Original

Removal of Radioactive Cs from Nonwoven Cloth with Less Waste Solution Using Aqueous Sodium Metasilicate

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Summary

Remediation of nonwoven cloth contaminated with radioactive material such as ^{137}Cs is important for the reuse of protective garments. Here, we report the effectiveness of aqueous sodium metasilicate prepared with a microbubble crushing process (SMC) in the removal of radioactive ^{137}Cs from nonwoven cloth. The ^{137}Cs removal ratio obtained using SMC was found to be 78%, and multiple washings at low SMC concentrations were effective. In addition, the volume of the waste solution could be reduced by neutralizing the SMC and using gelation to remove the radioactive material.

Key Words: (Standardized) Cesium-137, Decontamination, Accident, Nuclear criticality safety

1. Introduction

The accident at the Fukushima Dai-ichi nuclear power plant following the Great East Japan Earthquake resulted in the dispersal of radioactive Cs into the environment, which contaminated an extensive area of soil. Various decontamination methods have been developed and applied in Fukushima Prefecture,[1] but we still need to determine the optimum methods for the specific types of contamination being treated.

Radioactive Cs is adsorbed on soil particles through ion exchange with potassium.[2,3] The cleaning of protective fabric contaminated by such soil is difficult, and currently, the contaminated cloth is simply put into storage. Finding appropriate storage facilities for used protective fabrics is proving to be difficult, so it would be desirable to reduce the quantity of such fabrics. Furthermore, the quantities of contaminated fabric are so vast in some districts of eastern Japan, including Fukushima Prefecture, that storage is not practical. Therefore, a new cleaning detergent that can effectively treat the fabric is needed. However, the waste solution produced by washing contaminated fabrics also presents a problem, since reducing its volume by evaporation is not practical owing to the large specific heat of water. Thus, a facile method of reducing the volume of waste solution is also needed.

This research focuses on aqueous sodium metasilicate as a new detergent and possible decontamination agent. Since aqueous sodium metasilicate is not a surfactant, it has a low environmental load and does not display foaming characteristics. It can be used with hard, soft, or sea water, and furthermore, it is a “peeling detergent” in terms of its cleaning characteristics, which differentiates it from dissolving detergents such as organic solvents. As a peeling detergent, it is suitable for foaming, jet streaming, and high-pressure, ultrasonic-wave, and spray cleaning. The microbubble crushing process[4,5] can also be used to suppress precipitation during long-term storage.[6]

For this research, the treatment of nonwoven fabrics is considered with respect to the waste solution produced. Nonwoven fabrics such as Tyvek products are generally used as protective wear for the handling

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of contaminated dust and soil, since they help protect against dust particles and are easy to dispose of. While they are currently in use in work areas around the Fukushima Dai-ichi nuclear plant because of these qualities, methods for cleaning contaminated items should also be evaluated in order to reduce the total amount of radioactive ^{137}Cs. For reference purposes, we roughly estimate the current amount of waste created per day by nonwoven cloth protective garments as follows. If we assume that in 1 day 1,000 people use and dispose of such garments, then in just 1 day, approximately 150 kg of waste products are accumulated. This amount of waste cannot simply be ignored.

In order to decrease the volume of waste solution produced, coprecipitation can be used, since sodium metasilicate turns to a gel that can trap the cesium when neutralized with acid.[7)] Coprecipitation following the gel formation can be used to separate the ^{137}Cs gel from the soil, yielding a decontaminated waste product.

2. Experimental methods

2.1 Preparation of aqueous sodium metasilicate

A 0.47 mol/kg solution of sodium metasilicate nonahydrate ($Na_2O_3Si \cdot 9H_2O$) was prepared by dissolution in filtered water (manufactured using G-20B from Organo Corporation). The microbubble generator (capable of generating > 20,000 microbubbles per mL) was manufactured by Kyowa Engineering and used to interfuse microbubbles into the solution. Ultrasonic irradiation (40 kHz, ultrasonic wave generator UT-1204U and ultrasonic transducer UI-12R3, Sharp Corporation) was employed to crush the bubbles, and the resulting solution, SMC which is an abbreviation of "aqueous Sodium metasilicate prepared with a Microbubble Crushing process", was used as the nonsurfactant aqueous detergent. Purified water and aqueous sodium hydroxide with the same pH as SMC (pH = 13.1) were prepared for comparison.

2.2 Cleaning method

While microbubbles can only remain in water for several minutes depending on their individual diameters and buoyancy, it is known that they can remain in such environments for longer periods if their sizes are shrunk through the use of ultrasound treatment.[8)] Ultrasound pretreatment of aqueous sodium metasilicate to form SMC and reduce the bubble size does not decrease the eduction rate of aqueous sodium metasilicate and offers the possibility of sustained cleansing. In this experiment, we conducted a cleaning test in a standing solution, rather than in an agitated solution, in order to focus on the chemical cleansing effects due to the synergy between the aqueous sodium metasilicate and microbubbles rather than physical cleansing effects.

