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Durability of alkali-activated concretes containing cement kiln by-pass dust

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Abstract. The aim of the presented work was evaluation of an effect of various conditions on the performance of two developed concretes based on alkali-activated slag and cement kiln by-pass dust (BD). BD was used as a partial replacement of natural aggregates while slag as an aluminosilicate precursor activated by a combination of waterglass and sodium hydroxide solution (resulting silicate modulus of 0.5). The concretes differed only in an activator dose which was 4 and 6% of Na₂O with respect to the slag weight. The prepared specimens were sealed-cured for the first 28 days and then their resistance to freeze-thaw cycles and aggressive solutions (ammonium nitrate, acetic acid and sulphates) was tested. Evolution of dynamic modulus showed that both concretes resisted well to freeze-thaw cycles as well as to most solutions, where their dynamic modulus tended to increase in most cases or did not change significantly. Only the concrete with 4% Na₂O showed poor resistance to acetic acid solution as the specimens completely disintegrated until 50 days.

1. Introduction

Nowadays, alkali-activated materials (AAMs) undergo an unprecedented scientific interest. One of the most popular subgroup of AAMs is alkali-activated slag (AAS) due to high early strength achieved even at room temperatures. One of the key parameters for their practical utilization is their durability and resistance to various aggressive conditions. Although wider discussion about the needs for standardization of AAMs and their testing procedures have already started, it is not finished yet. Therefore, durability aspects of AAMs are usually tested on the basis of standards for ordinary Portland cement (OPC) systems and compared to them.

Chemical degradation of the silicate binders can take place via two basic mechanisms and their combinations. These are (i) the formation of new products with deteriorating effect on a binder or a composite structure such as ettringite formed during the sulphate attack and (ii) chemical changes in a binder phase. The main hydration product of AAS is calcium-aluminium-silicate-hydrate (C-A-S-H) [1] from which particularly calcium cations can be leached out that consequently causes polymerization of silicate chains. Calcium cations can also be replaced by other ions.

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Typical combination of the above mentioned degradation processes is the action of magnesium sulphate which induces the formation of gypsum but also destabilization of C-A-S-H due to the replacement of Ca^{2+} by Mg^{2+} [2, 3]. Unlike MgSO₄, sodium sulphate was reported having much lowereffect on AAS [2, 3] or can be even better than curing in a humid chamber [4].

Decalcification of the C-A-S-H gel can be caused by the action of various organic and inorganic acids as well as acidic salts, typically ammonium nitrate [5, 6]. Very important factor that affects the degradation extent is a solubility of a resulting calcium salt, because the insoluble products can act as a barrier for further degradation [7].

AAS is usually found being more resistant to the above mentioned degradation effects compared to OPC [2, 4, 6, 8, 9]. which is attributed to the different composition of starting materials as well as the nature of hydration products, porosity etc. Also the frost resistance of AAS, key durability parameter particularly in cold and mild climate, was reported being better than that of OPC [7, 10, 11], while AAS is usually more prone to carbonation [12, 13].

Nevertheless, this work is not focused on the comparison of AAS and OPC but to the evaluation of performance of two AAS-based concretes developed within the projects mentioned in the acknowledgement at the end of this paper. These concretes have a potential to be used in practice but before that it is necessary to test them in terms of various durability criteria. Therefore, the selected results are presented in this paper. They can also serve for comparison with other similar materials.

2. Experimental part

2.1. Materials and concrete composition

Ground granulated blast furnace slag with the Blaine fineness of 400 m²/kg was alkali-activated with the combination of waterglasshaving silicate modulus of 1.85 and 50% sodium hydroxide solution. The silicate modulus of the resulting activator mixture was 0.5 and dry matter (Na₂O + SiO₂) content of 44.2%.Slag was combined with a natural aggregate, namely sand (0–4 mm) and gravel (4–8 mm) in the portions calculated using Füllergranulometric curve. Total aggregate to slag ratio was 3:1 by weight. Sand was partially replaced by BD whose amount was 10% by the slag weight. To ensure the desired workability 1% (relative to slag weight) of a lignosulphonate-based plasticizer was also added. Water to slag ratio of both concretes was 0.37 including water from the activator.

