

STUDY ON REMOVAL OF CESIUM AND STRONTIUM FROM MARINE AND LAKE MUD

Keiichiro Shibata¹, Hidenori Yoshida² and Naomichi Matsumoto³

¹Graduate School of Engineering, Kagawa University, Japan

^{2,3}Faculty of Engineering, Kagawa University, Japan

ABSTRACT: The serious nuclear disaster in the Fukushima Daiichi nuclear energy plant was occurred by the Tsunami on March 11, 2011. The radioactive materials leaking from the power plant were widely diffused in and around Fukushima prefecture including the Pacific Ocean by wind, rain and river flow. It can't be always said that there is no risk of the condensation of radioactive materials in human body by ecological chain if fish take in radiation in the ocean contaminated by the radioactive materials. However the decontamination is less-advanced. The establishment of a new decontamination method is urgent need. Thus, in this study, it is aimed to establish a new decontamination technology of radioactive materials deposited on seabed or lake bed. In particular, the new adsorption material which can adsorb radioactive materials is developed and the new method which can move them from the bottom sediment to the adsorption material is proposed. It is expected that the proposed method and the developed adsorption material are efficient to remove radioactive materials from seabed or lake bed when they are expansively applied to the real decontamination.

Keywords: aeration, adsorbent, decontamination, radioactive material

1. INTRODUCTION

The serious nuclear disaster in the Fukushima Daiichi nuclear energy plant of the Tokyo Electricity Power Company was occurred by the tsunami which was caused by the Great East Japan Earthquake on March 11, 2011. The radioactive materials leaking from the power plant were widely diffused in and around Fukushima prefecture including the Pacific Ocean by wind, rain and river flow. Though more or less 5 years have passed since the accident, the target of decontamination is still limited to land compared with marine and river. Actually, the appropriate decontamination method for hydrosphere is not established. As the example of comprehending current situation, the radiation dose of radioactive cesium has been measured by the Ministry of the Environment are published as in [4].

The investigations of radiation dose are conducted at the bottom sediment of river, lake and seacoast. First, as for river, the measurement points are 118 places in Fukushima, Miyagi, Gunma, Ibaraki and Chiba prefectures. The measured results of radiation dose in 21 places exceeded 200 Bq/kg and those in 6 places exceeded 500 Bq/kg. Generally, the value of radiation dose in terms of radioactive cesium around downstream basin is larger than that around upstream basin, which means that the radioactive material moved from river to marine. Secondly, as for lake, the measurement points are 164 places in Fukushima, Miyagi, Gunma, Ibaraki, Tochigi and Chiba

prefectures. The storage reservoirs and dams are the targets of investigation in the case of the lake. The measured results of the radiation dose in a number of places exceeded 50,000 Bq/kg in Fukushima prefecture. The accumulation of radioactive cesium in the enclosed water area like the storage reservoirs is significant compared with that in other place. The decontamination of lake mud is also urgent task from the light of cesium concentration. Thirdly, as for seacoast, the measurement points are 32 places in Fukushima, Miyagi and Ibaraki prefectures. The measured results of radiation dose in 10 places exceeded 200 Bq/kg. Especially, the concentration of radioactive cesium is increasing in Sendai bay, which indicates that the radioactive pollution of marine is progressing. From these facts, it is noticed that the pollution is widespread and the decontamination is not progressing in hydrosphere.

Alternatively, the progress of the pollution may lead to cause a negative effect on ecology because the ecological chain consists in hydrosphere. For example, the survey results of radiation-contaminated in aquatic product are shown as Table. 1 which is published by Fisheries Agency as in [3]. Table. 1 shows that the high detection value of cesium are extracted from a various types of fish. The total value of cesium is equal to the sum of cesium-134 and cesium-137. These values exceed 100 Bq/kg that is configured as the upper limit of common food. It can't be always said that there is no risk of the condensation of radioactive materials in human body by ecological chain if fish

take in radiation in the ocean contaminated by the radioactive materials. Though a number of media often feature the contents of radioactive cesium, the strontium-90 should be paid attention in case of considering its features.

