Suppression of Alkali Silica Reaction Using H^+ -type Geopolymer

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An H^+ -type geopolymer powder was prepared by grinding a Na^+ -type geopolymer hardened paste and processing it with sulfuric acid. At pH 7, the extent of cation exchange with Na^+ and K^+ ions of the H^+ -type geopolymer powder was one-fourth of that of the original Na^+ -form geopolymer at the same pH. The ion-exchange capacity of the H^+ -type geopolymer powder shows pH dependence, that is, has a tendency to increase with higher pH levels. A 10 mass% addition of the H^+ -type geopolymer reduced both pH and the soluble alkali quantity of the hardened cement pastes to a greater extent than when no addition to the cement paste was made. Further, the injection of cement paste of 40 mass% addition of the H^+ -type geopolymer suppressed expansion of Alkali-Silica-Reaction more compared to that of the non-addition one.

Keywords: geopolymer, coal ash, hydrogen ion, ion-exchange, pH, alkali-silica-reaction

1. Introduction

Hardened geopolymers (GP) are polymerized silicates that are obtained from reactions between amorphous powder containing silicon and aluminum components and alkali silicate solutions [1]. Davidovits saw similarities between that reaction and the forming process of rock and thus, named the hardened material that results from the reaction “geopolymer” [2]. Portland cement concrete is known to dissolve in acid solutions. On the other hand, hardened geopolymers are highly resistant to acid [3] and for that reason, studies are underway on hardened geopolymers for possible applications in places with acidic water where Portland cement concrete cannot be used [4].

Most studies on hardened geopolymers are indeed about the possible applications of geopolymers as a substitute for Portland cement concrete. However, hardened geopolymers also have a cation exchange capacity and thus, are being studied for possible applications utilizing this capacity for adsorption of heavy metals, for example [5]. As a possible application of the cation exchange capacity, the authors et al. have been developing concrete alkali silica reaction (ASR) suppressants [6]. Alkali silica reactions occur when solutions in concrete pores become high in pH when reacting with alkali components, causing silica components in the aggregate to dissolve and forming an alkali silica gel. The alkali silica gel then absorbs water and expands, causing the concrete body to crack and also possibly causing the reinforcing bars to break. As a suppressant of the alkali silica reaction, the authors et al. developed a grouting material containing Li-EDI type zeolites [6]. The material exchanges its lithium (Li) components for alkali components, such as potassium (K) and sodium (Na) components, to suppress the expansion of alkali silica gel. However, currently used materials containing lithium are too expensive, so reducing costs is important. Another possible option would be to find a material that has a high ion exchange capacity and hydrogen ions (H^+) as an exchange-

able cation, exchanging its hydrogen ions (H^+) for Na^+ and K^+ ions to lower the pH of concrete bodies and thereby suppress the alkali silica reaction. However, high-capacity, H^+ -type ion exchangers in general are difficult to manufacture economically. As such, yet another possibility would be a hardened geopolymer that is highly resistant to acid and could be turned into an H^+ -type ion exchanger through an inexpensive process of acid treatment. Based on the above, the authors et al. started attempts to turn hardened geopolymers into an H^+ -type ion exchanger through acid treatment and evaluate the exchanger's performance in suppressing alkali silica reactions.

2. Experiments

As H^+ -type hardened geopolymers cannot be produced in a single process, Na^+ -type hardened geopolymers were produced first, and then treated with acid to produce H^+ -type geopolymers. The following materials were used to produce Na^+ -type hardened geopolymers: JIS A6201 type I fly ash, and alkali silicate solutions made from a mixture of sodium hydroxide (NaOH) and fine silica powder. As shown in Table 1, Na/ H_2O mole ratios (hereafter “A/W” ratios) of 0.10 to 0.50 were used, in each case the Si/Na mole ratio (hereafter “Si/A” ratio) was set to 0.40 while the water/binder weight ratio (hereafter “W/B” ratio) was set to 0.30.

