Radioactive Waste Water Treatment for Fukushima Daiichi Nuclear Power Plant – 16081

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ABSTRACT

The Great East Japan Earthquake of 11th March 2011 caused serious damage to the Fukushima Daiichi Nuclear Power Station (NPS) of the Tokyo Electric Power Company, Inc. [1]. Toshiba and Shaw/AVANTech installed a Simplified Active Water Retrieve and Recovery System (SARRY^{TM} [2, 3]) to remove radioactive cesium (Cs) from the contaminated water. Toshiba, in partnership with EnergySolutions, also developed and installed the Multi Radionuclide Removal System (MRRS^{TM} [4]), which can remove radioactive nuclides being treated, except tritium, to a level less than the concentration limit in water. As contaminated water treatment has progressed, the composition of the contaminated water has changed. Both salinity and radioactive Cs concentration in the contaminated water have been decreasing. Thus, a new adsorbent that is suitable for the present water chemistry conditions is required.

In order to provide an appropriate contaminated-water treatment system, Toshiba has been examining the removal of not only radioactive Cs but also radioactive strontium (Sr) by SARRY^{TM}. SARRY^{TM} has been operated for removing Cs by using a Cs adsorbent. Instead of a Cs adsorbent, a new media that has high selectivity for both Cs and Sr should be installed. This paper describes the results obtained when using the newly developed adsorbent for removing Cs and Sr at once.

As the Cs and Sr adsorbent, we have selected crystalline silicotitanate (CST). The distribution coefficient (K_d) of CST was determined by the batch method. The lifetime of the adsorbent was evaluated by a column examination. The selected CST had a K_d value of over 10^4 ml/g for both Cs and Sr. The highest-selectivity CST had a lifetime (defined as the period for the outlet concentration to decrease to one tenth of the inlet level) of more than 125000 BV (bed volume) for Cs and more than 18000 BV for Sr, when the test was conducted at 10BV/h. Calculation code was also developed for estimating the relation between the BV and the decontamination factor (DF) using an adsorption rate model for diffusion and adsorption [5]. The calculation results of the Cs and Sr adsorption behavior agreed well with the experimental results. To evaluate the replacement cycle of adsorption tower in actual equipment, the radiation exposure during the replacement operation and the required Cs and Sr removal performance were used as limiting conditions for the estimation. The results of the evaluation showed that the selected CST has sufficient performance for practical usage. Based on this finding, Toshiba proposed loading the CST in SARRY^{TM}, and SARRY^{TM} loaded with this CST started removing Cs and Sr in December 2014 resulting in decreased contaminated water. It has been continuously working since then.

INTRODUCTION

The Great East Japan Earthquake of 11th March 2011 caused serious damage to the Fukushima Daiichi Nuclear Power Station (NPS) of the Tokyo Electric Power Company, Inc. The reactor has been cooled by circulating water injection system after the accident. Injected water is recovered and purified for reuse. A schematic diagram of the contaminated water treatment facilities [1] is shown in Fig. 1. The contaminated water treatment system consists of Cs/Sr filtering devices, a desalination facility, and a multi-nuclide removal facility.

There are two Cs/Sr filtering devices: The first one is the combination of a Kurion system [6-9] and an AREVA system [10]. The Kurion system is composed of several adsorption towers, and the AREVA system is composed of coagulation-sedimentation equipment. The other is SARRY^{TM}, developed by Toshiba and Shaw/AVANTech. The contaminated water is pumped from the reactor buildings and turbine buildings and is sent to Cs filtering devices. Then the water from which Cs has been removed is desalinated by a reverse-osmosis (RO) system [11]. After that, the desalinated water is reused for reactor cooling. High-salinity contaminated water generated from the RO system is sent to the multi-nuclide removal facility to remove radioactive nuclides being treated, except tritium, to a level less than the concentration limit in water and is stored in tanks. The multi-nuclide removal facility consists of three facilities, named MRRS^{TM}, Improved MRRS^{TM} and a High-performance Advanced Liquid Processing System. Two of them, MRRS^{TM} and Improved MRRS^{TM}, were manufactured and installed by Toshiba in partnership with EnergySolutions.

