

Evaluation on the Surface Modification of Recycled Fine Aggregates in Aqueous H_2SiF_6 Solution

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Abstract: Recycled aggregates (RAs) production techniques are essential for the material circulation society because RAs from demolished concrete waste can sustainably be reused as a concrete material. However, RAs can bring about several performance decreases when they are used for recycled aggregate concrete (RAC) because of the low qualities (i.e., high water-absorption rate and low density) caused by the attached hydrated cement paste on the RA surface. Therefore, both the production of high-quality RAs and the surface modification of RAs are significantly important for the extension of RAC utilization. This paper focuses on the surface modification of RFA to reduce the water absorption rate and increase density. Hydrofluorosilicic acid (H_2SiF_6), which is one of the by-products in phosphoric acid manufacture, is used herein for the surface modification of the RFA. The physical properties and mechanical performance of mortar using RFA were evaluated after RFA modification. Consequently, the proposed method is effective in reducing water absorption rate and increasing density of RFA. The density of RFAs was slightly increased by 0.5–2.6% after modification. On the other hand, the water absorption rate decreased by 4–18% after modification. The compressive strengths of mortar at 28 days ages showed 18.1 MPa with modified RFA and 16.2 MPa with RFA.

Keywords: recycled aggregate, recycled fine aggregate, surface modification, hydrofluorosilicic acid, mortar.

1. Introduction

The current annual industrial waste in South Korea amounts to approximately 130 million tons, with more than 50% of that being construction waste such as excess concrete. Specifically, the amount of concrete waste comprises 70% of construction waste, which is approximately 40% of all industrial waste (46 million tons). More than 90% of concrete waste, or 40 million tons each year, is produced as recycled aggregates (RAs) after going through recycling processes. The reproduced RAs are mainly reused as sub-base materials for roads, roadbed materials, and RAs for concrete (Noguchi et al. 2015; Shi et al. 2015). The quality of RAs produced from waste concrete via processes such as crushing, rubbing, smashing, and heating varies, and standards dependent on the physicochemical properties of the aggregates have been established for various countries as shown in Table 1 (AS 1996; DIN 4226–100 2002;

Construction standard 2013; BS 812: Part 2 1994; JIS A 5021 2005; JIS A 5022 2007; JIS A 5023 2007; KS F 2573 1999; RILEM TC 121-DRG 1994; Spanish Minister of Public Works 2008).

The current standardized quality grades of RAs are divided according to aggregate absorption rate and specific gravity, and they are classified into structural concrete aggregates, non-structural concrete aggregates, roadbed materials, and so on, based on these grades as shown in Table 2 (Shi et al. 2015; Behera et al. 2014). In general, the reason that RAs are lower in quality than natural aggregates is because mortar adheres to the surface of RA (cement matrix). Low-quality RAs having a high absorption rate and low weight have limitations in terms of being reused for concrete (Behera et al. 2014; Choi et al. 2014; Ismail and Ramli 2014). Accordingly, most RAs are not used as concrete aggregates, but as roadbed and sub-base materials; however, this demand is gradually decreasing, while the demand for their use in concrete is continuously required. In addition, regarding RAs for roads and landfills, there are concerns about alkali extraction due to $\text{Ca}(\text{OH})_2$, which is contained in adhered mortar (cement matrix) on the surface of aggregates, and also other long-term problems of environmental concern (Shi et al. 2015; Chen et al. 2017; Tam et al. 2007).

For the sustainable recycling of resources, in order to recycle the waste concrete that is produced in large quantities, not only an active use, but also an eco-friendly use of RAs is important (Choi et al. 2014; Ismail and Ramli 2014; Chen et al. 2017; Tam et al. 2007; Kong et al. 2010). This

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Table 1 Acceptance criteria regarding RA

| Country or standard | RA type | Oven-dry density (kg/m ³) | Absorption rate |
|-----------------------------------|----------------|---------------------------------------|-----------------|
| Australia (AS1141.6.2) | Class 1A | ≥ 2100 | ≤ 6% |
| | Class 1B | ≥ 1800 | ≤ 8% |
| Germany (DIN 4226-100) | Type 1 | ≥ 2000 | ≤ 10% |
| | Type 2 | ≥ 2000 | ≤ 15% |
| | Type 3 | ≥ 1800 | ≤ 20% |
| | Type 4 | ≥ 1500 | No limit |
| Hong kong | – | ≥ 2000 | ≤ 10% |
| Japan (JIS A 5021, 5022 and 5023) | Coarse—class H | ≥ 2500 | ≤ 3% |
| | Fine—class H | ≥ 2500 | ≤ 3.5% |
| | Coarse—class M | ≥ 2300 | ≤ 5% |
| | Fine—class M | ≥ 2200 | ≤ 7% |
| | Coarse—class L | No limit | ≤ 7% |
| | Fine—class L | No limit | ≤ 13% |
| Korea (KS F 2573) | Coarse | ≥ 2500 | ≤ 3% |
| | Fine | ≥ 2500 | ≤ 3% |
| RILEM | Type 1 | ≥ 1500 | ≤ 20% |
| | Type 2 | ≥ 2000 | ≤ 10% |
| | Type 3 | ≥ 2500 | ≤ 3% |
| Spain (EHE) | – | ≥ 2000 | ≤ 5% |

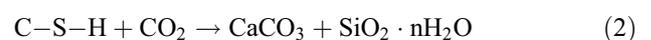
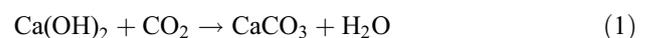
Table 2 Reference for categorizing concrete made with recycled coarse aggregate (RCA).

| Category | Coarse aggregate | | | Aggregates for concrete |
|-----------------------------------|---|--|---|-------------------------|
| | High quality | Medium quality | Low quality | |
| Dried density (t/m ³) | Over 2.5 | Over 2.3 | – | Over 2.5 |
| Absorption rate (%) | Below 3.0 | Below 5.0 | Below 7.0 | Below 3.0 |
| Fine aggregate content (%) | Below 1.0 | Below 1.5 | Below 2.0 | Below 7.0 |
| No. JIS | A 5021 | A 5022 | A 5023 | A 5005 |
| Categorization of usage | Identical to natural aggregate or structural concrete | Concrete construction elements not affected by dry shrinkage | Non-structural elements that do not require durability and strength | – |

requires taking measures to simultaneously address the problems of low weight, high absorption rate, and alkali extraction that RAs currently have, and also requires the quality improvement of aggregates for use in concrete (Kong et al. 2010; Al-Bayati et al. 2016; Zhan et al. 2014).

