1. Introduction

In March 2011, meltdown accidents of the Fukushima Daiichi Nuclear Power Station occurred, and radioactive materials-contaminated water continues to stay in the nuclear power station site even after more than six years have passed. Various methods to reduce the contaminated water have been taken so far. The building of frozen water-barrier walls has started in March 2016 to reduce groundwater flowing from mountains into the reactor. Purification of the contaminated water stored in tanks has been carried out using Multi-nuclide Removal Facility (ALPS) [1]. Outside the station site, water-decontamination treatments have started in the early stage of the accidents, but those in the forests and lakes are rather slowish. Thus, development of effective water-decontamination technologies is required both within and outside Fukushima Daiichi Nuclear Power Station.

The following treatments as examples have been attempted for the water-decontamination; 1) the contaminated water is passed through a tower containing various inorganic adsorbents such as zeolite, ferric ferrocyanide, and sodium titanate to remove radioactive ions such as Cs⁺ and Sr²⁺ from the...
water, and 2) the inorganic adsorbent powders are directly added to the contaminated water [2–4]. However, these methods have some problems in exchanging the used adsorbents for new ones in the tower or correcting and discarding the used inorganic powders in water mixtures. Therefore, a new method to use adsorbent-containing filtration fabrics was studied to improve handling and processing before and after the use in water-decontamination [5,6]. As a result, composite sheets sandwiching zeolite powders such as mordenite and clinoptilolite between two nonwoven fabrics have been developed [7]. The zeolite-containing composite sheets can be used as filters installed in a drainage channel inside the Fukushima Daiichi Nuclear Power Station for water-decontamination.

In a previous paper [8], we prepared composite sheets containing A-type zeolite which efficiently and selectively adsorbs Sr\(^{2+}\) ions, and reported their adsorption behavior of Sr\(^{2+}\) in simulated seawater. These sheets were effective in adsorbing Sr\(^{2+}\) in simulated seawater contaminating various competing metal ions, and thus expected to be used as decontamination filters. However, because the type zeolite is a fine powder, it was found that a part of zeolite powder insufficiently adhered to the composite sheets were detached from the sheets by water flow during filtration. Moreover, the filtration time increased with increasing the amount of water flow, because clogging of the pores in the composite sheets with the detached zeolite particles more or less occurs during the filtration. These problems should be overcome for practical use. In this study, therefore, we prepared new zeolite-containing composite sheets, and their filtration performance and adsorption behavior of Sr\(^{2+}\) in water were evaluated to solve the problems described above.

2. Experimental

2.1 Materials

A-type zeolite (Zeolum A 4 HA pellet, Tosoh Nikkemi Co., Ltd.) was crushed with a roll mill (KGO-1000, Kowa Industrial Co., Ltd.). The crushed zeolite particles were screened into the following four particle-size groups using four wire meshes: 300–500 µm, 150–300 µm, 150–100 µm, and 100 µm or lower. Three fabrics used were “nonwoven fabric I (made of polyester)” with a 45 g/m\(^2\) basis weight (Precise Alpha Seal, Asahi Kasei Co., Ltd.), “nonwoven fabric II (made of polypropylene/polyester)” with a 50 g/m\(^2\) basis weight (Melphit II, UNICEL Co., Ltd.), and “nonwoven fabric III (made of polyester)” with a 30 g/m\(^2\) basis weight (Elta E 01030, Asahi Kasei Co., Ltd.). A polyethylene-vinyl acetate copolymer (Q 16190N, Sumitomo Seika Chemicals Co., Ltd.) was used as a binder for the composite sheets.

2.2 Preparation of zeolite-containing composite sheet

A-type zeolite of each particle-size group was mixed with the binder at weight ratios from 25 to 100% based on dry weight of zeolite. The zeolite/binder mixture adhered to each other to form a sheet using a rotating roll at a uniform thickness with a blade, and the zeolite/binder sheet was transferred on one nonwoven fabric at a constant speed. By controlling the rotation speed of the roll and the feeding speed of the nonwoven fabric, the amount of the zeolite was controlled to be 180 g/m\(^2\). Another nonwoven fabric was placed on the zeolite/binder side (or the opposite side of the first nonwoven fabric), and the zeolite/binder sheet sandwiched with nonwoven fabrics was pressed at 8 kgf/cm\(^2\) for 5 s at 150 ℃ using a heat-press machine to prepare a zeolite-containing composite sheet.

