Development of Zeolite Nonwoven for the Adsorption of Radioactive Cesium-13288

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ABSTRACT

The zeolite nonwoven fabric produced by TDS (Totally Dry System) process has some advantages such as the control of zeolite content, flexibility, strength and water-resistant property depending on the purpose. Hence the zeolite nonwoven fabric is expected for the application in various fields of the decontamination of Cs-contaminated water. In this study, Cs adsorption properties of zeolite nonwoven fabrics were examined by batch experiments, and the radiation stability, thermal stability and chemical durability were evaluated. As for batch adsorption properties, relatively large uptake rate of Cs^+ was obtained; the uptake equilibrium attained within 20 min and the uptake (%) was above 95%. The differences in zeolite content had no effects on the Cs^+ uptake (%). The uptake (%) of Cs^+ in seawater was slightly lowered compared to that in the presence of HNO_3. The uptake (%) of Cs^+ in seawater was estimated to be above 90% after 2 h-shaking, indicating the considerable enhancement of uptake rate compared to the conventional granular zeolites. The uptake (%) of Cs^+ for the zeolite high content type was estimated to be above 99% by using ^{137}Cs tracer. As for the comparison of sealing treatment, the uptake (%) for the zeolite sheet treated with edge sealing was larger than that with rapping treatment. The uptake (%) for the zeolite sheet (zeolite high content type) was estimated to be about 95%, which is independent of sealing treatment and NaOH concentration. As for the stability, the surface morphology and the structure of zeolite sheet were not altered by the treatment with acid and alkaline solutions under the experimental conditions. The zeolite sheets were also stable after ^{60}Co- γ ray irradiation up to 7.01×10^6 R. On the other hand, color change for both fiber and zeolite and the shrinkage of the fiber were observed after heat treatment at 150ºC for 2 h. Thus the considerable enhancement of adsorption properties was observed by using zeolite nonwoven fabrics compared to the conventional granular zeolites.

INTRODUCTION

The development of highly functional adsorbent, instead of the conventional granular zeolites, is very important subject for the advanced decontamination of water contaminated with radioactive cesium dispersed by Fukushima NPP-1 accident.[1]-[4] The zeolite nonwoven fabrics produced by TDS (Totally Dry System, OJI KINOCLOTH K.K., **Fig. 1**) process has some advantages such as the control of zeolite content, flexibility and strength depending on the purpose. Hence the zeolite nonwoven fabric (zeolite sheet) is expected for the application in various fields of the decontamination of Cs-contaminated water such as high-activity-level water in NPP site and effluent liquid wastes from contaminated soil. In particular, zeolite sheets have excellent properties for both adsorption and filtration in the decontamination processes. As for the adsorption, the enhancement of Cs uptake rate is also expected. The present study deals with the evaluation of Cs adsorption properties of zeolite nonwoven fabrics by batch experiments, and the characterization of this adsorbent considering the irradiation stability, thermal stability and chemical durability.

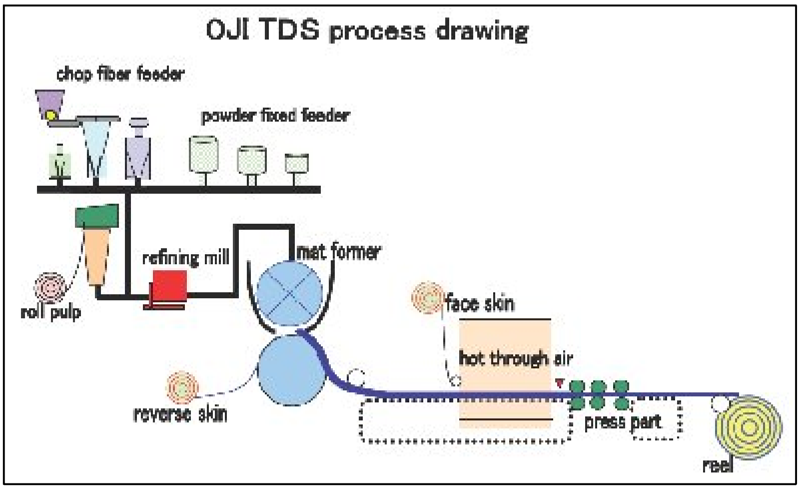

Fig. 1. Flow sheet of OJI TDS process.

