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Influence of different artificial additives on Portland cement hydration and hardening

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HIGHLIGHTS

- Tribochemically activated biomass fly ash (AFA) does not have a pozzolanic activity and acts as an inert microfiller.
- Synthesized clay–silica gel additive (CSG) is a pozzolanic material.
- Both AFA and CSG additives have a positive effect on the compressive strength of cement samples.

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ABSTRACT

This study investigated two artificial materials—biomass fly ash (AFA) and a new synthesized composite from clay and silica gel waste (CSG)—as additives for Portland cement. AFA has very weak pozzolanic properties and acts as an inert microfiller, whereas CSG is a pozzolana. It was determined that up to 15 wt.% of ordinary Portland cement (OPC) can be replaced with either additive without impairing the strength properties of the samples. The positive effect of AFA additive on the strength properties of OPC is associated with significant acceleration of the calcium silicate hydration process, whereas this effect for the CSG additive is related to the formation of stratlingite (C_2ASH_8), hydrogarnet ($C_3AS_xH_{6-2x}$), and an additional amount of calcium silicate hydrates.

1. Introduction

The cement industry is one of the most energy-intensive industries. The incorporation of industrial mineral wastes as additives in the cement manufacturing industry presents two principal benefits: an ecological benefit (environmental protection and reduction of pollution) and an economic benefit (reduction of consumption of clinker and improvement of land conditions) [1,2].

Recently, attention has been paid to the replacement of ordinary Portland cement with various pozzolanic materials. These materials are used in order to improve the compressive strength of mortar or concrete [3]. The fine additives used in cement systems are classified into reactive and "inert" substances [4]. "Inert" additives (quartz, limestone or dolomite) in normal processing conditions fill up the void spaces remaining between the coarser particles and contribute to an increase of compressive strength without any chemical reaction [3,4]. The reactive additives (i.e., pozzolanas, ground blast furnace slag) also fill the void space between the larger particles, which is otherwise occupied by water, and in contrast to "inert" additives, with time they react chemically to produce additional hydrates. This causes a compaction of the matrix and interface transition zone [4,5]. Tasdemir determined [6] that mineral admixtures having high values of fineness and pozzolanic activity increase the compressive strength of concrete.

Burned clay is one of the earliest known pozzolanic materials. Depending on the pozzolanic activity of the burned clay, this material allows replacement of part of the cement in concrete to improve its long-term strength and durability [7,8]. It has been proposed that the burning temperature producing the active state is usually in the range of 600–800 °C, which causes destruction of the crystalline structure of the clay and formation of amorphous silica and alumina [9].

A new source of pozzolana could be a waste from the aluminum fluoride industries: silica gel. The structure of the precipitated silica depends on many variables, including reaction temperature and time, concentration of reagents, structure of aluminum hydroxide used, purity of fluorosilicic acid [10], degree of impurity elution, and washing technology of the silica [11]. Using this waste (silica

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gel) as a pozzolanic additive in concrete, similar reactions must take place during the curing of cement paste as in the use of SiO_2 fume [12]. The admixture of SiO_2 in concrete reduces cement consumption and increases the strength and density of the concrete. Thomas and Jennings [13] stated that the SiO_2 particle surfaces serve as the source of C–S–H crystallization centers, which result in a faster cement hydration process. From silica gel waste one can obtain a pozzolanic additive for Portland cement through combustion of a silica gel–clay–limestone composite [14]. During the combustion process, the fluorine ions from silica gel were combined into a stable CaF_2 compound, and the pozzolanic activity of the obtained material is 260 mg CaO/g. Up to 15 wt.% of a pozzolana additive increased the compressive strength of the cement samples cured for 28 days under normal conditions.

Biomass ash is the solid waste that results from the combustion, complete or incomplete, of biomass, and it shows a heterogeneous mix of variable composition with both organic and inorganic components [15,16]. The quantity and quality of the ash produced in biomass plants strongly depend on the characteristics of the biomass used. Therefore, the biomass composition can be highly variable, depending on the geographic locations and industrial processes [17–19]. The chemical composition of biomass fly ash is an important characteristic to consider when using it as a supplementary cementing material in blended cement. Tkaczewska [20] found that, during hydration, the cement samples that contain coal and biomass fly ash show lower heat flow values, a higher quantity of $Ca(OH)_2$, and slower C_3S hydration in comparison with samples containing bituminous coal fly ash as an additive. Researchers have noted that a wood ash concrete requires a higher quantity of water [21]. The compressive strength grows with an increasing duration of curing, but it decreases with an increasing amount of additive. It was determined that the compressive strength of waste wood ash concrete is lower than that of concrete without additives [22–24]. This is associated with the different behavior of waste wood ash: in the concrete matrix it acts more as microfiller than as a binder.

Thus, the research into economic binders using industrial byproducts (blast furnace slag, silica fume, fly ash, rice husk ash, and other materials) is a major concern in reducing the deficit recorded during the manufacture of Portland cement.

In this work, two different artificial additives (tribochemically activated biomass fly ash (AFA) and a newly synthesized composite from clay and silica gel waste (CSG)) were used. Both artificial additives contained about 50 wt.% of SiO_2, but CSG is a pozzolana, whereas AFA acts as an inert microfiller. The aim of this work was to determine the influence of two artificial additives with different properties on the hydration process of ordinary Portland cement (OPC).