The feature of strontium-90 is described further below. Simply stated, the strontium-90 has a habit similar to calcium. Therefore, the strontium-90 is absorbed into the bones and hardly egested once it is taken in human body. The decontamination of mud in hydrosphere makes little headway despite the existence of these risks since the decontamination of mud in hydrosphere has the annoying problems of disposal and diffusion of dredged soil in dredging as in [2]. As for past studies in terms of decontamination in hydrosphere, for example, there is the method in which the polluted mud is dredged. Concretely speaking, the bottom deposit is resuspended by a jet blast. The resuspended solids which is stirred up by the jet blast is collected in fluid. At the same time, aerobic is promoted by the stirring. However, in this method, there is the view that the radioactive materials can be diffused widely in hydrosphere. Additionally, it will be difficult to secure intermediate storage facilities enough for hydrosphere. Thus, in this study, the decontamination method for radioactive materials without dredging mud in marine and lake is proposed with keeping in mind of the shortage of the intermediate storage facilities for the sand polluted by radioactive materials.

Table 1 Radiation-contaminated aquatic products

Fish species	Catch area	Release date	Total value of cesium (Bq/kg)
Gin-buna	Tega pond	H27.4.3	110
Char	Kamisawatari river	H27.4.17	130
Char	Nuno river	H27.5.20	110
Land-locked trout	Ishida river	H27.6.17	180
Ayu	Hirose river	H27.7.8	100
Eel	Tega pond	H27.7.24	100
Ayu	Abukuma river	H27.9.2	110
Carp	Tega pond	H27.9.10	110
Char	Horonai swamp	H27.9.24	240
Land-locked trout	Syakadou river	H27.9.25	160
Char	Amato river	H27.9.30	110
Broun trout	Cyuuzenji lake	H27.10.9	120
Land-locked trout	Gotou river	H27.11.5	120

2. THE TARGETED MATERIAL FOR EXPERIMENT

In this study, the circumstances of lake or marine are reproduced by experiments. A wide variety of radioactive materials are released by the accident of the Fukushima Daiichi nuclear energy plant. In the experiments, the cesium and strontium are target materials which are moved from the mud sand to an adsorbent material in the solution, because two materials are released vigorously and their half-life are relatively long. The properties of cesium and strontium are explained in below since it is necessary to grasp their features for the experiment.

2.1 Feature of cesium

The cesium is a fusible alkali metal element. It exists as a monovalent positive ion in solution. The cesium which is spread from the Fukushima Daiichi nuclear power plant is captured by the negative charge in soil as well as an exchangeable base such as the potassium. The cesium has several isotopes. Among those, the cesium-137 is the main target of decontamination. The half-time of cesium-137 is about 30 years. The cesium-137 changes to the stable barium-137 by releasing gamma ray after releasing beta ray. The cesium has the chemical properties similar to those of potassium. In the case of plant, the cesium is absorbed from the root of plant. Meanwhile, in the case of animal, it is absorbed through water and food. Once the cesium is absorbed in human body, it spreads throughout the body. However, the cesium is easily discharged to the outside of the body with urine and sweat.

2.2 Feature of strontium

The strontium is a fusible alkali-earth metal. It exists as a divalent positive ion in solution. The strontium which is spread from the Fukushima Daiichi nuclear power plant is also captured by the negative charge as well as an exchangeable base such as calcium. The strontium also has several isotopes. Among those, the strontium-90 is representative for the decontamination target. The half-time of strontium-90 is about 29 years. The strontium-90 changes to the stable zirconium-90 by releasing beta ray twice. The cesium has the chemical properties similar to those of zirconium. Thus, the strontium is absorbed into bones, which is different behavior from that of cesium. Therefore, it is took for granted that the strontium is hardly discharged to the outside of the body and accumulated in the body.

From the above facts, it can be said that the strontium is threat to human rather than the cesium and should be decontaminated as quickly as possible.

