Development of fibrous zeolite-polymer composites used for decontamination of radioactive cesium.

（放射性セシウム除染のためのゼオライト―ポリマー複合繊維の開発）

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Abbreviation list

Chapter 1 General introduction

1.1 Accident of Fukushima daiichi nuclear power plant

Due to the east Japan great earthquake disaster with a magnitude of 9.0 occurred in the northwest pacific of northeastern Japan on March 11, 2011, a tremendous amount of radioactivity was discharged to Fukushima area and surrounding eastern Japan. The radioactive pollution was caused by the serious damage of nuclear reactors of the Fukushima Daiichi electric power plant. Afterword, Fukushima and their adjacent prefectures have been contaminated with the fission products from the accident power plant. Consequently, high volatility fission products including ^{131}I, ^{134}Cs, ^{137}Cs, ^{89}Sr, and ^{90}Sr were discharged into the nearly environment [1]. According to the report of Tokyo Electric Power Company (TEPCO) [2], the amounts of ^{131}I, ^{134}Cs, ^{137}Cs, ^{89}Sr, and ^{90}Sr were known as radionuclides released into the surrounding environment, as shown in Table 1-1. In a major three nuclides of I, Cs and Sr, their tremendous amounts were present with a total 165.44 PBq in the natural field. Here, the unit of Becquerel (Bq) represents the radioactive number of atoms for the radioactive substances collapsing per second. Among their nuclides, especially, the ^{137}Cs in the Cs radioisotopes has a long half-life about 30 years. On 2017, Table 1-1 is seen that the ^{134}Cs is attenuated to 0.34 PBq and the ^{137}Cs is to 1.34 Bq. At the present, about six years after the accident, the total

1

amounts of the radioactive Cs (^{134}Cs + ^{137}Cs) are decreased by attenuation to about one-half of the initially released ones. But, Table 1-1 also describes that still a vast amount of radioactive Cs exists in the natural environment in Fukushima area.

Table 1-1 Radioactive substances emitted from Fukushima daiichi power plant after the east Japan great earthquake accident on 2011 and 2017*.

Radioactive nuclear species	Half life	2011 Emission amount 10^{15}Bq	2017 Emission amount 10^5Bq
^{131}I	8.02d	160	0
^{134}Cs	2.065y	1.8	0.34
^{137}Cs	30.167y	1.5	1.34
^{89}Sr	50.53d	2	0
^{90}Sr	28.79y	0.14	0.12
Total		165.44	1.8

* There are surmised with TEPCO reports [2]

Because Cs belongs to a chemically similar group including sodium and potassium to ingestion, the Cs radioisotopes are possible to be radiation exposure to skin and human body, presenting an internal hazard risk to our human health. Therefore, decontamination to remove Cs is necessary. Therefore, conventional decontamination in Fukushima has been worked in primarily removal, washing and sequestration of substances contaminated with radioactivity in order to reduce the dose to the environment. As currently six years

have passed since the accident, the radioactive pollutant is mainly radioactive ^{137}Cs which

has a long life time. Now, on 2017, the diffusion of the radioactive ^{137}Cs becomes main

problem in pollution. This becomes that the radioactive Cs has a property of being easily

dissolved in water. The pollutant radioactive Cs contained in water should be removed

from contaminant in natural water and others like soil and ash. On the other hand, soon

after the Japan accident, the Government of Japan formulated a program for the recovery

of these areas. In International Atom Energy Agency (IAEA) final report [3], the

progmatic approach for the radioactive remediation strongly indicated that the special

decontamination area was further divided into the three following categories as shown in

Figure 1-1 on 2013:   In Figure 1-1, the area 1 (Green) is that estimated annual dose level

is shown in range of 20 mSv - 1 mSv, the area 2 (Yellow) is   between 20 mSv and 50

mSv, and the area 3 (Red) is over 50 mSv [3]. Here, the unit of Sievert (Sv) represents

the magnitude of the biological effect of exposure to living bodies. At the International

Radiation Protection Committee, the exposure tolerance of ordinary people is set at 1 mSv

per year [4]. According to the Nuclear regulation authority [5], the annual effective dose

was expected to be more than 20 mSv after six years. As seen in Figure 1-1, not only the

distance from the nuclear power plant, but also the area with high space dose is existed

in the Fukushima map. This is reason that extensive decontamination has been carried out

for a long time in wide range of Fukushima. Figures 1-2 show maps of a great effort to

decontaminating through these six years after the accident occurred. It is seen that the

dose rate was reduced on 2016 [6], meaning the attenuation of radionuclide and broad

decontamination. However, as a result, huge-scale decontamination work generated large

amounts of radioactive waste. For example, in various categories, cleaning waste,

including soil, and municipal solid waste and etc. The amount of radioactive waste

delivered to intermediate storage is estimated at 22 million m^3 in Fukushima [7]. In

addition, on year 2012, about 22.5 million tons of their wastes have been collected from

the Tohoku area [8]. For their huge amounts of wastes, the Ministry of Environment,

Japan (MEJ) has defined criteria for categorization of contaminated material regarding

origin and activity concentrations [9]. The responsibilities of agencies are specified at

national and local levels for the management of the different categories of contaminated

materials throughout their lifecycle. Due to effective and efficient development of

radioactive Cs decontamination in Fukushima area, the decontamination demonstration

programs were carried out on 2011 – 2013, by organization of Fukushima prefecture. For

example, Figures 1-3 are pictures for the decontamination program carried on 2012 at

Date city of Fukushima for "The development of the compact decontamination equipment

with Cs adsorbents" for corporative participation of Kasai co. Ltd, Fukushima National

College and Nagaoka University of Technology. In this project, decontamination
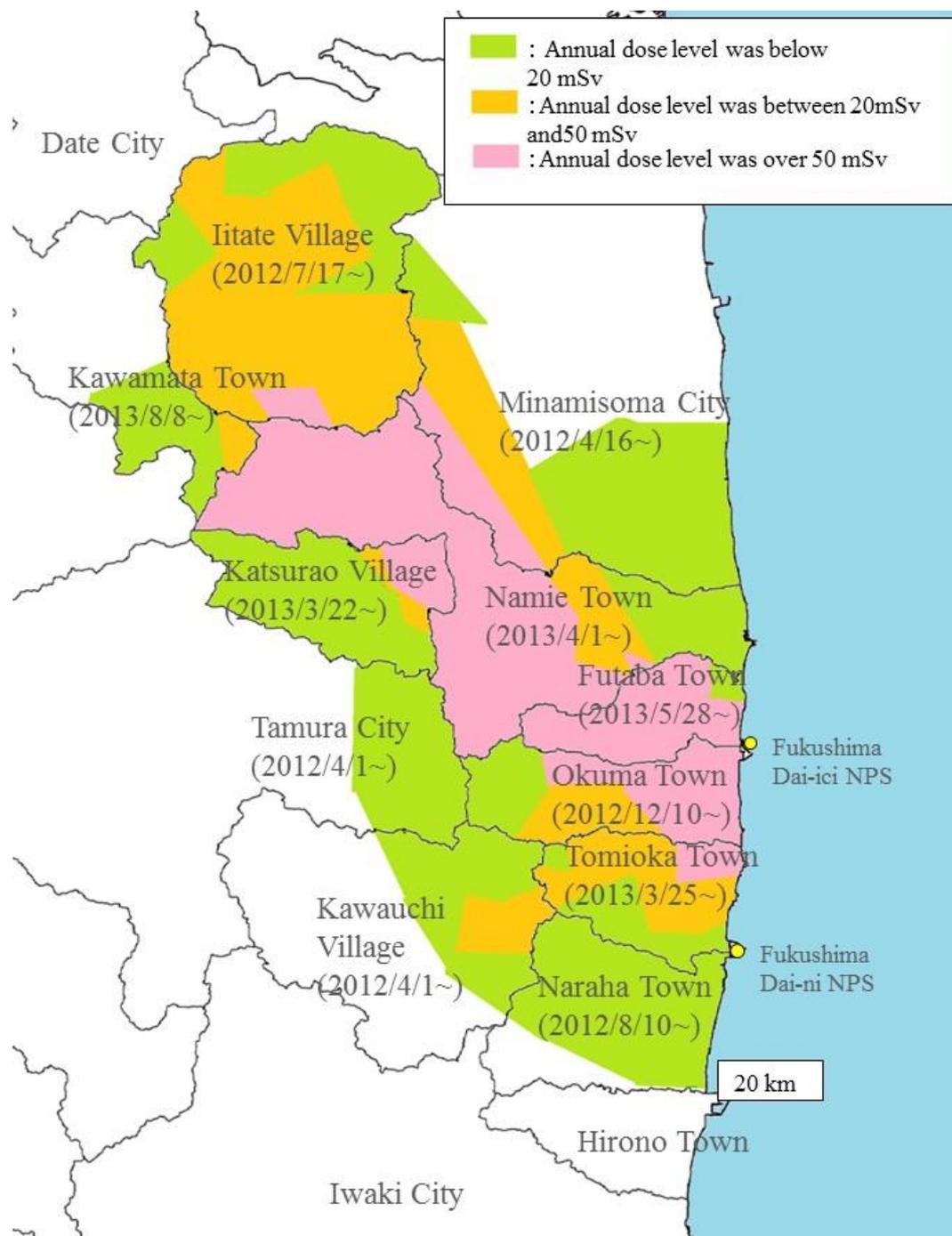
Figure 1-1 Arrangement of the areas to which evacuation orders had previously been issued (7 August 2013) [3]

April 2011

Dose of 1 m height from the ground surface

(pink)	$19.0 <$
(orange)	$9.5 < \text{Data} \leqq 19.0$
(yellow)	$3.8 < \text{Data} \leqq 9.5$
(yellow-green)	$1.9 < \text{Data} \leqq 3.8$
(green)	$1.0 < \text{Data} \leqq 1.9$
(dark green)	$0.5 < \text{Data} \leqq 1.0$
(cyan)	$0.2 < \text{Data} \leqq 0.5$

← Fukushima Daiichi Nuclear Power Plant

March 2013

November 2016
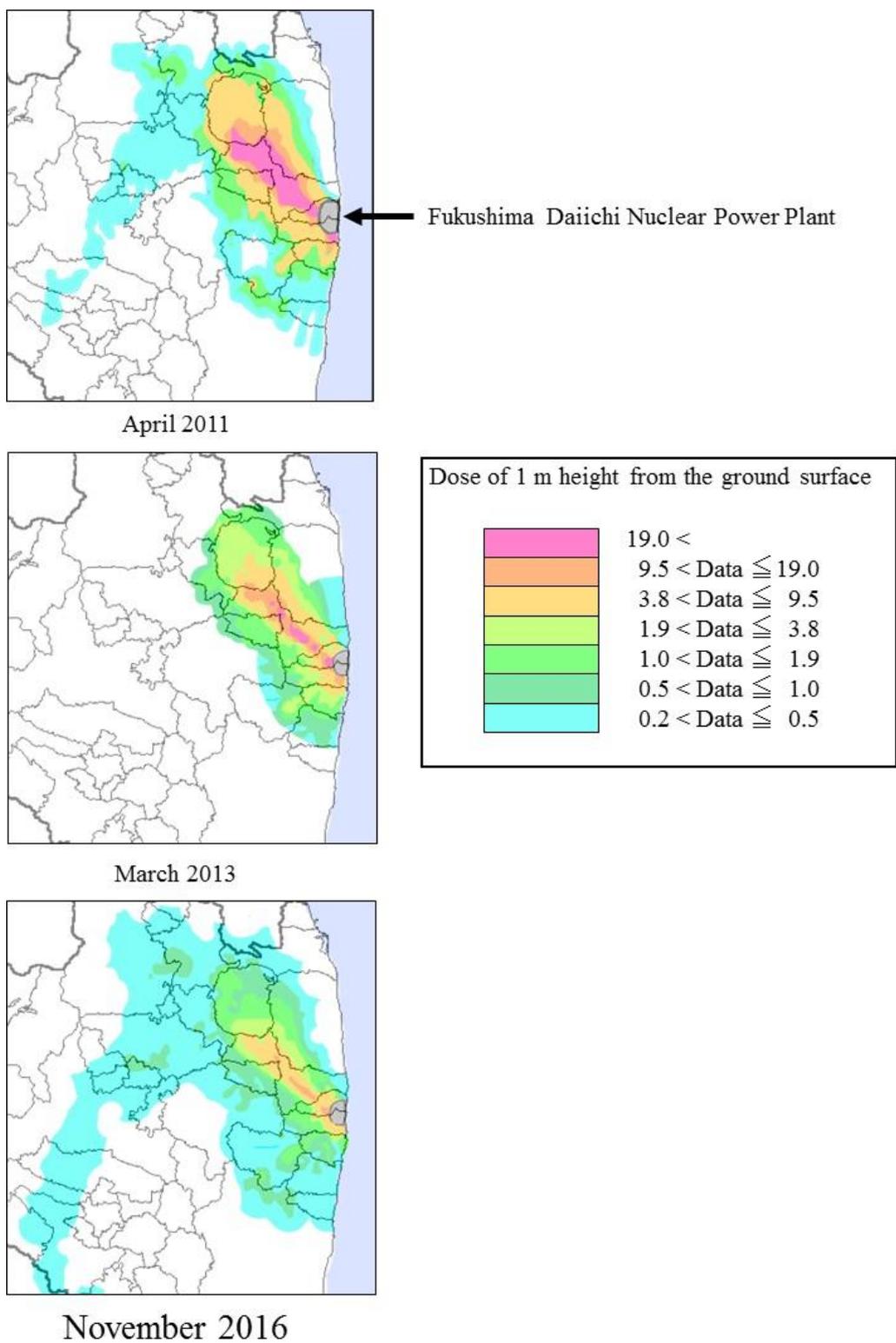
Figure1-2 Changes in the dose around Fukushima Daiichi electric power plant.

test was conducted to recover radioactive Cs contained in agricultural water with zeolite-

polymer adsorbents fiber, which were packed in nylon net bag (Figure1-3 A). Figure 1-2

Changes in the dose around Fukushima Daiichi electric power plant [6]. Figure 1-3 (B)

presented view for installed container containing adsorbent-nylon nets in the side groove

of agricultural water. After a certain period of time, the stain less container was taken out

(Figure1-3 C) and then, the concentration of radioactive Cs in the adsorbent contained

therein was measured.

Figure 1-3 Pictures of decontamination demonstration project in Yuzan at Date City of

Fukushima on 2012, October-December. The decontamination was carried out by Kasai

co. Ltd., as support with Fukushima prefecture.

1.2 Problems of radioactive wastes in Fukushima

For radioactive wastes having ^{137}Cs, definition of categories and allocation of responsibilities have provided and stepped forward a clear path in the management of Cs contaminated materials year by year. As shown in Figure 1-4, the flow diagram presents radionuclide treatments in specified waste water and soil for the decontamination in Fukushima Prefecture. In the flow diagram of governmental treatment radioactive Cs, there are two kinds of decontaminated wastes like specified waste, waste in countermeasure area and designated one with over 8,000Bq/kg. In the point of B, the waste generated in the contaminated area should be disposed as general waste at 8,000 Bq / kg (Figure 1-4 at point A) or less depending on the radioactive Cs concentration and above 8,000 Bq / kg (Figure 1-4 at point B). In treatment processing to the waste of 8,000 Bq / kg by the usual treatment method, the radiation dose to workers and surrounding residents is estimated as less than 1 mSv / year. In the radiation dose of the surrounding residents of the final disposal site the landfill disposal is completed at below 10 μSv / year [7]. On the other hand, after incineration, combustible wastes are transported to intermediate storage (Figure 1-4 at point C). But those are exceeding 100,000 Bq / kg due to concentrate of the burning process, meaning that extremely high radioactive ^{137}Cs retains in the wastes. Similar concentration of the radioactive Cs has been seen in the
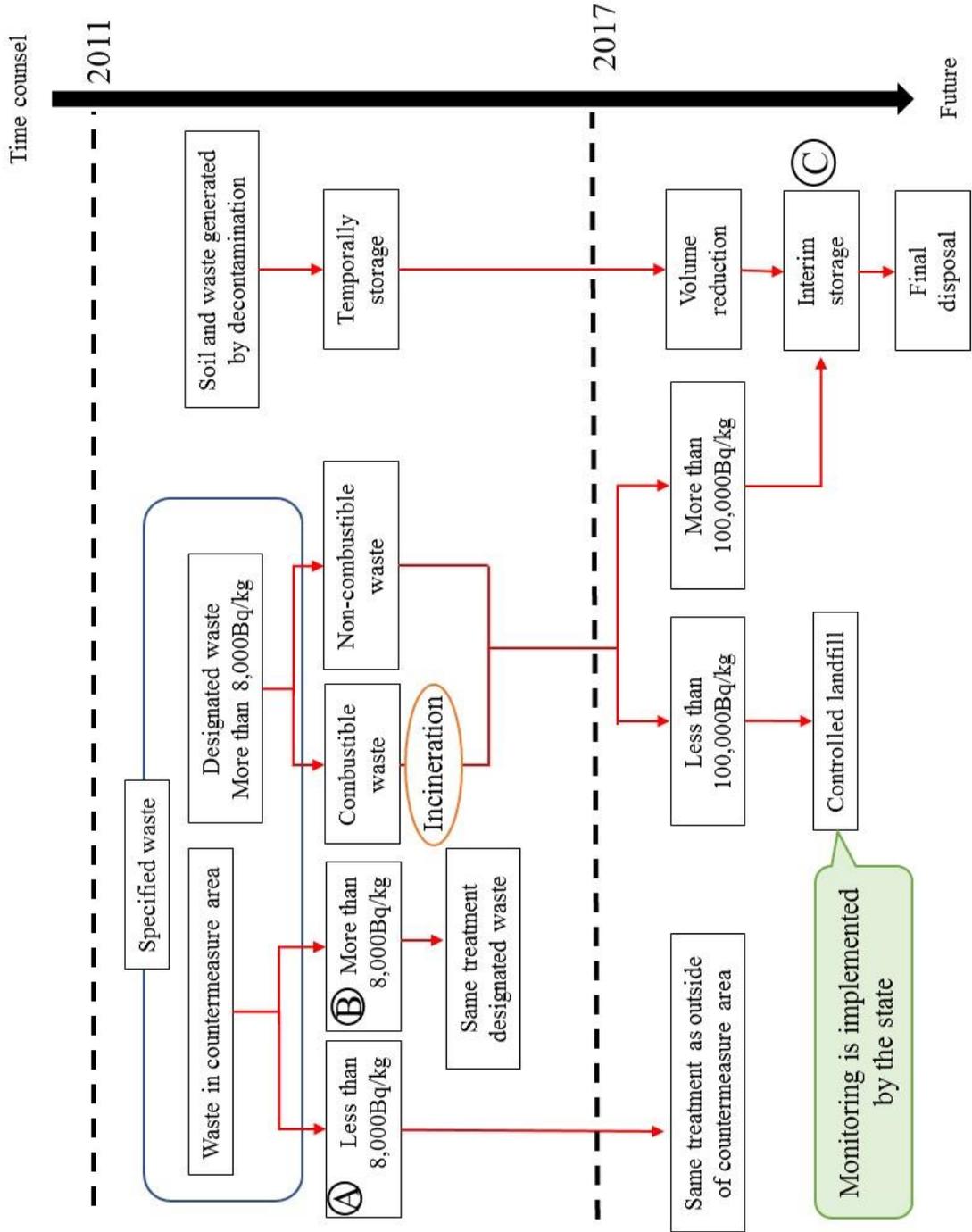
Figure 1-4 Flow diagram for treatment of specified waste and decontamination waste and soil

contaminated soil and waste generated by the decontamination operation. There are

transported to an intermediate storage facility irrespective of radioactive Cs concentration.

It has been regulated by the MEJ that such waste containing radioactive Cs is classified

by concentration on over 100,000 Bq / kg which is transported stored and to an

intermediate storage facility. Untile now, the conventional decontamination at Fukushima

was mainly the collection and transport of such radioactive waste (Figure1-5). However,

in future, the decontamination system might be a problem to reduce volume of radioactive

waste, in order to keep long-term storage of the huge amounts of high Cs concentration

waste. Therefore, at this time the reduction of the ^{137}Cs included waste becomes to be

required for the safe keeping of a huge quantity of radioactive waste.

Figure 1-5 Picture of storage radioactive waste in Tomioka town.

1.3 Separation technology to radioactive wastes

As mentioned, the treatment of radioactive Cs waste is also very important in the

decontamination technology. For that reason, separation process for the nuclides becomes

a key technology. It is necessary to develop a radioactive Cs separation and then to store

in long-termed safety storage without generating a large amount of waste. Table 1-2

shows the separation technology of radioactive Cs that has been previously reported. Here

in practical separation technology of radioactive Cs contaminated in soil, ash and water,

there are several methods for flotation melting treatment method, a hydrothermal

extraction and aqueous medium separation. In the flotation method [10], radioactive Cs

tends to be adsorbed on fine soils of a particle. Thus, this technique is to collect to

radioactive Cs as the fine particles are need as buoyancy. In melting treatment, the method

is to vaporize the radioactive Cs from waste at a high temperature of 1300 °C in a melting

furnace [11]. The hydrothermal extraction method is a technique to bring radioactive Cs

into the water layer by pressure water treatment bringing it into contact with superheated

steam under high temperature and high pressure [12]. For the pollutant extracted in the

water, the separating process of radioactive Cs in aqueous medium is taken place. Here,

the Cs salt can be in a bag filter. It is also known that radioactive Cs is recovered in the

ion state in water. In the aqueous medium separation for the pollutant, the method is

Table 1-2 Cs separation methods from waste substance or water.

Method	Target	Separation mechanism	References
Flotation method	Soil	radioactive cesium is adsorbed on fine particles, it captures fine particles and separates radioactive Cs from radioactive waste	[11]
Melting Treatment	Soil, Ash	The radioactive Cs containing waste is vaporized with high temperature, separated from radioactive waste	[12]
Hydrothermal extraction	Soil, Ash	Extract radioactive Cs with high temperature and high pressure water	[13]
Membrane separation	water	Concentrated separation of radioactive Cs using RO membrane	[14]
Coagulative precipitation	Water	Add radioactive Cs adsorbent and coagulant, filter and separate radioactive cesium in water	[15]
Adsorbent	water	Adsorb and separate radioactive cesium in water with adsorbent	[16].[17]

subject for radioactive Cs contained in aqueous solution which is present as radioactive

pollutant. For example, there are several processes of RO membrane method, coagulation

sedimentation, and adsorbent in order to treat such aqueous pollutant waste. The RO

membrane method is already used, when people have prepared ultrapure water and

desalination of sea water. By the membrane process for contaminated water, radioactive

Cs is concentrated and separated by the membrane separation to the ions contained in

water [14]. However, a high concentration of wastewater still remains. In the coagulation

sedimentation method, Prussian blue and zeolite, are typical radioactive Cs adsorbents

for treating radioactive wastewater. Although the adsorbent method is simple and

effective in the separation technique of the radioactive Cs as advantages, the flocs are

formed by a coagulant, precipitated, and separated after the decontamination treatments.

This problem happened are due to that when radioactive Cs contained in water can be

separated, radioactive waste is generated by a large amount of floc. The flocs generally

contain high concentration of radioactive Cs and also become serious problem after the

treatment is finished, becomes of extra thermal, high concentration of nuclides. This

residence of the huge flocs is disadvantage to the method. Also, in the separation method

using an adsorbent, wastewater is passed through an adsorbent to adsorb radioactive Cs

[15,16]. As well as the sedimentation, it should be noted that high concentrated

radioactive Cs waste is generated in the adsorbents. This is become that the separation process has concentration by adsorption of the radioactive Cs to the adsorbents. As a results, the treatment process includes the adjustment of the radioactive Cs concentration in the radioactive waste by controlling the radioactive Cs adsorption.

1.4 Development of radioactive Cs adsorbents

For the large amounts of radioactive Cs that still exist after about six years passed, several adsorption technologies have been developed and seen for the purpose of Cs decontamination. Many works were focused to adsorbent materials, which almost were applied for Cs removal from aqueous radioactive wastes. Table 1-3 lists adsorbent materials of radioactive Cs reported to such pollutant decontamination; Prussian blue [17-20], crown ether and its hybrid [21-24], clay [25-29], cement [30-33], and zeolite [34-36]. As seen, extensive research has been conducted with Prussian blue [17-20]. Here, Prussian blue is excellent performance of the adsorption capacity by the fine particles. However, since cyano group are main components in Prussian blue as shown in Figure 1-6, harmful cyano group desorption occurs under high alkali. In addition, Prussian blue is present in nanosize dispersion in water [18], meaning that the separation of Prussian blue having radioactive Cs from the dispersion water medium becomes serious problem in the

Table 1-3 Radioactive Cs adsorbent materials development

Cs adsorbent material	Description	References
Prussian blue (cyanogen compound)	· Sparingly soluble metal ferrocyanide (M-FC) salts are formed in liquid by mixing a metal salt solution with a potassium ferrocyanide solution. · A simple procedure at room temperature using non-toxic and cost-effective precursors has been developed to prepare magnetic Prussian blue/graphene oxide ($PB/Fe_3O_4/GO$) nanocomposites for the removal of radioactive cesium in water.	[18-21]
Crown ether hybrid	The conjugate adsorbent was prepared by direct immobilization of dibenzo18-crown-6 ether onto mesoporous silica monoliths. the prepared adsorbents could be used as low-cost potential adsorbents for the selective radioactive Cs decontamination from Fukushima wastewater samples.	[22-25]
Clay	· A series of experiments were performed to quantify the adsorption of cesium on ceiling tiles as a representative of urban construction materials. · The state and dynamics of water and cations in pure and mixed Na-Cs-montmorillonite as a function of the interlayer water content were investigated in the present study, using Monte Carlo and classical, molecular-dynamics methods.	[26-30]
Cement	· Geopolymer foam materials could function as adsorbents for cesium ions. Geopolymer foams showing cesium adsorption were prepared by condensing a mixture of metakaolin and alkali solution at 100° C in the presence of silica from rice husk powder, and they showed effective adsorption of cesium.	[31-34]
Zeolite	· In the river water samples, Cs-134 and Sr-85 were successfully removed using bentonite and zeolite, and I-131 was removed using activated carbon. In the seawater samples, Cs-134 was removed using bentonite and zeolite. · A nonwoven fabric containing zeolite was tested for the removal of cesium. Ion exchange selectivity of the natural zeolite was $Ag^+ > Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Cr^{3+} > Ni^{2+}$ with almost 100% removal of Ag^+ and Pb^{2+} ions.	[35-37]

well mixed water. For this reason, radioactive Cs adsorbents were produced with support

on solid polymer materials by immobilizing such nano size Prussian Blue have been

studied [19].

Figure 1-6 Desorption of cyano group from Prussian blue under high alkali image.

On the other hand, natural zeolite is microporous in the aluminosilicate structure

(Figure1-7) as known as molecular sieve functionality to hosting to several cations.

Higher capacity adsorbents to the radio nuclides with high selectivity for Cs ions [34-36],

is reported in the aluminosilicate having stable even under high alkalinity [37]. The

natural zeolites, mordenite zeolite having $(Na^+_8)[(AlO_2)_8(SiO_2)_{40}] \cdot 24H_2O$ (Figure 1-7)

was found by Meier for the building framework units linked edge-sharing 12-membered

ring [38]. Its two-dimensional pore structure consists of 12-membered ring channels ($7 \times$

6.5 Å) connected by 8-membered ring channels (3.4×4.8 Å) [39]. In general, adsorption

of Cs by zeolite is carried out by ion exchange. Nakamura etc. al. examined the ion

exchange mechanism between Na ion and Cs ion of mordenite zeolite using

computational analysis and was the high selectivity clarified to Cs [40]. Furthermore, the

zeolite is thermochemically stable and its crystal structure can be maintained up to 600 °

C [41]. There are advantages as followed for zeolite adsorbents; 1) high capacity

adsorbent of cation, 2) excellent chemical stability, 3) safe substance derived from natural.

However, since most of the zeolite adsorbent is in the form of powder type, it is necessary

to recover by the coagulation sedimentation method after the decontamination treatment.

As well as Prussian blue, therefore, fixing such powder adsorbents is strategy for efficient

adsorbents. So, such development of an adsorbent is capable of easily recovering without

increasing radioactive waste and is preferred in practical operation.
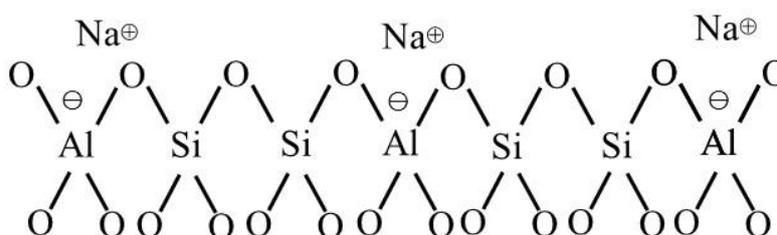
Figure 1-7 Picture and chemical structure of zeolite.

