

CARBONATION RESISTANCE OF ALKALI-ACTIVATED SLAG UNDER NATURAL AND ACCELERATED CONDITIONS

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Introduction

The use of alkali-activated slag (AAS) has been recognised for a long time as an alternative solution to Ordinary Portland cement-based binders. However, the durability of AAS-based binders is still unknown¹, which limits their application in engineering practice. Carbonation is of the great interest for AAS since it induces both chemical and physical changes. The change of the pore structure after carbonation and CO₂ uptake for AAS are rarely reported. This paper investigates the carbonation of AAS pastes in natural (laboratory and outdoors (unsheltered)) and accelerated conditions. The effect of the different exposure conditions on AAS pastes was studied in terms of the gel pore structure, chemical and mechanical properties.

Materials

The chemical composition of the blast furnace slag (BFS) was 39.17% CaO, 34.40% SiO₂, 11.53% Al₂O₃, 7.81% MgO, 1.42% Fe₂O₃, 1.6% SO₃, 0.23% Na₂O and 0.58% K₂O. The alkaline activator was prepared by mixing two solutions, 4M NaOH and sodium silicate with modulus ratio Ms=3.37 (SiO₂/Na₂O, mol-based ratio), and liquid to BFS ratio was 0.5. The pastes were cast in cylinder moulds of 54x100 mm². The samples were sealed and cured for 28 days in fog room. After 28 days of curing the samples were removed to the laboratory conditions at 20°C and about 55% relative humidity for additional 28 days (preconditioning of the samples). At the age of the 56 days, the samples were exposed to different environmental conditions as described in Table 1.

Table 1: Exposure conditions

	Reference (sealed)	Natural laboratory	Natural outdoors	Accelerated
CO ₂ concentration	0	0.039%	0.039%	1%
Relative humidity	60-99%	50-60%	80-98%	60%
Temperature	20°C	20°C	0-20°C	20°C

Methods

The pH measurements were carried out on the simulated pore solution, by dissolving 1 g of powdered sample in 10 ml of de-ionised water. The suspension was magnet rotated and maintained during 1 hour at ambient temperature. Subsequently, the pH was measured by a standard colour chart and pH meter 827 Metrohm. XRD was performed with a step size of 0.02° for a 2θ angle range between 25 and 60 degrees. Thermogravimetric analysis was carried out using a heating rate of 10°C/min between 40°C and 1000°C, with an argon purge at 70 ml/min. The release of H₂O and CO₂ gasses were monitored from the mass loss by means of mass spectroscopy (MS). ESEM was used to collect images in backscattered electron detector mode. Pore structure was investigated by nitrogen adsorption tests. The compressive strength was examined on cube samples, with dimensions of 40x40x40 mm³.

Results and Discussion

Figure 1 presents the pH measurements of the pastes in different exposures and time intervals (Table 1). The minimum pH is 12.18 that was detected in natural outdoors conditions. Generally, the high pH values suggested strong alkaline media under all exposures after 1 year, indicating slightly carbonated or noncarbonated pore solution of AAS pastes. However, minerological composition analysis was performed to ensure that reaction phases of AAS in addition to pore solution also did not undergo carbonation. The XRD patterns of AAS pastes under different exposure conditions have shown that the C-S-H peak is the main found peak and presence of carbonation products was not identified (Figure 2).

