Effects of wetting and drying on alkalinity and strength of fly ash/slag-activated materials

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HIGHLIGHTS

- Alkali leaching was found to be a main cause of neutralization of geopolymer (GP).
- Alkalinity drop of GP subjected to wetting, drying and carbonation was examined.
- Inside alkalinity gradient of GP in wetting and drying environments was clarified.
- Color reaction to the phenolphthalein indicator was clarified for wetted or dried GP.
- Strength change of GP subjected to wetting, drying and carbonation was investigated.

ARTICLE INFO

ABSTRACT

The alkalinity of alkali-activated materials, so-called geopolymer (GP), is attributed to the alkali activator remained in the pores. For the application of GP in reinforced concrete as binder, it is necessary to investigate the alkalinity change of GP concrete in various environments. In this study, after GP concrete (GPC) and GP mortar (GPM) specimens, which used active fillers of fly ash (FA) and ground granulated blast furnace slag (GGBS), were stored in water, wet-dry repeating, accelerated carbonation (AC), and AC-dry repeating environments for a certain period, we observed the coloring reaction to the spraying phenophthalein indicator, measured pH values in different depths and the compressive strengths, and did microstructure analysis by SEM. A comparison was also performed between GPM and Portland cement (PC) mortar specimens. It was found that, the alkalinity of GP mortar is much easier to decrease no matter in any of above environments, compared to PC mortar. Heat-cured GP has a higher alkali leaching resistance in the wet-dry repeating environment than ambient air-cured GP. Carbonation only decreases the alkalinity in the outer zone, but drying and wetting redistributes the alkalis and promotes the movement of internal alkalis to the outer zone even to the surface of GP, resulting in an alkalinity drop in both the outer zone and the inner zone. The AC-dry repeating causes a greater alkalinity drop than the wet-dry repeating. The AC results in a faster and greater alkalinity drop in the outer zone, compared to the water immersion. Carbonation and water immersion can raise GP's strength, but intense drying causes cracks to harm the strength of GP.

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1. Introduction

Alkali-activated material (AAM), so-called Geopolymer (GP), has been thought as an environment-friendly binder for its less CO$_2$ emission and massive waste recycling [1–3]. GP also has many desirable characteristics, such as early strength development, high fire and acid resistances, and no alkali aggregate reaction [4–6]. However, if GP is used practically in reinforced concrete as binder, GP concrete must have desirable neutralization resistance in various environments like Portland cement (PC)-based concrete since the corrosion of reinforced steel bars is mainly caused by the decline of concrete alkalinity.

In PC-based concrete, pH is mainly controlled by the amount of portlandite (Ca(OH)$_2$). Dissolution of Ca(OH)$_2$ and outside diffusion causes the deposit of calcium carbonate on concrete surface, so-called efflorescence. However, because calcium carbonate is not soluble and uneasily eliminated by washing, continuous leaching

of $Ca(OH)_2$ is inhibited. Thus, the alkalinity drop of PC concrete is mainly resulted from carbonation, which is well-known carbonate reaction between $Ca(OH)_2$ and CO_2.

However, the pH of GP is mainly controlled by the pore solution. According to Rowles et al. [7], Na^+ of alkali activator is partially bound to the aluminum inside the gel structure with a relatively strong Na-O bond, neutralizing the charge of $Al(OH)_4^-$ group, and partially bound weakly to part of the silicon in the $SiO-(Na^+)-Si^-$ form, associated with molecular water $(Na(H_2O)_n^+)$. That is to say, a part of Na^+ in the alkali activator is taken up during the formation of reaction products, while other Na^+ ions are present in the pore solution. The pH reduction is a result of three concurrent mechanisms: continuous precursor dissolution, alkalis leaching, and carbonation of NaOH in the pore solution [8,9].

Some previous accelerated carbonation tests showed that the carbonation resistance of GP concrete is lower than that of PC concrete [10–14]. It was reported that GP concrete has lower carbonation resistance in an atmospheric environment too [15–18]. Bernal et al. concluded that the effect of carbonation on the pH of pore solution is highly dependent on the partial pressure of CO_2 [8,19]. In addition, in the carbonation process, the crystallization pressure due to the precipitation of sodium carbonates in the pores of GP may introduce internal stress, which consequently affects the mechanical properties of GP in great or less degree varying with the pore structure [20,21].

The alkalis of pore solution are able to diffuse toward the surface of GP, particularly when GP material is exposed to cycles of wetting/drying or moisture transfer. GP is generally more prone to efflorescence formation, compared to Portland cement. This feature is related to its high porosity, to the high alkali concentration or excess alkali oxide (sodium, potassium, etc.) in the pore solution, and to the weak bond of alkali cations in the aluminosilicate framework [22–24]. The diffusion of alkalis toward the GP surface will affect or suppress the later activation of residual precursors, which would be harmful to the strength development [25]. Alkali leaching also damages the microstructure of GP [20], and leads to a faster propagation rate of carbonation front in GP [9]. These latest results clearly showed that efflorescence, usually attributed to alkali leaching, is a durability issue rather than aesthetic problem, since the drop of alkalinity may damage the protective layer around the steel reinforcement [26].

On the other hand, Škvára et al. [23] observed a greater reduction in compressive strength of fly ash-based GP samples after immersed in the water, compared with those exposed to the air. It should be noted that in this specific case, the water-immersed samples only lost the alkalis by leaching, and no crystallization process occurred. The negative effect of water immersion was attributed to the instability of sodium aluminosilicate gel.

It is natural that water moves into or out of concrete with humidity fluctuation in the air or getting wet with rain. Concrete may also be used in underground structure or marine structure in contact with water. As stated above, leaching of alkalis reduces the alkalinity and harms the mechanical property of GP. There are some studies focused on the influencing factors of efflorescence, such as slag content [21,27], curing temperature [26,27], alkali activator sort [26]. However, the effects of sole action of alkali leaching and concurrent action of carbonation and alkali leaching on the alkalinity and strength change are not fully clear now.

As popular precursors, fly ash (FA) and ground granulated blast furnace slag (GGBS) are usually blended to prepare geopolymer due to their low cost, widespread availability, and good strength development even cured in room temperature, etc. In this study, for clarifying the effects of alkali leaching and concurrent action of carbonation and alkali leaching on the alkalinity and strength of GP materials, we investigated the changes of superficial and inner alkalinity of the FA & GGBS-based GP concrete and mortar

specimens during stored in the wetting and drying environments besides only carbonation by pH measurement and the phenolphthalein indicator method, in comparison with PC mortar. Seven environmental condition regimes were designed, which were single or alternation of water immersion, drying, and accelerated carbonation (AC). We also discussed the changes in compressive strength and microstructure of GP mortar specimens after they were stored in the water or exposed to the wet-dry-wet repeating, the AC, and the AC-dry-AC repeating environments.

2. Experimental program

2.1. Raw materials

Table 1 shows the physical properties and the chemical compositions of precursors and alkali activator (AS) of GP as well as PC. The FA and the GGBS, which meet respectively with the grade II of Japanese industrial standard (JIS) and the JIS class 4000, were used as active fillers (AF) or precursors of GP binder. The AS was prepared by mixing the 10 mol. NaOH solution and the sodium silicate solution at a volume ratio of 1:3. The AS had 1.315 of specific gravity and 1.1 of SiO_2/Na_2O (S/N) molar ratio. The sodium silicate solution had 1.27 of specific gravity, which was an aqueous solution of sodium-based JIS No.1 water glass with 2.1 of S/N, diluted with de-ionized water in a volume ratio of 1:1. After prepared by mixing the two solution, the AS was stored in the laboratory with the temperature of around 20 °C to cool down for 24 h prior to the mixing of GP concrete or GP mortar.

