



Alkali-activated blends of calcium aluminate cement and slag/diatomite

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Abstract

The present study deals with the formulation of new cementitious materials via the alkaline activation of an industrial by-product (blast furnace slag) or a natural rock (diatomite) in the presence of reactive aluminium sourced from calcium aluminate cement (CAC). Two blends, one containing 20% CAC and 80% slag and the other 20% CAC and 80% diatomite, were prepared and activated with sodium sulphate or a sodium hydroxide solution. The hardened materials were characterised with X-ray diffraction (XRD) as well as ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) and tested for their 2-day mechanical strength. The main reaction product was a cementitious gel that precipitated with crystalline phases such as ettringite, U phase and katoite. While the slag blend reacted to generate a C–(A)–S–H-like gel under moderately alkaline conditions, diatomite reactivity proved to be very low under such conditions. The greater reactivity of both slag and diatomite at high pH (high alkalinity) favoured their interaction with CAC.

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1. Introduction

Since the entry into effect of the Kyoto protocols (1997), the cement industry, which is estimated to account for 6–7% of world-wide CO_2 emissions [1], has made earnest attempts to modernise cement manufacture and design alternative binders, primarily to improve energy efficiency and reduce polluting emissions. One of the avenues being explored is the alkali activation of aluminosilicates found in nature or industrial waste (such as metakaolin, fly ash and slag) [2–10]. Although such binders have been under study since the 1950s [11], it was not until the 1990s that cementitious systems based on the alkaline activation of aluminosilicates became a research target for teams the world over [12–19].

More specifically, calcium- and silicon-rich materials ($\text{SiO}_2 + \text{CaO} > 70\%$) such as blast furnace slag are being explored with particular intensity in an attempt to develop a new generation of binders based on alkaline activation

technology [20–23]. The chemical interaction between slag and alkaline solutions (NaOH , KOH , $\text{M}_2\text{O} \cdot \text{SiO}_3 \cdot n\text{H}_2\text{O}$ ($\text{M}=\text{Na}$, K), Na_2CO_3) triggers a series of reaction mechanisms (dissolution, nucleation, condensation and precipitation) and ultimately the formation of cementitious products. These calcium silicate hydrates are similar to the gel obtained during Portland cement hydration [23,24], but with a small amount of Al in their structure (C–(A)–S–H gel). The cohesive properties of this latter gel largely explain the strength and durability of the materials obtained by alkali-activating slag.

Given its amorphous silica content, diatomite holds potential for the cement industry. Nonetheless, most of the studies conducted to date address its microstructural characterisation [25–28], its use in brick manufacture [29] or, more recently, the possible application of diatomite–limestone blends as a base binder in concrete [30,31].

At this time, alkaline cements are the object of in-depth study, for many unknowns relating to the mechanisms that govern the activation of the materials involved are yet to be clarified. Further research is also needed on the nature of the hydration products formed, their interaction with activating

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substances and the mechanical behaviour of the resulting cements. Prior studies have shown that the main product of the alkaline activation of aluminosilicates is an aluminosilicate gel (typically N–A–S–H gel [3,4]), and that aluminium, which links silica tetrahedra, plays a key role during gel formation (especially in the initial stages of the reaction) [32,33] and hence the need for a minimum amount of reactive aluminium in the starting materials to guarantee the formation of N–A–S–H gel and with it, satisfactory strength development in the cement obtained. As a reactive aluminium-bearing material, CAC is a constituent of promise for future formulations [34,35]. Depending on the alkalinity and silicon content in the starting materials, CAC hydration may be governed by the usual or other mechanisms [36,37].

The present study focuses on the formulation of new cementitious materials by alkali-activating blends compositionally located in the CaO/SiO₂/Al₂O₃ ternary system, and more specifically blends M1=(20% CAC+80% BFS) and M2=(20% CAC+80% diatomite). The microstructure of the cement matrices is analysed with XRD as well as ²⁷Al and ²⁹Si NMR to acquire a deeper understanding of the mechanisms that govern alkaline activation in this type of CAC-containing systems.