There have been numerous studies reporting on surface modifications of RAs using carbonation and acid treatment, focusing on the fact that mortar adhered to the surface of RAs (cement matrix) contains profuse Ca(OH)₂ (Chen et al. 2017; Tam et al. 2007; Kong et al. 2010; Al-Bayati et al. 2016; Zhan et al. 2014). The surface modification with carbonation is a method that uses accelerated carbonation,

which reacts highly concentrated carbon dioxide with Ca(OH)₂ of the adhered mortar on the aggregate surface under dry or wet environments (Zhan et al. 2014; Zhang et al. 2015). The mechanism of surface modification used for RAs by accelerated carbonation is described below.



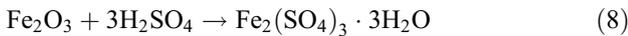
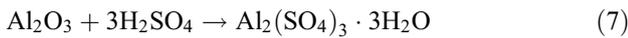
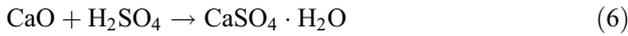
On the other hands, the hydration products of cement in hardened paste can be dissolved in acid solution (Shi et al. 2015; Tam et al. 2007; Al-Bayati et al. 2016). Thus, acidic

solution can be used to remove the adhered mortar effectively and enhance the quality of RA. Phosphoric acid, Sulfuric acid and hydrochloric acid are used in a typical acid treatment. The mechanisms of surface modification used for RAs by acid treatments are described below.

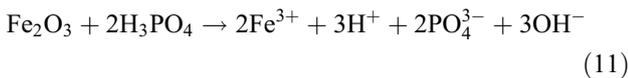
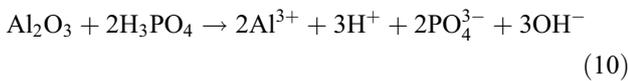
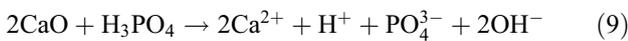
Reactions under HCl:



Reactions under H_2SO_4 :



Reactions under H_3PO_4 :



In the “mechanical” first processing stage, RAs are produced and then subjected to the “chemical” second processing stage, in which carbonation and acid treatment are applied. Ultimately, both methods improve the physical properties of RAs. $\text{Ca}(\text{OH})_2$ within the adhered mortar is converted to CaCO_3 by carbonation, and the porosity of the adhered mortar decreases, leading to an increase in the specific gravity of aggregates and a decrease in its absorption rate (Ryou and Lee 2014; Ondova and Sicakova 2016). The acid treatment results in an increased specific gravity of the aggregates and a decreased absorption rate through partially removing the adhered mortar and neutralizing the hydroxide (OH^-) ions simultaneously. However, carbonation is associated with problems such as high costs of equipment, limited processed amount of aggregates per unit time, and difficult retrieval of unreacted carbon dioxide (Al-Bayati et al. 2016; Zhan et al. 2014; Zhang et al. 2015). Furthermore, for acid treatment, there are issues with high processing costs, secondary contaminated water, and contaminated water (Shi et al. 2015; Chen et al. 2017; Tam et al. 2007; Kong et al. 2010; Al-Bayati et al. 2016). Thus, a new processing method that can both achieve surface modification of RAs and improve the issues associated with existing methods is required.

This study focused on achieving efficient surface modification of RAs through acid treatment. In order to overcome the problems of high costs and secondary contaminated water generation, we applied strongly acidic hydrofluorosilicic acid (H_2SiF_6) as an industrial by-product that is

usually generated in processing and production stages of phosphogypsum or phosphatic fertilizer (Yang et al. 2005; Kim et al. 2004). The uses of H_2SiF_6 are various such as metal refinement, soil hardening agent, surface treatment agent, sterilizer and water system purification. In this research, for RFAs, we evaluated the decrease in absorption rate, increase in specific gravity, and reduction in pH, in order to develop a method to achieve surface modification of RAs using H_2SiF_6 . In addition, we evaluated the physical properties of mortar with modified RFAs using a physico-chemical analysis, through which we were able to verify the usefulness of the RFAs, surface-modified by the method proposed in this study, as concrete aggregates.

2. Experimental Procedure

2.1 Materials

In the experiments, H_2SiF_6 of pH 1.0 (10% solution) was used as acid treatment for surface modification of RFAs. And both natural fine aggregate (NFA) and RFAs were used, and the basic physical properties of the fine aggregates are shown in Table 3. Three types of recycled aggregates (RFA 1, 2 and 3) were used in this study. As shown in Tables 1 and 2, RFA-2 and 3 are considered low-quality recycled aggregates used as roadbed. RFA-1 can be used as aggregate for mortar or concrete because it has higher physical quality than relatively different recycled aggregate. The chemical composition of cement is shown in Table 4.

2.2 Experiment Outline

In order to evaluate the surface modification of RFAs by the H_2SiF_6 proposed for use in this research, we measured the change in pH, specific gravity, and absorption rate of the fine aggregates. To evaluate the physical–mechanical properties of the mortar before and after surface modification of the fine aggregates, the setting time, flow, and compressive and flexural strengths were measured. Additionally, we performed Scanning Electron Microscope (SEM), Thermogravimetric Differential Thermal Analysis (TG/DTA), Mercury Intrusion Porosimetry (MIP), and X-ray diffractometer (XRD) as chemical analyses. The mortar specimens were created by using natural, recycled, and modified-RFAs. Table 5 shows the test items and methods for RFAs pre-soaking in water and acid. And Table 6 shows the test items and method for mortar and their related standards.

