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Reduction of Discard Glass Fiber Reinforced Plastics (GFRP) Using Thermal Decomposition after Immersion in Sodium Hydroxide Solution

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Abstract

In this study, the reduction of discarded glass fiber-reinforced plastics (GFRP) using thermal decomposition with sodium hydroxide was attempted as a new technology. After immersing GFRP in NaOH solution to adhere NaOH on the surface of GFRP, thermal decomposition treatment was performed under an inert atmosphere to occur gasification of resin and conversion of glass fiber into soluble sodium silicate in the GFRP. As a result, the gasification of the resin and the conversion of the glass fiber into soluble sodium silicate were promoted by thermal decomposition treatment after immersion in the NaOH solution. Furthermore, it was confirmed that the reduction of the weight and strength of the residue was promoted by the treatment with HCl due to the extraction of silica and calcium.

Keywords

GFRP
NaOH
Thermal decomposition
Alkali fusion
Volume reduction

1. Introduction

Glass fiber-reinforced plastic (GFRP) is a composite material consisting of resin (mainly thermosetting resins such as epoxy and phenolic resins) and glass fibers. Calcium carbonate ($CaCO_3$) is commonly used as a filler in the resin to enhance properties such as reinforcement, heat resistance, and cost-effectiveness [1]. GFRP is widely used in applications such as boats, bicycles, helmets, bathtubs, etc., due to its high strength, lightweight, corrosion resistance, and water resistance. In Japan, approximately 300,000–400,000 tons of GFRP are discarded annually. However, the disposal of waste GFRP is limited due to its unique characteristics, such as high strength making it difficult to crush, and the presence of a significant amount of glass, which makes incineration challenging. As a result, more than 90% of waste GFRP is currently disposed of in landfills [2].

The current situation is further compounded by the fact that over half of the municipalities in Japan do not accept GFRP-containing products for disposal, and outsourcing the disposal to specialized companies is costly, leading to an increase in illegal dumping and associated problems. Therefore, there is a need for effective methods of processing waste GFRP. Various methods for processing GFRP have been researched, including thermal decomposition and dissolution using high temperatures and pressures to treat the resin portion. Nevertheless, challenges such as processing time, cost, and the disposal of remaining glass residues remain, and practical solutions have not been achieved [3,4].

The authors have previously attempted to recycle various waste materials using sodium hydroxide (NaOH). For example, the authors have recovered tantalum capacitors through the thermal decomposition and gasification of the resin under alkaline conditions in the presence of alkali hydroxide [5] and have also reduced the volume of waste glass wool insulation materials by thermally decomposing the resin and dissolving the glass fiber [6]. In this context, the authors have demonstrated that thermal decomposition treatment using NaOH can simultaneously gasify the resin portion of waste GFRP and dissolve the glass fibers through alkaline chlorination. This process allows for the reduction of waste GFRP into powder form, carbonization of resin components, and extraction of glass components into a liquid medium [7].

This study aims to develop a new waste reduction technology for waste GFRP by immersing it in a NaOH aqueous solution, causing NaOH to adhere to the surface of the waste GFRP. Subsequently, thermal decomposition treatment is applied to gasify the resin and attempt to dissolve the glass fibers. The study investigates the thermal decomposition behavior of waste GFRP based on the concentration of NaOH aqueous solution used for immersion and examines the extraction behavior of glass components (silica) from waste GFRP based on the type of solvent used. The study explores the potential of this waste GFRP reduction technology.

2. Sample and experimental methods

2.1. Samples

The experiments utilized domestically generated waste GFRP. The sample used was a typical waste GFRP containing epoxy resin in the resin component. **Figure 1** presents the powder X-ray diffraction pattern of the waste GFRP, and **Figure 2** shows the results of differential thermal weight analysis conducted by heating the sample at a rate of 10°C/min under a nitrogen atmosphere. The waste GFRP was pulverized to a particle size of below 250 µm using a planetary ball mill (P-6, manufactured by Fritsch) and the powder X-ray diffraction patterns were analyzed using a powder X-ray diffractometer (MiniFlex 600, manufactured by Rigaku), while differential thermal weight analysis was conducted using a differential thermal weight analyzer (STA6000, manufactured by Perkin Elmer).

