



Resistance to acid attack of alkali-activated binders: Simple new techniques to measure susceptibility



Ana Mellado, Martha Iris Pérez-Ramos, José Monzó, María Victoria Borrachero, Jordi Payá*

Grupo de Investigación en Química de los Materiales (GIQUIMA), Instituto de Ciencia y Tecnología del Hormigón (ICITECH), Universitat Politècnica de València, Camino de Vera s/n, E-46022 Valencia Spain

HIGHLIGHTS

- Two new, simple methods for assessing resistance to acid attack have been proposed.
- Low calcium alkali-activated pastes showed the best resistance to acid attack.
- Acid neutralisation capacity (ANC) was measured for at pH 7, 4 and 2.
- The proposed ANC combined-pH assay is a good alternative for individual tests.
- Mass loss and acid consumption were proposed tests for studying monolithic samples.

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ABSTRACT

Two rapid tests were developed to evaluate the resistance to acid attack by ordinary Portland cement (OPC) and alkali-activated pastes. Acid neutralisation capacity (ANC) at pH 7, 4 and 2 was monitored with powdered pastes. In parallel, a 'combined-pH assay' with a single sample was used to sequentially assess ANC at different pH values. A mass loss/consumed acid monitoring technique has been also developed in order to assess monolithic samples. The OPC paste showed the most degradation. Among the alkali-activated pastes, those with the lowest calcium content (fly ash and spent-FCC catalyst) had the best performance.

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1. Introduction

Ordinary Portland cement (OPC) is one of the most used binders in the world. However, their manufacture generates a large amount of carbon dioxide emissions. It needs to be replaced by other more environmentally friendly binders which guarantee durability performance. A promising alternative is the production of other binders such as alkali-activated materials (also called geopolymers).

Geopolymers are formed by a reaction between an aluminosilicate solid material (precursor) and a highly alkaline solution (activating solution) under controlled curing conditions to form a strong dense binding gel [1–4].

Alkali activated binders have either nano-crystalline or amorphous microstructures depending on their reactivity or the

percentage of aluminosilicate in the material (precursor), on its nature (mineralogy, fineness), on the alkalinity of the activating solution and on the curing procedure. Most of the previous work in this area used metakaolin, fly ash (FA) and blast furnace slag [5,6]. Other alternative inorganic precursors such as hydrated-carbonated cement, waste glass, spent fluid catalytic cracking catalyst of petroleum (FCC), ceramic waste (CW) or other aluminosilicate materials have been tested to produce alkali-activated materials [7–11].

From the engineering point of view, one of the most important properties in concrete is its durability. As concrete interacts with its external environment, its durability may be threatened, especially by acid attack [12–14] which can reduce its lifetime of service.

The spectrum of aggressive acid media to which concrete can be exposed is broad [12]. Sources usually originate from industrial or agricultural processes, but can also be due to urban activity. Acids can be more or less aggressive towards hydrated compounds:

* Corresponding author.

E-mail address: jjpaya@cst.upv.es (J. Payá).

particularly and among others, nitric (HNO_3), hydrochloric (HCl), sulphuric (H_2SO_4) acids are strong acids and behaves very damaging to concrete: hydration products in OPC decompose resulting in a very intense attack.

A practical consequence of chemical degradation caused by an acid attack is the gradual weakening of the mechanical strength and solid cohesiveness of concrete. Decay starts by deterioration at the surface of the concrete, resulting in crushing and dropping of material, and continues its destructive progression into the interior portions. As the effects of an acid attack intensify, the strength of the concrete gradually decreases. An acid attack increases total porosity and the percentage of the volume composed of coarse pores as a result of the decomposition and leaching of hydration products.

In addition, usually dissolution of the products during an acid attack on hydrated cement results in the formation of a degraded layer which, in many cases, is an easily visible layer, often characterised by a light brown colour marking the front of the attack due to the formation of ferric compounds [15].

The severity of an acid attack is significantly dependent on the acid strength. Strong acids (e.g., nitric or hydrochloric acids) can reach very low pH values even when there is a relatively small amount of them in the solution. The acid attack progress also depends on the nature of the resulting salt: in some cases, insolubility of this salt reduces the inorganic corrosion rate of the matrix [13].

The corrosion rate of concrete subjected to acid solutions is a complex process resulting from a combination of dissolution, precipitation and transportation processes. Several factors control this phenomenon of degradation, mainly the chemical composition of the cement, the reactivity of the aggregate and the dosage of the concrete [16].

Many authors [17] have claimed that geopolymers cements are much more resistant to acid attack than OPC. Shi and Stegmann [18] compared the acid resistance of alkali-activated slag and OPC binders when immersed in solutions of nitric acid (pH 3) and in acetic acid (pH 3 and 5). They reported that alkali-activated slag binders had lower mass losses than OPC binders. According to these authors, after acid corrosion hardened alkali-activated and OPC binders formed a surface layer whose composition is mainly $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ gel. This layer provides a barrier which prevent further corrosion of the internal, non-corroded cores. However, there is a noticeable difference between the layers formed by alkali-activated slag and OPC. Alkali activated slag produce a protective dense silica gel layer, but hardened OPC leave a porous layer. Differing calcium content (greater in OPC than in alkali-activated slag) could be responsible for this effect.

Identical conclusions were obtained by other authors, such as Bakharev et al. who demonstrated that when alkali-activated FA concrete was exposed to an acetic acid attack [19] or alkali-activated slag concrete was exposed to acetic or sulfuric acid attacks [20]. In both cases, the resistance of materials was studied by immersion of cylindrical concrete specimens in acid solutions. The durability of alkali-activated materials when exposed to acid solutions was higher than that found for OPC systems.