EXPERIMENTAL

Materials

Three kinds of zeolite nonwoven sample (zeolite sheet, **Fig. 2**) were used for the batch adsorption experiments. In order to avoid the release of zeolites particles from nonwoven fabrics, two kinds of sealing treatment were adopted as shown in **Fig. 2**; sealing of sample edge (condition 1) and wrapping of the sample with thin nonwoven (condition 2).

Specification/Type	High content type	Low content type	Water repellence type
Sample name	11-048④	11-048②	11-103①
Basis weight (g/m^2)	1,000	700	700
Zeolite weight (g/m^2)	800	400	400
Zeolite content (%)	80	57	57

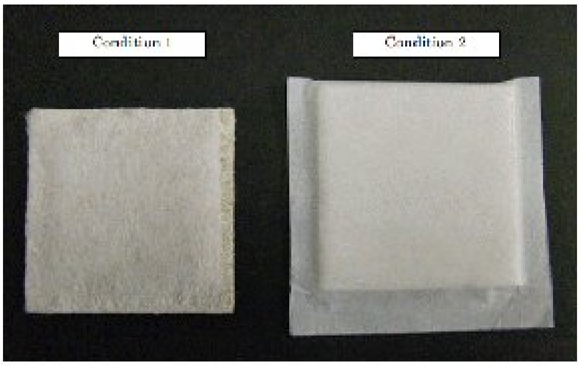

Fig. 2. Specification of zeolite sheets and sealing.

TABLE I. Sample No. and concentrations.

System	Sample No.	Concentration/M
HNO3	A-1	0.1
	A-2	0.5
	A-3	1.0
	A-4	3.0
	A-5	5.0
Sea water	—	—
NaOH	C-1	0.1
	C-2	0.5
	C-3	1.0

Determination of Uptake

The uptake of Cs^+ ions for zeolite sheets (5 cm x 5 cm) was estimated by batch method. An aqueous solution (30 cm^3) containing 10 ppm Cs^+ was contacted with zeolite sheet sample at

25±1°C up to 120 min., which was found to be sufficient for attaining equilibrium. Three kinds of Cs^+ solution (acid, seawater and alkaline solution) were used for the batch experiments (**Table I**). The concentrations of Cs^+ ions were measured by atomic absorption spectrometer (AAS, Thermo Fisher Scientific K.K., AA-890). ^{137}Cs tracer experiments were further carried out under the experimental conditions of $[Cs^+]$= 10 ppm, initial ^{137}Cs activity= 10^4 cpm, $[HNO_3]$= 0.1 M, high content zeolite sheets (5 cm x 5 cm) and V= 30 cm^3. The ^{137}Cs activity was measured by NaI(Tl) scintillation counter (Chiyoda Technol, JDC-715). The uptake percentage (R, %) of Cs^+ ions removed from the solution is defined as :

$$R= ((C_0 - C_f) / C_0) \times 100, \quad (\%) \qquad \text{(Eq. 1)}$$

where C_0 and C_f (ppm) are the concentrations of Cs^+ ions at initial and at equilibrium.

Stability Tests

Radiation stability, thermal stability and chemical stability were estimated by instrumental analyses; the surface morphology of zeolite sheets before and after treatment was observed by digital microscope (DM, HiROX, KH-1300) and SEM (Hitachi TM-1000). The structural change were examined by FT-IR (Horiba, FT-730) and EDS (EDS, SwiftED-TM, Hitachi, TM-1000).

RESULTS AND DISCUSSION

Uptake Rate of Cs^+ for Zeolite Sheets in the Presence of HNO_3

The uptake rate of Cs^+ ions for the high content zeolite sheets (condition 1 and condition 2) are examined at different HNO_3 concentrations (**Fig. 2 and Fig. 3**). In either case, similar uptake profile was obtained. The uptake rate tends to enhance with decreasing HNO_3 concentration as A-1 > A-2 > A-3 > A-4 > A-5, and relatively large uptake (%) above 90% was obtained below 0.5 M HNO_3 (A-2). In particular, the uptake (%) above 94% was obtained for all samples in the presence of 0.1 M HNO_3. In the case of high content of zeolite sheet (condition 2), the uptake data tends to scatter compared to that of zeolite sheet (condition 1) probably due to the contact problem between zeolite and aqueous phase.