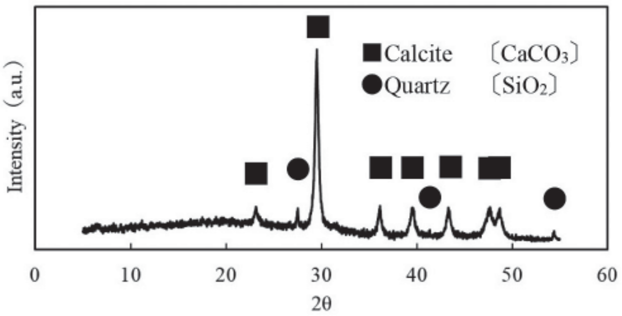

Figure 1. XRD pattern of waste GFRP

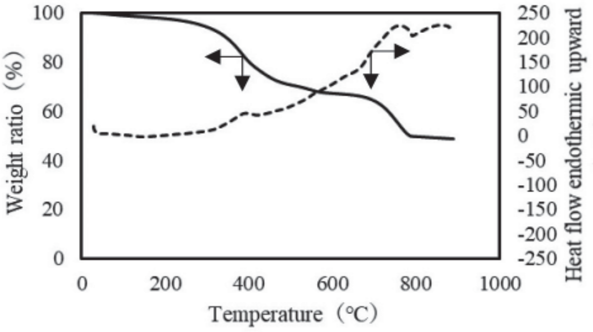

Figure 2. TG-DTA analysis of waste GFRP

In the sample, quartz (SiO_2) and calcite ($CaCO_3$) were identified as crystalline phases (**Figure 1**). Quartz is believed to originate from the glass fibers, while calcite is likely derived from the filler material used in the waste GFRP resin. In the thermogravimetric-differential thermal analysis (TG-DTA) of waste GFRP, a weight loss, and exothermic reaction were observed around 300–500°C, indicating thermal decomposition of the resin component in this temperature range. Based on these results, it is estimated that the resin component accounts for approximately 36 wt% of the total. Additionally, at around 700–800°C, another weight loss and exothermic reaction were observed, indicating the decarbonization reaction of calcium carbonate. It is estimated that calcium carbonate comprises approximately 36 wt% of the total based on these results. From these observations, it can be inferred that other components, including the remaining glass fibers, make up approximately 28 wt% of the total.

2.2. Viscosity of NaOH aqueous solution and adhesion to waste GFRP

In this study, waste GFRP was cut into dimensions of 1×1×0.2 cm (**Figure 3**). For the experiments, NaOH aqueous solutions with concentrations ranging from 0 to 30 M were used, and the viscosity of the NaOH aqueous solution at room temperature was measured using a viscometer (Viscotester VT-06, manufactured by RION Corporation). Waste GFRP was immersed in NaOH aqueous solutions of various concentrations, and the relationship between NaOH solution concentration and adhesion amount was investigated. Distilled water was used as the 0 M NaOH aqueous solution.

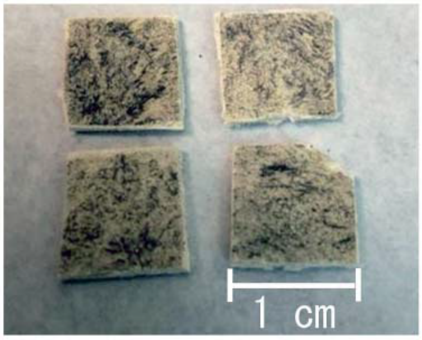

Figure 3. Photo of waste GFRP

The cut waste GFRP samples were immersed in NaOH aqueous solution for 3 hours, then allowed to stand on a Büchner funnel for 10 minutes, allowing any NaOH solution that did not adhere to the waste GFRP to flow down. The adhesion amount was calculated based on the difference in mass before and after immersion. However, the 30 M NaOH aqueous solution was measured immediately after immersion as it solidifies quickly and does not require a settling period.

2.3. Thermal decomposition treatment after immersion in NaOH aqueous solution

The flow of this experiment is illustrated in **Figure 4**. Waste GFRP (4 g) was immersed in NaOH aqueous solutions of various concentrations, placed in a stainless-steel reactor, and subjected to nitrogen substitution (100 mL/min, 45 min). Subsequently, the sample was heated at 600°C for 60 min under a nitrogen flow rate of 20 mL/min and then allowed to cool naturally for 40 min. The gas generated during the experiment was collected using a gas pack. The collected gas was analyzed for yield and composition using a gas chromatograph (GC-8A, manufactured by SHIMADZU).