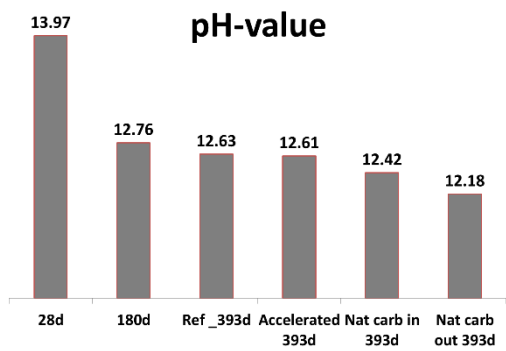


Figure 1: pH of AAS pastes

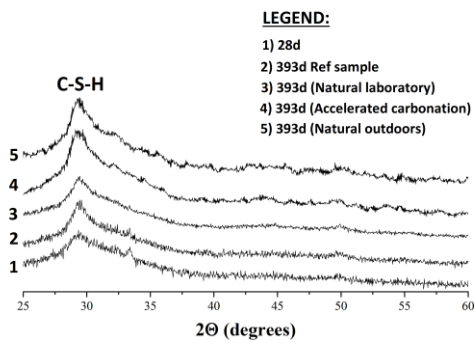


Figure 2: XRD patterns of AAS pastes

The TGA results are presented in Figure 3 (left). The respective MS curves for release of H₂O and CO₂ are plotted in the Figure 3 (right). The TGA curves of all the pastes exhibited a one-stage thermal degradation process during raising temperature, suggesting homogeneous reaction product. The mass loss at about 105–345°C corresponds to the emission of chemically bound water from the gel. From the TGA curves, the highest mass loss is measured in the conditions of accelerated carbonation. It is assumed that in these conditions gel was continuously developing due to the constant control of relative humidity value (Table 1). The MS curves clearly show that

the release of water was dominant. Very little CO₂ was released for AAS paste in the natural outdoors conditions suggesting slight carbonation of the paste.

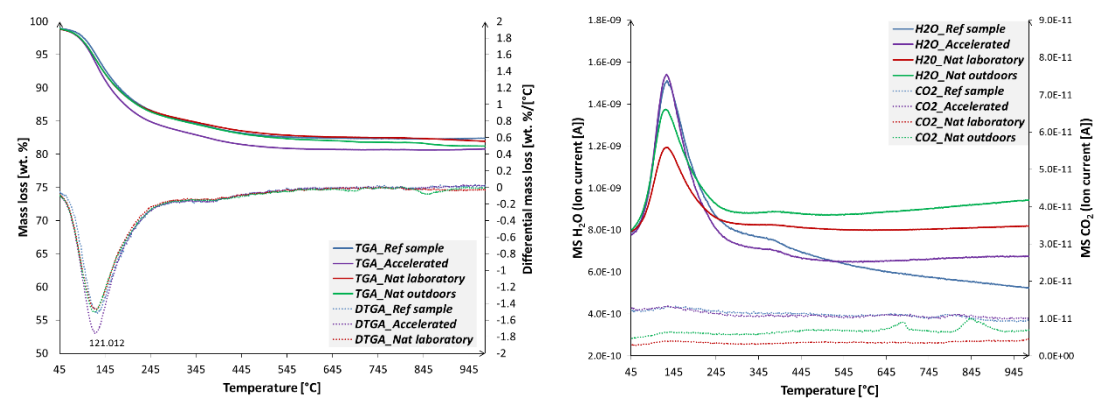


Figure 3: TGA/DTGA curves (left) and MS curves (MS_H₂O and MS_CO₂) (right) of AAS

Influence of the exposure conditions on porous network of AAS was also studied. The pore structure was tested first by Mercury intrusion porosimetry (MIP) method². The intrusion volume was very little so it was not possible to detect any characteristic pore diameter by MIP². Therefore, nitrogen adsorption was used to test pore structure. It was found that the pore size distribution (PSD) is in the range of the gel pores, with minimum pore diameter of 2 nm and maximum pore diameter of 10 nm. The PSD indicates dense and compact pastes, where CO₂ can hardly diffuse and react. Nevertheless, the pore volume was significantly higher for AAS in outdoors conditions (5*10⁻³ cm³/g) compared to others (<1*10⁻³ cm³/g). This can be due to much severe outdoors weathering of material. The visually observed microcracking of the samples beside gel pores might contribute to pore volume increase.

