

**Removal of Radionuclides from Waste Water at Fukushima Daiichi Nuclear Power Plant:
Desalination and Adsorption Methods – 13126**

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ABSTRACT

Waste water containing high levels of radionuclides due to the Fukushima Daiichi Nuclear Power Plant accident, has been treated by the adsorption removal and reverse-osmosis (RO) desalination to allow water re-use for cooling the reactors. Radionuclides in the waste water are collected in the adsorbent medium and the RO concentrate (RO brine) in the water treatment system currently operated at the Fukushima Daiichi site.

In this paper, we have studied the behavior of radionuclides in the presently applied RO desalination system and the removal of radionuclides in possible additional adsorption systems for the Fukushima Daiichi waste water treatment. Regarding the RO desalination system, decontamination factors (DFs) of the elements present in the waste water were obtained by lab-scale testing using an RO unit and simulated waste water with non-radioactive elements. The results of the lab-scale testing using representative elements showed that the DF for each element depended on its hydrated ionic radius: the larger the hydrated ionic radius of the element, the higher its DF is. Thus, the DF of each element in the waste water could be estimated based on its hydrated ionic radius.

For the adsorption system to remove radionuclides more effectively, we studied adsorption behavior of typical elements, such as radioactive cesium and strontium, by various kinds of adsorbents using batch and column testing. We used batch testing to measure distribution coefficients (K_{ds}) for cesium and strontium onto adsorbents under different brine concentrations that simulated waste water conditions at the Fukushima Daiichi site. For cesium adsorbents, K_{ds} with different dependency on the brine concentration were observed based on the mechanism of cesium adsorption. As for strontium, K_{ds} decreased as the brine concentration increased for any adsorbents which adsorbed strontium by intercalation and by ion exchange.

The adsorbent titanium oxide had higher K_{ds} and it was used for the column testing to obtain breakthrough curves under various conditions of pH and brine concentration. The breakthrough point had a dependency on pH and the brine concentration. We found that when the pH was higher or the brine concentration was lower, the longer it took to reach the breakthrough point.

The inhibition of strontium adsorption by alkali earth metals would be diminished for conditions of higher pH and lower brine concentration.

INTRODUCTION

The Fukushima Daiichi Nuclear Power Plant (NPP) accident resulted from the massive earthquake and the ensuing tsunami that hit northeastern Japan on March 11, 2011. Thousands of tons of contaminated waste water have been produced from the reactors by injection of sea water in the early stage of the accident and the following continuous injection of treated waste water to cool the reactors.

Waste water treatment systems are being used to remove oil, radionuclides and brine. Figure 1 outlines the waste water treatment system being used in Fukushima Daiichi NPP. The waste water is pumped from the reactor buildings and the turbine buildings and is processed to remove oil in the oil removal process, then sent to the cesium (Cs) removal process to remove contaminant Cs which has the highest impact on the dose rate. After that, the waste water is sent to the RO desalination system to remove brine, and the desalinated water is re-used to cool the reactor. Owing to the stable operation of the waste water treatment system, the concentration of Cs and Cl in the waste water has been decreasing as shown in Fig.2.

Several investigations have been conducted on the removal of radionuclides in the waste water after the accident. Since the waste water contains brine, we have focused on two methods for

