Characterisation of reactive magnesia and sodium carbonate-activated fly ash/slag paste blends

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HIGHLIGHTS

- Na_2CO_3 activated fly ash/slag pastes were thoroughly characterised.
- Increasing Na_2CO_3 from 5% to 10% has notable impacts on the pastes' properties.
- Reactive MgO has a notable influence on the reaction rate and the microstructure.
- Hydration products include C–(N)–A–S–H, hydrotalcite, calcite, and gaylussite.

ARTICLE INFO

ABSTRACT

A system of alkali-activated fly ash (FA)/slag (AAFS) mixtures as a clinkerless cement was investigated with different dosages of Na_2CO_3, as a sustainable activator. The effect of incorporating various proportions of reactive magnesia (MgO) was also examined. Mechanical, mineralogical, and microstructural characterisation of the cement pastes was carried out using the unconfined compressive strength, X-ray diffraction, thermogravimetric analysis, infrared spectroscopy and scanning electron microscopy. It was found that the strength of Na_2CO_3 activated FA/slag mixtures generally increased with time and the Na_2CO_3 dosage. The hydration products were mainly C–(N)–A–S–H gel of low-crystallinity, which is rich in Al and may have included Na in its structure, and hydrotalcite-like phases. Adding reactive MgO in the mixes showed an accelerating effect on the hydration rate as suggested by the isothermal calorimetry data. Additionally, findings revealed variations on the strength of the pastes and the chemical compositions of the hydration products by introducing reactive MgO into the mixtures.

1. Introduction

Portland cement (PC) and concrete are extensively used in the construction industry because of their remarkable technical performance and durability as well as their low cost. However, they are responsible for detrimental impacts on the environment because of their large consumption of natural resources, mass disposal of wastes, and the energy intensiveness and high carbon dioxide (CO_2) emissions of cement production. The production of PC, currently at more than 3 billion tonnes annually, is predicted to reach more than 4 billion tonnes per year by 2050 [1,2]. Approximately 0.85–1.0 tonne of CO_2 is emitted per tonne of cement clinker produced [3], which is responsible for 8–10% of the total man-made CO_2 emissions [4]. This places huge pressures on the cement and concrete industries to apply more sustainable

practices. Optimising the production process of PC, using waste as fuel and raw materials, using renewable energy, and replacing the clinker partially or completely with industrial by-products, are all applied to minimise the negative environmental impact of PC production [5]. Another promising and more sustainable alternative is the use of alkali-activated cements (AACs) using industrial by-products. In this system, alkalis are introduced to silica aluminate materials (e.g., natural waste or industrial by-products) to raise the pH of the solution, thereby facilitating the breakage of the Si–O–Si and Al–O–Si bonds and starting the reactions to form a condensed structure [6,7]. Rashad [8] stated that AAC concrete compared to PC concrete could be 70% and 60% lower in global warming potential and energy consumption, respectively.

The extensively used materials for AACs are slag and fly ash (FA) [9]; the former is called alkali-activated slag (AAS) and the latter is known as geopolymer. Many previous studies investigated either alkali-activated slag or FA. As for the combined use of both, only a few studies were reported recently [10,11]. Given the limited

global resources of the individual by-products, combining them would provide a much bigger resource and counterbalance the disadvantages of each activation process [12]. The main hydration products of the alkali-activated FA/slag (AAFS) system are calcium silicate hydrates (C–S–H) gel, hydrotalcite-like phases (Ht), pirssonite (Na$_2$Ca(CO$_3$)·H$_2$O), and calcite [12]. Chi and Huang [13] studied the binding mechanism and properties of AAFS mortars and concluded that better properties, compared to PC, have been obtained in terms of compressive strength, flexural strength and water absorption, but drying shrinkage was a major problem.

