Porous Ceramics Adsorbents Based on Glass Fiber-Reinforced Plastics for NO\(_x\) and SO\(_x\) Removal

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Abstract: To reuse waste glass fiber-reinforced plastics (GFRPs), porous ceramics (i.e., GFRP/clay ceramics) were produced by mixing crushed GFRP with clay followed by firing the resulting mixture under different conditions. The possibility of using ceramics fired under a reducing atmosphere as adsorbent materials to remove NO\(_x\) and SO\(_x\) from combustion gases of fossil fuels was investigated because of the high porosity, specific surface area, and contents of glass fibers and plastic carbides of the ceramics. NO\(_2\) and SO\(_2\) adsorption tests were conducted on several types of GFRP/clay ceramic samples, and the gas concentration reduction rates were compared to those of a clay ceramic and a volcanic pumice with high NO\(_2\) adsorption. In addition, to clarify the primary factor affecting gas adsorption, adsorption tests were conducted on the glass fibers in the GFRP and GFRP carbides. The reductively fired GFRP/clay ceramics exhibited high adsorption performance for both NO\(_2\) and SO\(_2\). The primary factor affecting the NO\(_2\) adsorption of the ceramics was the plastic carbide content in the clay structure, while that affecting the SO\(_2\) adsorption of the ceramics was the glass fiber content.

Keywords: waste GFRP; reuse; adsorbent; ceramics; NO\(_2\) adsorption performance; SO\(_2\) adsorption performance

1. Introduction

Currently, most glass fiber-reinforced plastic (GFRP) wastes are sent to landfills without recycling because they are difficult to recycle using the existing recycling technologies due to the content of glass fibers [1,2]. Leachates from landfills are causing several health and environmental problems. Thus, an efficient waste GFRP recycling technology is required [3–6].

In previous studies, authors have proposed a method for waste GFRPs reuse involving the production of porous ceramics by mixing crushed waste GFRPs with clay and firing the resulting mixture [7–9]. The types of clay and GFRPs used for the ceramic production are selected according to the type of the required products. In the ceramic manufacturing process, the resin components in GFRPs thermally decompose during the firing process, and the glass fibers remain in the clay matrix. The generation of fine glass fiber dust is
reduced during this process because both the clay and glass fibers or the glass fibers alone are sintered during the firing process of ceramics [8,9].

Focusing on the high porosity of GFRP/clay ceramics, we aimed to develop ecofriendly products [10–14]. Ceramics produced by firing the mixture of GFRPs and clay powders under an oxidizing atmosphere exhibit high porosity and a relatively high specific strength because the clay matrix is reinforced by the glass fibers. Moreover, this type of ceramics can also have high permeability by adjusting the particle size and the mixing ratio of GFRPs in the manufacturing process. These ceramics were investigated as filtering materials for turbid water treatment [12] and water-permeable paving blocks [13].

However, ceramics produced by firing the mixture of GFRPs and clay powders under a reducing atmosphere contain a small amount of plastic carbide residue with the glass fibers. Consequently, these ceramics exhibit higher specific surface area than those produced under an oxidizing atmosphere [14,15]. Because of the high specific surface area and porosity of the ceramics as well as the high ion exchange function of the clay [16–19], this type of ceramics was studied as a dye adsorbent material to remove pigments from dye-contaminated wastewater [14,15].

The GFRP/clay ceramics produced under reducing conditions may also be used as an adsorbent for toxic gases because the performance of a gas adsorbent is typically linked to its high specific surface area and porosity [20]. Further, they contain glass fibers and plastic carbides with fine pores. Carbides with fine pores or activated carbons exhibit high adsorption for specific substances [21–27]. Glass fibers also contain a large amount of calcium, which easily reacts with sulfur oxides [28]. Thus, the authors investigated the possibility of using GFRP/clay ceramics as adsorbent materials to remove NOx and SOx from gas emissions from fossil fuel combustion. In the study, the authors aimed to develop ceramics with a high adsorption ability for both NOx and SOx gas [29].