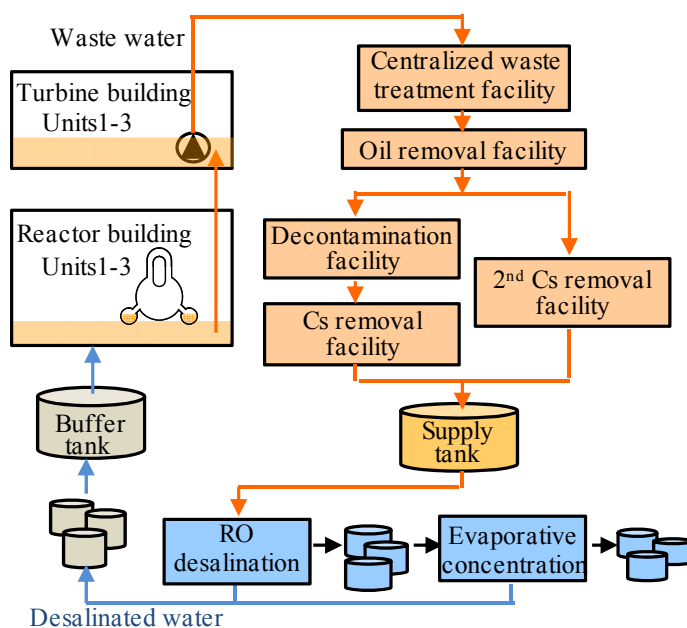
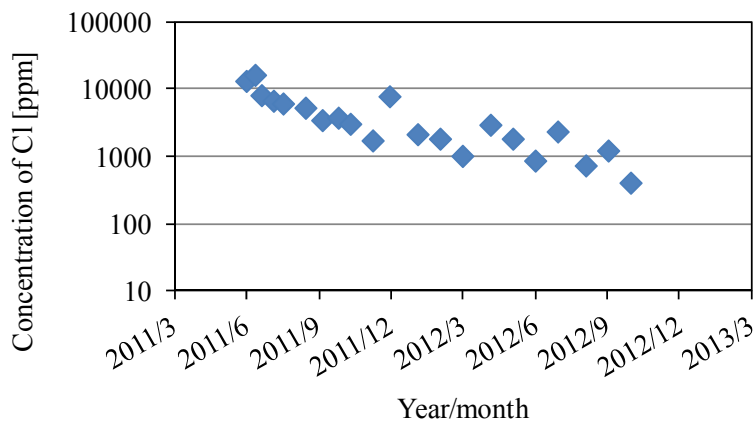


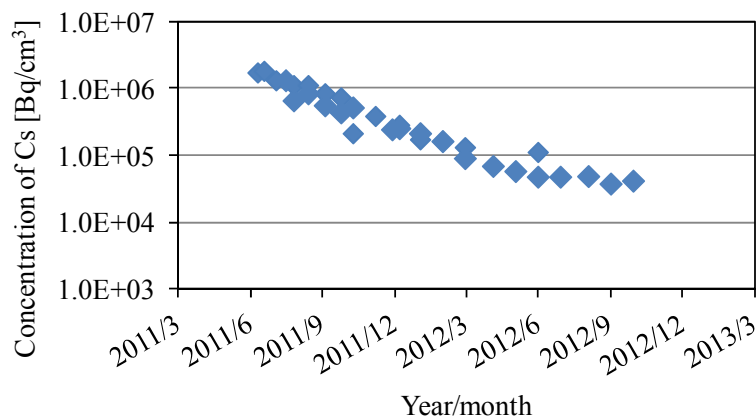
Fig. 1. Outline of the waste water treatment system being used in the Fukushima Daiichi NPP.

radionuclide removal: one is the RO desalination method being used to remove brine and the other is the adsorption method in the changing brine concentration environment based on progress in the waste water treatment. The RO desalination system can remove radionuclides with some decontamination factor (DF) because the RO system can separate brine elements such as Na, Cl, Ca and so on from the treatment water. With regard to the adsorption method, the removal efficiency of radionuclides will be affected by the changing brine concentration because the brine contains high concentrations of Na, Mg and Ca, which are in the same group of elements as Cs and Sr.

In this paper, we have studied the behavior of radionuclides in the presently applied RO desalination system and the removal of radionuclides in possible additional adsorption systems for the Fukushima Daiichi waste water treatment.



(a) Concentration of Cl at the inlet of the RO desalination



(b) Concentration of Cs in the waste water at the centralized waste treatment facility

Fig. 2. Variation in the concentration of Cl (a) and Cs (b) in the waste water with progression of waste water treatment [1].

EXPERIMENTAL

RO desalination method

Behavior of radionuclides in the RO desalination system was investigated using a lab-scale experimental module with polyamide membranes. Feed solutions were prepared by suitably diluting the simulated sea water (Marin Art SF-1, Tomita Pharmaceutical Co., Ltd.). Typical elements found in the waste water at the Fukushima site, such as Cs, Ru and Sb, were added to the test feed solutions using non-radioactive reagents. Each test feed solution was supplied to the RO module with applied pressure of 5.5 MPa and feed rate of 0.3 m³/h.

