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Properties of alkali activated slag–fly ash blends with limestone addition

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ABSTRACT

In this article, the effects of raw materials' composition on fresh behavior, reaction kinetics, mechanical properties and microstructure of alkali activated slag–fly ash–limestone blends are investigated. The results indicate that, with the increasing content of fly ash and limestone, the slump flow increases. The setting times are shortened when increasing the slag content, while both fly ash and limestone show a negligible influence. The reaction process is slightly accelerated by the presence of limestone due to the extra provided nucleation sites, but the reaction process is mainly governed by the slag. The slag content exhibits a dominant role on strength in this ternary system, while for a constant slag content, the compressive strength increases with the increasing limestone content up to 30%. The microstructure analysis shows that the gel characteristics are independent of the limestone powder content. The presence of limestone in initially high Ca and Al conditions does not lead to the formation of additional crystalline phases, which is different from Portland cement systems. Both physically and chemically bound water contents are slightly increased when limestone powder is incorporated.

1. Introduction

The utilization of alkali activated materials (AAMs) as a substitute for ordinary Portland cement has attracted great attention in recent years. This type of material generally exhibits better performance, such as enhanced mechanical properties [1], durability [2,3], thermal properties [4] and lower environmental impacts [5] when compared to ordinary Portland cement. Alkali activated materials can be classified into two types according to the calcium content in the raw materials [6]. One is the high calcium system, the typical precursor is ground granulated blast furnace slag (GGBS), having a C–A–S–H type gel as the main reaction product [7]. Class F fly ash and metakaolin are representative raw materials for the low calcium system, having N–A–S–H type gels within a three-dimensional network as the major reaction product [8]. However, although excellent performances can be achieved from both systems, drawbacks that limit their practical application are also obvious such as fast setting, high shrinkage of alkali activated slag [9,10] and the requirement of elevated curing temperatures, as well as the relatively long setting times of alkali activated aluminosilicates [11,12].

Approaches to avoid the disadvantages in individual system were widely studied; among those studies, attention was paid to blended alkaline systems (Na_2O–CaO–Al_2O_3–SiO_2 systems) that are produced by mixing calcium enriched precursors and aluminosilicates, due to the modified properties such as setting times [13], workability [14], shrinkage [15], mechanical properties and durability [16]. The reaction products in the blended system are C–A–S–H, N–A–S–H and calcium substituted (N,C)–A–S–H type gels [17,18] with a higher degree of cross-linking [19] that are simultaneously formed during the activation, indicating an ideal gel compatibility. Besides, the influences of key manufacturing factors on reaction kinetics, gel characteristics, mechanical properties and durability issues were also intensively investigated, in which the significance of activator type and dosage, raw materials' composition, water content and curing conditions [20–24] were highlighted. The recent progress in understanding these blended systems and those modified properties indicates a promising future for the application of alkali activated materials.

On the other hand, limestone powder has been widely utilized in Portland cement systems for the purpose of energy saving and carbon reduction [25]. A maximum limestone replacement of 35 wt.% in Europe is allowed according to the standard EN 197-1 [26]. Beside the environmental benefits, limestone has also been known to improve the workability and strength by the filler effect [27], to accelerate the hydration of C_3S by providing nucleation sites [28], to partly participate in the formation of C–S–H gels [29] and to interact with aluminate-containing phases to form monocarboaluminate [30]. Those studies indicate both physical and chemical modifications of limestone on the Portland cement system. Meanwhile, attention has also been paid to apply this more

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sustainable material in alkali activated systems. Moseson et al. [31] incorporated limestone powder into a sodium carbonate activated slag; the optimum synthesizing parameters and some environmental issues were discussed. The reported maximum limestone content was up to 68 wt.%, while the mechanical properties were comparable to Portland cement. Moreover, the carbon emission and energy consumption were reduced by more than 90%. Yip et al. [32] studied the effect of calcite on silicate activated metakaolin, showing that a calcite content of less than 20% benefits the compressive strength; higher contents may lead to disruption of the gel structure. It was suggested that the increase of strength was not only due to the filler effect, as a small amount of released Ca^{2+} from calcite also plays a limited role. Cwirzen et al. [33] investigated the effect of limestone on sodium hydroxide activated metakaolin, showing that limestone slightly promotes the dissolution of metakaolin, and both activator concentrations and curing temperature significantly affect the leaching equilibriums of Ca, Al and Si. As can be noticed, the previous studies showed the superiority of limestone powder addition in sustainable development and mechanical properties, as well as its reactive potential in alkali activated low calcium system. However, there are limited mechanism studies concerning the role of limestone powder in the blended alkaline system ($Na_2O–CaO–Al_2O_3–SiO_2$), where large amounts of reactive calcium, silica and alumina units are present simultaneously, generated gels of different types are coexistent, and the synthesizing parameters and curing conditions exhibit a more sensitive influence on the final performance.