Each of these mixtures was stirred with a mortar mixer for three minutes before being filled into a mold measuring 10 cm in length and 5 cm in diameter and then sealed. The mixtures were then heated at 80°C for 48 hours to be turned into hardened geopolymers. Each of these pieces of hardened geopolymers was then pulverized and all the powder put through a 75 μm sieve. The powder was then cleaned with pure water and put used for the experiments to be described below. The test pieces were named based on the A/W ratios used in preparing the sodium silicate solutions. For example, the test piece prepared using an A/W

Table 1 Mixing proportions for the GP

Sample name	0.1GP	0.2GP	0.3GP	0.4GP	0.5GP
Fly ash	1000 g	1000 g	1000 g	1000 g	1000 g
NaOH	68.7 g	137.3 g	205.6 g	275.0 g	342.6 g
Silica powder	42.6 g	85.1 g	127.6 g	170.5 g	212.6 g
Water	297.4 g	294.7 g	292.0 g	290.0 g	286.8 g
	80°C	80°C	80°C	80°C	80°C
Processing condition	48 h	48 h	48 h	48 h	48 h

ratio of 0.1 was named “0.1GP.”

Attempts were made to put the Na⁺-type hardened geopolymers of 0.1 to 0.5GP through acid treatment to turn them into H⁺-type versions by exchanging Na⁺ ions for H⁺ ions. The test pieces were mixed with sulfuric acid solutions with acid concentrations of 0.1 M to 4.0M (hereafter this sulfuric acid solution was described as “0.1M” to “4.0M”) to a solid-liquid ratio of 1:10 and stirred for one hour. These test pieces were renamed based on the acid concentrations used in the acid treatment. For example, a test piece with an A/W ratio of 0.2 was renamed “0.2 GP-4.0M” if it was treated with a sulfuric acid solution of 4.0M.

To evaluate their ion exchange properties, the H⁺-type geopolymer test pieces were mixed with either 1.0M sodium chloride (NaCl) solutions or 1.0M potassium chloride (KCl) solutions to a solid-liquid ratio of 1:250 and stirred for one hour to measure the amount of H⁺ ions exchanged for either Na⁺ ions or K⁺ ions.

H⁺-type geopolymer test pieces were added to normal Portland cement to measure the mixture’s pH and soluble alkali content and evaluate any effect of the mixture in lowering pH, which is effective in suppressing alkali silica reactions, as well as alkali adsorption performance. In the experiment, NaCl was added to a mixture of a 0.5GP-0.4M test piece and normal Portland cement (equivalent alkali (R₂O) content given by Na₂O content + 0.658K₂O content = 0.52%) in such a way that the R₂O content corresponded to 1.2% of the powder material, to form cement paste with a W/B ratio of 50%. For the purpose of comparison, one more cement paste was prepared that also had an R₂O percentage of 1.2% but did not contain H⁺-type geopolymer powder. These paste samples were left in moist air at room temperature for 28 days before being pulverized into particles of 75 μm or less and stirred in a form with a solid-liquid ratio of 1:1 to measure pH. In addition, pulverized samples were stirred in a form with a solid-liquid ratio of 1:30 at 30°C for 30 minutes and filtered. The filtered samples were then measured using the atomic absorption method for Na⁺ content to calculate their soluble Na₂O content.

Alkali silica reaction and gel expansion suppression tests were conducted on prepared mortar for its possible application as an H⁺-type geopolymer-based additive to grouting materials for suppression of alkali silica reactions. Pieces of mortar (40 mm × 40 mm × 160 mm) containing reactive aggregate were produced in the composition shown

Table 2 Mixing proportions of mortar for ASR expansion tests (R₂O = 1.6%)

OP cement	Water	NaOH	ASR reactive aggregate
600 g	300 g	8.3 g	1350 g

Table 3 Injection paste formulation

Sample name	BB cement	0.5GP-0.1M	Water
No addition	300 g	0 g	127.1 g
H ⁺ -type GP	180 g	120 g	153.0 g

in Table 2, and 36 holes measuring 6 mm in diameter were drilled into each of those pieces. H⁺-type geopolymer-based cement paste was prepared in the composition shown in Table 3 and injected into those holes, and resultant expansion rates were measured using the JIS A1146 mortar bar method. In the test, material with the 0.5GP-0.1M rating was used: the 0.5GP rating had been shown to have the highest ion exchange capacity while the 0.1 M rating had been shown to exchange H⁺ ions for nearly all Na⁺ ions with a solid-liquid ratio of 1:50.

