Construction and Building Materials 122 (2016) 54–62

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Preliminary electrochemical cementation of high volume fly ash mortars

Juan Lizarazo-Marriaga [*], Fredy García, Camilo Higuera

Department of Civil and Agricultural Engineering, National University of Colombia, Bogotá D.C., Colombia

HIGHLIGHTS

- The electrochemical activation of fly ash has been researched successfully.
- A qualitative model has been proposed to explain the electrical fly ash activation.
- The proposed fly ash activation process improved some mechanical properties.

ARTICLE INFO

Article history:
Received 3 February 2016
Received in revised form 3 June 2016
Accepted 14 June 2016
Available online 21 June 2016

Keywords:
Fly ash
Alkaline activation
Geopolymeric cementitious material
Electrochemistry
Electro-mutagenesis

ABSTRACT

This paper summarizes a research about the electrochemical activation of the cementitious properties of fly ash. Taking into account that in recent years there have been various environmental issues associated with the production of Portland cement (PC), the use of Fly Ash (FA) has been promoted in the production of concrete. Traditionally, the use of fly ash has been possible through its blending with Portland cement and as a geopolymeric cementitious material. In this research, a third technique for fly ash activation, known as electro-mutagenesis, was investigated. This treatment consisted in the late hydration of fly ash after the migration of ions from an external alkaline solution, by applying an electric field across the hardened mortar. Solutions of sodium hydroxide and sodium silicate with different molar concentrations were used as a source of alkaline ions. The electrical treatment was applied in many mortar samples using high volume proportions of fly ash, a constant water to binder ratio, and a fixed aggregate content. After treatment, the compressive strength, the ultrasonic pulse velocity, and the microstructure of the mortar matrices were investigated. Results showed that the alkaline ions migrated into the hardened mortar through the permeable capillary pores, reacted with the un-hydrated fly ash and mutated in new hydration phases, producing an improvement in the physical properties of mortar.

1. Introduction

Nowadays, environmental issues associated with the production of Portland cement (PC) are in the middle of a global debate. It is estimated that the CO_2 released during cement clinkering is around 0.7 to 0.9 tons per ton of PC, meaning that the cement industry generates around 7% of total CO_2 emissions worldwide [1,2]. For that reason, and because of the growing concrete demand, research on alternative materials has increased. Among those alternative materials, fly ash (FA) appears to be as one of the most industrially used, which is a by-product of thermal generation in coal power stations [3].

FA as a cementitious material has been used through "direct activation" using PC, in which the usual replacement percentages range from 15 to 25% [4]. Additionally, in recent years geopolymers have become popular, in which FA hydration is accomplished through a chemical "alkaline activation". This chemical process allows the transformation of a material with a partially or fully amorphous structure, in stable cementitious compounds [5]. FA is a silicon-aluminous material, which reacts in presence of an alkali hydroxide solution, producing synthetic silicon-aluminous solids, which can achieve similar characteristics of PC hydrates [3,6].

There are several chemical activators that can be employed with FA; however, the combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) has been successfully reported in literature. In this case, the sodium hydroxide generates the dissolution of FA in alumina (Al) and silicon (Si), which are the main precursors of the compounds produced in the hydration process. During the dissolution process, the sodium silicate acts as a catalyst, increasing the reactions velocity [3,7].

Electrochemical treatments in hardened concrete or mortar are based on electromigration, which can be defined as the transport of ionic species under the influence of an electric field. Ions must

---

* Corresponding author.
E-mail addresses: jmlizarazom@unal.edu.co (J. Lizarazo-Marriaga), fmgarciam@unal.edu.co (F. García), hchiguerraf@unal.edu.co (C. Higuera).

http://dx.doi.org/10.1016/j.conbuildmat.2016.06.070
0950-0618/

move through a tortuous path defined by the interconnection of capillary pores of the material, so, the transport equations are defined similarly to the equations of transport in porous medium [8]. The general law governing the ionic movements in cementitious materials is known as the Nernst–Planck equation [9].

$$J_i = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i c_i \frac{\partial E}{\partial x} \tag{1}$$

where J_i is the flux of species i [mol/m^2/s], D_i is the diffusion coefficient of species i [m^2/s], c_i is the ionic concentration of species i in the pore fluid [mol/m^3], x is the distance [m], R is the gas constant [8.31 J/mol/°K], T is the absolute temperature [°K], z_i is the electrical charge of specie i, F is the Faraday constant [9.65 × 104 Coulomb/mol], and E is the electrical potential [V].