2.2.1 Specific Gravity and Absorption Rate of Fine Aggregates

As shown in Tables 3 and 5, we measured the specific gravity and absorption rates of natural and RFAs that were used in our experiments and also the air-dried specific gravity and over-dry one for the specific gravity of aggregates.

2.2.2 pH Measurement

We measured the respective changes in pH by $\text{Ca}(\text{OH})_2$ within the cement matrices adhered to the RFAs and by

Table 3 Physical properties of fine aggregates.

| Aggregate type | Density (t/m ³) | Water absorption rate (%) |
|----------------|-----------------------------|---------------------------|
| NFA | 2.52 | 0.54 |
| RFA-1 | 2.34 | 5.12 |
| RFA-2 | 2.19 | 8.37 |
| RFA-3 | 2.27 | 7.64 |

Table 4 Chemical composition of cement.

| Chemical composition (%) | | | | | | | Specific gravity |
|--------------------------|--------------------------------|--------------------------------|-------|------|-----------------|------|------------------|
| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | LOI | |
| 21.95 | 6.59 | 2.81 | 60.12 | 3.32 | 2.11 | 2.58 | 3.15 |

LOI loss on ignition.

Table 5 Test items and methods (RFAs) (ASTM International 2012).

| Items | Fine aggregates | Conditions | Number of measurement | Standard |
|--------------------------------------|-----------------|---|------------------------|------------|
| Specific gravity and absorption rate | NFA, RFA | Air-dried specific gravity, over-dry specific gravity | More than twice each | ASTM C 128 |
| pH | RFA | [Method-1] RFAs (50 g) + distilled water (300 g) | More than 3 times each | – |
| | RFA | [Method-2] RFAs (50 g) + distilled water (300 g) 1st stirring → H ₂ SiF ₆ input → 2nd stirring | More than 3 times each | |
| | RFA | [Method-3] RFAs (50 g) + distilled water (300 g) + H ₂ SiF ₆ stirring | More than 3 times each | |

Table 6 Test items and methods (Mortar) (ASTM International 2006, 2012, 2013, 2013, 2014).

| Items | Fine aggregates | Conditions | Number of measurement | Standard |
|---|------------------------|----------------------------|----------------------------|------------|
| Setting time | NFA, RFA, Modified RFA | Initiation and termination | More than twice each | ASTM C 191 |
| Flow | NFA, RFA, Modified RFA | – | More than twice each | ASTM C 230 |
| Compressive strength, flexural strength | NFA, RFA, Modified RFA | Age of 3, 7, and 28 days | More than three times Each | ASTM C 109 |

H₂SiF₆ in the state of aqueous solutions under three different conditions, as displayed in Table 5. First, RFAs and distilled water were combined with a weight ratio of 1:6 and measured the pH values for different stirring times of the solution (0, 1, 3, and 5 min). Also, we conducted the first stirring of distilled water and RFAs for 5 min, deposited 8, 10, and 12 g of H₂SiF₆ into three different solutions, and measured their pH values based on second stirring times of 0, 1, 3, and 5 min. Lastly, we mixed RFAs and distilled water with a weight ratio of 1:6, and deposited 4, 6, 8, and 10 g of H₂SiF₆ into four different solutions, and measured their pH values based on different stirring times if 0, 1, 3, and 5 min.

2.2.3 Evaluation of Material Properties of Mortar

Mortar specimens were produced using natural and RFAs. For the mortar specimen with modified-RFAs, the method having the best surface modification was used.

3. Results and Analysis

3.1 pH

Table 7 displays the pH measurement results based on different stirring times of the distilled water and RFAs (Method-1 in Table 5). It was shown that the RFAs had a pH of about 10.51 when soaked in distilled water and the pH

Table 7 Stirring times of distilled water and RFAs and changes in pH.

| Number of tests | pH by stirring time | | | |
|-----------------|---------------------|-------|-------|-------|
| | 0 min | 1 min | 3 min | 5 min |
| 1 | 10.67 | 11.26 | 11.43 | 11.51 |
| 2 | 10.36 | 11.29 | 11.44 | 11.57 |
| 3 | 10.60 | 11.30 | 11.32 | 11.53 |
| 4 | 10.44 | 11.28 | 11.45 | 11.51 |

Table 8 Changes in pH by stirring times with H₂SiF₆.

| H ₂ SiF ₆ | pH before stirring | pH by stirring time | | | |
|---------------------------------|--------------------|---------------------|-------|-------|-------|
| | | 0 min | 1 min | 3 min | 5 min |
| 8 g mixed | 11.53 | 4.39 | 5.85 | 9.84 | 10.32 |
| 10 g mixed | 11.52 | 3.84 | 4.89 | 8.24 | 9.52 |
| 12 g mixed | 11.51 | 3.63 | 4.17 | 6.58 | 8.64 |

tended to increase depending on the stirring time of the solution. We also confirmed consistent alkali extraction due to the Ca(OH)₂ in the adhered cement matrices.

Table 8 shows the results of the pH measurements based on the second stirring times after conducting the first stirring of distilled water and RFAs for 5 min and depositing H₂SiF₆ into the solutions (Method-2 in Table 5). For the solutions containing 8, 10, and 12 g of H₂SiF₆, the pH values measured immediately after the addition of H₂SiF₆ were less than 5.0, implying that the solutions were acidic. The solutions that had less than 10 g of H₂SiF₆ added after 3 min of stirring showed pH values of less than 10, implying alkaline. For a solution to have a pH range under 10 in up to 5 min of stirring, more than 10 g of H₂SiF₆ was required.