A further study [21] revealed that alkali-activated FA cementitious materials prepared with sodium silicate solution had a lower crystallinity than those prepared with sodium hydroxide activator. With greater crystallinity, alkali-activated binders were more stable in acid environments, such as in sulfuric and acetic acid solutions.

Allahverdi and Škvára [22,23] determined the mechanism of nitric acid attack on hardened pastes of alkali-activated binders based on FA and granulated blast furnace slag. The authors proposed that the mechanism of acid attack consists on: a) dissolution process: sodium and calcium are leached and exchanged by

hydronium ions (H_3O^+) from the acid solution; b) electrophilic attack: polymeric Si-O-Al bonds are attacked and aluminium ions are removed from the aluminosilicate framework; c) realignment of chains: the framework vacancies are mostly re-occupied by silicon atoms and an imperfect highly siliceous framework is formed. The removed aluminium ions (tetrahedral complex) is converted to octahedrally coordinated aluminium, which is distributed in the intra-framework space. Also, volume contraction of the material during the leaching process resulted in the formation of shrinkage cracks.

This paper presents a study of the resistance to nitric acid attack of some alkali-activated pastes prepared from ground granulated blast slag (GGBS), fly ash (FA), spent fluid catalytic cracking catalyst of petroleum (FCC) and ceramic waste (CW) when exposed to nitric acid attack compared to hardened OPC pastes. Samples were stored at controlled pH values of 2, 4 and 7 to calculate the acid neutralisation capacity (ANC) of the powdered materials based the EA NEN 7371:2004 standard [24]. This study outlines a rapid test whereby the weight loss of prismatic specimens submerged in an acid solution (nitric acid, at a constant pH of 2) was measured over time. Also, optical microscopy and scanning electron microscopy (SEM) on samples attacked by nitric acid are presented. We have modelled ANC versus time for the samples at each pH tested in order to predict their behaviour during acid attack. Also equations were modelled to describe mass loss over time for each of the specimens tested.

2. Experimental

To prepare cement pastes, Spanish OPC (CEM I 52.5-R, supplied by Lafarge, Puerto de Sagunto, Spain) that complies with the specifications of EN 196-1 was used. In the preparation of alkali-activated binders, materials were supplied by different companies located in Spain: GGBS (Cementalva, Puerto de Sagunto), FA and CW (Balalva, Onda) and FCC (BP Oil, Grao de Castellón). These mineral additions were ground prior to use. Sodium hydroxide pellets (98% purity, Panreac S.A.) and a sodium silicate solution (waterglass; 28% SiO_2 , 8% Na_2O and 64% H_2O ; Merck) were used to prepare the activating solutions. Calcium hydroxide (95% purity, Panreac S.A.) was used to prepare alkali-activated paste with CW. Table 1 summarises the chemical composition of all materials used as precursors (as determined by X-ray fluorescence) and their mean particle diameter after milling.

A reference OPC paste was prepared at a water to cement ratio (w/c) of 0.4.

Activating solutions were prepared at least 1 h in advance and allowed to cool to room temperature prior to use. Then they were mixed with each material to prepare the pastes. Table 2 shows the composition of prepared alkali-activated samples. $\text{SiO}_2/\text{Na}_2\text{O}$ is the molar ratio of these oxides in the activating solution. A 5% by mass of $\text{Ca}(\text{OH})_2$ was used to replace CW in the CW paste.

The fresh pastes were cast in prismatic moulds (1 cm × 1 cm × 6 cm), sealed with a plastic film to avoid atmospheric carbonation and stored at $23 \pm 2^\circ\text{C}$ with 100% relative humidity for 24 h, except for FA and CW, which needed to be stored in a thermostatically controlled bath at $65 \pm 2^\circ\text{C}$ for 48 h before demoulding. After demoulding, all specimens were cured at $23 \pm 2^\circ\text{C}$ with 100% relative humidity for 28 days.

ANC studies were carried out in an 805 Dosimat Plus automatic titration system (Metrohm) coupled to a Delta-DO9765T pH transmitter (LabProcess). For ANC determination, cured pastes were ground in an agate mortar. One gram of powdered sample (particle size < 125 μm) previously dried at 60°C for 30 min. Samples were stored in a dried atmosphere until ANC tests. Deionized water (50 mL) were placed in a beaker and the solid sample was added (the L/S ratio was 50). The sample was magnetically stirred (spinning at 300 revolution per minute). After 10 min of stirring, HNO_3 (0.5 M for pH 7 and 4, and 1 M for pH 2) was added at a flow rate of 4 mL min^{-1} until the desired pH value was reached. The pH values selected for the single-pH assays were 7, 4, and 2. When the solution stabilised at the desired pH, the titration automatically stopped and the volume of acid required to reach this pH value was recorded. The assay was complete when the pH remained constant for longer than 15 min without any acid added by the automated titration system. All tests were carried out in triplicate. The total number of ANC curves measured was 45 (5 pastes × 3 tested pH values × 3 repetitions).

Additionally, a 'combined-pH assay' was carried out in which, after the stabilisation at the first pH value, more acid was added to decrease the pH further (e.g. from 7 to 4, and then from 4 to 2). In this case the sample was not removed from the beaker. HNO_3 (1 M) was used as the acid reagent for this 'combined-pH assay'.

The resistance of materials to acid attack was studied by immersion of the prismatic specimens in a HNO_3 solution at a constant pH of 2 with the same device used in the ANC studies. The specimens were suspended in 200 mL of deionised water

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