3. Results and Discussion

Figure 1 shows X-ray diffraction diagrams for the powdered samples of the fly ash (FA) used as the starting material and the test materials of 0.1 to 0.5GP made from the FA. The intensities of crystalline quartz and mullite

Fig. 1 Powder X-ray diffraction patterns for the Na⁺-type 0.1-0.5GP samples and starting material

of the Na^+ -type geopolymer materials were shown to have smaller changes than those of the fly ash, which indicates corresponding reactions of the fly ash's amorphous components. It was also found that the materials with higher A/W ratios had peak amorphous halos at greater degrees in the 2θ range of 20° to 30° . This agrees with the findings presented in the papers [7], indicating occurrences of the so-called geopolymer structure.

Figure 2 shows Al/Si and Na/Si mole ratios in the geopolymer structures of test materials obtained using fluorescent X-rays, with Si content used as the reference as it is least affected by acid treatment. Overall, as the A/W ratio increased, the Na content in the geopolymer-based test material showed an almost linear increase. At the same time, however, the increase slowed down and, with 0.5GP, the content decreased to around half of the initially prepared material. This is probably because surplus Na was not taken into the geopolymer structure and flew out during the cleaning process.

Figure 3 and Fig. 4 show respectively Al/Si mole ratios and Na/Si mole ratios of the Na^+ -type geopolymer test materials with GP ratings of 0.1 to 0.5 after they were treated with solutions of various acid concentrations. Overall, Na was shown eluted in larger quantities with higher acid concentrations, and almost completely eluted with 0.4M for 0.5GP, with 0.3M for 0.4GP and 0.3GP, with 0.2M to 0.3M for 0.2GP and with 0.1M for 0.1GP. On the other hand, almost no Al was observed up to 0.5M for 0.5GP while Al elution started accelerating above 0.4M for 0.4GP, above 0.3M for 0.3GP, between 0.2M and 0.3M for 0.2GP and between 0.1M and 0.2M for 0.1GP. The acid concentrations with which Al elution started accelerating were slightly higher than those with which Na was completely eluted from the geopolymer materials. It should be noted that with a high

Fig. 2 Al/Si and Na/Si atomic ratios of the Na^+ -type of 0.1-0.5GP samples

Fig. 3 Variations in the Al/Si atomic ratios of 0.1-0.5GP samples due to acid treatment

Fig. 4 Variations in the Na/Si atomic ratios of 0.1-0.5GP samples due to acid treatment

acid concentration of 4.0M, the quantities of Al elution were in the following order: $0.3\text{GP} \geq 0.5\text{GP} \geq 0.4\text{GP} > 0.2\text{GP} > 0.1\text{GP}$, indicating smaller quantities for materials of lower alkali contents. This is thought to be due to the lower reactivity of the geopolymer materials with lower A/W ratios such as 0.1GP, which is shown in the X-ray diffraction diagrams of Fig. 1, resulting in the Al content of non-reactive fly ash remaining in the materials during the acid treatment. On the other hand, the materials with higher A/W ratios showed higher geopolymer reactivity, retaining the geopolymer structure and allowing smaller quantities of Al to be eluted up to 0.5M. With high acid concentrations such as 4.0M, however, it is assumed that the higher-A/W ratio, higher-reactivity materials allowed larger quantities of Al to be eluted than those with lower A/W ratios.

