# Decalcification resistance of various alkali-activated materials

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**Abstract**. The resistance of alkali-activated materials (AAMs) to degradation processes, particularly the decalcification, was studied in this paper. The ground granulated blast furnace slag was alkali-activated using various activators with the same activator dosage 6% $Na_2O$ by slag weight (sodium hydroxide, sodium waterglass and sodium carbonate) and subjected to testing of decalcification resistance (immersion in 6M $NH_4NO_3$) for 84 days. The reference samples were stored in water. The progress of degradation was studied using the phenolphthalein technique, mechanical properties testing (compressive and flexural strength), and dilatometry analysis or weight measurements. The results obtained were compared to the CEM III/A 32.5R. The significant loss of mass along with the deterioration of mechanical properties were observed for all binder types, still some of the AAMs showed better durability than the cementitious one.

## 1. Introduction

The production of Ordinary Portland Cement (OPC) increases every year due to the needs of the building industry. However, the production of OPC represents a highly energetically and economically demanding process. Furthermore, the environmental aspects should be considered as well since the production of one tone of OPC is accompanied by the formation of one tone $CO_2$ [1]. Alkali-activated materials represent a suitable alternative from the economic and environmental point of view if properly composed (selection of suitable alkaline activator and aluminosilicate precursor). The current state of art remarks higher resistance against the action of aggressive media (high temperature [2], sulphates [3], chlorides [4] or acidic solutions [5]) for the AAMs contrary to OPC. Nevertheless, the real applications of the AAMs in the building industry are limited due to the absence of relevant standards and insufficient verification of long-term properties when exposed to degradation processes during the service life as well.

Degradation processes can be realized due to several reaction mechanisms: formation of new reaction products (e. g. carbonation, sulphate corrosion, alkali-silica reaction, …); processes of ionic exchange and regarding the topic of this paper mainly by processes of leaching of components of hydration products, thus through decalcification of binder gel or minor reaction products. The decalcification processes are based on the simultaneous leaching of $Ca^{2+}$ from the binder gel together with the formation of corresponding calcium salts. The decalcification is related to simultaneous reduction of C/S ratio in

binder gel to form only the residual S-H gel with limited utility value instead of the C-S-H or the C-A-S-H [6].

The alkali-activated blast furnace slag (AABFS) shows better resistance against the decalcification processes than the Ordinary Portland Cement, as stated in studies like [6–9] because of several aspects. Firstly, the AABFS binder gel has more intensely cross-linked silicate chains due to the incorporation of alumina units in C-A-S-H gel compared to the main hydration product of cement hydration (C-S-H gel). Besides this, the A-S-H can form a relatively stable passivation layer. Another benefit arises from the absence of portlandite in AABFS, since it represents a potential "first" target for decalcification. This causes opening of the porosity (an increase of permeability) after the complete leaching which is accompanied by the increase of degradation rate. Other like lower initial C/S ratio or lower porosity also explain the greater stability of the AAMs in acidic media.

The experimental study of decalcification resistance can be realized using the accelerated test – immersion in a solution of 6M $NH_4NO_3$ [10]. The benefit of this method contrary to other acidic leaching is that there are no changes in silicon concentration. Thus, the changes of microstructural and psychico-mechanical properties are related only to decalcification itself.

The present study analyses the influence of the type of alkaline activator used for the alkali-activation of blast furnace slag to the resistance against the degradation by decalcification reactions using the immersion in 6M solution of ammonium nitrate. A comparative study of CEM III/A-32.5R was carried out too.

## 2. Experimental procedure

### 2.1. Raw materials

*2.1.1. Blast furnace slag (BFS).* The slag was from Kotouč Štramberk, s.r.o. (Blaine specific surface area of 400 $m^2 \cdot kg^{-1}$). The chemical composition is shown in Table 1. The amorphous content was 84%, while the rest was crystalline (akermanite – 9.5%, calcite – 3.7%, merwinite – 2.3% and quartz – 0.5%) according to the X-ray diffraction (XRD) using Rietveld method.