GP mortar specimens and GP concrete specimens were produced in different laboratories. The sea sand, with a specific gravity of 2.57, was used in GP mortars, which was cleaned by freshwater beforehand. But in the GP concrete, the river sand with a specific gravity of 2.60 was used. Coarse aggregate of the concrete was crushed limestone with a specific gravity of 2.70, and a maximum size of 20 mm. Fine and coarse aggregates were prepared in the saturated surface-dry state beforehand. The retarder was added in the concrete and the mortar for making the GP materials to have enough working time, of which main ingredient is L-tartaric acid sodium.

2.2. Mix proportions of mortar and concrete

In this study, GP concrete (GPC) and GP mortar (GPM) were prepared according to the mix proportions shown in Table 2. GPC and GPM had the same AS/AF ratio by mass, but different GGBS/AF ratios, being 0.3 and 0.4, respectively.

For making a comparison, PC mortar (PCM) test was also performed. PCM's water-cement ratio and sand-cement ratio were 0.45, and 3.0 by mass, respectively, as shown in Table 3. Also, retarding type AE water-reducing agent was added at a dosage of 0.5 wt% of cement.

2.3. Preparation of specimens

2.3.1. GP concrete

A concrete mixer with two horizontal blades was used to mix the GP concrete. Firstly, the solid raw materials except the coarse aggregate were put into the mixer and mixed for about 1 min. Then, the alkali activator solution was added and mixed for 2 min. to get GP mortar. Lastly, the coarse aggregate was mixed into the mortar for another 2 min. After measuring air content and slump, fresh concrete were cast into the cylindrical molds with diameter of 10 cm and height of 20 cm, and then vibrated for 20 s by a rod vibrator.

Table 1
Raw materials of binders.

| | Chemical compositions (wt %) | | | | | | | | | Physical properties | |
	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	NaO	SO_3	Others	Specific gravity	Fineness (cm^2/g, Blaine)
FA	62.09	2.07	23.04	6.88	0.67	1.68	0.54	0.98	2.05	2.24	3550
GGBS	34.67	43.13	14.46	0.34	5.50	0.25	0.25	–	1.40	2.89	4180
PC	21.80	63.90	4.49	2.90	1.84	0.38	0.20	2.26	2.23	3.16	3110
Alkali activator	SiO_2	Na_2O	H_2O	Total	%Concentration			Specific gravity		SiO_2/Na_2O molar ratio	
	13.5	12.8	73.7	100	26.3			1.31		1.1	

Table 2
Mix proportions of GP mortar and GP concrete.

| Series | AS/AF | Unit weight (kg/m^3) | | | | | |
		AS	FA	GGBS	Sand	Crushed limestone	Retarder
AGPC/HGPC	0.5	200	280	120	756	1000	20
GPM	0.5	316	379	253	1264	–	32

Notes: AGPC: GP concrete (GPC) cured in the ambient air, HGPC: heat-cured GPC.

Table 3
Mix proportions of PC mortar.

| Series | W/C | S/C | AE/C | Unit weight (kg/m^3) | | | |
				W	C	S	R-WRA
PCM	0.45	3	0.005	229	509	1527	2.5

Notes: W: water, S: Sea sand, R-WRA: AE retarding type water-reducing agent.

The GP concrete specimens were cured at different temperatures. Part of the specimens, denoted as AGPC, were cured in the ambient air of 20 °C, R.H. 60 ± 5% for 28 days, while other specimens, denoted as HGPC, were first cured in the chamber of 60 °C for 6 h, then in the ambient air of 20 °C, R.H. 60 ± 5% until 28 days age. The HGPC specimens were demoulded after 60 °C curing. For the AGPC specimens used in the experimental environment e_{w+d}, and the environments e_c, e_{c+d} (e_{w+d}, e_c and e_{c+d} were described in Table 3), the demoulding ages were 1 day, and 3 days, respectively. The difference in demoulding time has been confirmed to have no distinct effect on the strength and carbonation resistance of GP concrete. At 28 days age, the AGPC and the HGPC specimens were moved into the laboratory of 20 ± 5 °C to further cure for about 100 days. Then, we placed them into an accelerated carbonation chamber or other experimental environments to conduct the neutralization resistance test.

2.3.2. GP mortar and PC mortar

The mixing process of GP mortar was the same to the GP concrete except the addition of the coarse aggregate, but a Hobart planetary mortar mixer was used. When producing the PC mortar, the Portland cement and sand was first mixed for 1 min, then water and the admixture (R-WRA) were fed into the mixer and mixed for 3 min. The GP mortar and PC mortar was poured into small prism molds with a size of 4 × 4 × 16 cm for producing test pieces of compressive strength, and into larger prism molds with a size of 10 × 10 × 40 cm for producing test pieces of the accelerated neutralization test. After pouring, vibration of 15–30 s was done by a vibrating table.

All the mortar specimens were cured in the ambient air of 20 °C, R.H. 60 ± 5% for 28 days. They were demoulded at 1 day age, and the accelerated neutralization test began after 28 days curing.

2.4. Environmental conditions

Seven kinds of environmental conditions were used to examine the effects of wetting and drying on the alkalinity and the strength of GP concrete and mortar, as shown in Table 4. It should be noted that the environmental conditions used for GPC and GPM were different in processing time or drying temperature or CO_2 concentration, etc., for discussing the effects of variation of these conditions on the test results. The environment condition E_w is water immersion. The mortar specimens were immersed into the water of 20 °C for 8 days per cycle. The environmental condition E_{w+d+w} is water immersion-dry-water immersion repeating. The mortar specimens were first immersed into the water for 3 days, then they were dried in a chamber of 60 °C for 2 days, and immersed into the water again for 3 days, before measuring neutralization depth and pH value. However, for GPC, the environmental condition e_{w+d} had only once water immersion of 3 days, and drying temperature was 80 °C. Hence, the internal humidity of GPM might be higher than the GPC when measuring the neutralization depth and the pH value. Preliminary investigations confirmed that water could enter into the center of specimen after water immersion of 3 days, and 60 °C or 80 °C drying of 2 days could make the water-saturated specimens to reach a constant weight, i.e. absolute dry state.

The environmental condition, detonated as E_c and e_c, for GP mortar, and GP concrete, respectively, was the accelerated carbonation environment with 20 °C, R.H. 60 ± 5%. The CO_2 concentration was 5% in the environment E_c, and 10% in the environment e_c, respectively. A lower CO_2 concentration was used in case of the GP mortar to prolong the full neutralization time for increasing the neutralization test cycle. After 7 days or 8 days of the accelerated carbonation, we measured respectively the neutralization depths and the pH values of the GPM and GPC specimens. Though the effect of carbonation on the pH of pore solution in GP is highly dependent on the partial pressure of CO_2, the pH induced by the elevated CO_2 levels of traditional accelerated carbonation tests is lower than after the carbonation of natural CO_2 level [8], and Bernal et al. [19] conducted that accelerated carbonation using CO_2 concentration beyond 1% will not accurately replicate the carbonation mechanism observed in service. But in order to accelerate the neutralization of specimen, and because the discussion of moisture

Table 4
Environmental conditions and regimes (one cycle) of accelerated neutralization test.

Denotation of specimen		Denotation of environmental condition	Environment		
			A	**B**	**C**
			Water immersion (pH 7.7, 20 °C)	Drying (**B$_1$**: 60 °C or **B$_2$**: 80 °C)	Accelerated carbonation test (**C$_1$**: CO_2 5%, 20 °C, R.H. 60%, or **C$_2$**: CO_2 10%, 20 °C, R.H. 60%)
Mortar: GPM / PCM	G$_w$ / P$_w$	E$_w$	Water immersion: **A** (8 days) → Measurement		
	G$_{w+d+w}$ / P$_{w+d+w}$	E$_{w+d+w}$	Wet-dry-wet repeating: **A** (3 days) → **B$_1$** (2 days) → **A** (3 days) → Measurement		
	G$_c$ / P$_c$	E$_c$	Accelerated carbonation (AC): **C$_1$** (8 days) → Measurement		
	G$_{c+c}$ / P$_{c+c}$	E$_{c+d+c}$	Accelerated carbonation - dry - AC repeating: **C$_1$** (3 days) → **B$_1$** (2 days) → **C$_1$** (3 days) → Measurement		
Concrete: GPC		e$_{w+d}$	Wet-dry repeating: **A** (3 days) → **B$_2$** (2 days) → Measurement		
		e$_c$	Accelerated carbonation: **C$_2$** (7 days) → Measurement		
		e$_{c+d}$	Accelerated carbonation - dry repeating: **C$_2$** (7 days) → **B$_2$** (2 days) → Measurement		

Notes: G$_w$ means the specimen of GPM tested in the environment E$_w$, P$_w$ means the specimen of OPCM tested in the environment E$_w$. Other specimens are denoted by the same method.

transfer's effects is a main purpose of this study, relative high CO_2 concentration was adopted in our accelerated carbonation test.