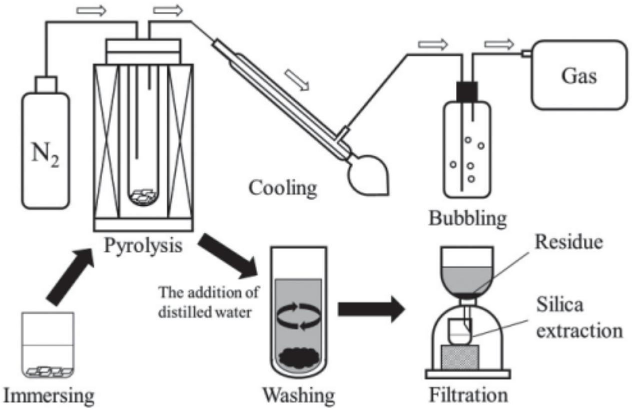

Figure 4. Experimental procedure

After gas collection, 200 mL of solvent (distilled water or 1 M HCl) was added to the reactor, stirred, and used to extract the dissolved components from the thermally treated waste GFRP, yielding a filtrate and solid residue. The filtrate was subjected to silicon and calcium concentration measurements using atomic absorption spectrometry (Analyst 200, manufactured by PerkinElmer), and the amount of dissolved glass components and calcium derived from calcium carbonate was calculated. The solid residue was dried at approximately 60°C and then examined for surface condition and weight using a scanning electron microscope (SEM) (JSM-6510A, manufactured by JEOL) and an electronic balance, respectively.

2.4. Strength testing of residues after treatment

The strength testing was performed using a strength measuring instrument (ZTS-500N, manufactured by Imada Corporation) as shown in **Figure 5**. The dried residue after treatment, which had retained the original form of the waste GFRP to a relatively high degree, was collected. The strength against penetration was measured at a descent rate of 30 mm/min. The tip diameter of the needle used for penetration was Φ1.5 mm.

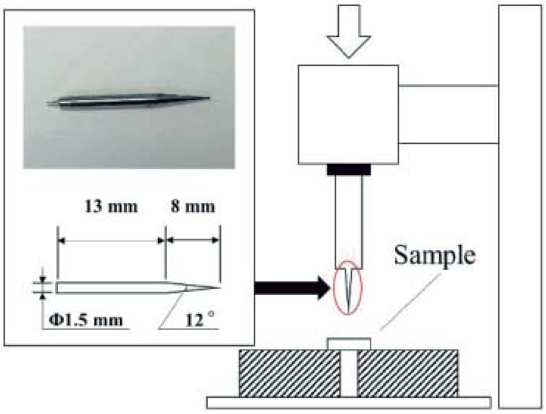

Figure 5. Strength testing

3. Results and discussion

The relationship between the concentration of each NaOH aqueous solution and its viscosity is shown in **Figure 6**, and the change in adhesion amount at each NaOH aqueous solution concentration is depicted in **Figure 7**. An increasing trend in the adhesion amount was observed with an increase in NaOH aqueous solution concentration. While GFRP generally possesses waterproof properties, it is believed that as the concentration of NaOH in the aqueous solution increases, the viscosity also rises, leading to an increase in the adhesion amount to the surface. In the case of the 30 M NaOH aqueous solution, approximately 0.2 g of NaOH adhered per 1 g of waste GFRP (**Figure 8**).