2. Materials and methods

In this work, fly ash from a biomass (wood chips and waste wood) fired power plant was used. The chemical composition and characteristics of the biomass fly ash (AFA) are shown in Table 1.

The CSG pozzolana was synthesized from the clay from an industrial quarry (consisting of quartz, illite, muscovite, feldspars, hematite, calcite, dolomite, chlorite and kaolinite) and silica gel (AlF_3 production waste ($SiO_2{\cdot}nH_2O$) with $AlF_3{\cdot}3H_2O$ impurity) mixed in proportions of 40 wt.% of waste and 60 wt.% of clay. The water-to-solid (w/s) ratio of the mixture was equal to 0.58. The formed granules (12 ± 2 mm) were dried at 100 ± 2 °C for 24 h and then burned at 700 °C for 1 h (10 °C/min). After burning, the obtained samples were crushed by a Fritsch jaw crusher Pulverisette 1 and ground with a Fritsch planetary disc mill Pulverisette 9 for 40 s at 600 rpm. The chemical composition and characteristics of the raw materials and CSG pozzolana are shown in Table 1.

The ordinary Portland cement (OPC) CEM I 42.5 R was used in this work. The chemical composition of the cement is shown in Table 1. The mineralogical composition of the OPC is as follows: $3CaO{\cdot}SiO_2$, 52.97 wt.%; $2CaO{\cdot}SiO_2$, 19.61 wt.%; $3CaO{\cdot}Al_2O_3$, 9.16 wt.%; $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, 9.74 wt.%; $CaSO_4{\cdot}2H_2O$, 5.37 wt.%.

Samples were formed of pure ordinary Portland cement and Portland cement with 5, 15, and 25% (by weight) replacement with artificial additives. The consistency of the cement paste and the initial and final setting times of the cement were estimated according to European Standard EN 196-3 [25]. Samples for compressive strength analysis (prisms $4 \times 4 \times 16$ cm) were formed according to European Standard EN 196-1 [26] (the cement-to-sand ratio was 1:3, and the water-to-cement ratio was 0.5). Samples were kept in molds at 20 ± 1 °C and 100% humidity during the first day of hydration. After 24 h of formation, the samples were transferred to deionized water and were stored there for 27 days at 20 ± 1 °C. In order to make a more exact estimation of the hydration process, the samples for instrumental analysis were prepared without the sand. The storage conditions of the samples were analogous to those used during the strength test. The hydration of samples was stopped using acetone: three samples were kept under the conditions described; then samples were crushed separately, milled together using a laboratory planetary disc mill, passed through an 80 micron sieve, washed with acetone, and dried in a CO_2-free atmosphere at 80 ± 5 °C for 8 h. A representative amount was selected from the lot to be analyzed, which upon further quartering (EN 196-2, EN 196-7 [27,28]) was reduced to a manageable amount for appropriate sample preparation. Powder samples were stored in sealed bags to prevent carbonation and hydration.

The particle size distribution and the specific surface area of the materials used were determined by a laser particle size analyzer (CILAS 1090 LD) in intervals from 0.04 to 500 μm. The distribution of solid particles in the air stream was 12–15 wt.%. Compressed air (2500 mbar) was used as a dispersing phase. The measuring time was 15 s.

The pozzolanic activity was assessed using the modified Chapelle method [29]. This test consists of placing 1.000 g of mineral admixture into 500 ml of lime solution (1.200 g/l CaO). The solution was kept for the first 48 h in a thermostat at 45 °C. At the end of this period, 50 ml of the solution was taken and the CaO content was determined by titration with 0.05 N hydrochloric acid (HCl) solution using methyl orange as the indicator. The results were expressed as milligrams of bound CaO per gram of pozzolanic additive. The rest of the solution (450 ml) was kept again for 24 h at 45 °C. The process was repeated until the estimated value of the pozzolanic activity was insignificantly low (7 days).

Table 1
Chemical composition and characteristics of raw materials.

Components	AFA (wt.%)	CSG (wt.%)	Clay (wt.%)	Silica gel (wt.%)	OPC (wt.%)
SiO_2	45.08	58.45	48.02	77.77	19.52
Al_2O_3	2.98	11.04	13.33	7,61	5.03
Fe_2O_3	1.37	3.83	6.69	–	3.05
CaO	16.58	6.11	10.19	–	61.39
MgO	1.90	2.57	4.59	–	3.93
K_2O	4.47	1.64	2.75	–	1.06
Na_2O	0.37	0.20	0.376	–	0.12
MnO	0.56	Not estimated	Not estimated	–	–
SO_3	2.26	–	–	–	2.5
P_2O_5	2.07	–	–	–	–
TiO_2	0.2	Not estimated	Not estimated	–	–
ZnO	0.12	Not estimated	Not estimated	–	–
BaO	0.10	Not estimated	Not estimated	–	–
F^-	Not estimated	3.45	Not estimated	8.64	Not estimated
Loss on ignition	8.89	12.71	14.81	9.56	Not estimated
Specific surface area, m^2/kg	430	400	30	400	350