2. Experimental procedure

The calcium aluminate cement (CAC) used in this study was furnished by Molins SA, Spain, while the blast furnace slag (BFS) and diatomite were sourced from South America. The experimental procedure began by mixing two blends of prime materials in the following proportions: M1=(20% CAC+80% BFS) and M2=(20% CAC+80% diatomite). The experimental design required the two binders to have similar Al₂O₃ contents but different CaO/SiO₂ and Al₂O₃/SiO₂ ratios. The chemical composition of the starting materials (CAC, BFS and diatomite) and working blends are given in Table 1.

Both blends were alkali-activated with a low alkalinity solid activator (6% Na₂SO₄) and a high pH liquid (8 M NaOH solution). The cement pastes were prepared with different liquid/solid ratios for each binder–activator combination to obtain similar consistencies. They were subsequently moulded into 10 × 10 × 60 mm³ prismatic specimens for curing in a chamber at 99% relative humidity. The specimens were removed from the moulds after 24 h and stored in the chamber until they reached the test age (2 days).

Bending and compressive strength were determined by testing the specimens to failure on an Ibertest Autotest 200/10-SW test frame.

The hardened materials were finely ground and submerged in acetone and ethanol to stop the hydration reactions prior to XRD mineralogical and NMR microstructural characterisation.

The chemical composition of the starting materials (Table 1) was found with X-ray fluorescence (XRF) on a Bruker S8 TIGER wavelength dispersive X-ray fluorescence spectrometer, with a 4-kW, 60-kV, 170-mA intermediate power X-ray generator. LiF 220, LiF 200, PET and XS-55 analyser crystals were used with 0.2- and 0.3-mm Cu as well as 0.8-, 0.2-, 0.5-, 0.1- and 0.0125-mm Al filters.

The samples were analysed on a Bruker D8 ADVANCE X-ray diffractometer with a high voltage 4-kW generator, a 40-kV, 30-mA copper anode X-ray tube, an automatic divergence slit, a graphite monochromator and an automatic sample changer. In most cases the patterns were recorded in a 5–60° 2θ interval at a rate of 0.01973° per 0.5 s.

The nuclear magnetic resonance spectra were obtained at ambient temperature on a Bruker Avance 400 (9.4 T) spectrometer. The resonance frequency settings were 104.26 MHz (²⁷Al) and 79.49 MHz (²⁹Si). The ²⁹Si MAS-NMR spectra (*I*=1/2) were recorded by irradiating the sample with a π/2 (4-μs) pulse, using a 500-kHz filter. The analogous pulse and filter settings for the ²⁷Al (*I*=3/2) MAS-NMR spectra were π/8 (1.5-μs) and 100-kHz and 2-MHz, respectively.

Table 1
Chemical analysis of the starting materials and working blends.

Constituent	CAC	BFS	Diatomite	M1	M2
SiO ₂	3.46	37.42	66.98	30.63	54.28
Al ₂ O ₃	42.6	11.47	4.94	17.70	12.47
Fe ₂ O ₃	14.93	0.66	2.10	3.514	4.67
MnO	0.02	0.19	0.01	0.15	0.012
MgO	0.38	10.62	1.16	8.57	1.00
CaO	35.8	32.71	3.34	33.33	9.83
SO ₃	0.08	2.96	1.16	2.38	0.94
Na ₂ O	–	1.47	2.32	1.17	1.86
K ₂ O	0.10	1.19	0.88	0.97	0.72
TiO ₂	1.65	0.50	0.23	0.73	0.51
P ₂ O ₅	0.07	0.05	0.62	0.05	0.51
Cl	–	–	2.04	–	1.63
Other	0.91	0.76	0.80	0.79	0.82
Loss on ignition	0.61	0.77	13.42	0.74	10.90
Total	100	100	100	100	100
Al ₂ O ₃ /SiO ₂	12.31	0.30	0.07	0.58	0.23
CaO/SiO ₂	10.31	0.87	0.05	1.08	0.18

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