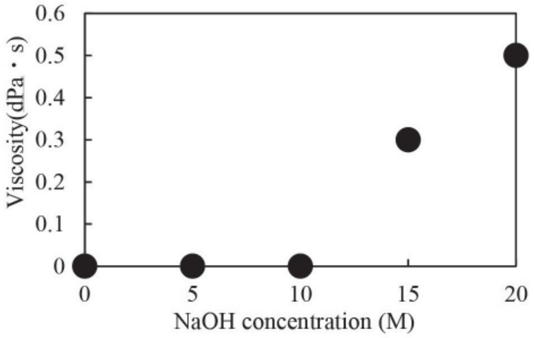

Figure 6. Viscosity of NaOH solution

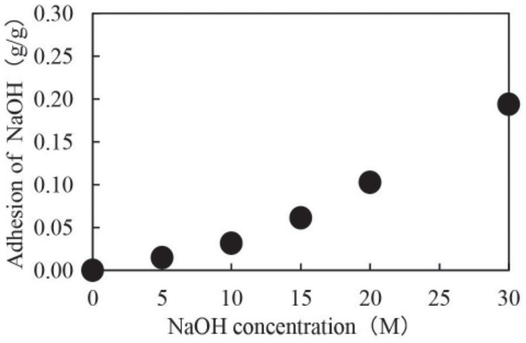

Figure 7. Adhesion of NaOH on waste GFRP

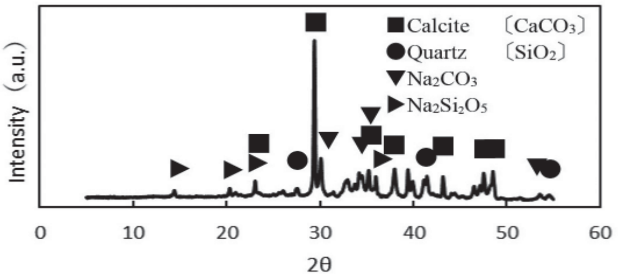

Figure 8. XRD pattern of waste GFRP after immersion in 30 M NaOH solution and thermal decomposition.

Figure 9 displays the gas yields resulting from the thermal decomposition of waste GFRP immersed in NaOH aqueous solutions of various concentrations. The amount of generated gas increases with the immersion in NaOH aqueous solution, gradually increasing with higher NaOH concentrations. With increasing NaOH concentration, there was a tendency for the yield of CO_2 in the generated gas to decrease, while the yield of H_2 increased. This suggests that higher concentrations of NaOH in the solution promote the thermal decomposition of the resin component of waste GFRP and lead to increased H_2 generation. In the case of waste GFRP immersed in the 30 M NaOH aqueous solution, the H_2 concentration in the generated gas was approximately 14.6%, and the CH_4 concentration was approximately 5.9%, which are concentrations suitable for use as combustible gas (H_2: 4%, CH_4: 5%) [8]. Additionally, as the adhesion amount of NaOH increases, it is likely that the reaction of CO_2 absorption ($2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$) was enhanced, leading to a decrease in CO_2 yield.

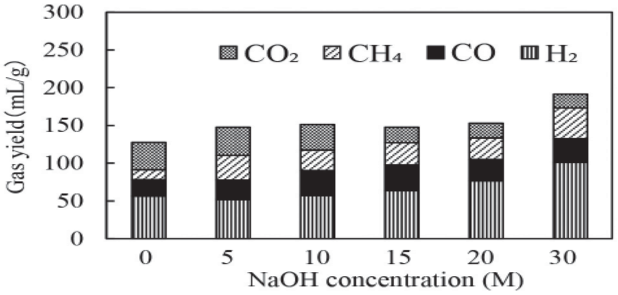

Figure 9. Gas yield generated from waste GFRP immersed in NaOH aqueous solution

Figure 10 illustrates the dissolution of glass components (silica) in each leachate from waste GFRP subjected to immersion in NaOH aqueous solutions of different concentrations. An increase in the concentration of NaOH aqueous solution used for immersion leads to an increase in the amount of silica dissolved. It is believed that the alkaline fusion reaction between the adhered NaOH and glass fibers occurs more readily with higher concentrations of NaOH in the solution, resulting in increased silica dissolution. Furthermore, in all conditions, the leachate obtained after treatment with HCl showed a higher amount of silica dissolution compared to treatment with distilled water.

Figure 11 shows the calcium dissolution from waste GFRP treated with each concentration of NaOH aqueous solution. In the case of treatment with distilled water, the calcium dissolution was nearly 0 mg/g, while treatment with HCl resulted in dissolution ranging from 95 to 120 mg/g. Moreover, the dissolution of calcium gradually increased with an increase in the concentration of the NaOH solution used for immersion.

