INVESTIGATION OF POROSITY AND CARBONATION DEPTH IN ALKALI-ACTIVATED GGBS MORTAR

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Abstract

The effect of type of activator on porosity and CO_2 penetration of the alkali activated ground granulated blast furnace slag (GGBS) mortar is an important behavior which is required for designing a durable concrete mixture. This research article investigates the influence of three types of activators consisting of NaOH, $Na_2.nSiO_2$ and $K_2.nSiO_2$ on the porosity, pore size and distribution, as well as carbonation depth in activated GGBS mortar which will affect the compressive strength, shrinkage, water penetration and durability of the concrete incorporating these types of pastes. It was observed that the GGBS activated by NaOH showed higher porosity than the other activators, while mixtures with $Na_2.nSiO_2$ and $K_2.nSiO_2$ demonstrated lower porosity, respectively. The results of carbonation depth were also coincident with the porosity of specimens, in which the one activated by NaOH was fully carbonated. In contrast, the least affected mortar was activated by $K_2.nSiO_2$. This trend was also observed for the compressive strength, while $K_2.nSiO_2$ provided the highest compressive strength stored in the air, although its rate of reduction due to CO_2 exposure was also the highest among other activators.
Keywords: Porosity, carbonation, GGBS, alkali-activated slag, mortar

1. INTRODUCTION

Alkali activated binders as one of the replacement alternatives for Ordinary Portland cement (OPC) has become more popular over the last 60 years. Different behaviors of this type of binders are proposed to be investigated by researchers [1]. In spite of its practices in China, Russia and Ukraine, there are uncertainties about the long-term and durability of concrete using this types of binders [2].

Several test methods are using for measuring the carbonation in concrete and mortar. One of the specific procedure for mortar specimens was described in RILEM TC56-MHM by using phenolphthalein spray on the cutting section of mortar prism [3]. The unclear point in this testing procedure is the method of splitting or cutting the specimens. Wet cutting always will influence the phenolphthalein procedure in comparison with dry splitting procedure and subsequently will give different results for OPC mortar.

The Portland cement carbonation occurred due to the reaction of CO_2 in atmosphere with $Ca(OH)_2$ and/or Ca rich C-S-H gels to form calcium carbonate (CO_2 could be dissolved in rain

drops or in the water inside the concrete pores) [4,5]. Alkali-activated binders are low in calcium content, in contrast its gel structure is enriched in aluminum and alkalis. Therefore, different mechanisms should be expected from these types of binders depending on their source materials and activators. Moreover, the rate of both natural carbonation, as well as, accelerated carbonation should be influenced by source materials. The carbonation process of the Portland cement exposed to 3 % CO_2 is almost similar to the corresponding process with 0.03 % CO_2 [5], although no other proof for change of carbonation mechanism was found yet, specifically for the higher concentrations of carbon dioxide.

The accelerated carbonation is a method of specimen's carbonation exposure that it could be influenced by CO_2 in the condition including higher concentration of CO_2. Shi et al stated the rate of natural carbonation in alkali silicate-activated binders are lower than 1 mm/year [2]. On the other hand, another experimental investigation declared that the carbonation depth in alkali-activated concrete will be between 13 mm to 25 mm after 240 hours exposure to 7 % CO_2 [6].

A study performed by Bernal et al showed that the carbonation progress is highly dependent to the CO_2 concentration, as well as difference of total and capillary porosity of hardened concrete [5,8].

The hydroxide activators have different effect on the CO_2 absorption in comparison with other types of activators, since hydroxide activators are well known in carbon dioxide absorption in CO_2 flow or air [4,9].

The accelerated carbonation has completely different effect on the behavior of the alkali-activated concrete in comparison with the natural condition carbonation which provided far more damaging condition for steel corrosion in reinforced concrete elements than in the natural carbonation condition. Actually, in natural carbonation of alkali-activated binders no considerable reduction could be observed in PH value of pore solution, while in accelerated condition the PH of pore solution decreased sharply [4].

