Sulfuric acid resistance of one-part alkali-activated mortars

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ABSTRACT

One-part alkali-activated (geopolymer) mortars based on three different silica-rich starting materials and sodium aluminate, with and without ground granulated blast furnace slag (GGBFS) addition, were tested regarding sulfuric acid resistance according to DIN 19573:2016-03 (70 days at pH = 1). Corresponding pastes were characterized by XRD, SEM, chemical analysis, ^{29}Si MAS NMR and ^{1}H-^{29}Si CPMAS NMR after water storage and after acid exposure. The mortars exhibited a high resistance against sulfuric acid attack, with the best ones conforming to the requirements of DIN 19573:2016-03. The analytical results showed that this was due to precipitation of silica gel at the acid-mortar interface, which formed a mechanically stable layer that protected the subjacent mortar and thus inhibited further degradation. The addition of GGBFS decreased the acid resistance via formation of expansive calcium sulfate phases.

1. Introduction

The long-term chemical resistance of concrete structures is of major importance for sustainable economies; one aspect in this context is that cementitious materials with a high acid resistance are required in many different important infrastructures, either for construction or for repair. In particular, concretes and mortars with high sulfuric acid resistance are needed for the construction and the repair of sewer structures, in which biogenic sulfuric acid attack is the major degradation mechanism [1–4]; improved acid resistance is also required in agricultural structures and biogas plants [2,5,6]. Important progress has been achieved in this regard with materials based on Portland cement (OPC)/supplementary cementitious materials (SCM) blends or calcium aluminate cement (CAC) [3,7–11], but ever-increasing demand justifies the search for alternative, potentially more durable binder systems.

Low-calcium alkali-activated materials (geopolymers and mortars/concretes produced from these) have been repeatedly observed to exhibit high acid resistance [12–18], making them promising materials for applications in the aforementioned environments, though exceptions from this general trend, i.e. unsatisfactory or ambiguous results of acid resistance tests, have been reported too [12,19–21]. Different parameters of the mix-design have been found to influence the acid resistance of geopolymers. The alkali ion of the activator solution appears to affect the pore size distribution of the binder matrix, potassium leading to larger pore sizes and thus lower acid resistance than sodium [12]. The addition of nano-silica or microsilica modifies the particle

size distribution of the dry binder, potentially increasing the packing density of the solid particles in the fresh paste and thus improving its microstructure after hardening; furthermore, it is a way to modify the chemical composition (increase the SiO_2 content) of the system [16,17]. The presence or absence of dissolved silicate in the activator solution influences the crystallinity of the reaction products, which can impact the chemical resistance too [12]. Apparently the most important parameter is the CaO content of the binder: During sulfuric acid or sulfate attack, calcium may precipitate as gypsum, thereby causing expansion and damage [14,16,21]; under some circumstances, however, gypsum appears to block pores, inhibiting further corrosion [22].

All the above-mentioned studies were conducted on conventionally produced alkali-activated materials (AAMs), i.e. materials that were produced by addition of an alkali hydroxide or alkali silicate solution to a solid aluminosilicate powder. However, AAMs that need only to be mixed with water to initiate hardening (termed 'one-part mix' AAMs [23,24]) provide significant advantages regarding transport and storage of feedstocks, occupational health and safety, and adaption to conventional mixing and processing equipment, thus providing potentially a higher commercial viability. Different routes to precursors for one-part AAMs have been devised, including calcination or intense grinding of aluminosilicate materials together with alkali-bearing compounds, and dry mixing of (alumino)silicate materials with readily soluble solid activators [23–26].

One of these approaches is to dry-mix a silica-rich starting material and solid sodium aluminate ($NaAlO_2$), and subsequent mixing with

water [23,25]. In this approach, the properties and the phase assemblage after curing depend strongly on the employed silica material and the starting SiO_2/Al_2O_3 ratio, leading either to geopolymer-zeolite composites or to virtually fully amorphous geopolymers [27–29]. Besides the fact that the use of an alkaline solution for activation is avoided here, advantages of these binder systems include easy control of the SiO_2/Al_2O_3 ratio in a wide range as well as the possibility to use various industrial and biogenic by-products as silica-rich starting materials.

To the authors' knowledge, no previous studies of the acid resistance of one-part AAMs are available. In the present study, mortars were made with these binders, based on three different silica starting materials, with and without addition of ground granulated blast furnace slag (GGBFS). The mortars were tested for sulfuric acid resistance according to DIN 19573:2016-03 (70 days at pH = 1), and their binder microstructure characterized, using XRD, ^{29}Si MAS NMR, ^{1}H-^{29}Si CPMAS NMR, and SEM with regard to the mechanisms that are responsible for the observed acid resistance.

2. Materials and methods

2.1. Starting materials

Three different silica materials were employed as feedstocks: a microsilica (hereafter referred to as MS), a silica resulting from thermal treatment of residues from chlorosilane production and subsequent scrubbing and neutralization of the flue gas (CR), and a rice husk ash (RHA). The employed solid activator was sodium aluminate (nominally $NaAlO_2$). GGBFS was added to some formulations as a source of calcium. Chemical analysis of the solid feedstocks was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) after total microwave digestion; the results are shown in Table 1. MS and RHA contained ~94 wt% SiO_2, while the SiO_2 content of CR was considerably lower (~84 wt%); RHA contained significant amounts of K_2O and P_2O_5. The sodium aluminate had an almost stoichiometric Na/Al ratio of 1.003 mol/mol.