Chemical composition of both slag and BD is given in table 1. Mineralogical composition of these raw materials was determined using X-ray powder diffraction with Rietveld evaluation method where fluorite (CaF₂) was used as an internal standard. The measurement was carried out in Bragg-Brentano configuration in the range of 5–90° 20, X-ray tube with copper anode with voltage of 30 kV and electric current of 40 mA was used. It revealed that the slag consisted predominantly of an amorphous phase (~84%), calcite (CaCO₃, ~9%) and minor crystalline phases typical for slags (akermanite, melilite, merwinite) while BD consisted mainly of amorphous phase (~44%), free CaO (~16%), sylvite (KCl, ~20%), larnite (C₂S, ~10%) and arcanite (K₂SO₄, ~9%) and traces of quartz (SiO₂). Particle size distribution of both slag and BD determined using laser granulometer (in a dry state) is given in figure 1. It can be seen that both these materials have very similar median (around 10 μ m), but BD has much broader distribution of particles which is due toits origin.

Table 1. Chemical composition of slag and by-pass dust as determined using X-ray fluorescence.

	CaO	SiO ₂	Al_2O_3	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO_3	Mn ₂ O ₃	TiO ₂	P_2O_5	Cl
slag	39.6	38.9	8.9	0.27	8.8	0.39	0.40	1.4	0.83	0.32	0.01	_
BD	25.9	6.5	2.5	1.6	0.48	0.44	17.1	5.2	_	0.14	0.08	10.3

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Figure 1. Particle size distribution of the slag and cement kiln by-pass dust.

2.2. Specimens preparation and curing regime

Mixing was performed in a 50l laboratory pan mixer. Firstly, all liquid components were combined together, then slag was added and after that BD and aggregates. A fresh concrete was cast into the moulds to prepare specimens with the dimensions of 40 mm \times 40 mm \times 160 mm and sealed with a stretch foil. After 24 hours, specimens were demoulded, sealed with stretch foil to prevent moisture loss and stored at laboratory conditions at a temperature of \sim 25°C until the age of 28 days. After that the specimens were unsealed and transported tovarious degradation media (see section 2.5).

2.3. Strength testing

During the storage in autogenous conditions, flexural and compressive strengths were tested at the age of 1, 2, 3, 7, 14, 21 and 28 days. At each time, 2–3 specimens were used to test flexural strength while compressive strength was tested on their broken parts.

2.4. Dynamic modulus determination

Determination of the dynamic modulus E_d was carried out using the device Pundit PL-200 with the frequency of 150 kHz according to equation (1), where the factor k was assumed being 1, v_p was ultrasonic pulse velocity calculated from the time of the passing of the signal and length of the prism and ρ was bulk density of the specimen. Three prisms of each concrete were tested for each degradation conditions (see section 2.5) and each prism was measured three times at each testing time, i.e. just before the start of the degradation and from time to time within the period up to about half of a year.

$$E_d = k \cdot v_p^2 \cdot \rho \tag{1}$$

2.5. Degradation conditions

Degradation of the specimens took place in basically two ways – by freezing and thawing cycles and in various aggressive solutions. Also water-cured specimens were tested for comparison.

Freezing-thawing cycles were performed according to ČSN 73 1322, i.e. one cycle comprised storage at -20° C for four hours and at 20°C for two hours. Dynamic modulus of the specimens was determined after 68, 125 and 250 cycles.

Aggressive solutions were namely sodium sulphate and magnesium sulphate (concentration of both was 50 g/l of water, i.e. 0.32 and 0.38 mol \cdot dm⁻³, respectively), ammonium nitrate (6 mol \cdot dm⁻³) and acetic acid whose pH was maintained between 3–4 by regular checking using pH meter and additions of a concentrated acid. These tests were carried out at laboratory temperature (~25°C). The concentration of each solution was selected based on a literature review: Sulphate resistance tests across various national standards for Portland cement are summarized in [7], while concentration

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of ammonium nitrate was selected the same as in [5, 6] used for AAS testing. And finally, acetic acid

3. Results

renewed every month.

Before the degradation of both concretes started, evolution of their compressive and flexural strength was monitored. The results given in figure 2 showed that increased dose of activator from 4 to 6% Na₂O led to increase in compressive strength which corresponds well with the expectations and also with the previously published results [14]. Such effect was not observed in the case of flexural strength which was similar for both concretes. Although flexural strength values are more scattered, which can also affect the results, the observed trend is related rather to higher internal stresses as a consequence of shrinkage increased by the dose of activator [14, 15]. After 28 days, concretes with 4 and 6% Na₂O reached around 43 and 57 MPa with obvious tendency to further increase.

with pH around 4 was have been already used for the degradation of AAS [9]. The solutions were





Performance of both concretes in aggressive solutions is expressed as a relative values of dynamic modulus to its initial values obtained just before the degradation is given in figures 3 and 4. Absolute values of dynamic modulus water-cured specimens can be seen later in table 2 showing the results from frost resistance determination and were very similar for all sets of specimens used for the degradation in various solutions, i.e. around 37.0 GPa at the beginning of degradation.