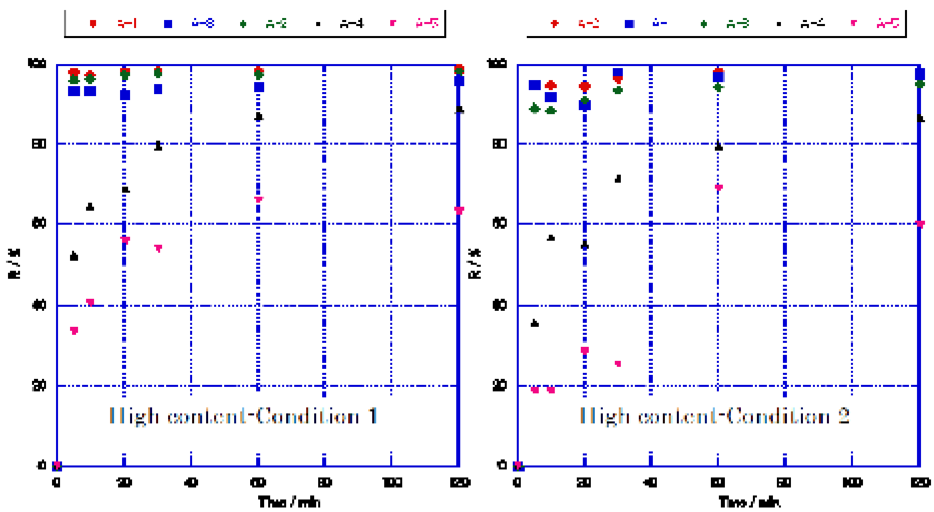

Fig. 2. Effects of shaking time on uptake (%) of Cs^+. High content zeolite sheets (5 cm x 5 cm); 10 ppm Cs^+ in HNO_3; 25°C.

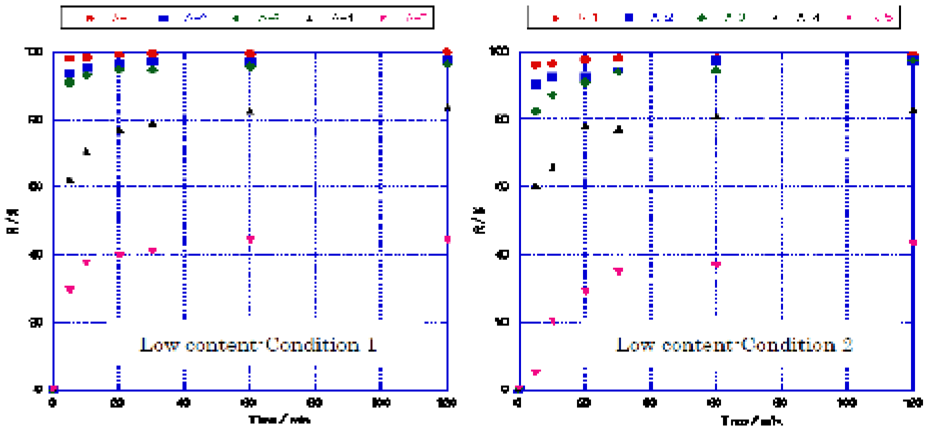

Fig. 3. Effects of shaking time on uptake (%) of Cs^+. Low content zeolite sheets (5 cm x 5 cm); 10 ppm Cs^+ in HNO_3; 25ºC.

Comparison of Uptake Rate of Cs^+ for Different Zeolite Sheets

The comparison of uptake rate of Cs^+ ions for different zeolite sheets is shown in **Fig. 4**. In the presence of 0.1 M HNO_3, the uptake equilibrium attained within 20 min and the uptake (%) was above 95% except for the case of high content zeolite sheet (condition 2). Thus the differences in zeolite content and sealing treatment had no effects on the Cs^+ uptake (%) under these experimental conditions. In the case of ^{137}Cs tracer experiments, similar results were obtained; the uptake equilibrium attained within 5 h and the uptake (%) above 95% was obtained (**Fig. 5**).