Pieces of nonwoven cloth (made of polypropylene) used in farm work that were exposed to the fallout from the nuclear accident in Fukushima Prefecture were used as the specimens for cleaning. The average weight of the nonwoven cloth to be cleaned was 2.65 g, and the average amount of ^{137}Cs exhibited approximately 1633 Bq/sample (616,226 Bq/kg) of radioactivity. The nonwoven cloth samples were immersed in 100 mL of the solution mentioned above at several concentrations for 20 hours. A total of 28 samples were prepared and placed into four groups of 7 samples each. One group was washed in water, and the remaining three were washed with solutions of SMC in concentrations of 1, 10, and 100 wt%. To examine the effects of multiple washings, samples were tested after 6 hours of immersion for second and third washes. After these immersion tests, the nonwoven cloth specimens were dried at 40°C for 40 hours until they were sufficiently free of moisture. In order to reduce the volume of the waste solution, hydrochloric acid (HCl) was added to neutralize the detergent solution after washing, which resulted in gelation. Then, the gel and clear supernatant were separated by filtration, and the radiation intensity (counts per second, cps) of the gel and supernatant were measured.

In addition, we conducted neutralization tests on standardized ^{133}Cs solutions (Wako, 030-21341) to form gels using potassium ion electrodes (LAQUA F-73, 8202-10C, mfg. by Horiba) to provide a basis of comparison for evaluating the volume reduction. The use of a potassium ion electrode makes it possible to quantify the concentration of ^{133}Cs ions. In this experiment, for comparison, we used a solution containing dissolved aqueous sodium metasilicate (0.47mol/L, pH=13.1) and an SMC solution and measured the ^{133}Cs ion concentration by performing concentrated HCl (0.36 g, 3.6 g, and 36 g) titration three times respectively, hypothesizing that some ^{133}Cs ions would remain in the solution.

2.3 Radiation measurement

The background radiation intensity of these nonwoven cloth specimens was measured using the germanium semiconductor detector at the Radioisotope Research Center, Kyoto University. The main unit of the detector is a high-purity germanium detector (GMX-18200-S manufactured by EG & G Ortec), and the size of the germanium crystal is 10^2 cm^3 with a relative efficiency of 22.3% (efficiency ratio of a 3” × 3” NaI (TI) (76 × 76 mm) crystal relative to that of the ^{137}Cs 662 keV gamma ray). The entrance window is a 0.5-mm-thick beryllium plate, which allows for the measurement of X-rays of energy 3 keV or higher, as well as high-energy gamma rays. The energy resolution was 0.54 keV for ^{55}Fe 5.9 keV (Mn Ka) and 1.8 keV for ^{60}Co 1.33 MeV gamma rays. A specific container (100 mL) was used for analysis of the nonwoven cloth specimens. The removal ratio was determined as the ratio of the intensity of the sample after and before immersion as following calculation.

$$\text{Removal ratio [\%]} = \frac{\textit{After immersion [cps]}}{\textit{Befor immersion [cps]}} \times 100$$

3. Results and discussion

To investigate the cleaning performance of SMC (Fig. 1), the performance of 1, 10, and 100 wt% solutions of SMC and pure water were compared. The respective radiation intensities were measured, and the removal ratios were calculated. The average removal ratios for the respective samples and their standard deviations are plotted in Fig. 1.

Almost no ^{137}Cs was removed with pure water, as expected, but significant decontamination was achieved as soon as SMC was introduced. Since the nonwoven cloth samples were actually used in agricultural fields, they contained traces of fertilizers and other organic materials from areas where relatively high levels of ^{137}Cs were detected. As mentioned previously, the sodium metasilicate detergent used for this technique has generally been used because of its demonstrated capacity for breaking down organic materials via saponification, which results from its alkaline nature. We anticipate that we will be able to increase the efficiency of this material through the use of microbubbles and ultrasound treatment, because the organic components such as sebum and oil that are contaminated with ^{137}Cs can likely be eluted from nonwoven cloth owing to the alkalinity of SMC. The average removal ratios for 1, 10, and 100 wt% SMC were 45%, 60%, and 78%, respectively (Fig. 1). Even with only 1 wt% SMC, the removal ratio was 60% of that achieved with 100 wt% SMC, which is important if the amount of detergent used is to be reduced.

In order to study the effects of performing multiple washings, the 1 wt% solution of SMC was used (Fig. 2). The samples were washed three times, and the removal ratio (we measured the radiation intensity of each sample beforehand as a standard procedure) for each wash was determined. Furthermore, the radiation intensity of the waste solution and nonwoven cloth specimens were evaluated afterward to determine the amount of ^{137}Cs transferred. The removal ratios for the first, second, and third washes were 45%, 35%, and 21%, respectively, yielding overall removal ratios of 64% for the second wash and 71% for the third wash. This indicates that even at a concentration of 1 wt%, significant decontamination of the nonwoven cloth can be achieved with multiple washings.