The sorptivity of geopolymer concrete increases with the age of concrete, while the sorptivity of OPC concrete decreases by age which shows the opposite behavior during the long-term reaction. Moreover, the porosity of geopolymer concrete increases by exposing to the carbonation field [10].

2. EXPERIMENTAL PROCEDURE

2.1 GGBS
The GGBS used in this research was including the following chemical composition, listed in Table 1. The activity indexes of the GGBS were 1.02 and 1.25 at 7 and 28 days, respectively, based on EN 450-1 [12]. Moreover, the density of mentioned GGBS determined 2.5 g/cm^3 by pycnometer test method and the blain of 4,050 cm^2/g was measured according to EN 196-6 [13].

Table 1: Chemical composition of ground granulated blast furnace slag (GGBS)

	Fe	Mn	MnO	SiO$_2$	TiO$_2$	Al$_2$O$_3$	CaO	MgO	S	Na$_2$O	K$_2$O
GGBS	0.24	0.12	0.16	36.62	0.91	11.34	42.13	6.48	1.42	0.3	0.53

2.2 Aggregates
The aggregates which were used for the production of mortar, were standard reference sand according to EN 196-1 [14].

2.3 Activators

Three types of activators were used in this research that all were solutions in water. Two types of water glasses including $Na_2.nSio_3$ (Betol 52) and $K_2.nSiO_2$ (Geosil 14,517) which contained the 45 % concentration of solid material in the solution having density of 1.55 g/cm^3 and 1.50 g/cm^3 and molar ratio (SiO_2/Na_2O) of 2.1 and 1.7, respectively. The other activator was sodium hydroxide which was solved in water with the concentration of 16 mol/L and 24 hours before preparing the mortar in order to equalize the temperature of solution with the room temperature.

2.4 Mixture design

In this study more than 20 mixtures designs with water to binder ratio (W/B) of 0.5 were provided based on EN 196-1 in order to evaluate the effect of activator type on the GGBS paste separately and combination of two or three of them on the GGBS as binder. However, five mixtures compositions which were more highlighted are presented in this article, listed in Table 2. Regarding the previous studies, the final compressive strength of the alkali-activated GGBS could be reached by curing the specimens in 60°C for 24 hours due to the acceleration of hydraulic reaction. Thus, the specimens in this study cured for 24 hours in 60°C in order to obtain their final strength, then exposed to the accelerated CO_2 condition.

Table 2: Mixture composition

Mixture	Sand (g)	GGBS (g)	Water (g)	NaOH (g)	$Na_2.nSiO_3$ (g)	$K_2.nSiO_3$ (g)	A.A./Binder (%)
1	1,350	450	203	-	40	-	4
2	1,350	450	203	-	-	40	4
3	1,350	450	203	40	-	-	4
4	1,350	450	184	14	30	30	8
5	1,350	450	182	19	-	60	8

2.5 Sampling and curing

The mortar mixture was produced according to EN 196-1. Then, the mortar was poured in the triple prismatic mold having the dimensions of 160×40×40 mm and it was put on the vibrating table for two minutes to be compacted. Thereafter, the filled mold was covered by a glass plate and cured for (24 ± 1)°C hour in a climate chamber having (92 ± 2) % humidity and (20 ± 1)°C as well as (60 ± 1)°C temperature regarding the experiment plan respectively. The specimens were demolded after 24 hours and for alkali-activated specimens, they were wrapped in cling film in order to keep the humidity of the specimens constant until the considered curing time reached.

2.6 Carbonation test

The provided mortar specimens were tested according to the RILEM TC56-MHM (CPC-18 Measurement of hardened concrete carbonation depth). Based on the mentioned recommendation, the mortar specimens must be produced in 160×40×40 mm prisms and exposed to the target condition. While in RILEM recommendation CPC-18 that is proposed to consider the natural carbonation condition (0.03 % CO_2 concentration) [3], based on the previous studies on the accelerated carbonation of Portland cement paste, the mechanism of

carbonation will be similar to the natural condition when the specimens are exposed to 3 % carbon dioxide concentration [5]. Therefore, the 3 % concentration of CO_2 was considered for this study to apply carbonation on the provided specimen.

