



# Influence of different additives on the properties of sodium sulfate activated slag



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## HIGHLIGHTS

- Activated slag blended with 5% limestone showed the highest workability.
- Activated slag blended with 5% SF or limestone showed high compressive strength.
- Activated slag blended with 5% Portland cement showed the lowest compressive strength.
- Activated slag blended with 5% Portland cement showed the lowest drying shrinkage.
- Activated slag blended with 5% silica fume showed the highest drying shrinkage.

## ARTICLE INFO

### Article history:

Received 18 August 2014  
 Received in revised form 21 December 2014  
 Accepted 4 January 2015  
 Available online 28 January 2015

### Keywords:

Activated slag  
 Additives  
 Workability  
 Compressive strength  
 Drying shrinkage

## ABSTRACT

In this work, the effect of some additives namely condensed silica fume (SF), fly ash (FA), limestone (LS), hydrated lime (HL) and Portland cement (PC) on the workability, compressive strength and drying shrinkage of 1% Na<sub>2</sub>O equivalent of Na<sub>2</sub>SO<sub>4</sub> activated granulated ground blast-furnace slag (hereafter referred to as slag) has been investigated and compared to slag activated with other common activators. These additives were used as a partial replacement of slag at level of 5%, by weight. Traditional neat PC and activated neat slag (AS0) pastes were used as references. The various decomposition phases formed were identified using X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Compared to AS0, the results indicated that the inclusion of LS increased the workability, whilst HL, FA, PC and SF reduced it. The inclusion of SF and LS enhanced the compressive strength, whilst FA, HL and PC decreased it. The inclusion of FA, HL, PC and LS reduced the drying shrinkage, whilst SF greatly increased it.

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is one of the major greenhouse gases, the increasing emission of which may lead to higher temperatures and cause climate change. Global emissions of CO<sub>2</sub> from human activity have increased from an insignificant level two centuries ago to more than  $24 \times 10^9$  t/year in 2003. Roughly half of the anthropogenic emissions are absorbed into oceans and forests, but the other half accumulates in the atmosphere, where the concentration of CO<sub>2</sub> is currently 379 ppm, about 33% above the preindustrial level. It is rising at a rate of more than 1 ppm/year. It has been estimated that CO<sub>2</sub> emission will increase to  $38.8 \times 10^9$  tonnes by 2025 [1]. The major CO<sub>2</sub> producing sectors are power generation, transportation, oil refining and manufacturing of steel and concrete. Concrete is produced mainly from PC clinker and it is the most widely-used

material on the world after water. The annual production of cement is of the order of 1.8 billion tonnes and about 3 billion tonnes of natural resource per year are needed for its production [2]. However, within the concrete industry, cement manufacturing is the main culprit [3,4] where the production of PC is an energy-intensive [5] process that release a very large amount of greenhouse into the atmosphere [6]. The use of supplementary cementitious materials is a possible solution. During recent decades the use of pozzolans, mainly in the form of industrial by-products and waste materials, as construction materials has also increased as their use offers beneficial effects from both environmental and thermal viewpoints. These blends can reduce CO<sub>2</sub> emissions by approximately 13–22% [7], although this estimate can vary depending on local conditions at the source of raw materials, binder quantity and amount of PC replacement, type of manufacturing facilities, climate, energy sources and transportation distance. Another effective alternative binder is the use of alkali-activated materials such as slag, FA, burned clay and other aluminosilicate

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materials [8–10]. The CO<sub>2</sub> emission reduction rate of alkali-activated concrete relative to PC concrete commonly ranges between 55% and 75%, although the CO<sub>2</sub> reduction of alkali-activated concrete is somewhat dependent on the type, concentration and dosage of the added alkali activators [11]. Today the focus is no longer on obtaining new binders, but on developing materials with sustainable, high mechanical strength, fire resistance, higher durability and other characteristics. One option to improve some especial properties of alkali-activated slag (AAS) system is to replace part of source slag with other supplementary materials such as SF, FA, LS, HL and PC.