1.5 Cs Decontamination by zeolite adsorbents

In the decontamination works at Fukushima, buildings and roads were mainly subjected to wet blasting work [42]. As shown in Figure 1-8, the wet blasting operation is removing radioactive substances with scraping the surface. Thus, used abrasive water be collected as radioactive waste containing Cs. The collected waste water is discharged after the waste water was removed for radioactive Cs by treating with zeolite and then coagulation sedimentation. The standard is followed with Act on Special Measures concerning the Handling of Radioactive Pollution in Japan [41], in according to the standard Cs concentration calculated by the followin$\dfrac{^{134}\text{Cs Bq/L}}{60} + \dfrac{^{137}\text{Cs Bq/L}}{90} \leqq 1$
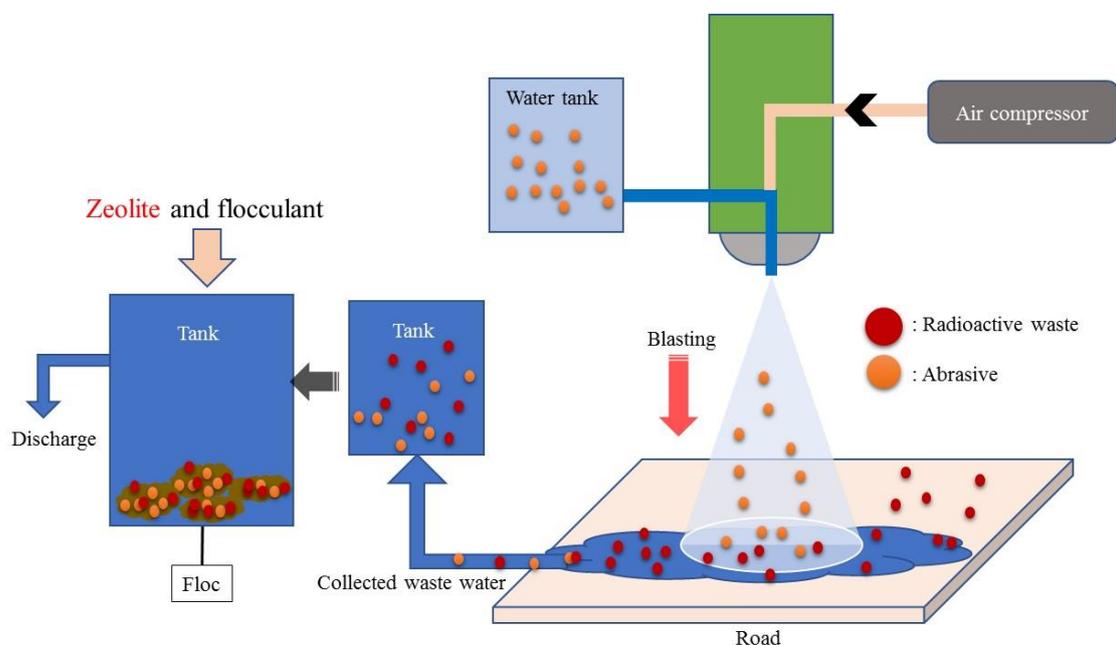
Figure 1-8 Decontamination method of road with wet blast.

  Since the floc which is generated in large amount by the coagulation sedimentation,

treatment becomes serious problem. For instance, as seen in the illustration, there has

been used zeolite and flocculant for decontamination of radioactive Cs to the wet blast

waste water.

    Actually, such landfill disposal of contaminated soil and radioactive waste of

incineration ash showed be less than 8,000 Bq / kg in the radioactive Cs level. So, zeolite

decontaminated agent is spread down as shown in Figure 1-9 in one of other methods.

This could prevent outflow of radioactive Cs [9] according to the MEJ guides for the

landfill disposal method of radioactive waste. However, the radioactive Cs concentration

to zeolite sometime occurs over time, meaning that high-concentration radioactive waste

in zeolite powder remains in the landfill.
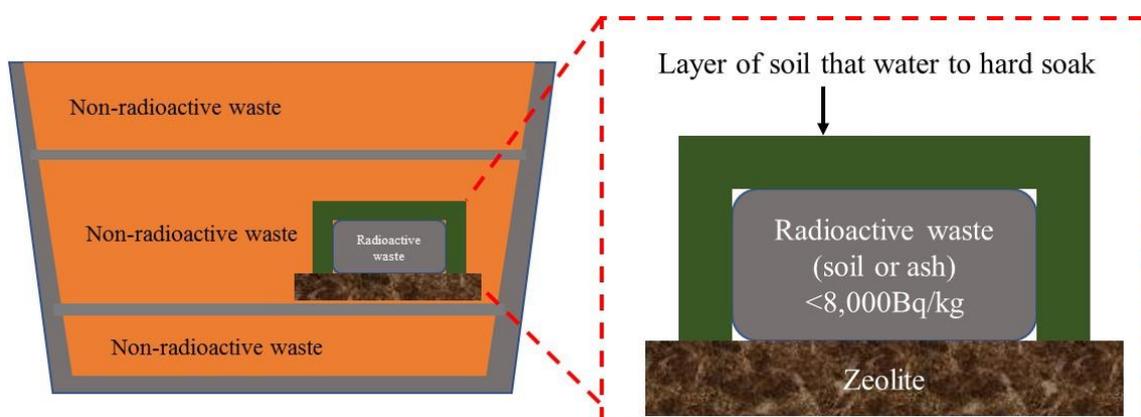
Figure 1-9 Landfilling method of radioactive waste

Furthermore, it is also used to suppress the transfer rate of radioactive Cs to agricultural crops by spraying zeolite to agricultural land [42]. However, the sprayed zeolite has not been recovered, meaning problem in radioactive Cs concentrated on farmland without removal. As mentioned, although zeolite mainly is used in many decontaminations works at Fukushima, the recovery of zeolite powders adsorbed with highly radioactive Cs is still remained as technical to solve.

1.6 Development of zeolite composite fiber

Generally, conventional radioactive Cs adsorbents have a shape in powder materials like zeolite. As introduced in previous section for Prussian blue and powder zeolite, it is seen that difficulty is happened to recover them after their decontamination. In such powder adsorbent, thus, such serious problem should be solved. So, there were reports on the decontamination site for Cs adsorbent introduced to be complexed with other solid matrix. Awual et.al. was prepared by direct immobilization of dibenzo-18-crown-6 ether onto mesoporous silica monoliths. The Cs sorption behavior was examined using batch equilibrium technique [21]. Table 1-4 shows research reports on adsorbent loaded on polymer and inorganic materials. Adsorbents having a powder, shaped adsorbent by ion exchange resin beads [43], silica gel [44], pulp [45] were reported.

Zohreh reported synthesize Cs adsorbent of beads shape using polyvinyl alcohol [43].

Also, there was report on a phosphate-modified radioactive Cs adsorbent on silica gel

reported by Knneth [44]. Umezaki et.al. prepared a sheet of zeolite powder hybridized

with pulp to make handling easier [45]. This radioactive Cs adsorbent sheet produced by

Umezaki was actually installed in the river of Kawauchi village by Toppan Printing Co.,

Ltd. as shown in Figure 1-10. Here, porous supports using ion exchange resin or silica gel

also was noted for reaching the efficiency in addition with the shape of bead shape, gel

and sheet. However, in their porous matrix adsorbents, having the forms of beads or sheets

has a limited contact area with water [46]. In order to improve the adsorption efficiency

of radioactive Cs, fibrous from of the adsorbent shape was seemed to be better handling

properties, improving in the adsorbent performance and separation from pollutant

medium. Therefore, the requirements are for decontamination adsorbent for practical used

and following advantages are including; 1) high contact area, 2) simple handing, 3) easily

collecting. In conclusion for strategy of the present work, fibrous adsorbents are focused.

However, for the radioactive Cs adsorbent with fiber form, very little has been known.

For example, Okamura et.al. reported on Cs adsorbent fiber with inorganic cyanide

compound supported on synthetic fiber by graft polymerization using gamma ray [47].

This was attempted to improve adsorption rate and efficiency. Duangkamo et. al. coated

chitosan on surface of the rayon and prepared fibrous adsorbent to precipitate

ferrocyanide [48]. However, since the cyanide chemicals for example, for such Prussian

blue decomposes in the high alkali region and emit cyanide, the practical uses are serious

in the chemical stability, although the Cs absorptivity is excellent. To consider the stability

and efficiency, zeolite system has been used in practical purpose in the adsorbents (Figure

1-8 and 1-9). Therefore, composite zeolite fiber is worth challenging and better to be

applicable for practical decontamination to Fukushima. On this policy for purpose

practical decontamination material, research and development in new Cs adsorbents

having fibrous form were performed in this this thesis.

Figure 1-10 Picture of installation case of zeolite sheet. The decontamination was carried
out by Toppan Printing Co., Ltd.

Table 1-4 Cs adsorbents sharp, material and preparation.

Adsorbent sharp	Adsorbent material	Base material	Preparation	References
Bead	Potassium iron(III)-Hexacyanoferrate(II)	Polymethylmethacrylate	Precipitation	[43]
Gel	Phosphotungstic acid	Silica gel	Precipitation	[44]
Sheet	Zeolite	Polypropylene	Fixing agent	[45]
Fiber	Potassium cobalt hexacyanoferrate	Dimethyl methacrylate	Graft-polymerized onto gamma ray	[47]
Fiber	Chitosan, Prussian blue	Rayon	Precipitation	[48]

1.7 Scope of present thesis

In the present thesis, preparation and properties of zeolite composite fiber is described as the novel adsorbent of radioactive Cs for the purpose of the decontamination technique in Fukushima.

My thesis is described as followed in consisting of 5 chapters. **Chapter 1** presents a brief introduction to Fukushima Daiichi Nuclear Power Plant accident and the problem of radioactive waste of decontamination. The work ground importance of the work for the development of adsorbent is mentioned in the point of views of decontamination of radioactive Cs. In this chapter, therefore, the uses of zeolite in actual decontamination work and strategy in the development of fibrous radioactive Cs adsorbents. **Chapter 2** describes preparation method of the zeolite-polymer composite fibers having unique structure and characterization for radioactive Cs adsorption. Also, this chapter describes decontamination properties of extra-diluted radioactive Cs in Fukushima areas by using zeolite−polymer composite fibers. Here, the adsorption performance of radioactive Cs for the fibrous composite adsorbent was compared with those of zeolite powder under naturally practical environment. For example, the decontamination of radioactive Cs was carried out in Date during October−December 2012 for 28 days. The comparison indicated that the fiber adsorbent was excellent during

their long-termed immersion in the field river. Evidence was noted that the fiber adsorbent effectively remediated contaminant water. In **Chapter 3**, fibrous zeolite-polymer composites were used for decontamination of radioactive waste water extracted from radio-Cs fly ash. Here, fly ash polluted in Fukushima was treated by washing water and then the radioactive pollutant water was treated with zeolite polymer composite fiber. The behavior of the composite fibers was compared with that of zeolite and Prussian blue (PB). The strong alkali condition of the radioactive waste water strongry damaged in PB, while zeolite and the composite fiber successfully treated the radio-Cs by sorption process of batch and column experiments. **Chapter 4** describes compact storage of radioactive Cs in compressed pellets of zeolite composite fibers by immobilization. In this chapter, the immobilization of radioactive Cs in the pellets was studied, when the pollutant was prepared at different temperatures for the composite fibers and radioactive Cs. To facilitate safe storage of radioactive Cs in the composite fiber, such compact storage forms the effects of volume reduction and stability of the fibrous adsorbents were shown. The technique was suggested in the usefulness for long-term storage without leakage of radioactive Cs. In **Chapter 5,** this doctoral thesis is summarized. Especially in this chapter, the practical application of Fukushima decontamination for the fibrous composite adsorbents was introduced to the MEJ project 2016, for recovery and removal of

radioactive Cs extracted from incinerated fly ash.

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Chapter 2 Preparation and property of zeolite–polymer composite fibers and application to decontamination of extra-diluted radioactive cesium in Fukushima water

Abstract

The authors have developed and applied new technologies using zeolite composite fibers to prevent radioactive Cs pollution of water in Fukushima, Japan. During approximately four years in the area, decontamination has been conducted to reduce radioactive cesium (Cs) in the field. However, water contaminated with extra-diluted radioactive Cs has prevented residence within about 30 km of the damaged nuclear facilities. Great efforts at decontamination work should be undertaken to alleviate social anxiety and to produce a safe society in Fukushima. Decontamination using fiber-like decontamination adsorbents was examined in actual use for radioactive Cs in water in Date city in 2013 and in Okuma town in 2015. This report describes preparation and properties of the fiber-like decontamination adsorbents. Furthermore, this report is the first describing results of radioactive Cs decontamination using a fiber-like adsorbent for water with extra-low-level concentrations of radionuclides. Even four years after the accident, results strongly suggest the decontamination still distributed in Fukushima area,

depending on the distance of the nuclear power plant. Evidence indicates the importance

of preventing extension of radioactive Cs further downstream to human residential areas.

2.1 Introduction

After the Great East Japan Earthquake and Tsunami damaged the Fukushima

Daiichi Nuclear Power Plant during and after March 11, 2011, long-term radiation

contamination ensued, presenting severe difficulties to human life and the local

environment. Radioisotopes were released. Therefore, the area was left with

contaminated soil, air, and water. Thousands of people evacuated from their homes have

been prohibited from returning, or are hesitating to do so. Human life even in less-affected

areas is also still affected strongly, although four years half have passed since the disaster.

Now, potential exposure to radioactivity persists as an important problem with long-

active Cs (Cs) radioisotopes, [134]Cs and ^{137}Cs, which are distributed widely throughout

affected areas [1–3]. The release of Cs caused environmental contamination for which

mitigation, especially for ^{137}Cs, requires considerable effort. It has a 30-year half-life. The

release of the radioactive Cs into the environment has created severe environmental

problems and human health hazards. Among the huge volumes of contaminated materials

of various categories, millions of tons of matter require urgent disposal, including soil,

vehicles, buildings, roads, plants, and cleaning wastes. Therefore, emphases of earlier

studies have been assigned to volume reduction, which mainly includes methods for

solid-waste compaction and incineration [4,5]. Aqueous wastes that contain long-lived

radionuclides require treatment using chemical precipitation, evaporation, filtration, and

solvent extraction. Such decontamination processes have been recommended by the

International Atomic Energy Agency [6]. A designated disposal system is necessary for

such wastes. Currently, great concern persists over the effects of contaminated soil and

water on the health and safety of the local inhabitants.

However, the treatment level for extra low-level pollution on the radioactive Cs

in Fukushima is insufficient. Regarding the abundance of sources of radioactive Cs and

its damaging effects, extensive research related to the adsorption of Cs on various

materials with Prussian blue [7–9], clays, and cements [10–15]. Among them, for the

efficient removal of radioactive Cs from low-level radioactive liquid wastes, natural

zeolites like mordenite (Scheme 2-1), because of their low cost and selectivity, are

important alumino-silicates used in sorption processes [16–18]. For example, efficient

removal of Cs from low-level radioactive liquid wastes was reportedly improved by the

use of substances impregnated with natural zeolite minerals [19,20]. Natural zeolite is

known to have higher capacity as well as high selectivity for Cs ions. Unfortunately,

practical uses of zeolite for actual Cs decontamination have been little reported. It is

noteworthy that powder zeolites cannot be used continuously for long-term removal

because of the difficulty of powder recovery and the apparent limitations of the adsorption

capacity at the powder surface. Therefore, efforts have been undertaken to develop new

materials that are suitable for use as radioactive Cs adsorbents. The Fukushima area

continues to confront exposure to radioactivity, but the distribution of contamination

clearly depends on the area and circumstances. Nevertheless, some exposure risk to

residents Fukushima persists in each area. Effective methods to treat and dispose of the

hazardous substances should be developed quickly to protect local residents.
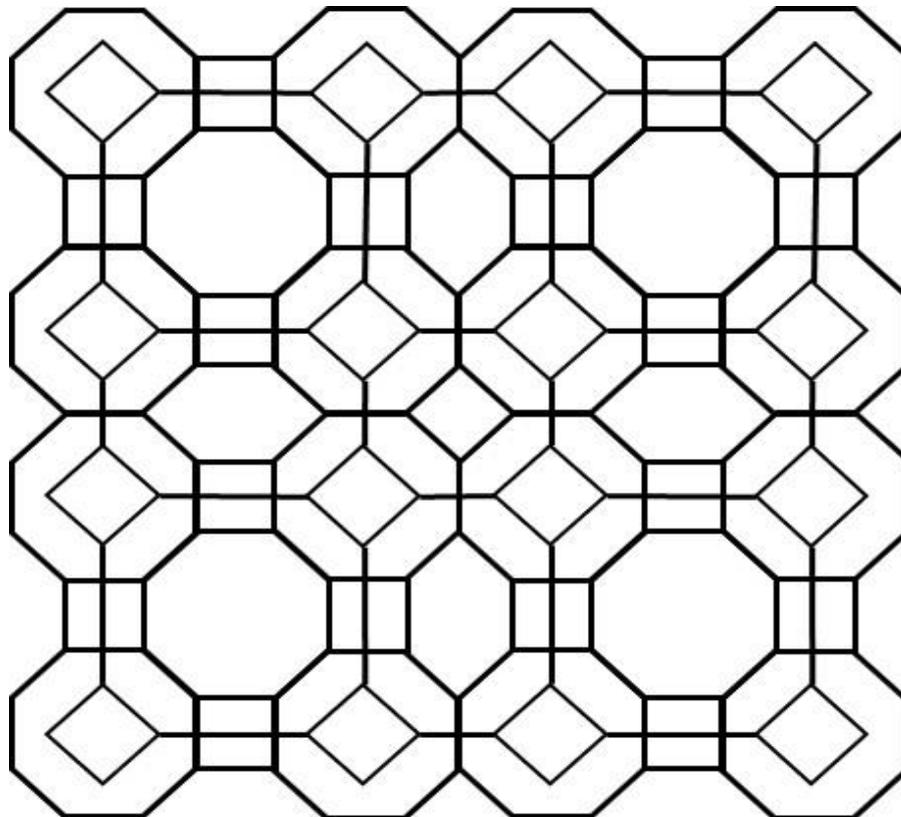
Scheme 2-1 Structure of mordenite zeolite.

This study assesses zeolite composite fibers as a radioactive Cs decontamination technology. It is noteworthy that the composite material enables recovery after decontamination treatment. Consequently, fiber adsorbents were actually used for decontamination in Fukushima to investigate decontamination of Cs from extra-diluted water in exposed areas of Date, Iwaki, and Okuma. Its operation is simple and beneficial, entailing installation of the zeolite composite fibers in a living environment. When a contaminant in a river flows downstream, it is transferred from mountain areas to plains and fields near residents. Figure 2-1 shows that the fibers can be used for passive decontamination to prevent radioactive Cs penetration to downstream residential areas. Composite fiber barriers reduce exposure risks while requiring no driving force or energy for the decontamination. In addition, the detection of radioactive Cs in composited fibers settled in water can be used as alarms notifying residents of the spread of radioactive Cs.

  The present paper describes preparation of the zeolite composite and includes evidence related to decontamination of radioactive Cs from a natural water environment. Evidence shows that passive decontamination using zeolite composite fibers eliminated radioactive Cs from water environments of surrounding fields that have extremely diluted radioactive Cs.
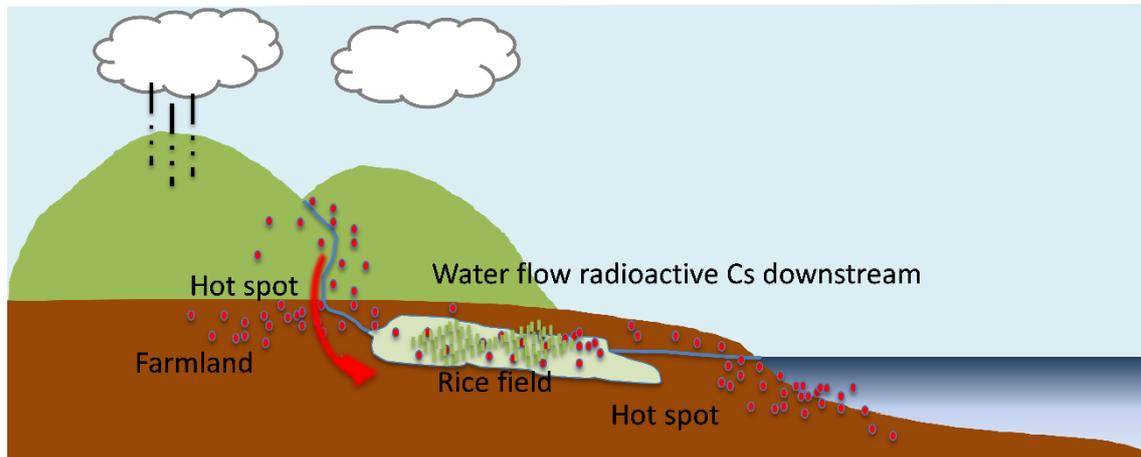
Figure 2-1 Illustration of radioactive Cs running off and infiltration at downstream residential areas and picture of agricultural river in Okuma town.

2.2 Materials and methods

2.2.1 Materials

All chemicals and reagents used for this study were of analytical grade purity.

They were used without further purification. Natural mordenite zeolite was acquired from

Japan Nitto Funka Trading Co. Ltd. (Miyagi, Japan). Poly(ethersulfone) (PES) was used

as received (PES, MW=50,000; BASF Japan Ltd., Ludwigshafen, Germany). Also, *N*

methyl-2-pyrrolidone (NMP; Nacalai Tesque Inc., Kyoto, Japan) was used without

purification.

2.2.2 Methods

Preparation of zeolite composite fibers was conducted using a modified dry–wet

spinning process [21,22], as presented in Figure 2-2. Figure 2-3 presents the procedure

process for fabrication of zeolite composite fibers. In 44 mL NMP as a dope solution,

PES (20 g) was dissolved and added to 36 g of zeolite. Then, the mixture was stirred with

constant speed at 50 °C to prepare the blending solution. The zeolite powder content was

50 wt% in the PES dope solution. Dope solutions containing zeolite powder were

extruded through a spinneret at 3 mL/min using a high-pressure gear pump (GP Driving

Unit CDS-18G-0.8; Kyowa Fine Tech. Co. Ltd). The extruded spinning solution was

introduced into a water bath located at a distance of 10 cm below the nozzle. Then, the

extruded spinning solution was coagulated at 25 °C in water to form zeolite composite

fibers. They were kept underwater to remove the solvent from the resultant fiber.

The composite fibers were treated with excess hot water at 90 °C three times to

eliminate the remaining NMP. They were then stored at room temperature in a wet

condition until use. Here, in the phase-transition condition, the PES and zeolites of the

dope solution were both coagulated simultaneously in the water medium when the

solution was put in the water medium. The NMP solvent is well known to have solubility

in the water but not for both PES and zeolite powders. Consequently, the PES with the

imbedded zeolites was used after coagulation in the water medium. Figure 2-4 presents

scanning electron microscopy (SEM) images taken using an SEM microscope (JSM-

5310LVB; JEOL, Japan). The zeolite composite fibers were characterized using Fourier

transform infrared scanning (FT-IR, IR Prestige-21 FTIR 8400s; Shimadzu Corp., Japan)

and a scanning electron microscope (SEM, JSM-5310LVB; JEOL, Japan). The

Brunauer–Emmer–Teller (BET) surface area was measured using N_2 adsorption–
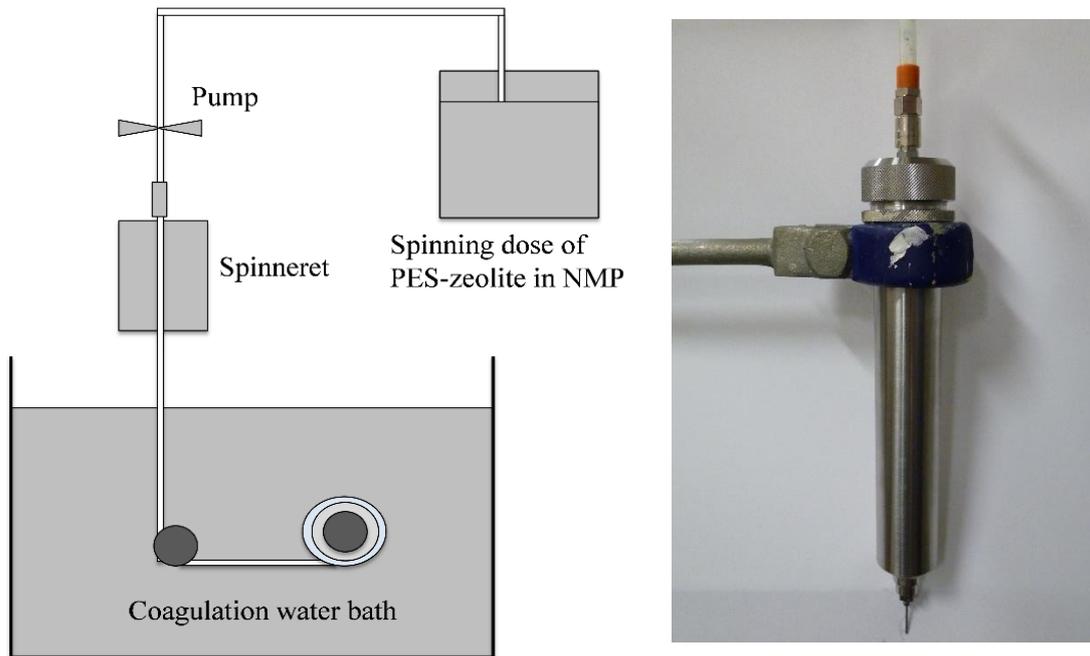
desorption (Tristar II 3020; Micrometric Inc.).

Figure 2-2 Preparation scheme and picture of the equipment for zeolite composite fibers
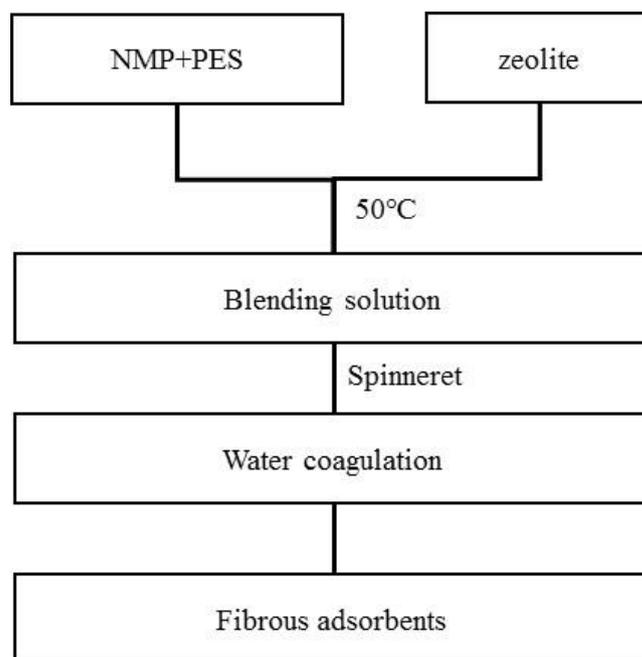
by dry–wet spinning process.

Figure 2-3 Flowchart of preparation method for zeolite composite fibers.