After the specific period of time of exposure, the specimens were cut into the slices having 2 cm thickness. Then, the cross sections of specimens were sprayed with the 1 % phenolphthalein solution in 70 % ethyl alcohol. The dark pink parts of the sprayed area showing the non-carbonated part having PH value of higher than 9 and the carbonated areas will be colorless. The depth of carbonation was determined by measuring the depth of colorless parts from the edge of the specimen with 0.5 mm precision. Moreover, the compressive strength of specimens after a period of time exposure to carbon dioxide was measured based on the EN 196-1.

2.7 Mercury intrusion porosimetry

In order to evaluate the volume of capillary pores, as well as its distribution, the mercury intrusion porosimetry method according to ISO 15901 was used [15]. For this purpose, the Pascal 140/440 (low/high pressure porosimetry) was used to measure the porosity of carbonated, as well as non-carbonated parts in mixture 1-4. In this experiment, the 3-4 gram of dried specimen in vacuum desiccator was prepared to put in the equipment canister to start the test by increasing the mercury pressure up to 200 MPa. Subsequently, the pores distributions graph was drawn by calculating the volume mercury penetration at specific pressure.

2.8 Compressive strength

Compressive strength of produced mortars in this research was tested according to EN 196-1 [14].

3. RESULTS AND DISCUSSION

The capillary porosity of the mortar as one of the most effective criteria in rate of carbonation, as well as other durability hazards is considered. By increasing the capillary porosity, specifically the larger pores the probability of CO_2 penetration will be increased that leads to increase the carbonation occurrence through the specimens.

In Fig. 1 the cumulative pore volume distribution, as well as relative pore volume is demonstrated with respect to the variation of pore size. It could be clearly observed that more than 85 % of the pores are smaller than 1 μm and the rest of 15 % are smaller than 0.1 mm. The total volume of the pores in the GGBS mortar using $Na_2.nSiO_2$ activator was 93.85 mm^3/g measured. Another mixture which was activated by another type of silicate based activator, $K_2.nSiO_2$ was tested in mercury intrusion apparatus and the results are shown in Fig. 2. This type of activator made lower porous structure 82.36 mm^3/g in the mortar of alkali-activated GGBS which had a considerable influence on the mechanical, as well as the durability properties of these types of binders. The distribution of pore size also showed the lower pore diameter than the first mixture which was stating the lower penetration potential for the penetration of the fluids through the mortar or concrete matrix.

The effect of NaOH as an activator on the porosity of alkali-activated GGBS is moderately different from the two previous silicate based activators, specifically in pore size distribution which included larger pores than the two previous mixtures, shown in Fig. 3. The pore volume of alkali-activated GGBS with NaOH was 99.88 mm^3/g measure that with respect to activated mortar with $Na_2.nSiO_2$ showed 8 % increase and with $K_2.nSiO_2$ demonstrates 21 %

enhancement. On the other hand, the dispersion of the pores according their sizes is completely different as for sodium and potassium silicate based activated GGBS 18 % and 16 % of the pores volume were larger than 1 μm, respectively, whereas in NaOH activated GGBS mortar, 28 % of pores were larger than 1μm.
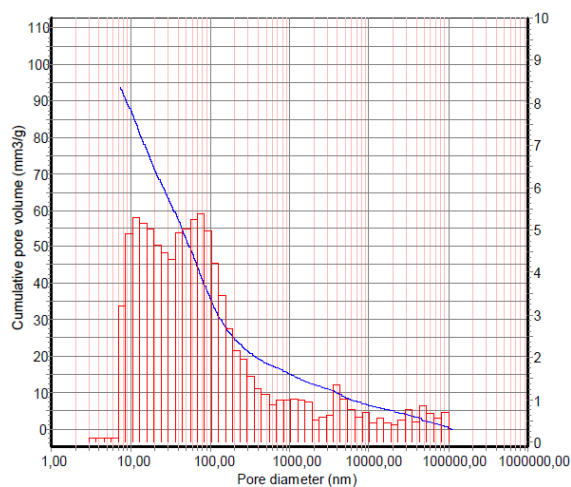