The environmental condition, detonated as E$_{c+d+c}$, was an accelerated carbonation (AC)-dry-AC repeating environment. After 3 days accelerated carbonation in the environment E$_c$, the mortar specimens were dried in an oven for 2 days at 60 °C, then returned back into the carbonation chamber for other 3 days. After each cycle, we measured the GPM's neutralization depth and pH value in the air-dried state of R.H. 60 ± 5%. However, the GPC specimens in the environmental condition e$_{c+d}$ were firstly carbonated for 7 days then dried at 80 °C for about 2 days until their masses became nearly constant. The neutralization depths and the pH values of the GPC specimens were measured in the air-dried state too.

2.5. Measurement of neutralization depth and pH

The phenolphthalein solution method, which is always used for PC concrete, was adopted to measure the neutralization depths of GPC and GPM specimens. The neutralization depth of GPM specimen was measured on the two side rather than the top and bottom surfaces for removing the effect of segregation, as shown in Fig. 1 (a). And because the color border between the neutralized and non-neutralized area was unstable, pointed out by previous researchers too [28], the neutralization depth was measured within 5 min after splitting the specimen and immediately spraying 1 wt% phenolphthalein solution on the fractured surface, as described in detail in Ref. [14]. The recorded neutralization depth was an average of 8 locations, as shown in Fig. 1.

Fig. 2 presents the pH measurement positions of GPC specimen. The powder was drilled from two positions: outer surface within a thickness of 2 mm and inner circular zone of concrete specimen's fractured surface, which are briefly noted as O (outer), and I (inner). The inner circular zone located in the central of cross section, with a diameter of 4 cm. For avoiding the influence of coarse
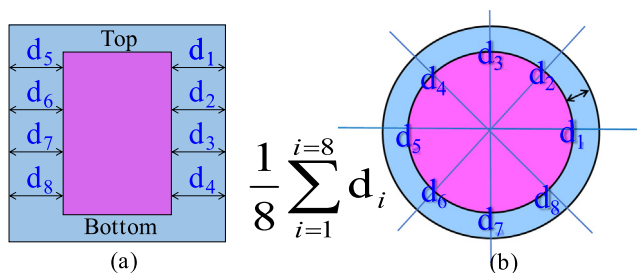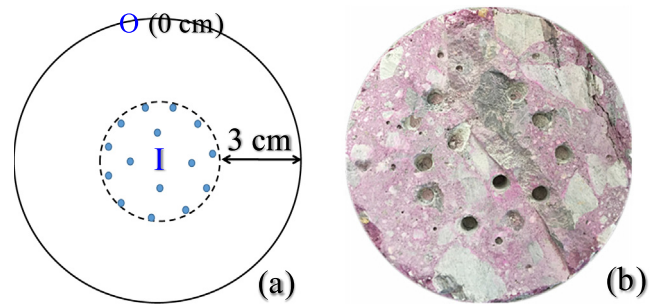
Fig. 2. Two pH measurement positions of GPC: (a) Sample drilling depth, (b) Photograph of specimen section. (O: outer surface of specimen section, I: inner circular zone with a diameter of 4 cm).

aggregate, the powder sample of GPC was drilled from the matrix mortar. The drilled powder sample was firstly sieved with a sieve of 150 μm opening, then dissolved in the de-ionized water with pH of 7.7. Finally, a pH meter with 0.1 of precision was used to measure pH value of the solution dissolving the powder sample. The authors [10] found that the pH increased with increasing the concentration of powder sample, but when the concentration was above 8 wt%, the measured pH approached to a stable value. Moreover, the measuring value of pH decreased gradually with soaking time of powder sample, i.e. standing time before measurement, because the solution carbonates in the air. But the pH measurement within 1 h of standing time only resulted in a difference of 0.1 ∼ 0.2 in pH. Hence, we mixed 2.4 g of the powder sample with 30 ml de-ionized water at ambient temperature, and measured pH value within 1 h. The pH was an average of three measurements for the same depth. The powder sample concentration of our experiment was similar to Ref. [9], but standing time was longer, which equilibrated 1 g of powdered paste (bulk pastes were crushed and ground into a powder) with 10 ml of de-ionized water during 15 min. On the other hand, pH measurement positions of the GPM are shown in Fig. 3. The sample drilling depths were 0 cm, 1 cm and 3 cm. The measuring method of pH was the same to the GPC.

2.6. Compressive strength test

The compressive strength of GPM was measured, using three prism specimens for each series. Three prism specimens were first broken by bending load to get six pieces, then the compressive test was performed. The compressive strength was an average of six pieces. The strength measurement was at the 28 days age, and 68 days age, respectively. The accelerated neutralization test of
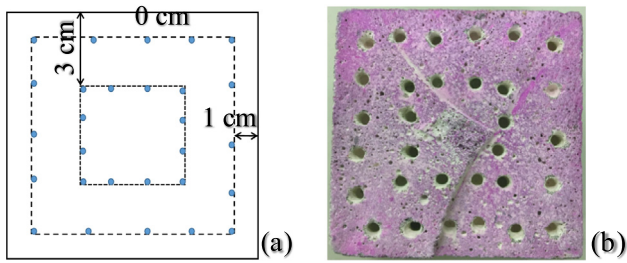
Fig. 1. Measurement positions of neutralization depth after spraying the phenolphthalein indicator: (a) Prism specimen section of GPM, (b) Cylindrical specimen section of GPC.

Fig. 3. Three pH measurement positions of GPM: (a) Sample drilling depth, (b) Photograph of specimen section.

GPM started from 28 days age, and complete neutralization of the GPM specimens took 40 days.

3. Test results and discussion

3.1. Alkalinity change of GP concrete in different environments

Table 5 shows the neutralization situation of AGPC (20 °C-cured) and HGPC (heat-cured) specimens in three environments. It was found that only the specimens experienced in the accelerated carbonation (AC) presented clear borders of pink area. The heat-cured GP concrete (HGPC) showed a higher carbonation resistance than the 20 °C-cured GP concrete (AGPC), according to the depth of colorless zone. Before the accelerated carbonation, the neutralization depths (colorless depths) of the AGPC specimens had already reached to about 12 mm, the HGPC specimens were, however, zero. With increasing the carbonation time in the environment e_c, the neutralization depth of the AGPC specimen increased faster than the HGPC specimen.

On the other hand, after the accelerated neutralization in the environments e_{c+d} and e_{w+d} with an additional drying process to the AC or wetting, the pink color on the freshly fractured surfaces of the AGPC and the HGPC specimens was so pale even in the first

circle that color border could not be exactly determined to measure their neutralization depths, though the color of the inner zone was slightly deeper than the outer zone in case of the environments e_{c+d}. And the pink color of the AGPC and the HGPC specimens stored in the environment e_{c+d} was thinner than in the environment e_{w+d} from the first circle, though the color faded throughout the whole fractured surface of the specimen in the environment e_{w+d}. These results indicate that drying promoted the movement of internal alkalis to the outside so that the alkalinity of inner zone decreased, and a combination of carbonation and alkali leaching resulted in a rapid and great alkalinity drop.