The purpose of this study is to understand the influence of limestone powder on fresh behavior, early age reaction kinetics, mechanical properties and reaction products of alkali activated blended systems. Ground granulated blast furnace slag and class F fly ash are chosen as solid raw materials due to their worldwide availability, while ambient temperature curing is used because of its advantage in field applications. Both paste and mortar samples are produced and analyzed. The flowability and setting times of slag–fly ash–limestone pastes are identified. The micro-scale analyses are carried out by using isothermal calorimetry, thermogravimetry/differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The potential physical and/or chemical effects of limestone on the blended alkaline system are discussed.

2. Experiment

2.1. Materials

The solid materials used in this study were ground granulated blast furnace slag (GGBS, provided by ENCI B.V., the Netherlands), Class F fly ash and limestone powder. Their chemical compositions were analyzed by X-ray fluorescence and are shown in Table 1. The median particle size (d50) is 12.43 μm for slag, 22.06 μm for fly ash and 10.12 μm for limestone powder. The specific density (kg/m^3) of the used slag, fly ash and limestone powder are 2930, 2300 and 2710, respectively. The detailed particle size distributions, measured applying a light scattering technique using a Master 2000 particle size analyzer, are given in Fig. 1. CEN standard sand in accordance with EN 196-1 [34] was used for the mortar mixes. The activator used was a mixture of sodium hydroxide pellets (analytical level) and sodium silicate solution. The sodium silicate solution has a composition of 27.69% SiO_2, 8.39% Na_2O and 63.92% H_2O by mass. The desired activator modulus (Ms, SiO_2/Na_2O molar ratio) was achieved by adding the appropriate amount of sodium hydroxide pellets into the sodium silicate solution. The mixed activator solution was cooled down to room temperature prior to further use. Distilled water was added in order to reach the desired water/binder ratios.

Table 1
Major chemical compositions of raw materials.

Oxides (wt.%)	Fly ash	GGBS	Limestone
SiO_2	54.6	34.4	0.84
Al_2O_3	24.4	13.3	0.24
CaO	4.44	37.4	53.96
MgO	1.43	9.89	1.01
Fe_2O_3	7.2	0.47	0.32
Na_2O	0.73	0.34	0.21
K_2O	1.75	0.47	0.34
SO_3	0.46	1.23	–
LOI	2.80	1.65	43.01

2.2. Sample preparation

The activator used in this study has an equivalent sodium oxide (Na_2O) content of 5.7% by mass of the solid material and an activator modulus (Ms) of 1.4 for all mixes, determined based on the preliminary study, which would provide sufficient alkalinity without efflorescence. The target activator modulus was reached by mixing the sodium silicate solution and sodium hydroxide pellets with a solution/pellets mass ratio of 6.42. Three levels of slag content (60%, 50% and 40% by mass) and limestone powder additions from 0% to 30% by mass were used. The water/binder ratio by mass was 0.35 for pastes and 0.45 for mortar specimens, the water consisted of the added distilled water and the water contained in the sodium silicate solution. The binder/sand ratio was 3.0 for all mortar samples. The detailed information of the mixture proportions is listed in Table 2. The samples were prepared in a laboratory mixer; the solid raw materials were added into the mixer followed by the activating solution, then the standard sands. The mixtures were mixed at a slow speed for 30 s, then rested for 30 s before another 120 s at a medium speed. The fresh paste/mortar was poured into plastic molds of 40 × 40 × 160 mm^3 and vibrated for 1 min, then covered with a plastic film on the top surface for 24 h; finally all specimens were demolded and cured at a temperature of 20 °C and a relative humidity of 95% until their testing age.

2.3. Testing methods

The workability of the pastes and mortars were evaluated by the flow table tests according to EN 1015-3 [35]. The fresh samples were transferred into a standard conical ring and a free flow without jolting was allowed. Two diameters that are perpendicular to each other were determined and the mean value was recorded as

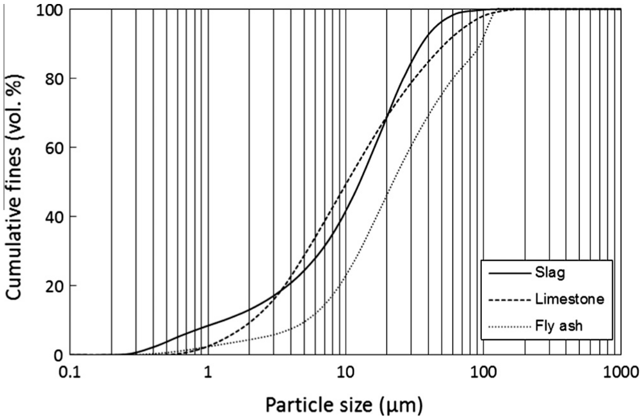

Fig. 1. Particle size distributions of raw materials.