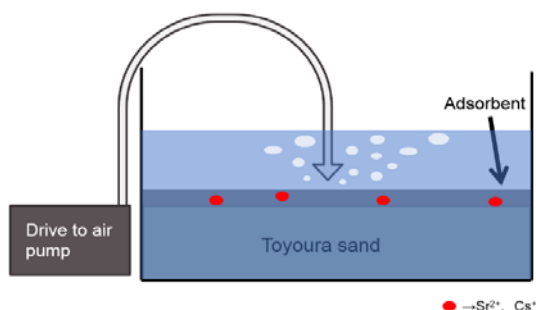


Fig.1 Schematic of aeration test

3. EXPERIMENT AND ANALYSIS

There are two issues in terms of the decontamination in hydrosphere, the non-proliferation and volume-reduction of radioactive materials. In this study, the new adsorption material which can adsorb radioactive materials is developed and the new method which can move them from the bottom sediment to the adsorbent is proposed so as to solve the issues. To be more precise, the new adsorption material which consists primarily of hydroxyapatite (HAp) is developed and the aeration is employed for the convection of fluid. The HAp is made of burnt fish bones. The adsorption tests were conducted to confirm the adsorption property of the HAp. First, 5.0 mg of strontium is added into 300 mL of pure water or sodium chloride fluid. The sodium chloride is 3 % of concentration in the solution to be close to that in seawater. Secondly, 6~7g of the HAp which is set in the net for drain is soaked in the pure water or the sodium chloride fluid. There is two types of specimens; one is uncontrolled immersion test and another is stirred by a screw agitator during the immersion so as to take the flow in river or marine into account. The immersion time is 24 hours. It is noted that same tests for cesium were not conducted since both cesium and sodium belong to alkali metal which makes it difficult to analyze the quantity of cesium by AAS (Atomic Absorption Spectrometer). Table 2 shows the test results of adsorption test for HAp, respectively. The HAp was employed as an adsorbent because it is confirmed that the HAp has enough adsorption performance. The adsorption tests by which cesium and strontium are adsorbed are conducted with using the HAp and the

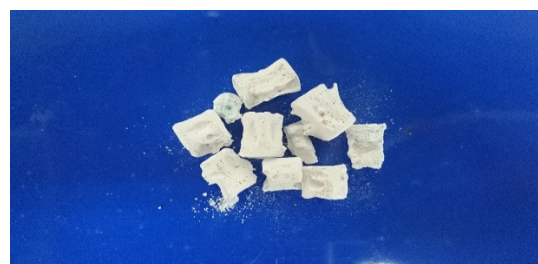


Fig. 2 Hydroxyapatite (Bone HAp)

Table 2 Adsorption test for HAp (1 day)

proposed method to examine their validity and availability.

First, Toyoura sand is laid at the bottom of cylindrical chamber to simulate the decontamination in marine or lake. In the test, 200 g of Toyoura sand which has more or less uniform size of grains is utilized so as to keep the reproducibility of tests. Secondly, 38.1 mg of cesium or 5.0 mg of strontium is added into the sand, and the HAp sheet and the convection device are set on the sand (see Fig.1). Subsequently, pure water is poured into the chamber to simulate the decontamination in lake, and sodium chloride fluid is poured into the chamber to simulate the decontamination in marine. As for specimens, three types of the specimen are prepared to evaluate the validity and availability of contamination; one is the specimen in which only the HAp sheet is set, another is the specimen in which the HAp sheet and the convective device are set, and the other is the specimen in which nothing is set. And they are left for a given length of time. After the tests, the cesium or strontium contained in Toyoura sand is extracted by washing the sand. For the extracted water solution, the cesium is analyzed by AAS to measure its remained amount of the pure water, and the strontium is analyzed by ICP-AES (Inductively-coupled Plasma Atomic Emission Spectrometry) to measure its remained amount of the sodium chloride solution. The availability of convective method and adsorption material are examined by the comparison of remained amount of three type specimens.

	Residual ratio (%)	
	Pure water	Sodium chloride fluid
Screw	4.39	26.51
Immersion	16.87	17.81

4. THE CONFIRMATION OF ADSORBENT OF MATERIALS TO HAp

In the previous chapter, not the adsorbed amount of the cesium or strontium in the HAp sheet but their remained amount in the solution is measured so as to confirm their adsorbed amount in the adsorbent quantitatively. It is supposed that