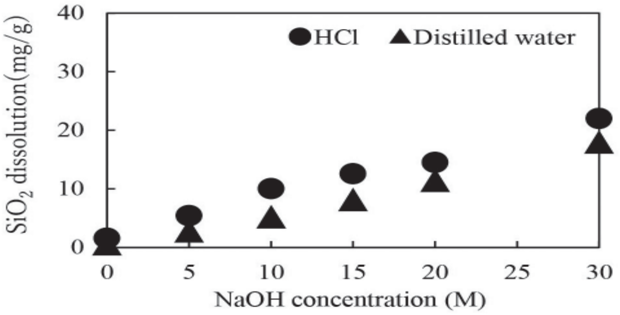

Figure 10. SiO_2 dissolution from thermal decomposed waste GFRP immersed in NaOH solution

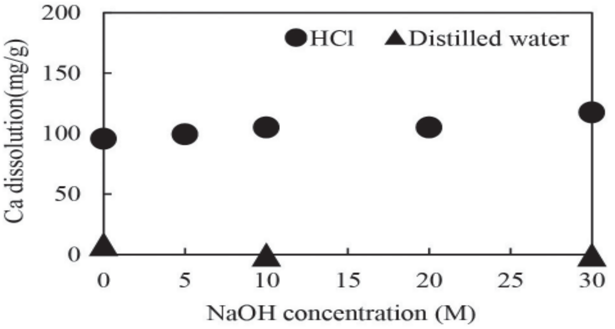

Figure 11. Ca dissolution from thermal decomposed waste GFRP immersed in NaOH solution

Figure 12 presents the pH of each leachate, irrespective of the concentration of the NaOH aqueous solution used for immersion. Leachate treated with distilled water displayed alkaline pH, whereas leachate treated with HCl exhibited acidity. Therefore, it is believed that the leachate treated with HCl is acidic due to the reaction of calcium carbonate with HCl ($CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$), resulting in the dissolution of calcium in the solution. Additionally, the pH of the leachate treated with HCl was acidic, indicating a high concentration of hydrogen ions. Consequently, the dissolution of sodium silicate, a base, increased, resulting in a higher silica dissolution compared to treatment with distilled water.

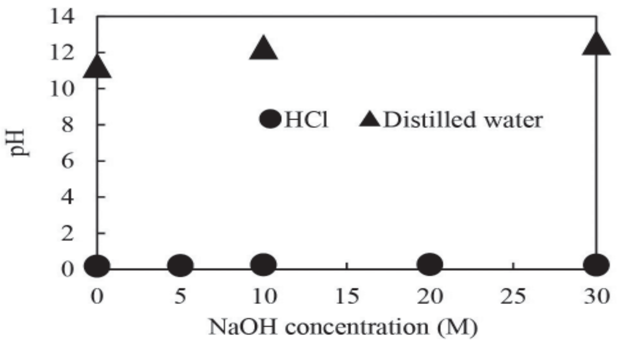

Figure 12. pH of the solution after dissolving thermal decomposed waste GFRP immersed in NaOH solution

Figure 13 depicts the state of the dried residues obtained from thermal decomposition of waste GFRP treated with distilled water, NaOH aqueous solution immersion, and HCl treatment. Residues from NaOH aqueous solution immersion exhibited more damage to the original form of waste GFRP compared to those treated with distilled water. Therefore, it is suggested that an increase in the concentration of NaOH in the solution affected the residual shape. In addition, treatment with HCl resulted in the dispersion of glass fibers. It is believed that the dissolution of calcium carbonate and the ease of dispersion of resin and glass fibers occurred more readily when treated with HCl.

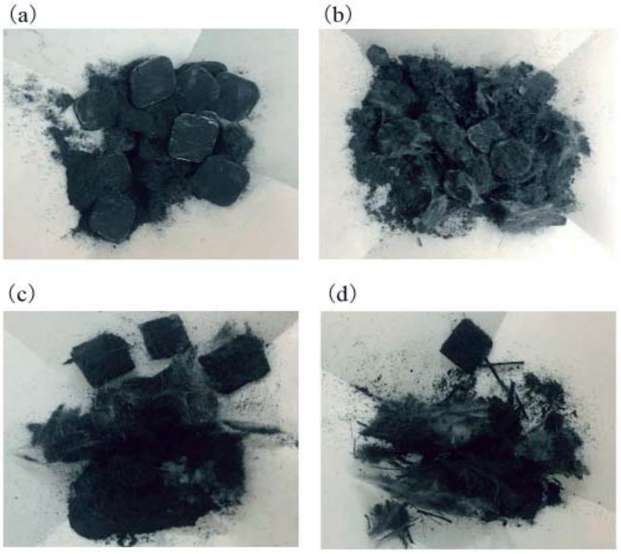

Figure 13. Photos of the residue: **(a)** distilled water immersion and washing; **(b)** NaOH immersion and distilled water washing; **(c)** distilled water immersion and HCl washing; **(d)** NaOH immersion and HCl washing.