Batch binding experiments were conducted in aqueous solution aliquots (50 ml), each with diluted non-radiative Cs (Nacalai Tesque Inc.) with 20–500 mg/L concentration in the presence of the composite fibers (0.1 g). The original aqueous solution of non-radiative Cs solution was dispersed with the composite fibers and was shaken at 25 °C in a 50 ml glass container. The incubation time for a saturated binding process was specified as 48 h. The Cs concentration after batch binding experiments was determined using an atomic adsorption spectrophotometer (AA-6300; Shimadzu Corp., Japan). Here, the 852.11 nm emission band for the characterized Cs was detected using an emission lamp (L233-55NB; Hamamatsu Photonics K.K., Japan). The gamma radioactivity of ^{134}Cs radionuclide in the tested samples was quantified using a typical non-destructive γ-ray spectroscopic technique with an automated gamma analyzer (WallacWIZARD-1480) with a well-type NaI (Tl) detector and Ge semi-conductive detector (SEG-EMS MCA7600; Seiko easy and G company).
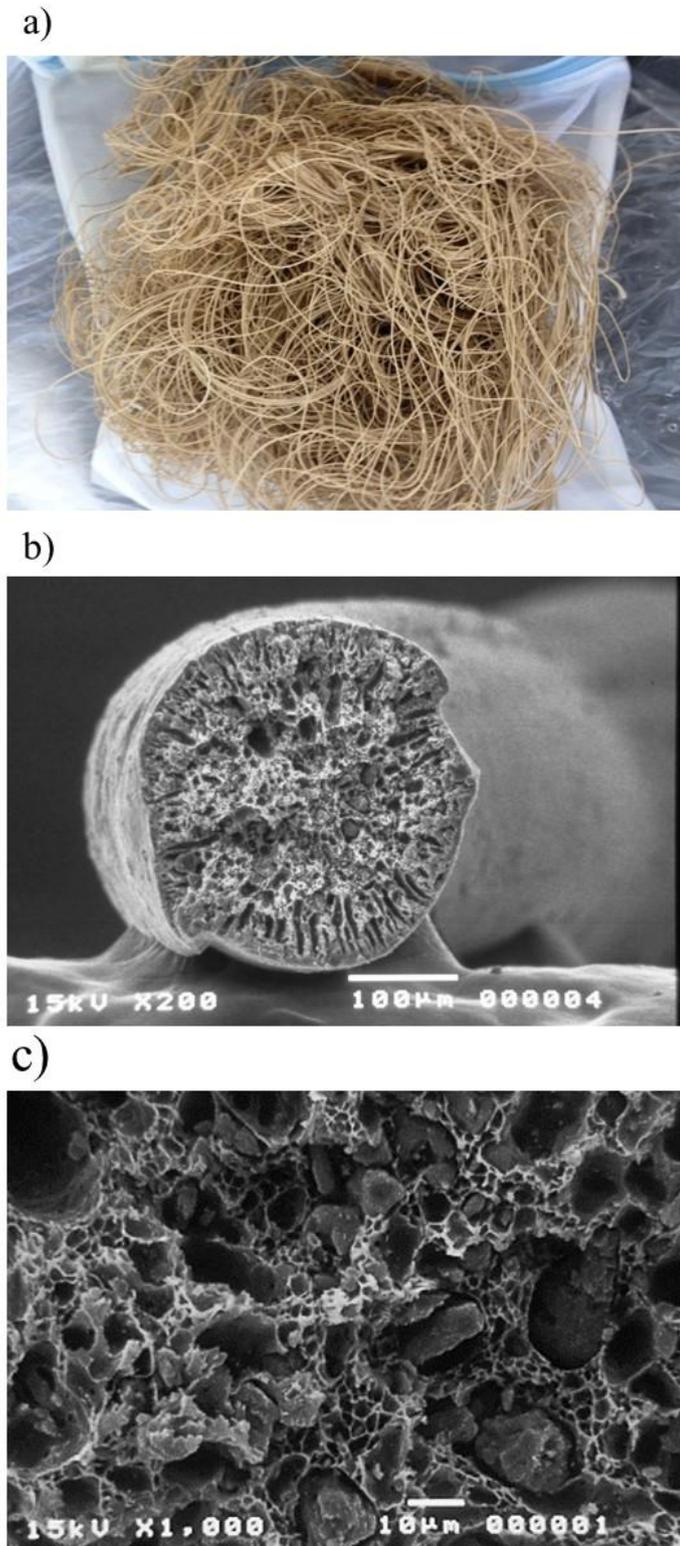
Figure 2-4 Picture (a) and scanning electron microscopy images of zeolite composite fiber in the cross section (b) and the inside (c).

2.3 Results and discussion

2.3.1 Characteristics of zeolite composite fibers as Cs adsorbents

The prepared composite fibers, which were opaque, were satisfactorily strong fibers. Figure 2-4a) shows that the resultant fibers had approximately 300 μm diameter. Their length was about 50−100 cm. The SEM images (Figure 2-4b)) of the cross-sections for the zeolite composite fibers presented a porous structure. The phase-inversion method showed that the fibers contained a sponge-like pore structure showing typical porous polymers that were prepared. Expansion of the fiber section at 1000× magnification (Figure 2-4c)) reveals that zeolite powder particles are distributed and embedded in the sponge-like polymer medium. Therefore, the water and ion can permeate into the interior fiber. On the image, the fibers show that the zeolite particles were smaller than 10 µm.

Figure 2-5 shows comparison of the FT-IR spectra of PES, zeolite and the fibers. In the spectra of PES and the composite fiber, PES had strong phenyl bands at both 1211 and 1360 cm^{-1} and $>S(O)_2$ band at 1730 cm^{-1}. The stretching band of Si-O group near 1029 cm^{-1} represented zeolite powders for the composite fiber. The asymmetric stretching bands of $>S(O)_2$ group near 1411 cm^{-1} represented the PES scaffold. Both were found in the composite fiber spectra. The Si–O band of the zeolite was shown to be shifted slightly toward 1032 cm^{-1} with a somewhat broader band. The 1411 cm^{-1} band was weakened in
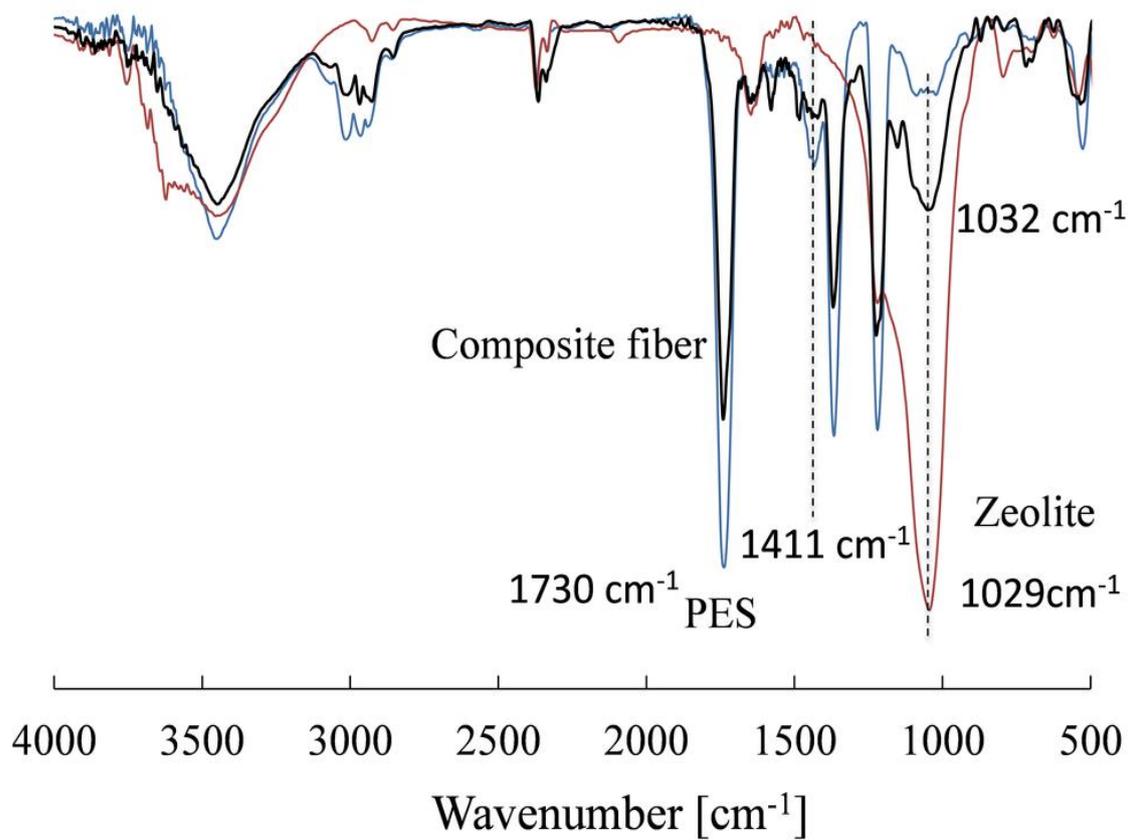
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Figure 2-5 FT-IR spectra of zeolite composite fiber, zeolite powder and PES.

the composite fibers, demonstrating that the zeolite powder interacted with the PES and

that it was held in the scaffold. This observation confirmed that the zeolite powders were

hybridized in the PES scaffold fibers. The SEM micrographs (Figures 2-4b) and 2-4c))

show that the porous structure provides greater surface area, which constitutes an

advantage for the adsorption. To evaluate the porosity, nitrogen adsorption was conducted

at 25 °C for zeolite, the zeolite composite fiber, and the PES fiber without the zeolite.

Figure 2-6 shows amounts of adsorbed N_2 in their materials at different relative N_2

pressures. As reported in the IUPAC classification [23], the adsorption isotherms can be

summarized as six types. The isotherms of six types are characteristic of adsorbents that

are microporous (type I), nonporous or macroporous (types II, III, and VI), or mesoporous

(types IV and V). Types II and IV are associated with strong fluid–solid interactions.

Types III and V are associated with weaker fluid–solid interactions. According to their

adsorption behavior, the PES fibers belonged to type II isotherms, which meant the fibers

consisted of macroporous structures. Comparison of results of the PES fibers with those

of the zeolite composited fibers shows that the zeolite powders have higher N_2 adsorption

capability than a PES fiber having no zeolite. When the relative pressure was increased,

the amounts of N_2 adsorbed to the zeolite and composited fibers increased gradually.

Consequently, both zeolite and zeolite composite fibers showed mesoporous isotherms

with types IV and V. The zeolite composite fibers exhibited somewhat lower N_2

adsorption relative to the zeolite, but it was much higher than that of the PES fibers. The

composited fiber loaded with 59 wt% of the zeolites showed greater surface area than the

PES fiber (Table 2-1). Similar adsorption profiles of both zeolite and the composite fiber

demonstrated that the greater surface area resulted from the zeolites composition in the

PES fiber. The large surface area, 27 m^2/g, is attributed to its porous morphology. Figure

2-7 shows relationship between pore size and pore volume for their samples. It is sure

that the zeolite composite fiber had higher pore volume, when the comparison was made

in the zeolite and PES fiber. As seen in the SEM picture of the composite fibers, the

composite also causes that the porous structure enables the fibers to hold 40% water inside,

exhibiting wetting properties.

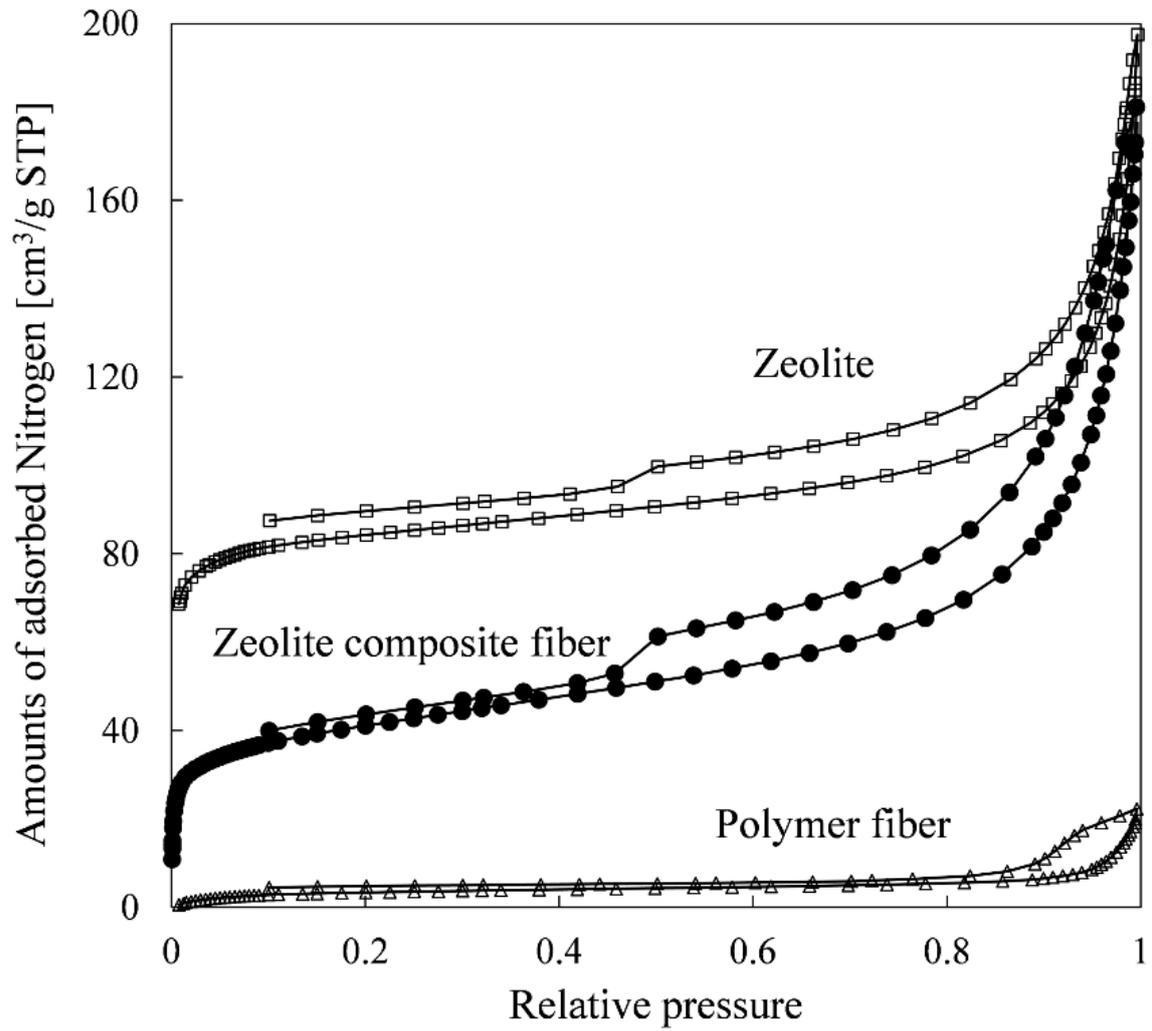Figure 2-6 Adsorption and desorption isotherms of N_2 for zeolite composite fiber, zeolite powder and PES at different relative N_2 pressures.
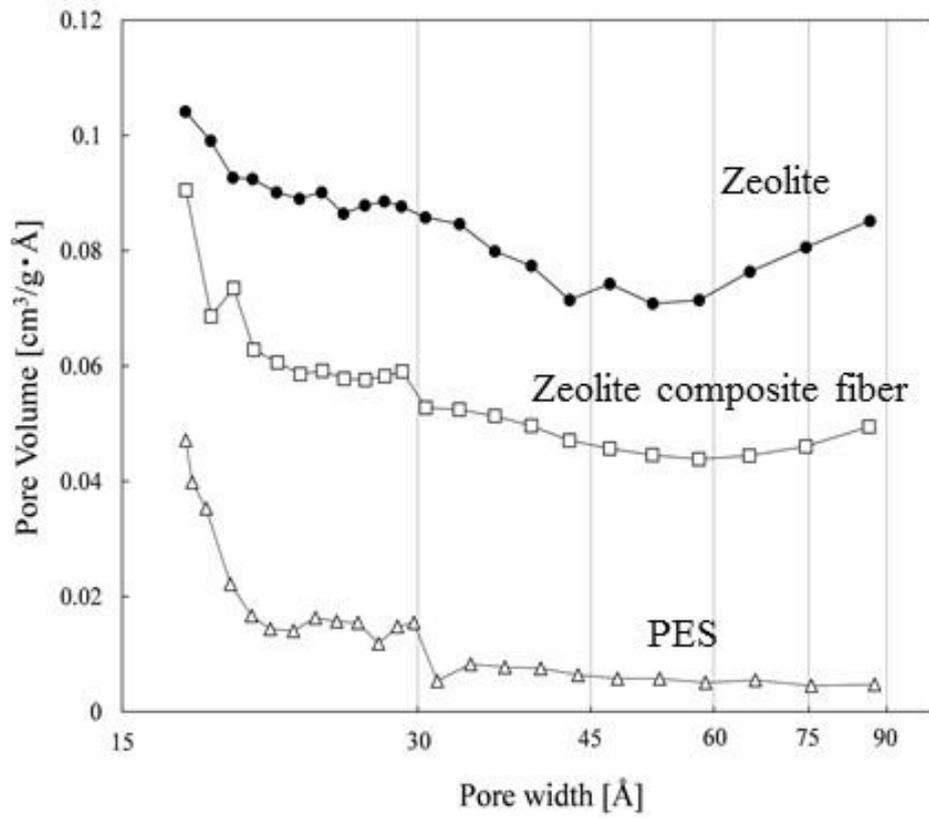
Figure 2-7 Relationship between pore size and pore volume for zeolite composite fiber,

zeolite powder and PES.

Table 2-1 Properties of zeolite composite fiber

	Diameter (mm)	Water content (%)	Density (cm^3/g)	Tensile strength (N/mm^2)	Surface area (m^2/g)	ζpotential (mV)
Zeolite composite fiber	0.55	40	1.5	7	136	-5.7
Zeolite	-	50	2.1	-	263	-8.6

2.3.2 Cs binding to zeolite composite fibers

As reported in the literature, zeolites have been used for Cs removal [17–20]. These zeolite composite fibers were used to examine Cs adsorption in batch binding experiments. The zeolite loading amount in the composite fibers was fixed as 59 wt%. Figure 2-8a) shows changes of Cs binding over time. The zeolite shows saturation of binding and capture of Cs within 3 h, to approximately 130 mg/g. The composited fiber reached saturation in 48 h. The PES fibers showed no binding to Cs. Therefore, the binding behaviors of the composited fibers are attributable to the zeolite loading. Actually, the composite fibers were able to concentrate Cs at the different concentrations. This character strongly obeyed the saturation model, suggesting that the zeolites imbedded by the PES scaffold acted as Cs absorbers. Because of the saturation behavior of Cs in both cases, the Cs binding obeyed monolayer bonding on the composite fibers and zeolite powders. For the Cs-substrate, the saturation binding amounts were confirmed respectively as 136 mg/g and 145 mg/g for the zeolite composite fibers and zeolite powders. The comparison results indicated that the composite fibers had somewhat lower saturation on the Cs binding relative to the zeolite powders. This result derived from the PES scaffold coverage by the zeolite powders. Langmuir analysis showed that, for the composite fibers, the adsorbent was mostly able to capture Cs, with maximum adsorption

capacity of 139 [mg/L] and respective Langmuir constants of 0.12 [L/mg] and 149 [mg/L]

and 0.15 [L/mg] for the zeolite powders. The zeolite powders exhibited somewhat higher

performance than that of the composite fibers.

2.3.3 Decontamination using zeolite composite fibers in Fukushima

In Fukushima, especially for people residing near concentrations of radioactive

contaminants, severe hazards have threatened human life. This threat can be mitigated by

the decontamination of radioactive Cs, thereby limiting exposure near living

environments. People residing in those areas are exposed daily to radioactive Cs.

Although decontamination work is advancing, such work has been done by transporting

earth from other places and mixing it into the soil and by washing the deposited Cs.

However, the contaminants remain in the water flowing downstream as illustrated in

Figure 2-1. Although the radioactive Cs concentration is extremely low, and less than

Japanese government criteria [24], the radioactive Cs might persist in hot-spot areas,

where the Cs is concentrated near larger populations. Therefore, the present composite

fibers were loaded into rivers and ponds in Fukushima on 2012, 2013, and 2015 to provide

artificial hot spots in natural water environments to ascertain the detectable radioactive
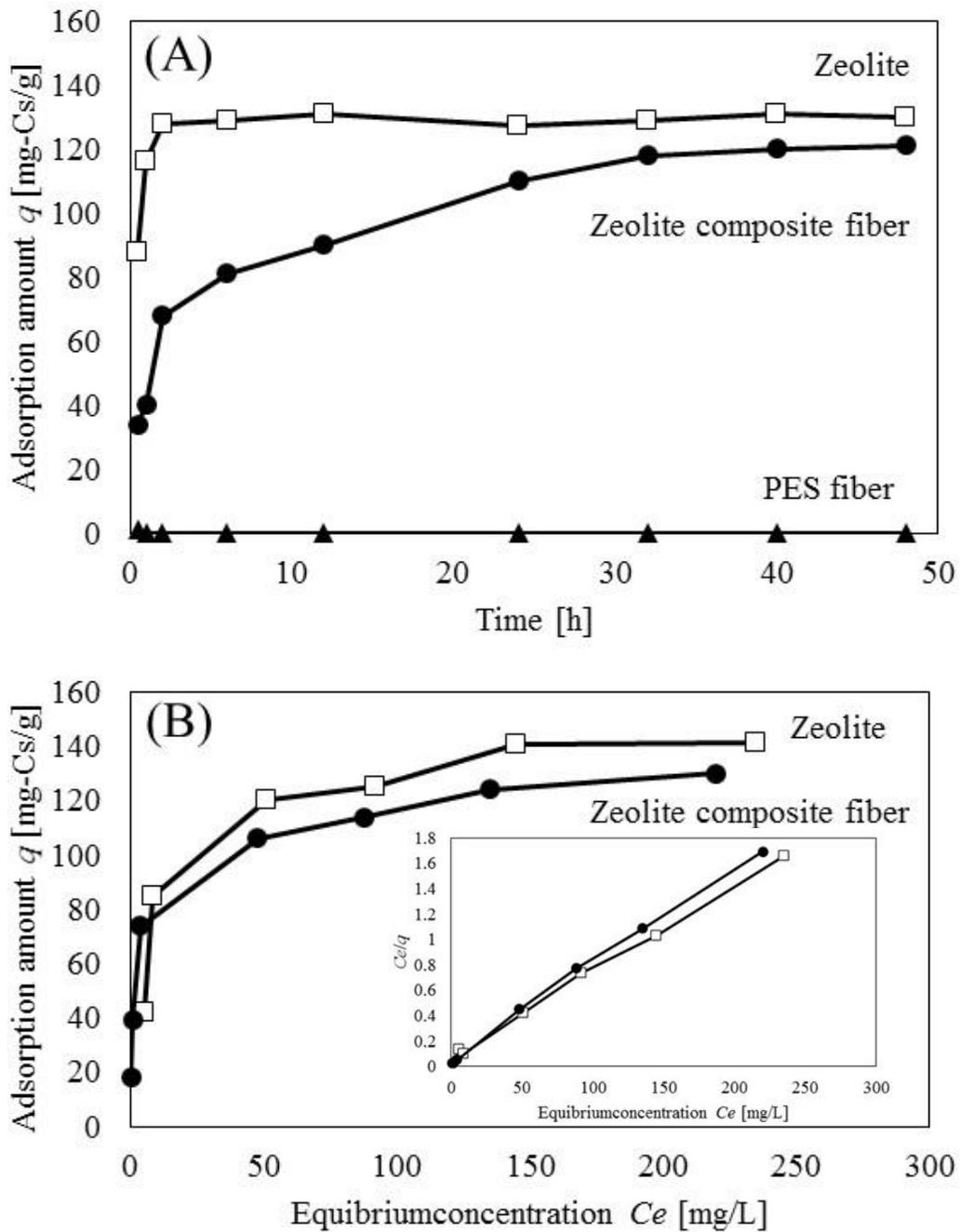
Cs for the fiber adsorbents.

Figure 2-8 Changes of Cs binding over time (A) and equilibrium isotherms (B) for zeolite composite fiber, zeolite powder and PES. The inserted figure is Langmuir plots. The (A) side experiments were carried out in 264 mg/L of Cs aqueous solution as immersed with 0.1 g of their adsorbents.

Figure 2-9 shows an area map of Date city, Oguni area at Kakinouchi, which was used

for field experiments. The map was referred from the web site of the Geospatial

Information Authority of Japan at Kakinouchi, Shimooguni, Yuzan town.

Decontamination was conducted at a water pool located upstream and in a rice field

irrigation area downstream during October–December 2012. Regarding the degree of

pollution, the water of the pond and river showed extremely low concentrations of

radioactive Cs. The Cs contamination was not detected normally at pollutant

concentrations in the water, but the concentrated water contained less than 1–2 Bq/kg of

radioactive Cs. As the pictures show, the zeolite composite fibers were immersed in the

water environment for about one month. In the pictures, the fibers were covered with a

nylon net (25 cm × 15 cm mesh size) and were set in the rice field irrigation area at Okuma

(Figure 2-8 c), with a porous stainless steel box ($45 \times 30 \times 30$ mm^3) (a) at river side. Also,

the nyron nets including the fibrous adsorbents were immersed in a water pool located

upstream (Figures 2-9 b) at Date and Kashiko march (Figure2-9d). Table 2-2 presents the

radioactive Cs detected in the zeolite composited fibers and zeolites, which was used as

a reference. Zeolite cubes of about $2 \times 2 \times 2$ mm^3 were also set similarly in the nylon net.

When the fibers were immersed in the water pool located upstream, 250 Bq/kg was

detected after 28 days. Data for the rice field irrigation area showed highly enhanced

values of the adsorbed radioactive Cs in the fibers, which reflects the capability of water

penetration into the fibers in the irrigation area because the river water, which was

contaminated with extra low concentrations of Cs, flowed through the fiber arrangement.

It is particularly interesting that until 28 days, a total of 7700 Bq/kg of the radioactive Cs

was captured in the composited fibers. To ensure the adsorption capability of the

composited fibers, the fibers and zeolites were washed with ultrasound cleaner (450 W

and 43 kHz) for 1 h and then applied for Cs detection. Both values of the composited

fibers and zeolites were decreased by washing with the sonic cleaner. For example, in 28

days, the 7700 Bq/kg and 33 Bq/kg were reduced respectively to 2,200 Bq/kg and 17

Bq/kg for the composited fibers and zeolites by washing. Consequently, the fibers might

hold non-adsorption Cs such as colloidal Cs. Actually the values of radioactive Cs in the

fibers were increased somewhat in the case of the fibers. The values were higher than that
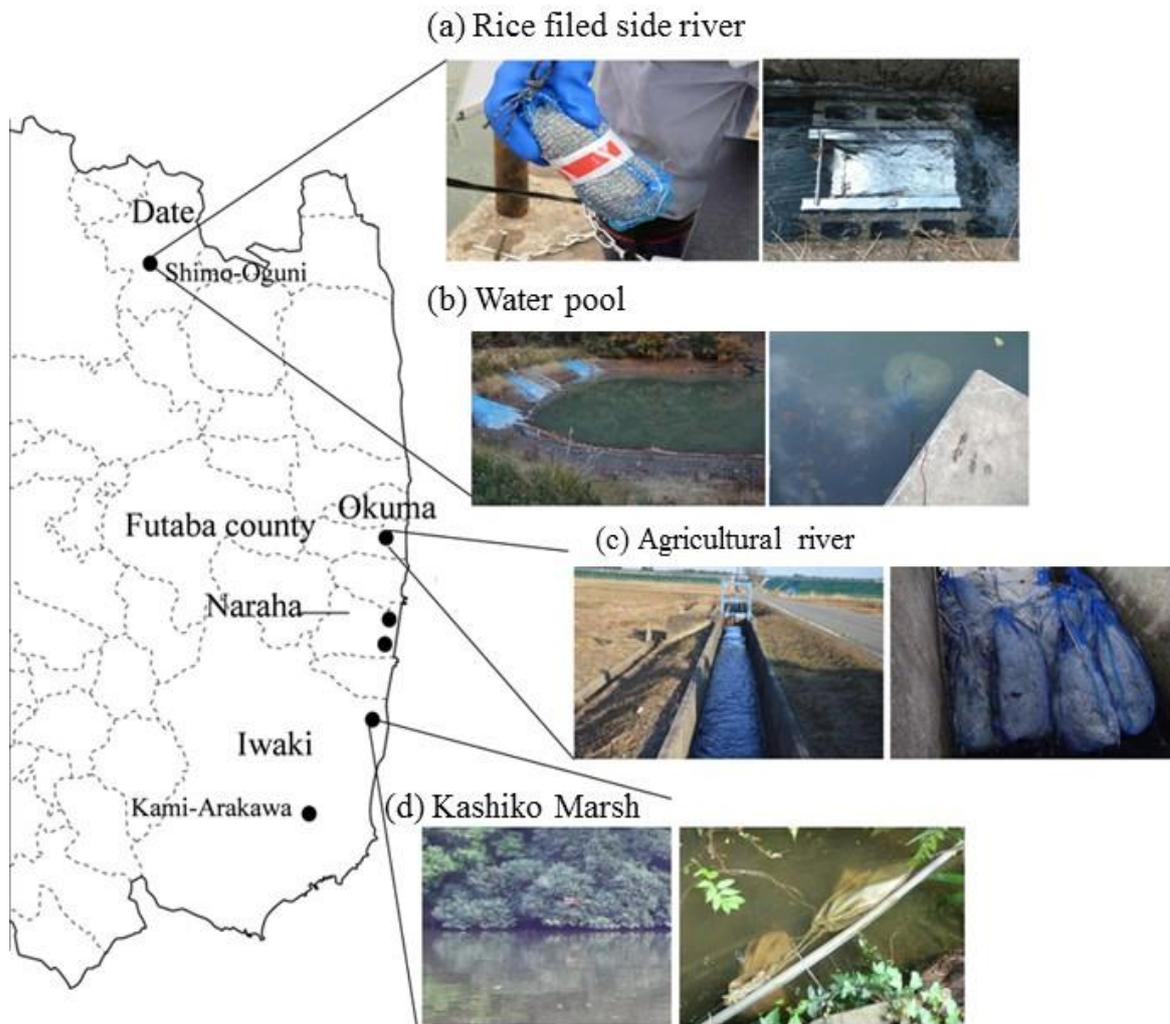
of zeolite.

Figure 2-8 Map of Fukushima area in Japan and pictures of the decontamination using zeolite composite fibers.

