Resistance of alkali-activated binders to organic acid attack: Assessment of evaluation criteria and damage mechanisms

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HIGHLIGHTS

- Resistance of low-Ca AABs under organic acid attack was proved.
- Strength rise during acid attack is linked to new phase formation near the surface.
- Organic acid resistance of AABs decreases with increasing CaO content of the binder.
- CaO-limit of 10 m.-% seems appropriate to differentiate AABs regarding durability.

ARTICLE INFO

ABSTRACT

This paper summarizes the results of investigations into the material resistance of mortars and concretes based on alkali-activated binders (AABs) under organic acid attack (acetic, propionic, lactic acid with pH ≈ 3). The development of the residual strength, degradation depth and mass loss over time were recorded after six, twelve and 18 weeks of storage. Additionally, the damage mechanisms were examined by different imaging techniques, mainly micro X-ray computer tomography (μXCT) and microscopy, including spatially resolved porosity as well as phase analyses. The degree of degradation, especially in the pre-damaged zone, decreases with a decreasing Ca-content of the binder. No damage zones, an increased residual strength and a densification (detected as a reduction in porosity) at the acid-exposed fringe zone was observed for so-called Geopolymer binders (low-Ca AABs) the longer the exposure to acid was. A lower degree of degradation was detected for high-Ca AABs compared to cementitious reference mortars/concretes.

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1. Introduction

The acid resistance of cementitious materials is influenced by the impermeability of the concrete matrix and the resistance of the strength forming phases. Apart from technological concrete optimizations, such as a decreasing w/c-ratio [1] or an optimized grading curve [2], the best potential for improvement with respect to acid resistance is to generate more stable phases. The use of Supplementary materials such as fly ash or particularly silica fume leads to a reduction of the acid-soluble $Ca(OH)_2$ in Portland cement-based binders, and at the same time to the formation of C-S-H-phases with lower C/S ratios [3–6]. In contrast to fly ash and silica fume, the addition of metakaolin results in the formation of C-A-S-H-phases with an enhanced acid resistance compared to ordinary C-S-H-phases [3]. In order to reduce the amount of acid-soluble $Ca(OH)_2$ and thereby to generally improve the acid resistance, a reduction of the clinker content in cements is decisive. Accordingly, the aforementioned pozzolans are often combined to form cementitious composites [7,8].

Nevertheless, the advances in cementitious materials regarding the durability are limited due to the thermodynamic instability of hydrate phases for pH-values below nine [9,10]. The resistance of cementitious materials is reduced in many applications with challenging exposure conditions, e.g. biogenic sulfuric or organic acid attack [6,11]. Initially, alternative cements such as high alumina cements [12,13] or sulfate-activated granulated blast furnace slag [13,14] were used to improve the acid resistance of concretes. More recently, alkali-activated binders became a promising alternative for highly durable concretes due to their high resistance within aggressive environments, which was already demonstrated for sulphate [15], sulfuric acid [16–18], hydrochloric acid [19], nitric acid [18] or acetic acid [17].

Next to mineral acids, organic acids can be of particular importance for sewage or agricultural concrete applications. Even if the acidity of organic acids like acetic, propionic, lactic or butyric acids is lower than mineral acids, concrete attack isn't less aggressive (i.e. due to buffer effects and the solubility of the organic salts). A more detailed description of the damage mechanism of weak acids is published in [20].

This paper presents a detailed experimental program to characterize the damage mechanisms of mortars and concretes based on four alkali-activated binders exposed to organic acids. An organic acid mix of acetic, propionic and lactic acid with a pH of 3 was chosen to represent typical exposure conditions for highly-stressed agricultural constructions, i.e. silage clamps [11]. The experimental results obtained on alkali-activated mortars with different CaO contents are compared with reference mortars based on ordinary Portland cement (OPC) as well as on OPC partially enhanced by fly ash (OPC + FA). Finally, recommendations based on the findings that were obtained are formulated for the future evaluation of acid resistance.

2. Significance of work

The broad spectrum of investigated binder compositions and assessment criteria herein, will thereby enable a sufficient and comparative assessment of different AAB systems as well as the used evaluation criteria and is at the same time highlighting the novelty of the paper.

3. Materials and methods

3.1. Cementitious materials and testing conditions

3.1.1. Experimental program

This paper assesses the acid resistance of four different types of alkali-activated binder, an alkali-activated granulated blast furnace slag (AAS), an alkali-activated low-calcium fly ash (AAFA), a high-Ca multi-component AAB consisting of fly ash and slag (80-20, 50-50) as well as two reference mixes (OPC, OPC + FA) in terms of the development of mass loss, residual compressive strength and degradation depth. Moreover, the damage mechanisms of the binder systems which are quite different from one another (OPC, AAS, AAFA) were comparatively evaluated by X-ray diffraction (XRD), micro X-ray computer tomography (μXCT) and mercury intrusion porosimetry (MIP).

3.1.2. Compositions of raw materials and mix designs

A low-calcium fly ash (FA) according to EN 450-1:2012-10, granulated blast furnace slag (S) and two ordinary Portland cements (CEM I 32.5 R, CEM I 52.5 R) according to EN 197-1:2011-11 were used. The chemical composition, amorphous percentage and loss of ignition of the raw materials used were determined by X-ray fluorescence (XRF), X-ray diffraction analyses (XRD) and gravimetric analysis. The results are shown in Table 1.