The DF of each element was calculated from the feed and permeate concentration of the element except for NaCl; its DF was calculated from the feed and permeate conductivity. Concentrations of each element in the feed (C_0) and permeate (C_i) solutions were measured using an ICP-MS. The DF was calculated by Eq.1.

$$DF = \frac{C_0}{C_i} \quad (\text{Eq.1})$$

Adsorption method

Adsorption behavior of typical elements, such as radioactive Cs and Sr, was investigated by batch and column testing. Adsorbents for Cs and Sr used are shown in TABLE I. Test feed solutions were prepared by appropriate diluting the simulated sea water (Marin Art SF-1) and adding a radionuclide solution containing Cs-137 or Sr-85 for the batch testing and only Sr-85 for the column testing.

In the batch testing, distribution coefficients (K_{ds}) were obtained by a laboratory batch method for estimation of removal efficiency of radionuclides. An adsorbent of known mass (M_{ad}) was put into a plastic bottle and a test feed solution with known volume (V_{sol}) and concentration of radionuclide (C_0) was added. The V_{sol}/M_{ad} ratio was selected as 100:1 (w/w). The bottle was capped and kept on a rotating bench at room temperature for 1 to 7 days. A portion of the

TABLE I. Adsorbents used in the batch testing

ID	Cs adsorbents	ID	Sr adsorbents
A	Potassium hexacyanocobalt-ferrate	F	Sodium titanate (1)
B	Ammonium iron hexacyanoferrate	G	Sodium titanate (2)
C	Crystalline silicotitanate (CST)	H	Synthetic zeolite
D	Mordenite	I	Chelate resin
E	Chabazite	J	Layered metal sulfide

solution was filtered through a 0.45 μ filter and the concentration of radionuclide (C_i) was measured. The K_d was calculated by Eq.2.

$$K_d = \frac{V_{sol}(C_0 - C_i)}{M_{ad}C_i} \quad (\text{Eq.2})$$

The column testing was done using a plastic column (10mm ID) filled with 5-10 mL of an adsorbent. Examination of the breakthrough curve was carried out with test feed solutions of different brine concentrations and different pH values (TABLE II). The flow rates of the solution were kept in the range of 10-20 bed volume/h (BV/h). At selected time intervals the concentration of Sr-85 in effluent was measured.

TABLE II. Test feed solutions used in the column testing

No.	Concentration of test feed solution (dilution ratio)	pH	Cl concentration [ppm]	Sr concentration [ppm]
1	1	8	18000	7.2
2	0.35	8	6300	2.4
3	0.11	8	2000	0.8
4	0.056	8	1000	0.4
5	1	12.5	18000	7.2
6	0.11	9.0	2000	0.8

RESULTS AND DISCUSSION

RO desalination method

The DFs of various elements are listed in TABLE III. The DF value of Ru was calculated using the detection limit value of Ru measurement as C_i in Eq.2 because the concentration of Ru in the permeate solution was under the detection limit. The DF value of 210 for Na and Cl means the percent separation of Na and Cl was about 99.5%. Taking the DF of Na and Cl as the reference, Cs has a similar DF to that of Na, a much higher DF is observed for Mg, Ca and Ru, and a lower DF is observed for Sb.

Arnal et al. [2] reported the treatment of Cs-137 liquid wastes by RO. Their result showed the percent separation of Cs-137 was around 96%, and reached values around 99% when using a membrane with the applied pressure of 4 MPa. Since the DF of Cs-137 based on the percent separation around 99.5% is calculated as about 200 and the DF of Cs obtained in this study is close to the value calculated from their data, the results of DF measurement in this study are regarded as valid.

TABLE III. Decontamination factors and Stokes radii of various elements

Element	Chemical formula of species in the test feed solution	DF	Stokes radius [pm]
Na	Na ⁺	210	180
Cs	Cs ⁺	210	120
Mg	Mg ²⁺	1070	350
Ca	Ca ²⁺	1090	310
Ru	Ru(OH) ₄	>500*	-
Sb	Sb(OH) ₆ ⁻	110	-
Cl	Cl ⁻	210	70
Sr	Sr ²⁺	1000 (estimate)	310

*DF of Ru was calculated using detection limit value for C_i in Eq.2.

In principle, the RO membrane separates water from brine solution by permeation of water molecules through the membrane. Transport of water molecules through the membrane may be through physical pores present in the membrane, or by diffusion from one place to another within the membrane. That mechanism suggests that permeability of salt molecules accompanying the water molecules would depend on the molecular (or ionic) size of the salts. The results listed in TABLE III clearly show the dependency of DF on the ionic (Stokes) radius [3]. Cesium with the closest value to the ionic radius of Na had the same DF, while Mg and Ca, which have ionic radii two times larger than Na, making it hard for them to pass through the membrane, show five-fold higher DFs. The DF of Sr, one of the radionuclides observed in the waste water at the Fukushima site, is estimated as about 1000 based on the Stokes radius shown in TABLE III.