Table 2-2 Radioactive Cs detected in the zeolite composited fibers and zeolite

Radioactive cesium	Places		Periods in field experiments			
			7 days	14 days	21 days	28 days
^{134}Cs+^{137}Cs Bq/kg	Water pool	Composite fiber	49	33	130	250
		Zeolite	<19	<15	<18	33
	Rice field side river	Composite fiber	3,600	3,100	7,300	7,700
(After ultrasound washing) ^{134}Cs+^{137}Cs Bq/kg	Water pool	Composite fiber	19	23	35	74
		Zeolite	<13	<8	<17	17
	Rice field side river	Composite fiber	850	1,300	1,800	2,200

Figure 2-10 presents images of a radioactive Cs adsorption experiment conducted in the

Iwaki area at Kashiko Marsh on April 19, 2012 and in Futaba county, Okuma town,

Ohgawara area during January–February, 2015. Here, a 1 kg weight of zeolite composite

fibers was packed in a nylon net bag in Iwaki, with an additional 1 kg in Okuma. The

nylon net including the composite fibers was maintained inside the pond water for one

month at Iwaki and Okuma for about 3 months in the flowing river. In these works, the

pond water was polluted with radioactive Cs to less than 10 Bq/L, which was a safe

concentration level [24,25], although the Okuma area is known for its high concentrations

of radio Cs in 2014 [26]. For comparison, zeolite powders were maintained similarly in

the pond or flowing river. Their amounts of radioactive Cs of the zeolite composite fibers

and zeolite powders were examined on each treatment day. Results show that the

radioactive Cs value was detected as about 4600 Bq/kg at 80 days in the immersion.

Figure 2-10 also presents comparison of the values measured at different years in 2012

and 2015 for detectable radioactive Cs in the marsh. Here, the closed symbol is shown

for 2012 and the opened one is for 2015. It was noteworthy that, in the Iwaki data, the

value of the detectable radioactive Cs was much lower in March 2015. This fact strongly

reflected that the presence of the Cs might be decreased in the marsh. In these cases for

the marsh tests, the fibers exhibited higher detection for radioactive Cs relative to that of

zeolite. The figure 2-10 (B) presents results obtained in Okuma in 2015, where is close

to the Nuclear Power Plant within 7.5 km distance. The pictures show that the net block

is dammed up by a zeolite composite fiber arrangement in the flow. The experiments were

conducted for 42 days. The fibers detected markedly high radioactive Cs to reach to about

2,300 Bq/kg for 42 days. Although each dose was increased day by day in the fiber, the

zeolite block was mostly lost after 32 days in the immersion by some natural accident.

The amount of the radioactive Cs for the zeolite was 1,700 Bq/kg at 32 days. After 42

days, the zeolite block was lost by the river flowing, meaning that the comparison

between the fiber and the zeolite cube could not be halted, but the fiber experiment was

maintained until November 2015 for 334 days. The detectable radioactive Cs reached

6,800 Bq/kg during the 334 days of immersion. The comparison was also made between

the Okuma area and Iwaki one in the figure. Apparently, the Iwaki data described lower

radiation level. Here, the Iwaki portion is located with 59.5 km distance from the Nuclear

Power Plant. Figure 2-11 shows the values recorded at a particular date at different areas.

A comparison was made at Futaba county in Naraha town on May–August 2015 for the

Kamishigeoka area (north) and Shimouchi area (south) and Iwaki city at Kami-arakawa

during March–May 2015 and for Niigata at Niitsu area during July–August 2015. The

Niigata area, where located distance was 174 km from the distance, showed extremely

low-level detection with 50 Bq/kg for 33 days. Then the Iwaki area in Kami-arakawa

showed 360 Bq/kg for 33 days. At Kashiko Marsh in Iwaki city, the value was 613 Bq/kg

for 38 days. In that city at the Kami-arakawa and Kashiko marsh, different values of

detectable Cs were found. Similar tendencies were found in Naraha town (13.4 km

distance from the nuclear power plant) in the north and south areas with 500 Bq/kg and

1,500 Bq/kg respectively found in 88 days. Actually, the highest value of the Okuma area

was 6,800 Bq/kg for 334 days in the present comparison.

Consequently, results suggest strongly that the increased dose contributed to hot-

spots on the composite fibers, although an extremely low dose was found in each body of

water. Decontamination condenses the low-dose radioactive material where the

composite fiber is merely zeolite composite fibers immersed in the water of a river. The

method's simple operation is beneficial, merely requiring the installation of the zeolite

composite fiber in a living environment. The importance of cutting off the transfer of Cs

through water is evident. This method enables passive decontamination. The surrounding

composite fibers are expected to reduce exposure risk with no driving force or energy
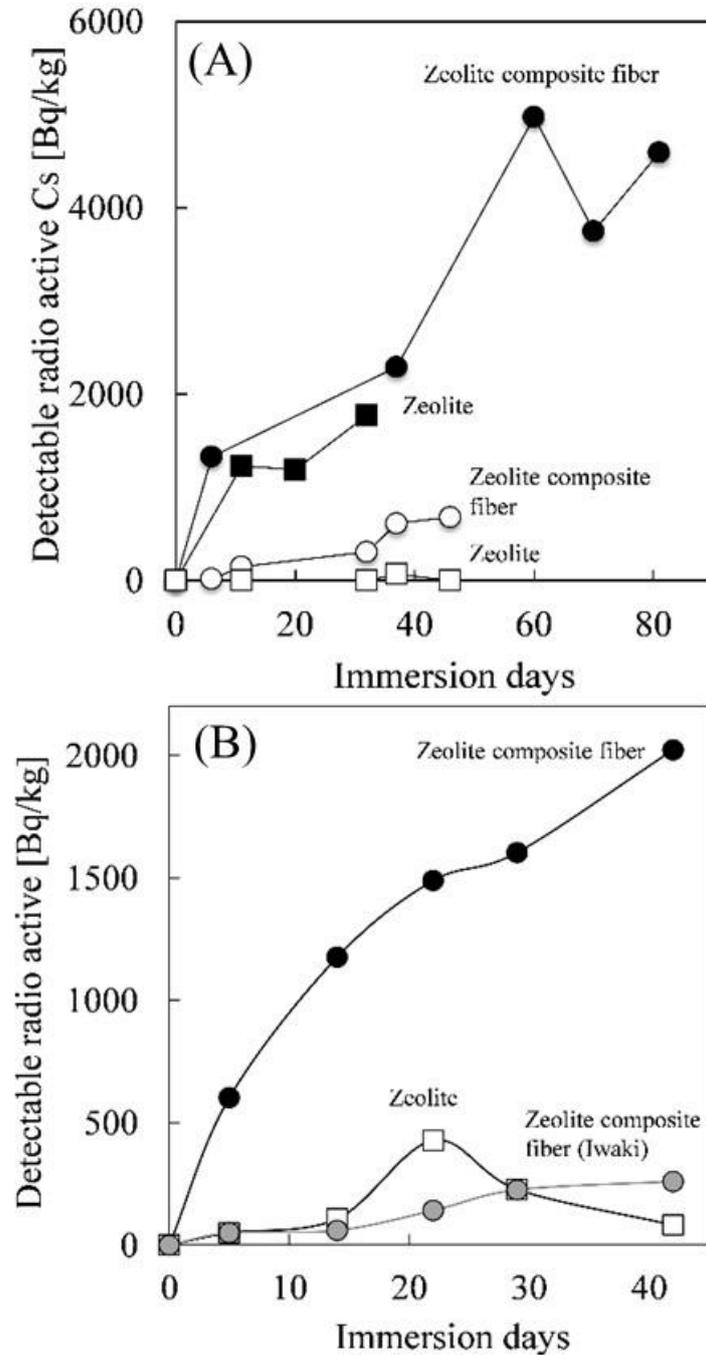
used for decontamination.

Figure 2-10 Observation of radioactive Cs adsorption experiments conducted in the Iwaki area at Kashiko Marsh on April 19, 2012 (A) and in Futaba county, Okuma town, Ohgawara area during January–February, 2015 (B). The (B) contains results of the Iwaki area for the comparison.
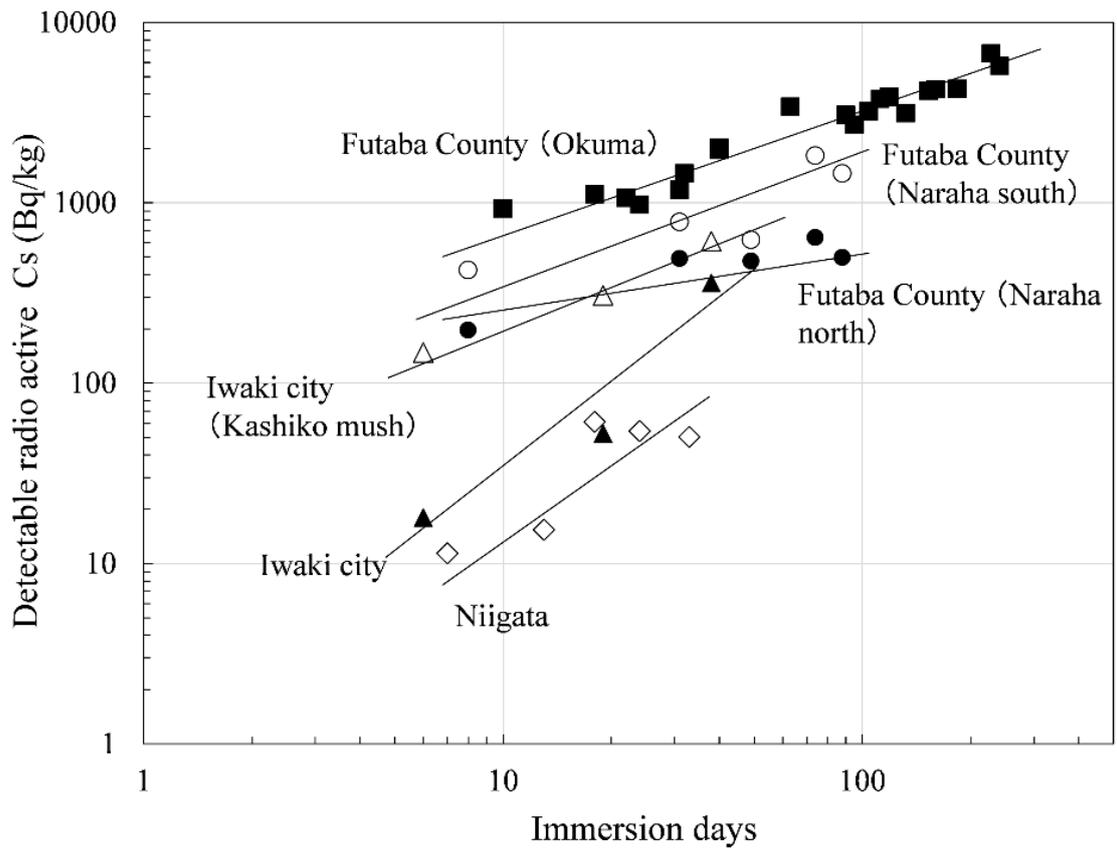
Figure 2-11 Comparison of detectable radioactive Cs in the zeolite composite fiber at different immersion days.

2.4 Conclusion

The preparation and properties were described for this fibrous zeolite–polymer material. Furthermore, the importance for decontamination of radioactive Cs is that this is a passive process, especially for field results in Fukushima, for pollution originating from the Fukushima Daiichi nuclear power plant accident. These methods were applied to remove radioactive Cs effectively from the water environment. To diminish the radioactive Cs risk in surrounding areas, such decontamination material is expected to be used to realize a safe society. Composite fiber applications can protect people from exposure risk without the need for any driving force for decontamination. Figure 2-9 shows the possibility of using prepared fibers to cut flows of contaminants downstream in flowing water. The composite fiber layer allows water to flow through the fibers, which is not possible with zeolite powders. Therefore, low-level Cs is concentrated in the decontaminant layer, preventing its flow further downstream and preventing the diffusion of radioactive Cs through water migration in natural environments.

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6 9

Chapter 3 Decontamination of radioactive waste water extracted from radio-Cs fly ash by using fibrous zeolite-polymer with different zeolite loading

Abstract

Fly ash polluted in Fukushima was treated by washing water and then the radioactive waste water was decontaminated with zeolite polymer composite fiber. The character was compared in zeolite, Prussian blue and the composite fiber. The strong alkali condition of the radioactive waste water damaged in PB, while zeolite and the composite fiber successfully treated the radio-Cs by sorption process of batch and column experiments. The ability of the composite fiber was superior performance in the time course of the sorption process. The radioactive Cs binding to the composite fiber and zeolite was followed in Freundlich mechanism, showing multibanding to their adsorbents in the extra-diluted condition, but, each adsorbent obeyed saturated mechanism for non-radioactive Cs.

3.1 Introduction

A large quantity of radioactive material radiated in Fukushima environment by an accident of the Fukushima first Nuclear Power Plant started from East Japan great earthquake disaster of March 11, 2011 [1-4]. The decontamination work to radiocesium (Cs) has been pushed forward and implemented for removal of radioactive materials zealously at the present after particularly times have passed for six years [5-7]. A method of decontaminating includes there in various ways, but, as a radioactive Cs adsorption material, zeolite attracts attention to be really used. However, problems of the zeolite are pointed out in the real decontamination that is necessarily to recovery the waste zeolite after the decontamination [8-13]. Therefore, there are various kinds of improvement and demands of the advancement utilization. Among them, for the efficient removal of radioactive Cs from low-level radioactive liquid wastes, natural zeolites, because of their low cost and selectivity, are important alumino-silicates used in sorption processes [14, 15]. However, it is noteworthy that powder zeolites cannot be used continuously for long-term removal because of the difficulty of powder recovery and the apparent limitations of the adsorption capacity at the powder surface [16]. Therefore, efforts have been

undertaken to develop new materials that are suitable for use as radioactive Cs adsorbents.

On the other hands, consumption of fossil fuels in power plants for energy production is increasing in Fukushima, leaving fly ash waste for radioactive landfills with low lever contaminants [17,18]. The action to utilize destruction by fly ash having radioactive contamination effectively becomes the situations such as interruption and the review for recycling to become raw materials of cement and the metal refinement. By the policy of the Japanese country [18], all Cs contaminant levels decide for the thing more than 8000Bq/kg to process undergrounding in the last disposal place established as designated waste in the national land. It is a policy of Ministry of the Environment for less than 8000 Bq/kg that such fly ash has been in the management type disposal ground that after appropriate measures giving leaking. A gross quantity actually has kept in large quantities by processing facilities without being handled (Figure 3-1). As seen in the picture, the huge amounts of radioactive fly ash have been stored in plastic flexible container packs. But the waste destruction by fired fly ash with more than 8,000 Bq/kg in radioactivity concentration was designated as radioactive fly ash waste on of December 31, 2013 approximately 97,000t (Ministry of the Environment) [19]. However, the present

conditions are kept without being handled in 8,000Bq/kg or less. A technique to separate

radioactive Cs from fly ash, where the Cs attached, includes a washing method. The

washing method shows the solution that Cs is highly extracted from radioactive fly ash.

Here, the procedure of removal of the radioactive Cs from such fly ash in the water

washing of radioactive fly ash in National Institute for Environmental Studies (NIES) for

the recovery of radioactive Cs with zeolite adsorbent [20]. Aqueous wastes that contain

long-lived radionuclides require treatment using chemical precipitation, evaporation,

filtration, and solvent extraction. Such decontamination process has been recommended

by the International Atomic Energy Agency [7]. A designated disposal system is necessary

for such wastes. In addition to zeolite, it has been known that extensive research has been

conducted related to the adsorption of Cs on various materials with Prussian blue (PB)

[21-24]. Therefore, the present work paid attention to a characteristic of the zeolite and

developed the fibrous adsorbent, which was made by composite of zeolite polymer [16],

for the character comparison in the waste water treated with radioactive fly ash. This

chapter introduced the decontamination behavior of strong alkali waste water

contaminating radioactive Cs. The decontamination function to such fly ash waste water

contaminating radioactive Cs was described by using different loading amounts of zeolite in zeolite polymer composite fibers.

3.2 Materials and Methods

3.2.1 Materials

All chemicals and reagents used for this study were of analytical grade purity. They were used without further purification. Natural mordenite zeolite was acquired from Japan Nitto Funka Trading Co. Ltd. (Miyagi, Japan). Poly(ethersulfone) (PES) was used as received (PES, MW = 50 000; BASF Japan Ltd., Ludwigshafen, Germany). Also, *N* methyl- 2-pyrrolidone (NMP; Nacalai Tesque Inc., Kyoto, Japan) was used without purification. Preparation of zeolite composite fibers was conducted using a modified wet spinning process [16, 17]. The zeolite polymer composite fiber composed 30wt% of zeolite in porous polymer fibers. Therefore, when the decontamination process of the polluted washing water was carried out, the amounts of zeolite was 6 g relative to the 2g of the composite fibers. PB was product of Kanto Kagaku (Japan). Scanning electron microscope (SEM) of the composite fiber was measured with Hitachi TM3030Plus

Tabletop SEM, which was equipped with highly sensitive low-vacuum secondary electron detector with reflective electron images. The secondary electron images were determined for C, S, O, Si and Al components in the cross section and fiber surface.

3.2.2 Methods

Batch binding experiments were conducted in aqueous solution aliquots (50 mL), each with diluted non-radiative Cs (Nacalai Tesque Inc.) with 20−500 mg/L concentration in the presence of the composite fibers (0.1 g). The original aqueous solution of non-radiative Cs solution was dispersed with the composite fibers and was shaken at 25 ° C in a 50 mL glass container. The incubation time for a saturated binding process was specified as 48 h. The Cs concentration after batch binding experiments was determined using an atomic adsorption spectrophotometer (AA-6300; Shimadzu Corp., Japan). Here, the 852.11 nm emission band for the characterized Cs was detected using an emission lamp (L233− 55NB; Hamamatsu Photonics K.K., Japan). The gamma radioactivity of 134 Cs radionuclide in the tested samples was quantified using a typical nondestructive γ-ray spectroscopic technique with an automated gamma analyzer (WallacWIZARD-1480)

with a well type NaI (Tl) detector and Ge semi-conductive detector (Segemsmca7600;

Seiko easy and G company). The circulation of the radioactive waste water was taken

place with Iwaki metering pump (model EHN-B31VC4R, Iwaki co. Ltd, Japan). To

investigate Cs adsorption selectivity in alkali metal ions, 0.05 g of composite fiber was

added to 50 ml of a mixed solution of lithium, potassium, sodium and Cs at 20 ppm and

shaken at 100 rpm for 48 hours. In addition, 110 ml of alkali metal ion 20 ppm solution

was passed through a sample (Figure 3-1) in which composite fiber was processed into a

membrane shape at a water flow rate of 1.35 ml / min. The value of binding amount of

alkali metal ions was determined by Atomic Adsorption Spectrophotometer (AA-6300;

Shimadzu Corp., Japan). Here, the 852.11nm, 766.49nm, 589nm and 670.78nm emission

band for the for the characterized Cs, K, Na, and Li was detected using an emission lamp

(Cs: L233-55NB, K-Na: L733-201NB, Li: L233-3NB; Hamamatsu Photonics K.K.,

Japan).

3.3 Results and discussion

3.3.1 Radioactive Cs fly ash in Fukushima

As followed with the Tohoku earthquake and tsunami of March 11, 2011, the explosions at the Fukushima Daiichi Nuclear Power Plant on March 15 released massive quantities of radionuclides into the atmosphere. It was reported that the total amount of ^{137}Cs released into the atmosphere was estimated to be approximately 8.6×10^{15} Bq [25]. After 6 years have passed, still the contamination is seriously influenced to people life in Fukushima area. The radioactive leveled fly ash has been stored now without treatments in the anywhere fields in Fukushima near people living house (Figure 3-1). Especially the treatments of radioactive fly ash are problems even though the radioactive amounts are less than 8,000 Bq/kg, which NIES in Japanese government set up guide line for the fly ash contaminated by radioactive Cs [20], because the majority of radioactivity fell on fly ash after burning. However, very little was reported in the decontamination of radioactive waste water used for the radioactive extraction in the fly ash. In the guide line, it has been recommended that the radioactive fly ash should be washed with water [20] to remove the radioactive Cs from the ash and used zeolite. However, little is known about the

reports for the radioactive waste water used for the water washing of the fly ash.

In the present work, fly ash was sampled in Kohriyama city on April 10, 2014 and the radioactive Cs measured was 6843 Bq/kg and comparison was made for decontamination of the radioactive waste water by using each PB, zeolite and zeolite polymer composite fiber. Here, the washing process with water was carried out as followed extraction process. The fly ash (200g) was suspended in 2 L water according to the guide line for 6 hours. Then, the suspension water polluted with radioactive Cs was filtrated with paper filter and then was decontaminated with adsorbents. The pH was at 13 after washing and then 500 mL was used to soak with 2g of each adsorbent, PB, zeolite and fibrous zeolite polymer composite. The radioactive waste water polluted with radioactive ^{137}Cs was used for following decontamination processes in batch treatment and also column one in following sections. Here, the composite fiber composed of PES and zeolite was prepared by wet spinning process [16, 17]. The fiber diameter was 3 mm and about 1,000 mm length in each fiber.

Figure 3-1 Pictures of fly ash and storage state of radioactive Cs in flexible containers at

Fukushima.

Figures 3-2 show pictures of both reflective electron images and secondary electron images for the composite fiber containing carbon (e) and sulfur (c) for the polymer section and Si, Al and oxygen (g) for zeolite. The pictures of (a) and (h) are reflective electron images of the cross section and surface of the composite fibers and the color images of (b)-(g) are secondary electron images. The latter images suggested that the cross section contained their color components mainly for yellow and pink of C and S, respectively. The Si and Al components (orange colors) were resulted from the loading 30 wt% zeolite powders. On the side surface portion of the fiber, it was also apparent that the zeolite section was found. In our previous report [16] for practical field experiments in Fukushima, the characteristics of zeolite composite fibers was seen as Cs adsorbents. The prepared composite fibers were opaque and were satisfactorily strong fibers composing of microporous structures.
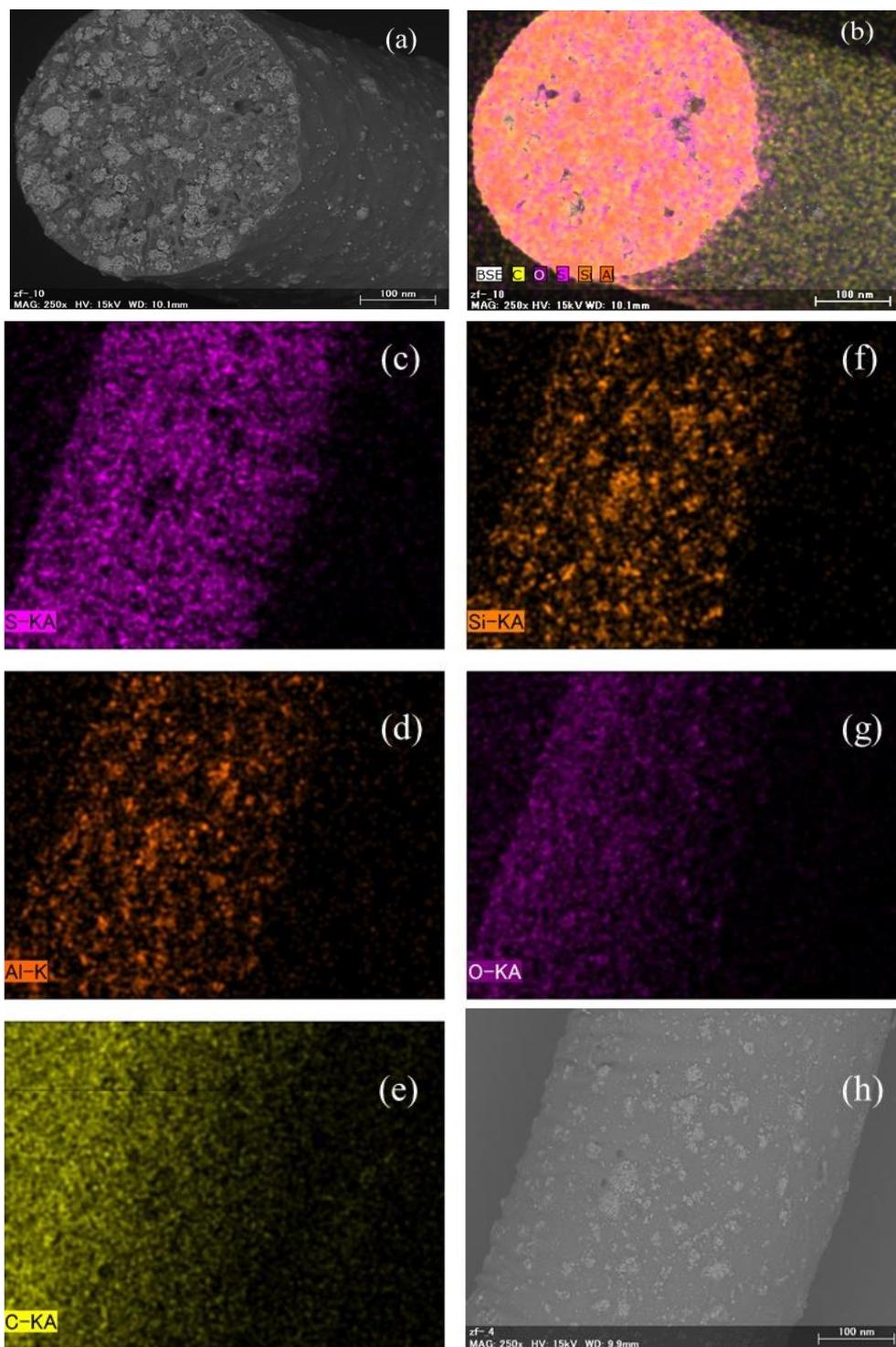
Figure 3-2 Reflective electron images and secondary electron images of composite fiber having 30% loading with zeolite.

3.3.2 Removal of the radioactive cesium from radio cesium contaminated washing water for radio fly ash

Figure 3-3 shows pictures of the radioactive waste water and PB powders which were used for the decontamination process of the waste water. The color of the radioactive waste water was transparent with pH 13 and the radioactive Cs level was in the range of 2,500-3,000Bq/kg for the radioactive waste water. After the extraction and the contaminated amounts of ^{137}Cs for 120 min, the waste water was changed to yellowish color in the case of PB treatment. As seen in the picture for the PB, the dark black blue powders were changed to be brown color in the waste water, meaning that the PB powders were dissoluble into the aqueous layer during the process and the iron ligand changed to oxidized species having brown color. It was noted that this color leakage to the waste water began, when the decontamination process was started, although the natural water at neutral pH had no such color change for the PB. The comparison indicated that PB was unfavorable to use for the decontamination to the strong alkali solution. On the other hand, there was no color change like such PB experiment in zeolite and the composite fibers after 720 min treatment in the alkali waste water was not changed in the observation of

the cross section and the surface of the composite fiber in SEM view. Figure 3-4 shows

time change of the radioactive Cs (Bq/kg) at different decontamination times for PB,

zeolite and the composite fiber. As well seen in the PB system, the reduction of the

radioactive Cs was reached to 2,000 Bq/kg after 720 min passed, while the zeolite powder

system was to 500 Bq/kg. Contrary, the value of the composite fiber system was reached

to 500 Bq/kg when the time was 120 min and then gradually decreased to 260 Bq/kg at

720 min, meaning that most of the radioactive Cs was adsorbed to the composite fibers

within 120 min. At 720 min, about 90% of the Cs was decontaminated by the composite

fibers. Relative to the composite fibers, the value of the PB was 34% in the reduction to

the initial Cs concentration and remained brown color solution. This noted that batch

experiment as the composite fiber was used effectively decontaminated the radioactive

Cs in the strong alkali waste water.

Figure 3-3 Pictures of the radioactive waste water and PB powders (a) before adsorption test, (b) after adsorption test.