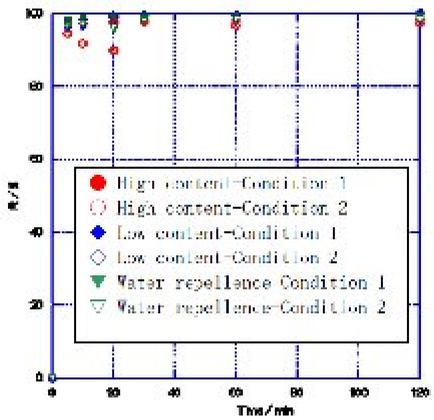

Fig. 4. Effects of shaking time on uptake(%) of Cs^+. Zeolite sheets (5 cm x 5 cm); 10 ppm Cs^+ in 0.1 M HNO_3; 25ºC.

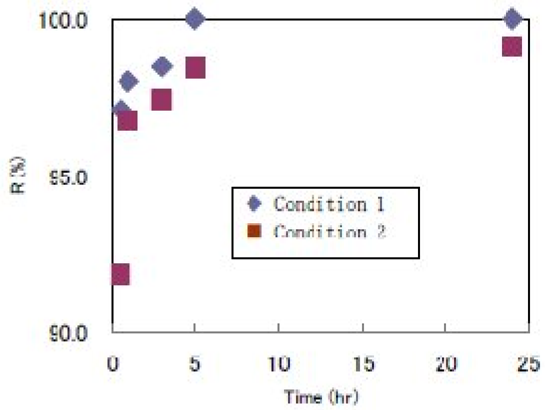

Fig. 5. Effects of shaking time on uptake (%) of Cs^+. $[Cs^+]$= 10 ppm; initial ^{137}Cs activity= 10^4 cpm; $[HNO_3]$= 0.1 M; high content zeolite sheets (5 cm x 5 cm); V= 30 cm^3.

Uptake Rate of Cs^+ for Zeolite Sheets in Seawater

The high-activity-level water from Fukushima NPP-1 accident contains seawater. Here the uptake rate of Cs was evaluated using actual seawater (Matsushima bay, Miyagi Prefecture). As shown in **Fig. 6**, the uptake (%) of Cs^+ in seawater was slightly lowered compared to that in the presence of HNO_3. The uptake (%) of Cs^+ in seawater was estimated to be above 90% after 2 h-shaking, indicating the considerable enhancement of uptake rate compared to the conventional granular zeolites. The zeolite sheet seems to be effective for the decontamination process as a filter with Cs adsorbability.

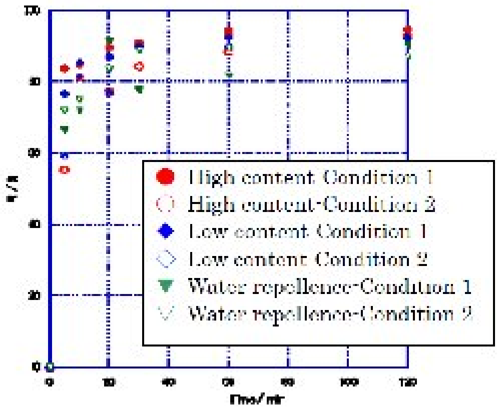

Fig. 6. Effects of shaking time on uptake (%) of Cs^+. Zeolite sheets (5 cm x 5 cm); 10 ppm Cs^+ in seawater; 25ºC.

