External sulfate attack on alkali-activated slag

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HIGHLIGHTS

- External sulfate attack on alkali-activated slag (AAS) was studied.
- Sulfate attack was performed by 5% Na_2SO_4 solution.
- Portland-slag cement (CEM II/A-S 42.5N) was used as a benchmark material.
- Sulfate attack led to a decrease in strength of CEM II, but not of AAS.
- Alkali-activated slag showed higher resistance to sulfate attack.

ARTICLE INFO

ABSTRACT

This paper analyses the effects of external sulfate attack (5% Na_2SO_4 solution) on mechanical and microstructural properties of alkali-activated slag (AAS). Portland-slag cement (CEM II/A-S 42.5N) was used as a benchmark material.

External sulfate attack led to a decrease in strength of CEM II, but not of AAS. Under the investigated experimental conditions, AAS showed significantly higher resistance to sulfate attack with respect to the benchmark CEM II. A very pronounced resistance of AAS to sulfate attack can be explained by the absence of portlandite and unavailability of aluminum, present in C–S–H(I) and hydrotalcite gels, for the reaction with sulfates.

1. Introduction

Durability of structure during long-term exploitation is of key importance for safe and efficient functioning of concrete constructions. Durability of concrete is determined by its ability to resist weathering action, abrasion, chemical attack, or any other process of deterioration [1,2].

Chemical reactions, which alter the microstructure of cement paste, are among fundamental causes of concrete degradation. Pores of cement paste are generally filled with a highly basic solution (pH > 12.5). Therefore, any medium with a lower pH value represents an aggressive environment for cement matrix.

An important process of degradation of cement-based materials is external sulfate attack, which is the consequence of impact of sulfate ions present in soils, underground waters, sea water or industrial waste waters, on hardened concrete [3–6].

Sulfates generally cause harm to cement, but their adverse effects depend on types of cement used, nature and concentration of aggressive sulfate solution, presence of different cations and/or salts in sulfate solution, the quality of concrete, as well as concrete exploiting conditions [7,8].

External sulfate attack has been most often analyzed in ordinary Portland cement: OPC [9,10], CEM I [6,11–13], and ASTM Type I [14,15]. Hydrated cement phases most vulnerable to sulfate attack are calcium hydroxide (portlandite) as well as aluminum containing phases, whereby gypsum and ettringite are generated as reaction products. It is clear that cements which contain the lowest amount of aluminum containing phases, primarily sulfate resistant Portland cement – SRPC, show the strongest resistance to external sulfate attack, [6,9,15,16]. Reducing the amount of portlandite increases the resistance of hydrated cement to sulfate attack, therefore different materials were used as additives to Portland cement: blast furnace slag – BFS [9,16–18], fly ash – FA [9,15,18], silica fume – SF [15,19], metakaolin – MK [20], nanosilica or microsilica [18], as well as limestone – LS [9,10]. Along with these materials, the effects of external sulfate attack on properties of other types of cement were also examined: CEM II [6,12,13,21], CEM III [12,21], CEM IV [21], white Portland cement-WPC (with BFS and sodium sulfate as an activator) and high early-strength Portland cement [22]. External sulfate attack on hydrated clinker mineral tricalcium silicate (C_3S) was also investigated [14].

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Strength loss, expansion, cracking and, ultimately, disintegration are indicated as consequences of external sulfate attack [23]. Different methods were used to study the process of external sulfate attack, whereby ASTM C1012 standard method [21,22] or its modification [6] was often used. The ASTM C1012 test procedure is the only internationally recognized and standardized test procedure. However, ASTM method was criticized due to its limitation (orientation to expansion effect) [3]. Taylor indicates that, whereas laboratory studies concentrate on expansion and cracking, field experience shows that loss of adhesion and strength are usually more important [23].

In the last few decades, alkali-activated materials (AAM; material: binder, mortar or concrete) have unquestionably drawn attention of scientific and professional public as an environmentally friendly alternative to Portland cement systems [24,25].

Based on main elements the reaction products (gels) are made of, AAM can be divided into two basic groups: (a) $CaO–Al_2O_3–SiO_2–H_2O$ (C–A–S–H gel) and (b) $Na_2O–Al_2O_3–SiO_2–H_2O$ (N–A–S–H gel). Alkali-activated slag (AAS) belongs to the first group [26], while alkali-activated metakaolin (AAMK) and fly ash (AAFA) belong to the second group [27–29].

Main obstacle towards wider practical application of AAM is a lack of reliable durability data which is, above all, the consequence of non-existence of standardized methods for durability testing and evaluation criteria [25]. The majority of existing standardized methods for durability testing, which have been used for construction materials testing, were developed specifically for Portland cement systems [30]. This means that these methods are partially or entirely unsuitable for application to the analysis of AAM durability [31].

Despite the lack of appropriate standards, the importance of AAM durability testing is recognized [32,33]. Special attention was paid to the resistance of AAM to acid attack [34–36] acidic salt attack [37], sulfate attack [38–40], sea water attack [38,41], decalcification resistance [42], carbonation resistance [32,43,44], freeze/thaw and wet/dry cycles [45], rapid chloride permeability [32,44], water sorption [44] and alkali–silica reaction [32].

Microstructural and microanalytical properties of different types of cement and different slag-cement blends under the sulfate attack were studied intensively by Gollop and Taylor [46,47]. However, the effects of sulfate attack on AAS were not studied.