In addition, the average amount of radiation from the initially contaminated materials was approximately 1,633 Bq and cleaning using 100 wt% SMC reduced this

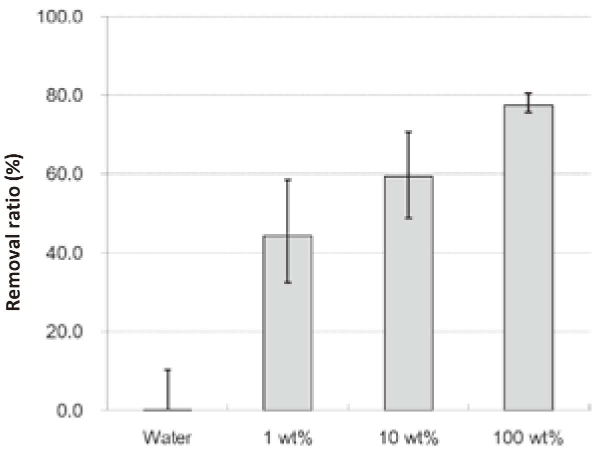

Fig.1 ^{137}Cs removal ratio obtained using purified water and SMC (1 wt%, 10 wt%, and 100 wt%) to decontaminate nonwoven cloth

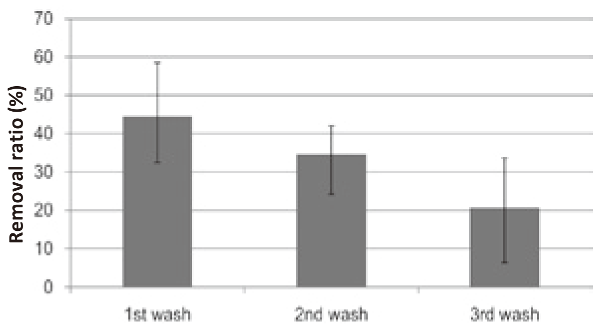

Fig.2 ^{137}Cs removal ratio obtained using 1 wt% SMC (multiple washes) for decontamination of nonwoven cloth

Table 1. Residual 133Cs ion concentration after aqueous sodium metasilicate and SMC neutralization with concentrated HCl (0.36 g, 3.6 g, and 36 g) determined by potassium ion conversion

Amount of concentrated HCl (g)	Concentration (ppm)	
	Aqueous sodium metasilicate	SMC
0.36	7.2	0.4
3.6	7.5	0.4
36	4.4	0.0

SMC; aqueous sodium metasilicate prepared with a microbubble crushing process

value to approximately 346 Bq. When other samples including clay particulate in addition to the usual contaminants were cleaned with SMC and water, 1 wash cycle using 100 wt% SMC resulted in approximately 1,292 Bq/kg in using water, and 3 wash cycles using 1 wt% SMC resulted in a ^{137}Cs radiation level of approximately 122 Bq/kg in the third using water. As such, we conclude that it is necessary to reduce the volume of waste solution less than 100 Bq/kg when washing using water.

Next, the reduction in waste solution volume obtained by using SMC was investigated. The radiation intensity of the waste solution after washing was 2,597 cps, and the separated gel and clear supernatant solution showed values of 1,904 and 167 cps, respectively. This confirms that the ^{137}Cs was captured in the gel after coprecipitation. In terms of becquerels, this represents a decrease from the original radiation intensities of 1,292 Bq/kg and 122 Bq/kg in the gel and supernatant to approximately 78 Bq/kg and 7.2 Bq/kg, respectively. This radioactivity level could decay to the levels found in the natural environment within a reasonable time. Thus, these results indicate that reuse of the water would be possible, and the volume of waste material will be small. In addition, because the gel is composed of an alkali silicate, it can be easily vitrified by heating.

Finally, in the test involving HCl reduction of standard ^{133}Cs solutions, the results of which are displayed in Table 1, we observed that the typical concentration of sodium metasilicate initially contained in the aqueous solution (approx. 7 ppm) was retained almost entirely in the solution after conversion. However, retained almost entirely in the solution after conversion. However, when SMC was used, we observed reductions in the eduction rates for the sodium metasilicate (through the use of the gel) and the ^{133}Cs ions less than 0.4 ppm. As mentioned previously, this resulted in a reduction across the board in the amount of solution used to wash the nonwoven cloth, which we recognize as a special feature of SMC. In summary, the results of this study demonstrate that aqueous sodium metasilicate is a promising candidate for the decontamination of polluted nonwoven cloth.

4. Conclusions

In order to examine the cleaning performance of aqueous sodium metasilicate treated by crushing microbubbles (SMC), we compared the radioactivity of the waste solution before and after the washing of contaminated nonwoven cloth. The ^{137}Cs particulate attached to the nonwoven cloth was effectively removed by SMC cleaning, and even after cleaning, the remaining dissolved aqueous sodium metasilicate from the SMC had better treatment capacity (after neutralization) than the standard aqueous solution. Thus, the use of SMC could significantly contribute to the decontamination work currently being undertaken in urban areas as well as in forests, where decontamination cannot be performed simply using water.

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