

STUDY ON ADSORPTION ABILITY OF ADSORBENTS FOR STRONTIUM IN DIFFERENT SOLUTIONS

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ABSTRACT: The Tsunami due to the Great East Japan Earthquake on March 11, 2011 indirectly caused a nuclear disaster at the Fukushima Daiichi nuclear energy plant of the Tokyo Electric Power Company. The radioactive strontium dispersed by the accident has spread to the soil, lake, river and marine environments. In addition, contaminated groundwater continues to be generated by the flow under the damaged facilities of the plant. The increase of collected tainted water makes it difficult to secure the storage facility. In the face of such situation, the decontamination work for the radioactive strontium has not been completed. It is possible that humans may be exposed as a result of transfer through the food chain and biomagnification when the tainted water, including the major quantity of strontium leak to the marine environment. Therefore, the decontamination of strontium is an urgent requirement. To help address this risk, we previously conducted an experiment to sequester strontium into an adsorbent so as to decrease the degree of contamination. The results of this earlier study confirmed that the uptake ability of adsorbent for strontium varied in different solutions. In this study, the adsorption test of adsorbent is conducted to understand its ability in solution composed of magnesium, potassium or chloride. The hydroxyapatite derived from fish bones is developed and used as the adsorbent. From the result of tests, it is confirmed that the adsorption ability of the hydroxyapatite for divalent cation is high in the various solutions.

Keywords: decontamination, hydroxyapatite, strontium, radiation tainted water

1. INTRODUCTION

The nuclear disaster at the Fukushima Daiichi nuclear energy plant (1F) of the Tokyo Electric Power Company was indirectly caused by the Great East Japan Earthquake and the Tsunami on March 11, 2011. The radioactive materials discharged from the 1F due to the accident has contaminated in the surrounding land and ocean. The impact on aquatic products is of special concern as a result of the release of radioactive materials into the marine environment. Figs. 1-4 are developed based on the Report of Radioactivity Surveys conducted by the Hydro-graphic and Oceanographic Department Japan Coast Guard. These figures show the contaminated situations of cesium-137 (¹³⁷Cs) and strontium-90 (⁹⁰Sr) as shown in references [1]-[5]. The vertical axis in the graphs is the detected value of ¹³⁷Cs or ⁹⁰Sr, and the horizontal is the measured year. They are surveyed in Off Otaru, Sendai bay, Tokyo bay, Ise bay and Osaka bay. The detected values of ⁹⁰Sr and ¹³⁷Cs in the marine water are shown in Fig. 1 and Fig. 2, respectively. The detected values of ⁹⁰Sr and ¹³⁷Cs in the marine mud are shown in Fig. 3 and Fig. 4, respectively. The radioactive concentration of strontium in Tokyo bay is almost the same as that in Sendai bay. However, the radioactive concentration of cesium in Tokyo bay is the highest. The spreading of the radioactive

materials is evident from the survey results. Alternatively, it is confirmed that a large quantity of cesium and strontium were detected from marine water on 2011 and they were high in the sediment after 2012. After that, the detected of strontium did not change. On the other hand, the level of cesium remains the same until 2014. These survey results indicate that the radioactive contamination in hydrosphere is due to the cesium. It is important to take note of the matter of tainted water in the 1F. The groundwater, which is transferred to the nuclear reactor building, is contaminated and the securing the storage facility is a serious problem. Table 1 is recreated on the basis of the results, which are obtained from the analysis for groundwater in the 1F by the Tokyo Electric Power Company Holdings [6]. The groundwater is collected from the thirty points which are located around the seawall of the Units 1-4 of the nuclear reactor building so as to investigate the contaminated situation by ¹³⁷Cs and beta ray. The average of detected value of ¹³⁷Cs and beta ray in the groundwater are shown in Table 1. Though the Tokyo Electric Power Company sets out to decrease the inflow of groundwater through the nuclear reactor building and steps down the contamination degree of tainted water, the sign of solution is not shown. The detected value of beta ray is very high to compare with that of ¹³⁷Cs. It is considered that

the tainted groundwater may include the major quantity of ^{90}Sr , because ^{90}Sr is the representative radioactive material that emits the beta ray. Therefore, the removal of strontium in the tainted water and cesium in marine mud are respectively