Many authors blended slag with other materials in AAS system activated with the common activators such as sodium silicate, NaOH and their combinations. Rashad et al. [12] and Rashad [13] reported higher compressive strength of AAS pastes activated with sodium silicate with the inclusion of quartz powder (QP) up to 30% as partially replacement of slag, by weight. Rashad [13] reported that the inclusion of QP up to 30% as partially replacement of slag, by weight, in AAS activated with sodium silicate greatly increased the workability. Furthermore, the inclusion of QP reduced the degradation in the compressive strength caused by heating/cooling cycles. This degradation decreased with increasing QP content. Rashad and Khalil [14] reported that replacing slag with 5% SF in AAS pastes activated with sodium silicate enhanced the compressive strength and the residual compressive strength after exposure to elevated temperatures ranging from 200 °C to 800 °C. Recently, Rashad [15] reported that neat slag activated with 1% Na<sub>2</sub>O equivalent of Na<sub>2</sub>SO<sub>4</sub> exhibited higher elevated temperatures resistance ranging from 200 °C to 800 °C than that of containing 5%, 10% and 15% PC as slag replacement, by weight. Rashad [16] reported that the inclusion of FA in FA/slag concretes activated with sodium silicate and NaOH decreased the compressive strength, but reduced the drying shrinkage.

Although strong alkaline activators, such as sodium silicate, NaOH and their combinations, are preferred for high strength, but none of them exists naturally and their production process is quite energy intensive. On the other hand, Na<sub>2</sub>SO<sub>4</sub> can be obtained from natural resources and hence is more environmentally friendly [17]. There are too limited investigations in the literature in relation to activate slag with Na<sub>2</sub>SO<sub>4</sub> of which Na<sub>2</sub>SO<sub>4</sub> activated slag suffers to be unusable in practice due to its very low early strength [18]. In the literature, Rashad et al. [17,19] activated slag with Na<sub>2</sub>SO<sub>4</sub> at concentrations of 1–3% (Na<sub>2</sub>O equivalent). They reported that increasing the Na<sub>2</sub>SO<sub>4</sub> concentration caused a significant increase in the compressive strength at early ages. By 28 days, the compressive strength of hardened slag pastes activated with either 1% or 3% Na<sub>2</sub>O equivalent of Na<sub>2</sub>SO<sub>4</sub> seemed to converge to the same value. The compressive strength of PC was significantly higher than that of Na<sub>2</sub>SO<sub>4</sub> activated slag pastes. On the other hand, Douglas and Brandstetr [20] reported that at 1 day, strength of slag mortar activated with Na<sub>2</sub>SO<sub>4</sub> at 1 wt.% Na<sub>2</sub>O equivalent was comparable to that of PC. Wu et al. [18] reported that slag pastes activated with Na<sub>2</sub>SO<sub>4</sub> were stronger than that of slag pastes without Na<sub>2</sub>SO<sub>4</sub> activation at early hydration times, but were weaker later on during hydration. Puertas [21] showed that slag activated with an optimized mixture of Na<sub>2</sub>CO<sub>3</sub> + Na<sub>2</sub>SO<sub>4</sub> + Ca(OH)<sub>2</sub> showed similar strength value to that obtained by NaOH. Wang et al. [22] reported that Na<sub>2</sub>SO<sub>4</sub> plus small amount of PC, lime or clinker dramatically improved the strength of fine ground basic slag. Bai et al. [23] reported that the corrosion of aluminum in terms of pot expansion could be reduced with the inclusion of 20% pulverized FA (PFA) as slag replacement, by weight, in Na<sub>2</sub>SO<sub>4</sub> activated slag pastes.