Uptake Rate of Cs^+ for Zeolite Sheet in the Presence of NaOH

The uptake rate of Cs^+ ions for the zeolite sheets are examined at different NaOH concentrations up to 1.0 M. For example, the uptake rate of Cs^+ for the high content zeolite sheets (condition 1 and 2) is shown in **Fig. 7**. In either case, similar uptake profile was obtained. The uptake rate tends to enhance with decreasing NaOH concentration as C-1 > C-2 > C-3, and relatively large uptake (%) above 90% was obtained within 20 min in the presence of 0.1 M NaOH. In particular, the uptake (%) above 95% was obtained for the high content zeolite sheet (condition 1) in the presence of 0.1 M NaOH. In the case of high content of zeolite sheet (condition 2), the uptake data tends to scatter, compared to that of zeolite sheet (condition 1), probably due to the contact problem between zeolite and aqueous phase. As for low content zeolite sheet, similar uptake rate was obtained, and the scattering of the uptake data for condition 2 was improved (**Fig. 8**). However, considering high solubility of Si in alkaline solution, more detail analysis data are essential for the estimation of the resistance against alkaline solution.

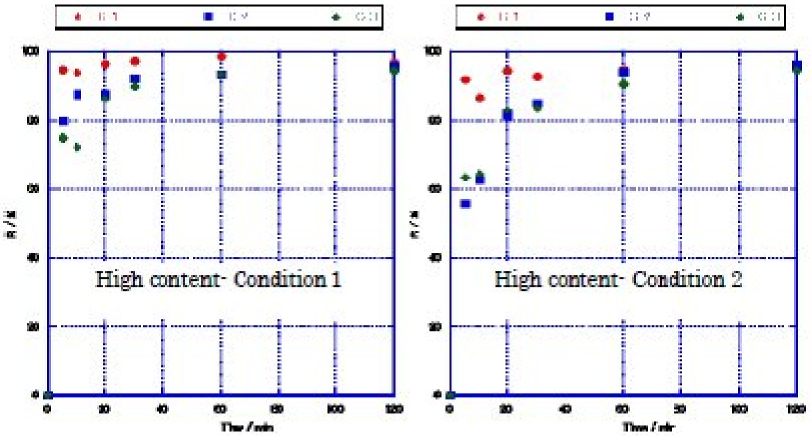

Fig. 7. Effects of shaking time on uptake (%) of Cs^+. High content zeolite sheets (5 cm x 5 cm); 10 ppm Cs^+ in NaOH; 25ºC.

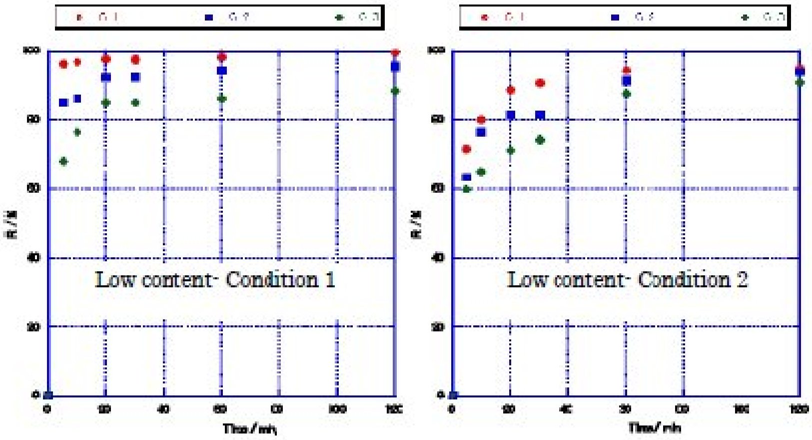

Fig. 8. Effects of shaking time on uptake (%) of Cs^+. Low content zeolite sheets (5 cm x 5 cm); 10 ppm Cs^+ in NaOH; 25ºC.

Characterization and Stability

As for the radiation stability test, different zeolite sheets were irradiated by ^{60}Co-γ ray up to 86 d at 3.4×10^3 R/h of exposure rate (^{60}Co irradiation facility, Tohoku University), and the surface morphology of irradiated specimens was examined by SEM observation. As shown in **Fig. 9**, there is no appreciable alteration on the surface of the irradiated specimens after irradiation of ^{60}Co-γ rays at 7.01×10^6 R.

Surface morphology of zeolites sheets heated up to 150℃ is shown in **Fig. 10**. There is no alteration for the surface morphology of the specimens heated below 110℃ for 2 h and IR spectra up to 150℃, while the shrinkage of fibers and color change were observed at 150℃, probably due to the thermal alteration of polymers, desorption of adsorbed water and oxidation of impurities on the natural zeolite surface. The thermal stability is thus estimated to be less than 110℃.

