



Decalcification resistance of alkali-activated slag

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H I G H L I G H T S

- ▶ The effects of decalcification on properties of alkali-activated slag were studied.
- ▶ Decalcification was performed by concentrated NH_4NO_3 solution (accelerated test).
- ▶ Portland-slag cement (CEM II/A-S 42.5 N) was used as a benchmark material.
- ▶ Decalcification led to strength decrease and noticeable structural changes.
- ▶ Alkali-activated slag showed significantly higher resistance to decalcification.

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This paper analyses the effects of decalcification in concentrated 6 M NH_4NO_3 solution on mechanical and microstructural properties of alkali-activated slag (AAS). Portland-slag cement (CEM II/A-S 42.5 N) was used as a benchmark material. Decalcification process led to a decrease in strength, both in AAS and in CEM II, and this effect was more pronounced in CEM II. The decrease in strength was explicitly related to the decrease in Ca/Si atomic ratio of C–S–H gel. A very low ratio of Ca/Si ~ 0.3 in AAS was the consequence of coexistence of C–S–H(I) gel and silica gel. During decalcification of AAS almost complete leaching of sodium and tetrahedral aluminum from C–S–H(I) gel also took place. AAS showed significantly higher resistance to decalcification in relation to the benchmark CEM II due to the absence of portlandite, high level of polymerization of silicate chains, low level of aluminum for silicon substitution in the structure of C–S–H(I), and the formation of protective layer of polymerized silica gel during decalcification process. In stabilization/solidification processes alkali-activated slag represents a more promising solution than Portland-slag cement due to significantly higher resistance to decalcification.

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1. Introduction

Stabilization/solidification (S/S) is accepted as a well-established technique for the treatment of hazardous and radioactive wastes prior to re-use or final disposal [1–4]. The degree of effectiveness of S/S products is defined basically by mechanical and structural stability. Cement-based materials are most commonly used due to their low cost, significant durability and simple processing techniques [5–10].

The main purpose of the leaching studies of radioactive or other hazardous wastes that are incorporated in blocks of suitable embedding materials is to assess their potential hazard to the environment, when these blocks come into contact with water during long-term storage or disposal [7].

An important and widespread process of degradation of cement-based materials is decalcification, which is the consequence of calcium ions migration from solidified cement matrix into surrounding aggressive medium [11]. Since decalcification is a very slow reaction, this is not the degradation process frequently seen in cement-based structures. Decalcification of cement-based materials has been identified as an important issue for the long-term radioactive waste disposal in deep geological formations [12–24]. As some radionuclides show stability over a longer period of time (period of half-decay of several hundred years), decalcification of cement-based materials affected by water represents the worst case scenario, which is to be considered seriously when designing containers for radioactive waste disposal. Decalcification also affects concrete structures which have been in contact with pure or acidic waters for a longer period of time: dams, tunnels, pools, water pipes, etc. [25].

Most often, decalcification has been analyzed in ordinary Portland cement (OPC or CEM I) [12–17,26–34]. Different methods have been developed to study the process of decalcification. Water was frequently used as the aggressive medium: pure and mineralized [33,34], distilled [27], as well as deionized [11,14,15,29,31].

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A whole palette of accelerated tests was developed in order to examine the process of decalcification in real time. In some cases organic acids were used [30], while in others gradient of electric potential [14]. Sulfate salts, such as $(\text{NH}_4)_2\text{SO}_4$ [26,28,35] and Na_2SO_4 [35], were also used.

Chemical, mineral and mechanical similarity of leaching by water and concentrated solution of ammonium nitrate was established by Carde and François [13]. Decalcification by highly concentrated 6M NH_4NO_3 solution offers some key advantages compared to leaching by water. The rate of leaching is increased by two orders of magnitude and additionally, the leaching reaction in 6M NH_4NO_3 solution is almost entirely a pure decalcification, i.e. there is a small loss of silicon, even at very low ratios of $\text{Ca}/\text{Si} = 0.3$ [11]. Therefore, instead of deionized water, most tests are carried out with strongly acidified solutions, such as ammonium nitrate [11–13,16,17,19,24,26,28,32,35–37].