**Table 1.** The chemical composition of the BFS determined by X-ray fluorescence (XRF) analysis.

| Chemical composition in wt. % | | | | | | | | | |
|------|------|------|------|------|------|------|------|------|------|
| CaO | $SiO_2$ | MgO | $Al_2O_3$ | $SO_3$ | $TiO_2$ | $K_2O$ | MnO | $Na_2O$ | $Fe_2O_3$ |
| 41.1 | 34.7 | 10.5 | 9.1 | 1.4 | 1.0 | 0.9 | 0.6 | 0.4 | 0.3 |

*2.1.2. Alkaline activators.* Liquid sodium water glass (NaWG) obtained from Vodní sklo, a.s.  – Silicate modulus ($M_s$) = 1.89; Sodium hydroxide (SH) 50% solution – PENTA s.r.o. (pure); Sodium carbonate (SC) – INCHEMA s.r.o (pure).

*2.1.3. Other materials.* Standard siliceous sand according to ČSN EN 196-1 was used for the mortar preparation. The cement for universal use – Optimcem – CEM III/A 32.5R (Cemmac, s.r.o.) served as comparison binder to the AAMs. The pure ammonium nitrate of obtained by Lachner s.r.o. was used as degradation medium in concentration of 6M.

### 2.2. Tests and methods
The samples of individual binders had dimensions of 40 × 40 × 160 mm and were prepared according to the ČSN EN 196-1. The samples were stored in sealed moulds for 24 h hours, and then they were demoulded and stored in water up to 28 days (to reach a certain degree of hydration before the degradation tests took place). The leaching method consisted of submerging the 28-day water cured specimens (time zero in all of the figures below) in 6M $NH_4NO_3$ and water.

The testing temperature was kept constant (25°C) during the experiment (28, 56 and 84 days of exposition to the media). The sampling and analysis of the samples with selected techniques took place in the same period. The immersion solutions were renewed every 28 days.

The binder systems were mortars with sand to binder (slag or cement) ratio of 3:1. The water to binder ratio was the same for all alkali-activated materials (0.45), same as the activator dosage (6% $Na_2O$ by the slag weight). Water to binder ratio was equal to 0.45 in case of the cementitious system as well, but there was no alkaline activator added.

*2.2.1. Mechanical properties testing.* The determination of mechanical properties (compressive and flexural strength) was done as prescribed in ČSN EN 196-1 using the Desttest 4310 Compact A (Beton System, s.r.o.). The flexural strength was measured in the three-point arrangement. The flexural strength was determined on three samples of each binder type in each interval, meanwhile the compressive strength was tested on six samples. The final values below were calculated as the mean values.

*2.2.2. Phenolphtalein technique.* The phenolphthalein technique was used for the determination of the progress of the degradation reactions since they are accompanied by the decrease of pH of matrices. The phenolphthalein is an acid-base indicator, which changes colour with dependence on the pH. It changes colour from purple-red (alkaline pH) to colourless. The fracture surfaces of the samples after the three-point bending test were treated with a 1% solution of phenolphthalein in ethanol. The purple-red colour can be seen in case of the non-degraded sample. On the other hand, the damaged samples show no colour change (since the decrease of pH took place) and remain colourless. The treated fracture surfaces were then photographed, and the dimension of the colourless area was measured and evaluated using the optical analysis method.

*2.2.3. Dilatometry analysis, weight measurement.* The samples with dimensions of 40 × 40 × 160 mm with implemented brass contacts were used for dilatometry analysis, same as the weight measurement. The samples were measured before and during the degradation tests in a defined period and the data obtained were then evaluated.

## 3. Results and discussion

According to the literature that for the decalcification in 6M $NH_4NO_3$ to take place pH below the 9.25 is necessary [9]. Thus, the pH was monitored for various systems and reached values of 8.10; 8.35; 8.58 and 8.66 after 84 days for NaOH; NaWG, $Na_2CO_3$ and CEM, respectively. The most noticeable changes in pH were observed during the initial 14 days period since the pH increased to 9.01; 9.22; 9.31, and 9.48 in the same order. Thus the need of solution exchange during the degradation reactions was confirmed.