2.3 Evaluation of water permeation time and zeolite-detachment rate during filtration

The zeolite-containing composite sheets were cut into 5 × 5 cm\(^2\) and set in a filter holder with an effective filtration area of 9.6 cm\(^2\) for filtration (KGS-47, ADVANTEC Co., Ltd.). Water (200 mL) was added to the funnel of the filter holder, and the filtration time required for removal of water through filtration under reduced pressure using a water aspirator was measured. Additional 1800 mL water was filtrated under the same conditions through the composite sheet, and all the filtrates were combined (i.e., totally ~2000 mL) was filtered through a membrane filter with a pore size of 0.65 µm. The zeolite particles collected on the membrane filter were dried at 105 ℃ for 2 h, and the weight was measured. The zeolite detachment ratio was calculated according to the following equation (1),

\[
\text{Zeolite-detachment ratio (\%)} = \frac{Z_{\text{detached}}}{(4 \times Z_{\text{basis}})} \times 100
\]

where \(Z_{\text{detached}}\) is the zeolite weight (g) collected on the membrane filter (g), \(4 \times Z_{\text{basis}}\) is the effective filtration area (m\(^2\)), and \(Z_{\text{basis}}\) is the basis weight of zeolite in the original composite sheet (g/m\(^2\)).
2.4 Observation of composite sheets by scanning electron microscopy

The surface of composite sheets, the zeolite/binder layer exposed by peeling off the one-side nonwoven fabric, and the cross section of the sheets were observed using a scanning electron microscope (SEM) (SU 8020, Hitachi High-Technologies Co., Ltd.) at 1.0 kV without any coating. Samples for cross section observation were prepared through cutting a sample on a glass plate with a stainless steel blade.

2.5 Evaluation of Sr\(^{2+}\) distribution coefficient

The simulated seawater was prepared through dissolution of 27.3 g sodium chloride, 4.3 g magnesium sulfate heptahydrate, 7.2 g magnesium chloride dihydrate, and 0.7 g potassium chloride in 1000 g pure water. The strontium carbonate/nitric acid standard solution at 1000 ppm was diluted with the simulated seawater to Sr\(^{2+}\) concentrations from 5 to 100 ppm. The zeolite-containing composite sheet was cut to 4.5 × 14.4 cm\(^2\). A heat sealer was partly applied at 5 mm from the sheet edge by thermal pressing to prevent detachment of zeolite particles from the sheet edge. A Sr\(^{2+}\) solution (100 mL) and one composite sheet were placed in a 250 mL screw-capped polypropylene bottle, in which the zeolite content in one test piece was adjusted to 1 g. The bottle was shaken at 25 °C for 24 h, and then the mixture was filtered through a membrane filter with a pore size of 0.65 µm. The concentration of Sr\(^{2+}\) (mg/L) in the filtrate was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (ICP-740 AES, Agilent Technologies Inc.) according to a previously report method to measure the adsorbed amount of Sr\(^{2+}\) in the composite sheet, \(C_i\) (mg/L) [8]. The initial Sr\(^{2+}\) concentration, \(C_0\) (mg/L), in the solution was also determined using ICP-AES before the adsorption experiment. As a reference, the original A-type zeolite powder (1 g) in place of the composite sheet was subjected to the adsorption test of Sr\(^{2+}\) under the same conditions. The adsorbed amount of Sr\(^{2+}\) on zeolite, \(q_i\) (mg/g), was calculated by subtracting \(C_i\) from \(C_0\) (mg/L) according to the following equation (2):

\[
q_i = (C_0 - C_i) \times \frac{V}{m}
\]

where \(V\) is the volume of Sr\(^{2+}\) solution (100 mL in this experiment), and \(m\) is the weight of zeolite (1 g). The distribution coefficient \(K_i\) and the adsorption amount \(q_i\) of the composite sheet for Sr\(^{2+}\) are expressed in the following equations (3) and (4).

\[
K_i = \frac{(C_0 - C_i)}{C_i} \times \frac{V}{m}
\]  
\[
q_i = K_i \times C_i
\]

2.6 Water flow test

The strontium carbonate/nitric acid standard solution at 1000 ppm for Sr\(^{2+}\) was diluted to 6 ppm with the simulated seawater. The zeolite-containing composite sheet was cut into a circle with a diameter of 40 mm, and it was set in a filter holder (PFA-47, ADVANTEC Co. Ltd.). Three composite sheet-containing filter holders and a metering pump were connected in series. The Sr\(^{2+}\)-containing solution was flowed through the three filters at a flow rate of 15 mL/min, and the filtrate was intermittently collected from the filtrate during the filtration at 0–100 min after starting. The Sr\(^{2+}\) concentration of the filtrate was determined using ICP-AES and the adsorption rate of Sr\(^{2+}\) was calculated from the following equation (5).