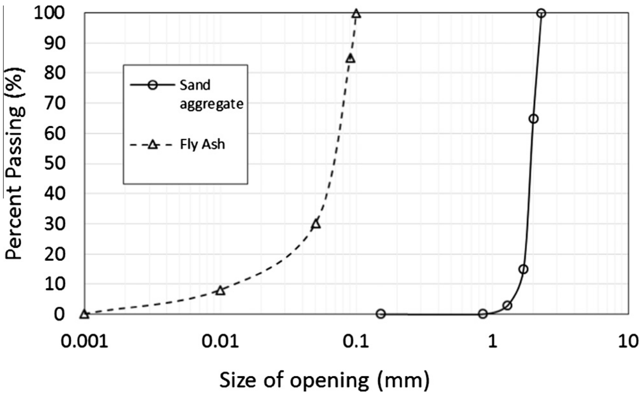

Fig. 1. Fly ash and sand particle size distribution.

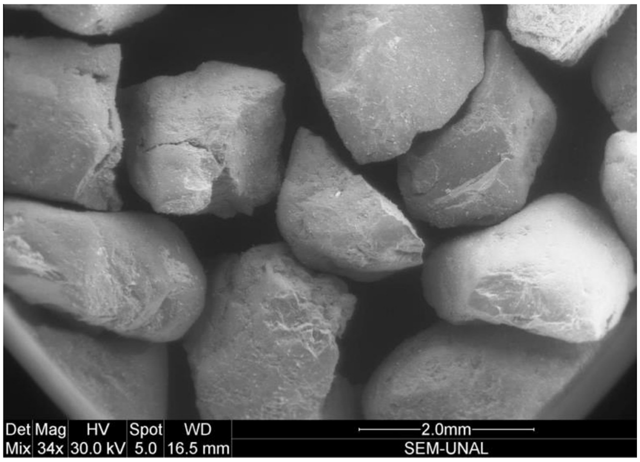

Fig. 2. Appearance of aggregate.

Table 1
Aggregate physical properties.

Average aggregate particle size (mm)	Apparent specific gravity	Loose bulk density (g/cm^3)	Compacted bulk density (g/cm^3)	Effective absorption (%)
1.68	2.63	1.64	1.79	2.86

Recently, a new process of electromigration has been used to mitigate damage and densify cementitious matrices. This technique corresponds to the electrodeposition of nanoparticles within the capillary pores of cementitious materials [10–12]. It has been reported that if in a reinforced concrete structure an electric current is applied between the steel reinforcement (cathode) and an outer electrode (anode), it is possible to lead the electrodeposition of external nanoparticles that could serve as a physical barrier and prevent the entry of gases or contaminants within concrete [13,14].

Electrodeposition is a novel and promising technique because it can help in many durability issues. It also improves other physical properties such as the compressive strength and density. That increase is related to the porosity reduction within the material during the electrochemical treatment, which is provided by the pozzolanic materials that migrate into concrete. The driving electrical forces produce late hydration products. In literature, this process is better known as electro-mutagenesis [15].

Based on a preliminary research [16], a more detailed research program was carried out regarding the electrochemical activation of high volume fly ash mortars. This paper summarizes the results of that experimental study about the activation process of FA by applying an electrochemical method. The treatment consisted on the electrical migration of alkali ions within hardened mortar samples previously cast using high volume FA. For the experimental setup, cells with external reservoirs containing sodium hydroxide and sodium silicate solutions, with different molar concentrations, were used. After the electrochemical process, the compressive strength, the ultrasonic pulse velocity and the microstructure were assessed.

2. Experimental programme

2.1. Raw materials

All mortar mixes were cast using natural sand and a constant aggregate content. Fig. 1 shows the size distribution for the aggregate used in this research. Fig. 2 shows the physical appearance of the aggregate, with individual particles viewed through SEM at a magnification of 34×. From X-ray fluorescence, it was determined that the natural sand (aggregate) was mainly siliceous holding a 98% SiO_2 content. The physical properties of aggregates are summarized in Table 1.

Commercial hydraulic ASTM C1157 cement for general construction, classified as GU type (general use) according to the manufacturer [17], without a representative amount of mineral admixtures was used. Fly ash class F was obtained from a Colombian power station, which had an average loss of ignition value of 8% and the particle size distribution shown in Fig. 1. Specific gravities of cement and fly ash were 3.0 and 2.2 respectively. The chemical characterization of both binders in terms of oxides is shown in Table 2. In addition, Fig. 3 shows the physical appearance of fly ash, in which individual particles can be seen at a magnification of 500× and 4000×.

Table 2
Chemical oxide composition of binders used.

Compound% by weight	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	K_2O	Na_2O	Cl	TiO_2	MnO	P_2O_5	Cl	Ba
Cement	60.41	21.46	5.57	4.65	3.83	1.41	0.71	0.62	0.43	0.35	0.05	–	–	–
Fly Ash	1.01	62.21	23.86	1.09	5.61	0.64	1.91	0.56	–	1.35	–	0.75	0.53	0.12