The XRD patterns (Fig. 1; for measurement conditions see Section 2.4) showed a major hump with its maximum around 21.5° 2θ for CR and MS, evidencing a virtually fully amorphous silica with only minor crystalline impurities quartz (PDF # 00-046-1045), calcite (PDF # 01-086-0174) in CR, and residues of silicon (PDF # 00-027-1402) and silicon carbide (PDF # 00-049-1429) in MS. RHA contained, besides amorphous phase, a considerable amount of cristobalite (PDF # 00-039-1425) and minor amounts of tridymite (PDF # 00-042-1401). In a previous study on one-part AAMs [28], a fully amorphous rice husk ash was employed; the presence of cristobalite in the RHA used in the
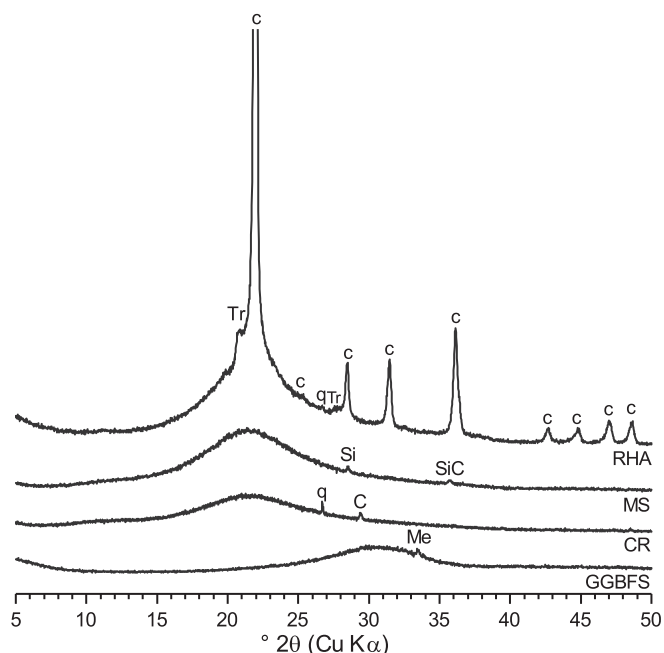

Fig. 1. XRD patterns of the starting materials RHA, MS, CR, and GGBFS (q = quartz; Tr = tridymite; c = cristobalite; C = calcite; Si = silicon; SiC = silicon carbide; Me = merwinite).

present work indicates a higher calcination temperature for the rice husks, probably above 800 °C [30]. The sodium aluminate consisted almost completely of anhydrous $NaAlO_2$ (PDF # 00-033-1200), and contained only minor amounts of hydrated sodium aluminates and natrite [27]. The GGBFS was almost fully amorphous (diffraction maximum at ~30.6° 2θ), and included minor amounts of merwinite ($Ca_3Mg(SiO_4)_2$; PDF # 00-035-0591).

MS consisted of spherical primary particles with a diameter of approx. 50–200 nm, fused together to form larger agglomerates, as is typical for microsilicas. As seen in SEM micrographs [25], silica CR had a very similar particle morphology. The RHA exhibited angular particle shapes, and rough particle surfaces with many pore openings with sizes up to ~500 nm. The specific surface areas of the silica materials were determined by N_2 sorption at 77 K, employing the BET method for data evaluation, to be 20.1 m^2/g for MS, 32.3 m^2/g for CR, and 13.9 m^2/g for the RHA. The medium particle size, d_{50}, determined by laser granulometry, was 24.1 μm for RHA and 17.3 μm for the sodium aluminate.

CEN Standard sand (quartz; max. grain size: 2 mm) in accordance with DIN EN 196-1:2016-11 was used as aggregate for all mortars.

2.2. Sample preparation

Table 2 gives the compositions of the investigated mortars in terms of the molar SiO_2/Al_2O_3 ratio of the binder, the water/binder weight

Table 1
Chemical composition of the starting materials.

Oxide	MS (wt%)	CR (wt%)	RHA (wt%)	Sodium aluminate (wt%)	GGBFS (wt%)
SiO_2	94.57	84.23	93.72	1.07	35.10
Al_2O_3	0.17	4.18	0.05	60.89	11.03
Fe_2O_3	0.04	0.43	0.10	0.02	0.42
TiO_2	0.01	0.06	0.01	< 0.01	< 0.01
CaO	1.15	2.97	0.97	0.52	40.64
MgO	0.23	0.17	0.38	0.01	8.26
Na_2O	0.14	0.22	0.26	36.78	0.55
K_2O	0.71	0.03	1.33	0.56	0.49
SO_3	0.21	0.16	0.35	0.08	2.20
P_2O_5	0.14	-	0.63	-	-
LOI	1.84	5.08	1.74	1.00	1.05
CO_2	-	4.20	-	0.03	0.36
Residual	0.82	2.51	0.49	0.16	0.29

LOI: loss on ignition (1000 °C); includes CO_2.
-: not determined.

Table 2
Mix-designs of the one-part alkali-activated mortars.

Sample designation	SiO_2/Al_2O_3 (mol/mol)	w/b (g/g)	Paste content (wt%)	Na_2O/CaO (mol/mol)	$H_2O/(Na_2O + CaO)$ (mol/mol)
MS_6	6.03	0.40	31.5	10.66	11.44
MS_6_b	6.03	0.40	37.4	10.66	11.44
MS_6_SL	6.31	0.38	30.0	0.80	6.74
RHA_6_b	6.05	0.40	37.6	12.40	11.30
RHA_6_SL_b	6.38	0.38	38.2	0.80	6.67
CR_3.5	3.52	0.50	30.7	6.36	11.10