### 3.1. Mechanical properties

The development of mechanical properties in time as a function of activator type and the storage medium (water/6M $NH_4NO_3$) is depicted in Figure 1 and Figure 2. The lowest absolute values of compressive and flexural strength were obtained for the NaOH activated blast furnace slag. Nevertheless, this system showed the lowest drop of compressive strength when exposed to 6M ammonium nitrate compared to water. The residual compressive strength (calculated as percentage difference compared to water) follows: NaOH>NaWG>$Na_2CO_3$>CEM with values of 80.2; 77.7; 58.3, and 27.3% after 84 days of deposition to the ammonium nitrate solution. Secondly, residual flexural strength compared to water storage about 82.5; 69.6; 54.6 and 21.6% was observed in the following alkaline activator order NaWG; NaOH; $Na_2CO_3$ and ending with the cementitious system after 84 days of deposition to ammonium nitrate solution. The whole development of residual compressive and flexural strength over the testing period is shown in Figure 3.

The cementitious system showed the lowest residual compressive and flexural strength, same as the highest loss of mass as specified below. Both trends have simultaneous character and increase

with prolonging time of deposition to $NH_4NO_3$. This is related to the decalcification reactions taking place and simultaneous leaching of $Ca^{2+}$ from the gel structure. The highest resistance to the decalcification was observed for the NaOH and NaWG activated systems. This can be related to factors like higher pH of pore solution or character of hydration products. Quite similar trends were reported in Komljenović et al. [7] study, where residual compressive strength about 41; 19, and 18% after 30; 60, and 90 days of the exposition were determined. Meanwhile, the residual strength for AABFS system activated using the mixture of NaWG+NaOH ($M_s$=0.6) was 94; 91 and 85%. These results are comparable with the ones in the present study and confirm higher resistance of the AAMs, especially when water glass is used. In contrary to study [7] no signs of retardation of degradation rate for the cementitious system were not detected in the present paper. Significant deterioration of mechanical properties of OPC and AABFS (NaWG+NaOH; $M_s$=1.2) due to the decalcification in 6M $NH_4NO_3$ was also presented in the study of Varga et al. [8]. They stated a decrease of compressive strength about 34% and 77% for AABFS and OPC after 21 days of immersion. Both research groups attribute better resistance of AABFS against decalcification to more cross-linked C-A-S-H gel structure along with the absence of portlandite, lower porosity and permeability and last but not least positive effect of alumina units forming protective barrier retarding the further progress of decalcification. The degradation in a solution of ammonium nitrate is accompanied by a decrease in the C/S ratio and deterioration of mechanical properties.
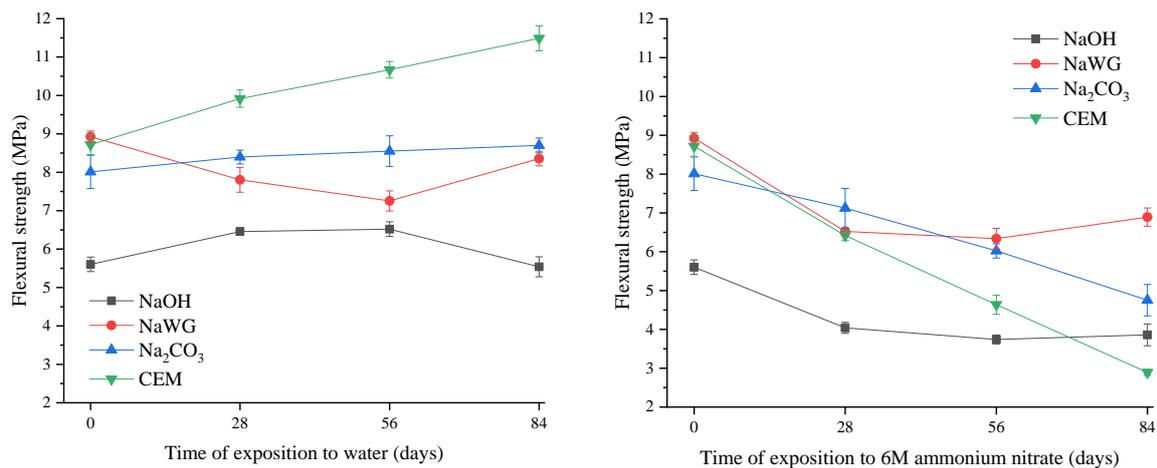