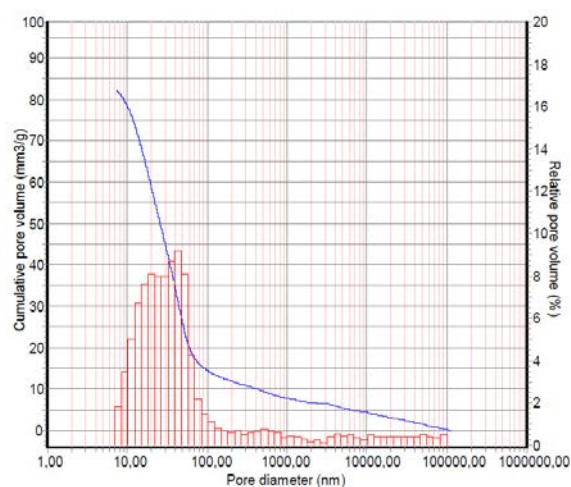**Figure 1: Pore volume distribution of GGBS activated by Na$_2$.nSiO$_2$ with respect to pore size**

Figure 2: Pore volume distribution of GGBS activated by K$_2$.nSiO$_2$ with respect to pore size
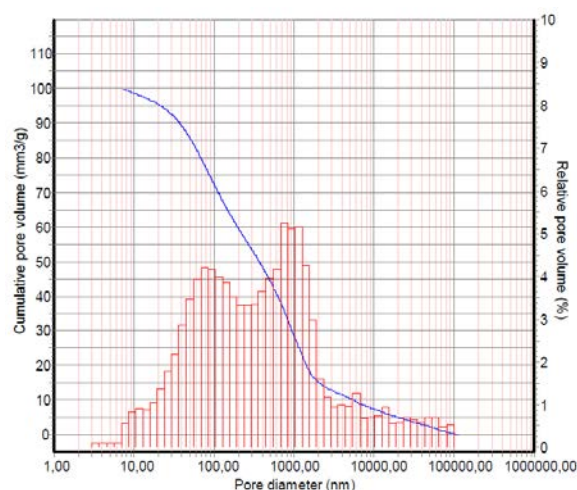
Figure 3: Pore volume distribution of GGBS activated by NaOH with respect to pore size

The photos of the mortar prisms after exposing to the CO$_2$ (Bottom) as well as natural air condition (Top) with (Left) and without spraying phenolphthalein (Right) are shown in Fig. 4-6. By comparing the cross section of mixture 1 (Fig. 4) and mixture 2 (Fig. 5) which were the activated GGBS with Na$_2$.nSiO$_2$ and K$_2$.nSiO$_2$ respectively, it could be concluded that the sodium silicate based activator was highly affected by CO$_2$ than potassium silicate based activator. Apart from chemical composition of both activators, the higher porosity of the Na$_2$.nSiO$_2$ can be one of the main reasons for the higher depth of carbonation in the similar

condition. It can also be observed from the cross section of the specimens that the gray parts are already carbonated or affected by carbonation and the green parts are not influenced by the carbonation mechanism yet.
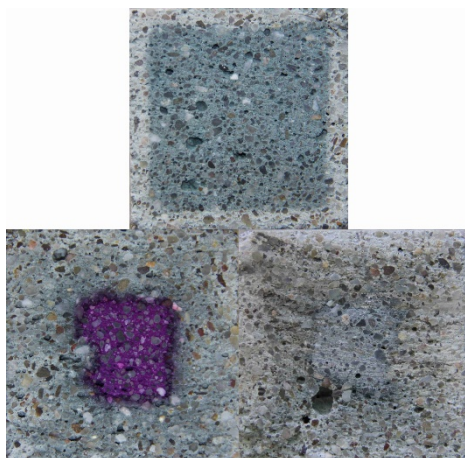

