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Mutual activation of blast furnace slag and a high-calcium fly ash rich in free lime and sulfates

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HIGHLIGHTS

- Certain ground slags and fly ashes can be matched to activate one another chemically.
- Binders without Portland cement or added chemicals can be made.
- Blending slag and fly ash gives higher strength than when either is used alone.
- Ettringite and CSH are the main hydration products.

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ABSTRACT

Alkaline activation of fly ash and blast furnace slag has gained interest due to a desire to avoid Portland cement in mixtures. Outstanding mechanical performance and durability is reported, but often when the activator dosage is high which can have various negative environmental impacts that can overshadow the carbon reduction benefit. This study investigates the use of a ground slag, and a high-lime fly ash, rich in free lime and sulfates, to activate each other and render mortars which don't incorporate any Portland cement or an added chemical activator, but still have useful strengths. The ash, which does not conform to standards for use in concrete, hence is nearly completely landfilled, is used as-received or after grinding. 28-day compressive strengths surpassing 13 MPa and 20 MPa were recorded, for samples cured at 23 °C or at 80 °C. Various combinations of the two powders have heats of hydration lower than that of a typical Portland cement. Ettringite and CSH are determined to be responsible for the early and ultimate strength gain. The effect of adding gypsum to the system as a low-impact activator is also investigated.

1. Introduction

More than 4 billion tons of Portland cement (PC) are produced annually, worldwide ([1,2]. Since this process emits large and ever increasing amounts of CO_2 [3,4]; researchers have been seeking alternatives to PC concrete. Possibly the most popular of these is alkali-activated materials (AAM) in which a ground aluminosilicate is "activated" with a small amount of a chemical like an alkali hydroxide, silicate, carbonate or sulfate that raises pH and results in dissolution of the powder and formation of reaction products [5]. AAM can offer economical or technical advantages over PC systems [6–9] but their main benefit is considered to be environmental; a reduced carbon footprint due to the avoidance of the carbonate raw materials and high kiln temperatures required for PC production. Although reduction of carbon emissions, which contribute to global warming, is important, a complete assessment of the environmental impact of a binder requires a broader approach, such as life-cycle assessment [10], which considers impact categories like aquatic and terrestrial toxicity, acidification, eutrophication, ozone depletion, photochemical smog, human toxicity, etc. The impacts of seemingly small amounts of chemical "activators" used in a binder can be quite large on some categories. Habert et al. [11], for example, calculated the fresh water ecotoxicity of metakaolin-, fly ash-, and slag-based geopolymer concretes as roughly 30×, 10×, and 8× that of ordinary PC concrete, respectively. The impact of slag and fly ash geopolymers were 3–10× that of PC concrete in various categories. Accurate calculation of the impact of chemical activators is not easy, since more than one production route exists for them [12,13]. Nonetheless, the sustainability of these chemicals is debatable and their use should be reduced or avoided if possible. Hence, the ideal PC alternative binder would not use a factory-made chemical activator but rather match various wastes or less preferably unprocessed natural materials to

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Table 1
Physical and chemical properties of the powders used.

Oxide	S (%)	FA (%)	G (%)
CaO	34.56	33.30	36.00
SiO_2	39.90	19.40	3.67
Al_2O_3	11.13	9.50	1.25
Fe_2O_3	0.26	5.64	0.46
MgO	9.37	1.88	0.53
SO_3	0.09	12.90	42.50
K_2O	1.18	0.68	0.16
Na_2O	0.35	0.23	0.06
Loss on ignition (%)	2.93	4.93 (7.94[a])	4.7
Free CaO (%)	N/A	9.5	N/A
Physical properties			
Specific gravity	2.87	2.41 (2.67[a])	2.31
Blaine fineness (cm^2/g)	4100	2200 (7540[a])	5140

[a] The values in parentheses are for the ground fly ash (FG).