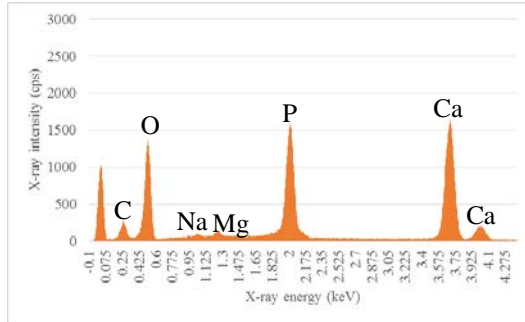


Fig. 3 Spectrum for added nothing specimen

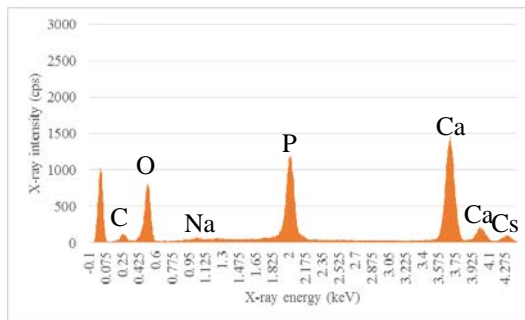


Fig. 4 Spectrum for added cesium specimen

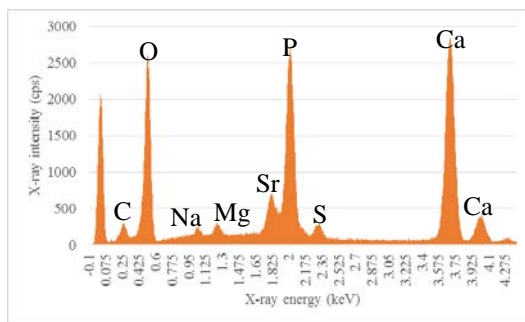


Fig. 5 Spectrum for added strontium specimen

the adsorbed amount of adsorbent is equivalent to their added amount minus their remained amounts, because it is extremely difficult to be derived the cesium or strontium which is adsorbed to the adsorbent once. Though it is difficult to estimate the cesium or strontium which is adsorbed to the adsorbent quantitatively, it is important to examine that not the untested adsorbent but the tested adsorbent contains them.

Therefore, in this chapter, the cesium or strontium which is adsorbed to the adsorbent is analyzed qualitatively and the movement from the solution to the adsorbent is confirmed.

The existence of cesium or strontium in or on the HAp is examined by a SEM-EDX facility. The SEM-EDX is the measurement device which consists of Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy. The HAp which is utilized in the aeration test explained in the previous chapter is target of the analysis by the SEM-EDX. In the analysis, 300 mL of pure water is poured into a cylindrical container, and 38.1 mg of cesium or 5 mg of strontium is added to it. After that, 10 pieces of the bone HAp are soaked in the solution. In the analysis, there are three specimens in which cesium, strontium or neither of them is added into the pure water, respectively. The each result is shown in the following tables and the figures of spectrum. The vertical axis in the graph is for the X-ray intensity of each element, and the horizontal for the X-ray energy of each element. The elements in sample are shown as the wavelength. The elements which the wavelength is similar in are recognized at fault. In that case, the same element is shown as the different element at multiple sites. However it is no problem because the highest intensity of the element is recognized as the wavelength of the element. The calcium and oxygen are detected

Table 3 Analysis result for added nothing specimen

Element	Mass concentration (%)	Atomicity concentration (%)
C	7.15	15.05
O	38.06	60.13
Na	0.29	0.32
Mg	0.42	0.43
P	12.20	9.95
Ca	22.39	14.12

Table 4 Analysis result for added cesium specimen

Element	Mass concentration (%)	Atomicity concentration (%)
C	2.79	9.19
O	23.48	58.11
Na	0.26	0.44
P	9.18	11.74
Ca	19.36	19.12
Cs	4.68	1.39

Table 5 Analysis result for added strontium specimen

Element	Mass concentration (%)	Atomicity concentration (%)
C	3.87	9.25
O	35.11	62.97
Na	0.42	0.52
Mg	0.50	0.59
P	10.82	10.03
S	0.92	0.82
Ca	19.85	14.21
Sr	3.99	1.31

highly at the three spectrums. The reason is which the analyzed sample is the fishbone. Alternatively, the detected elements by SEM-EDX are shown by the mass and atomicity concentration in the tables. First, Table 3 and Figure 3 are the analysis results of specimen in which nothing is added. It is took for granted that the neither of cesium or strontium is detected qualitatively and quantitatively.

Secondly, Table 4 and Figure 4 are the analysis results of specimen in which cesium is added. The adsorption of cesium is confirmed by the test results. The analysis results of specimen which the strontium is added are same as that of the cesium (See Table 5 and Figure 5). It is confirmed that the cesium and strontium are adsorbed to the HAP by these test results.

