline cements. A detailed study was also conducted on the effects of the fluxing oxides used (Na_2O and CaO) and synthesis temperature on the aluminosilicate glass obtained. The mineralogical, morphological and compositional characteristics of the glass and the alkaline cements obtained were analyzed with XRD and SEM-EDX and TEM-EDX microscopic techniques.

2. Experimental

2.1. Alkaline earth and/or alkali glasses

Ball clay (BC) and potassium feldspar (KF) were used to synthesize the alkaline earth and/or alkali aluminosilicate glasses studied. Both materials were characterized and their reactivity studied by the authors in prior research [9,20]. The findings showed that for both, compositional (initially inappropriate Si/Al ratios) and structural (high crystallinity) causes, these materials could not be satisfactorily used to prepare alkaline cements. For that reason, these aluminosilicates were chosen for the present study.

Table 1
Composition of the starting mixes and experimental conditions for glass synthesis.

Mix	Composition (wt%)	*T* (°C)	*t* (h)	Glass
M1	46.9% BC + 39.3% KF + 13.8% Na_2CO_3	1250	1	A
M1	46.9% BC + 39.3% KF + 13.8% Na_2CO_3	1400	1	B
M1-C	42.2% BC + 35.4% KF + 12.4% Na_2CO_3 + 10.0% $CaCO_3$	1250	1	C

The two materials were mixed to obtain a Si/Al (molar) ratio of approximately 2 [21–23]. That mix was partially replaced with anhydrous sodium carbonate (M1), in which the Na_2O added with the flux came to 8.0 wt% (see Table 1). Similarly, 10 wt% of the M1 mix was replaced with anhydrous calcium carbonate (5.6 wt% of CaO) to study the effect of that oxide on the glass and the alkaline cements obtained (see Table 1, M1-C). The sodium carbonate used was supplied by Panreac (r: 99.5%) and the calcium carbonate by Merck (r: 98.5%).

Mix M1 was heated to one of two temperatures to assess the effect of that parameter on glass synthesis: 1250 °C (glass A) and 1400 °C (glass B). The mix containing a small amount of additional calcium was only heated to 1250 °C (glass C) to determine whether, at a given temperature, its inclusion induced any variation in the nature of the vitreous materials obtained (see Table 1). In all cases, the firing time was one hour, after which, the crucibles where the glass was synthesized were flash-cooled (near total immersion in cold water) to prevent crystal phase formation. The cooled vitreous materials were then carefully removed from the crucible and ground with a disk grinder until at least 80% of the material passed through a 45micron sieve.

The composition of the glass obtained was found with XRF on a PHILIPS PW-1004 X-RAY spectrometer fitted with a Sc-Mo X-ray generator tube (see Table 2).

The mineralogy of the starting mixes and glass obtained was characterized by XRD on a BRUKER-AXS D8 ADVANCE diffractometer. The diffractograms were recorded with Cu-Kα1,α2 radiation at 2θ values ranging from 5 to 60, a step size of 0.019736 and a step time of 0.5 s. Glass nano-composition was studied with TEM-EDX. The TEM study was conducted on a JEOL 2000FX LaB6-source transmission electron microscope at an accelerating voltage of 200 kV and a point-to-point resolution of 0.31 nm.

2.2. Preparation of alkaline cements

The alkali aluminosilicate glasses obtained by melting and quenching were mixed with an 8 M sodium hydroxide solution and the resulting pastes were used to prepare $1 \times 1 \times 6$ cm^3 prismatic specimens. The alkaline solution/binder (*s/b*) ratio was 0.35 throughout and the specimens were cured for 20 h in an oven at 85 °C and over 90% relative humidity. The compressive strength of the cured cements was found on an IBERTEST AUTOTEST-200/10 SW test frame. Mechanical strength, expressed in mega pascals (MPa), was calculated as the arithmetic mean of twelve compressive strength values.

After stopping hydration reactions with acetone/ethanol, a small fraction of the specimens was analyzed under a JEOL 5400 scanning electron microscope linked to an OXFORD LINK-ISIS EDX energy-dispersive X-ray spectrometer. The samples were vacuum dried and carbon coated. Another small fraction of the cements was finely ground. These powdery samples were analyzed by means of XRD and TEM-EDX on the instruments described in the preceding item.