During the waste incineration process, several techniques, such as combustion control as well as non-catalytic and catalytic denitrification equipment, are used to reduce or remove NOx from combustion gases. Combustion control reduces the generation of nitrogen oxides by adjusting the combustion conditions of the wastes in the incinerator to suppress the generation of incomplete combustion gases. The non-catalytic denitrification equipment reduces nitrogen oxides by directly spraying ammonia gas into the incinerator. Catalytic denitrification reduces NOx to N2 via a catalytic reaction [30–32].

SOx are removed from the combustion gases of fossil fuel by either the dry method or the wet method. In the wet method, sulfur oxides are collected by spraying a large amount of an alkaline solution, such as caustic soda, into the incinerator to form a solution, such as Na2SO4. The dry method involves (1) spraying an alkaline agent, such as slaked lime, into the incinerator to neutralize the acidic substances in the exhaust gas and (2) collecting the reaction products as fly ash [33]. Moreover, NOx can be reduced using zeolites [34,35], activated carbons, and photocatalytic technology [36]. Several studies, such as that of Kitagawa et al., investigated the production of activated carbon from plastics [37].

Here, the effect of the specific surface area as well as the plastic carbides and glass fiber contents on the NOx and SOx adsorption performance of GFRP/clay ceramics were studied using several types of ceramic samples produced by adjusting the GFRP mixing ratio and the firing atmosphere. Next, NO2 and SO2 adsorption experiments were conducted using the prepared ceramic samples, and the reduction rates of their concentration were compared to those treated using a clay ceramic and Bora, a volcanic pumice stone, with a high NO2 adsorption ability [38]. Furthermore, to determine the primary factor affecting NOx and SOx adsorption, adsorption tests were conducted on the glass fibers in GFRPs and GFRP carbides. NO2 and SO2 adsorption performances of the GFRP/clay ceramics were evaluated based on the experimental results. In addition, their adsorption mechanisms were investigated based on the difference in the contents of plastic carbide and glass fibers in the ceramics and their specific surface area.
2. Materials and Methods

2.1. Samples Used for NO₂ and SO₂ Adsorption Tests

Several types of oxidatively and reductively fired GFRP/clay ceramics, a clay ceramic (without glass fibers), and unfired Bora were used for the NO₂ and SO₂ adsorption tests. Table 1 presents the inorganic chemical compositions of GFRP, clay and Bora [14,15]. Their compositions were measured by an energy dispersive X-ray analyzer (EDX-720, Shimadzu Corporation, Kyoto, Japan) using a fundamental parameter method after firing at 1073 K.

Table 1. The compositions of inorganic substances in the glass fiber-reinforced plastic (GFRP), clay, and Bora.

| Samples       | Component (Mass%) |
|---------------|-------------------|
|               | SiO₂  | Al₂O₃ | Fe₂O₃ | K₂O  | MgO  | CaO  | TiO₂ | Others |
| GFRP (40%GF)  | 54.9  | 16.3  | 0.77  | 0.15 | -    | 26.7 | 0.56 | 0.62   |
| Clay          | 65.8  | 21.9  | 4.79  | 3.37 | 1.67 | 1.31 | 0.87 | 0.29   |
| Bora (unfired)| 67.2  | 20.1  | 5.0   | 2.98 | 0.77 | 3.19 | 0.55 | 0.18   |

Polyamide (PA) thermoplastic pellets (Renny, Mitsubishi Engineering-Plastics Co., Tokyo, Japan) containing glass fiber (~40 mass%) were used as a substitute for waste GFRPs. The glass fibers in the GFRPs were E-glass type fibers with diameters of ~10 μm, lengths of ~1.0 mm, and a high CaO content.

The clay (Sougoo Co., Miyakonojo, Japan) was mined and produced in Miyazaki, Japan [39]. It is typically used as a raw material for bricks and tiles. The clay comprises chlorite group as major minerals.