**Figure 1.** Dependence of flexural strength of various binder types on the time of exposition to water and 6M ammonium nitrate.
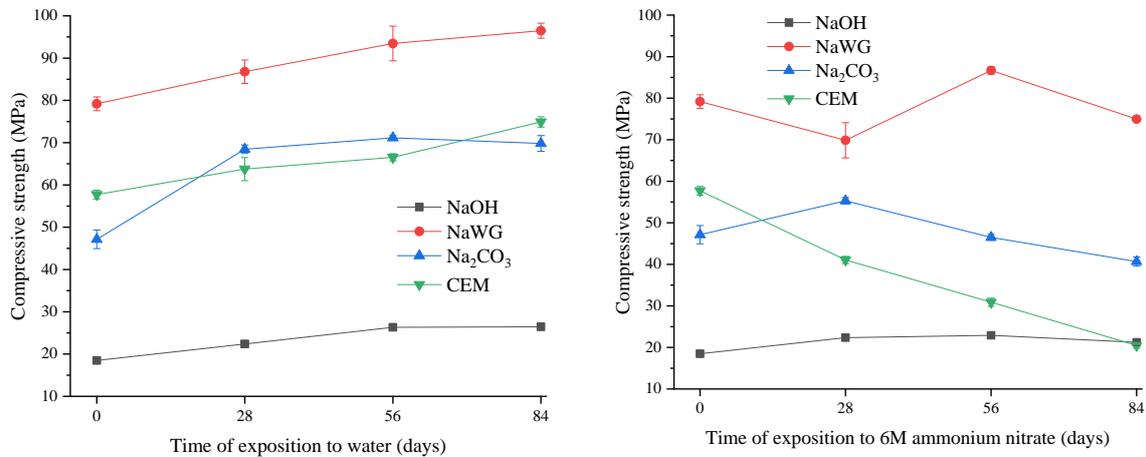
**Figure 2.** Dependence of compressive strength of various binder types on the time of exposition to water and 6M ammonium nitrate.
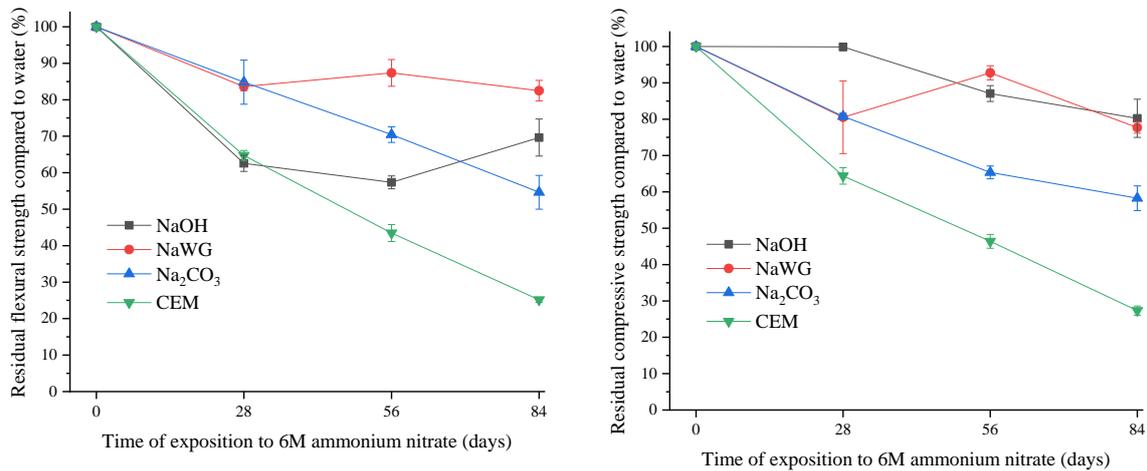


**Figure 3.** Residual flexural and compressive strength of various binders stored in 6M $NH_4NO_3$ compared to water as a function of time.

### 3.2. Dimensional and weight changes

None of the tested binder systems showed a remarkable loss of mass due to the water storage. The weight changes were between -0.2% (NaWG) and +0.5% (NaOH) after 84, respectively total of 112 days of exposition to water. Those changes are not related to degradation processes but only different sorption of water and leaching of activator in time. On the other hand, the significant loss of mass was observed for the cementitious system stored in 6M $NH_4NO_3$, since the simultaneous drop of the weight of the samples about 1.1; 1.7; 2.6 and 3.3% after 14; 28; 56 and 84 days was observed. The loss of mass of the cementitious system is noticeably higher than for any of AAMs. The loss of mass of the AAMs decreased in the following alkaline activator order NaOH>NaWG>$Na_2CO_3$. Still, the values of weight change are only about -1.1; -0.7 and -0.4%, thus not such crucial compared to the CEM. Overall comparison is presented in Figure 4.