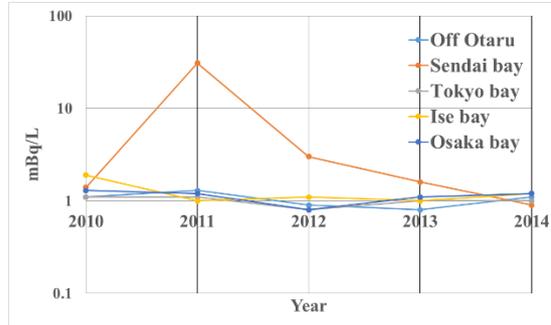


Fig. 1 Secular change of ^{90}Sr in marine water

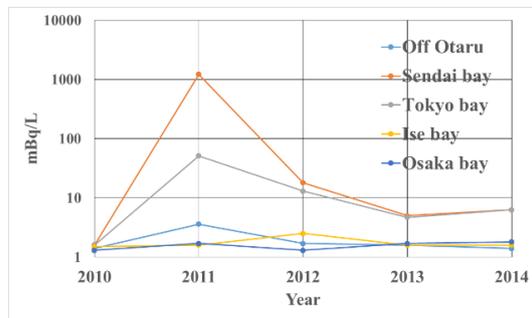


Fig. 2 Secular change of ^{137}Cs in marine water

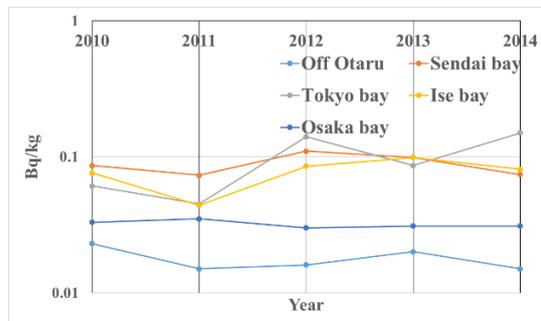


Fig. 3 Secular change of ^{90}Sr in marine mud

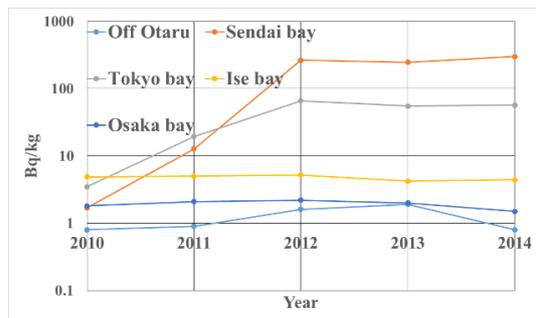


Fig. 4 Secular change of ^{137}Cs in marine mud

required for remediation. Alternatively, the strontium is more dangerous than the cesium due to the following fact. When cesium is taken in the human body, it is mainly absorbed into muscle.

After that, it is released from the body as sweat or urine. Strontium, on the other hand, is absorbed into bone and is stored there for a long time. When the tainted water including the major quantity of strontium released to marine environment, it is possible that humans are exposed by ecological chain and biological concentration. Therefore, the decontamination of strontium is urgently needed. The authors have conducted the experiments in which strontium is adsorbed to the adsorbent under the marine and tainted water so as to solve this problem in the past (see the reference [7]). It was confirmed that the adsorption ability of adsorbent for strontium is varied in different solutions. Thus, in this study, the adsorption ability of adsorbent is examined to maximize the performance of adsorbent for strontium under the various environmental conditions. In concrete terms, a number of water solutions were prepared, and the adsorption tests of the adsorbent for strontium in each water solution were conducted. The adsorption ability of adsorbent is understood by comparing the test results.

Table 1 Analysis results of tainted water in around F1 (seawall of Unit 1-4)

	^{137}Cs (Bq/L)	Sum of beta ray(Bq/L)
Around seawall of Unit 1	6.75	28.17
2	4797.38	129294.20
3	43.33	1200.00
4	3.43	5478.67

2. UTILIZED ADSORBENTS IN EXPERIMENT

There are two important issues for decontaminating the hydrosphere. One is the non-