As reported before, the early strength of Na<sub>2</sub>SO<sub>4</sub> activated slag is usually low, which hinders its wider applications. On the same line, activated slag suffers from higher drying shrinkage which is still

the main problem of this system. Replacing part of slag with other supplementary materials in Na<sub>2</sub>SO<sub>4</sub> activated slag system may be help to solve these problems. In this study the workability, compressive strength at different ages and drying shrinkage up to 200 days of Na<sub>2</sub>SO<sub>4</sub> activated slag blended with different additives namely SF, FA, LS, HL and PC were investigated. Each of neat PC paste and neat Na<sub>2</sub>SO<sub>4</sub> activated slag paste was employed for comparison. In addition, the comparison of the trends of Na<sub>2</sub>SO<sub>4</sub> activated slag blended with different additives regarding to workability, compressive strength and drying shrinkage versus that activated with other common activators such as sodium silicate, NaOH and their combinations, quoted from the literature, were reported. Hence, this investigation will therefore add valuable knowledge to the Na<sub>2</sub>SO<sub>4</sub> activated slag system which the literature is still missed.

## 2. Experimental details

### 2.1. Materials

Industrial grade of Na<sub>2</sub>SO<sub>4</sub> was used as the activator. Slag that supplied by UK Hanson Cement was used as the raw material to produce activated slag paste. Slag Blaine surface area was 500 m<sup>2</sup>/kg. Condensed SF obtained from disposal of local ferro-silicon alloys was used as additive. SF Blaine surface area was 22,000 m<sup>2</sup>/kg. LS was supplied by UK Omya with a very high purity (98% of CaCO<sub>3</sub> content, 0.8% of SiO<sub>2</sub>, 0.17% of Al<sub>2</sub>O<sub>3</sub>, 0.1% of Fe<sub>2</sub>O<sub>3</sub>, 0.5% of MgO, 0.002% of Cl<sup>-</sup>). LS Blaine surface area was 486 m<sup>2</sup>/kg. Class F FA was obtained from local power plant. FA Blaine surface area was 230 m<sup>2</sup>/kg. HL was supplied by UK Omya with a Blaine surface area of 486 m<sup>2</sup>/kg. CEMI Class 42.5R, with a Blaine surface area of 270 m<sup>2</sup>/kg complies with EN 197-1: 2001, was used as either an additive or as a reference in PC mixture. The chemical compositions of the PC, slag, SF and FA were determined by X-ray fluorescence (XRF) spectrometry and the results are shown in Table 1.

### 2.2. Mixture proportions

Six Na<sub>2</sub>SO<sub>4</sub> activated slag pastes and one PC paste were prepared. Among the six activated slag pastes there was one mixture being manufactured from the neat slag without any additive. The remaining five mixtures were manufactured from slag coupled with one additive, of which slag was partially replaced with a certain type of additive at a level of 5%, by weight. Five different types of additives have been used namely condensed SF, FA, LS, HL and PC. A water binder ratio (w/b) was fixed at 0.3, for all mixtures. 1% Na<sub>2</sub>O equivalent of Na<sub>2</sub>SO<sub>4</sub> by binder mass was used as an activator. All mixture proportions are detailed in Table 2.

**Table 1**

Oxide composition of PC, slag, FA and SF (% by mass) after calculation from XRF results.

Composition	PC	Slag	SF	FA
CaO	63.47	40.89	0.98	4.76
SiO <sub>2</sub>	20.18	34.94	95.2	55.95
Al <sub>2</sub> O <sub>3</sub>	4.83	11.69	–	23.3
MgO	2.47	7.42	0.431	1.85
Fe <sub>2</sub> O <sub>3</sub>	3.16	3.32	1.0	4.84
SO <sub>3</sub>	3.26	1.19	0.02	0.65
K <sub>2</sub> O	0.52	0.34	1.03	1.82
Na <sub>2</sub> O	0.16	0.16	0.91	0.91
TiO <sub>2</sub>	0.3	0.49	–	1.03
MnO	0.22	0.27	–	0.05
P <sub>2</sub> O <sub>5</sub>	0.09	0.01	–	0.73
Loss of ignition	2.18	-0.93	0.429	3.47
Total	100.34	100.71	99.571	99.36

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