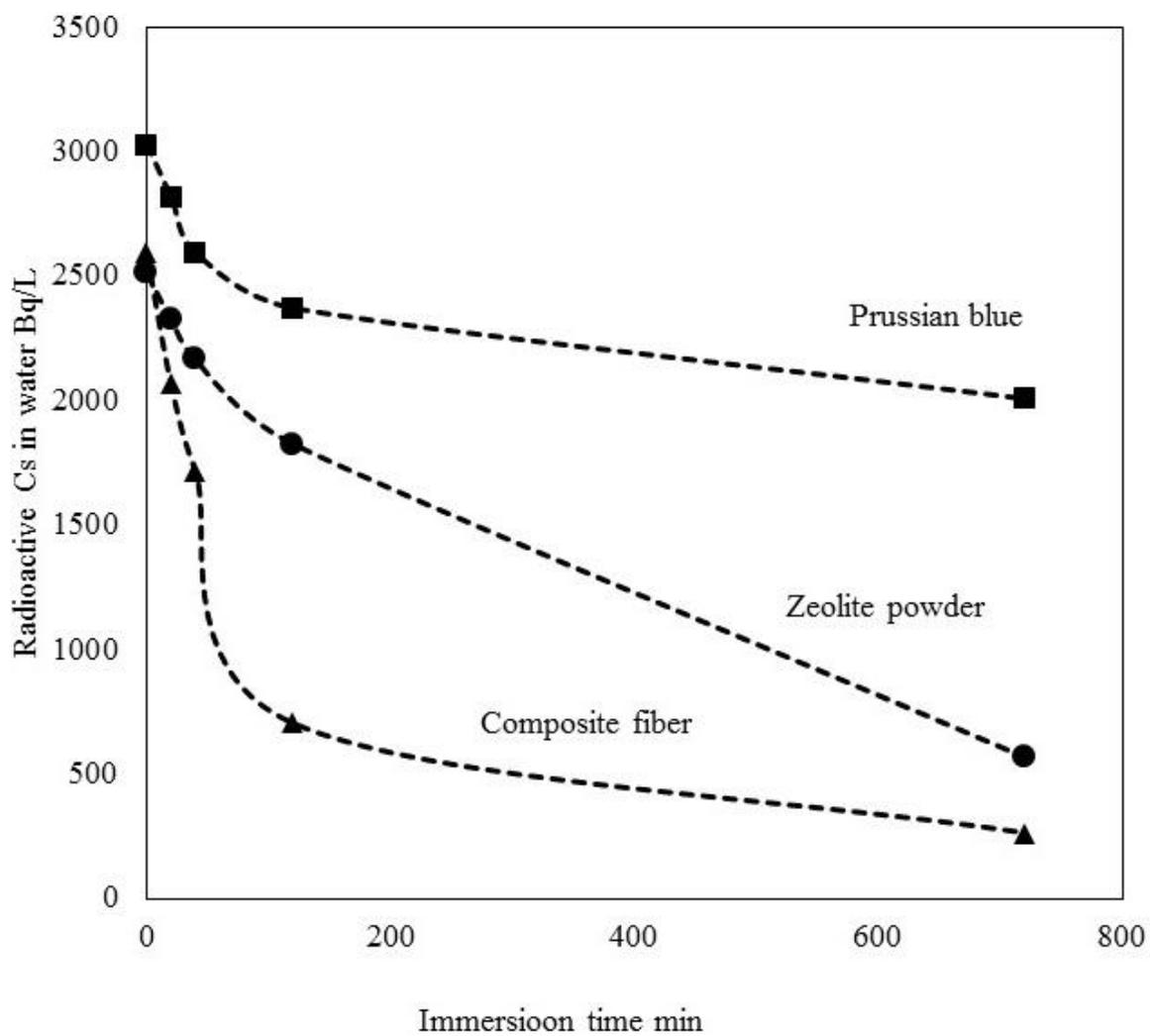Figure 3-4 The radioactive Cs concentration change different time for PB, zeolite and composite fiber.

8 5

For the adsorption isotherm, comparison was made in both of zeolite and the composite fiber in the alkali waste water. Here, radioactive Cs fly ash, which was sampled in Naraha town on October 8, 2015 and the radioactive Cs concentration was 3,141 Bq/kg. The extraction of the Cs to the water phase was carried out as mentioned above and the prepared Cs concentration and pH for the radioactive waste water was 823 Bq/L and 12.5, respectively. Different amounts of both adsorbents of zeolite and the composite fiber were used, as the amounts of Zeolite powders or the composite fibers were changed in 0.05g, and 10 g for the alkali waste water. In their conditions, the ratio of the amount of adsorbent to the constant radioactive Cs, 823 Bq/L, was varied in 200 ml at 30 °C. The saturation adsorption was confirmed at 24 h by starring at 80 rpm in the solution and then the resident amounts of radioactive Cs was measured to evaluate the adsorbed amount to the fiber and zeolite. These isotherm results for the zeolite powder and the composite fiber are presented in Figure 3-5. To elucidate the mechanisms of adsorption and adsorption capacity, adsorption isotherm data were subjected to two sorption isotherms of Langmuir and Freundlich. As seen in (a), the relationship between the adsorbed amounts vs. equilibrium concentration in the range of 50-600 Bq/L showed non-linear in the

composite fiber, while the zeolite was linearly in the relation. So the relation was not

obeyed in Langmuir. Figure 3-5 (b) shows Freundlich plots for both cases. The Freundlich

equation is an experimental model equation based on a heterogeneous and multilayer

adsorption system. Its empirical equation can be used to describe non-ideal adsorption on

heterogeneous surfaces and multilayer adsorption, as $q_e = K_F C_e^{(1/n)}$, where q_e stands for

the equilibrium adsorption amount [Bq/L], K_F and n, respectively, denote Freundlich

constant [–], and C_e signifies equilibrium concentration [Bq/L]. Therein, the Freundlich

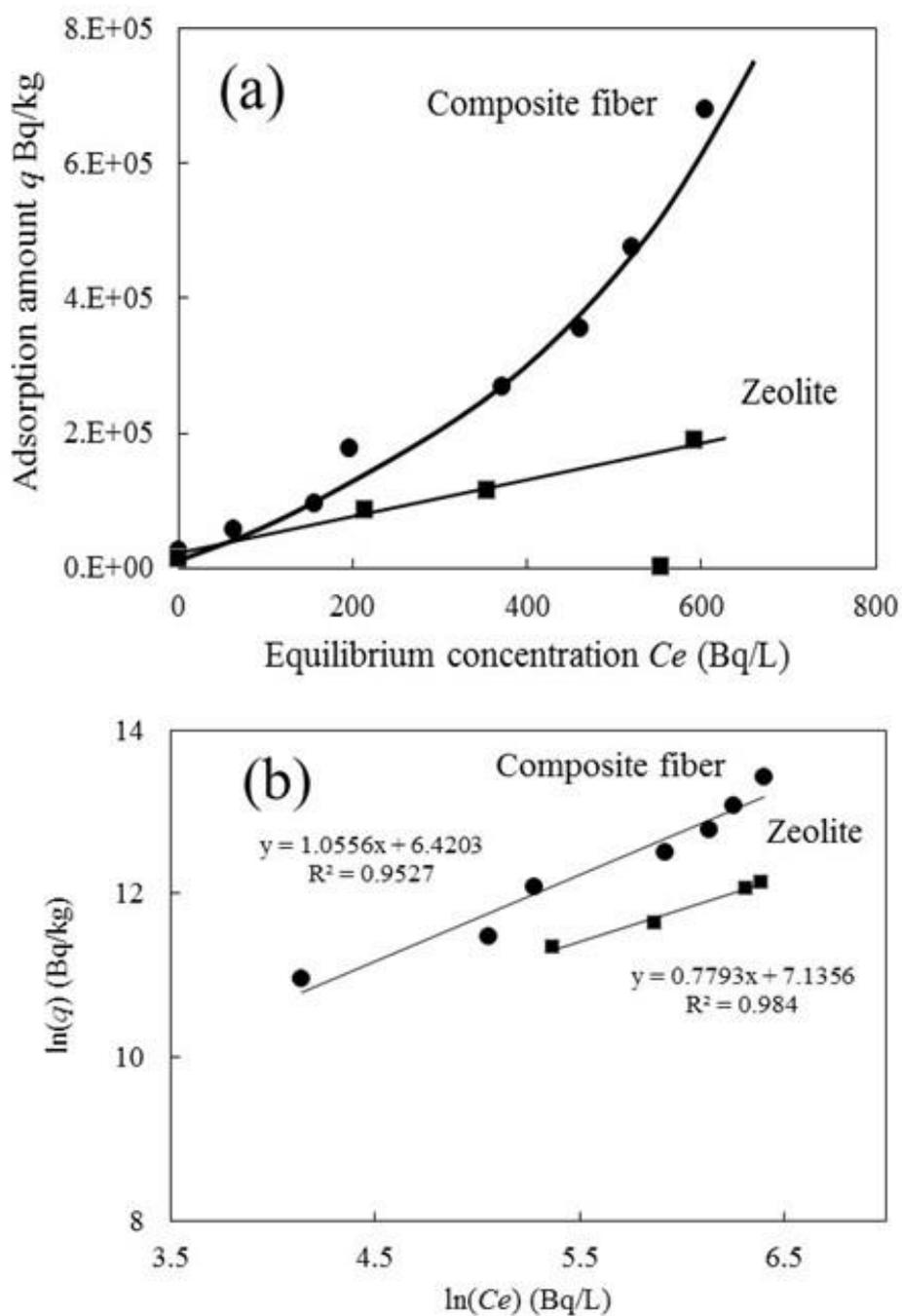constant KF is obtainable by plotting ln (q_e) against ln(C_e) (Figure 3-5 (b)).

Figure 3-5 (a) Adsorption isotherm, (b) Freundlich plot of radioactive Cs for composite

fiber and zeolite.

Actually, the equilibrium isotherm curves could be compared with non-radioactive Cs in the equilibrium concentration for mmol/L range (Figure 3-6) for the both adsorbents. The curve well obeyed Langmuir relationship, meaning saturation binding of non-radioactive Cs. Because of the saturation behavior of Cs in both cases, the Cs binding obeyed monolayer binding on the composite fibers and zeolite powders. For the Cs-substrate, the saturation binding amounts were confirmed respectively as 97 mg/g and 145 mg/g for the zeolite composite fiber and zeolite powder as seen in Figure 3-6. The comparison results indicated that the composite fibers had somewhat lower saturation on the Cs binding relative to the zeolite powders. This result derived from the PES scaffold coverage by the zeolite powders. Langmuir analysis showed that, for the composite fibers, the adsorbent was mostly able to capture Cs, with maximum adsorption capacity of 139 [mg/g] and respective Langmuir constants of 0.12 L/mg, 149 mg/g, and 0.15 L/mg for the zeolite powders. The zeolite powders exhibited somewhat higher performance than that of the composite fibers.
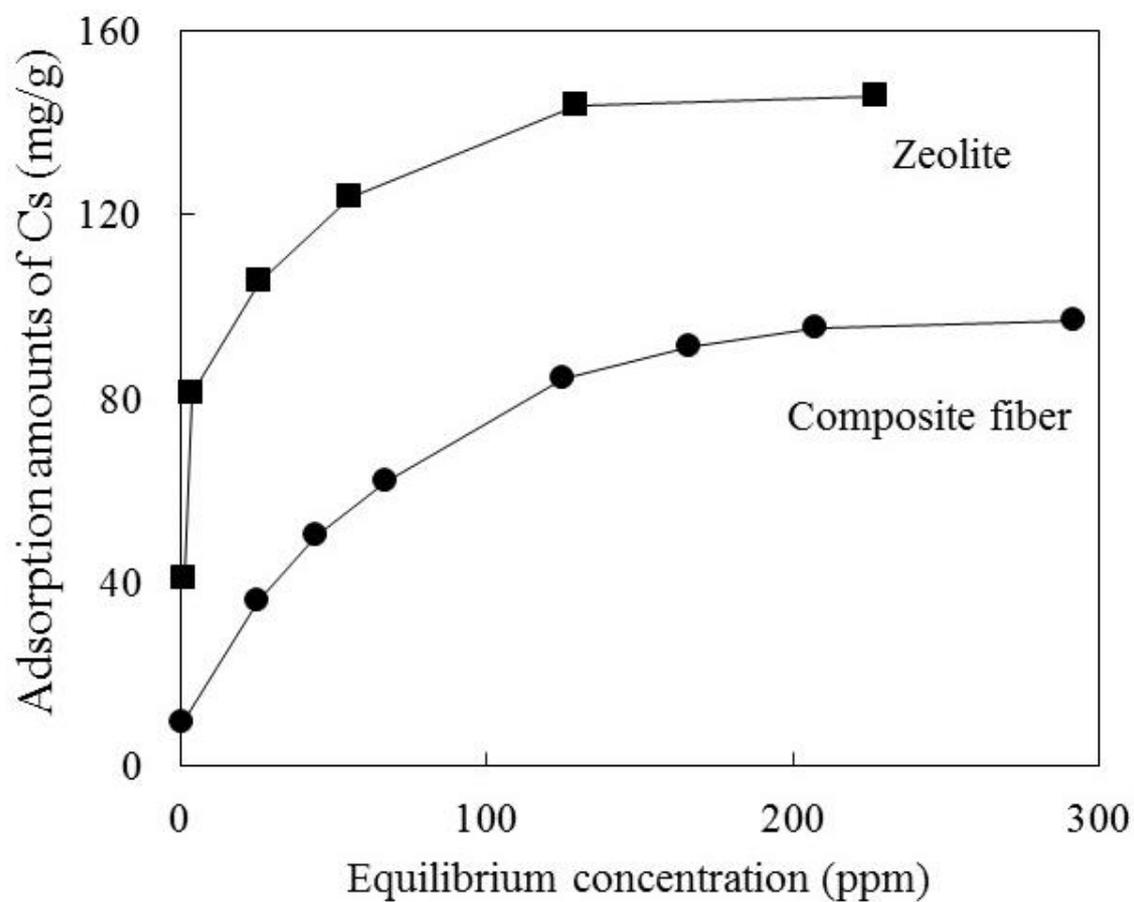
Figure 3-6 Adsorption isotherm of non-radioactive Cs for composite fiber and zeolite.

3.3.3 Circulation decontamination process using column binding to contaminated radio aqueous solution

 Decontamination of radioactive Cs for fly ash aqueous solution containing radioactive Cs with 823 Bq/L concentration and pH 12.5 was conducted. Figure 3-7involves the circulation scheme for the experiment. The composite fibers were filled in a 40cm length column with a 4 cm inner diameter with different loading % of 10, 38 and 78% for 10 g, 50 g and 135 g in the column volume, respectively. For the composite fibers-column, then the radioactive waste water with 823 Bq/L was passed to flowing by the circulation pump at 200 ml/min. Figure 3-7 shows radioactive Cs concentration measured at several circulated time for the waste water in the water bath container with 10L volume. After circulation started, the value was decreased with the circulate time within 120 min and then gradually decreased to be 40 Bq/L at 480 min for the case of the 78% loading. This meant that the radioactive Cs was adsorbed to the composite fibers during the circulation of the radioactive waste water. When the comparison was made at different amounts of composite fibers, significant decrease of the radioactivity in the water bath was observed, meaning that lower loading of the composite fibers easily reached to the saturated

condition of the zeolite components in the column, while the higher loading column could almost 95 % decontamination by the column treatment at 480 min. In Figure 3-8, similar circulation experiments were carried out at different circulation speeds of the radioactive Cs waste water. Here, the radioactive fly ash was obtained in Iwaki city on 2012, May 2nd. The concentration of radio Cs was 6,560Bq/kg and the resultant radio waste water contained 488 Bq/L. For the decontamination of the Cs by the composite fiber, the loading amounts was 78% in the column. Water flow was changing with 242 mL/min and 121 ml/min for the column permeation. Both flow experiments show reduction of the radioactive Cs in the water bath container, meaning that the composite fiber successfully adsorbed the radioactive Cs in the waste water by column permeation. Relative to 121 mL/min permeation, the 242 mL/min one had efficient reduction of the Cs concentration.
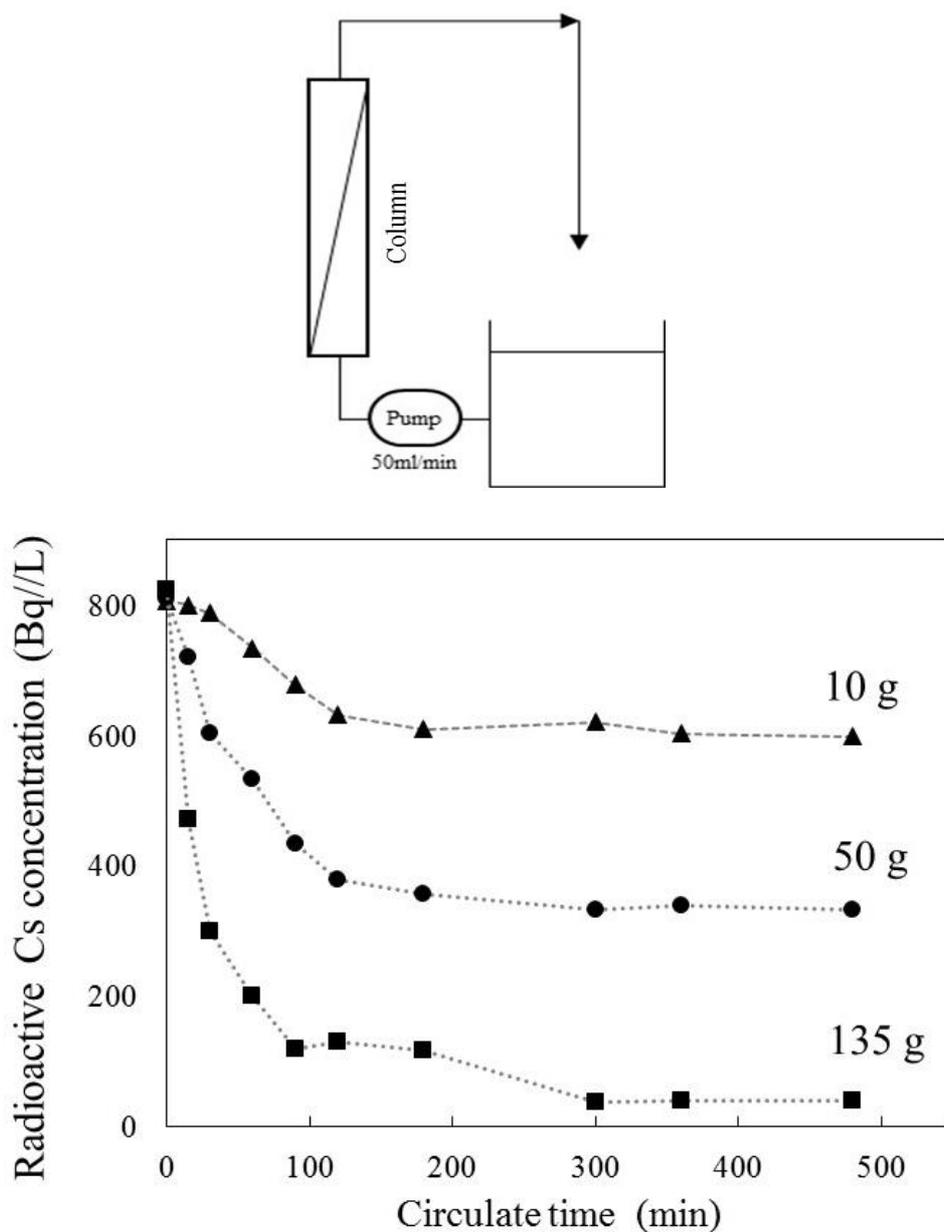
Figure 3-7 Schematic representation of the circulation experiment with column. Packed

fibrous composites and eluted radioactive Cs after the column treatment at different
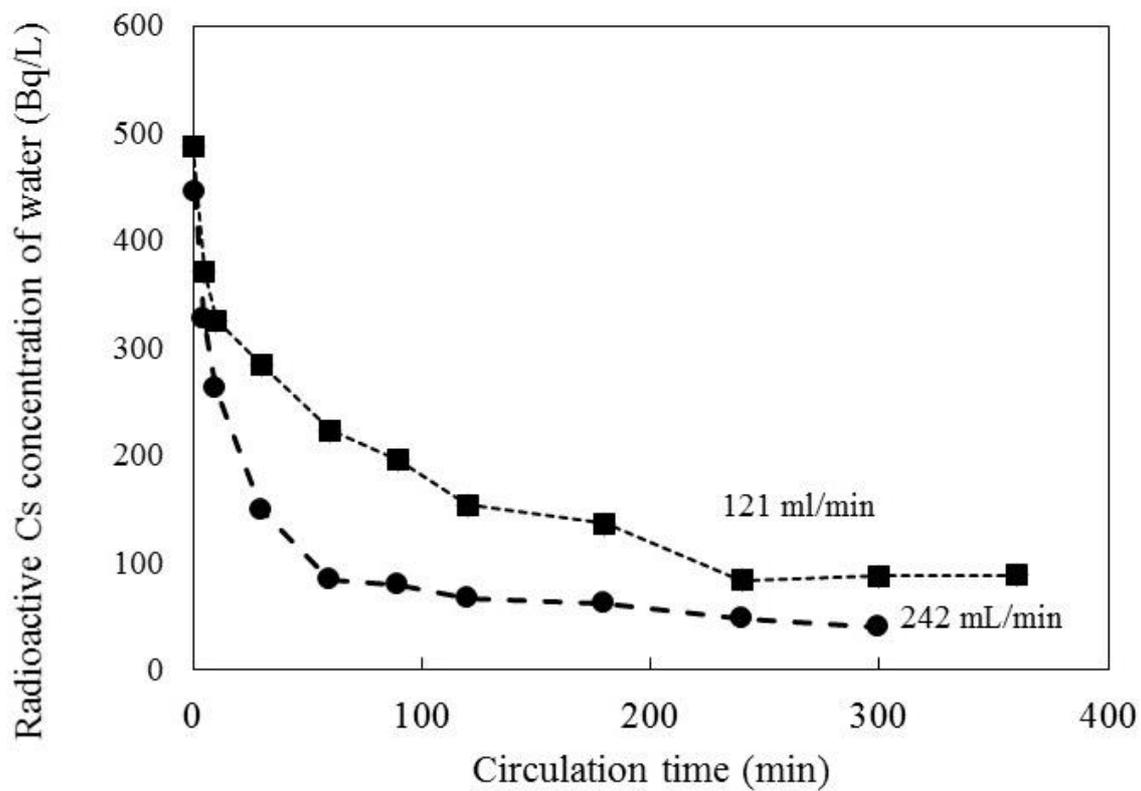
operation time.

Figure 3-8 Radioactive Cs removal performance of different flow ratio.

3.3.4 Consideration of Cs binding to fibrous adsorbents

As shown in Figure 2-4 and 3-2, the composite fiber had porous morphology having the surface skin layer and sponge like macrovoid. Therefore, the asymmetric structure of the porous fiber seemed to have different solute perpetration, when the ion was accessed from the skin surface or the macrovoid into the immobilized zeolite sites. In the radioactively contaminated Cs solution, so the extract of other salts was contained at Ca^{2+}=4,000 ppm, Na^+= 2,000 ppm and K^+=2,000 ppm. So, these ions were interfered the ion exchange mechanism of the zeolite sites for the adsorption of radioactive Cs. Here, the value of the radioactive Cs concentration at 600 Bq/L in the extracted solution was corresponded to 1.8×10^{-9} mg/L, meaning that the Cs was very low concentration relative to other ions. However, the fibrous adsorbent had resulting high sensitive adsorption against the radioactive Cs in the extra diluted condition. Therefore, it was very difficult to explain the ion exchange mechanism for the binding of the radioactive Cs in the strong alkali condition, as higher concentrations of Ca^{2+}, Na^+ and K^+ were present. The result of the Freundlich mechanism in the present work suggested that the radioactive Cs in the radioactively contaminated Cs solution prepared from the fly ash suspension was

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experienced by multilayer binding to the adsorbent sites of zeolite.

In order to test the Cs selectivity to be asymmetric fibrous adsorbent in composite fiber in the presence of alkali metal ions in immobilized zeolites powders, several ions of K^+, Na^+, Li^+ and Cs^+ were mixed with each 20ppm and their adsorption amounts were measured. Figure 3-9 shows removal ration % of these each ion from the quaternary ion mixture solution for composite fibers, zeolite powder and ground powder mixture of the fibrous adsorbent loading with 30wt% of zeolite. Actually, after 48 hours immersion of each adsorbent into the quaternary ion mixture solution, Cs^+ removal ratio was in the range of 75-82% in the highest adsorption performance. On the other hand, the composite fiber had less adsorption to Li^+=14%, Na^+=0% and K^+=10%. Thus, comparison meant that the composite fibers had a less ability of such Li^+, Na^+ and K^+ adsorption, although other two system of zeolite powders and the ground powder of the composite fibers.
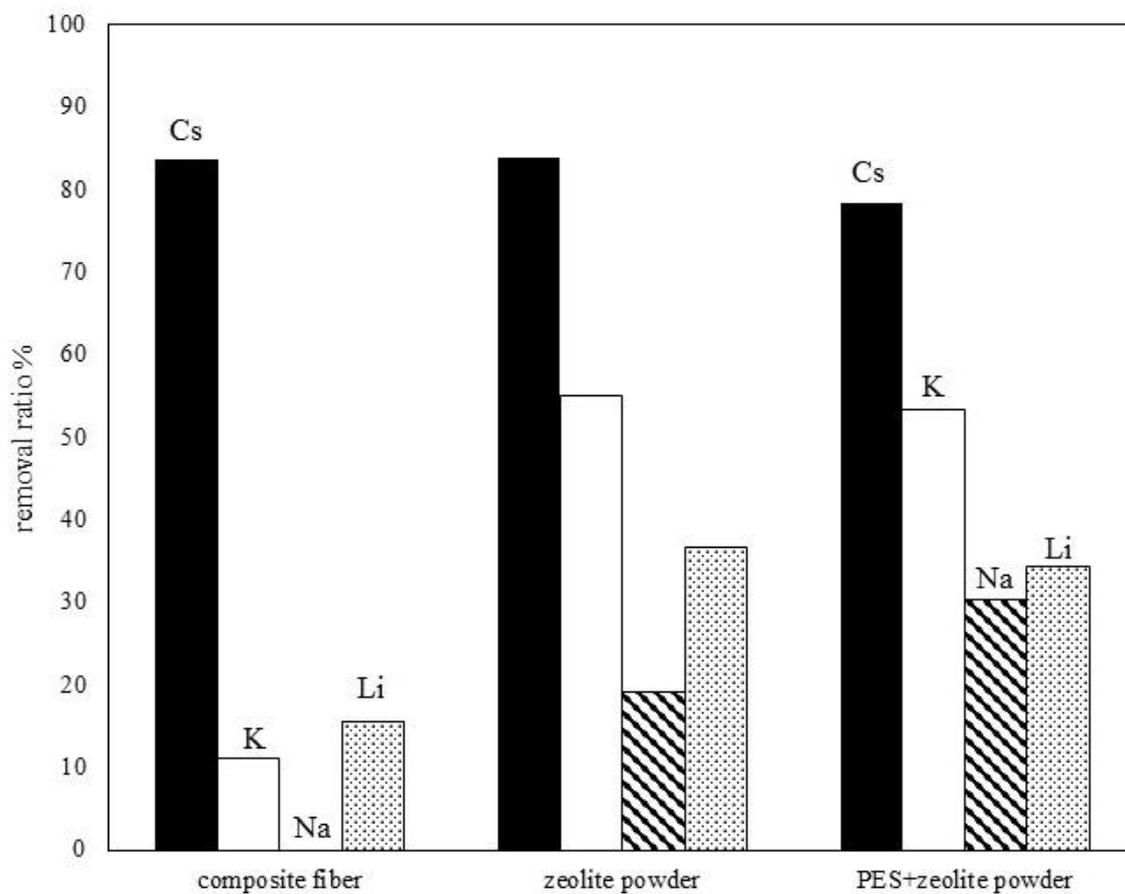
Figure 3-9 Adsorption behavior of composite fiber, zeolite powder and PES + zeolite powder under mixed alkali metal ion.
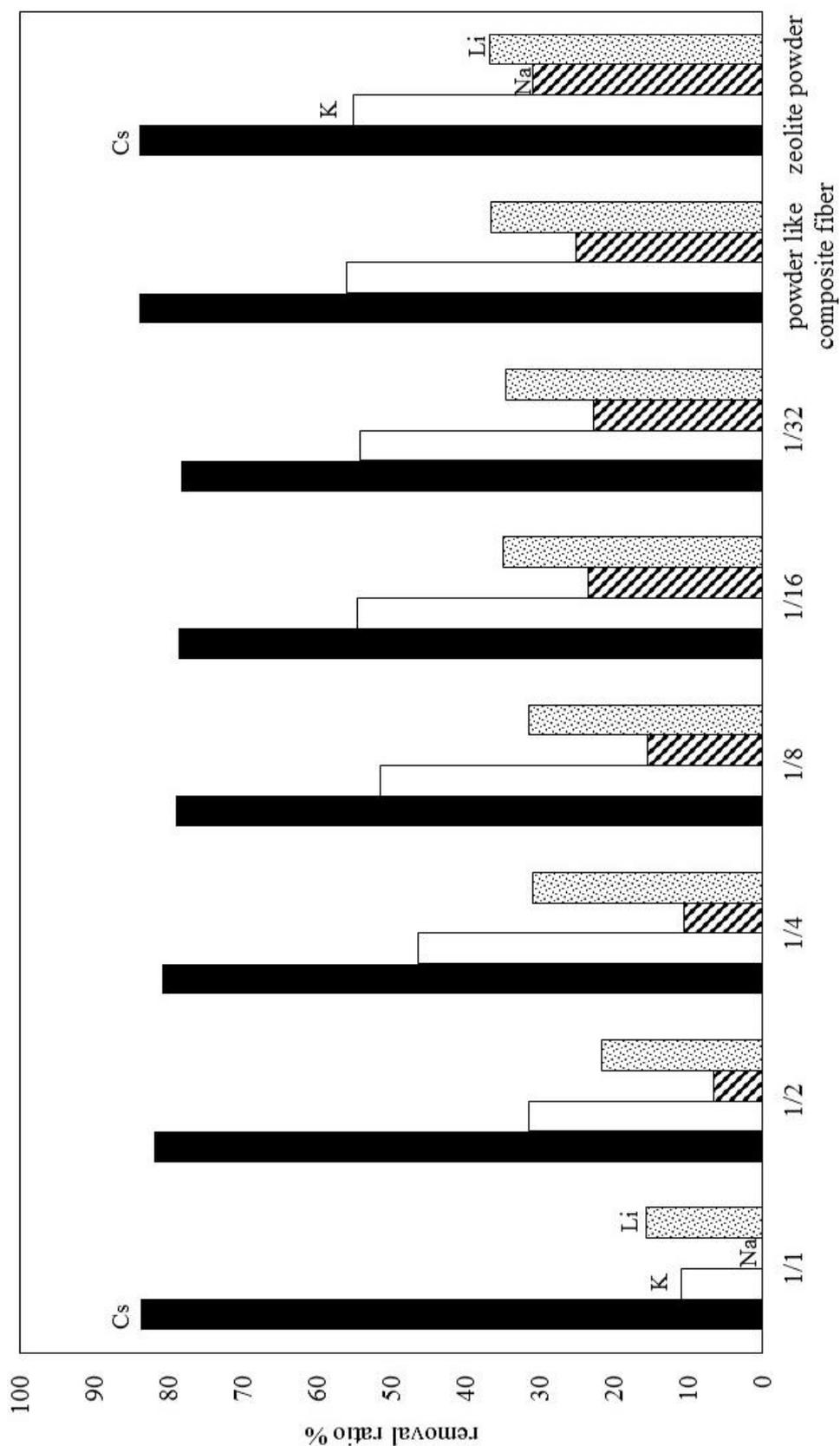
Figure 3-11 Removal ratio (%) of alkali metal ions in the presence of fibrous composite fibers. The each sample meant that 185 mm length fiber was cut with different length as mentioned in Figure 3-10

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Different experiments for quaternary ions mixture were carried out, when the 185mm length of composite fiber was cut to be 1/2, 1/4, 1/8, 1/16, 1/32 and powder like composite fiber. Here, 1/1 meant no cutting of the composite fiber as shown in Figure 3-10. The results of the adsorption experiments of quaternary ions for the cutting composite fiber are shown in Figure 3-11. Interestingly, as the size of the composite fiber decreased by cutting it, the removal ratio of K^+, Na^+ and Li^+ was increased, although the Cs^+ removal ratio was almost 80%. This comparison meant that the skin side accessing and macrovoid side one for each ion was quaternary different behavior to the capture, for example, especially, Na^+ ion. As shown in Figure 3-12, the cross section of the composite fiber had a thinner skin layer on the surface with less 0.1-0.5 μm thinness. And the cross section view should about 550 μm diameter as seen (A). Actually, the zeolite powders are exposed to the surface of the macrovoid cross section. Therefore, when the cut number of the composite fibers was increased from 1/2 – 1/32, the cross sectional area of macrovoid s was increased and the zeolite numbers to expose to the void surface also increase.
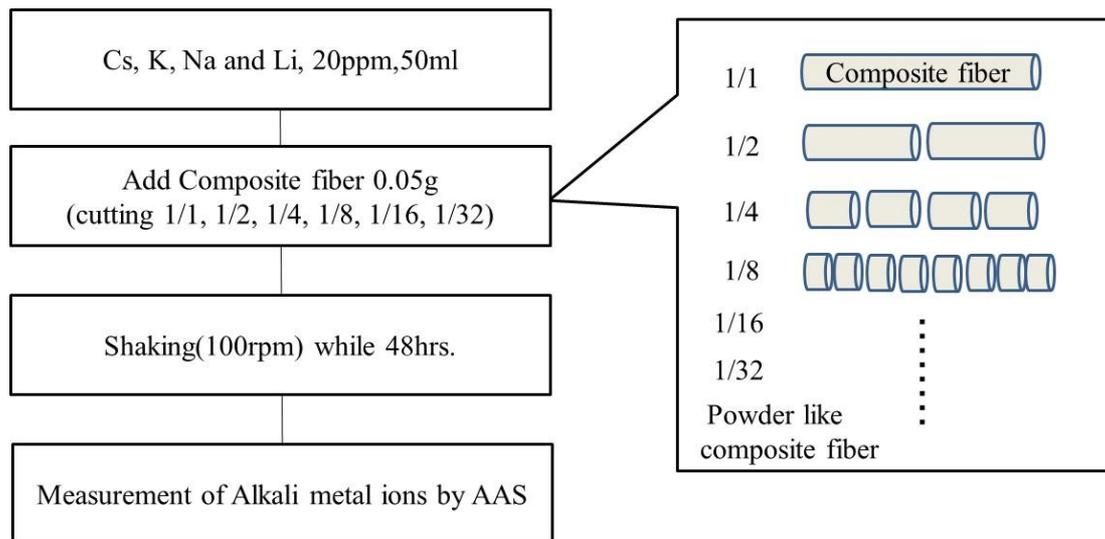
Figure 3-10 Flow diagram of binding experiment for quaternary ions mixture and image of cutting composite fiber.