Gradual increase in dynamic modulus of the reference water-cured samples shows the well-known long-term hydration potential of AAS, far beyond 28 days, which was also suggested by the compressive strength development. Approximately the same dynamic modulus evolution in time was observed in the solution of sodium sulphate. Similar trends (in strength evolution) were recorded in [2, 4] where also microstructural analyses were performed but did not show the formation of products related to sulphate attack. Therefore, Sodium sulphate is not an aggressive medium for AAS. This was explained by low availability of calcium and aluminate ions as well as low permeability of AAS. Sodium sulphate can be also used as an activator for AAS and in that case, formation of ettringite, C-A-S-H and layered double hydroxides are formed [16].

Contrary to sodium sulphate, magnesium sulphate has deleterious effect on AAS. According to literature [2, 3], its effect lies in the decalcification and therefore destabilization of C-A-S-H with simultaneous formation of gypsum from leached calcium ions. This results in volume expansion, cracking and thus contribute to AAS degradation. In spite of these findings, it can be surprising that dynamic modulus of both tested concretes did not markedly change in time. Probably, longer exposure is needed to observe more pronounced degradation. However, it is also important to note, that the evaluation of the degradation extent is strongly dependent on the used approach. In this study,

the values of dynamic modulus were related to the initial values before the immersion to the solutions, while relating to water-cured specimens is also possible and probably more common. When the latter approach is used, unchanged properties in an aggressive solution and simultaneously their increase in water results in increasing degradation extent. Taking this into account, the results obtained in this work correspond well with the results published in [2]. Also for the case of ammonium nitrate, dynamic modulus did not change noticeably over the testing timescale which is in good agreement with the already published results [6].



Figure 3. Evolution of the dynamic modulus of concrete with 4% Na₂O in various environments.



Figure 4. Evolution of the dynamic modulus of concrete with 6% Na₂O in various environments.

The last degradation solution was that of acetic acid. Dynamic modulus of concrete with 4% Na₂O only slightly decreased after 21 days but then rapid degradation leading to complete disintegration

of the specimens within a few weeks occurred as can be seen from figure 5. Such result was unexpected for us since during some similar tests on AAS the degradation was limited to the first several millimetres from the surface and did not progress deeper even from long-term viewpoint. One possible explanation could be different curing conditions, because in the present study, the specimens were sealed to ensure autogenous conditions, while they were immersed in water in the former case. It was expected that self-desiccated specimens can quickly absorb much higher amount of acid which consequently induces much severe degradation. Therefore, two series of specimens made of later prepared concrete with 6% Na₂O were tested. The first one was immersed in water for five days and then in acetic acid, while another one was left at 20°Cfor five days. In figure 4, they are denoted as soaked and dried, respectively. However, the results (figure 4) showed that none of the two series disintegrated within the first 50 days indicating that there is another reason for the inconsistent performance in acidic environment.

The only difference in composition of both concretes is the activator dose. Better performance of the concrete with the higher activator dose can be related to increased C-A-S-H formation supposed by about one third higher compressive strength compared to concrete with lower activator dose after 28 days. This probably results in lower permeability which reduces the penetration of aggressive media into the specimen. Additionally, it was reported [8] that residual aluminosilicate gel acts as a barrier for further ingress of acid into the specimen. Increased dose of activator and thus higher amount of silicates could also reduce the Ca/Si ratio in the matrix which is also considered contributing to higher stability of C-A-S-H [9].

Both concretes showed very good resistance to freezing and thawing because, up to at least the first 125 cycles (see table 2), the changes in dynamic modulus were only negligible and the above mentioned issue of relating the values arises again. Hopefully, it could be overcome by prolonged curing of the specimens before the start of the degradation as also e.g. ČSN 73 1322 prescribes for blast furnace slag cements, pozzolanic cements etc.



Figure 5. Specimens of concrete with 4% Na₂O in acetic acid after 49 days.

Table 2. Freezing-thawing resistance of AAS concretes with various dose of activator expressed as changes absolute values of dynamic modulus in GPa ± standard deviation (first line) and in relative values to the start of experiment (second line, in brackets).