Meanwhile, the pH measurements after depositing RFAs into distilled water and adding H₂SiF₆ are shown in Table 9 (Method-3 in Table 5). When the properties of the solutions with 4, 6, 8, and 10 g of H₂SiF₆ were evaluated, for the unextracted RFAs, the pH values of the solutions fell within the “acidic” range under 3.0; when each specimen was stirred, its pH tended to increase inversely proportional to the amount of H₂SiF₆ added.

3.2 Specific Gravity and Absorption Rates of Fine Aggregates

The results of testing the specific gravity and absorption rates of NFA and RFAs are shown in Table 10. The test

results of the modified RFAs correspond to the case with 10 g of H₂SiF₆ added and 5 min of stirring in Table 9 (Method-3 in Table 5). The density of RFAs was slightly increased by 0.5–2.6% after modification. On the other hand, the water absorption rate decreased by 4–18% after modification. The decrease of the absorption rate of the aggregate due to the modification was found to be an increase of the aggregate density.

3.3 Mortar Setting Times and Flows

Three types of recycled aggregates (RFA 1, 2 and 3) were used in this study. RFA-2 and 3 are considered low-quality recycled aggregates used as roadbed materials because of their high water uptake after modification. However, it has confirmed the alkali leaching reduction effect and can be used as a more environmentally stable roadbed material. RFA-1 can be used as aggregate for mortar or concrete because it has higher physical quality than relatively different recycled aggregate. Therefore, RFA-1 and modified RFA-1 were used in the preparation of mortar specimens for the following experiments and analyzes.

Table 11 indicates the results of testing the flows and setting times of mortar using NFA, RFA-1, and modified RFA-1. In this case, the modified RFAs with 10 g of H₂SiF₆ added and 5 min of stirring in Table 9 was used for mortar.

The RFA had relatively smaller flows when compared to the NFA, and the flows of the modified RFA were found to

Table 9 Changes in pH pH by stirring time after mixing H₂SiF₆.

| H ₂ SiF ₆ | pH before stirring | pH by stirring time after mixing H ₂ SiF ₆ | | | |
|---------------------------------|--------------------|--|-------|-------|-------|
| | | 0 min | 1 min | 3 min | 5 min |
| 4 g mixed | 10.64 | 3.80 | 9.15 | 10.78 | 11.04 |
| 6 g mixed | 10.45 | 3.50 | 6.54 | 9.24 | 10.20 |
| 8 g mixed | 10.36 | 3.30 | 4.01 | 8.04 | 9.80 |
| 10 g mixed | 10.52 | 3.00 | 3.52 | 7.85 | 8.24 |

Table 10 Changes in the specific gravity and absorption rate of fine aggregates.

| Aggregate type | Before | | After | |
|----------------|---------------------|---------------------------|---------------------|---------------------------|
| | Density (t/m^3) | Water absorption rate (%) | Density (t/m^3) | Water absorption rate (%) |
| NFA | 2.52 | 0.54 | 2.51 | 0.55 |
| RFA-1 | 2.34 | 5.12 | 2.39 | 4.88 |
| RFA-2 | 2.19 | 8.37 | 2.20 | 6.84 |
| RFA-3 | 2.27 | 7.64 | 2.33 | 6.58 |

Table 11 Mortar setting times and flows.

| Used aggregate type of mortar | Flow (mm) | Initiation (min) | Termination (min) |
|-------------------------------|-----------|------------------|-------------------|
| NFA | 180 | 250 | 450 |
| RFA | 130 | 200 | 400 |
| Modified-RFA | 150 | 220 | 410 |

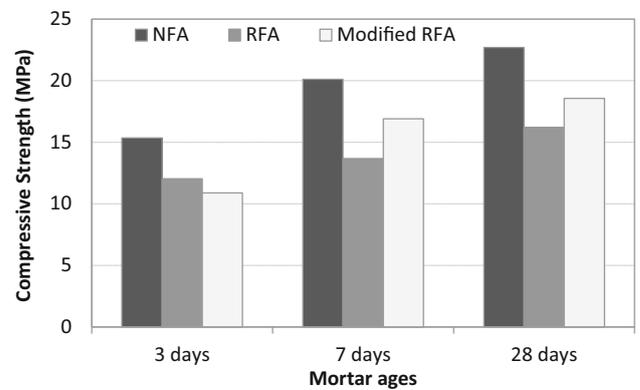
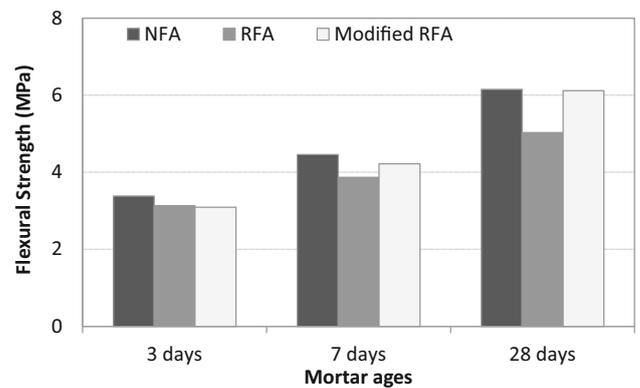
be greater than those of the RFA (unmodified). Because of the high absorption rates of RFA, the values of their flows appeared to be relatively low, but on the other hand, there was a positive effect on the flows of the modified RFA. Even though there were relative differences among the mortar samples with different setting times, it was found that the initiation and termination times satisfied their prescribed ranges in all levels.

3.4 Mechanical Properties of Mortar

The results of the compressive strength test and flexural strength test of the mortar using each type of aggregates are shown in Figs. 1 and 2. The results show that the compressive strength of mortar with RFAs was lower than that of mortar with NFA, and the compressive strength of mortar with modified RFA was smaller than that of mortar with NFA, but greater than that of mortar with RFA. The improvement in compressive strength of the modified RFA appears to result from the enhancement of its specific gravity and reduction in its absorption rates. Because of the characteristics of fine aggregates, it is very difficult to control their moisture content in a surface-dry state, but even when taken into consideration, it can be seen that there is an evident relationship between the enhancement of material properties of RFA through surface modification and the compressive strength of mortar. In addition, after testing the flexural strength of mortar, the flexural strengths of mortar were in the same descending order as the compressive strengths (28 days ages): NFA (22.7 MPa), modified RFA (18.1 MPa), and RFA (16.2 MPa).