Chapter 3 Composite fiber for decontamination of radioactive waste water extracted from radio-Cs fly ash

 As well known about by phase inversion prosses, the NMP used as a solvent was exchanged with an excess of water, leading the high-density structure of the PES on surface of composite fiber. This was origin to form the skin layer on the surface of the composite fiber.

 As seen in results of zeta potential of zeolite, PES, the composite fiber and the cut fibers are shown in Figure 3-13. It was confirmed that the composite fibers and PES were almost neutral, whereas both zeolite and the cut fiber had charges. The potentials results were different in the composite fiber and the cut fiber, meaning that the surface of the composite fiber coverd with PES skin layer could not detected the negatively charges of zeolite. In addition, the ion needed to access to the internal zeolites by passing through the skin layer surface for the composite fiber. But the cut fibers increased the access from the exposed zeolite in the macrovoids. Therefore, it seems that different of Na^+ selectivity was provided.
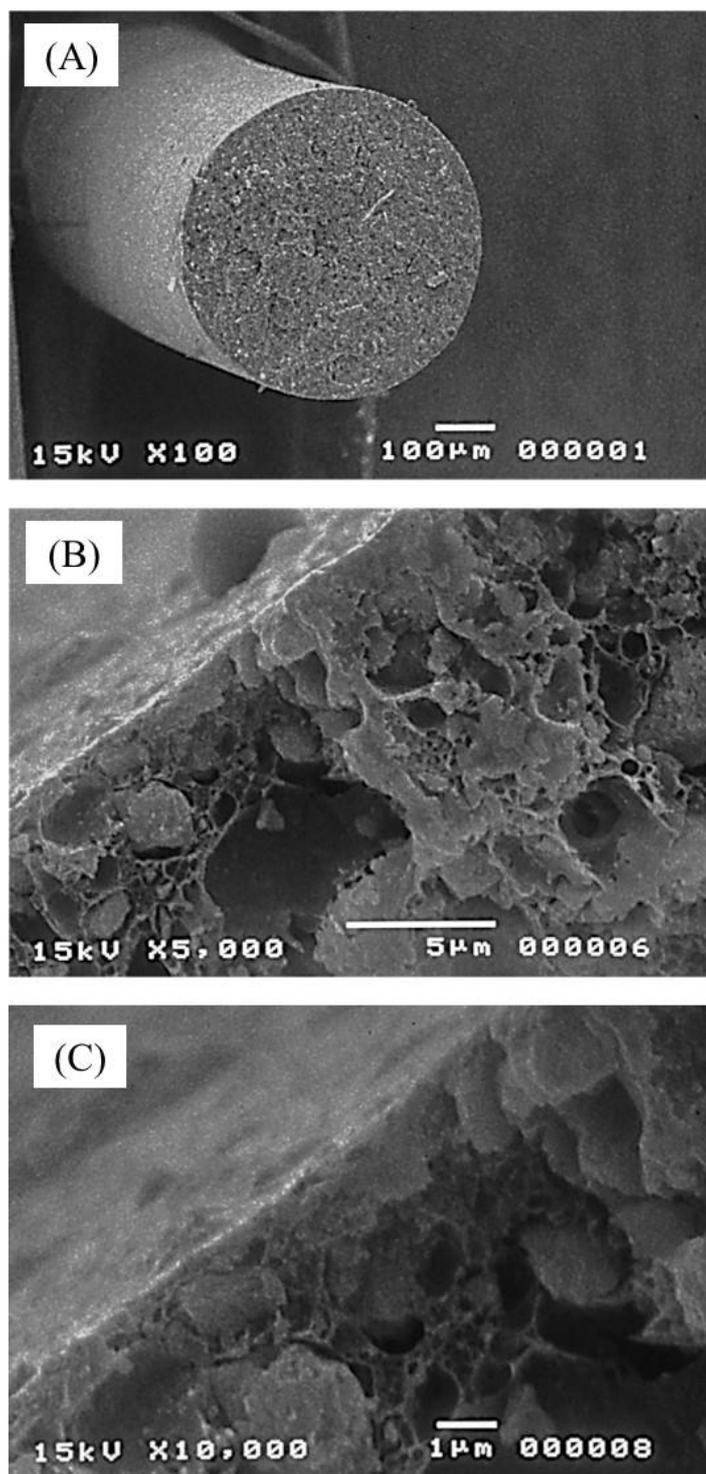
Figure 3-12 SEM images of (A) cross section of composite fiber having diameter Φ=0.55mm at ×100 magnitude, and top surface of the fiber at (B) ×5,000 and (C) ×10,000.
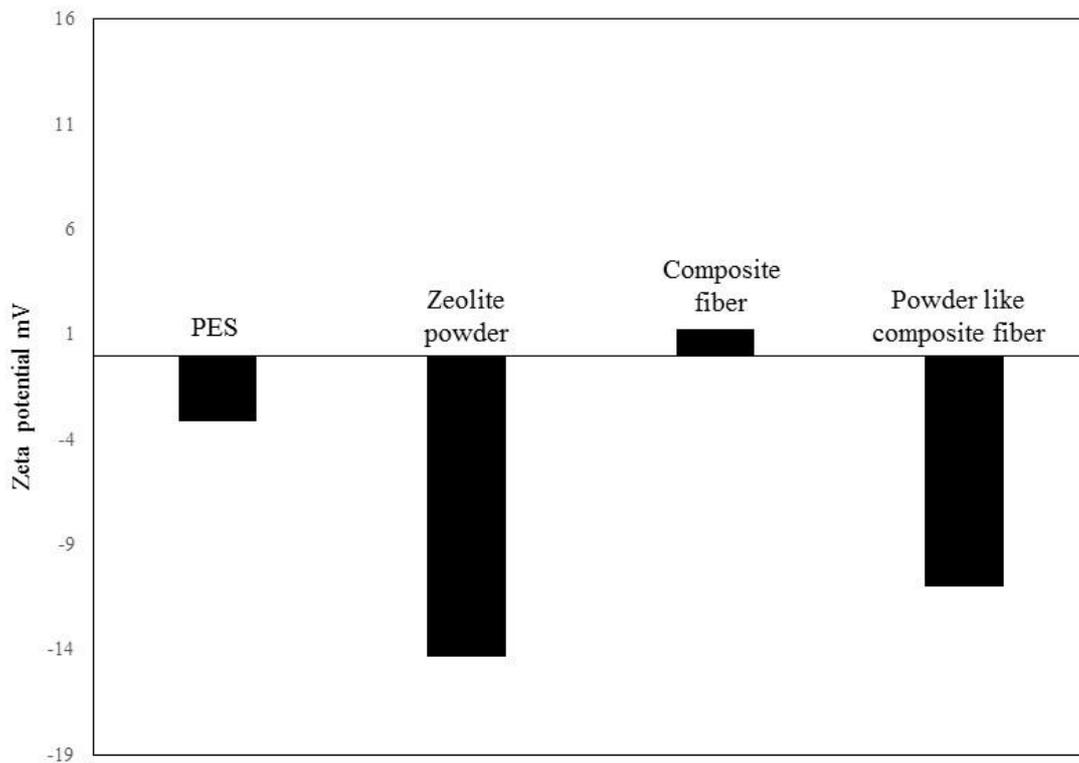
Figure 3-13 Zeta potential of PES, Zeolite powder, composite fiber and powder like composite fiber.

Chapter 3 Composite fiber for decontamination of radioactive waste water extracted from radio-Cs fly ash

Table 3-1 shows the cross sectional area, when each was cut with 1/4 and 1/16 for the composite fibers. In order to investigate influence of the composite fibers on different diameter to such alkali metal adsorption the comparison of fiber diameter in 1,230 μm with 550 μm was made. Figure 3-14 show the SEM images of 1,230 μm fiber fabricated. The experiments of the alkali metal ion were carried out and compared in the two composite fibers having 550 μm and 1,230 μm diameters with the zeolite loading as seen in Table 3-1, the cross sectional area was increased, when the cutting numbers of the fiber was increased. Here, C/L was defined with the ratio of the cross section and the lateral area. It can be thought that the adsorption of Cs^+ and other alkali ions, especially for Na^+, depend upon the C/L ratio as shown in Figure 3-15. Here, the C/L ratio was defined as

C/L = Cross sectional area (mm^2) / Lateral area (mm^2). Thus, as increased as the cutting number, the exposed zeolites on the cross section occurred to be similar adsorption behavior of zeolite. It was interesting to note similarity of the ground powder of the composite fiber. This might be due to the increase in the cross sectional area in the cases of higher cutting numbers. Therefore, when the ion penetration was occurred thought the skin thin layer at the surface, the PES barrier interfered the Na^+ ion accessibility to the
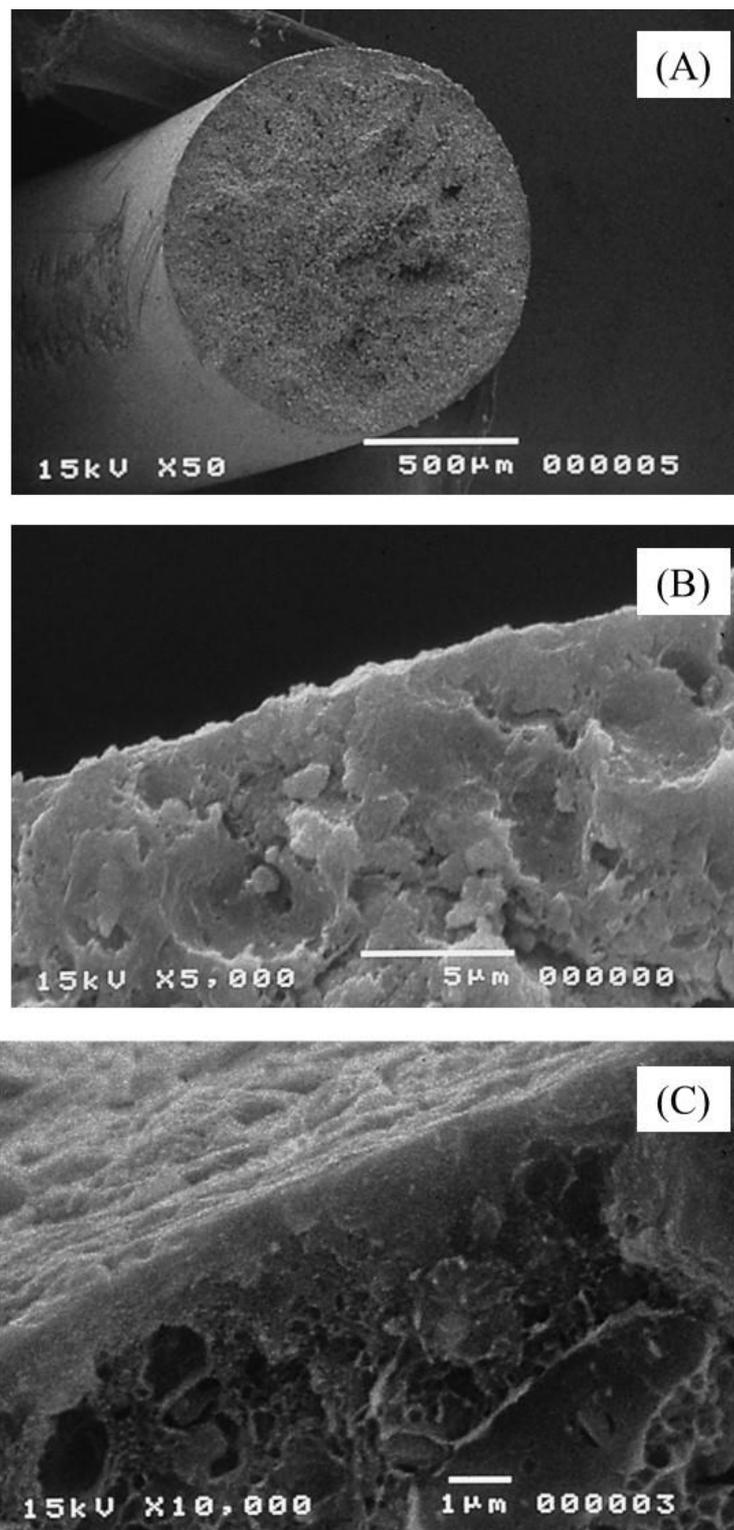
Figure 3-14 SEM images of cross section of composite fiber. Φ = 1230μm for the cross

section of (A) ×100 and top surface of (B) ×5,000 and (C) ×10,000.

Table 3-1 Relationship between side area and cross sectional area of composite fiber with different fiber diameters.

Fiber diameter mm	Length mm	Division number	Lateral area mm^2	Cross sectional area mm^2	C/L
0.55	185	1/1	319.5	0.47	0.0014
		1/4		1.9	0.0059
		1/16		7.6	0.023
1.23	38	1/1	146.8	2.38	0.016
		1/4		9.50	0.064
		1/16		38	0.258

C/L: Cross sectional area mm^2 / Lateral area mm^2

Figure 3-15 Removal ration of alkali metal ions at different C/L for the cut composite

fibers.

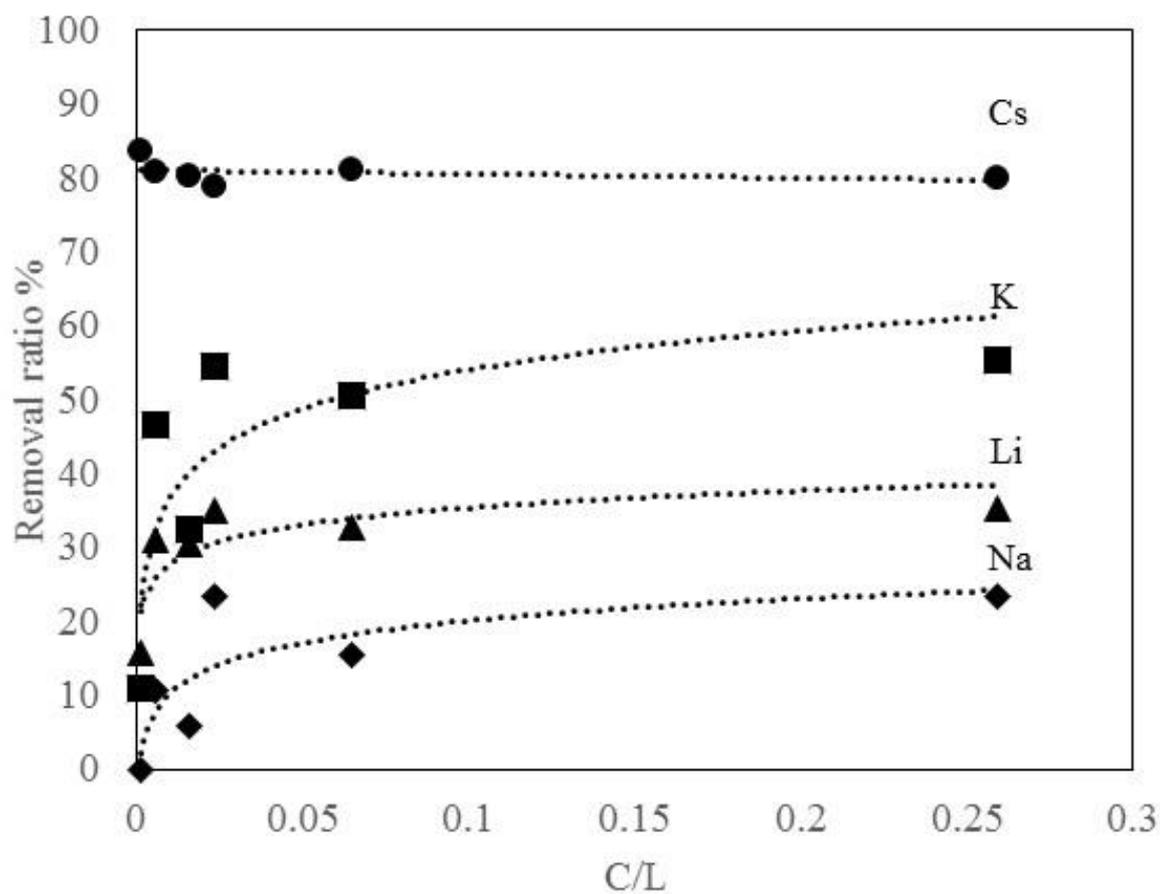imbedded zeolite sites. This result suggests the selectivity of Cs^+ and that others are accessing to the zeolite sites.

3.4 Conclusion

Radioactive Cs water wastes obtained for radioactive fly ash decontamination were used in removal tests for the sorption processes of zeolite, zeolite composite fiber and PB. While the strong alkali pH was damaged to PB, zeolite and zeolite composite fiber were behaved reduction of radioactive Cs by the batch and column sorption processes. Relative to zeolite, the composite fiber having 30wt% loading zeolite had excellent character in the decontamination of radioactive Cs. Furthermore, Cs adsorption selectivity of composite fiber has caused by side adsorption. As a result, it was found that even highly alkaline solution containing radioactive Cs extracted from ash can be adsorbed effectively. In extra diluted radioactive Cs relative to the batch sorption test for 823 Bq/kg concentration of radioactive Cs solution, the binding was obeyed in Freundlich mechanism with multilayer binding to the adsorbent sites of zeolite.

3.5 References

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Chapter 4 Compact storage of radioactive cesium in compressed pellets of zeolite composite fibers

Abstract

To facilitate safe storage of radioactive Cs, zeolite polymer composite fiber fabricated to serve as a compact storage form for radioactive Cs immobilization was investigated for its effects of volume reduction and stability of adsorbent. Using compressed heat treatment at 100–800°C, composite fiber containing Cs was changed from a fiber form into a pellet form, which decreased its volume to about one-sixth. The Cs leakage behavior of the composite fiber matrix was examined using non-radioactive Cs and radioactive Cs for different fabrication conditions. The elution ratio of non-radioactive Cs from the matrix was minimal, 0.05%, when composite fiber was compressed with heat treatment at 300°C. Because the poly(ethersulfone) (PES) of the composite fiber component was thermoplastic, striking composite fiber surface area reduction was observed after heat treatment. When using radioactive Cs, the pellet form also had no elution of radioactive Cs from the matrix, when the heat treatment under 300°C. Pellets compressed by heat treatment at 500°C and higher tempeatures exhibited elution of radioactive Cs from the matrix, meaning that the component was burning PES

from the pellet. Comparison of composite fiber and natural zeolite shows that composite

fiber was not eluted, which suggests its usefulness as a compact stable adsorbent for long-

term storage.

4.1 Introduction

The severe accident that occurred on March 11, 2011 at the Fukushima Daiichi

Nuclear Power Plant resulted from difficulties related to the catastrophic earthquake and

its subsequent tsunami. The event damaged the plant, which released great amounts of

radioactive ^{134}Cs and ^{137}Cs. Since then, the residual radioactivity has persisted as a hazard

for local residents [1]. The huge volume of contaminants was estimated in 2013 as about

$15-28 \times 10^6$ m^3 [2]. The estimated amounts of radionuclides released into the atmosphere

in 2012 in Fukushima were 6.1–62.5 PBq and 65–200 PBq, respectively, for ^{137}Cs and

^{131}I. Especially, the Cs radioisotopes have been found frequently in aqueous radioactive

wastes, mostly at levels exceeding the standards set for the areas. Because Cs belongs to

a chemically similar group that includes sodium and potassium, ingestion of Cs

radioisotopes can engender their deposition in tissues throughout the human body, thereby

presenting an internal hazard to human health.

Over the years that have passed since the accident, external exposure to ^{137}Cs,

which has a long half-life of 30.5 years, has come to dominate radionuclide exposure. The

trapped ^{137}Cs wastes now present a health risk in Fukushima because of the huge amounts

of radioactive waste in the environment. Along with increased concern related to the Cs

radionuclide waste, people feel threatened in human life environments. Consequently,

decontamination processes have continued to cope with the huge amounts of radioactive

Cs. An effective mitigation method must be found through consideration of attractive

technologies. Among such methods, immobilization techniques have been presented for

the remediation of radioactive Cs [3–5]. For the large amounts of radioactive Cs that still

exist, development of some adsorption technology is needed. Additionally, for proper

management and storage of radioactive waste, volume reduction of secondary wastes

from adsorption treatments is necessary.

To immobilize radioactive Cs, diverse methods have included solidification. In

some studies of radioactive fly ash treatment, embedding radioactive materials in a

solidified form was accomplished using a nanometallic Ca/CaO suspension for

wastewater [6]. Reportedly, pyrolytic carbon-coated zeolite is effective [7]. Radioactive

wastewater has been immobilized in a concrete matrix and in struvite ceramics [8].

Moreover, immobilization has been achieved in a $HZr_2(PO_4)_3$ matrix [9] and in ash-based

geopolymers [10,11] or in rice husk silica geopolymers [12]. Nevertheless, no report of

the relevant literature has described immobilization by polymeric envelopment of a radioactive species with zeolite. Flammable wastes have been incinerated to accumulate enormous amounts of fly ash containing radioactive Cs. Zeolite polymer composite fiber is an effective agent for water treatment to achieve radioactive Cs decontamination [5]. However, post-adsorption treatment of the composite fiber containing radioactive Cs presents storage problems for coming decades because of the greater volume of wastes. In post-adsorption treatment processes for radioactive Cs, reducing the volume of such decontaminated agents becomes important for later storage processes. Therefore, several methods of immobilizing radioactive Cs in a matrix have been proposed as described above. For radioactive Cs remediation, the composite fiber used with this method holds it strongly in matrix, even though the radioactive Cs was concentrated from an extra diluted solution of radionuclides. However, after adsorption treatment of the ^{137}Cs, the fiber adsorbent must be stored for long periods, which requires compaction of the fiber volume for safe storage. This study tested composite fiber, used as a radioactive Cs immobilization matrix, to assess leakage of radioactive Cs from the matrix using the radioactive Cs source from actual radioactive fly ash. Results show that the reductive volume fiber has excellent capabilities for Cs immobilization.

4.2 Materials and methods

4.2.1 Materials

Natural mordenite zeolite powder (≤100 μm) was purchased from Nitto Funka

Trading Co. Ltd. (Miyagi, Japan). Poly(ethersulfone)(PES) was used as received (PES,

MV = 50,000; BASF Japan Ltd., Ludwigshafen, Germany). *N*-methyl-2-pyrrolidone

(NMP; Nacalai Tesque Inc., Kyoto, Japan) was used for the composite fiber without

purification. The radioactive Cs adsorbed into composite fiber was prepared as shown in

Figure 4-1. An aqueous solution containing radioactive Cs was prepared using

hydrothermal extraction of fly ash for 2 h at 200°C and 1.5 MPa. The fly ash was sampled

in Namie, Fukushima (Figure 4-1). After the supernatant dispersed with fly ash was

filtrated, the radioactive aqueous solution was used for experiments to fill into the

composite fiber. Then the Cs-adsorbed fibers were prepared. Total radioactivity in the

weighted fibers was measured in Becquerel per kilogram (Bq/kg) units. As Figure 4-1

shows, after Cs binding to the composite fiber, the following procedure for

immobilization by compressed heat treatments of different temperatures was tested for

the pellet. We evaluated the Cs release and the heat-treated matrix properties. The Cs

adsorption process was conducted as follows. Radioactive fly ash (4 kg) having about

30,000 Bq/kg with Cs was dispersed in water (16 L). Then composite fiber was immersed

for 12 h. After this binding process, the composite fiber was used to measure the

radioactive Cs concentration. For example, the radioactive Cs was 13,100–33,000 Bq/kg

after immersion.