Concrete	Conditions	0 cycles	68 cycles	125 cycles	250 cycles
40/ No O	Water (reference)	36.3 ± 0.8 (100%)	37.0 ± 0.7 (102%)	37.2 ± 0.8 (102%)	$\begin{array}{c} 40.2\pm 0.7 \\ (111\%) \end{array}$
4% Na ₂ O	Frozen- thawed	$\begin{array}{c} 37.0 \pm 0.4 \\ (100\%) \end{array}$	35.0 ± 0.5 (94.6%)	$\begin{array}{c} 36.1 \pm 0.5^{*} \\ (97.6\%) \end{array}$	30.0 ± 2.8 (81.1%)
(0/ N= 0	Water (reference)	37.4 ± 0.6 (100%)	_	$41.8 \pm 0.5 \\ (112\%)$	$\begin{array}{c} 42.3 \pm 0.8 \\ (113\%) \end{array}$
0% Na ₂ U	Frozen- thawed	37.0 ± 0.6 (100%)	_	36.2 ± 0.4 (97.8%)	$\begin{array}{c} 23.9 \pm 0.7 \\ (64.6\%) \end{array}$

*Between the first 125 cycles and the next 125, specimens were immersed in water for 49 days without freezing and thawing. Nevertheless, their dynamic modulus did not change during this period as it was 36.3 ± 0.6 GPa just before the start of the last 125 cycles.

4. Conclusions

In this study, resistance of two AAS-based concretes to freezing and thawing cycles and to various aggressive solutions was evaluated in terms of their dynamic modulus development. Both concretes showed very good performance in most of these aspects. Their dynamic modulus started to noticeably decrease after around 250 freezing and thawing cycles. Both concretes behaved similarly also in most solutions showing unchanged or even increasing dynamic modulus compared to that at the beginning of degradation and therefore good resistance to these solutions. Only acetic acid had negative effect on concretes, particularly on that with 4% Na₂O, which completely disintegrated during the first 50 days of exposure.

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References

- Puertas F, Palacios M, Manzano H, Dolado J S, Rico A and Rodríguez J 2011 A model for [1] the C-A-S-H gel formed in alkali-activated slag cements J. Eur. Ceram. Soc. 31 pp 2043-56
- Bakharev T, Sanjayan J G and Cheng Y-B 2002 Sulfate attack on alkali-activated slag concrete [2] Cem. Concr. Res. 32 pp 211-6
- [3] Ismail I, Bernal S A, Provis J L, Hamdan S and van Deventer J S J 2012 Microstructural changes in alkali activated fly ash/slag geopolymers with sulfate exposure Mater. Struct. 46 pp 361–73
- Komljenović M, Baščarević Z, Marjanović N and Nikolić V 2013 External sulfate attack on [4] alkali-activated slag Constr. Build. Mater. 49 pp 31-9
- Varga C, Alonso M M, Mejía de Gutierrez R, Mejía J and Puertas F 2014 Decalcification [5] of alkali-activated slag pastes. Effect of the chemical composition of the slag Mater. Struct. **48** pp 541–55

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- [6] Komljenovic M M, Bascarevic Z, Marjanovic N and Nikolic V 2012 Decalcification resistance of alkali-activated slag J. Hazard. Mater. 233-234 pp 112–21
- [7] Provis J L and van Deventer J S J 2014 Alkali activated materials (Dordrecht: Springer)
- [8] Bernal S A, Rodríguez E D, Mejía de Gutiérrez R and Provis J L 2012 Performance of alkaliactivated slag mortars exposed to acids *J. Sustain. Cem.-Based Mater.* **1** pp 138–51
- [9] Bakharev T, Sanjayan J G and Cheng Y B 2003 Resistance of alkali-activated slag concrete to acid attack *Cem. Concr. Res.* **33** pp 1607–11
- [10] Shi C, Krivenko P V and Della R 2006 Alkali-Activated Cements and Concretes (Oxon: CRC Press)
- [11] Pacheco-Torgal F, Abdollahnejad Z, Camões A F, Jamshidi M and Ding Y 2012 Durability of alkali-activated binders: A clear advantage over Portland cement or an unproven issue? *Constr. Build. Mater.* 30 pp 400–5
- [12] Puertas F, Palacios M and Vázquez T 2005 Carbonation process of alkali-activated slag mortars J. Mater. Sci. 41 pp 3071–82
- [13] Bakharev T, Sanjayan J G and Cheng Y-B 2001 Resistance of alkali-activated slag concrete to carbonation *Cem. Concr. Res.* **31** pp 1277–83
- [14] Aydın S and Baradan B 2014 Effect of activator type and content on properties of alkaliactivated slag mortars *Compos. Part B-Eng.* **57** pp 166–72
- [15] Melo Neto A A, Cincotto M A and Repette W 2008 Drying and autogenous shrinkage of pastes and mortars with activated slag cement *Cem. Concr. Res.* **38** pp 565–74
- [16] Mobasher N, Bernal S A and Provis J L 2016 Structural evolution of an alkali sulfate activated slag cement J. Nucl. Mater. 468 pp 97–104