Figure 5 and Fig. 6 respectively show X-ray diffraction diagrams for powdered samples of acid-treated 0.2GP

Fig. 5 X-ray diffraction patterns of acid-treated 0.2GP samples

Fig. 6 X-ray diffraction patterns of acid-treated 0.5GP samples

and 0.5GP materials. It has been shown that with higher-concentration acid treatments, the peak amorphous halo occurred at smaller angles. With the 0.5GP-0.5M material, which had almost no Al elution and therefore is assumed to have had no major structural change, the peak amorphous halo occurred at a smaller angle than the materials

treated with acid of lower concentrations. This is assumed to be due to H^+ being the exchangeable cation, causing changes in the bond angle and resultant average surface separation of Si-O-Si, Si-O-Al or other bonding. With the 0.2GP-0.4M to 4.0M and 0.5GP-4.0M materials, which experienced Al elution in large quantities, the occurrence of peak amorphous halos at a smaller angle than the materials treated with acid of lower concentrations indicates that the geopolymer structure broke into a state similar to silica gel. The above indicates that the appropriate sulfuric acid concentration for acid treatment that enables exchange of H for nearly all Na without breaking the geopolymer structure, or lowering of Na/Si ratio while minimizing the drop in Al/Si ratio, is determined by the A/W ratio for geopolymer preparation: with higher A/W ratios, geopolymer structures stay unbroken even with higher acid concentrations.

Figure 7 shows the quantities of Na exchanged (in Na/Si mole ratio) in a Na exchange test conducted on initial and acid-treated 0.5GP materials. Figure 8 shows the quantities of K exchanged (in K/Si mole ratio) in a K exchange test conducted on identical 0.5GP materials. In both tests, a greater drop was observed in the quantity of ions exchanged with a material treated with a higher acid concentration. The greatest drop was observed especially with the 4.0M material that had experienced significant Al elution. The materials of 0.5M or less with relatively insignificant Al elution also showed a drop in the quantity of ions exchanged.

In Fig. 2, the 0.5GP material is shown to have a Na/Si ratio of 0.32. In Fig. 8, the quantity of K exchanged with the 0.5GP material at around pH7 is about 0.32, which indicates that the non-acid-treated Na^+ -type geopolymer material exchanged nearly all Na for K. The H^+ -type geopolymer 0.5GP-0.5M material had a Na/Si ratio of 0.062 and a K/Si ratio of 0.076, both of which are small, corresponding to 19% and 24% of the ratios respectively for the 0.5GP

Fig. 7 Na/Si atomic ratio of 0.5GP samples treated with NaCl solutions of varying pH

Fig. 8 K/Si atomic ratio of 0.5GP samples treated with KCl solutions of varying pH

Fig. 9 Al/Si atomic ratio of 0.5GP samples treated with NaCl solutions of varying pH

material.

The 4.0M materials, considered to have a broken geopolymer structure with eluted Al, thus resembling silica gel in structure, show a linear increase in both Na/Si and K/Si ratios with an increase in pH. Figure 9 and Fig. 10 show H^+ -type geopolymer materials exchanging increasing quantities of ions with an increase in pH, or pH dependency, although their Al/Si ratios stayed constant between pH9 and pH11. That is probably because H^+ -type geopolymers have an amorphous structure, with silanol groups located on the outer faces of the geopolymer networks being negatively charged. In a test segment conducted with pH12.5, however, an increase in the content of Al relative to Si was observed, indicating the occurrence of Si elution in that range. Given the above, the increased adsorption of Na and K with pH12.5 was due in part to the Si elution pushing up the Na and K contents relative to Si.

