Resistance of blended cement pastes subjected to organic acids: Quantification of anhydrous and hydrated phases

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ABSTRACT

Concrete for agricultural construction is often subject to aggressive environmental conditions. Ground granulated blast furnace slag (GGBFS) or metakaolin (MK) largely improve the chemical resistance of the binder. Anhydrous particles seem particularly resistant to the acid solution. The purpose of this study is to quantify anhydrous particles in blended cement pastes as a function of acid exposition time in order to evaluate their acid resistance.

Cement pastes were moist cured for 28 days and then immersed in an acetic acid solution for 2 months. The quantification of the anhydrous phases was carried out using ^{29}Si MAS NMR, selective dissolution and back-scattered electron (BSE) images analysis, while the hydrated phases content was evaluated by TGA. After 28 days of hydration, 60% of OPC, 44% of GGBFS and 76% of MK particles were hydrated. The amount of anhydrous particles drops for all materials during acid immersion. After 2 months of immersion, the amount of anhydrous particles drops by 49%, 23% and 15% for OPC, GGBFS, and MK respectively. This study confirms that GGBFS and MK anhydrous and hydrates phases present higher acid resistance than OPC.

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1. Introduction

Agricultural effluents contain organic acids that constitute a severe chemical threat toward the concrete of agricultural structures. Acidic environments are among the most aggressive media for concrete. Cement hydration products are stable only in solutions with well defined Ca^{2+} and OH^- concentrations and in contact with an acidic environment, the constituents of the hardened cement pastes are altered by decalcification [1]. Organic acids react with hydrated and anhydrous compounds of the cement paste to give mainly calcium salts. Depending on their solubility, these salts may precipitate or may be dissolved in solution. Acids such as nitric, hydrochloric or acetic acids form easily soluble Ca-salts and have a strong decalcifying effect [2–5]. Bertron et al. [5] showed that the four acids of the liquid manure (acetic, propionic, butyric and iso-butyric acids) have an equivalent aggressiveness while lactic acid presents a greater aggressiveness according to its dissociation constant value (pKa). Moreover, it was demonstrated that an acetic acid solution of pH 4 mimics well the aggressiveness of organic acids found in animal manure. Due to the formation of easily

soluble Ca-salts, acetic acid forms a porous altered layer with relatively weak diffusion resistance [1].

Previous studies [6–9] has shown that cement pastes blended with ground granulated blast furnace slag (GGBFS) and metakaolin (MK) largely improve the chemical resistance of the binder when submitted to an acidic environment. Chemical composition profiles measured by electron probe microanalyser (EPMA) of paste samples immersed in acetic acid solution according to the distance to the surface of the specimen have demonstrated the good chemical resistance of GGBFS and MK samples. These samples presented a reduced altered depth that is less decalcified compared to other binders [6]. Anhydrous GGBFS particles seemed particularly resistant against the acid attack and their presence can partly explain the good performance of that binder. The positive effect of residual anhydrous grains was also reported by Bertron et al. [10]. These authors reported that the amount of some anhydrous grains (slag grains, silica fume agglomerates and C_4AF) may improve the durability because they are not dissolved in the altered zone and their presence can help preserving the integrity of the matrix. These authors observed that the C_4AF grains were well preserved when subjected to an acetic acid solution at pH 4, while C_2S and C_3S grains were mainly dissolved.

According to Macias et al. [11], the acidic attack decomposes the unhydrated and hydrated cement paste phases. Portlandite is dissolved and the hydrated silicate and aluminate phases are decom-

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posed. The resistance of cement pastes is due to the nature of the hydration products rather than the porosity of the hardened cementing materials and depend on the protective silica layer precipitated on the surface [12]. As stated by Beddoe and Dorner [13], the dissolution of ferrite or aluminate hydrates is slower and occurs at lower pH values than the release of Ca^{2+} from C–S–H and portlandite. They indicated that as the pH decreases, portlandite (12.6), ettringite (10.7), C–S–H ($\approx$10.5) and finally calcium aluminate and ferrite hydrates decompose successively.

All these studies have shown the beneficial effect of some SCMs on the durability of concrete submitted to acidic environments. However, although observations have shown large amounts of anhydrous grains presented in the degraded zone of samples submitted to organic acids, no study has focused on the quantification of anhydrous grains. The quantitative assessment of the rate of hydration of SCMs is still a challenge in the scientific community. Much effort is made to improve the methods. Some methods have been tested for slag cements, others for metakaolin. In this work, we evaluated different techniques recently developed to directly quantify the cement and SCMs anhydrous phases during the acid immersion.

The purpose of this study is to quantify anhydrous GGBFS and MK particles in blended cement pastes as a function of acid exposition time. This is done to evaluate their acid resistance and improve understanding of their role in the durability of cementitious material subjected to acid attack. The quantification of the anhydrous particles is measured by ^{29}Si MAS NMR, selective dissolution method and back-scattered electron (BSE) images processing while the evolution of the hydration process is evaluated using thermogravimetric analysis (TGA). This last method allows the monitoring of the mass loss occurring during the thermal decomposition of cement hydrated phases. The non-evaporable water content, or bound water, is directly function of the amount of C–S–H, portlandite, ettringite and AFm phases presented in the sample. The amounts of residual anhydrous and hydrate phases of metakaolin, slag and OPC mixtures was measured after a curing period of 28 days prior to acid immersion. The same parameters were evaluated on the altered zones of samples after 15 days, 1 and 2 months of immersion in an acetic acid solution.