Figure 4: The cross section of activated GGBS mortar specimen with $Na_2.nSiO_2$ exposed to room condition (Top) and 3 % CO_2 condition phenolphthalein sprayed (Left) without phenolphthalein (Right)
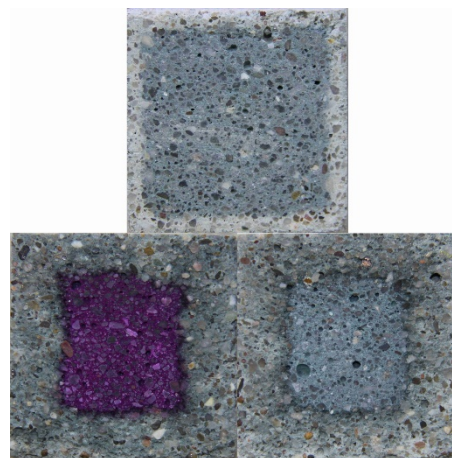

Figure 5: The cross section of activated GGBS mortar specimen with $K_2.nSiO_2$ exposed to room condition (Top) and 3 % CO_2 condition phenolphthalein sprayed (Left) without phenolphthalein (Right)
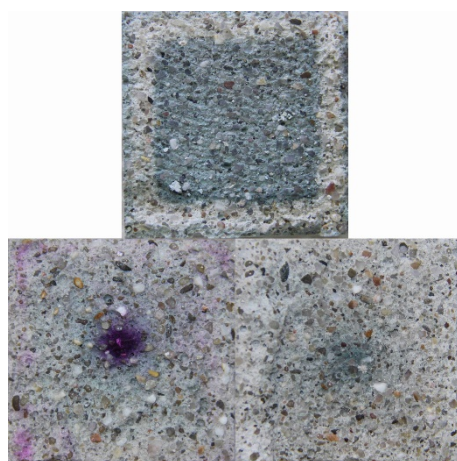

Figure 6: The cross section of activated GGBS specimen with NaOH exposed to room condition (Top) and 3 % CO_2 condition, with (Left) and without phenolphthalein (Right)

The carbonation depth in Fig. 6 which is showing the carbonation through alkali-activated GGBS specimen using NaOH as activator is completely different from the other mixtures using silicate based activators, shown in Fig. 4 and Fig. 5.

By comparing the depth of carbonation after 7 days, it can state that the depth of carbonation in mixture 4 does not have a considerable difference with mixture 2 including $K_2.nSiO_2$ which is the main reason of resistance against carbonation in alkali-activated GGBS (Fig. 7). Whereas

the corresponding porosity of mixture 4 that was considerably lower than mixture 2, is not highly affecting the carbonation mechanism in alkali-activated GGBS. The compressive strength of alkali-activated GGBS specimens after 7 days in room condition $((21 \pm 1)°C$, relative humidity of (55 ± 5) %) and also 3 % carbon dioxide are represented in Fig. 8. The highest reduction in compressive strength was experienced 33 % decrease by activated GGBS with $K_2.nSiO_2$.