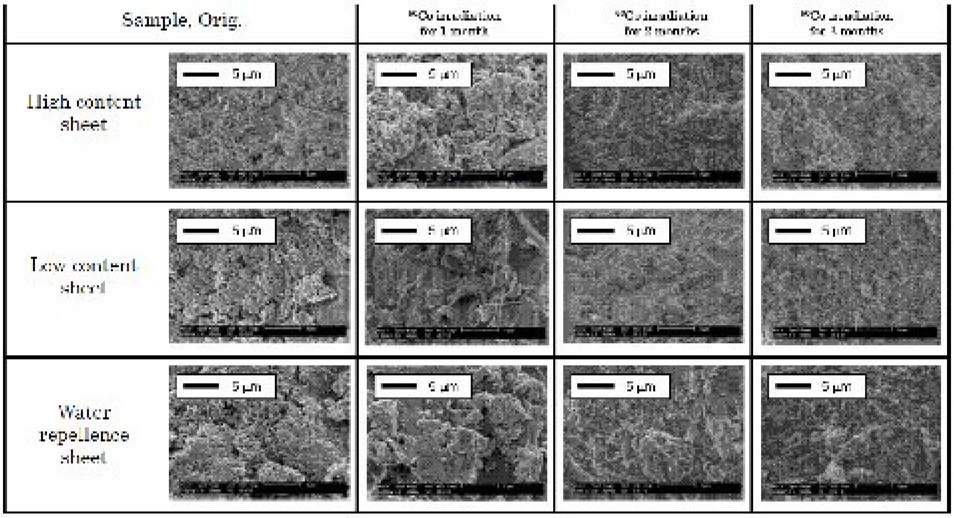

Fig. 9. SEM images of irradiated specimens of three kinds of zeolite sheet.
Exposure: 2.28×10^{6} R (1 month), 4.73×10^{6} R (2 months), 7.01×10^{6} R (3 months).

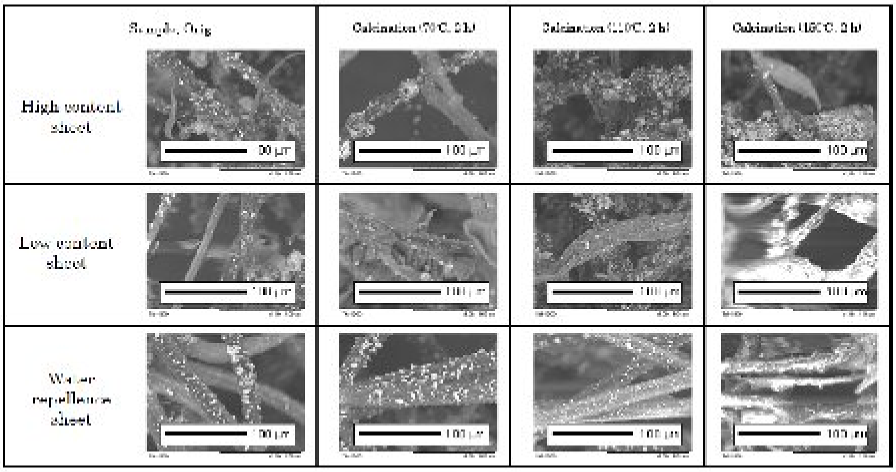

Fig. 10. SEM images of calcined specimens of three kinds of zeolite sheet (fiber).

As for the chemical durability, the specimens after batch experiments were submitted to SEM observation, EDS and IR analyses. As shown in **Figs. 11 and 12**, no surface alteration was observed for the specimens treated with 5 M HNO_3 or 1 M NaOH. On the other hand, slight spectral changes are observed by EDS and IR analyses; spectra of K^+ and Fe^{3+} ions in natural zeolites were disappeared after the treatment with 5 M HNO_3 and 1 M NaOH, respectively, while the zeolite structure was still maintained.