Similar to the clay, the volcanic pumice Bora (Nanken kougyo Co., Miyakonojo, Japan) was mined in Miyazaki, Japan. Bora is mined in large quantities in the southern Kyushu area of Japan. The chemical composition of Bora was very similar to that of the clay although it had a slightly higher calcium content.

Figure 1 shows the manufacturing process of the GFRP/clay ceramic samples. The sample manufacturing procedure was as follows [14,15]:

1. The clay was crushed using a rotary mill (New Power Mill ABS-W, Osaka Chemical Co., Ltd., Osaka, Japan) and was then sifted using a 0.3 mm mesh screen.
2. GFRPs were also crushed using the same rotary mill and were then sifted using a 0.5 mm mesh screen.
3. The crushed GFRPs were mixed with the clay at the mass rates of 20%, 40%, and 60%.
4. The GFRP/clay mixture was solidified by being pressed into a mold under 10 MPa. The molded samples had a diameter of 74 mm and a thickness of 50–60 mm.
5. The molded samples were heated under oxidizing or reducing atmospheres to 1073 K in an electric furnace (KY-4N, Kyoei Electric Kilns Co., Ltd., Tajimi, Japan). The samples were then held at the firing temperature for 1 h and then allowed to cool to room temperature in the furnace. For oxidative firing, the samples were heated at 100 K h⁻¹ to the firing temperature. For reductive firing, the samples were heated at 400 K h⁻¹. The reducing atmosphere was obtained by closing the intake port attached to the bottom of the electric furnace.
6. The produced GFRP/clay samples were then crushed using a hammer, and the particles with sizes of 1.4–2.0 mm were selected.
Glass fibers and GFRP carbides were prepared to be used in the experiments investigating the factors affecting the gas adsorption for GFRP/clay ceramics. The glass fibers were prepared by heating the GFRP pellets at a rate of 100 K h\(^{-1}\) to 1073 K under an oxidizing atmosphere followed by holding them at the firing temperature for 1 h until the plastic component decomposed. The GFRP carbides were prepared by heating the GFRP pellets at a rate of 400 K h\(^{-1}\) to 1073 K under a reducing atmosphere. The particle size of both samples was adjusted to 1.4–2.0 mm by sieving.

Figure 1. The manufacturing process of GFRP/clay ceramic samples.

Table 2 presents the inorganic chemical compositions of the samples [14,15]. The GFRP/clay ceramics had greater CaO contents than the clay ceramic, and the ratio of CaO to the total mass of the ceramics increased with the GFRP mixing ratio because of the increase in the glass fiber content.

Table 2. Inorganic chemical compositions of the GFRP/clay ceramic samples.

| Samples                | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | K\(_2\)O | MgO  | CaO  | TiO\(_2\) | Others |
|------------------------|-----------|-----------------|-----------------|---------|------|------|----------|--------|
| Oxidatively fired ceramics |          |                 |                 |         |      |      |          |        |
| 20% GFRP/clay          | 62.6      | 22.1            | 4.87            | 3.26    | 1.66 | 4.02 | 0.86     | 0.58   |
| 40% GFRP/clay          | 59.1      | 20.7            | 4.16            | 2.91    | 1.75 | 9.93 | 0.8      | 0.71   |
| 60% GFRP/clay          | 50        | 17.7            | 4.09            | 2.0     | 1.51 | 23.2 | 1.03     | 0.45   |
| Reductively fired ceramics |        |                 |                 |         |      |      |          |        |
| 20% GFRP/clay          | 62.2      | 18.5            | 6.13            | 3.73    | 2.24 | 5.34 | 1.21     | 0.65   |
| 40% GFRP/clay          | 61.2      | 9.13            | 7.56            | 3.77    | 2.43 | 12.9 | 1.56     | 1.46   |
| 60% GFRP/clay          | 56.2      | 4.79            | 7.34            | 3.11    | 2.14 | 22.7 | 1.49     | 2.22   |