As contaminated water treatment has progressed, the concentrations of the impurities (i.e. Cl, Na, etc.) of the contaminated water have changed. The concentration of radioactive Cs has been decreased to approximately 1/100 (~10^4 Bq/ml) in 2015 compared with the level in 2011 (~10^6 Bq/ml). The concentration of seawater materials has also been decreased to approximately 1/10 in the case of chloride ion (several hundred ppm). Sr is the second most abundant radioactive nuclide in the contaminated water, at approximately 10^4 Bq/ml. In such a situation, not only radioactive Cs but also the β-ray exposure caused by Sr in the circulating cooling water has become a problem. The purpose of the development work described here was to reduce the risk of exposure to workers by removing both Cs and Sr in SARRY^{TM}. To remove radioactive Sr, we examined the use of an adsorbent that can remove Cs and Sr simultaneously, instead of existing Cs adsorbents. Here we describe the performance of the CST developed by Toshiba.

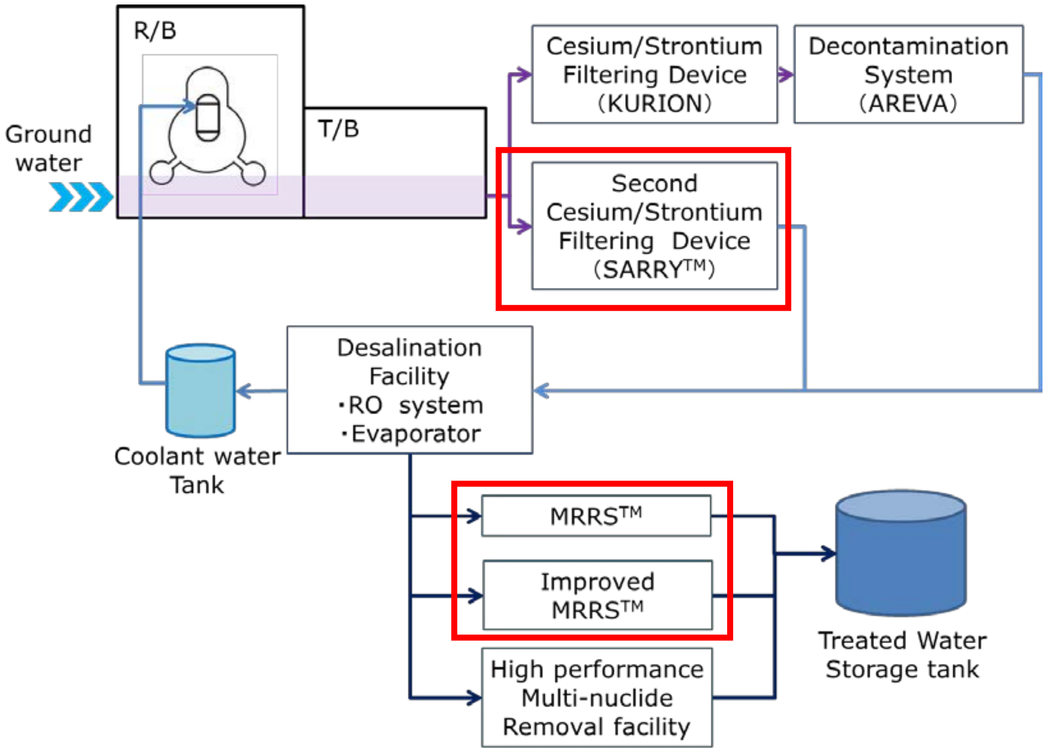


Fig. 1. Schematic diagram of contaminated water treatment facilities.

OUTLINE OF SARRY^{TM}

SARRY^{TM} was designed by Toshiba and Shaw/AVANTech, as a second cesium adsorption apparatus. Figure 2 shows schematic diagram of SARRY^{TM}. SARRY^{TM} consists of two individual trains each having two sand filters and five adsorption towers and one media filter to prevent adsorbent leakage. It is used two types of adsorbent to remove radioactive Cs from the contaminated water. One is Chabazite zeolite (IE-96, UOP), which is used for the four primary towers, and the other is crystalline silicotitanate (IE-911, UOP), which is used for the last tower. IE-911 has higher K_d than IE-96 and is used as a water polisher. The adsorption tower is replaced when: 1) Cs is sufficiently adsorbed and it has the allowable temperature of the adsorbent in storage due to decay heat, or 2) the adsorption tower surface has the allowable radiation dose. SARRY^{TM} has achieved stable operation since it started operation in August 2011. Because of its stability and high performance, SARRY^{TM} has been used as the main system for removing radioactive Cs from the contaminated water. The initial adsorbent formation can remove Cs but it cannot remove Sr.