activate one another. An example is activation of slag or fly ash with gypsum [14,15] or a combination of gypsum and lime [16,17]. A better example is activation of slag with the highly-alkaline cement kiln dust (CKD) [18,19]. The high free lime and sulfate CKD reacts with slag to give ettringite and calcite, and strengths ~35 MPa [20,21]. However, availability of CKD is dependent on the existence of the PC industry. In another example of wastes activating one another, Sadique et al. [22] combined two different fly ashes, one rich in calcium and the other in alkali sulfates, with silica fume to obtain a binder with ~30 MPa strength. In yet another, Kuo et al. [23] activated blast furnace slag using desulfurization slag with a high pH and high CaO and MgO, to produce samples with 12–14 MPa strength. Complex zero-cement binders involving four or more different powders have also been reported [24]. These studies suggest that carefully matching wastes based on their chemical compositions can give binders that set and harden without the use of chemical activators. The binders can possess properties superior to those obtained when the wastes are hydrated by themselves. In addition, the use of certain wastes could be deemed even more beneficial than others. For example, the use of high-calcium ashes, which are generally less effective pozzolans and as such preferred less for blending into PC concrete, could be advantageous. Bricks with moderate strength made with pastes containing only a high-calcium fly ash and application of compaction pressure have been reported [25,26]; largely owing to their self-cementing property [27,28]. Any excessive free lime, SO_3, etc. in such an ash could also be expected to activate another fly ash or slag mixed with it. Some fly ashes don't meet the relevant standards for use as a mineral admixture in PC concrete [29,30]; due to having excessive free lime or SO_3. Nearly all of such an ash is landfilled where it can eventually cause groundwater contamination or air pollution [31–33]. Hence its use is preferable over that of a standard ash which can find other uses.

The present study attempts the activation of a ground slag with a non-standard, high-calcium, high-SO_3 fly ash, first without any additional activators and then with the addition of gypsum as a low-environmental-impact activator. Strength and hydration product development of various combinations, at close to room temperature or with elevated-temperature curing, are investigated. Cementless binders without any added activating chemicals could have a truly low carbon footprint, and would reduce the consumption of natural resources.

2. Materials and methods

Three different powder materials, a ground granulated blast furnace slag (S), a fly ash (FA), and a natural gypsum (G), were combined in different proportions to prepare mortars. Table 1 shows the physical properties of the materials and their oxide analyses determined using inductively-coupled plasma spectroscopy.

The slag was obtained from Kardemir Iron Steel Industry and Trade Co., in Northwest Turkey. The fly ash was obtained from Afşin Elbistan (AE) thermal power plant in Southeast Turkey, which produces the greatest amount of fly ash in the country, ~3 million tons/yr. The ash was used "as received" (FA) or after being "ground" (FG) in a laboratory ball mill. Mechanical activation of fly ash by grinding is well-known [34,35]; but this high-energy operation also impacts the environment. Grinding does not significantly affect the oxide composition of the ash (the oxide composition of FG was very similar to that of FA) but surprisingly, greatly increases its loss on ignition. Payá et al. [36] suggested that grinding causes the formation of calcium carbonate, due either to carbonation of free lime during grinding, or to oxidation of unburned carbon with atmospheric oxygen and further acid-base reaction with free lime. FA has mostly irregular shape, with some spheres, and was mostly gray with dispersed white particles (identified as calcium sulfate). It has a high calcium content, with ~10% free lime and ~13% SO_3, exceeding the EN standard limits of 3% and 2.5%, respectively [37]. Previous attempts to use this ash to

Table 2
Mixture proportions of the various mortars made.

Mixture ID	Mixture ingredients								
	S (%)	FA (%)	FG (%)	G (%)	S (g)	FG (g)	FG (g)	G (g)	Water (g)	W/P (by mass)
S100	100	0	0	0	450	0	0	0	225.0	0.50
S75FA25	75	25	0	0	337.5	112.5	0	0	235.7	0.52
S50FA50	50	50	0	0	225	225	0	0	246.5	0.55
S25FA75	25	75	0	0	112.5	337.5	0	0	257.2	0.57
FA100	0	100	0	0	0	450	0	0	267.9	0.60
S75FG25	75	0	25	0	337.5	0	112.5	0	229.2	0.51
S50FG50	50	0	50	0	225	0	225	0	233.4	0.52
S25FG75	25	0	75	0	112.5	0	337.5	0	237.6	0.53
FG100	0	0	100	0	0	0	450	0	241.9	0.54
S100-G	90	0	0	10	405	0	0	45	230.4	0.51
S75FA25-G	67.5	22.5	0	10	303.75	101.25	0	45	240.1	0.53
S50FA50-G	45	45	0	10	202.5	202.5	0	45	249.7	0.55
S25FA75-G	22.5	67.5	0	10	101.25	303.75	0	45	259.4	0.58
FA100-G	0	90	0	10	0	405	0	45	269.0	0.60
S75FG25-G	67.5	0	22.5	10	303.75	0	101.25	45	234.2	0.52
S50FG50-G	45	0	45	10	202.5	0	202.5	45	238.0	0.53
S25FG75-G	22.5	0	67.5	10	101.25	0	303.75	45	241.8	0.54
FG100-G	0	0	90	10	0	0	405	45	245.6	0.55