3.5 Chemical Analysis

Figure 3 shows the SEM results based on different mortar curing periods. CSH and ettringite were clearly observed in the NFA and RFA in the early age. CH, CSH, and ettringite were observed on the 28th day regardless of the fine aggregate type. When modified RFA was used, the hydration reaction proceeded relatively late, but the effect of porosity and compressive strength was better than that of RFA. The

**Fig. 1** Compressive strength of mortar.**Fig. 2** Flexural strength of mortar.

effect of CaF_2 , SiO_2 and residual H_2SiF_6 formed on the modified aggregate surface were affected. However, the decrease of the water absorption rate and the density of the aggregate increased the compressive strength of mortar. TG–DTA regarding three different types of mortar at the ages of 3 and 28 days, and the contents of $Ca(OH)_2$ and $CaCO_3$ are shown in Table 12.

In addition, Fig. 4 represents the result of TG/DTA for the mortar at the age of 28 days. There were changes in weight

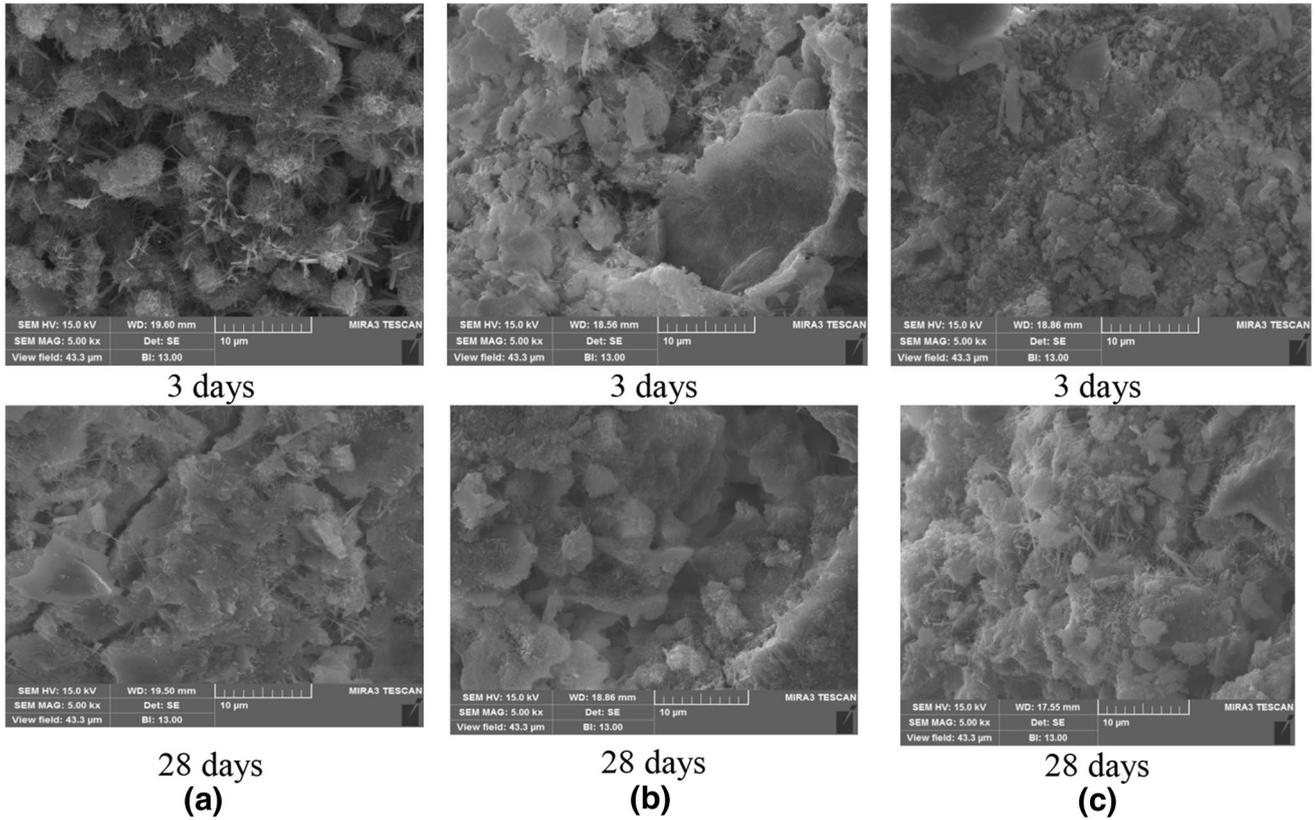


Fig. 3 SEM analysis based on mortar curing ($\times 5000$). **a** NFA, **b** RFA, and **c** modified RFA.

Table 12 Analysis of contents of Ca(OH)_2 and CaCO_3 by the age of mortar.

| Fine aggregates | Ca(OH)_2 content (%) | CaCO_3 content (%) |
|------------------------|-------------------------------|-----------------------------|
| NFA (3 days) | 2.96 | 4.54 |
| NFA (28 days) | 3.12 | 5.56 |
| RFA (3 days) | 2.71 | 5.33 |
| RFA (28 days) | 2.42 | 4.65 |
| Modified RFA (3 days) | 2.18 | 3.97 |
| Modified RFA (28 days) | 2.22 | 5.54 |

for all specimens during the pyrolysis of Ca(OH)_2 and CaCO_3 , and based on this result, the existence of Ca(OH)_2 and CaCO_3 was verified within the analyzed specimens. At up to 100°C on DTA, the physically bonded water within the matrices evaporated, and there was physical dehydration of C_3A ettringite between 140 and 180°C , ettringite and aluminate-based hydrates between 270 and 330°C , and aluminate-based hydrates at around 570°C . In the case of mortar with RFA and modified RFA, their Ca(OH)_2 contents were lower than that of mortar with NFA, and the CaCO_3 contents of mortar with NFA and modified RFA, respectively, were measured lower than that of mortar with RFAs. As a result, the modification of RFA by H_2SiF_6 appeared to be effective.