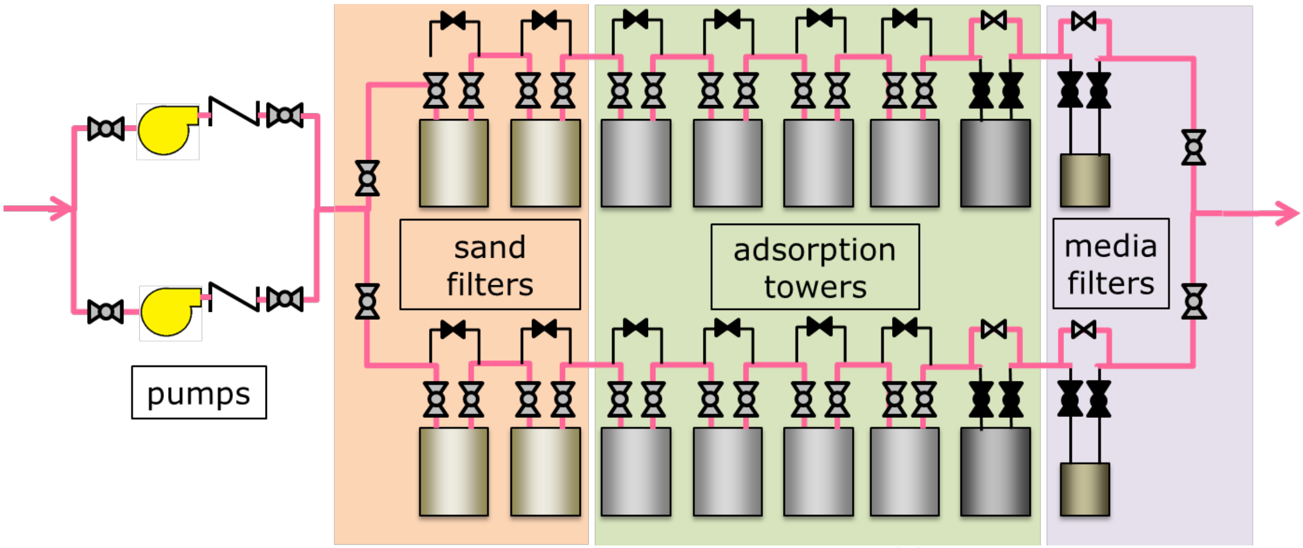


Fig. 2. Schematic diagram of SARRY^{TM} [2].

EXPERIMENTAL

Batch Adsorption Test

For the batch adsorption experiment, we selected three types CST of adsorbent to remove both Cs and Sr. TABLE I shows the adsorbent types. Simulated seawater was prepared using simulated seawater salt (Marine Art SF-1, Tomita Pharmaceutical Co., Ltd.). As the batch experimental solution, the simulated seawater was diluted 25 times with pure water, and $CaCl_2$ was added to the diluted seawater to a concentration corresponding to 80 ppm of Ca, and then $CsCl_2$ was added to a concentration corresponding to 33 ppb of Cs. Radionuclide solution containing ^{134}Cs and ^{85}Sr was also added. The major components of the simulated seawater are shown in TABLE II. To perform the batch adsorption test, 0.3 g of CST was added to 30 ml of the test solution (liquid-to-solid ratio of 100 ml/g). The mixture solution was shaken on a rotary shaker at 25 °C for 7 days. A portion of the test solution was filtrated through a membrane filter (pore size 0.45 μm). The counting rate of radioactive nuclide in the solution was measured with an NaI scintillation counter (2480WIZARD23, PerkinElmer). The K_d value was calculated using Eq. 1.

TABLE I. Adsorbent Type

Name	Binder Material
CST-1	Organic binder
CST-2	Inorganic binder
CST-3	Binderless (Toshiba)

TABLE II. Major Components of Simulated Seawater (solution of Marine Art SF-1)

Materials	Chemical Formula	Content / 1L Solution
Sodium chloride	$NaCl$	22.1 g
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	9.9 g
Calcium chloride	$CaCl_2 \cdot 2H_2O$	1.5 g
Sodium sulfate anhydrous	Na_2SO_4	3.9 g
Potassium chloride	KCl	0.61 g
Sodium hydrogen carbonate	$NaHCO_3$	0.19 g
Strontium chloride anhydrous	$SrCl_2$	0.013 g

$$K_d = \frac{A_0 - A_{eq}}{A_{eq}} \times \frac{V}{m} \qquad \text{(Eq.1)}$$

K_d : distribution coefficient (ml/g) A_0 : initial counting rate (cps)
A_{eq} : counting rate after reaching equilibration (cps)
V : solution volume (ml) m: weight of adsorbent (g)