Fig. 5 Zeolite (left) and Hydroxyapatite (right) proliferation of radioactive materials and the other is the volume reduction of radioactive waste. In this

study, new adsorption material that can adsorb radioactive fallout is developed to solve the issues. To be more precise, the new adsorption material consists of hydroxyapatite (HAp, see Fig. 5). The chemical formula for the HAp is $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$ and is the hydroxyl end member of the complex apatite group. The apatite is the clump of crystalline compound which has the basic structure of $\text{M}_{10}(\text{ZO}_4)_6\text{X}_2$. For example, fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) is the representative component of phosphate rock, and it is the industrial resource for phosphorus [10]. The HAp receives a lot of attention as the biomaterials for modern tooth and bone implants. The artificial combination is conducted by a lot of methods [9]. The HAp utilized in this study was developed by Suenaga, et.al. (application number: 2014-58267, invention name: hydroxyapatite made from fish bones, merely calcined, applicant: national university corporation Kagawa University and Nihon Kogyo CO.LTD, apply date: April 2nd, 2014). It is expected that strontium similar to calcium is adsorbed into the HAp because the HAp has many fine pores. Each single size of the HAp is about 1 cm squares, weight is about 0.6 g (The HAp has varied size and weight because the ingredient is fish bones).

Alternatively, zeolite is utilized in the



Fig. 6 Filter bag containing zeolite(left) or HAp (right)



Fig. 7 Immersion test experiments to compare the performance of the HAp due to its ability to highly adsorb cesium [11].

Each single size of the zeolite is about 0.2 ~ 0.5 cm squares, and the weight is about 0.05 ~ 0.3 g (The zeolite is a quantity of variable in size and weight as same as the HAp, see Fig. 5).

3. TARGETED MATERIAL FOR EXPERIMENT

A wide variety of radioactive materials were released from the accident at the 1F. For experiments using the HAp, strontium was selected as a target material because it is released in large quantities and its half-life is relatively long. Also, the property of strontium is more or less same as those of calcium which is absorbed into the bones after entering the body [8]. The properties of strontium are explained below in detail since it is necessary to grasp their features for the experiment.

Strontium is a fusible alkali-earth metal that exists as a divalent positive ion in solution. Strontium also has several isotopes. Among those, ^{90}Sr , a by-product of nuclear fission found in the nuclear fallout from the 1F, is the removal target. The half-life of ^{90}Sr is about 29 years. ^{90}Sr changes to stable zirconium-90 (^{90}Zr) after twice beta collapse. Radiation exposure is divided into two categories; one is the external exposure, and the other is the internal exposure. The external exposure occurs when an organism receives radiation from outside the body. Internal exposure allows strontium to be substituted for calcium in bone, it is rare that the strontium is expelled from the body. This behavior is different from that of cesium which is absorbed into the muscles in the body.

The above facts indicate that strontium 90 is a health threat to humans and that the strontium should be de-contaminated as quickly as possible.

4. EXPERIMENT AND ANALYSIS METHOD

In the experiment, five water solutions and pure water were prepared to compare the adsorption ability of the HAp or zeolite for strontium in different environments. One specimen is prepared in terms of comparison; it is pure water, while the other contains sodium chloride, sodium acetate, potassium chloride, magnesium chloride and sodium nitrate 3%. The reason why the sodium chloride and etc. was a 3 % concentration in the each solution was because this is close to that in seawater.

First, 300 ml of each solution are poured into cylindrical containers, and 5.0 mL of liquid strontium hydroxide is added. After that, the filter bag containing the HAp absorbent is placed on the bottom of cylinders. The filter bag is frequently used as the household kitchen sinks (see Fig. 6).

Secondly, it is immersed for the set period of time (see Fig. 7). After a set immersion time, the HAp is picked up, and the remaining amount of strontium in the solutions is analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). In this study, the residual ratio is utilized as the evaluation of experimental result. The residual ratio is defined by the following equation, Eq. (1),

$$R(\%) = \frac{r}{a} \times 100 \quad (1)$$

where, “r” is the remained amount of strontium, and “a” is the additive amount of strontium. An average result is recorded after three times experiments are conducted for each set of 5 solutions and pure water.

5. PRELIMINARY TEST

Preliminary test was conducted so as to examine the limit amount that strontium which was adsorbed into the 10 pieces of HAp. First, 300 ml of pure water is poured into cylindrical containers, and 3.0, 5.0, 8.0, 10, 15 or 20 mL of liquid strontium hydroxide is added. After that, the filter bag containing the HAp is placed on the bottom of cylinders. Secondly, it is immersed for the set period of time. After a set 7 days, the HAp is picked up, and the remaining amount of strontium in the solutions is analyzed by ICP-AES. The analysis result is shown in Fig. 8. The vertical axis in the figure is the residual ratio of strontium, and the horizontal one is the additive amount. It is confirmed that the remained amount of strontium increases with the increase of additive amount. Alternatively, almost all strontium is adsorbed into the HAp when the additive amount is 5.0 mL. However, a few strontium remains in the pure water when the additive amount is 8.0 mL. From these results, it is decided that the additive amount of strontium is 5 mL in the immersion test.