Because of the limitation of phenolphthalein indicator method, we measured the pH to evaluate the alkalinity drop of GP concretes. Fig. 4 shows the pH change of the GPC specimen with the increase of test cycle in the three environments. The initial pH of AGPC's outer surface (position "O") was 10.7. In the AC environment e_c, as shown in Fig. 4(a), the pH in the position "O" decreased with the carbonation time, but the pH of inner zone did not change. The pH of the AGPC in the position "O" after 2 circles of the AC reduced to below 9.6. If comparing the pH values at the position "O" of the AGPC and the HGPC in the environment e_c, it was clearly found that the pH of the HGPC was higher than that of the AGPC for the same AC time. Since heat curing can improve the compressive strength of GP concrete [29], it is considered that the higher carbonation resistance of the HGPC was attributed to its higher compactness.

Fig. 4(b) shows the pH change of GPC specimens in the AC-dry repeating environment e_{c+d}. The pH was measured after concrete specimen was dried. The pH in the outer surface kept around 10.9 or even increased as test cycles increased. However, in the inner zone, the pH decreased greatly with the test cycle. This can be explained that the alkali matters in the inner zone moved to the outer zone, even to the surface of concrete with moisture movement, resulting in that the color of uncarbonated inner zone faded away. As explained above, Na^+ is weakly associated with H_2O molecule in form of $Na(H_2O)_n^+$ [7]. With water evaporation due to drying, alkali Na^+ moves out. This alkali movement led to

Table 5
Color and neutralization depth of GPC specimens after the accelerated neutralization in three environments and spraying the phenolphthalein indicator.

Period	AGPC (20 °C-cured)			HGPC (60 °C-cured)		
	e_{w+d}	e_c	e_{c+d}	e_{w+d}	e_c	e_{c+d}
Cycle 0 (Before the accelerated neutralization test)		D_n=12.2 mm			D_n=0.0 mm	
Cycle 1		D_n=25.0 mm			D_n=9.4 mm	
Cycle 2		D_n=29.6 mm			D_n=18.0 mm	
Cycle 3		–				–

Notes: D_n is neutralization depth. The neutralization depth of the GPC in the environments e_{w+d} and e_{c+d} couldn't be measured.

a) Environment e_c

b) Environment e_{c+d}

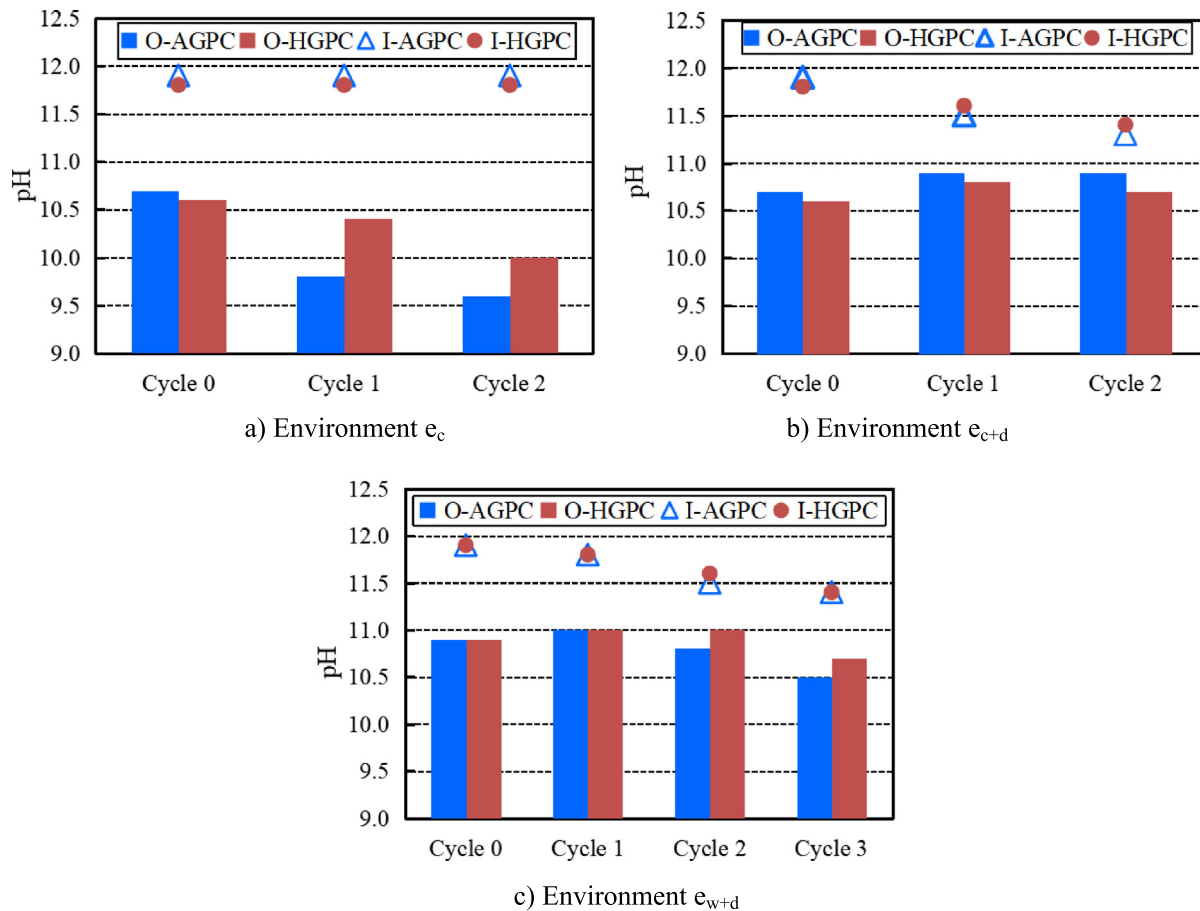
c) Environment e_{w+d}

Fig. 4. The pH change of GPC with the elapsed time in the three environments.

an indistinct color border and alkalinity drop of inner zone. Bernal et al. [8] reported that the pH of GP does not drop below 10 after carbonated under the CO_2 concentration of 0.04–4%. However, this pH measurement was for the simulated pore solution with different concentration of NaOH, formation of soluble bicarbonate (Na_2CO_3, $NaHCO_3$) may be a reason of the limited pH reduction of pore solution. In the AC-dry repeating environment, stabilization of pH above 10 at outer surface was attributed to the movement of internal alkalis.

According to Fig. 4(c), in the environment e_{w+d}, the pH values in the outer surface of the GP concrete specimens were maintained as their initial values, but a decrease occurred in their inner zones in the first cycle (5 days). This can explain why the pink color of the inner zone faded away with the wet-dry repeating, and clearly implies that alkali leaching in water neutralizes GP concrete. From the second circle of AGPC or after the second circle of HGPC, the pH decreased obviously even at the outer surface. The wet-dry repeating resulted in an alkalinity drop of whole concrete specimen not only the inner zone.

According to the outer surface pH, the heat-cured GP concrete had a relatively higher resistance to alkali leaching in the wet-dry repeating environment, compared to the 20 °C-cured concrete. Also, as shown in Fig. (b), the inner zone pH of the HGPC was little higher than the AGPC, but the outer surface pH of the HGPC was lower than the AGPC in the AC-dry repeating environment without wetting process. It was concluded that alkali movement in the HGPC due to drying was slower than in the AGPC. As explained above, heat curing makes concrete denser than ambient curing. If further comparing the inner zone pH of the GPC specimens in the two environments e_{c+d} and e_{w+d}, recorded in the first and the

second circle, it is found that the AC in combination with drying results in a greater alkalinity drop than the wet-dry repeating, which is consistent with the results shown in Table 5.

From the results shown in Table 5 and Fig. 4, we found that the zone with below 10.5 of pH was colorless, the zone with 10.5–11.5 of pH had faded color, and above 11.5 of pH resulted in a dark purple color. This result is consistent with Ref. [30], which reports the accelerated carbonation test results of FA-based GP concrete. The zone with 10.5–11.5 of pH was regarded as partially carbonated zone in Ref. [30] Hence, in case of the accelerated neutralization test, the zone or whole specimen with 10.5–11.5 of pH may be called briefly partially neutralized zone or concrete. The phenolphthalein indicator method can detect the border of neutralized and partially neutralized zones, but the detection of the border of non-neutralized and partially neutralized zones is difficult.