Column Adsorption Test

The adsorbent (10ml) was filled in a plastic column (10 mm inner diameter). As the column test solution, the simulated seawater was diluted 25 times with pure water, $CaCl_2$ was added to a concentration corresponding to 80 ppm of Ca, and $CsCl_2$ was added to a concentration corresponding to 0.5 ppm of Cs. The flow rate of the solution was kept at 10 (1/h), which is the same space velocity (=superficial velocity of contaminated water / height of adsorbent) as that in actual equipment. ICP-AES (IRIS Advantage, Thermo Fisher Scientific) was used to determine the concentration of Cs and Ca. ICP-MS (7500i, Agilent) was used to determine the concentration of Sr. The relative concentration was calculated using Eq.2. The bed volume (BV) was defined as in Eq. 3.

$$\text{Relative concentration of Cs } (-) = \frac{C_{out}}{C_{in}} \qquad \text{(Eq.2)}$$

C_{out}: Cs or Sr concentration of column outlet (mol/m^3)
C_{in}: Cs or Sr concentration of column inlet (mol/m^3)

$$BV\,(-) = \frac{\text{volume of liquid to be treated } (m^3)}{\text{volume of adsorbent } (m^3)} \qquad \text{(Eq.3)}$$

Evaluation of Replacement Cycle

The required removal performance of radioactive Cs and Sr from the contaminated water is shown in TABLE III. From the viewpoint of the radiation exposure limit of workers, the maximum amount of adsorbed radioactive Cs per tower was set to 2.1×10^{15} Bq. We developed code for estimating the relation between BV and DF using an adsorption rate model for diffusion and adsorption. The adsorption behavior of Cs and Sr was estimated using this calculation code. Evaluation equations are shown in Eqs. 4 - 8. In Eq. 5, erf the means error function. *X* is a parameter for the height of the adsorbent, *v* is a parameter for the diffusion of the boundary film, and *Y* is a parameter for the contact time of the adsorbent with Cs and Sr.

TABLE III. Required Performances

Nuclide	required performance
Cesium(^{134}Cs&^{137}Cs)	Less than 10 Bq/ml at outlet
Strontium(^{90}Sr)	More than DF1000

$$u\left(\frac{\partial C}{\partial z}\right)+\frac{\partial C}{\partial t}=-\frac{(\partial q/\partial t)}{m} \qquad \text{(Eq.4)}$$

$$C_{out}\ /\ C_{in}[-]=\frac{1}{2}\left[1+erf\left\{\frac{(3Y/2X)-1}{2\sqrt{v/X}}\right\}\right] \qquad \text{(Eq.5)}$$

$$X=\frac{3D_p\rho_pK_d(1-\varphi)Z}{\varphi ub^2} \qquad \text{(Eq.6)}$$

$$v=\frac{D_p\rho_pK_d}{h_fb} \qquad \text{(Eq.7)}$$

$$Y=2D_pb^2(t-Z/u) \qquad \text{(Eq.8)}$$

C: concentration of Cs or Sr (mol/m^3) *q*: adsorption quantity (mol/kg)
m: weight of adsorbent (kg) ρ_p: adsorbent density (kg/m^3)
D_p: intra particle diffusion coefficient (m^2/s)
φ: porosity (-) *Z*: adsorbent column length (m)
u: linear flow rate (m/s) *b*: adsorbent radius (m)
h_f: boundary film mass transfer coefficient (m/s)
t: time (s)

RESULTS AND DISCUSSION

Batch Adsorption Test

Figure 3 shows the K_d values of CST-1 to CST-3, for Cs and Sr. The selected CST had a K_d value of over 10^4 ml/g, for both Cs and Sr. K_d was 10 times as high as that of the Cs adsorbent used in SARRY^{TM}. This result means that the selected CST has a possibility of removing both Cs and Sr from contaminated water.