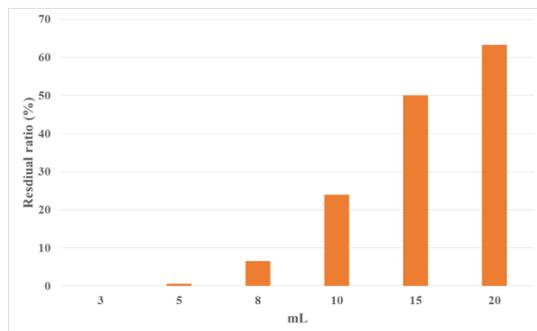


Fig. 8 Preliminary test

6. EXPERIMENT AND ANALISYS RESULTS

The residual ratio of strontium in each solution is shown in Figs.9-19. Also, Figs. 9-14 are test results when the HAp is utilized as the adsorbent, Figs. 15-19 are test results when the zeolite is utilized as the adsorbent. The vertical axis in the figure is the residual ratio of strontium, and the horizontal one is the immersion time. About 10 pieces (6.0~7.0g) of the HAp, 6.0g of the zeolite, were used in each experiment and the immersion times were 24, 72, 120 or 168 hours.

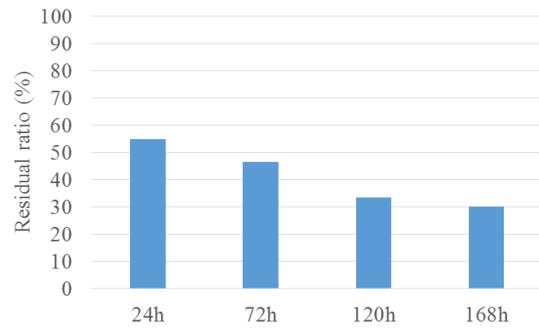


Fig. 9 Residual ratio of strontium in magnesium chloride solution for HAp

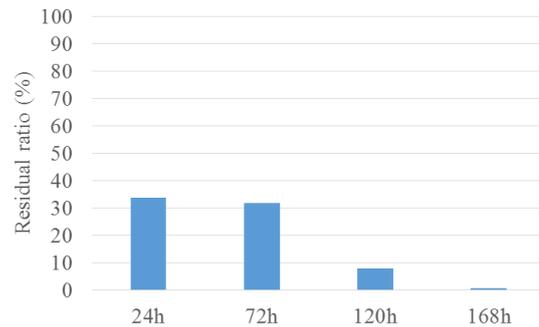


Fig. 10 Residual ratio of strontium in sodium chloride solution for HAp

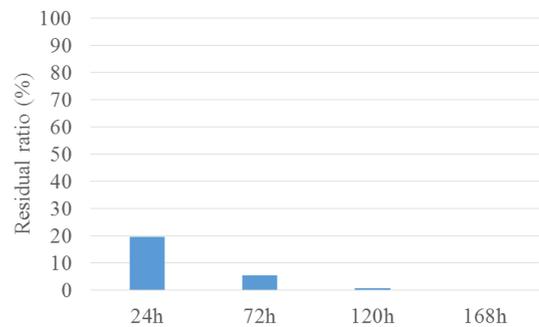


Fig. 11 Residual ratio of strontium in potassium chloride solution for HAp

6.1 Solutions containing chloride for HAp

The experimental results of the three solutions

with involvement chloride are shown in Figs. 9-11. It is confirmed that the residual ratio of strontium in three specimens decreases with the passage of time. Especially, when potassium chloride solution or sodium chloride solution is employed as the solution, the residual ratio of strontium is almost zero percent after 168 hours, and it is the lowest in the potassium chloride solution after 24 hours. It is possible that the adsorption of the HAp for strontium is prompted by the potassium. On the other hand, when magnesium chloride solution is employed, almost thirty percent of strontium remained in the solution. Furthermore, the adsorption ability of the HAp for strontium is clearly influenced by divalent cationic magnesium.