The mortar porosity rate distribution dependent on mortar age is displayed in Fig. 5. The porosity at 3 days of age showed 20.025, 20.295, and 19.428% of NFA mortar, RFA mortar and modified RFA mortar respectively. On the other hand, the porosity at 28 days of age showed 16.950, 15.991, and 15.903% of NFA mortar, RFA mortar and modified RFA mortar respectively. The all mortar showed similar porosity. The smaller the pore size, the higher the distribution in NFA mortar. Modified RFA mortar showed a distribution of pores similar to NFA mortar than RFA mortar.

An XRD compound analysis was conducted on the test bodies of NFA, RFA, and modified RFA, and the results from day 3 and day 28 are shown in Fig. 6. Modified RFA mortar showed different compound composition compared

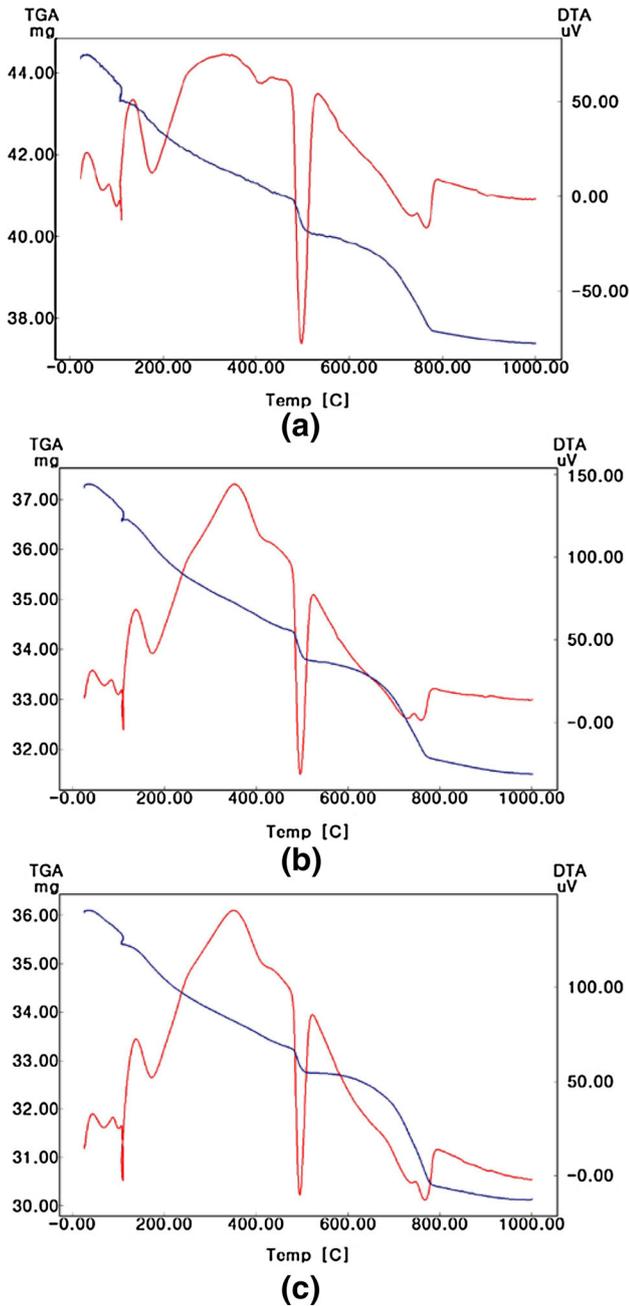


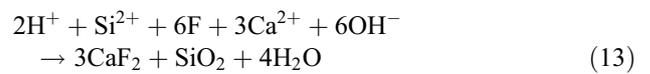
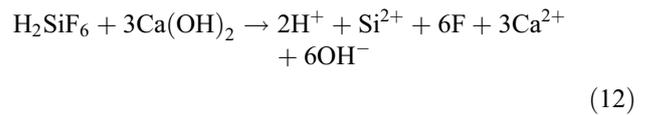
Fig. 4 Mortar TG/DTA (28 days). **a** mortar using NFA (28 days), **b** mortar using RFA (28 days), and **c** mortar using Modified RFA (28 days).

to RFA mortar. For the mortar on day 3, the early stage amount of $\text{Ca}(\text{OH})_2$ was relatively higher for mortar with RFA than for mortar with modified RFA. This is considered to result from the increase in the hardened cement paste attached to the surface of the RFA resulting from $\text{Ca}(\text{OH})_2$. Meanwhile, a relatively higher CSH generation was verified for mortar with modified RFA. For the mortar on day 28 with modified RFA, the amount of CSH generation was found to be increasing, which was considered to result from the supply of Si ions in the H_2SiF_6 .

To investigate the RA surface modification method proposed in this paper, the absorption rates and specific gravity of RFA before and after treating with H_2SiF_6 were

measured. Additionally, a physicochemical property evaluation and chemical analysis of mortar with modified RFA were conducted. The results verified the surface modification effect and the presence of changes in the physical properties of the RFA owing to the H_2SiF_6 in each experiment. The values of various mechanical properties of the modified RFA mortar were also found to be relatively high. The RFA surface modification method proposed in this study is based on the chemical reaction mechanism between H_2SiF_6 and abundant $\text{Ca}(\text{OH})_2$ contained in the hardened cement paste in the aqueous solution state as below.