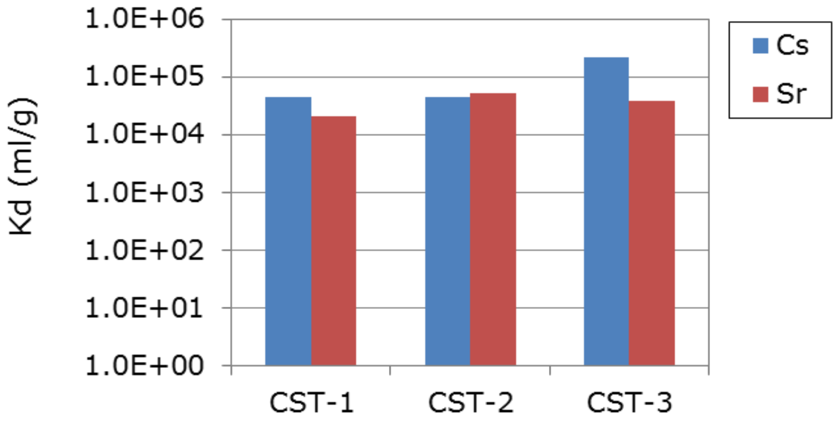
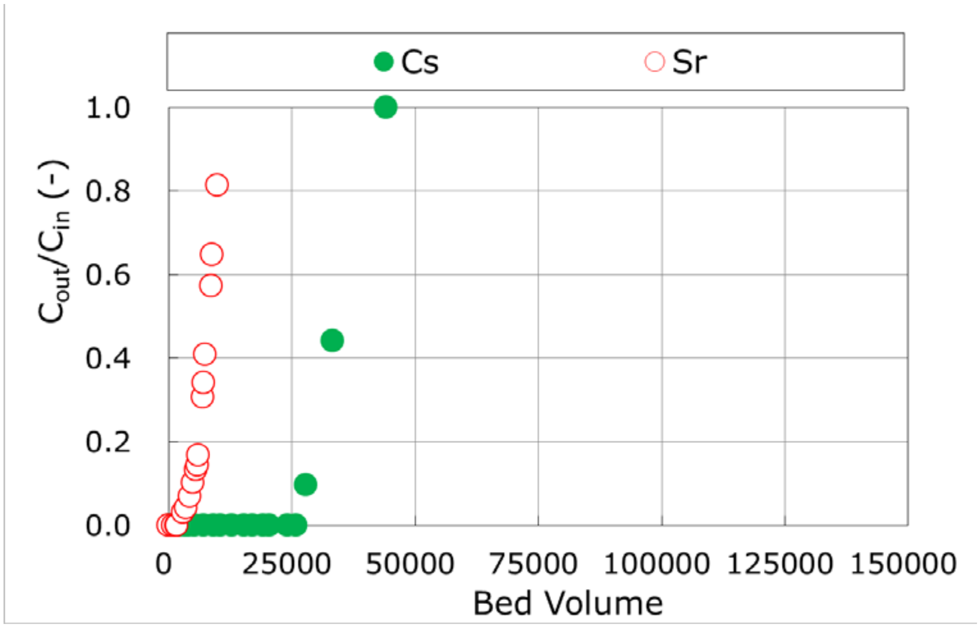


Fig. 3. Distribution coefficients of Cs and Sr adsorbents.