6.2 Solutions without chloride for HAp

The experiment results of the three solutions with non-involvement chloride are shown in Figs. 12-14. It is confirmed that the residual ratio of strontium in three solutions decreases with passage of time. Alternatively, when three solutions are compared in the light of existence or non-existence of sodium, the residual ratio of strontium in the solution containing of sodium is relatively higher

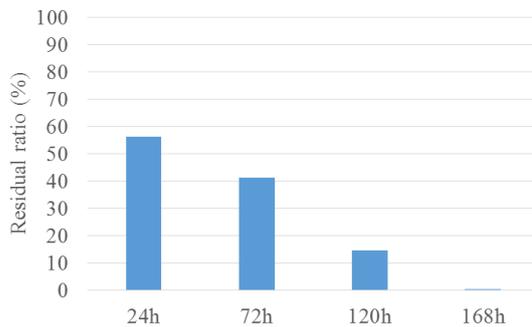


Fig. 12 Residual ratio of strontium in pure water for HAp

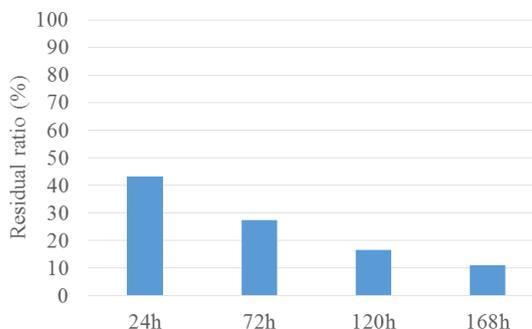


Fig. 13 Residual ratio of strontium in sodium nitrate solution for HAp

than the specimen of using pure water. It is considered that the adsorption ability of the HAp for strontium is slightly influenced by sodium.

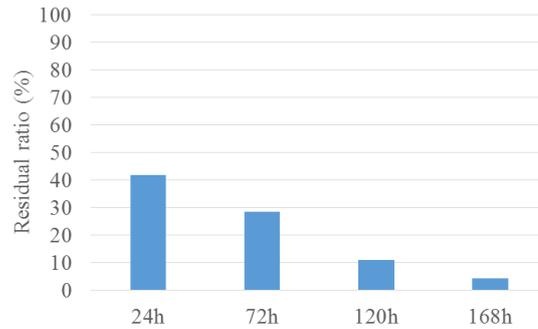


Fig. 14 Residual ratio of strontium in sodium acetate solution for HAp

Nevertheless, more than ninety percent of strontium is adsorbed to the HAp in case of utilizing each solution.

6.3 Solutions containing chloride for zeolite

The experimental results of the three solutions with involvement chloride are shown in Figs. 15 and 16. The residual ratio of strontium remained virtually unchanged with passage of time when the sodium chloride solution or potassium chloride solution was utilized. It is confirmed that the adsorption of strontium is inefficiently conducted because the residual ratio after 168 hours is about 80 %.

6.4 Solutions without chloride for zeolite

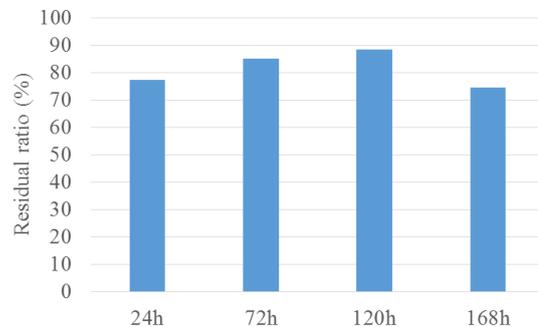


Fig. 15 Residual ratio of strontium in sodium chloride solution for zeolite

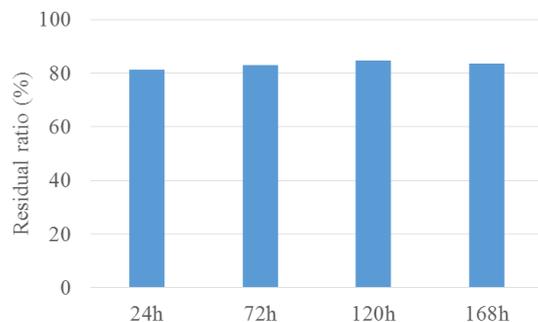


Fig. 16 Residual ratio of strontium in potassium chloride solution for zeolite

The experiment results of the three solutions with non-involvement chloride are shown in Figs. 17-19. The residual ratio of strontium remained virtually unchanged with passage of time when the sodium nitrate solution or sodium acetate solution was utilized. The residual ratio after 168 h is about 90 %. Alternatively, the residual ratio after 72 h decreased by 50 % when pure water was utilized. However, it remains unchanged after 72 hours. It is confirmed that the zeolite is not suitable as the adsorbent for strontium because the adsorption ratio of the zeolite is lower than that of the HAp.