3.2. Difference of GP mortar and PC mortar in neutralization resistance

Although the effects of wetting and drying on the neutralization depth and the pH of GP concrete were discussed above, the drilled powder samples, used to measure the pH, might contain a little of coarse aggregate (crushed stone) powder so as to somewhat influence the test results. For doing a reliable investigation, we further investigated the neutralization resistance of GP by using GP mortar specimens, in comparison with Portland cement mortar (PCM). The wetting and drying conditions were different from GP concrete, as shown in Table 4.

Table 6 shows the color of the freshly fractured surfaces of GPM and PCM specimens after stored in the four kinds of environment, which were E_w (only water immersion (WI)), E_{w+d+w} (WI-60 °C

drying-WI repeating), E_c (only the AC in 5% CO_2 atmosphere and constant humidity of 60%), and E_{c+d+c} (AC-60 °C drying-AC repeating). It was firstly found that, after cured for 28 days in the ambient air, the GP mortar specimens had already a pronounced neutralization depth about 3.3 mm. But for the PCM specimens, initial neutralization depth was almost zero. It is thought that this was

attributed to high porosity and high permeability of GP mortar, which led to a high diffusivity of CO_2 and a high alkali leaching. This result indicates again that the neutralization resistance of GP is inferior to PC-based materials [14].

After spraying the phenolphthalein indicator, whole freshly fractured surface of the GPM specimen G_w, G_{w+d+w} presented pink

Table 6
Color change and neutralization depth of mortar specimens stored in the different environments.

Series	Specimen	Environment	cycle 0	cycle 1	cycle 3	cycle 5
PC mortar	P_w	E_w				
	P_{w+d+w}	E_{w+d+w}				
	P_c	E_c				
		D_n (mm)	0	9.0	Uncertainty	
	P_{c+d+c}	E_{c+d+c}				
		D_n (mm)	0	6.4	Uncertainty	
GP mortar	G_w	E_w				
	G_{w+d+w}	E_{w+d+w}				
	G_c	E_c				
		D_n (mm)	3.3	10.1	17.4	21.0
	G_{c+d+c}	E_{c+d+c}				
		D_n (mm)	3.3	10.5	21.3	25.8

Notes: D_n means neutralization depth.

a) 0 mm depth
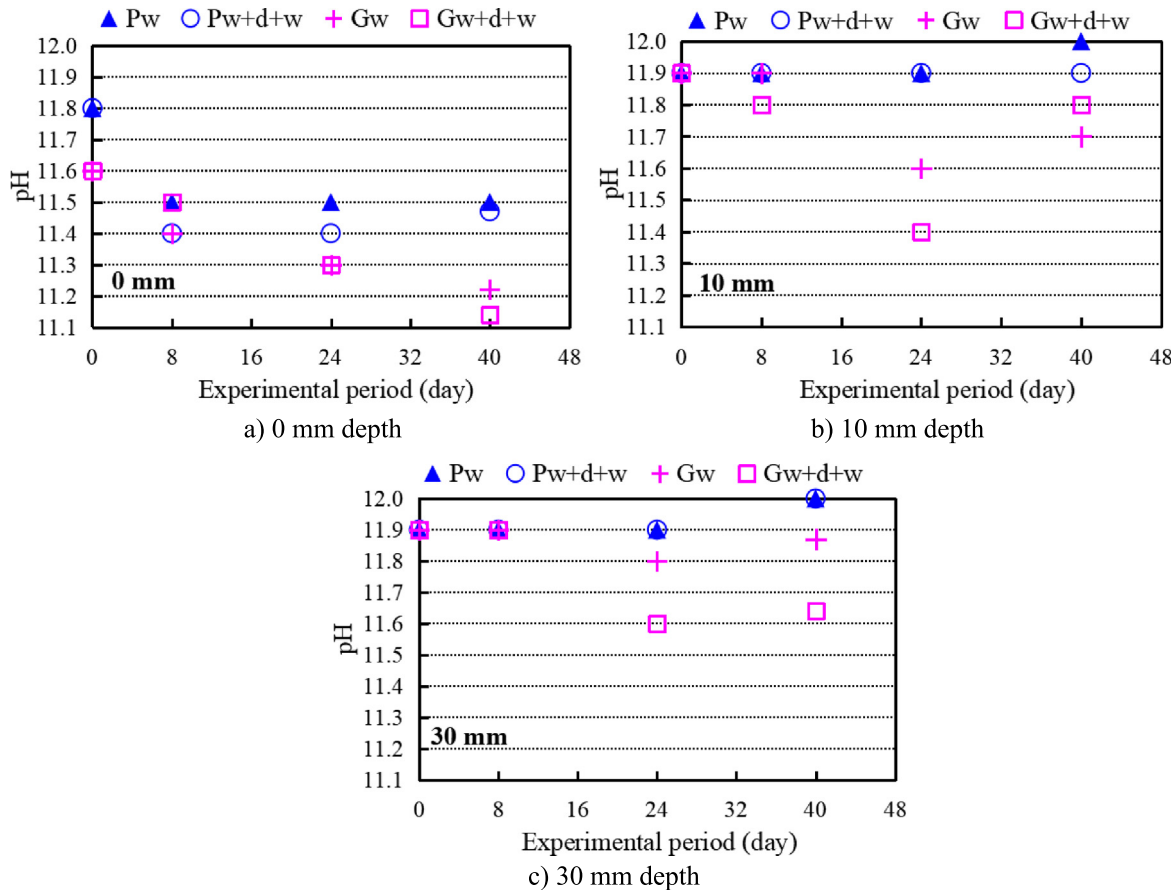

b) 10 mm depth

c) 30 mm depth

Fig. 5. The pH change with the test period in the three depths: 0 mm, 10 mm, and 30 mm of GPM and PCM in the environments E_w and E_{w+d+w}.

color, and there was a light pink color zone in the center with a dark belt-shaped border. Hence, the neutralization depth could not be measured. If the dark red in the center of 0 cycle specimen's section is due to plenty of alkalis, it is considered that the dark belt-shaped border should have many alkalis that came from the central zone. The specimen G_{w+d+w} had a wider light pink color zone and a broader dark belt-shaped border than the G_w. This means the outward diffusion of the alkalis in the central zone was intenser in the environment E_{w+d+w}. But only according to the color change, we can not yet conclude in which environment the GPM has high neutralization resistance. On the other hand, the pink color of the P_w, P_{w+d+w} faded away with the increase of test cycle. Especially, the pink color of the PCM specimen P_{w+d+w} was very pale even from the first cycle. However, as shown in the later, the pH of the PCM specimen's inside did not obviously decrease. The reason is unknown now. Color change after spraying the phenolphthalein indicator may be affected by wetting state of specimen.

The GPM specimens G_c and G_{c+d+c}, stored in any of the environments E_c and E_{c+d+c}, displayed clear color borders so that their neutralization depths could be measured, as shown in Table 6. The neutralization depth of GPM increased with test cycle, and the drying process increased obviously the neutralization depth of G_{c+d+c}. Carbonation in combination with drying promoted the alkalinity drop of GPM like GPC. However, the neutralization depths of PC mortar specimens P_c and P_{c+d+c} had almost no difference, i.e. the weak drying that was from R.H. 60% to 0% did not cause a definite alkalinity drop of PC mortar.