5. TEST FOR CESIUM ADSORPTION

The results of the immersion tests in which the adsorption performance of cesium by the HAP sheet is examined with changing the immersion time are shown and are discussed. In the tests for cesium, only pure water is utilized as for the solution. The remained amount of cesium in the water after 4 weeks and 13 weeks from the start of immersion are shown in Table 6. Figs. 6 and 7 show the ratio of the remained amount of cesium to the initial additive amount of cesium after 4 weeks and 13 weeks from the start of immersion, respectively. The ratio is decreased during 9 weeks of their interval. However, not only the test with both the sheet and the aeration but also the test

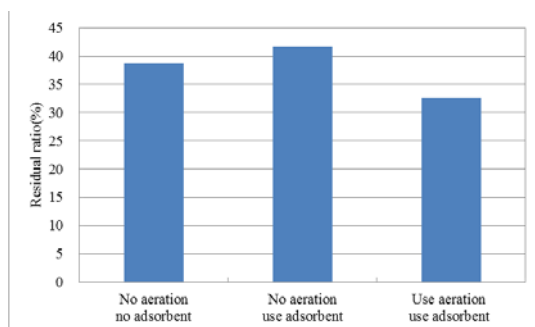


Fig.6 Residual ratio of cesium for 4 weeks.

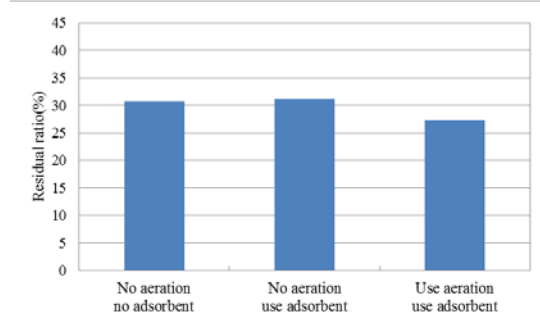


Fig.7 Residual ratio of cesium for 13 weeks.

with neither of them show the similar tendency in terms of the decrease of the ratio. Such a phenomenon as the decrease of ratio may be caused by the change of temperature and humidity. Since the reason why the remained amount of cesium in the water for the specimen left uncontrolled is decreased with time is unclear, the effectiveness and availability of the sheet or the aeration are not discussed. Hereafter, the additional tests such as the increase of specimens under varied conditions and the extension of immersion time are required.

Table 6 Test results for cesium

	4 weeks	
	Remained amount (mg)	Residual ratio (%)
No aeration no adsorbent	14.76	38.74
No aeration use adsorbent	15.85	41.61
Use aeration use adsorbent	12.42	32.60
13 weeks		
No aeration no adsorbent	11.70	30.70
No aeration use adsorbent	11.87	31.15
Use aeration use adsorbent	10.44	27.40

6. TEST FOR STRONTIUM ADSORPTION

The results of immersion tests in which the adsorption performance of strontium by the HAP sheet is examined with changing the immersion time are shown and are discussed. In the test for strontium, pure water and sodium chloride solution are utilized as the solution. The tests time are 1 week, 4 weeks and 13 weeks. The other conditions of strontium adsorption test are same as those of cesium adsorption test. The remained amount of strontium in the solution after 1 week, 4 weeks and

13 weeks from the start of immersion are shown in Tables 7, 8 and 9. Figs. 8, 9 and 10 show the ratio of the remained amount of strontium to the initial additive amount of solution after 1 week, 4 weeks and 13 weeks from the start of immersion, respectively. According to the figures, the residual ratio of strontium is relatively low in the case of 4 weeks immersion test with pure water and extremely low in the case of 13 weeks immersion test with pure water. The residual ratio decreases with increasing test time in the pure water case. On