2. Materials and methods

2.1. Materials

This study was conducted on three cement pastes made with OPC, designated in American Standard as GU (General Use, containing a maximum of 5% limestone filler), blended with 80% of GGBFS and with 20% of MK, respectively, as a partial cement replacement by mass of the cement. The control sample is made only of GU. No superplasticizer was added. The chemical composition of the binders is given in Table 1.

The immersion solution was composed of acetic acid (CH_3-COOH), a weak organic acid with a dissociation constant pKa of 4.76 at 25 °C. The concentration of the acetic acid solution was 0.5 M and the pH 2.8. To avoid hydration of anhydrous phases during the acid immersion of pastes, the acetic acid was dissolved in a solvent other than water. Referring to the miscibility data of acetic

acid, toluene ($C_6H_5CH_3$) was chosen. The aggressive solution was a mixture of acetic acid and toluene (0.01%). The solution was renewed every week throughout the duration of the experiment in order to maintain the pH of the solution at a value of 2.8.

2.2. Methods

The quantification of anhydrous phases consists to measure the quantities of OPC, GGBFS and metakaolin anhydrous particles as a function of acid exposition time in order to evaluate their chemical resistance. Acetic acid was diluted in toluene (0.01%) in order to avoid the presence of water causing the hydration of the anhydrous phases. Different methods were reported for the quantification of anhydrous particles of Portland cement or blended cements in order to evaluate the hydration degree of cementitious materials. These techniques included the selective dissolution method [14–18], ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) technique [19–21] and back-scattered electron (BSE) images processing techniques [22,23] while the quantification of the hydrated phase content was evaluated by thermogravimetric analysis (TGA). Some authors have combined the use of ^{29}Si MAS NMR and selective dissolution [24–26] while others have used the selective dissolution and image processing techniques [27]. In this study, anhydrous GGBFS and MK particles were quantified using the 3 methods. Results obtained by the different methods will be analyzed and compared.

2.2.1. Specimen making and treatment

Cement pastes were made at a water/cementitious material ratio of 0.27. Hardened cement pastes specimens are cylindrical, 100 mm high and 50 mm diameter. The specimens were demolded 24 h after pouring and stored in moist-curing room (23 °C, RH = 100%) for 27 days. Cement pastes were made according to ASTM C192/C192M procedure [55].

Samples were removed from the moist-curing room, wiped to remove water surface and then immersed in an acetic acid solution at a pH of 2.8 for 2 months at solid–liquid volume ration of 1/15. Some control specimens were kept in moist-curing room during the whole experiment. At the end of each immersion period (15 days, 1 and 2 months), specimens were wiped and dried at room temperature. The analyses were realized in the sound and altered zones of the specimens. The external altered zone was easily removed from the specimen due to shrinkage cracking. Samples were pulverised into powder to pass through a 200 mesh sieve of 74 μm apertures for the NMR analysis and pulverised into powder to particle size lower than 63 μm for the selective dissolution method. Polished flat sections were prepared for image analysis technique using standard procedure with SiC and diamond pastes as abrasive material.

2.2.2. NMR spectroscopy

Skibsted et al. [28] have shown that ^{29}Si MAS NMR spectroscopy is a very valuable tool for quantifying the silicate phases (C_2S and C_3S) in Portland cement. Due to the overlapping of resonance lines of these minerals, their amounts are obtained by decomposition of ^{29}Si MAS NMR spectra. According to Chao [26], ^{29}Si MAS NMR is not only a good method for characterizing the clinker (i.e. C_3S and C_2S) but can also be used to evaluate the amount of blast furnace slag which are essentially constituted by SiO_2, Al_2O_3 and CaO. In fact, the ^{29}Si MAS NMR spectra of hydrated cement paste consist of two parts: One related to residual anhydrous silica C_3S and C_2S (Q_0 and Q_4) and the other related to the hydrates of the chains component of C–S–H (Q_1 and Q_2). The spectrum of alite is characterized by a large broadened line ranging between −69 ppm and −74.5 ppm [26]. It consists on a monoclinic form of alite with isolated SiO_4, tetrahedra (Q_0) [29]. The spectrum of belite is illustrated

Table 1
Chemical composition of binders.

Binders	%CaO	%SiO$_2$	%Fe$_2$O$_3$	%Al$_2$O$_3$	%MgO	%K$_2$O	%Na$_2$O	%TiO$_2$
GU	62.5	19.6	2.27	4.9	2.61	0.9	0.24	0.25
MK	0.03	51.65	0.68	44.7	0.08	0.34	0.08	0.12
GGBFS	37.31	36.77	0.85	7.77	13.91	0.43	0.31	0.36