As stated above, the GPC specimens in the environment E_{c+d+c} (AC-dry repeating) displayed no clear color borders. In this case,

the phenolphthalein indicator was sprayed after the GPC specimens were dried. Though the carbonation process made a difference in alkalinity between non-carbonated and carbonated zones, the drying process distributed the alkalis in concrete to reduce the unevenness of alkalinity so that the color border of concrete section became unclear. However, the GPM specimen G_{c+d+c} was experienced the AC again later after drying, the twice carbonation process differentiated the alkalinity of non-carbonated and carbonated zones so that the clear color border was shown. This result indicates again that the water movement due to drying would change the distribution of alkaline matters so as to equalize the alkalinity of whole specimen, and also suggests that in an accelerated neutralization test considering comprehensively both carbonation and alkali leaching, the measurement of neutralization depth using the phenolphthalein indicator should be conducted after the accelerated carbonation process rather than after the drying.

Figs. 5 and 6 show the change of pH with the increase of experimental period, for the three depths of GPM and PCM specimens in the four environments: E_w, E_{w+d+w}, E_c, and E_{c+d+c}. For the GPM specimen G_w, in the environment E_w, the pH of the whole specimen decreased with the increase of water immersion time. The pH decrease in the 0 mm depth was rapid and large, but was very small in the 30 mm depth. The pH in the 10 mm depth displayed an intermediate reduction though there was a large measuring error in this position. Larger measuring error of pH at 10 mm depth was caused by an unstable alkali amount at this position due to the confused movement of alkali from outer zone to surface and from central zone to outer zone. That is to say, after the water immersion, a gradient of alkalinity was formed from inside to outside of the G_w. This result indicates that when GP materials contact
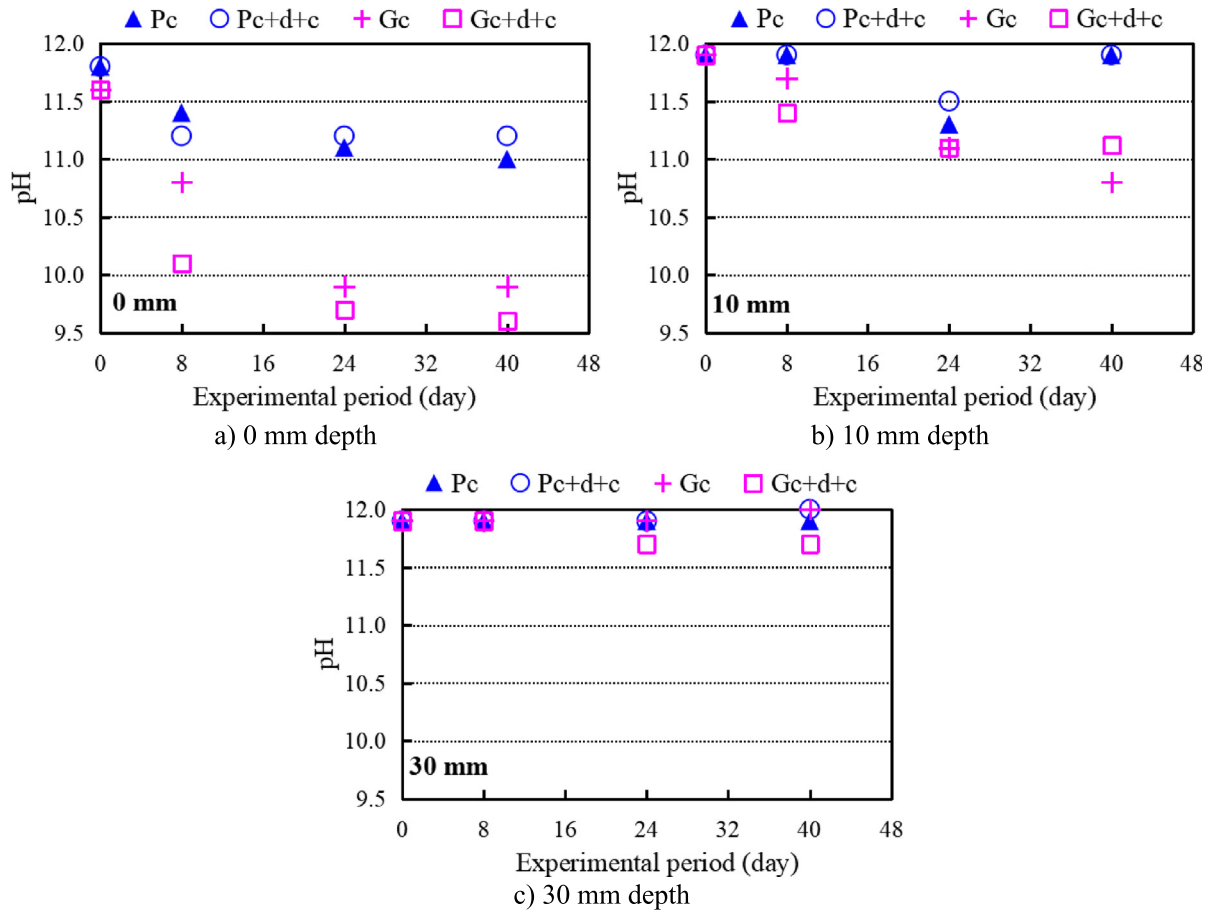
a) 0 mm depth

b) 10 mm depth

c) 30 mm depth

Fig. 6. The pH change with the test period in the three depths: 0 mm, 10 mm, and 30 mm of GPM and PCM in the environments E_c and E_{c+d+c}.

with water, alkali matters will dissolve and leach into water to reduce their alkalinity.

From Fig. 5, it was also found that the pH of the GPM specimen G_{w+d+w} decreased largely in the inner zone (30 mm depth), though the pH values of the G_w and G_{w+d+w} in the depths of 0 mm and 10 mm were near, and they were in a contrary order in the depth of 10 mm at 40 days of test period. Hence, in the wet-dry repeating environment, drying process promotes alkali leaching and accelerates inside neutralization.

From Fig. 6, we found that an alkalinity gradient was formed in the specimen G_c and G_{c+d+c} from inside to surface as observed in the specimen G_w and G_{w+d+w}. The pH values of the specimen G_{c+d+c} were lower than those of the specimen G_c in the depths of 0 mm and 30 mm, and the pH values of the specimen G_w and G_{w+d+w} decreased with the experimental period in the depths of 0 mm and 10 mm. Because the specimen G_c and G_{c+d+c} didn't carbonate completely, i.e. the carbonation did not yet reach to the depth of 30 mm, the pH values in the 30 mm depth were kept above 11.5. Moreover, if comparing the results shown in Figs. 5 and 6, it is found that the pH reduction of the specimen G_c and G_{c+d+c} was greater and faster than the specimen G_w and G_{w+d+w} in the depths of 0 mm and 10 mm. However, in the 30 mm depth, the specimen G_w and G_{w+d+w} had a greater pH reduction, the specimen G_c and G_{c+d+c} displayed a smaller pH reduction (the specimen G_{c+d+c}) or changeless (the specimen G_c). It is considered that the drying caused the smaller pH reduction of G_{c+d+c} in the 30 mm depth. That is, the carbonation resulted in a faster and greater alkalinity drop than the alkali leaching in water, called water-induced alkali

leaching. The water-induced alkali leaching caused a greater inner alkalinity drop than the drying-induced alkali leaching.

Harada et al. [28] reported that after spraying the phenolphthalein indicator, the colorless zone, i.e. carbonated zone was gradually colored with the elapsed time, as shown in Fig. 7. It is considered that this is because the alkalis in the non-carbonated zone diffuse outward. Though the neutralization depths of the specimens G_c and G_{c+d+c} were more than 10 mm, as show in Table 6, the pH values in the depth of 10 mm were above 10.5, as shown in Fig. 6. The powder sample was drilled for the pH measurement after spaying the phenolphthalein indicator and further measuring the neutralization depth was in a order of 0 mm depth, 10 mm depth and 30 mm depth. During measuring the neutralization depths of three positions and drilling the powder sample from the 0 mm depth, the alkalis in the non-neutralized might move outward to cause the pH rising in the 10 mm depth. Therefore, the pH of the 10 mm depth depends on the elapsed time from spaying the phenolphthalein indicator to drilling the powder sample so that there was a large measurement error. This resulted in that the variation of the pH values in the 10 mm depth of the specimen G_w and G_{w+d+w} with the experimental period was in disorder, as shown Fig. 5, and it can not be understood at present why the pH values in the 10 mm depth of G_{w+d+w} and G_{c+d+c} were higher than those of G_w and G_c, respectively, as shown in Figs. 5 and 6.