Reactions under H_2SiF_6

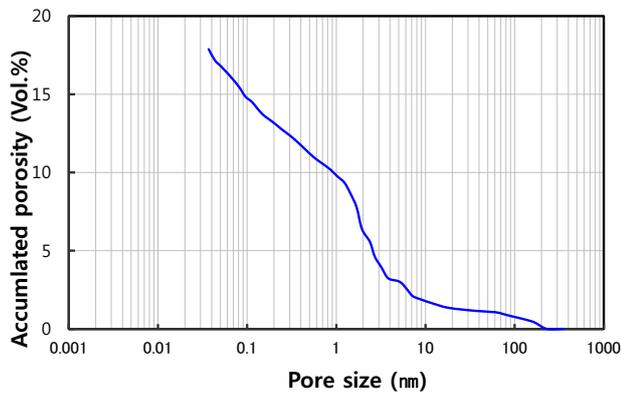


The reaction between the $\text{Ca}(\text{OH})_2$ and H_2SiF_6 involves a chemical reaction that produces inorganic fine powders of CaF_2 and SiO_2 . Wastewater is generated in recycled aggregate processing using the proposed method. Removal of fluoride from wastewater may be worse than acid wastewater. However, the fluoride in the wastewater is precipitated as an insoluble CaF_2 form as described in the paper. During the wet process, CaF_2 precipitate can be collected and disposed of separately.

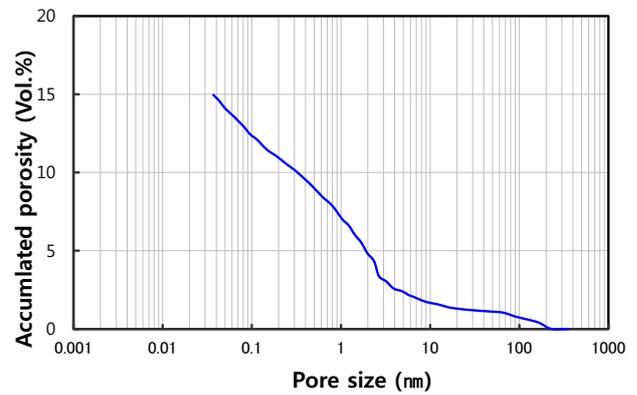
On the other hand, it is thought that this reaction progresses gradually from the surface of the hardened cement paste attached to the RFA towards the inside, causing the cement matrix to become denser. The decrease in the absorption rate and the consequent increase in specific gravity are considered to be the filling effect of the surface porosity due to the densification of the matrix inside the hardened cement paste. A decreased aggregate absorption rate and an increased specific gravity were revealed as increased mortar compression strength compared to before the modification as the compressive strengths (28 days ages): NFA (22.7 MPa), modified RFA (18.1 MPa), and RFA (16.2 MPa). Therefore, it has been confirmed that the acid treatment of the RFA and H_2SiF_6 in aqueous solution, as proposed in this study, shows a surface modification effect similar to that of conventional carbonation treatment and acid treatment.

4. Conclusions

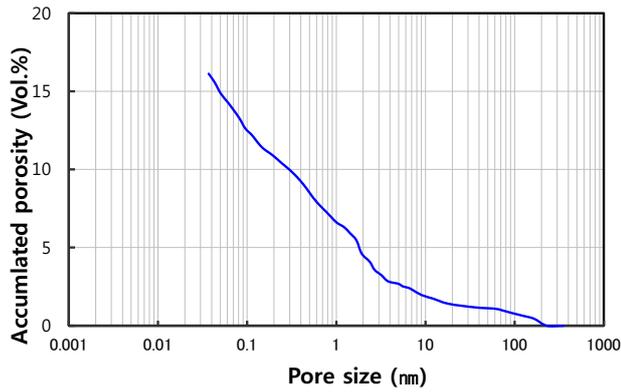
In this study, RFAs with high absorption rates and low specific gravities were wet-reacted with H_2SiF_6 having relative strong acidity, and various physical properties of the RFAs and mortar using the byproduct were confirmed. The results of this study are summarized as follows.



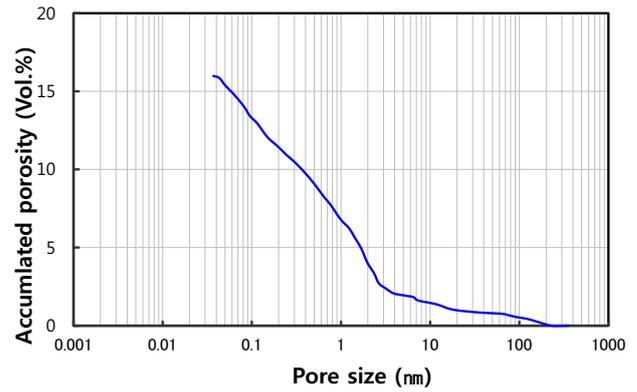
(a-1) Mortar using NFA (3 days)



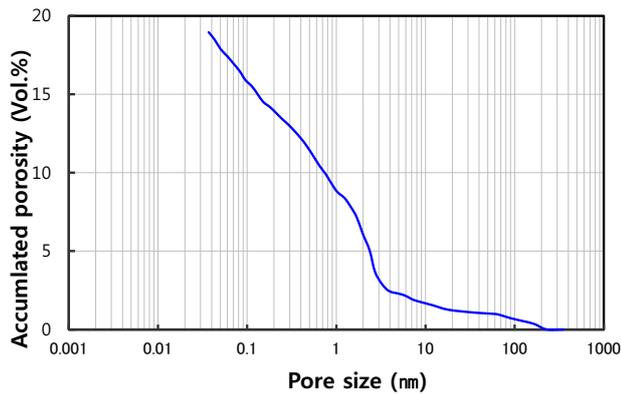
(a-2) Mortar using NFA (28 days)



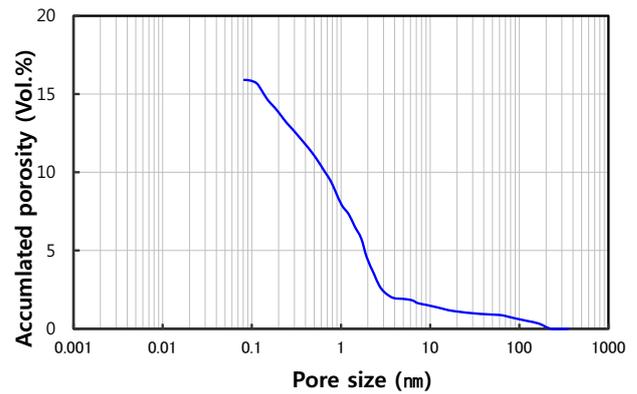
(b-1) Mortar using RFA (3 days)



(b-2) Mortar using RFA (28 days)



(c-1) Mortar using modified RFA (3 days)



(c-2) Mortar using modified RFA (28 days)

Fig. 5 Mortar MIP.