The most widely used activators are NaOH, waterglass (sodium silicate), and a combination of both. These activators, however, are a source of concerns because they are the most expensive component in the system and the primary source of greenhouse gas (GHG) emissions in the production of AAC concrete. In addition, these activators would cause the AACs to shrink and harden more rapidly than what is desirable [14]. The use of sodium carbonate (Na$_2$CO$_3$) as an activator is much less extensively studied in AACs although it has been shown that buildings made of Na$_2$CO$_3$-activated binders remained sound and increased in strength over their service life under conditions in which PC deteriorated rapidly [15]. Compared to other conventional activators, Na$_2$CO$_3$ yields a lower early age strength due to its lower pH but it can demonstrate higher strength at late ages than NaOH resulting from the effect of CO$_3^{2-}$ ions [16], which lead to the formation of carbonated compounds that improve the mechanical strength [17]. Li and Sun [18] used Na$_2$CO$_3$ with or without NaOH to activate slag alone and a combination of slag and FA. The compressive strength of 10% Na$_2$CO$_3$-activated slag developed from 0 MPa at 3 days to 60 MPa at 28 days. Recently, Bernal et al. [19] examined the activation mechanism of Na$_2$CO$_3$-activated slag. They proposed that the activation took place in three different stages starting with the dissolution of the slag and the formation of gaylussite and zeolite A in the first day. Then the reaction might go through an extended induction period of 4–6 days with the conversion of gaylussite to CaCO$_3$ and the formation of hydrotalcite. In the last stage, the precipitation of C–A–S–H gel started [19].

Magnesia, MgO, is mainly produced from the calcination of magnesite, MgCO$_3$, at different temperatures resulting in different grades [20]. The use of hard burned MgO, calcined at 900–1200 °C, as a shrinkage compensating additive in the construction of the Baishan dam in China in the mid of 1970s proved its efficiency and potential over the conventional admixtures [21]. Ground granulated blastfurnace slag (GGBS) normally contains a high content of MgO, which is in the slag glass network, sometimes up to 13%; whereas reactive grade MgO (calcined under 1000 °C) or hard burned MgO (calcined at 1000–1400 °C) are often chosen for use as additives. Recent work found that reactive MgO can efficiently activate the GGBS and showed higher strength than hydrated lime activated GGBS [22,23]. The main hydration products of MgO–GGBS system were C–S–H and Ht [24]. The reactions within such a system depend on the properties of MgO [24], which strongly depend on the source of the precursor and the calcination history [25].

There are very limited reports regarding the effect of reactive MgO in AACs. Ben Haha et al. [26] studied the effect of high inherent MgO content on AAS and found that for waterglass-activated slag paste, the compressive strength at 28 days increased by 50–80% with increasing MgO content from 8% to 13%. This was because the higher MgO content contributed to more Ht formed, resulting in up to 9% higher volume of hydrates and a lower porosity. Additionally, Shen et al. [27] studied the properties of reactive MgO modified alkali activated FA/slag cement (MAAFS) and concluded that the blends can reach the strength standard of 42.5 N. They also showed that adding MgO reduced the shrinkage and cracking tendency due to its expansive hydration [27]. Kwok [28]

studied the effect of reactive MgO in Na$_2$CO$_3$-activated slag/limestone systems and found that replacing limestone by reactive MgO remarkably increased the early strength and slightly increased the 28-day strength. The effect of MgO reactivity on the strength, shrinkage, and microstructure of sodium silicate and sodium carbonate-activated slag was studied by [29–31]. They found that adding reactive MgO into the AACs can effectively reduce the drying shrinkage and increase the strength depending on the reactivity and the content of reactive MgO. However, there is no literature on the role of reactive MgO in Na$_2$CO$_3$-activated slag/FA system.

Hence the aim of this paper is to examine the effect of combining reactive MgO and Na$_2$CO$_3$ for the activation of FA and slag blends on the strength, reaction kinetics, and hydration products and microstructure.