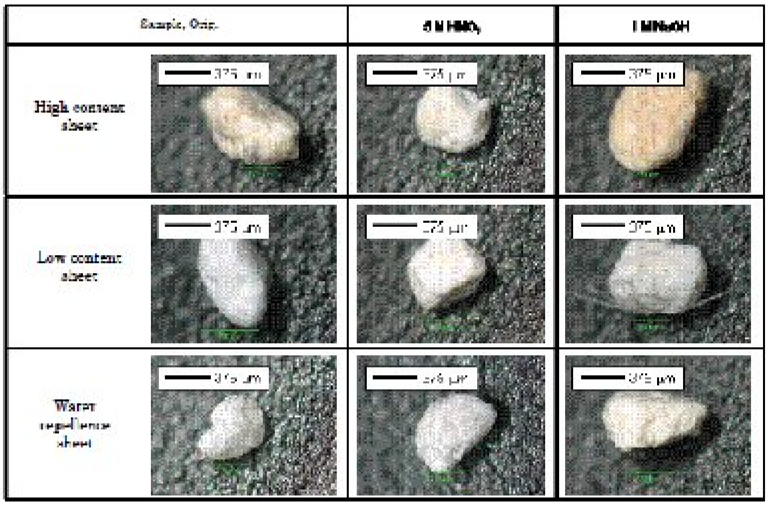

Fig. 11. DM images of specimens of three kind of zeolite sheet (zeolite) treated with 5 M HNO_3 and 1 M NaOH.

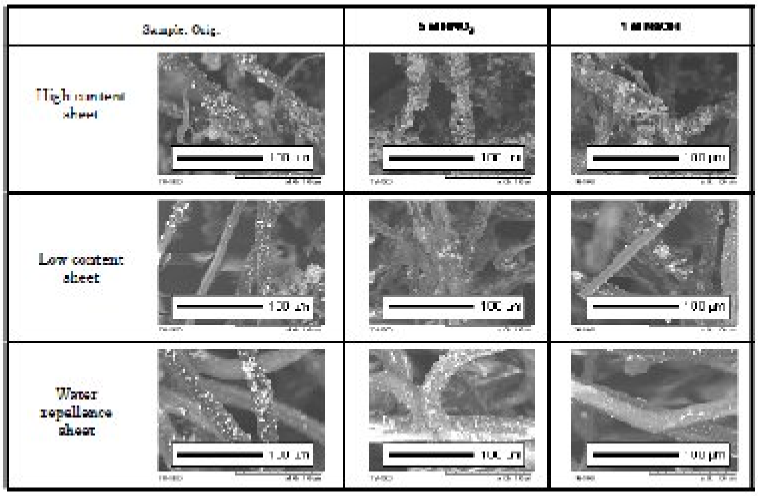

Fig. 12. DM images of specimens of three kind of zeolite sheet (fiber) treated with 5 M HNO_3 and 1 M NaOH.

CONCLUSIONS

The uptake properties of Cs^+ ions and the stability for zeolite nonwoven fabrics (zeolite sheets) were evaluated considering the application for the decontamination of contaminated water. As for batch adsorption properties, relatively large uptake rate of Cs^+ was obtained; the uptake equilibrium attained within 20 min and the uptake (%) was above 95%. The differences in zeolite content had no effects on the Cs^+ uptake (%). The uptake (%) of Cs^+ in seawater was slightly lowered compared to that in the presence of HNO_3. The uptake (%) of Cs^+ in seawater was estimated to be above 90% after 2 h-shaking, indicating the considerable enhancement of uptake rate compared to the conventional granular zeolites. The uptake (%) of Cs^+ for the zeolite high content type was estimated to be above 95% by using ^{137}Cs tracer. As for the comparison of sealing treatment, the uptake (%) for the zeolite sheet treated with edge sealing was larger than that with wrapping treatment. The uptake (%) for the zeolite sheet (high content type) was independent of sealing treatment and NaOH concentration. As for the stability, zeolite sheets were stable after ^{60}Co- γ ray irradiation up to 7.01×10^6 R. On the other hand, the discoloration of fiber and zeolite and the shrinkage of the fiber were clearly observed after heat treatment at 150ºC for 2 h. After treatment with HNO_3 and NaOH, the zeolite structure was still maintained. Thus the considerable enhancement of adsorption properties was observed by using zeolite sheets compared to the conventional granular zeolites.

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