For Ru, the primary chemical species in the test feed solution is calculated as Ru(OH)₄ by PHREEQC [4]. The ionic radius of Ru(OH)₄ is unknown in the present solutions studied, but it should be larger than that of Na due to the high DF value of Ru.

Antimony is mainly present as Sb(OH)₆⁻ in aqueous solution [5]. The removal of Sb in drinking water using RO membrane has been reported by Kang et al.[5], who obtained the percent separation of Sb of more than 97%. The percent separation of Sb in this study, nearly 99%, corresponds with that of Kang et al.

Based on the results in this study, we can estimate the DF of the elements in the RO desalination system. Figure 3 summarizes DF estimations. The circled elements were studied experimentally in this study. The DFs of the elements enclosed within the dotted lines (alkali and alkaline earth metal) would be predictable based on their ionic radii in aqueous solution. The elements enclosed within the dashed lines form anions in aqueous solution and their ionic radii do not seem to be applicable for DF estimation. For the elements enclosed in the solid line, proper understanding of the chemical species in the water plays an important role in the DF estimation.

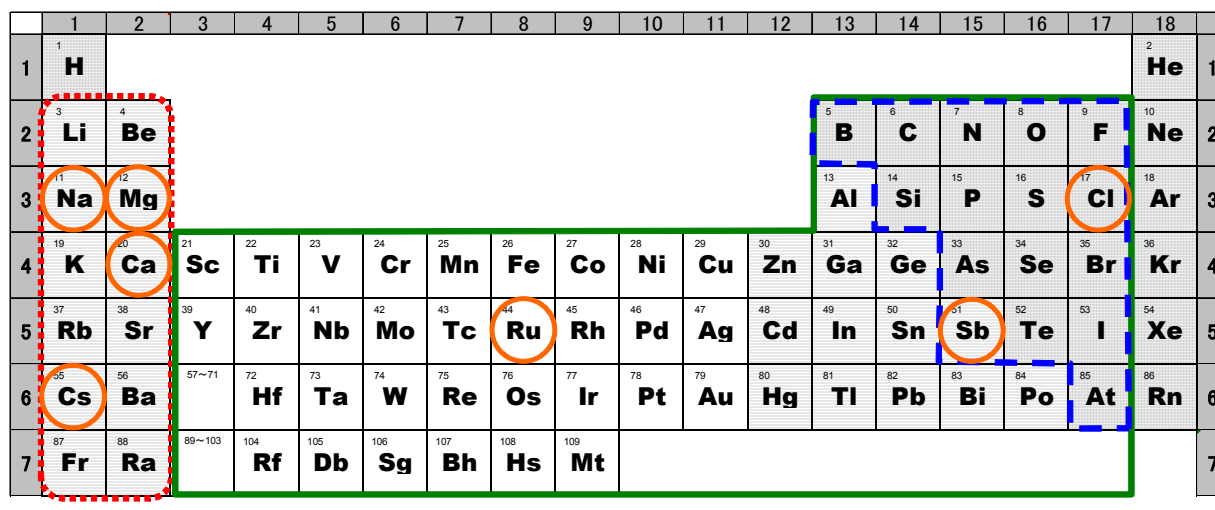


Fig. 3. Summary of DF estimation.

In addition, assuming use of a RO membrane under the condition that separates about 99.5% of Na and Cl from the feed solution, the DF of radionuclides present in the waste water at the Fukushima site would be expected as more than 100.

Adsorption method

Figures 4 and 5 show the K_{ds} for Cs and Sr adsorbents plotted against the concentration of test feed solutions shown as dilution ratio of simulated sea water given in TABLE II (No.1-4).