The compressive strength in mixture 1 and 2 using NaOH and $Na_2.nSiO_2$ decreased up to 30 % and 27 % respectively. Although the corresponding carbonation depth of activated GGBS with NaOH was the highest among the other two silicate based activators, the compressive strength reduction of $K_2.nSiO_2$ activated GGBS mortar was higher than NaOH activated GGBS mortar. Interestingly, the compressive strength of mixture 4 having 8 % activator showed 18 % reduction which was a little (about 1.5 %) lower than that of mixture 5 activated by 6 % $K_2.nSiO_2$ + 2 % NaOH instead of 3 % $K_2.nSiO_2$ + 3 % $Na_2.nSiO_2$ + 2% NaOH. It can be concluded that using potassium based silicate activator leads to higher decreases in compressive strength of alkali-activated GGBS mortar due to exposure to 3 % CO_2 condition.
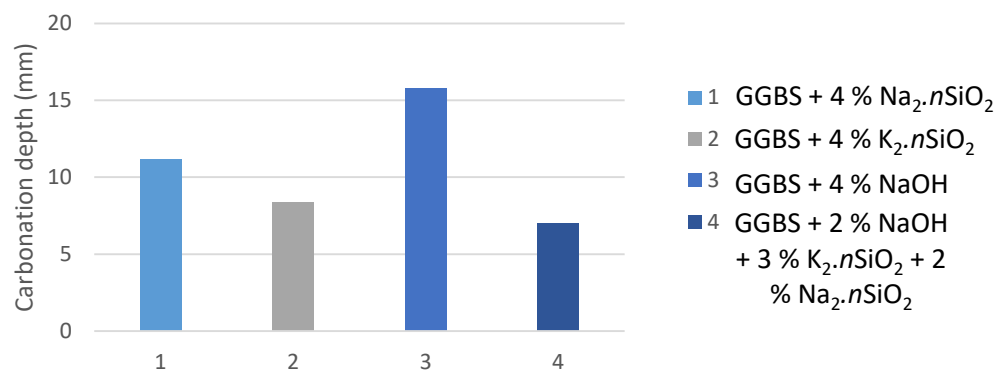

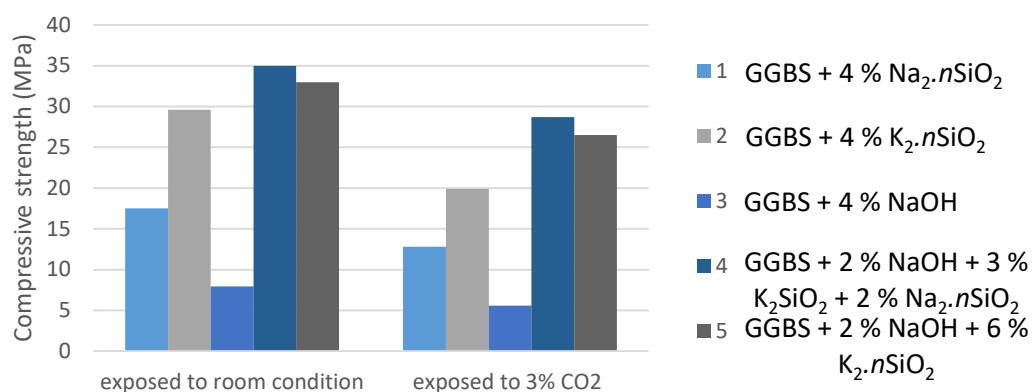**Figure 7: Carbonation depth of alkali-activated GGBS mortar mixtures 1-4, exposed to 3 % CO₂ after 7 days**

Figure 8: Compressive strength of alkali-activated GGBS mortar mixtures 1-5, exposed to room condition and 3 % carbon dioxide condition for 7 days

4. CONCLUSIONS

− Due to the higher absorption feature of CO_2 by NaOH activator, activated GGBS mortar using this type of activator shows highest porosity, as well as carbonation depth than $K_2.nSiO_2$ and $Na_2.nSiO_2$.

− Increasing the dosage of alkali activator improves porosity and in contrary reduces the carbonation depth, although the rate of decrease in carbonation depth is not linearly related to the porosity.

− The carbonation mechanism has lower effect on the reduction of compressive strength in alkali-activated GGBS with NaOH and $Na_2.nSiO_2$ than $K_2.nSiO_2$, although the compressive strength of $K_2.nSiO_2$ activated GGBS has considerably higher value than the two other activators. It means that the compressive strength of alkali-activated GGBS with $K_2.nSiO_2$ is the most affected mixture by carbonation.

ACKNOWLEDGEMENTS

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