Table 4 shows the pH and soluble Na (Na_2O) content measured of normal Portland cement containing NaCl as a source of alkali and those parameters measured of identical cement that also contained 0.5GP-0.4M material which had been added by a quantity corresponding to 10% of that of the powdered material before the addition. These measurements were part of this paper's stated attempt to use H^+ -type geopolymers as an alkali silica reaction suppressant. Generally, when NaCl permeates a concrete body as it comes into contact with seawater or is subjected to other external factors, the Cl components are retained by hydrocalumite etc. that are formed in the cement paste, which increases the pH of solutions in the concrete pores [8]. Back in the experiment, while the NaCl-added test materials were generally high in pH, the material to which 0.5GP-0.4M material had been added showed lower pH than the other 0.5GP-0.4M-free material. As for soluble Na_2O content, the material containing the 0.5GP-0.4M additive has a soluble Na_2O content of 0.41 mass%, which is about 30% lower than the 0.60 mass% of the 0.5GP-0.4M-free materi-

Fig. 10 Al/Si atomic ratio of 0.5GP samples treated with KCl solutions of varying pH

Table 4 The value of pH and the amount of soluble Na_2O in the cement paste adding GP

Sample	No addition	0.5GP-0.4M 10% added
Equivalent alkali amount.	1.2%	1.2%
Addition amount of 0.5 GP-0.4 M	0%	10%
pH	13.03	12.74
Amount of soluble Na_2O	0.60%	0.41%

No addition and H⁺GP: Processing period of 365 days
Li-EDI: Processing period of 365 days

Fig. 11 Expansion test results of mortar injected with cement paste adding H⁺-type GP or Li-EDI

al. The above suggests that H⁺-type geopolymers retain Na in cement while releasing H, in effect lowering pH, thus offering a possibility as an alkali silica reaction suppressant.

Figure 11 shows the results of mortar expansion testing using an H⁺-type geopolymer additive in the grouting paste as a possible alkali silica reaction suppressant. At 365 days, the expansion of the test piece into which cement paste containing H⁺-type geopolymers had been injected was about 70% less than that of the test piece into which cement paste free of H⁺-type geopolymers had been injected, showing that H⁺-type geopolymers are effective in suppressing alkali silica reactions and subsequent expansion. It was also found that the results achieved with the H⁺-type geopolymers used were equal to those of the testing with Li-EDI type zeolites that had been developed earlier [6].

4. Research activities in the future

Using metakaolin, which has a higher Al/Si ratio than fly ash, as the starting material, could offer a higher ion exchange capacity, and thus a higher alkali silica reaction mitigation effect. With that in mind, experiments are underway on the potential of metakaolin as the starting material in place of fly ash. Figure 12 shows results of ion exchange tests conducted under pH=12 conditions on various H⁺-type geopolymers made from metakaolin. It was found that test pieces with lower Si/A ratios (0.10 and 0.25) exhibited greater ion exchange capacities than H⁺-type geopolymers made from fly ash. Going forward, H⁺-type geopolymers made from metakaolin will be put through similar tests described in this paper to examine their effectiveness in suppressing alkali silica reactions.

5. Conclusions

Fly ash was converted into hardened geopolymers through treatment with sodium silicate solutions, and those geopolymers were then turned into H⁺ with ex-

Fig. 12 Cation exchange capacity for Na⁺ ion of H⁺-type GP prepared from metakaolin with different Si/alkali ratio

changeable cations, which were then tested to clarify their properties. The following were obtained:

- (1) Na⁺-type hardened geopolymers were pulverized and the pulverized geopolymers were treated with sulfuric acid. Through the acid treatment, the geopolymers were turned into H⁺-type geopolymers with nearly all of the exchangeable cations turned into H⁺ ions.
- (2) Under pH 7 conditions, the ion exchange capacity of H⁺-type geopolymers for Na⁺ and K⁺ was about one fourth of that of the initial Na⁺-type geopolymers.
- (3) H⁺-type geopolymers showed dependency on pH levels in ion exchange capacity, which tends to increase with higher pH levels. That said, some Si elution was observed with pH12.5, which indicates that in observing reactions of hardened cement, it is necessary to look not just at cation exchange but also at Si elution as mechanisms for consuming alkalis.
- (4) It was found that the expansion of mortar that has undergone alkali silica reactions can be suppressed more effectively by injecting cement paste containing H⁺-type geopolymers than cement paste that does not contain those geopolymers.

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