2.2. Material Properties of the Samples

The following material properties of GFRP/clay ceramics have already been reported [14,15]. However, they are shown here since it is necessary to discuss the NO\(_x\) and SO\(_x\) adsorption performance of the ceramics in terms of their properties.
Table 3 [14,15] presents the apparent porosity, specific surface area, and carbon content of the samples. The apparent porosity was measured using a mercury porosimeter (Auto Pore IV 9500, Micromeritics Instrument Corporation, Norcross, GA, USA). The specific surface area was measured using a high-precision gas and vapor adsorption analyzer (BELSORP-max, MicrotracBEL Corp., Osaka, Japan). The carbon content was measured using an elemental analyzer (CHNS/O Analyzer 2400, PerkinElmer Inc., Waltham, MA, USA).

| Samples                  | Apparent Porosity (%) | Specific Surface Area (m²/g) | Carbon Content (%) |
|--------------------------|-----------------------|-----------------------------|-------------------|
| Oxidatively fired ceramics | Clay                  | 31.9                        | 11.0              | 0.06 |
|                          | 20% GFRP/clay         | 38.2                        | 7.05              | 0.24 |
|                          | 40% GFRP/clay         | 52.7                        | 5.74              | 0.25 |
|                          | 60% GFRP/clay         | 62.9                        | 2.83              | 0.26 |
|                          | 20% GFRP/clay         | 43.1                        | 14.9              | 0.85 |
| Reductively fired ceramics | 40% GFRP/clay         | 53.8                        | 14.2              | 0.99 |
|                          | 60% GFRP/clay         | 66.2                        | 11.3              | 1.12 |
| Bora                     | -                     | 9.52                        | -                 |
| GFRP carbide             |                       | 26.4                        | 7.0               |

The apparent porosities of the oxidatively and reductively fired GFRP/clay ceramics were equivalent and were approximately twice that of the clay ceramic because the resin component decomposes during the firing to create voids in the clay structure.

The specific surface areas of the oxidatively fired GFRP/clay ceramics were smaller than that of the clay ceramic and decreased with the increase in the mixing ratio of GFRPs. By contrast, the specific surface areas of the reductively fired GFRP/clay ceramics were comparable to that of the clay ceramic or slightly larger. The specific surface area of Bora was slightly lower than that of the clay ceramic. GFRP carbides exhibited a remarkably high specific surface area.

The carbon content in the reductively fired GFRP/clay ceramics were higher than that in the oxidatively fired ceramics because plastic carbides remained in the ceramic structure after the firing process. The carbon content in the GFRP pellets used as the raw material for the ceramics was ~30%, and the content in the GFRP carbides was 7%.

Figure 3 [14,15] shows the pore size distributions in the samples. The pore size distributions were measured using the same high-precision gas/vapor adsorption measurement instrument, which was used to measure the specific surface area. The nano-sized pores in the structure of the oxidatively fired GFRP/clay ceramics decreased with the increase in the mixing ratio of GFRPs. Thus, the specific surface areas of the ceramics decreased with the increase in the mixing ratio of GFRPs. The nano-sized pores could have disappeared owing to the progress of sintering between the clay and glass fibers with the increase in the mixing ratio of GFRPs.

The reductively fired GFRP/clay ceramics had relatively more nano-sized pores than the oxidatively fired GFRP/clay ceramics. Therefore, the ceramics had higher specific surface areas. This can be attributed to the high specific surface area of the GFRP carbides in the clay structure of the ceramics. In addition, the sintering between the clay and glass fibers may be suppressed owing to the presence of plastic carbides. The GFRP carbides had many pores with a size of several tens of nanometers.