Although calcium leaching is a well-analyzed phenomenon, a solution that would lead to its prevention has yet to be found, notwithstanding serious efforts to minimize its harmful effect. As portlandite is the weakest link in the cement system, it is clear that cementitious materials, which contain the lowest amount of portlandite, show the strongest resistance to the process of leaching. In order to slow down the process of calcium leaching, along with the ordinary Portland cement, different authors have used various additives: silica fume [12,14,31,32], blast furnace slag [14], fly ash [31], and calcium-carbonate [27]. Along with these materials, the effect of the process of decalcification on properties of other types of cement was also examined: CEM II [24,34,37], CEM III [30,34], CEM V [34], white Portland cement (WPC) [11,35], sulfate resistant Portland cement (SRPC) [28,29,35], as well as low-heat Portland cement and high early-strength Portland cement [15]. The process of decalcification of hydrated clinker minerals was also investigated: tricalcium silicate (C_3S) [11,27,35,36], tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) [27], as well as C–S–H [36].

In S/S processes alkali-activated cements have been recognized as a more promising option than Portland cement, due to lower leachability of contaminants from alkali-activated cement stabilized hazardous and radioactive wastes [4,38–46].

Alkali-activated cement consists of an alkaline activator and cementitious material, such as blast furnace slag, coal fly ash, phosphorus slag, steel slag, red mud, and metakaolin, or a combination of two or more of them. However, to the best of our knowledge and according to available literature, there has been no research on the effects of decalcification process on the properties of alkali-activated slag.

This paper investigates the effects of decalcification process on mechanical and microstructural properties of alkali-activated slag (AAS).

2. Experiment design

The design of experimental research is based on two main states of examined materials:

- Non-degraded material – initial, i.e. reference state (cured in a humid chamber), and
- Chemically degraded material – asymptotic final state (exposed to accelerated leaching in concentrated NH_4NO_3 solution).

These two main states can be considered as asymptotic physical states of cementitious materials, especially those used in concrete structures exposed to long term impact of pure or mineralized water [17].

Table 1
Chemical composition (% m/m) and physical characteristics of GBFS and CEM II.

Composition/characteristics investigated	GBFS	CEM II
LOI at 1000 °C	2.13	2.80
SiO_2	37.50	21.70
Al_2O_3	7.27	4.62
Fe_2O_3	0.73	2.98
CaO	38.48	62.53
MgO	10.86	1.56
SO_3	0.39	2.44
S	1.51	0.00
MnO	0.30	0.22
Na_2O	0.54	0.45
K_2O	0.26	0.60
Sum	99.97	99.90
Density (kg/m^3)	2890	3020
Specific surface area (Blaine) (m^2/kg)	390	380

Decalcification was performed by concentrated 6M NH_4NO_3 solution in a period of 90 days. NH_4NO_3 solution was completely renewed every 30 days.

Kinetics of decalcification process was investigated based on the changes in mortar compressive strength. Microstructural changes were investigated on the paste by X-ray diffraction and SEM/EDS analysis.

Numerous differences in experimental conditions used to examine Portland cement systems leave little space for comparison of decalcification process of AAS and the data from literature referring to Portland cement. Consequently, in these experiments, Portland-slag cement (CEM II/A-S 42.5 N) was used as a benchmark material and the decalcification process was investigated under equal conditions for both systems, thus making this comparison credible.

2.1. Materials

The following materials were used:

- Granulated blast furnace slag (GBFS) – “U.S. Steel”, Serbia.
- Sodium silicate–water glass ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$) – “Galenika - Magmasil”, Serbia
- Sodium hydroxide (98% NaOH) – “Zorka-Pharm”, Serbia.
- Portland-slag cement (CEM II/A-S 42.5 N) – “Titan”, Serbia
- Ammonium nitrate (99% NH_4NO_3) – “Superlab”, Serbia.

Sodium silicate was used as an alkaline activator. Starting sodium silicate modulus $n = \text{SiO}_2/\text{Na}_2\text{O}$ (mass ratio) was 2.97 (9.43% Na_2O , 28.0% SiO_2). In order to reduce undesirable shrinking and avoid fast setting of AAS, low sodium silicate modulus ($n=0.6$) was used in all experiments, while Na_2O concentration was 4% in respect to the slag mass [47]. Sodium silicate modulus was adjusted by adding NaOH.

Chemical composition and physical characteristics of GBFS and CEM II are given in Table 1. GBFS was ground so that its specific surface area (Blaine) was approximately 400 m^2/kg .

2.2. Sample preparation

AAS paste was prepared by adding activator to water and then mixing it with ground slag. Water/binder ratio was 0.25 (water represents the total amount of water in the system, including water from the activator, while binder represents the total slag mass and solid part of the activator). Water/cement ratio was 0.25. Sample dimensions were 25 mm \times 25 mm \times 30 mm. Sample labels are given in Table 2.

Mortar prisms (40 mm \times 40 mm \times 160 mm) were prepared according to Serbian standard SRPS EN 196-1 (2008), which is in compliance with European EN 196-1 standard. Cement/sand

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