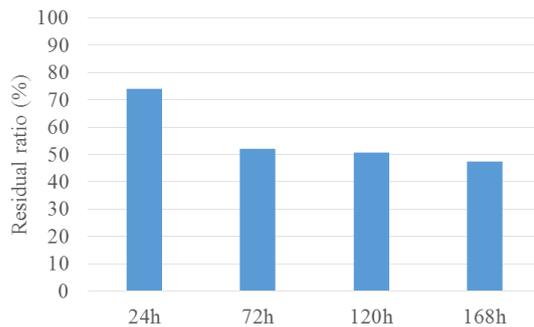


Fig. 17 Residual ratio of strontium in pure water for zeolite

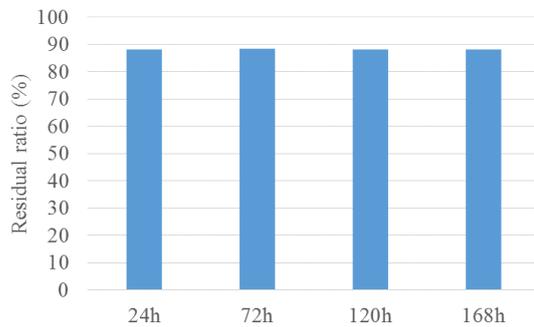


Fig. 18 Residual ratio of strontium in sodium nitrate solution for zeolite

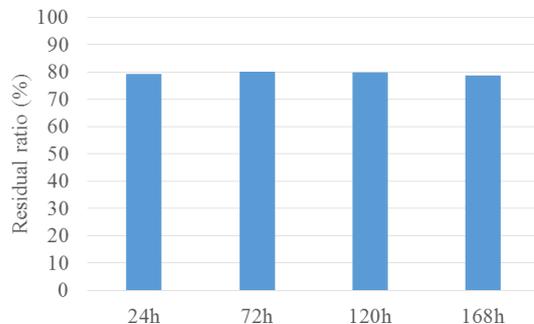


Fig. 19 Residual ratio of strontium in sodium acetate solution for zeolite

7. CONCLUSIONS

In this study, adsorption experiments are conducted in various solutions to determine the adsorption ability of the HAp for strontium. The results, confirmed that the adsorption ability of the HAp for strontium has a beneficial effect in each of the five water solutions and pure water. The residual ratio of strontium is more or less zero percent in case of pure water, sodium chloride solution or potassium chloride solution. In particular, the residual ratio of strontium already declines up to twenty percent after 24 hours in the case of potassium chloride solution. It is considered that the ionization tendency of potassium is higher than that of strontium, which has an effect on the adsorption performance of the HAp. The influence on the HAp will be examined by increasing the concentration of potassium in near future. On the other hand, when magnesium chloride solution is utilized, about thirty percent of strontium remained in the solution. It is considered that divalent cationic magnesium blocks strontium adsorption to the HAp. In fact, the seawater and the groundwater include various metal elements. Furthermore, it is necessary to examine the detailed influence on the HAp by conducting the experiment in which the concentrations of potassium, sodium and magnesium are changed. In addition, it was also confirmed that the adsorptive rate of the HAp was higher than the ratio of zeolite, which was selected as the comparative target. The adsorption ability of the zeolite for strontium has a beneficial effect in each of the four solutions and pure water. It is confirmed that the zeolite is not suitable as the adsorbent for strontium because the residual ratio exceeds 80 % in the case of these experiments with the four solutions.

It is confirmed that the HAp is the most effective adsorbent for strontium among various tested adsorbents, but it is necessary to conduct the laboratory experiment in environment including various environments so as to remove strontium from the seawater and marine mud in which the strontium is consisted to be included. Alternatively, the HAp may have the potential to adsorb a large number of contaminants in addition to strontium. The HAp can become the effective material for the cleanup of air and water pollution. A variety of artifices and many experiments are necessary to make use of the HAp in various fields. In this study, the adsorption ability of the HAp for the alkali metals and the alkaline-earth metal has been examined, but the adsorption ability for the other elements awaits future study.

8. ACKNOWLEDGEMENTS

The authors would like to express cordial gratitude to NIHON KOGYO. CO. LTD for provision of the HAp and the HAp sheet. This work

was supported by JSPS KAKENHI Grant Number 16K06492.

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