1. When large amounts of $\text{Ca}(\text{OH})_2$ from hardened cement paste were attached to the surface of the RFAs and mixed with distilled water, alkaline ions are continuously eluted, resulting in pH values exceeding 11.5. When low quality RFAs were chemically treated in an aqueous solution containing H_2SiF_6 , the absorption rate decreased and the specific gravity increased.
2. The proposed surface modification method is considered to result from the chemical reaction occurring on the RFA surface between H_2SiF_6 and $\text{Ca}(\text{OH})_2$, which is contained in abundance in the hardened cement paste attached to the surface of the RFA. Because of the production of CaF_2 and SiO_2 on the surface of the RFA

as the result of the reaction with H_2SiF_6 , an improvement in aggregate specific gravity and absorption rate was found to occur, and mortar test results confirmed enhanced strength.

3. By surface modification, mortar by using modified RFA showed improvements of mechanical properties in both compressive strength and flexural strength relatively in comparison with mortar by using RFA.
4. Therefore, it was confirmed that the proposed RFA surface treatment method using H_2SiF_6 , which is an industrial byproduct, is effective in improving the physical properties (high water absorption rate and low density) of RFA.

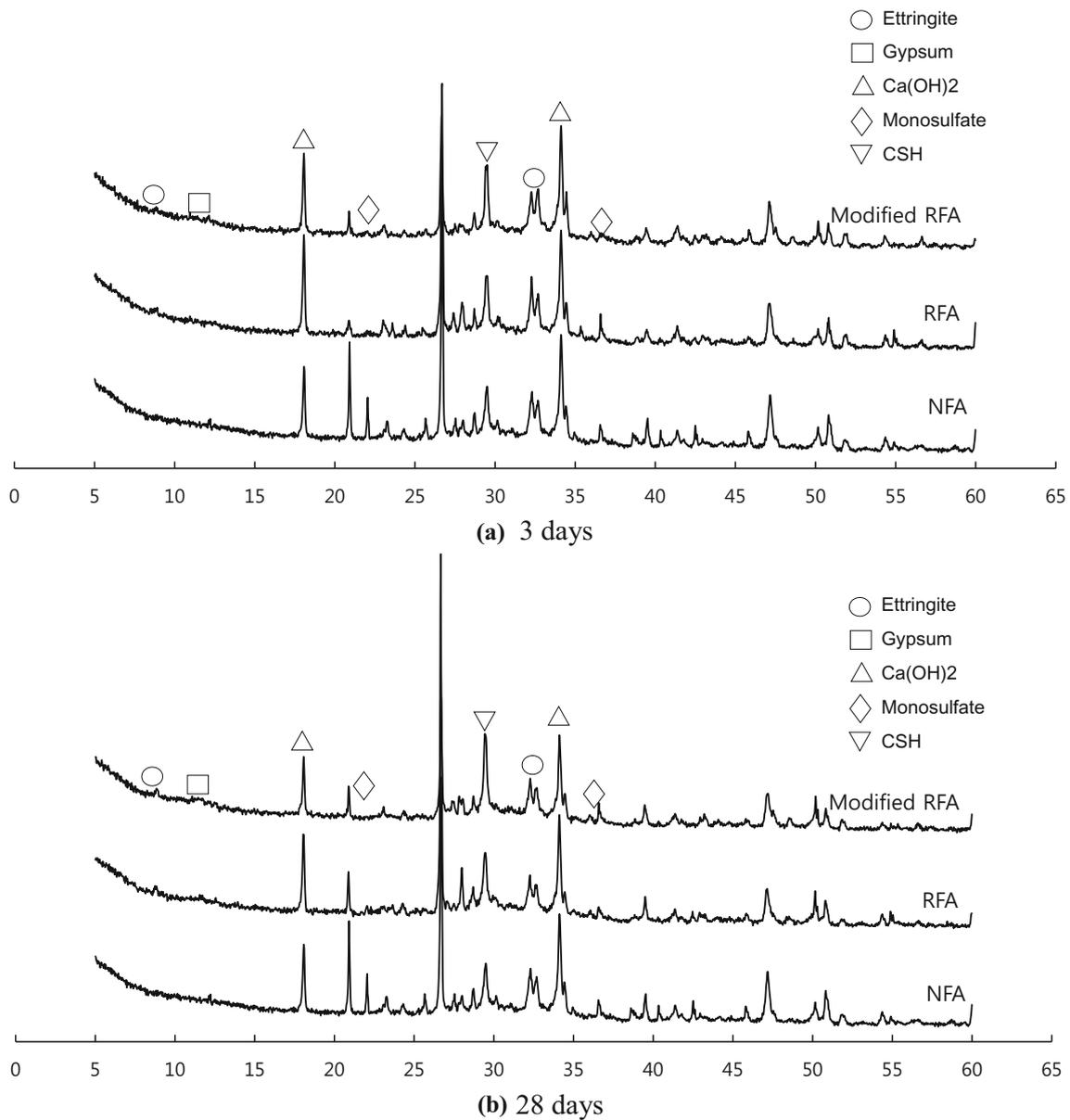


Fig. 6 XRD.

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