It can be also found from Figs. 4(c) and 5(a) that there was not difference in the reduction degree of pH of the outer surface (0 mm depth) between the GP concrete stored in the environment e_{w+d} and the GP mortar stored in the environment E_{w+d+w}. This may
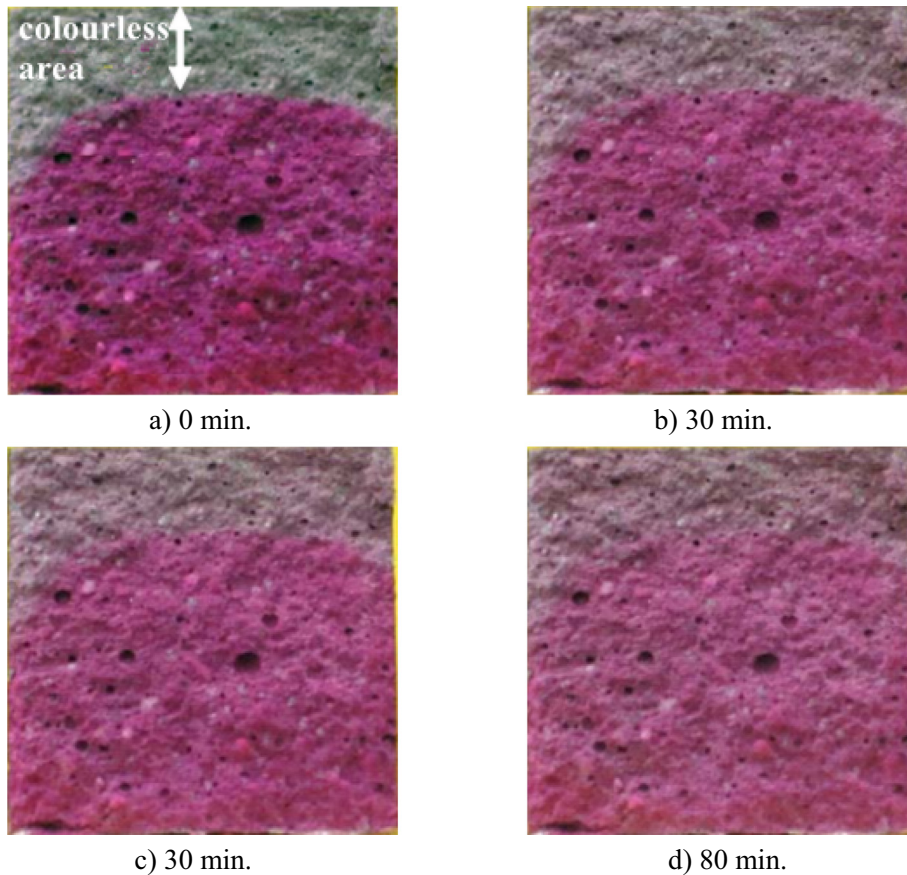
a) 0 min.

b) 30 min.

c) 30 min.

d) 80 min.

Fig. 7. The color change of initial colourless area of GP mortar with the elapsed time after spraying phenolphthalein indicator [26].

be because the drying or the water immersion before the pH measurement could result in alkali leaching of outer zone and inside alkali redistribution. However, between the environment e_{c+d}, and E_{c+d+c}, the pH change of outer surface with the experimental period was very different, as shown in Figs. 4(b) and 6(a). The outer surface pH of the former did not almost change during the experimental period, but the outer surface pH of the latter decreased with the experimental period. The drying before the pH measurement redistributed the inside alkalis, but the carbonation before the pH measurement caused a further reduction of pH. Hence, the measuring value of pH depends on the processing method (wetting, drying, carbonation) just before pH measurement.

On the other hand, as shown in Table 6, Figs. 5 and 6, the neutralization depth of the PCM specimen was small no matter in the environment E_c or E_{c+d+c}. The outer surface pH of PCM specimen decreased with the experimental period, but this reduction was smaller than the GPM, and the inside pH did not almost change even after 40 days accelerated neutralization. The neutralization resistance of the GPM specimen was obviously lower than the PCM specimen. From Fig. 5, it is found that, for the PCM specimen P_w, P_{w+d+w}, the water immersion resulted in alkali leaching to the outer surface, and the drying drove the alkalis from outer zone to outer surface, but both the wetting and the drying did not cause the inside movement or redistribution of alkalis (see Fig. 5b) and c)). This is the same for the PCM specimen P_{c+d+c} in the environment E_{c+d+c}, the effect of drying on the inside pH was not found (see Fig. 6c)). On the contrary, the pH reduction in the outer surface of the specimen P_{c+d+c} was little smaller when the drying process was added, compared to the specimen P_c that was only in the AC environment E_c. In summary, wetting and drying affect the

alkalinity of shallow outer zone of PC mortar, but do not result in inside alkalinity drop.

3.3. Microstructure after accelerated neutralization

It is not easy at present to observe the effects of alkali leaching and crystallization pressure of Na, Ca-carbonate on the pore microstructure by Scanning Electron Microscope (SEM). Therefore, we compared inside structure of GP mortars before and after the accelerated neutralization by a low SEM magnification for the same sample and the same position. Table 7 shows the SEM images of GP mortars before and after the accelerated neutralization of 2 cycles in the four environments. It was found that there were many pores in the specimen G_w before the water immersion, but these pores became few and small after the water immersion, as marked by square mark, and continuous reaction of FA and GGBS was also found, as shown by cycle mark. However, there is no much change in the cracks after the water immersion. The microstructure change may be thought as an evidence of strength growth of the specimen G_w. On the other hand, in the specimen G_{w+d+w}, after subjected to the wet-dry-wet repeating, part of pores and cracks were narrowed, as shown by square marks, but part of pores and cracks became wide, as marked by squares. That is to say, the drying process may cause new cracks and enlarge the existing cracks.

However, there is almost no obvious difference between the SEM images of the specimen G_c and G_{c+d+c} before and after the AC or the AC-dry-AC repeating, though little crack enlargement was found in the specimen G_c after the AC, as marked by circle. The drying from R.H. 60% to R.H. 0% was not sharp in case of the specimen G_{c+d+c}, i.e. the weak drying, compared to the intense

Table 7
SEM images of GPM before and after the accelerated neutralization in the 4 kinds of environment.