\[
\text{Adsorption rate} (\%) = 100 \times \left( \frac{C_0 - C_e}{C_0} \right)
\]

3. Results and discussion

3.1 Evaluation of the filtration time and detached amount of zeolite during filtration

In the previous paper [8], we used the nonwoven fabric I and the zeolite with a particle size <100 µm as a zeolite-containing composite sheet (hereinafter abbreviated as “SI#100”). Although SI#100 had sufficient Sr\(^{2+}\) adsorption performance, it had low filtration performance (or it took long filtration time,
because filter clogging with detached zeolite particles occurred). In this study, therefore, improvement of filtration performance of the zeolite-containing composite sheets to minimize the amount of detached zeolite particles from the sheets by selecting nonwoven fabrics, and controlling zeolite particle sizes and binder/zeolite weight ratios under the preparation conditions of the composite sheets.

Figs. 1 and 2 show the relationships between the binder/zeolite weight ratio in the composite sheets and either the filtration time or weight ratio of detached zeolite from the composite sheets during filtration with water. Three different nonwoven fabrics I, II, and III were used in the composite sheets. In the experiments of Figs 1 and 2, the zeolite powder with a particle size <100 µm was used. The composite sheet prepared with the nonwoven fabric III had lower filtration times (or better filtration performance) than that prepared with the nonwoven fabric I or II at the binder/zeolite ratios ranging from 25% to 70%. However, the weight ratios of detached zeolite powder from the composite sheets prepared with the nonwoven fabric III were higher than the others at the binder/zeolite ratios ranging from 40 to 70%. Thus, the filtration time and the detached zeolite weight ratio is the trade-off relationship; the shorter the filtration time, the higher the weight ratio of the detached zeolite. The high water flow rates (or high share forces of water flow) during filtration probably increased the amount of detached zeolite from the composite sheets because of incomplete adhesion between zeolite particles with binder. However, it does not seem from the results in Figs. 1 and 2 that the detached zeolite particles cause an increase in the filtration time because of clogging of the detached zeolite particles in the composite sheets during filtration.

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Next, the filtration performance of the zeolite-containing composite sheets was studied in terms of the different nonwoven fabrics I, II, and III, and different sizes of the zeolite powders (Fig. 3) under the same conditions shown in Figs. 1 and 2. The binder/zeolite weight ratio was fixed to 40% based on the results in Figs. 1 and 2. The corresponding weight ratios of the detached zeolite powder are shown in Fig. 4. The filtration time decreased and the weight ratio of detached zeolite powder decreased, as the particle size of zeolite was increased. The composite sheet prepared with the nonwoven fabric II and the zeolite powder 300–500 µm in size (hereinafter abbreviated as SII#300–500), and that prepared with the nonwoven fabric II and the zeolite powder 150–300 µm in size (hereinafter abbreviated as SII#150–
300) had filtration times shorter than half that of the SI#100 sheet. Moreover, the weight ratios of the detached zeolite were similar to or lower than that of the SI#100 sheet.

3.2 Observation of the sheet structures

Fig. 5 shows SEM images of the SII#300‒500, SII#150‒300, and SI#100 sheets. Only the nonwoven fabric fibers were observed on the surface of each sheet, showing that no migration of zeolite particles from the inside to the fabric surface occurred during the sheet making. In the interlayers and the cross-sections of the sheets, the zeolite particles and the nonwoven fabric fibers were partially fused to each other, probably resulting from thermal pressing in the sheet making process. The surfaces of zeolite particles were not completely covered with the binder component, and the binder seemed to bind between zeolite particles and the nonwoven fabric fibers. In the case of the SI#100 sheet, the zeolite particles existed with less amounts of pores or voids. In contrast, many pores or voids were observed in the interlayers of the SII#500‒300 and SII#150‒300 sheets, which may contribute to the improvement of filtration performance with shorter filtration times.

3.3 The distribution coefficient

The Sr$^{2+}$ adsorption isotherms for the three composite sheets, SI#100, SII#300‒500, and SII#150‒300, which were prepared at 40% binder/zeolite ratio, are shown in Figs. 6 and 7. The Sr$^{2+}$ distribution coefficients $K_d$ are calculated from the slopes of the adsorption isotherms, and listed in Table 1. The higher the distribution coefficient $K_d$, the quicker the response to the concentration of Sr$^{2+}$, showing that Sr$^{2+}$ ions efficiently adsorb in the composite sheets even when the Sr$^{2+}$ concentration is low.