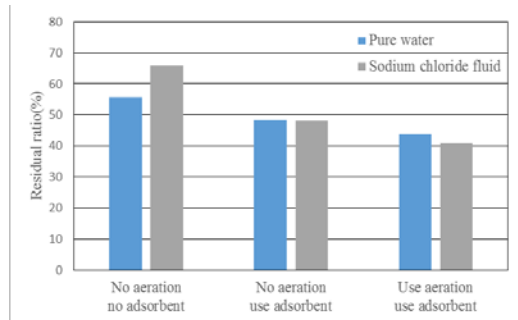


Fig.8 Residual ratio of strontium for 1 week

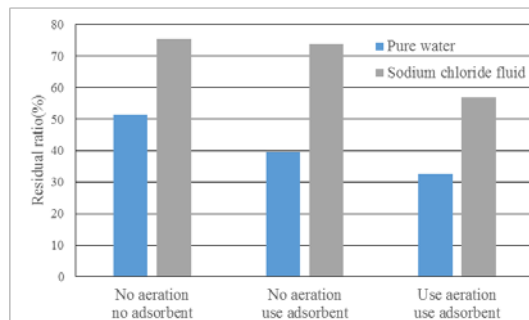


Fig.9 Residual ratio of strontium for 4 weeks

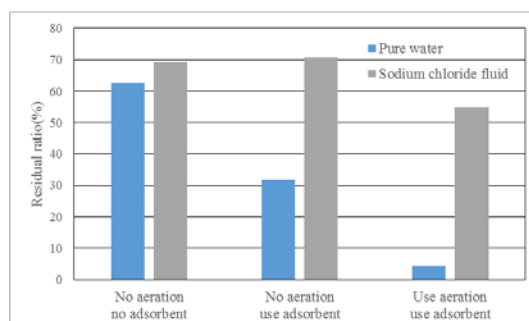


Fig.10 Residual ratio of strontium for 13 weeks

the other hand, that is relatively low in the case of 1 week immersion test with sodium chloride solution. As the reason, it is possible that the

strontium which firmly adhered to the soil is liberated from the soil into the solution. This phenomenon occurs in the case of abundant Na ion (Na^+). Additionally, the convective method may have the space to be improved. The strontium liberated from soil passes through the HAp sheet when the aeration is performed on the sheet. However, the strontium liberated into sodium chloride solution has less chance to pass through the HAp sheet. Therefore, it is needed to exam the setting method for the HAp sheet so as to adsorb cesium or strontium in not only soil but also solution effectively.

Table 7 Test results for strontium for 1 week

	Pure water	
	Remained amount (mg)	Residual ratio (%)
No aeration no adsorbent	2.79	55.74
No aeration use adsorbent	2.42	48.47
Use aeration use adsorbent	2.19	43.86
Sodium chloride solution		
No aeration no adsorbent	3.29	65.81
No aeration use adsorbent	2.41	48.20
Use aeration use adsorbent	2.05	40.93

Table 8 Test results for strontium for 4 weeks

	Pure water	
	Remained amount (mg)	Residual ratio (%)
No aeration no adsorbent	2.58	51.56
No aeration use adsorbent	1.98	39.66
Use aeration use adsorbent	1.62	32.47
Sodium chloride solution		
No aeration no adsorbent	3.76	75.29
No aeration use adsorbent	3.69	73.82
Use aeration use adsorbent	2.85	57.00

Table 9 Test results for strontium for 13 weeks

	Pure water	
	Remained amount (mg)	Residual ratio (%)
No aeration no adsorbent	3.13	62.67
No aeration use adsorbent	1.60	31.93
Use aeration use adsorbent	0.22	4.40
	Sodium chloride solution	
	Remained amount (mg)	Residual ratio (%)
No aeration no adsorbent	3.47	69.42
No aeration use adsorbent	3.53	70.69
Use aeration use adsorbent	2.74	54.82

7. CONCLUSIONS

In this study, a new decontamination method is proposed without dredging mud in marine and lake with considering the shortage of the intermediate storage facilities for the sand polluted by radioactive materials. To examine the validity and availability of the developed material and the proposed method, the adsorption tests by which cesium and strontium are adsorbed by the developed adsorption sheet are conducted. From the test results, it is found that the difference between the residual ratio of strontium in the tests with both the HAp sheet and the convective device and the residual ratio of strontium in the test with nothing is larger than the difference of the residual ratios of cesium in the both tests. From here onwards, the following two knowledge are obtained. One is that most of strontium maybe existed in the fluid rather than the sand. Another is that cesium maybe strongly adhering to the sand. As has already stated, the possibility that the strontium is not effectively adsorbed in the experimental environment in this study is not denied. Therefore, the additional issues such as the extension of immersion time and the increase of test specimen should be examined in near future. While at the same time, the settings of the HAp sheet should be also discussed. More to the point, in this study, the number of test is not enough since the longest terms of immersion test are 13 weeks for cesium and strontium. In concrete terms, the longer immersion test, 26 and 52 weeks immersion tests, are required. Alternatively, the residual ratios of strontium in the pure water case and the sodium chloride fluid vary with time. This work was supported by JSPS KAKENHI Grant Number 24520507.