Secondly, Figure 5 presents the development of length changes of the samples stored in water and the one exposed to 6M $NH_4NO_3$. It can be concluded that storage in water causes no changes in the dimension of the samples since it lies between -0.0005 and 0.009% after the 84days of water storage. The exposition of the NaOH and NaWG activated samples to ammonium nitrate did not cause any significant length changes (0.0015 and 0.004% after the 84 days), contrary to the $Na_2CO_3$ activated system where simultaneous shrinkage of the samples was observed. It reached the value of -0.1249%

after 84 days. Nevertheless, similar trend was as well noticed for the cementitious system but with a higher final shrinkage of about -0.1776%. To sum up, the highest shrinkage same as the loss of mass was observed in the case of cementitious system, which confirms that AAMs show better resistance against aggressive environments as presented in studies [6–9].
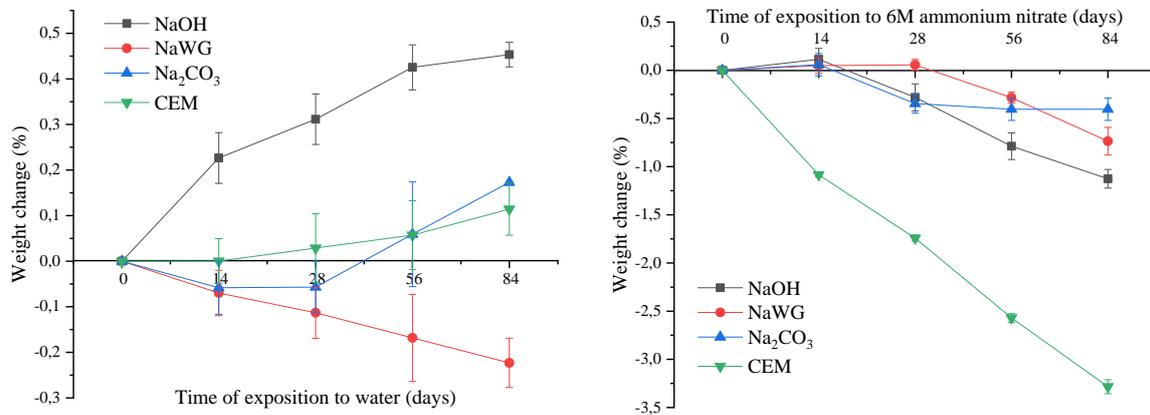


**Figure 4.** Time development of weight loss of the various binders due to the immersion in water and 6M $NH_4NO_3$.
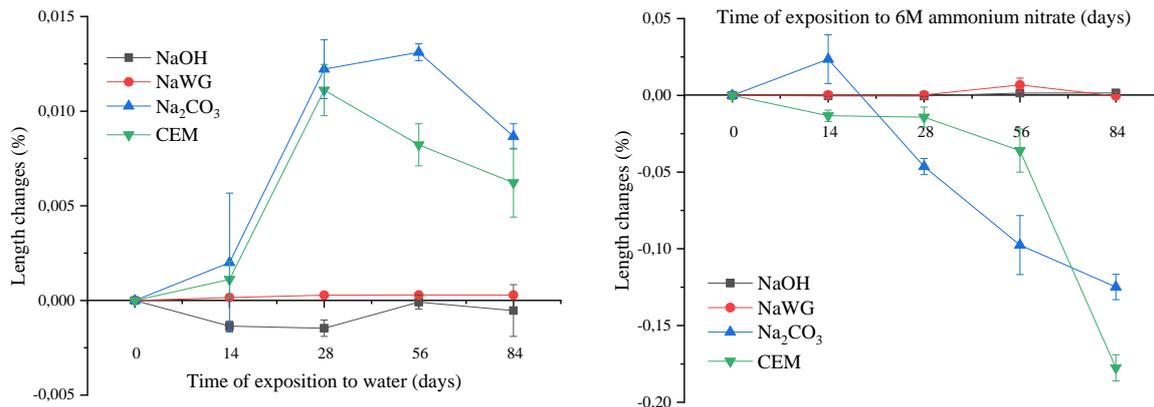