As shown in Fig. 4, K_{ds} with different dependency on the test feed solution concentration are observed for Cs adsorbents; the adsorbents A, B and C show less dependency on the test feed

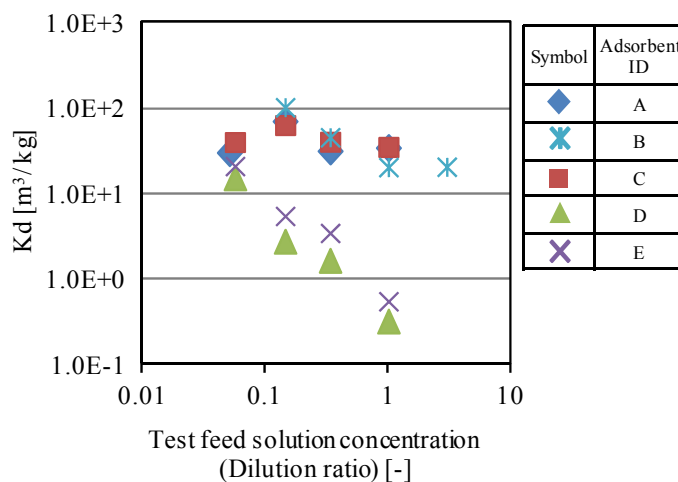


Fig. 4. K_{ds} of various Cs adsorbents.

solution concentration while the adsorbents D and E show clear dependency that their K_{dS} decrease with increasing the test feed solution concentration. Increase of the test feed solution concentration raises concentrations of Na and K, those are interfering elements for Cs adsorption, in the test feed solution. We can explain the dependency on the basis of the mechanism of Cs adsorption for each adsorbent, namely, the adsorbents that show less dependency on the test feed solution concentration have high selectivity for Cs adsorption. The adsorbents A and B include the crystal structure of hexacyanoferrate that it able to adsorb Cs by intercalation. The selectivity mechanism of the intercalation reaction allows Cs ions to be put into the crystal lattice but does not allow other cations present in the sea water, such as Na and K, to be put in due to the difference of ionic radii. The adsorbent C, CST, has high equilibrium constants for the exchange reaction of Na in Na_3X (CST) with Cs [6], that means CST is highly selective for Cs adsorption. On the other hand, the adsorbents D and E, which are both a sort of zeolite, are assumed to have lower selectivity for Cs in comparison with the adsorbents A, B and C. Since Cs and Na in the simulated sea water will be adsorbed onto the adsorbent by the competitive ion exchange reaction, the K_{dS} of the adsorbents D and E for Cs decrease with increasing the test water concentration (concentration of Na in the test water).

In the case of Sr adsorbents, all adsorbents tested in this study show K_{dS} decrease with increasing the test water concentration as shown in Fig. 5, although we tested adsorbents which have the mechanisms of intercalation and ion exchange. Calcium, one of the elements present in sea water and an interfering element for Sr adsorption, has the same value of ionic radius as Sr (TABLE III). This suggests that the adsorption of Sr onto both intercalation and ion exchange adsorbents is a competitive reaction with Ca, thus the K_{dS} for Sr decrease with increasing test feed solution concentration (concentration of Ca in the test feed solution).

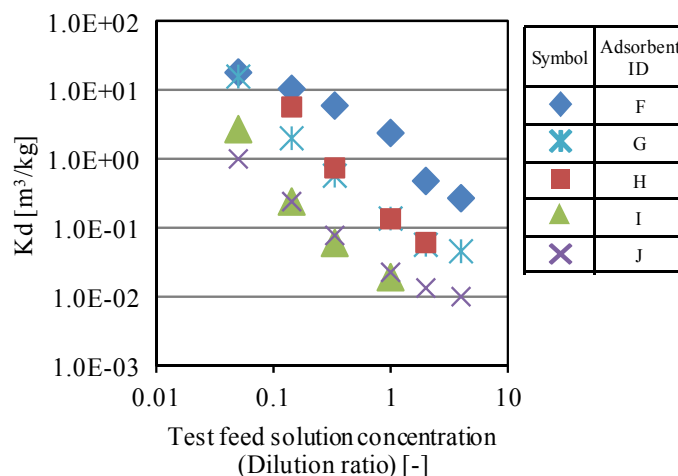


Fig. 5. K_{dS} for various Sr adsorbents.

In the column testing, we carried out detailed examinations for the breakthrough curves of SrTreat (Fortum Nuclear Services Ltd., Finland). Figure 6 shows the breakthrough curves obtained with various test feed solution conditions. Breakthrough of SrTreat has a clear dependency on the test feed solution condition: the test feed solution No.1 with the highest concentration of Cl and Sr exhibits the fastest breakthrough in the test feed solution examined, and the test feed solution No.4 with the lowest concentration shows no breakthrough within 600 BV of throughput. SrTreat is a sort of sodium titanate, and the K_d s of sodium titanate has a dependency on the test feed solution concentration as discussed above. The breakthrough curves of SrTreat are strongly correlated to the K_d s.