In the simulated seawater, the concentrations of sodium and magnesium ions are much larger than that of Sr$^{2+}$ ion, and the Na$^+$ and Mg$^{2+}$ ions compete with Sr$^{2+}$ ion during the adsorption in zeolite powder. However, the A-type zeolite can adsorb Sr$^{2+}$ to some extent even in simulated seawater, in which Na$^+$ and Mg$^{2+}$ ions are present. For both the zeolite-containing composite sheet and the zeolite powder, the distribution coefficient $K_d$ increased with decreasing the zeolite powder size (Table 1). This is because the specific surface area increases as the zeolite particle size is decreased. The Sr$^{2+}$ adsorption isotherms as well as the $K_d$ values were almost similar between the zeolite powder and the zeolite-containing sheets, irrespective of the sizes of zeolite powder. These results indicate that the Sr$^{2+}$ adsorption performance of the original zeolite powder can be almost maintained in the composite sheets in the batch experiment under equilibrium conditions. Actual seawater contains a significant amount of calcium ion, and the influence of Ca$^{2+}$ on the Sr$^{2+}$ adsorption performance in the sheets will be studied in future.
3.4 Water flow experiment

The Sr$^{2+}$ adsorption ratio on the three zeolite-containing composite sheets in the water flow experiment using Sr$^{2+}$ containing simulated seawater are shown in Fig. 8. The Sr$^{2+}$ adsorption ratio for the SII#300‒500 and SII#150‒300 sheets were lower than that for the SI#100 sheet. The Sr$^{2+}$ adsorption ratio continuously decreased with increasing the total filtered water volume. The SI#100, SII#300‒500, and SII#150‒300 sheets decreased in the Sr$^{2+}$ adsorption ratio by 13%, 5%, and 4%, respectively, at the total filtered water volume of 1500 mL.

The space velocity (SV) used in this experiment was set to be 360 h$^{-1}$. SV is an index calculated by dividing the water flow rate by the volume of adsorbent. Adsorbents with higher SV values can adsorb a target compound with lower adsorbent amounts. Standard SV values in filtration are 30 h$^{-1}$ or lower [9], and the SV value for the zeolite-containing composite sheets used in this study is 10 times higher than those in general filtration. When the Sr$^{2+}$ containing water is filtered at a standard SV, the contact time between zeolite particles and water would increase much higher, and correspondingly the amount of Sr$^{2+}$ adsorbed on the composite sheets would increase as well. Under these SV conditions, the Sr$^{2+}$ adsorption ratio of the composite sheets Sr$^{2+}$ likely become higher than those shown in Fig. 8.

The detached amounts of zeolite powder during the initial 300 mL filtration was 3.2%, 0.4%, and 1.1% for the SI#100, SII#300‒500, and SII #150‒300 sheets, respectively. No detachment of zeolite particles from the composite sheets was observed for all the composite sheets after 300 mL filtration. Thus, even though the Sr$^{2+}$ adsorption ratio was the highest for the SI#100 sheet (Fig. 8), the amount of the detached zeolite from the composite sheet during filtration at the initial stage should be reduced, based on the results for the SII#300‒500 and SII#150‒300 sheets.

4. Conclusion

The water filtration performance was in the order, fabrics III > II > I probably because of the low basis weight, when the binder/zeolite weight ratios
ranging from 25 to 70%. In contrast, the amount of detached zeolite particles during filtration was in the order, fabrics III > II > I. Therefore, the water filtration performance and the amount of detached zeolite particles during filtration is a trade-off relationship, which should be taken into account to design the zeolite-containing sheets for filtration of contaminated water. Similar results were obtained for the composite sheets containing zeolite powders with different particle sizes. However, the composite sheets containing zeolite powder with the largest particle size, i.e., #300‒500, had the highest filtration performance (or shortest filtration time) and the lowest amount of detached zeolite particles during the initial filtration. Because the $K_d$ values of the zeolite-containing composite sheets were almost similar to those of zeolite powders alone under equilibrium conditions. The Sr$^{2+}$ adsorption performance of zeolite powder was almost maintained for the zeolite-containing composite sheets at the same zeolite content. The Sr$^{2+}$ adsorption behavior was the highest, when the zeolite powder with the smallest size, i.e., #100, but the filtration performance of the #100-containing sheets was the lowest. Thus, the balance between the Sr$^{2+}$ adsorption and filtration performances should be taken into account in designing the zeolite-containing sheets for practical use.

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