**Figure 5.** Time development of length changes of the various binders exposed to water and 6M $NH_4NO_3$.

### 3.3. Phenolphthalein technique

There were no colour changes (samples remained purple-red after the treatment using the phenolphthalein solution) for any of the tested binder systems stored in water during the whole testing interval (0–84 days), as shown in Table 2. Only minor changes in colour intensity were observed between the various AAMs and the CEM. These minor changes correspond to the alkalinity of the pH of the pore solution. Thus, the system activated using the NaOH had the most intense-purple red colour contrary to the less intense purple-red colour of the cementitious system. The intensity of colouration decreases as follows NaOH>NaWG>Na$_2$CO$_3$>CEM. Overall, any of the tested AAMs same as the CEM did not show any signs of decrease of pH of matrices. Thus it indicates that no degradation took place in water.

**Table 2.** The pictures of phenolphthalein treated fracture areas of various AAMs and CEM binders.

| | H$_2$O | | | 6M NH$_4$NO$_3$ | | |
|---|---|---|---|---|---|---|
| | 28 days | 56 days | 84 days | 28 days | 56 days | 84 days |
| **NaOH** | | | | | | |
| **NaWG** | | | | | | |
| **Na$_2$CO$_3$** | | | | | | |
| **CEM** | | | | | | |
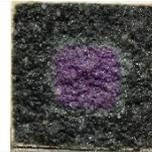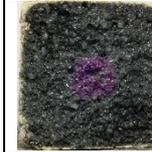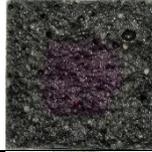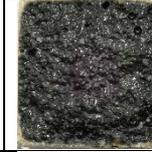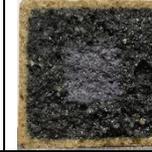
On the other hand, immersion of the samples to the 6M NH$_4$NO$_3$ was related to significant changes (corresponded with the presence of colourless area – degraded parts). The area of non-affected (non-degraded) layer decreases with prolonging exposition time to the ammonium nitrate for all binder types (Table 2). The depth of degraded area calculated using the optical analysis method (the value corresponds to the depth from one side of the sample to the middle) is in Figure 6. This graph shows that the depth of the degraded layer increases in time in the following order of binder systems NaOH>Na$_2$CO$_3$>NaWG>CEM. Still, the differences between the activators for the AAMs are not convincing. The cementitious systems showed the lowest degraded layer. However, the loss of mass or deterioration of mechanical properties was the highest.
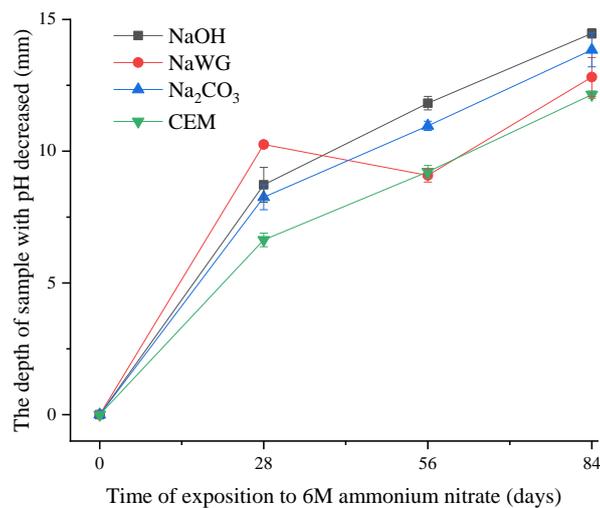


**Figure 6.** The depth of sample with pH decreased for various binder types as function of time.

## 4. Conclusion

This paper investigated the effect of alkaline activator type used for the alkali activation of blast furnace slag on the decalcification resistance. Decalcification was realized under the effect of 6M solution of ammonium nitrate for 28, 56 and 84 days. This resistance was characterized with a meaning of mechanical properties, weight and length changes and phenolphthalein technique. The CEM III/A 32.5R was used as comparison material. Based on the obtained results, the following conclusions can be drawn:

- AABFS showed superior durability compared to the cementitious system.
- Simultaneous decrease of residual strength was observed for all types of the binder. However, the cementitious system showed the highest deterioration (residual compressive and flexural strength about 30% after 84 days).
- Significant loss of mass was not detected for any of the AAMs tested (<1%), but CEM system showed a loss of about 3.3%.

## Acknowledgments

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