Figure 14 illustrates the volume of waste GFRP before thermal decomposition and the volume of each dried residue from **Figure 13**. The volume decreased due to thermal decomposition, and immersion in NaOH aqueous solution and treatment with HCl further reduced the volume. It was found that waste GFRP could be reduced to two-thirds of its original volume through immersion in NaOH aqueous solution followed by thermal decomposition and treatment with HCl.

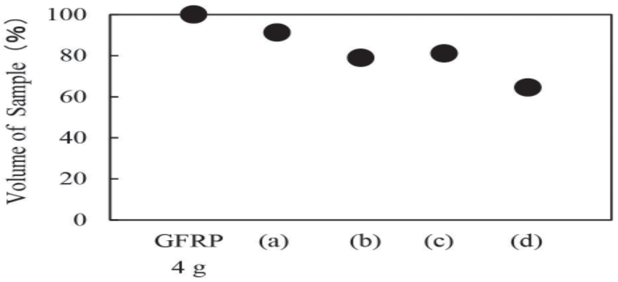

Figure 14. Residual ratio of waste GFRP after thermal decomposition treated

Figure 15 shows SEM images of the glass fibers in each dried residue from **Figure 13**, while **Figure 16** displays SEM images of the powder. Residues treated with distilled water showed smooth glass fiber surfaces (**Figure 15(a)** and **(c)**), whereas residues immersed in NaOH aqueous solution exhibited changes on the glass fiber surfaces, such as peeling and damage (**Figure 15(b)** and **(d)**). This is attributed to the partial dissolution of the glass fiber due to the alkali fusion reaction between NaOH and glass fibers. Furthermore, residues treated with distilled water exhibited clumping of particles in the powder (**Figure 16(a)** and **(b)**), while residues treated with HCl had smooth surfaces in the powder (**Figure 16 (c)** and **(d)**). In the case of residues treated with distilled water, calcium carbonate remained, whereas treatment with HCl resulted in calcium carbonate dissolving into the leachate, causing a difference in shape. Additionally, **Figure 16(d)** shows the presence of multiple hole-like structures.

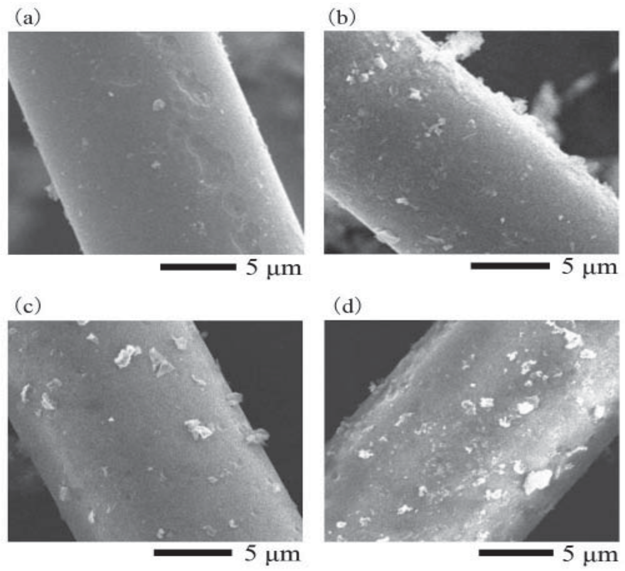

Figure 15. SEM of the residue (glass fiber): **(a)** distilled water immersion and washing; **(b)** NaOH immersion and distilled water washing; **(c)** distilled water immersion and HCl washing; **(d)** NaOH immersion and HCl washing.