4.2.2 Characterization of Composite Fibers

To fabricate the composite fiber pellet enveloping the radioactive Cs, processes

of immobilization and volume reduction were included in heat molding processing. After

the fibers (10 g) were pressed inside of a cylindrical stainless steel tube (50 mm height,

40 mm diameter, and 2.5 mm thickness), they were heated by a surrounding ribbon heater

for 2 h at different temperatures of 100, 200, 300, 400, 600, and 800°C. For experimental

procedures to assess radioactive Cs leakage from the fiber pellet matrix, the 10 g pellet

matrix was immersed in 100 ml water. Then the released radioactive Cs was evaluated by

measuring the Bq/kg amounts of the pellet and the washed water. In addition, scanning

electron microscopy (SEM) images were taken (JSM-5310LVB; JEOL, Japan) of the

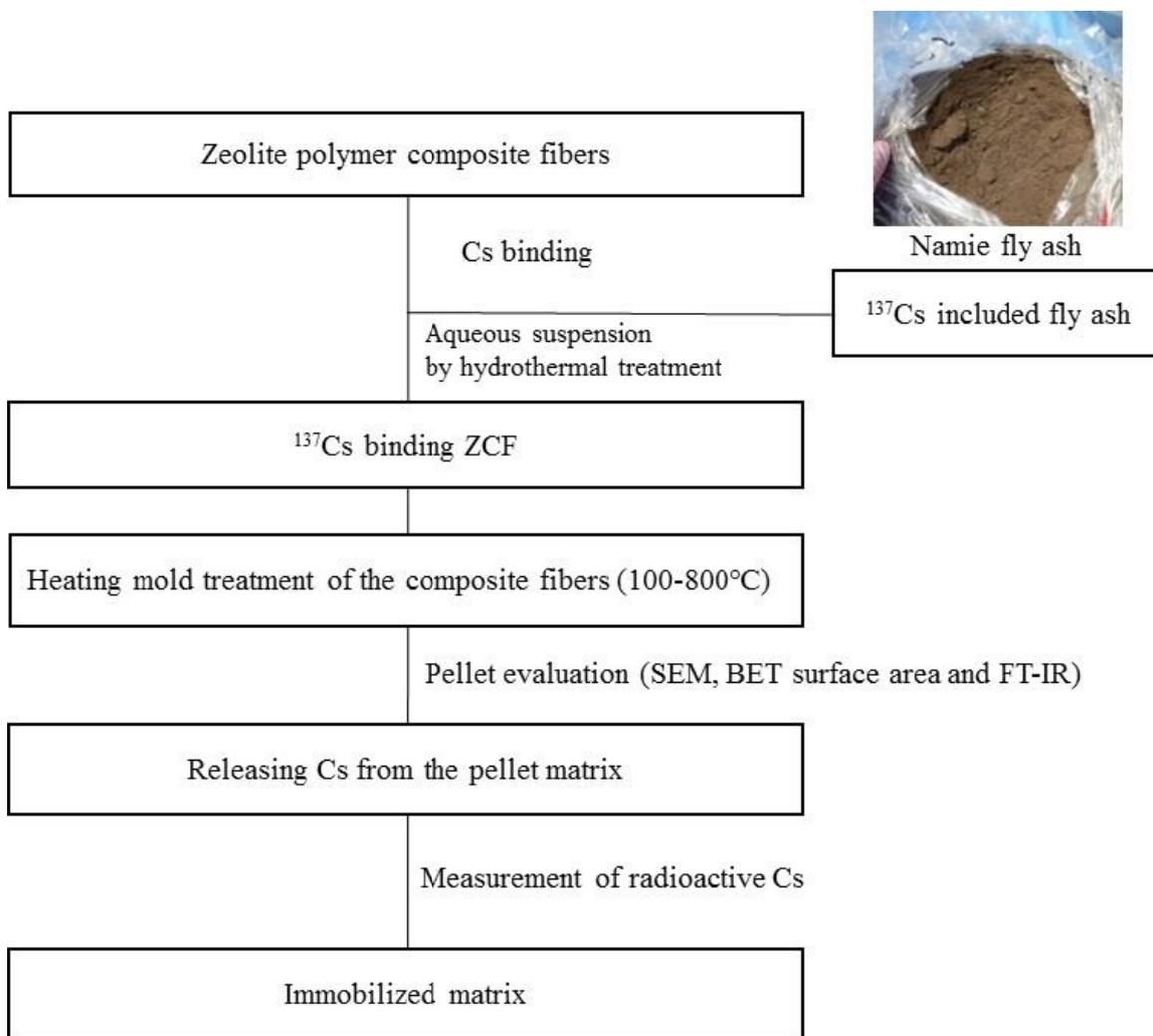composite fiber and the compacted pellet.

Figure 4-1 Flowchart of experiment procedure for Cs immobilization by heat treatment of zeolite polymer composite fibers and their Cs release processes.

Additionally, the sample was sputtered at 0.1 Torr for 40 s with Au for SEM measurements. A Fourier transform infrared spectrometer (FT-IR, IR Prestige-21 FTIR 8400s; Shimadzu Corp., Kyoto, Japan) was used with KBr method. The N_2 adsorption was analyzed using the Brunauer–Emmett–Teller (BET) surface area (Tristar II 3020; Micrometric Inc.). The radioactive Cs amount was found using a Ge semiconductor (SEG-EMS; Seiko easy and MCA7600 G Co.). During the release process, the pellet matrix enveloping the radioactive Cs was immersed in 100 ml of water. Then the Cs concentration of the matrix was monitored at different times until 6 h at 200 rpm. Similar experiments were also conducted with non-radioactive Cs.

4.2.3 Composite Fiber Pellet Fabrication and Release Tests

The heat molding process is depicted in Figure 4-2a). A stainless cylinder having a pipe shape was used for heat molding processing. In the cylinder with a ribbon heater attached to the outside of the cylindrical pipe, the temperature was measured using thermocouple thermometer (FINE THERMO DG2N 100; HAKKO Ltd., Japan). After 10 g of the composite fiber with 59 wt% zeolite was placed inside, the stainless steel cover (4 cm diameter× 2.5 cm thickness) was set on the fibers. Then, the cover was pressed using a hydraulic press machine (P-16B Air Valve; Riken Seiki) at 200 kg/cm^2 for 6 h.

After heat molding processing under pressure, the BET surface area and weight loss of

adsorbents were measured. The pellet form was prepared using heat mold processing.

Then the Cs release was conducted as follows. The fibers or the pellets, after accurate

measurement of their weight, were washed 10 times with water and were immersed in

100 ml of water for 6 h and 24 h with stirring at 200 rpm. Then, the matrix and the solution

were used to measure the resident Cs with a germanium semiconductor detector. The

remaining Cs was calculated as; Cs eluted rate (%) = $(C \times V/C_0 \times W) \times 100$,

where C stands for the Cs concentrations of eluted water, V denotes the eluted water

volume, C_0 represents the Cs concentrations of the fiber or pellet, and W stands for the
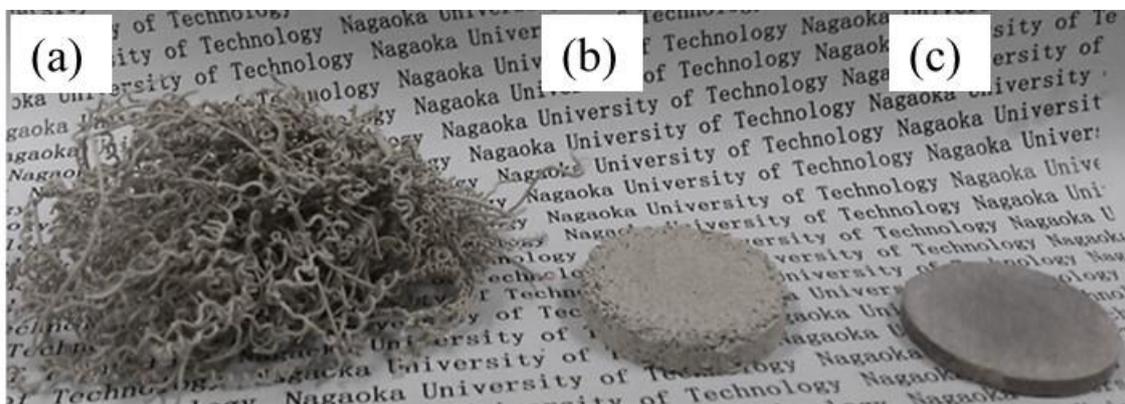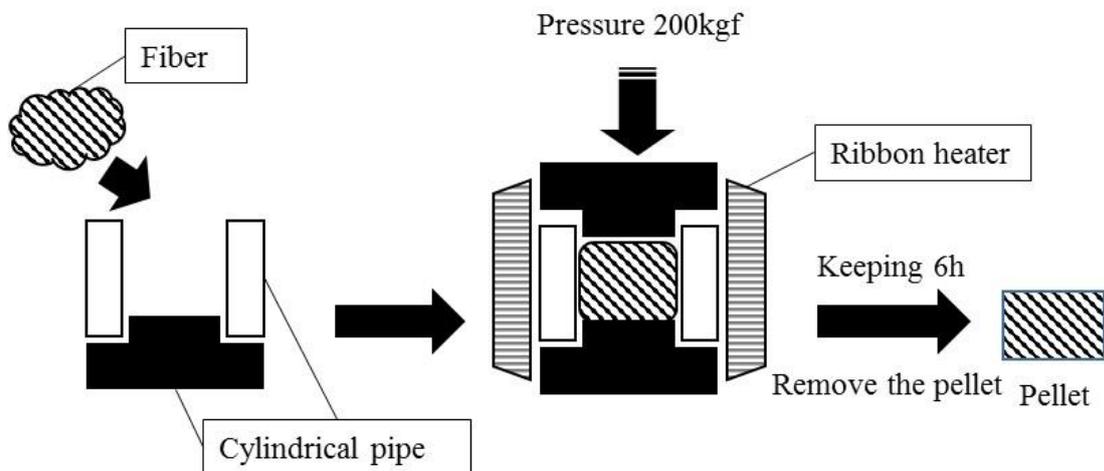
fiber or pellet weight.

Figure 4-2 Schematic illustration of heating mold processes for preparation of the pellet matrix. The picture shows, respectively, fibers (a) before and (b) and (c) after heating mold processes at 100°C and 300°C.

4.3 Results and discussion

4.3.1 Immobilization of Radioactive Cesium by Heating Mold Processing of

Composite Fibers

As Figure 4-2a) shows, heat molding processing of the composite fiber was

conducted after the radioactive Cs was bound in the dispersed fly ash solution. Then, to

fabricate the compacted shape of the fibrous sample, the fiber samples were heated at

different temperatures under pressure. To elucidate the heat molding processing, the

Differential Scanning Calorimetry (DSC) curves of PES fiber and the composite fiber

were found as shown in Figure 4-3. Endothermic peaks were found at 220°C and 227°C

for the PES and the composite fiber in each DSC curve, which indicated that heating to

temperatures higher than 230°C melted the PES in composite fiber and enabled

fabrication of a pellet matrix under a compressed mold condition. Results show that heat

molding processing was able to produce the pellet form. Additionally, it was apparent that

the pellet form could be made to different densities at 100°C and 300°C process

temperatures. Figure 4-4 presents the relation between the volume (cm^3) and density

(g/cm^3) changes of the pellets. The composite fiber volume was decreased from 40 cm^3

to 12.5 cm^3 under pressure during heat molding processing at 100°C. Then at 300°C, the

volume was decreased further to 6.3 cm^3. A comparison between 40 cm^3 and 6.3 cm^3

conducted before and after molding at 300°C showed volume reduction to about one-sixth of the original volume. Consequently, the pellet density increased from 0.25 to 1.52 g/cm^3 after compression processing. When the temperature was changed to greater than 500°C during heat molding processing, the density decreased to 1.1 g/cm^3. Probably, the decrease was attributable to the polymer decomposition of organic PES.
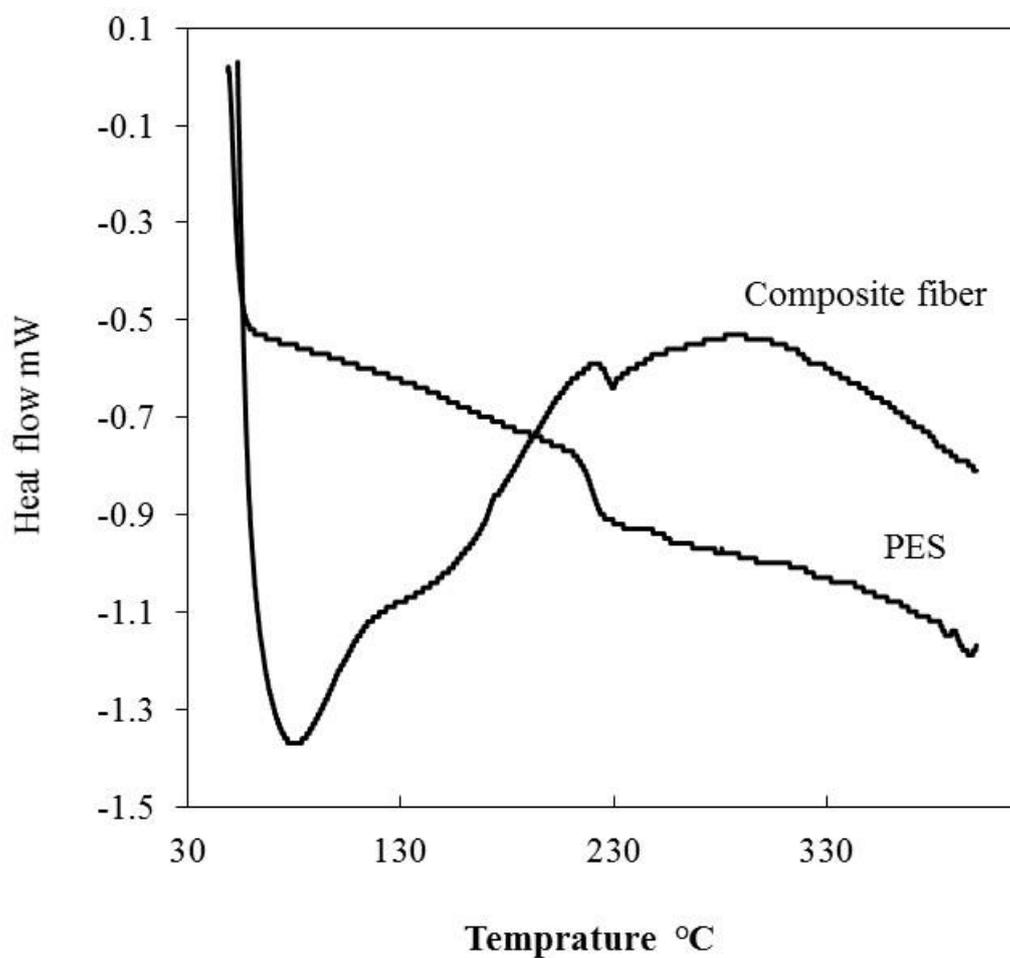
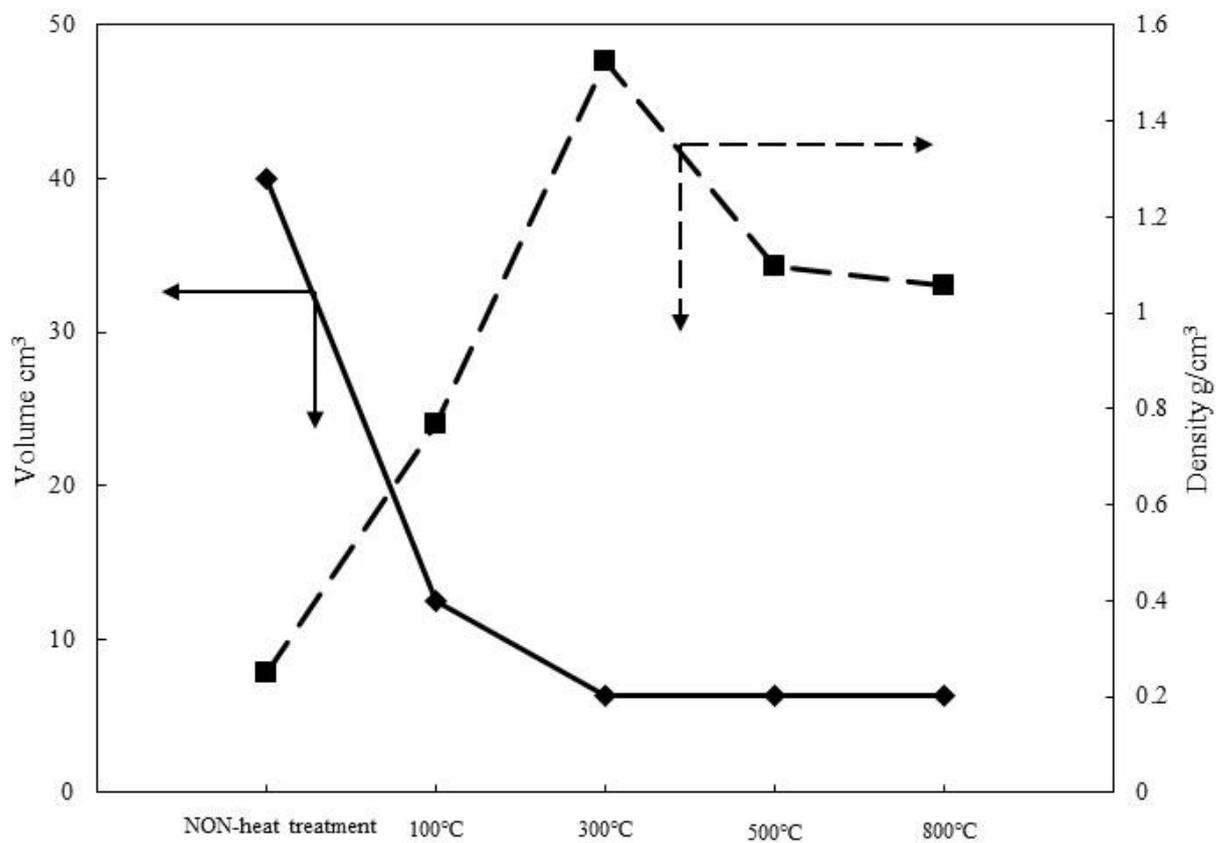Figure 4-3 Results of DSC analysis of composite fiber and PES.

Figure 4-4 Relation between heating mold press temperature and the pellet volume and density.

Figure 4-5 portrays SEM images of the surface and cross sections of composite fiber

treated at different temperatures with heat molding processing. Low-temperature molding

at 100°C revealed that the zeolite powders were embedded in the PES medium as they

were in the case of the non-heating mold. However, at temperatures higher than 300°C,

images show that the PES amounts decreased concomitantly with increasing temperature.

At temperatures, higher than 500°C, the fibers were in a brittle state. Moreover, the

polymer layer disappeared, reflecting the organic PES matrix decomposition. A cross-

section view (Figure 4-5) of the fibers remaining in the pellet revealed the dense structure

of the compressed fiber. The FT-IR spectral patterns for the 800°C sample (Figure 4-6)

revealed peaks at 1580, 1485, and 895 cm^{-1} corresponding to PES in the composite fiber

and peaks at 3460, 1658, and 1060 cm^{-1} corresponding to zeolite. Table 4-1 presents the

respective assignments for their FT-IR peaks. Actually, band broadening was apparent in

spectra obtained at 500°C and 800°C. Moreover, PES peaks were nonexistent. It was

inferred from these results that the SiO_2 component remained in the zeolite. The

appearance of the 1658 cm^{-1} peak in the heated pellets might be assigned to water

adsorbed from the atmosphere after heating. It is noteworthy that the peak appearance of

1580 and 1485 cm^{-1} is temperature-dependent. At 800°C, both PES peaks disappeared,

meaning that the PES in the pellet was burned out of the material. Therefore, the spectra

retained broad peaks at 1060 cm^{-1} for Si–O–Si and at 802 cm^{-1} for Al–O bands of zeolite.

To evaluate the porous and dense properties of the fibers and pellets, nitrogen (N_2) adsorption and desorption were measured at different pressures. Figure 4-7 portrays the N_2 adsorption isotherm of the PES and composite fiber in the absence (a) and presence (b) of heat molding processing. According to the isotherms, their samples presented that the adsorption behavior followed that of the type 2 isotherm, reflecting the presence of a macroporous structure [5] (Kobayashi et al., 2016). Compared to the PES and zeolite shown in Figure 4-7a), it was apparent that the PES fiber had lower capacity of the N_2 adsorption amounts relative to the zeolite powder. As Figure 4-7b) shows, the pellets molded at 500°C and 800°C showed similar isotherm curves to that of zeolite, as was true also for the non-heat treatment. However, it is noteworthy that the curve of the pellet heated at 300°C had much lower amounts of the N_2 adsorption. Consequently, the melted PES penetrated and covered the zeolite pores.
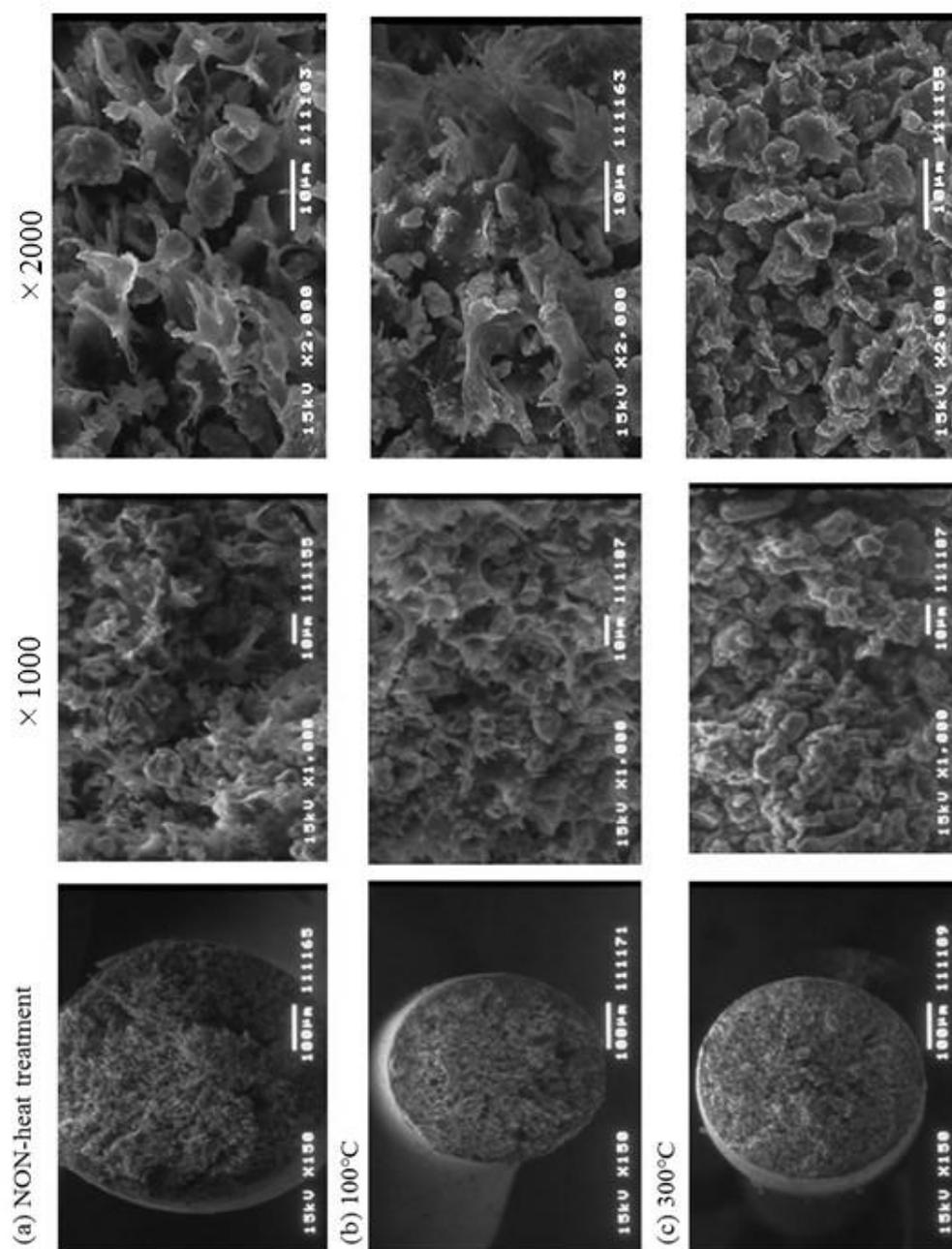
Figure 4-5 SEM view of fibrous cross section at different observation magnitudes for compressed heating.
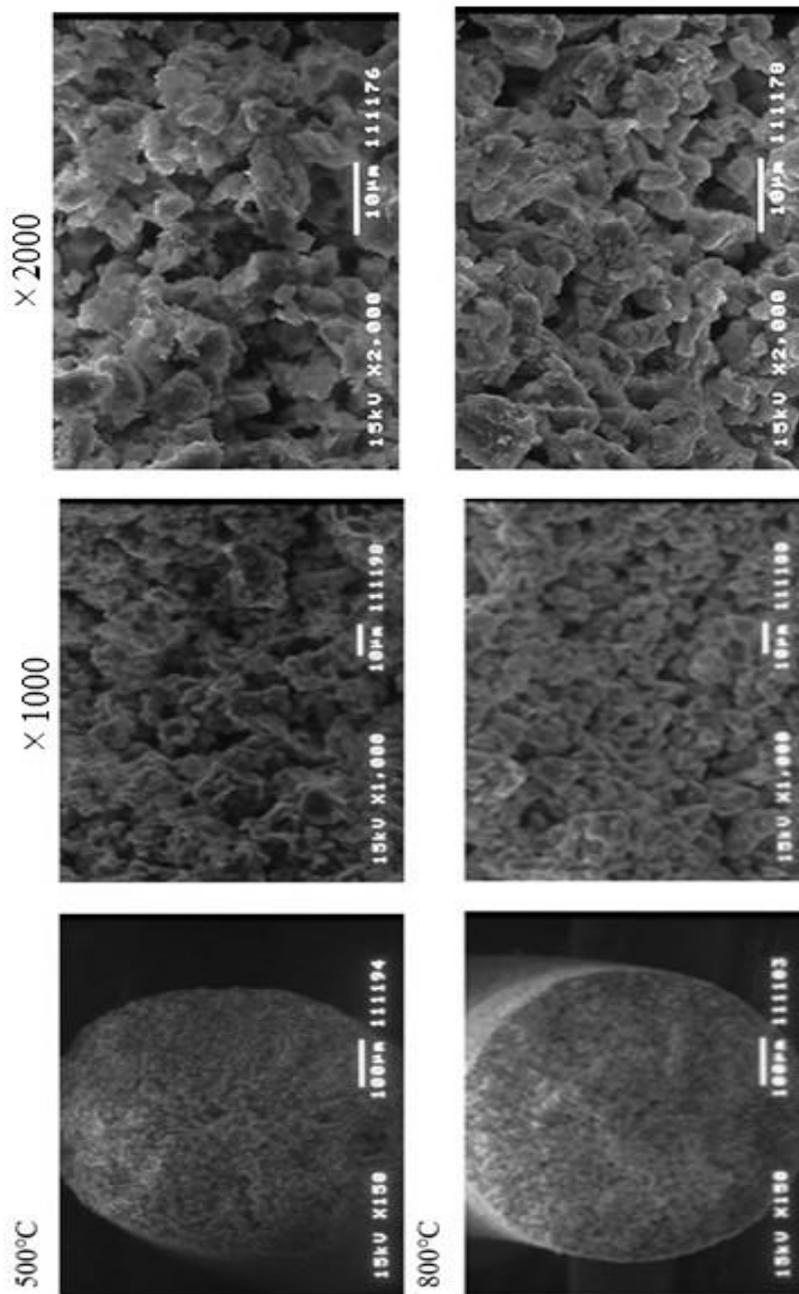
Figure 4-5 Continued.

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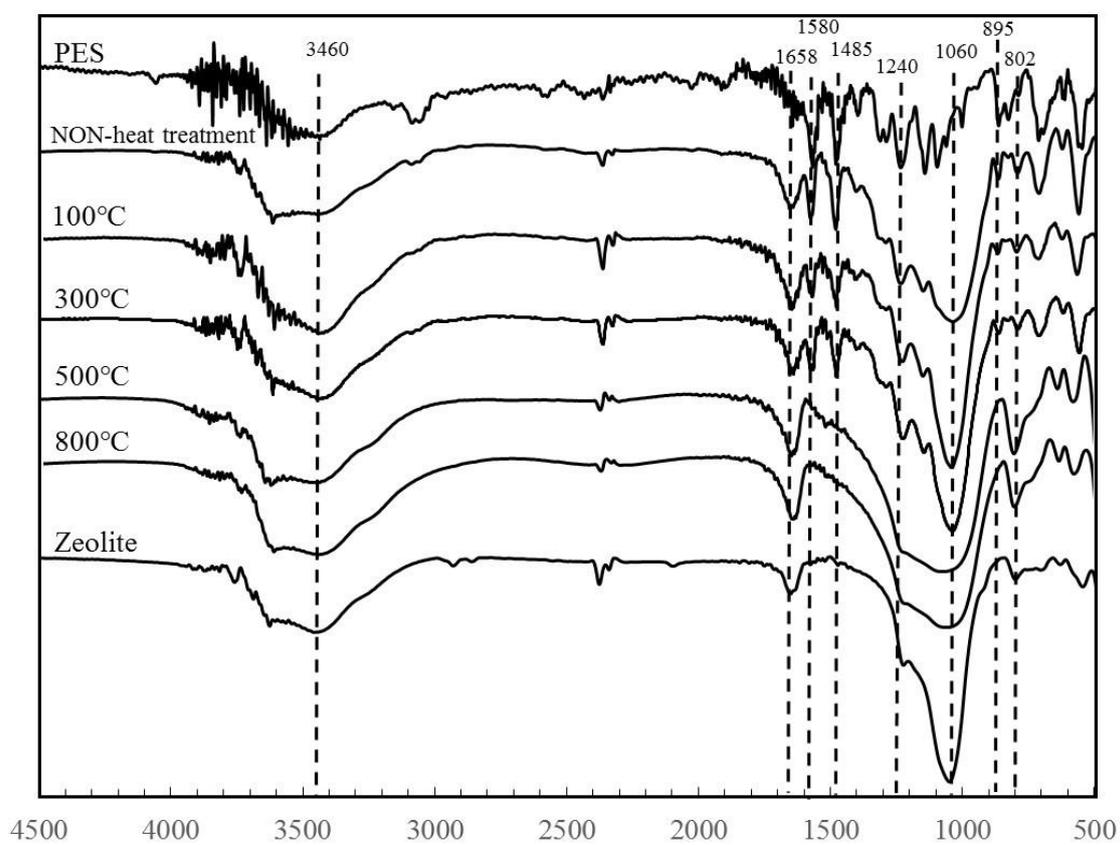
Figure 4-6 FT-IR spectra of composite fiber treated for 6 h at different temperatures.