Figure 4 shows examples of scanning electron microscope (SEM, S5500, Hitachi High-Technologies Corporation, Tokyo, Japan) images of the surface structures of the clay and 40% GFRP/clay ceramic samples. Further, the GFRP/clay ceramics had more pores than clay ceramic.
2.3. Methodology of NO$_2$ and SO$_2$ Adsorption Tests

Figure 5 shows a schematic diagram of the NO$_2$/SO$_2$ adsorption test. The experimental apparatus was constructed using a standard NO$_2$/SO$_2$ gas cylinder; a standard air cylinder (Sumitomo Seika Chemicals Co., Ltd., Osaka, Japan); a 50 L gas storage bag (chemical resistance sampling bag (Tedlar bag), Tech-Jam, Osaka, Japan); an air pump (APN-085E-D2-W, IWAKI, Tokyo, Japan); a digital flow meter (CMS0020BSRN, Azbil, Tokyo, Japan); a test tube, into which the samples were placed; and an instrument for measuring the NO$_2$ or SO$_2$ concentrations (XPS-7, New Cosmos Electric, Osaka, Japan). Standard gases are usually used for calibrating the gas concentration. The standard gases are manufactured in accordance with the standards of Japan Calibration Service System (JCSS) [40–43]. The standard air gas has a density of 1.20 kg/m$^3$ and a humidity of 65% (RH) at 293 K and 101.325 kPa. The NO$_2$ and SO$_2$ adsorption tests were performed following the subsequent procedures.

1. Samples were washed with distilled water and dried in an electric furnace at 378 K for over 24 h before the gas adsorption tests.
2. In the NO\textsubscript{2} adsorption tests, a 50 L gas storage bag was filled with NO\textsubscript{2} gas (20 L, NO\textsubscript{2} concentration = \textasciitilde5 vol ppm).

3. In the SO\textsubscript{2} adsorption tests, a 50 L gas storage bag was filled with SO\textsubscript{2} gas (10 L, SO\textsubscript{2} concentration = \textasciitilde10 vol ppm) and standard air (10 L). To homogenize the concentration of the gas mixture in the gas storage bag, the gas mixture was circulated in the circuit at a flow rate of 2 L/min for 20 min.

4. A portion of the sample (5 g) was placed into a test tube. The NO\textsubscript{2} or SO\textsubscript{2} gas was allowed to pass through the test tube containing the sample at a flow rate of 1.0 L/min, and the gas was circulated in the circuit for a maximum of 4 h.

5. The NO\textsubscript{2} and SO\textsubscript{2} concentrations in the gas storage bag were measured at 30 min intervals. The pump was momentarily stopped during the measurement of the gas concentration. The room temperature during the experiments was 287 K–299 K.

3. Results

3.1. NO\textsubscript{2} Adsorption Performance of GFRP/Clay Ceramics

Figure 6 shows the NO\textsubscript{2} reduction rates for all samples. Each graph represents the average reduction rates calculated based on the measurements of the three samples. Error bars represent the upper and lower limits of the measured values. The NO\textsubscript{2} reduction rate of the Bora is shown in all figures for easy comparison with that of each sample. The graph marked “without sample” shows the NO\textsubscript{2} reduction rate when the sample was not placed into a test tube. In other words, the graph represents the natural reduction in the NO\textsubscript{2} concentration with time. The error in the NO\textsubscript{2} reduction rate in the test without the sample is assumed to be mainly due to the difference in humidity caused by the difference in air temperature.

Figure 6. NO\textsubscript{2} reduction rates for the samples.

The NO\textsubscript{2} reduction rates of the oxidatively fired GFRP/clay ceramics were roughly comparable to that of the Bora, although those of 40% and 60% GFRP/clay ceramics were slightly lower. The reduction rate of the clay ceramic was almost comparable to that of the Bora. The NO\textsubscript{2} reduction rates of the reductively fired GFRP/clay ceramics were considerably higher than those of the oxidatively fired ceramics or the Bora regardless of the GFRP mixing ratio. The NO\textsubscript{2} reduction rates of reductively fired GFRP/clay ceramics were higher than those of a porous concrete sample coated with titanium oxide, which has a high NO\textsubscript{x} reduction rate reported in a previous study [39].