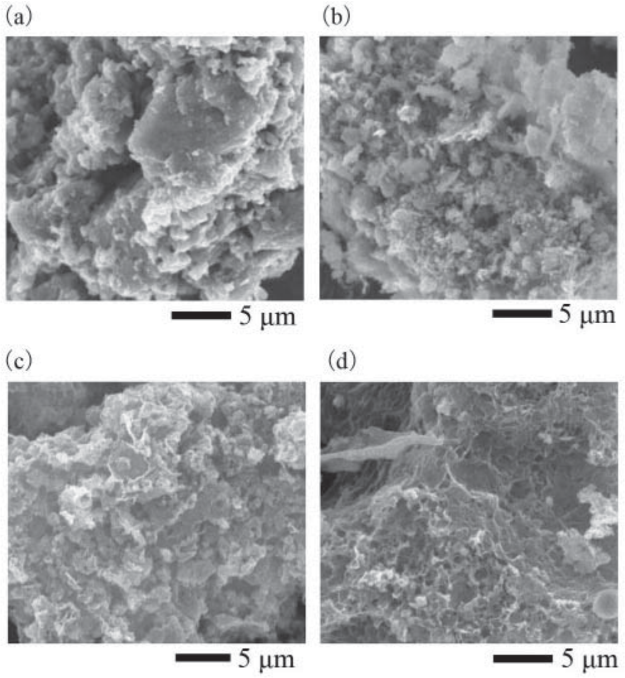

Figure 16. SEM of the residue (powder): **(a)** distilled water immersion and washing; **(b)** NaOH immersion and distilled water washing; **(c)** distilled water immersion and HCl washing; **(d)** NaOH immersion and HCl washing.

The residue remaining rate is shown in **Figure 17**. Regardless of the concentration of the NaOH aqueous solution, the residue remaining rate after treatment with distilled water was approximately 0.68 g/g, while it was approximately 0.38 g/g after treatment with HCl. Therefore, it is believed that the concentration of the NaOH aqueous solution had almost no effect on the residue remaining rate, and it was found that waste GFRP could be reduced by up to one-third through thermal decomposition and treatment with HCl.

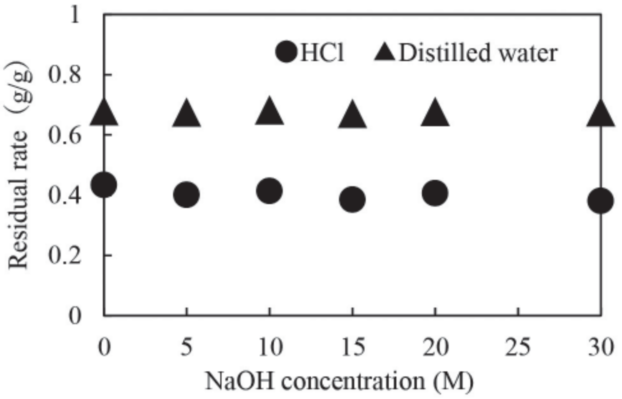

Figure 17. Residual ratio of waste GFRP after thermal decomposition treated

The strength for penetration was measured using each residue from **Figure 13**. Compared to the strength of the waste GFRP before treatment, the residue treated with distilled water showed a strength reduction of approximately 87% regardless of the concentration of the NaOH aqueous solution used for immersion, while the residue treated with HCl exhibited a strength reduction of approximately 93% for the residue immersed in distilled water and approximately 97% for the residue obtained from immersion in the 30 M NaOH aqueous solution. This suggests that thermal decomposition treatment in the presence of NaOH leads to a decrease in the strength of waste GFRP, and treatment with HCl further accelerates the reduction in strength. Currently, one of the recycling methods for waste GFRP involves using it as a cement raw material [1,2]. The treatment in this study significantly reduces the strength of waste GFRP which can lead to substantial energy savings in the crushing process, and the residue can be used as a cement raw material.

4. Conclusion

In this study, we attempted to develop a new volume reduction technology by immersing waste GFRP in NaOH aqueous solution followed by thermal decomposition treatment. As a result, immersion in NaOH aqueous solution and thermal decomposition treatment promoted the gasification of the resin in waste GFRP and the dissolution of glass fibers. Furthermore, treatment with HCl facilitated the dissolution of silica from the glass fibers and calcium from the filler material, leading to a reduction in residue weight and a decrease in strength.

Acknowledgments

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Disclosure statement

The authors declare no conflict of interest.

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