Forasmuch as AAS, in most cases, does not contain portlandite but predominantly C–S–H, and that aluminum is mainly present in C–A–S–H and hydrotalcite gels, this type of binding material might exhibit high resistance to sulfate attack. Other authors paid more attention to this type of binder predominantly studying physico-mechanical properties of AAS mortar and concrete, whereby different methods and criteria were used for resistance to sulfate attack testing: Koch–Steinegger (flexural strength) [38], ASTM C1012 (expansion) [38–40] and strength loss index [39,40]. Microstructural changes of AAS due to the external sulfate attack were not studied in detail.

This paper investigates the effects of external sulfate attack on mechanical properties of AAS expressed by strength loss index, with special attention being paid to the microstructural changes during sulfate attack. Commercially available Portland-slag cement (CEM II) was used as a benchmark material.

2. Experimental

2.1. Experiment design

It is well known that the selection of testing methods, for evaluation of properties of different cementitious materials in aggressive environment has dominant influence on experimental results.

Sulfate attack on Portland cement (OPC or blended) is an intensively studied process. However, experimental conditions significantly differ from each other in terms of the type of samples used (paste, mortar and/or concrete), w/c ratio, sample shape (prisms, cubes or cylinders) and dimension, curing conditions prior to sulfate attack (water, saturated limewater, temperature, time, humidity), aggressive medium type and concentration, as well as conditions of sulfate attack (full or partial immersion of samples, pH and SO_4^{2-} concentration control, time, solution agitation, recycling, etc.). Kinetics of sulfate attack is also monitored by different methods: expansion, mass loss, porosity, flexural and/or compressive strength.

Currently there is no European (EN) standard which defines experimental conditions for testing the resistance of cement systems to sulfate attack or the criteria which should be fulfilled. On the other hand, State of the art report CEN/TR 15697 [8], related to the performance testing for sulfate resistance of cement proposes the following experimental conditions and pass/fail criteria:

- Samples: $40 \times 40 \times 160$ mm mortar prisms prepared using EN 196-1 Standard sand. Water/cement ratio w/c = 0.60 (higher w/c ratio than EN 196-1 to achieve discrimination in a reasonable timescale; fixed w/c in order to improve reproducibility (compared to mortars gauged to constant flow)). Sand/cement ratio adjusted to 3.375 (limited to CEM I cements).
- Curing before exposure to sulfate solution: Minimum four weeks at 20 °C in limewater.
- Resistance testing: Prisms fully immersed in test solution (designed to test resistance of binder to sulfate attack alone, not sulfate attack and resistance to crystallization pressures).
- Aggressive solution: Na_2SO_4 solution prepared from deionised water (maximum SO_4^{2-} concentration of 10 g/l and performance at 3 g/l to be investigated). pH and SO_4^{2-} to be controlled by automatic titration (a pH of 8 ± 0.5 is suggested) and solution to be agitated/recycled. Temperature of test solution selected according to the relevant local conditions.
- Procedures to be introduced to minimize the possibility of specimen carbonation at any stage of testing.
- Pass/fail criteria: to be based on the relative strength of specimens stored in the sulfate solution and in limewater. Sulfate resistant binders will maintain 80% of strength at age of 2 years.

Unfortunately, recommended experimental conditions are not fully applicable for the AAS system, so certain modifications were necessary.

The basic goal of this investigation was to compare properties of AAS over a relatively short period of sulfate attack with properties of well-known material, such as Portland-slag cement. So, accelerated test of sulfate attack with 5% Na_2SO_4 solution was applied. pH of sodium sulfate solution was not kept constant, since eventual pH maintaining by (sulfuric) acid titration would represent combined acid–sulfate attack [3]. On the other hand, the strength change rate of slag-blended cement, due to sulfate attack, is higher when pH is not kept constant [48]. This means that appropriate mechanical and microstructural changes might be expected in a shorter period of time.

Controlling the pH simulates more closely field conditions where concrete is exposed to a mobile sulfate containing environment. However, it may not model stagnant situations [8].

It is well known that water/cement, i.e. water/binder ratio has a significant effect on degradation kinetics [49]. In AAS case high water/binder ratio of 0.6 could not be used due to the bleeding. In order to make the two systems comparable, the AAS water/binder ratio was determined providing the same rheological properties (flow table test) as the benchmark CEM II.

Water or limewater curing of AAS is not a desirable option, as it would lead to premature leaching and unavoidable loss of strength [40,50]. Instead of limewater, curing in a humid chamber was applied, whereby carbonation was not prevented [42].

Testing was performed in a period of 90 days with aggressive solution being completely renewed every 30 days. Portland-slag cement (CEM II) was used as a benchmark material.

Sulfate attack kinetics was monitored by mortar relative strength (strength loss index), while microstructural changes were monitored on paste by XRD and microscopic (SEM/EDS) analysis.

2.2. Materials

The following materials were used:

1. Granulated blast furnace slag (GBFS) – Smederevo, Serbia.
2. Sodium silicate – water glass ($Na_2O \cdot nSiO_2$) – Zemun, Serbia.
3. Sodium hydroxide (98% NaOH) – Sabac, Serbia.
4. Portland-slag cement (CEM II/A-S 42.5N) – Kosjeric, Serbia.
5. Sodium sulfate (99% Na_2SO_4) – Beograd, Serbia.

Sodium silicate was used as alkaline activator. Starting sodium silicate modulus $n = SiO_2/Na_2O$ (mass ratio) was 2.97 (9.43% Na_2O, 28.0% SiO_2). In order to reduce undesirable shrinking and avoid fast setting, low sodium silicate modulus