The above results demonstrate that the reductively fired GFRP/clay ceramics had a high adsorption capacity for NO\textsubscript{2}. This suggests that the high specific surface area of
the ceramics had a significant effect on the NO\textsubscript{2} adsorption performance or that plastic carbides in the ceramic structure are good NO\textsubscript{2} adsorbents.

3.2. SO\textsubscript{2} Adsorption Performance of GFRP/Clay Ceramics

Figure 7 shows the SO\textsubscript{2} reduction rates of all samples. Contrary to the results of NO\textsubscript{2} absorption tests, in which the concentration reduction rates of Bora and clay ceramic were equivalent, the SO\textsubscript{2} reduction rate of the clay ceramic was considerably lower than that of the Bora.

Figure 7 shows the SO\textsubscript{2} concentration reduction rates for the samples.

The SO\textsubscript{2} reduction rates of the oxidatively and reductively fired GFRP/clay ceramics were almost equivalent regardless of the difference in the firing conditions and were almost comparable to that of the Bora. Therefore, they were higher than that of the clay ceramic. However, the SO\textsubscript{2} reduction rates of the ceramics tend to slightly increase with the GFRP mixing ratio.

The above results demonstrate that the GFRP/clay ceramics had a high adsorption capacity for SO\textsubscript{2} regardless of the firing atmosphere. Based on these results, it can be concluded that the difference in the specific surface area between the oxidatively and reductively fired GFRP/clay ceramics did not significantly affect the SO\textsubscript{2} adsorption performance of the ceramics. This also indicates that the plastic carbides in the ceramic structure hardly affected the SO\textsubscript{2} adsorption performance. Therefore, another factor must have had a great influence on the SO\textsubscript{2} adsorption performance of GFRP/clay ceramics.

4. Discussion

4.1. The Primary Factor Affecting the NO\textsubscript{2} Absorption of the Reductively Fired GFRP/Clay Ceramics

To examine the effect of glass fibers and plastic carbide residues on the NO\textsubscript{2} adsorption performance of the reductively fired GFRP/clay ceramics, NO\textsubscript{2} adsorption tests were conducted on the glass fibers in the GFRPs and the GFRP carbides. Similar to the previous tests, the particle size of the samples used for NO\textsubscript{2} adsorption tests was 1.4–2.0 mm. The mass of each sample was also 5 g.

Figure 8 shows the NO\textsubscript{2} reduction rates of the glass fibers and GFRP carbides. The GFRP carbides exhibited a significantly high NO\textsubscript{2} adsorption ability. In contrast, that of the glass fibers was considerably low. Thus, the cause of the high NO\textsubscript{2} adsorption ability of the reductively fired GFRP/clay ceramics is the high NO\textsubscript{2} adsorption of the plastic
carbide residue in the clay structure. The high NO\textsubscript{2} adsorption of the plastic carbides can be attributed to its high specific surface area [25].

![Figure 8](image-url)  
**Figure 8.** The reduction rates of NO\textsubscript{2} concentration on the glass fiber and GFRP carbides.

Although we performed the elemental analysis by EDX on the GFRP carbides after the NO\textsubscript{2} adsorption test, nitrogen was not detected. NO\textsubscript{2} may be stored in the pores rather than adsorbed on the ceramic surface [21,22,24].

Regarding the NO\textsubscript{2} adsorption of activated carbon, Urano et al. [25] reported that NO\textsubscript{2} was adsorbed, without changing into other substances, to the activated carbon under a nitrogen atmosphere; the adsorption mechanism is physical adsorption with a weak binding force. However, NO\textsubscript{2} was adsorbed as nitric acid (HNO\textsubscript{3}) to the activated carbon under a nitrogen atmosphere containing water vapor.

Regarding the NO\textsubscript{2} adsorption on the reductively fired GFRP/clay ceramics, since NO\textsubscript{2} is a polar molecule, it seems that NO\textsubscript{2} and ceramic surface interacted electrically. Thus, it is presumed that the NO\textsubscript{2} adsorption mechanism of the ceramics is also physical adsorption.