2. Materials and methods

The GGBS used was supplied by Hanson cement, UK, and has basicity ($K_b = \frac{CaO+MgO}{SiO_2+Al_2O_3}$) and hydration modulus (HM $= \frac{CaO+MgO+Al_2O_3}{SiO_2}$) values of ~1.0 and ~1.60, respectively. The GGBS was mainly amorphous with a broad hump in the 2θ region of 25–38° in the XRD pattern (not shown). Merwinite (Ca$_3$Mg(SiO$_4$)$_2$) was identified as the only crystalline phase present. The FA was obtained from Cemex, Rugby, UK and is classified to meet the requirements of the British standard for use with PC (BS 3892: Part 1). The MgO was obtained from Richard Baker Harrison, UK, and has a reactivity of 170 s according to the acetic acid test, which indicates medium reactivity according to the classification of Jin and Al-Tabbaa [25]. The chemical compositions of all materials are shown in Table 1. Sodium carbonate was supplied by Fisher scientific, UK as a powder and has the purity of 99%. It was dissolved in the mix water until complete dissolution was reached.

Clinkerless systems were prepared from GGBS, FA, and MgO and activated by Na$_2$CO$_3$. All mixes had a water to binder (w/b) ratio of 0.31. Each material is given an appropriate notation for simplicity. G, F, M, and N refer to GGBS, FA, MgO, and Na$_2$CO$_3$, respectively. The ratio of GGBS to FA was fixed at 3 parts to 1 part by weight. The proportion of MgO changed from 0% to 10% by replacing GGBS + FA and the content of Na$_2$CO$_3$ varied from 0% to 10% by the weight of the total binder as shown in Table 2.

For the preparation of the paste samples, all the dry materials (GGBS, FA, and MgO) were mixed by hand in a bowl followed by 5 min dry mixing in a mixer to which the Na$_2$CO$_3$ solution was then added. The mixer was stopped after 3 min of slow mixing, to collect any unmixed solids scraped from the sides of the mixing bowl and the paddle into the bowl. Then 2 more minutes of slow mixing and 5 min of fast mixing were applied to ensure homogeneity. For each mix, the freshly mixed cement paste was placed into 40 × 40 × 40 mm steel cubic moulds in three layers, and in between each layer the mixture was tapped with a spatula for at least 25 times in two directions to remove the air voids. The samples were demoulded after 2 days of curing and then cured in a water tank at temperatures between 20 ± 2 °C until the designed testing age. The demoulding time was done after 48 h because some mixes were too soft to be demoulded after 24 h in agreement to [32].

Isothermal calorimetry experiments were conducted using a TAM Air Isothermal calorimeter, at a base temperature of 20 ± 0.02 °C. Fresh paste was mixed externally, weighed into an ampoule, and immediately placed in the calorimeter, and the heat flow was recorded for the first 140 h of reaction. All values of heat release rate were normalised by total weight of the paste.

The compressive strength testing was carried out using Controls Advantest 9 with a maximum capacity of 250 kN and a loading rate of 2400 N/s. Triplicate cubes were tested at ages of 3, 7, 28, 56 and 90 days and the strength reported was an average of the three specimens. Immediately after the compressive strength test at 28 days, selected samples for microstructural analyses were immersed in acetone

Table 1
Chemical composition and physical characteristics of the materials used (based on the suppliers' datasheets).

Component	GGBS	FA	MgO
CaO%	39.24	6.8 ± 3.6	1.9
SiO$_2$%	36.79	49.3 ± 6.2	0.9
Al$_2$O$_3$%	11.51	24.1 ± 0.4	0.1
Fe$_2$O$_3$%	0.42	9.7 ± 1.3	0.8
MgO%	8.10	1.1 ± 0.2	93.5
SO$_3$%	1.03	3.3 ± 1.3	–
K$_2$O%	0.63	3.5 ± 0.3	–
Na$_2$O%	0.37	1.2 ± 0.1	–
SSA (m^2/kg)	545	2600	–