Notes: The length of scalar in each SEM image is 10 μm.
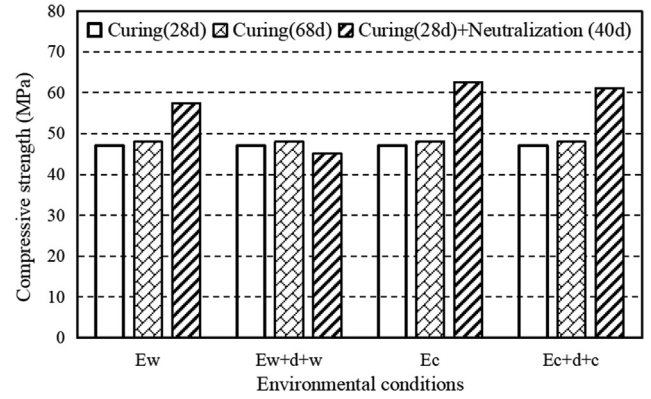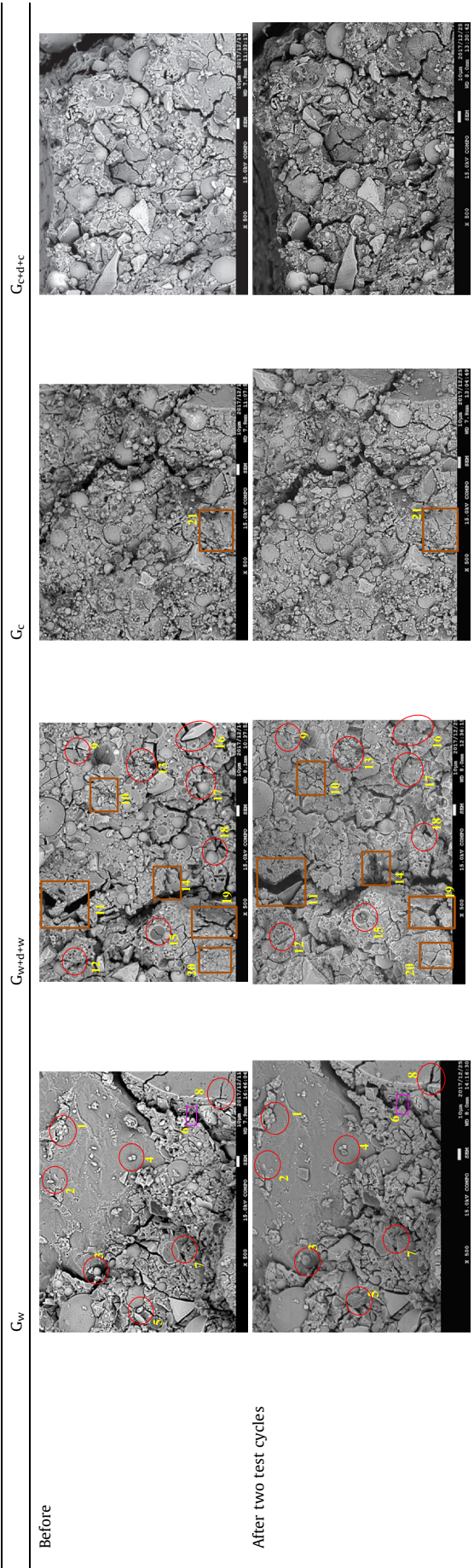
Fig. 8. Compressive strength of GPM at the age of 28 days, 68 days, and after neutralization.

drying from water-saturated state to absolute dry state in case of the specimen G_{w+d+w}, which almost did not cause the drying shrinkage-induced cracks.

3.4. Compressive strength after the accelerated neutralization

Fig. 8 shows the compressive strengths of GPM specimens before and after the accelerated neutralization in four kinds of environment. It can be found that the GPM specimen after cured in the ambient air of 20 ± 3 °C for 68 days had a higher compressive strength than the 28 days-cured specimen. That is to say, with the increase of age, the strength of GP grew. Moreover, compared to the specimen that was only stored in the ambient air of 20 ± 3 °C for 68 days, the compressive strengths of the GPM specimens, which were first cured for 28 days and then stored in the experiments E_w, E_c, E_{c+d+c} for 40 days, were large, especially for the specimens stored in the environments E_c, and E_{c+d+c}. However, the specimen stored in the wet-dry-wet repeating environment E_{w+d+w} had a lower strength.

It is generally considered that there are four reasons of strength reduction of GP caused by wetting and drying. One is alkali leaching that suppresses the later alkali-activation of residual precursors [20]. The second is damage of microstructure due to alkali leaching [25]. The third is the crystallization pressure due to the precipitation of sodium carbonates in the pores may also introduce inner stress, which consequently affects the mechanical properties of GP [20]. The fourth is drying shrinkage, resulting in cracks to reduce the strength. Because the polymerization reaction of GP is a dehydroxylation process, the drying shrinkage in the ambient air is so large to probably cause cracks [31].

Ref. [32] reported that water curing harms the strength growth of GP concrete due to alkali loss. However, the water immersion in this study was begun after 28 days ambient-curing rather than right after demoulding. Hence, the GPM specimens already gained strength to some degree before the water immersion so that much alkali loss is impossible. Though alkali leaching may harm the strength of the specimen immersed in the water, the strength growth of the specimen G_w in the environment E_w may be attributed to the absence of drying shrinkage and continuous polymerization reaction in the humid environment, as explained in the Section 3.3. Because the precipitation of a lot of Na, Ca-carbonate in the pores causes the declines in total porosity and in average pore size, carbonation enhances GP mortar dense to increase the mechanical strength [32]. Hence, the strength growth of the specimen G_c after the accelerated

carbonation was mainly attributed to the precipitation of carbonation products in the pores.

Since crack generation and enlargement was not found in the SEM image of the specimen G_{c+d+c}, it is considered that drying-induced alkali leaching other than drying shrinkage caused that the compressive strength of the specimen G_{c+d+c} was smaller than that of the specimen G_c. The crystallization pressure formed in the outer zone may be other reason of strength reduction of the specimen G_{c+d+c}. But it is almost impossible that natural carbonation of the specimen G_{w+d+w} during the drying process caused a great crystallization pressure of Na, Ca-carbonate in the outer zone, because the sodium carbonation could dissolve into water during the waster immersion process. As discussed in Section 3.3, the sharp drying process from water-saturated state to absolute dry state caused new cracks and enlarged the existing cracks, thus we consider that the strength reduction of the specimen G_{w+d+w}, compared to the specimen G_w, was resulted from drying shrinkage. Also, the strength reduction of the specimen G_{w+d+w}, compared to the specimen only stored in the air, was due to water-induced alkalis leaching and drying shrinkage-induced cracks.

4. Summary

This study aims to clarify the neutralization behaviors of fly ash/slag-activated materials (GP) in different environments due to carbonation reaction and alkali leaching. We measured the pH value and neutralization depth of GP concretes and mortars, after they were stored in water, wet-dry repeating, accelerated carbonation (AC), and AC-dry repeating environments. A comparison was also performed between GP mortar and Portland cement (PC)-based mortar. The effects of neutralization in different environments on the compressive strength and microstructure of GP mortar were discussed. Obtained main results are summarized as follows:

The heat-cured GP concrete (HGPC) showed a higher carbonation resistance and a higher alkali leaching resistance in the wet-dry repeating environment, compared to the ambient air-cured GP concrete (AGPC).

After the accelerated carbonation (AC), the alkalinity of GP only in the outer zone decreased, but after the water immersion (WI) or the alternation of drying and the AC or the WI, the alkalinity of the inner zone also decreased besides the outer zone, thus a gradient of alkalinity was formed from inside to outer surface of GP.

After the AC or the AC-dry repeating, a greater and faster alkalinity drop was caused in the outer zone of GP materials than after the WI or the WI-dry repeating. But the WI or the WI-dry repeating caused a greater alkalinity drop in the inner zone than the AC or the AC-dry repeating. The stronger the drying, the greater the inner alkalinity drop. The WI resulted in a greater inner alkalinity drop than the weak drying that dried the specimens stored in the environment of R.H. 60% to the absolute dry state.

The WI and the intense drying, which dried the water-immersed specimens to the absolute dry state, only slightly reduced the alkalinity of shallow outer zone of the PC mortar, but did not result in an inside alkalinity drop. The term of carbonation resistance is nearly able to describe the resistance of PC-based materials to neutralization. However, for GP materials, the alkalinity drop is not only due to carbonation but also because of water transfer-induced alkali leaching, neutralization resistance should include both carbonation resistance and alkali leaching resistance.

The WI and the AC increased the compressive strength of GP due to continuous geopolymerization reaction or precipitation of carbonation products in the pores. But the intense drying harmed the compressive strength because the drying caused crack growth and alkali leaching. In case of the AC-dry (weak drying) repeating,

the compressive strength of GP mortar was still greater than that only stored in the air.

The phenolphthalein indicator method can detect the border of neutralized zone (pH < 10.5) and partially neutralized zone (pH = 10.5 ~ 11.5) of GP, but the detection of the border of non-neutralized zone (pH > 11.5) and partially neutralized zone is difficult. Drying and wetting redistributes the alkalis in GP to reduce the unevenness of alkalinity so that the colorless border becomes unclear.

CRediT authorship contribution statement

Zhuguo Li: Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Sha Li:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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