4.2. The Primary Factor Affecting the SO\textsubscript{2} Absorption of GFRP/Clay Ceramics

Figure 9 shows the SO\textsubscript{2} reduction rates on the glass fibers and GFRP carbides. The SO\textsubscript{2} reduction rates of the glass fibers and GFRP carbides were equivalent and slightly higher than that of the Bora.

![Figure 9](image-url)  
**Figure 9.** The reduction rates of SO\textsubscript{2} concentration on the glass fiber and the carbide of GFRP.

The result indicates that the primary factor affecting the SO\textsubscript{2} adsorption of the GFRP/clay ceramics is the content of the glass fibers or plastic carbides. However, the plastic carbides in GFRP carbides represent only 7% of the total mass. Furthermore, the SO\textsubscript{2} reduction rates of GFRP/clay ceramics (Figure 7) did not depend on the carbon content. This indicates that the primary factor affecting the SO\textsubscript{2} absorption of the GFRP/clay ceramics is the glass fiber content. This is consistent with the fact that the SO\textsubscript{2} reduction
rates of the GFRP/clay ceramics tend to increase with the increase in the glass fiber content of the ceramics.

Since SO$_2$ is also a polar molecule, it may have interacted electrically with the ceramic surface. Thus, it is presumed that the SO$_2$ adsorption mechanism of the GFRP/clay ceramics involves a chemical reaction with glass fibers in addition to the interaction with the ceramic surface. Plastic carbides did not contribute to the adsorption.

Next, to verify that SO$_2$ was adsorbed onto the surface of the glass fiber, we performed elemental analyses of glass fibers before and after SO$_2$ adsorption tests using a SEM with an energy dispersive X-ray spectroscopy (EDS) analysis function (S-5500, Hitachi Ltd., Tokyo, Japan). Figure 10a,b shows the elemental analytical results of glass fibers before and after SO$_2$ adsorption tests. Sulfur was detected only in the sample after the SO$_2$ adsorption test. Figure 10c and d shows an image of the sulfur elemental mapping via EDS and the SEM, respectively. The sulfur element was locally distributed near the glass fibers.

SO$_2$ easily changes to SO$_3$ by combining with oxygen in the air. Further, SO$_3$ changes H$_2$SO$_4$ by reacting with moist air. H$_2$SO$_4$ may react with metals such as calcium to generate sulfates. Therefore, we measured the X-ray diffraction profile of the glass fibers after the adsorption test using an X-ray crystal structure analyzer (PANalytical, X’Pert-Pro MRD, Malvern Panalytical Ltd., Worcestershire, UK); however, sulfate was not detected. The adsorption mechanism of SO$_2$ and glass fibers is an issue to be addressed in the future.

5. Conclusions

The possibility of using GFRP/clay ceramics as NO$_x$ and SO$_x$ adsorbents was investigated for an effective reuse of waste GFRPs. The reductively fired GFRP/clay ceramics exhibited a high adsorption performance for both NO$_2$ and SO$_2$. The primary factor affecting the NO$_2$ adsorption of the ceramics was the plastic carbide content in the clay structure, while the glass fiber content was the primary factor affecting the SO$_2$ adsorption of the ceramics. Thus, the reductively fired GFRP/clay ceramics could be used as adsorbent materials to remove NO$_x$ and SO$_x$ from the combustion gases of fossil fuels.

6. Patents

Kinoshita H, Kaizu K., Ikeda K., (2013) Manufacturing method of porous ceramics using waste GFRP, Japanese Patent No. 5167520 (in Japanese).

Author Contributions: H.K. summarized the experimental results and wrote this paper. K.Y. made the gas adsorption system. T.H. (Taichi Hamasuna) conducted the gas adsorption experiments. T.H. (Tomohiro Haraguchi) conducted elemental analysis. N.M. (Naoki Misawa) and T.Y. investigated the mechanism of the gas adsorption. K.S. prepared ceramic samples. N.M. (Narong Mungkung).
examined the experimental results. All authors have read and agreed to the published version of the manuscript.

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