Figure 7 provides breakthrough curves obtained with various pH values of test feed solution. Test feed solutions No.1 and No.5 have the same concentrations of Cl and Sr but different pH, and test feed solutions No.3 and No.6 are similarly paired. The result clearly shows that increase in pH of test feed solution lengthens the time to breakthrough of the column, that is, the life of the adsorbent. The results for test feed solutions No.3 and No.6 suggest that pH change of 1 (pH=8 to pH=9) is enough to increase the life of the adsorbent more than two times as shown in Fig.7.

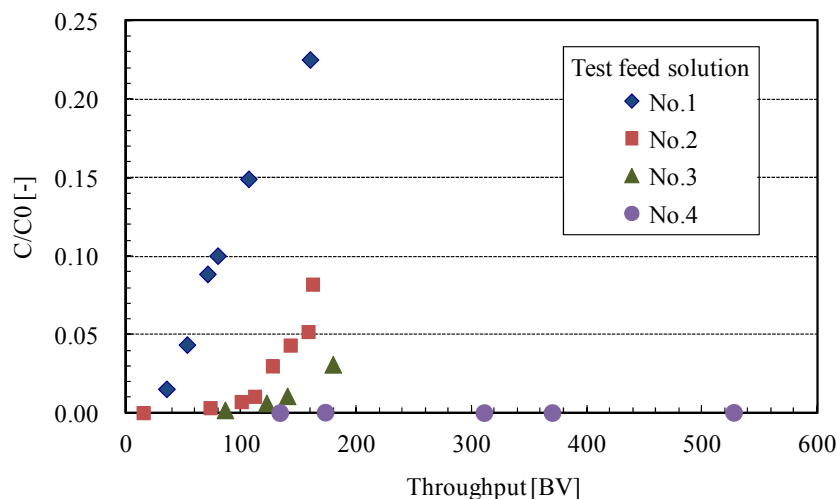


Fig. 6. Breakthrough curves for various test feed solution condition.

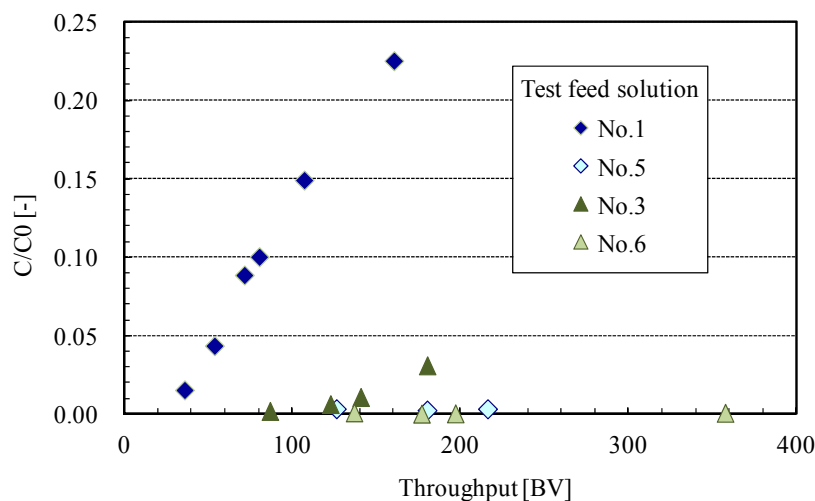


Fig. 7. Breakthrough curves for various pH values of test feed solution.

CONCLUSIONS

Removal of radionuclides by RO desalination and adsorption methods have been studied using simulated waste water of Fukushima Daiichi NPP. The RO desalination system holds great promise for removing radionuclides from the waste water; the DFs for major radionuclides Cs and Sr contained in the water expected to be more than 100. Adsorption behavior of Cs and Sr has much dependency on the adsorption mechanism of the adsorbent (intercalation and ion exchange) and the concentration of the competitive elements (Na, Ca, Mg) in the waste water.

Based on the results of this study, we concluded that an efficient waste water treatment system for Fukushima Daiichi NPP can be designed with an appropriate combination of desalination and adsorption methods.

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