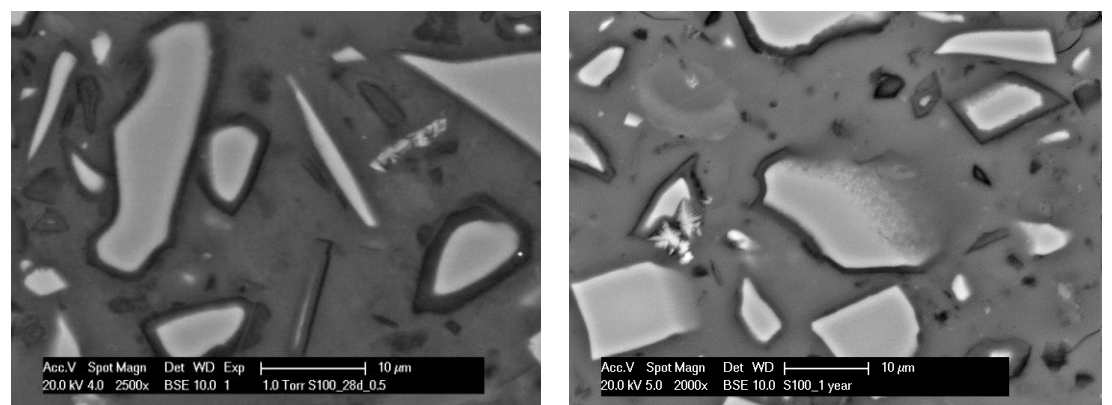


Figure 4: ESEM images of the AAS paste after 28 days of curing (left) and 365 days of natural laboratory carbonation (right)

The ESEM images of AAS pastes are presented in the Figure 4. It is demonstrated that the AAS pastes have similar microstructure where the gel was uniformly dispersed around the unreacted BFS particles regardless the age of the samples. No traces of the carbonation were observed, which was confirmed by strength measurements (Figure 5). The compressive strength of the samples under different exposure

conditions did not decrease compared to the strength values before exposure. The longer exposure time improved the strength due to the further hydration of the anhydrous BFS at the later ages (Figure 5).

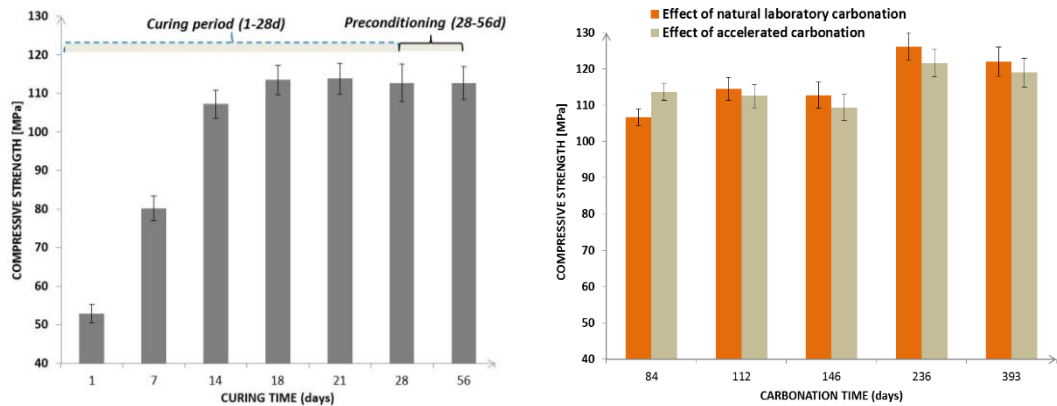


Figure 5: Compressive strength of AAS pastes

Conclusions

The dense microstructure and high pH values (>12.18) inhibited the carbonation and indicated the gel stability of AAS pastes in the studied conditions. The results from TGA/MS and XRD measurements demonstrated that the AAS pastes did not undergo chemical changes during exposure time. Nitrogen adsorption tests identified the gel pores (<10 nm) to be dominant in the system, which blocked the CO₂ to diffuse into the pastes within the exposure period. The dense AAS microstructure exhibited high mechanical strength (~110 MPa). The results of this study shed the light on the importance and the effect of the physical properties (pore size distribution; connectivity) and alkalinity (pH) on the carbonation resistance of AAS pastes.

Acknowledgement

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References

1. K. Arbi, M. Nedeljkovic, Y. Zuo and G. Ye, "A Review on the Durability of Alkali-Activated Fly Ash/Slag Systems: Advances, Issues and Perspectives", *Ind Eng Chem Res*, **55** (19) 5439-5453 (2016).
2. M. Nedeljkovic, K. Arbi, Y. Zuo and G. Ye, "Physical properties and pore solution analysis of alkali-activated fly ash-slag pastes", in *Proceedings pro113: International RILEM Conference Materials Systems and Structures in Civil Engineering (MSSCE 2016) on Concrete with Supplementary Cementitious Materials*, Lyngby, Denmark, 2016.