8. ACKNOWLEDGEMENT

The authors would like to express cordial gratitude to Professor Hidenori Yoshida of Kagawa University for his support and supervision. Also, we are grateful to Professor Yoshihiro Suenaga and NIHON KOGYO, CO. LTD for provision of HAp and HAp sheet. Of course, we gratefully acknowledge the work of past and present members of our laboratory.

9. REFERENCES

- [1] Atsushi N. Noriko Y, "The behavior of radioactive material in soil", Rural Culture Association. Latest agricultural technology. soil fertilization, Vol.4, Nov. 2011, pp. 1-9.
- [2] Tsutomu S, "Background and problematics of radioactive contamination by the accident at Fukushima Dai-ichi nuclear power plant", Journal of the Clay Science Society of Japan, Vol. 50, no. 2, Nov. 2011, pp. 26-32.
- [3] Fisheries Agency, 2015, http://www.jfa.maff.go.jp/j/housyanou/pdf/151214_result.pdf
- [4] Ministry of the Environment, 2014, http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-01-1.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-1.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-03-1.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-01-2.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-01-3.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-2.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-6.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-7.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-03-2.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-3.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-4.pdf
http://www.env.go.jp/jishin/monitoring/results_r-pw-h26/3-02-5.pdf
- [5] Satoshi T. Osamu M, "Similarity of crystal structure between Hydroxyapatite and its precursor crystal", A Journal of the College of Industrial Technology, Nihon University, Vol. 38, no. 2, Dec. 2005, pp. 35-39.
- [6] Yoshinobu K. *et al*, "Quantitative chemical analyses of silicate minerals using a Scanning Electron Microscope with Energy Dispersive X-ray Detector", National Institute for

- Environmental Studies, Vol. 12, 2010, pp. 99-107.
- [7] Shinji O. *et al*, “Long term temporal changes of ^{90}Sr and ^{137}Cs in seawater, bottom sediment and marine organism samples from the Chernobyl accident to immediately after the Fukushima accident”, BUNSEKI KAGAKU, Vol. 62, no. 6, June. 2013, pp.455-474.
- [8] Kenji S. *et al*, “Removal and adsorption of radioactive cesium from contaminated soil caused by the Fukushima Daiichi Nuclear Power Station accident”, BUNSEKI KAGAKU, Vol. 62, no. 6, June. 2013, pp. 535-540.
- [9] Akihisa S. *et al*, “A change in the concentrations of radioactive cesium in Tokyo-bay’s sediments released by the Fukushima Dai-ichi nuclear power station accident”, BUNSEKI KAGAKU, Vol. 62, no. 12, Dec. 2013, pp. 1079-1086.
- [10] Yuko M. *et al*, “Removal of radiocesium using cation exchange resin”, BUNSEKI KAGAKU, Vol. 62, no. 6, June. 2013, pp. 541-545.
- [11] Ko N. *et al*, “monitoring of radioactive cesium in Kawasaki derived from the Fukushima Daiichi Nuclear Power Plant Accident by a sequential leaching method for airborne particulate matter”, BUNSEKI KAGAKU, Vol. 64, no. 8, Sep. 2015, Special Articles : The First Papers of Prospective Analytical Chemists pp. 589-594
- [12] AOMI CONSTRUCTION CO., LTD.,
http://www.nikkenren.com/doboku/hukkou_pdf/001_004.pdf

International Journal of GEOMATE, Aug., 2016, Vol. 11, Issue 24, pp. 2259-2266.

MS No. 5127j received on July 30, 2015 and reviewed under GEOMATE publication policies. Copyright © 2016, Int. J. of GEOMATE. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors. Pertinent discussion including authors' closure, if any, will be published in April 2017 if the discussion is received by Oct. 2016.

Corresponding Author: Keiichiro Shibata