Table 4-1 Infrared adsorption peaks of zeolite and PES

Wavenumber (cm^{-1})	Component in ZCF	Assignment
3460	zeolite	OH st.
1658	zeolite	Si-O-Si st.
1580	PES	C=O st.
1485	PES	C-O st.
1240	PES	SO st.
1060	zeolite	Si-O st.
895	PES	Polymer group C-C st.
802	zeolite	Al-O st.

st. stands for stretching

The zeolite volume was decreased. It is noteworthy that the N_2 adsorption amounts were somewhat higher at temperatures of 500°C and 800°C, which indicates that the PES component in the pellets decomposed gradually because the temperature was higher than around 300°C, and that it increased concomitantly with increasing temperature to 800°C. Therefore, the PES component decomposition occurred gradually with increasing temperature. Results obtained at 800°C show that the zeolite surface was exposed without envelopment by the PES layer. Table 4-2 presents the BET surface area and weight reduction of the composite fiber pellets heated at respective temperatures. The BET surface area of the composite fiber was 32 m^2/g before heat molding processing. The value was remarkably lower at 300°C because the melted PES enveloped the porous structure of the zeolite. The pellet structure became denser. At 500°C, however, the surface area value increased to 32 m^2/g, suggesting that little zeolite remained after heating. Furthermore, the heating treatment decomposed the PES component and thereby exposed the zeolite surface. The experiment results of the composite fiber weight reduction at 500°C and 800°C were, respectively, 30.8% and 33.3% after heat molding processing. However, the volume was 2.17% at 300°C. Figure 4-3 depicts DSC spectra showing that the PES of thermoplastic polymer was melted at temperatures higher than 300°C. Then the melting PES seemed to cover the zeolite powder. Therefore, from weight

reduction results, one can reasonably infer that the melted PES surrounding the zeolite

powders produced an enveloping layer that decreased the zeolite surface area.

4.3.2 Immobilization of radioactive cesium in composite fiber pellets

Table 4-2 presents values of the radioactive Cs amounts observed with and

without heat molding processing. The composite fiber adsorbed up to 14,000 Bq/kg of

Cs. The Cs concentration amounts were increased as the temperature increased after heat

molding processing. The increased concentration derived from the fact that the PES

weight was lower at higher temperatures. The composite fiber form can be changed to a

pellet by heat molding processing. Therefore, it was interesting to observe the radioactive

Cs immobilization efficiency in the matrix. To measure changes in the radioactive Cs

concentration, Cs release tests were conducted in water for each sample. Figure 4-8 shows

the elution rate (%) of non-radioactive Cs. After the pellet was washed with diluted water

for 6 h, the elution rate (%) was evaluated. Figure 4-8 shows the rate of radioactive Cs

elution from pellet matrixes molded at different temperatures. These results indicate that

elution of the Cs from the fibers and pellets depend strongly upon the heat molding

process temperature.

Table 4-2 Relation between the BET surface area, weight reduction, and radioactive Cs concentration of composite fibers

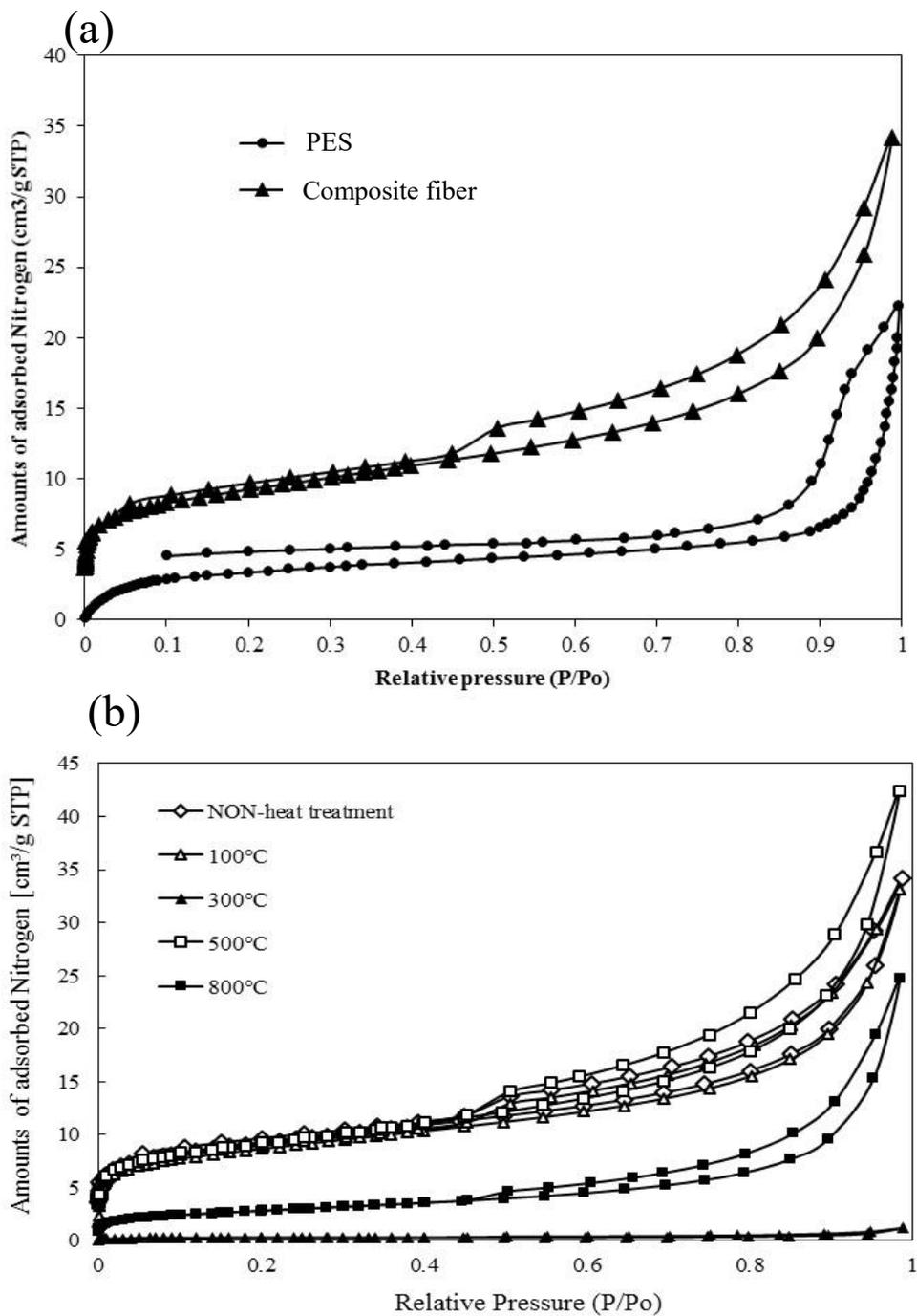| Heat treatment temperature	BET surface area m³/g	Weight reduction %	Adsorbent concentration Bq/kg	
			Before	After
NON-heat treatment	32.5	0	14,000	14,200
100°C	30.6	0.67	14,000	13,100
300°C	0.9	2.17	14,000	15,300
500°C	32.8	30.8	14,000	21,200
800°C	10.1	33.3	14,000	22,400

Figure 4-7 N$_2$ adsorption isotherms of (a) PES and composite fiber and (b) pellets obtained with heating mold treatment at different temperatures.

The rate of elution of the Cs was extremely low for about 0.05% at 300°C relative to 0.95% at 100°C and 2.49% at 500°C. Therefore, it was apparent that the melted PES influenced the Cs release. These results exhibited the same tendency as that for results of the surface area, as presented in Table 4-2. Therefore, for the 300°C treatment, envelopment within the polymer layer was effective for Cs immobilization in the pellet matrix. At 800°C, because heat processing greatly decomposed the PES layer surrounding the zeolite powders, the compacted pellet might be effective to fix the Cs component with the zeolite powder.

Table 4-3 presents results of radioactive Cs release tests conducted for 6 h and 24 h using different Becquerel per kilogram amounts of composite fiber. Here, the table shows radioactive amounts as evaluated at 0 h and at different times before and after water washing. The elution rates (%) are values obtained at 24 h. The elution rates were similar to those found for non-radioactive Cs. For example, the composite fiber had 14,200 Bq/kg before washing for the non-heat treatment sample. The sample was 14,000 Bq/kg at 6 h and 24 h after washing in water. For the pellet sample prepared at 300°C, the value of 15,300 Bq/kg after washing represented almost no change from the 15,500 Bq/kg. However, after 500°C mold treatment, the value of 21,200 Bq/kg was increased to 29,800 Bq/kg at 6 h and 24 h. As shown in Table 4-3, the observed weight reduction was about

30% after the elution tests for 500°C and 800°C, demonstrating that the component remaining after burning the PES from the pellet was water. The radioactive Cs concentration was increased in the pellet. Furthermore, the case at 800°C showed a similar phenomenon. In conclusion, heat molding processing of composite fiber containing Cs efficiently immobilized radioactive Cs in pellets formed at temperatures lower than 300°C. However, at temperatures higher than 300°C, the immobilization effect was less pronounced. Furthermore, results show that heat molding processing reduced the pellet volume. Results presented herein suggest that the composite fiber is a better matrix material for fixing radioactive Cs.
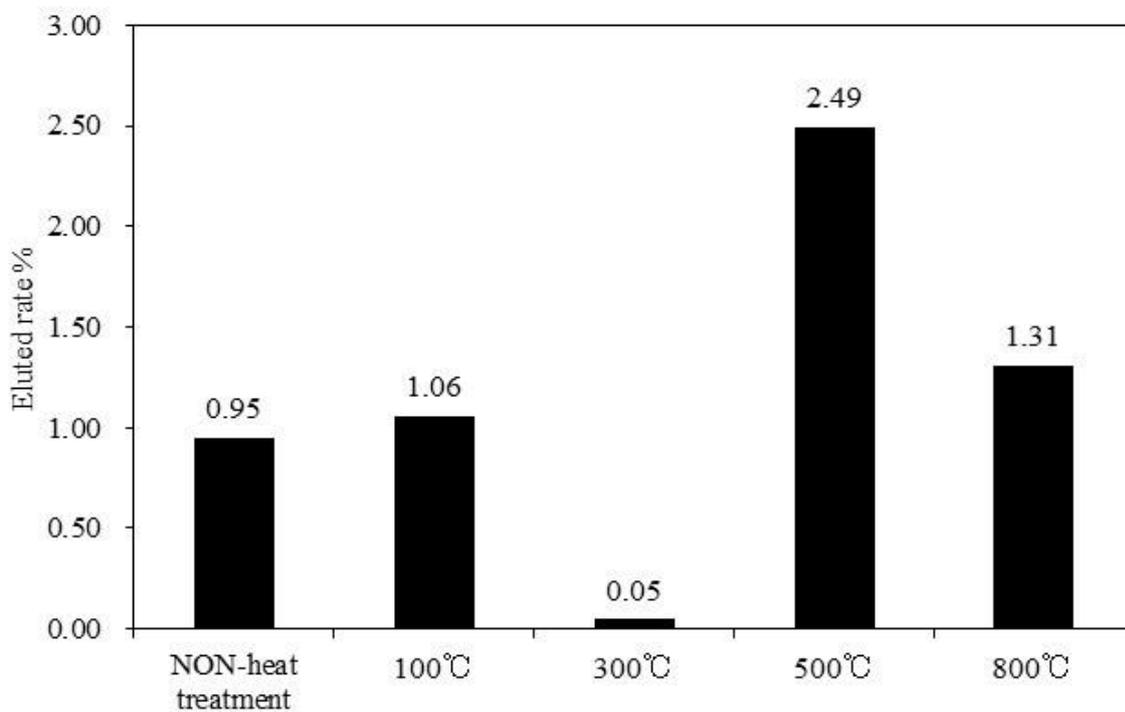
Figure 4-8 Elution rates of non-radioactive Cs from heating mold treatment of composite

fiber.

Table 4-3 Elution rate of radioactive Cs from heat treatment of composite fiber

Sample	Adsorbents concentration of ZCF Bq/kg (weight reduation %)			Elutied solution concentration of water Bq/L		Elution rate %
	0h	6h	24h	6h	24h	
non-heat treatment	14,200	14, 000 (0.1%)	14, 000 (0.1%)	< 1	< 1	0.07
100°C	13,100	13,300 (0.0%)	13,300 (0.1%)	< 1	< 1	0.08
300°C	15,300	15,500 (0.0%)	15,500 (0.1%)	< 1	< 1	0.07
500°C	21,200	29,800 (29.1%)	29,800 (29.2%)	60	62	4.10
800°C	22,400	33,000 (29.8%)	33,000 (30.0%)	25	26	1.73
zeolite	24,500	22,000 (0.1%)	22,000 (0.0%)	274	280	11.42

4.4 Conclusion

This study examined immobilization of radioactive Cs by heated mold treatment of composite fiber for safe storage. The properties of pellets formed at different temperatures using heat molding processing were compared. An effective decrease of the eluted Cs from the pellet was observed at 300°C, suggesting that the melted PES at 300°C enveloped the zeolite, thereby fixing the radioactive Cs. This inference was supported by several observations of the composite fiber pellet surface area, which decreased because of envelopment by the melted polymer surrounding the zeolite powders. Actually, elution of the radioactive Cs was extremely low: less than 0.07–0.08%. Moreover, volume reduction to 1/6 was achieved by heat molding of the composite fiber.

4.5 References

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Chapter 5　Summary

5.1 Summary

The present thesis described preparation and properties of zeolite composite fiber used as radioactive Cs adsorbents. In order to develop such new type of decontamination materials for Fukushima area decontamination process for the radioactive Cs, the decontaminated performance properties were mentioned. In the thesis, successfully applied adsorption process to the radioactive Cs, which was distributed in natural environment, was firstly reported to the treatment of low-level aqueous solution. Also, it was confirmed that the fibrous absorbent was suitable for treating at high alkali condition obtained from extraction of radioactive fly ash in Fukushima. Furthermore, in order to be immobilization in compact form, the fibrous adsorbents were compressed to be pellet form after the adsorption of radioactive Cs.

Chapter 1 introduced the influence of radioactive chemicals emitted from Fukushima Daiichi Nuclear Power Plant Accident and then the problem of radioactive waste the necessity of radioactive Cs adsorbent for the decontamination were described. In chapter 2, preparation and properties of fibrous zeolite composite adsorbents were present for used of radioactive Cs decontamination. It is shown that the resultant fibrous

adsorbents are well composited with zeolite and polyethersulfone (PES) with their

characteristic properties. The porous structure of the composite fibers was suitable to

adsorb radioactive Cs for the purpose of decontamination to reduce the risk in pollutant

area. This is due to that the structure of the composite fibers layers allows water to flow

through the matrix. Therefore, low-level Cs is concentrated in the decontaminant layer

without preventing the water flow toward further downstream and with restraining the

diffusion of radioactive Cs in to natural environments. In chapter 3, the fibrous zeolite-

polymer composites were applied to use for practical decontamination of radioactive

waste water extracted from radio-Cs fly ash. The radioactive Cs waste water obtained

from the extraction of radioactive fly ash was used for the Cs removal tests by zeolite, the

zeolite composite fiber and PB. While the strong alkali pH damaged strongly PB, both

zeolite and the zeolite composite fiber behaved efficient reduction of radioactive Cs by

batch and column sorption processes. Relative to the powder zeolite, the composite fiber

loading 30wt% zeolite had excellent character in the decontamination with longer time

operation. Furthermore, it was confirmed that the adsorption selectivity was obeyed in

Freundlich mechanism, meaning multilayer binding to the zeolite sites in the fibers.

Chapter 4 mentioned compact storage process of radioactive Cs in compressed pellets of

the zeolite composite fibers. The immobilization of the radioactive Cs was carried out by

compressing the fibrous adsorbent to be compact pellet with heated mold treatment in the

range of RT to 800°C. Then, leakage test of Cs from the pellet matrix was performed for

the purpose of long-termed storage. When the properties of pellets formed at different

temperatures were compared for each heat molding process, it was indicated that the

melted PES at 300°C enveloped well the radioactive Cs. The fixing performance of the

radioactive Cs in the matrix was optimized, actually, in the elution tests of the radioactive

Cs leading to be less than 0.07–0.08%. Moreover, volume reduction was 1/6 by the heat

molding of the fibrous adsorbents at 300°C.

Author would like to emphasize practical application of the developed fibrous

composite adsorbents for the decontamination screening facility [1]. As shown in the

pictures of Figure 5-1 (A), the facility was operated in Tomioka town in the periods of

2013-2015 for the decontamination of radioactive Cs waste water in construction spot of

express way load bound for Iwaki city and Sendai city (2013-2015). As seen in the

decontaminated results (Figure 5-1(B)), the emitted radioactive Cs levels were kept lower

than 1 Bq/L, for the three years. This screening facility was strongly contributed in the

radioactive waste water to be lower level.

On the other hand, the fibrous adsorbent was incorporated as column facility for decontamination process of radioactive fly ash in Fukushima by hydrothermal treatment process (Figure 5-2) [2]. The project of the Ministry of the Environment decontamination on 2015, "Verification of removal of radioactive Cs from incineration ash by hydrothermal extraction, volume reduction and stabilization of radioactive substances", was carried out on Hirono town in Fukushima prefecture Figure 5-3 depicts picture of the hydrothermal equipment to the treatment of radioactive Cs fly ash. As shown (Figure 5-4), the adsorption columns demised the radioactive Cs concentration in the extracted water waste, when the circulation time increased. This meant that the fibrous composite adsorbents (B) decontaminated the fly ash extracts to be about 48Bq/L. Although those the pH was over 14. This demonstration project attracted attention and many media participated in the achievements report meeting (Figure 5-5) on November 6th, 2018.
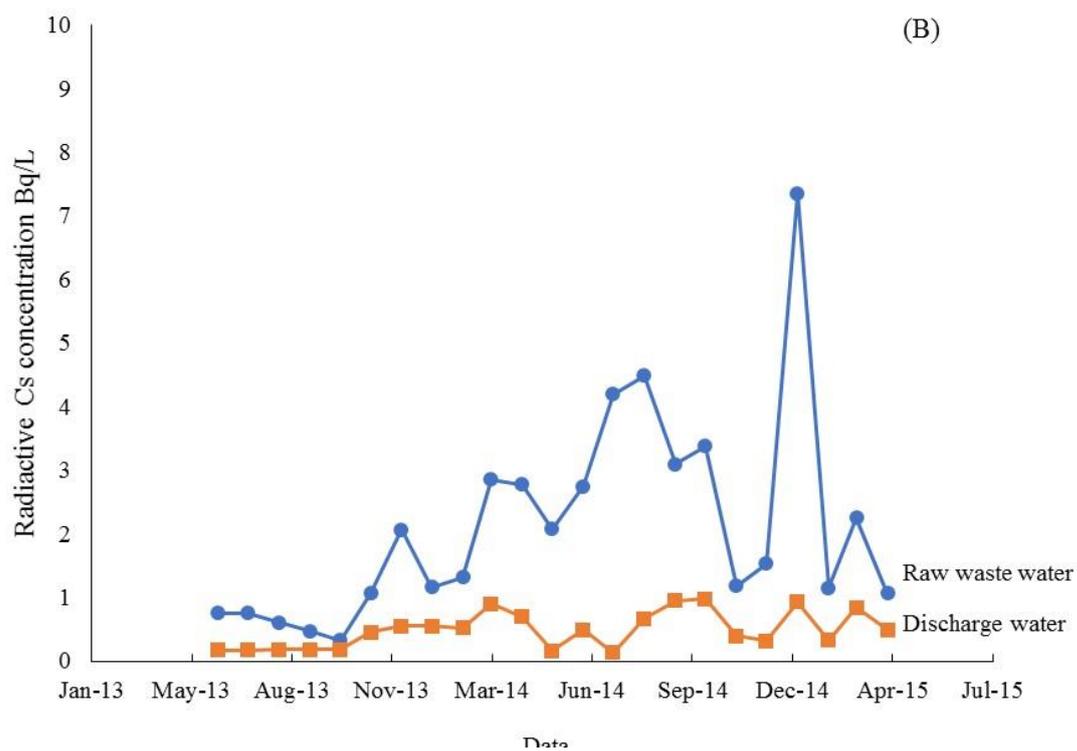
Figure 5-1 The picture of screening facility in Tomioka town (A) apparatus of removal

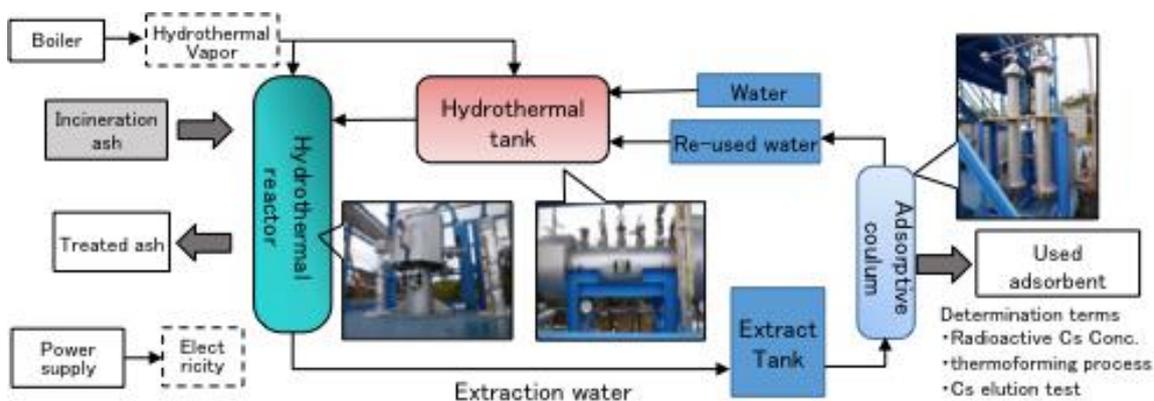radioactive Cs, (B) resultant of radioactive Cs concentration of emitted water.

Figure 5-2 Heat thermal treatment for radioactive ash in corporated with fibrous

composite adsorbent column.

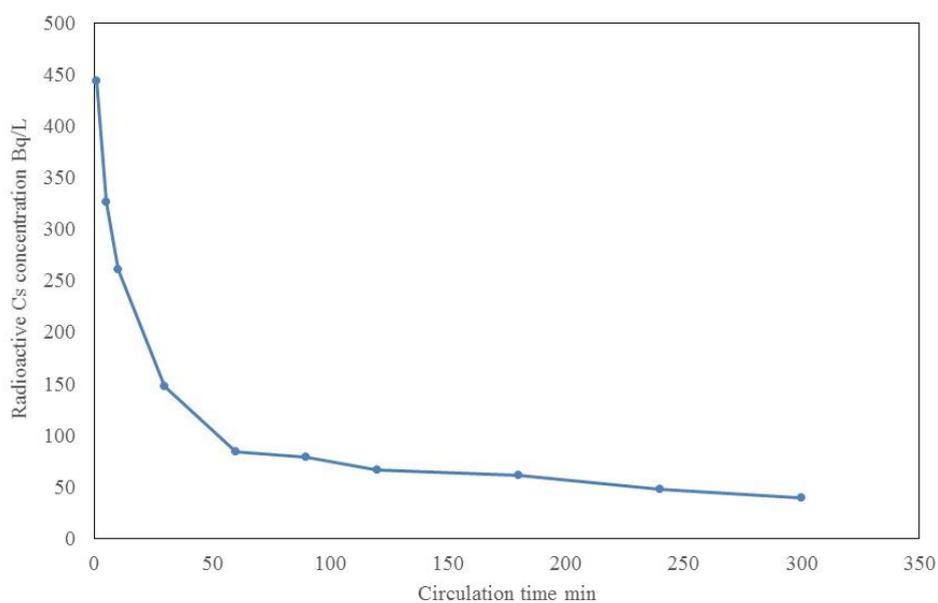

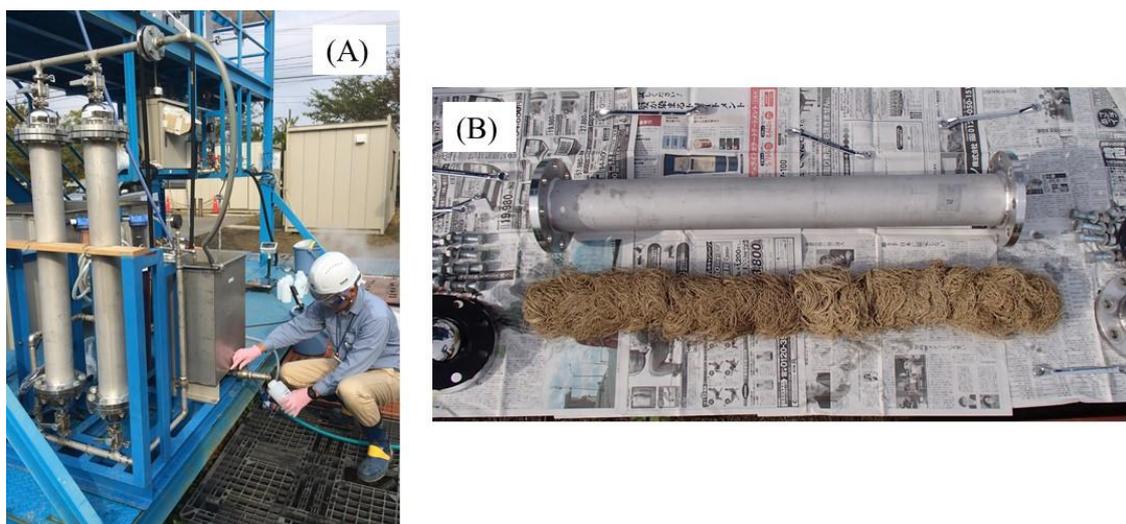Figure 5-3 Picture of heat thermal treatment device.

Figure 5-4 Pictures (A) Circulation adsorption device and (B) adsorption column with packed composite fibers (2kg/8L). The plots of radioactive Cs concentration showed change in the concentration of the circulation time for the column operation. The radioactive Cs at initial stage was 450 Bq/L.

Figure 5-5 Picture of achievements report meeting on November 6th, 2018.

In conclusion, zeolite composite fibers are excellent adsorbents for decontamination of radioactive Cs. Because of the excellent performance as introduced in this thesis, it will be applied that this strongly contribute several decontaminated problems in Fukushima.

5.2 Reference

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List of Achievements

Publication Papers

1. Decontamination of Extra-Diluted Radioactive Cesium in Fukushima Water Using

   Zeolite-Polymer Composite Fibers

   Takaomi Kobayashi, <u>Masaru Ohshiro</u>, Kohtaroh Nakamoto, Syuji Uchida

   Industrial & Engineering Chemistry Research, 55 (2016), pp6996-7002

2. Fibrous Zeolite-Polymer Composites for Decontamination of Radioactive Waste

   Water Extracted from Radio-Cs Fly ash

   Masaru Ooshiro, Takaomi Kobayashi, Shuji Uchida

   International Journal of Engineering & Technical Research, 7 (2017), pp1-6

International and National Conference Proceeding

1. The 2rd International GIGAKU Conference in Nagaoka, Japan, **DECONTAMINATION OF RADIACTIVE CESIUM IN NATURAL ENVIROMENT FUKUSHIMA BY USING ZEOLITE-POLYMERR COMPOSITE FIBERS,** <u>Masaru Ohshiro</u>, Syuji Uchida, Takaomi Kobayashi, (June 2013).

2. The 5th The Society for Remediation of Radioactive Contamination in Environment in Fukushima, Japan, **Compact storage of radioactive cesium in compressed pellets of zeolite composite fibers,** <u>Masaru Ohshiro,</u> Takaomi Kobayashi, Shuji Uchida (July 2016).

3. The International Conference of Science of Technology Innovation in Nagaoka, Japan, **IMMOBILIZATION OF RADIOACTIVE CESIUM IN COMPRESSED PELLET FORMS OF ZEOLITE COMPOSITE FIBERS FOR COMPACT STORAGE PRESERVING,** <u>Masaru Ohshiro</u>, Takaomi Kobayashi, Syuji Uchida, (January 2017).

Patents

1. 「放射性セシウム吸着繊維及びその製造方法」（特願 2012-134813）

2. 「放射性セシウム吸着繊維及びその製造方法並びに放射性セシウム吸着
繊維を用いた水中の放射性セシウム濃度の検出装置」（特願 2012-134813）

「RADIOACTIVE CESIUM-ADSORBING FIBER AND MANUFATURING
METHOD AS WELL AS DEVICE FOR DETECTING RADIOACTIVE
CESIUM CONCENTRATION IN WATER USING RADIOACTIVE CESIUM-
ADSORBING FIBER」（PCT/JP2013/066478）

3. 「焼却飛灰中に含まれる放射性セシウムの固定化方法及び固定化剤」
（特願 2012-245067）

4. 「焼却飛灰中に含まれる放射性物質の抽出及び抽出方法」
（特願 2014-211417）