Alkali-activated and multi-component mortars as well as concretes were activated by the addition of liquid sodium hydroxide (19 M) and sodium silicate with a SiO_2 /Na_2O molar ratio of 3.4 and solid content of 34.5 m.-%. The specific dosage was adjusted to the chemical composition of the raw materials (Table 2). Quarzitic gravel (ρ = 2.63 kg/dm^3) with a maximum size of 16 mm and locally available river sand were used as aggregates for the concrete mix. The mortars contained CEN sand according to EN 196-1:2005-05. The workability was adjusted in both cases by the addition of a polycarboxylate ether superplasticizer (PCE-SP) for OPC and by the addition of Lignosulphonate-superplasticizer (LSF-SP) for AAS, 80-20 and 50-50, to ensure good compatability and prevent segregation.

3.1.3. Casting

Mortars were produced in accordance to EN 196-1:2005-05 with a binder to sand ratio of 1:3, mixed in a TESTING Blum & Feuerherdt mortar mixer of the type 1.0205, consolidated via shock table and cast in molds of the size $40 \times 40 \times 160$ mm^3.

In addition, concrete prisms ($100 \times 100 \times 400$ mm^3) and concrete cubes with an edge length of 150 mm were cast. Dry and liquid constituents were mixed in a compulsory mixer for 3 min. Chemical additions were then added and mixing continued for a further 60 s. before the concrete mix was placed in steel molds and consolidated by vibration. Alkali-activated fly ash concretes were cast in plastic molds to avoid any loss of surface quality caused by a high bonding between the concretes and the steel molds.

3.1.4. Curing

The curing conditions depend on the type of binder, in particular their Ca-content and reaction mechanisms. Therefore, only alkali-activated fly ash (AAFA) mortars and concretes were cured at 75 °C for the first 48 h. The heat-cured specimens as well as all the other specimens stored at standard climate conditions (20 °C, 65% RH) were removed from the mold after 2 days. The OPC-based specimens were then stored under water until testing, whereas the AABs were wrapped in foil and stored in standard climate conditions.

3.1.5. Experimental set up

All samples were stored in water until saturation (at least three days) before the acid tests. This procedure ensures a diffusion-controlled process during the acid attack. A total of 54 mortar specimens, six concrete prisms and six concrete plates ($100 \times 100 \times 40$ mm^3, sawn from concrete cubes) were immersed in the organic acid for at least 28 days in accordance with an in-house testing procedure, presented in [20]. The test equipment and the testing procedure developed here enable a constant stress level and reproducible results. The accelerated test set up is primarily designed to compare the performance of different kinds of mortar and/or concrete. A reliable, probabilistic model for service life predictions is currently not available since the complexity of field conditions is not predictable [21].

The liquid test medium was a homogeneous mix of 1.5% acetic acid, 0.5% propionic acid and 3.0% lactic acid with a pH-value of ≈3. The acid mix is based on own investigations of agricultural constructions such as silage clamps [11]. The acid test solution had a volume of 320 dm^3 and a temperature of 25–28 °C. The samples had a total surface area of 246 dm^2. The pH value was regulated by an automatic titration unit filled with organic acid mix while the acid solution was homogenized by a mixer with a pump system. A flow rate of between 0.05 and 0.30 m/s prevailed in the acid container. The acid test solution was replaced every four weeks. The CaO-content of the continuously stirred test medium was determined by the complete replacement of the test solution at different times (6 wk.: 1345.0 mg/L, 12 wk.: 626.7 mg/L, 18 wk.:1237.0 mg/L). Furthermore, additional 48 mortar specimens and six concrete prisms were stored in a water bath as a reference for the corresponding removal date.

The damage potential was assessed after six, twelve and 18 weeks of immersion. Three mortar prisms were removed from the acid tank and two prisms were removed from water bath each time. The residual compressive strength was determined on four mortar cubes (two exposed and two unexposed references), which were sawn from the prisms. The third exposed specimen contained carbon rods (Ø 3 mm) and was used for image-generating analysis of the degradation depth. In contrast, all the concrete specimens were removed at the same time. After 18 weeks of immersion, one concrete prism was removed from the acid tank and one from the water tank to determine the residual compressive strength. The concrete plates which were also removed after 18 weeks of immersion were used to examine the depth of concrete degradation.

3.2. Mass loss

To ensure a suitable statistical basis, all mortar and concrete prisms that were exposed to acid and water were weighed using a digital scale with an accuracy of ±0.1 g; the results were recorded before exposure as well as at the specific removal date. For this purpose, the mortar and concrete prisms were roughly dried on a saturated surface. With a progressive exposure time, the number of samples gradually

Table 1
Chemical composition by XRF, X-ray amorphous percentage by XRD and Loss On Ignition (LOI) of the raw materials (%).

Raw material	Chemical composition								LOI	X-ray amorphous quantity
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O		
Portland cement (CEM I 32.5 R)	20.10	4.82	3.20	63.50	3.46	1.27	0.99	0.21	2.22	4.0
Portland cement (CEM I 52.5 R)	19.97	5.56	3.20	63.59	2.08	3.74	1.13	0.27	1.55	2.1
Fly Ash (FA)	52.85	25.57	9.41	3.26	1.74	0.48	2.42	1.44	1.55	63.2
Blast furnace slag (S)	35.35	11.18	0.57	40.33	6.83	2.69	0.68	0.18	–	98.8