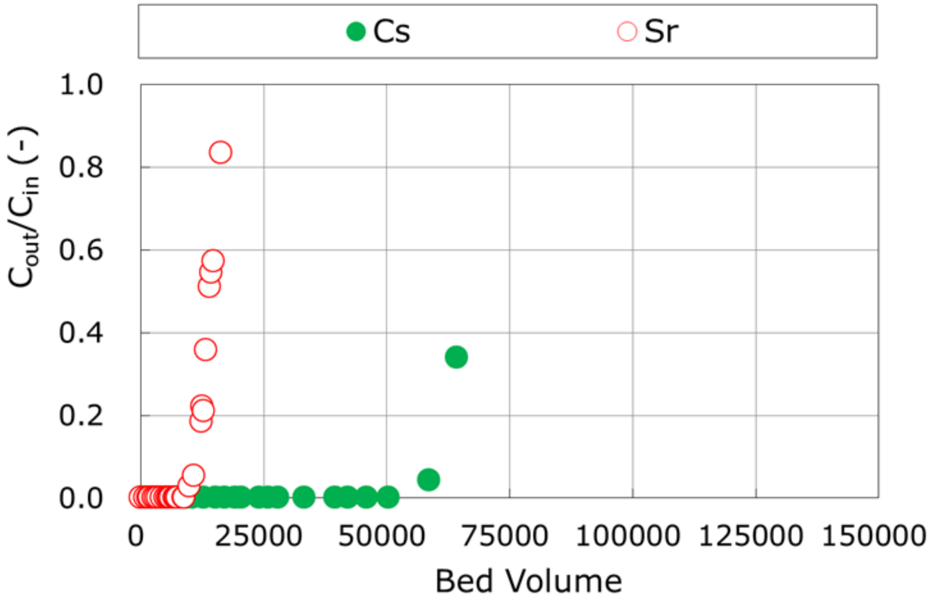
Column Adsorption Test

The results of the column adsorption test are shown in Fig. 4. The relative concentration of Ca was high from the start of the test, suggesting that the CST has high selectivity of Sr from Ca. CST-1 had a lifetime, defined as the period for the outlet concentration to decrease to one tenth of the inlet level, of 28000 BV for Cs and 5000BV for Sr. CST-2 had a lifetime of 60000BV for Cs and 11000BV for Sr. CST-3 had a lifetime of more than 125000BV for Cs and 18000BV for Sr. The test was conducted at 10 BV/h in each case. All of the selected CSTs showed high adsorption performance for both of Cs and Sr. The Cs and Sr adsorbing capacities of the selected CSTs were in the relationship CST-3 > CST-2 > CST-1.

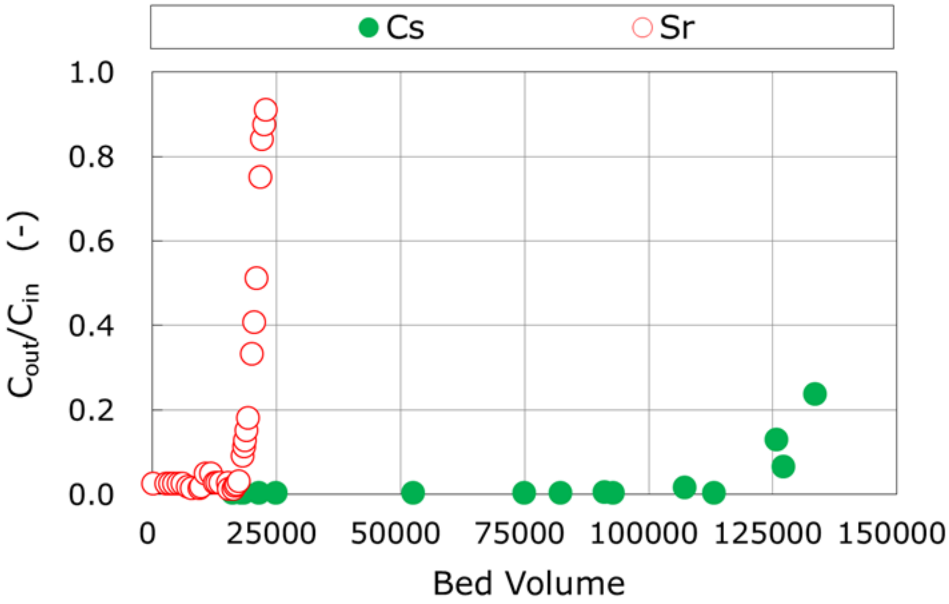


(a) CST-1

Fig. 4. Relative concentrations of each adsorbent.



(b) CST-2



(c) CST-3

Fig. 4. Relative concentrations of each adsorbent (continued).

Evaluation of Replacement Cycle

The results for estimating the CST adsorbing behavior are shown in Fig. 5. The results were calculated assuming that the adsorptions of Cs and Sr were independent. The calculation results for the adsorption behavior of Cs and Sr agreed well with the experimental results, suggesting that the calculation code can predict the adsorbing behavior. The replacement cycle was calculated based on the Cs adsorption limit. It was found that CST-2 and CST-3 had sufficient adsorbing capacity. At present, only CST-2 can be mass produced, and therefore, we proposed the use of CST-2. SARRY^{TM} has started removing Cs and Sr by using the CST-2 since December 2014 [12]. Figure 6 shows the trend of the relative concentration of Cs and Sr treated by SARRY^{TM}. The contaminated water treatment was performed by three adsorption towers. The adsorption tower was replaced before the concentration became one-tenth of the initial inlet concentration. After a new tower was installed, the flow path is rotated. SARRY^{TM} has achieved stable operation and reduced the concentration of Sr to less than 1/100. Figure 7 shows the total volume of contaminated water treated by SARRY^{TM}. By 18th December 2015, the total volume of treated contaminated water had reached 1,080,110 m^3 [13].

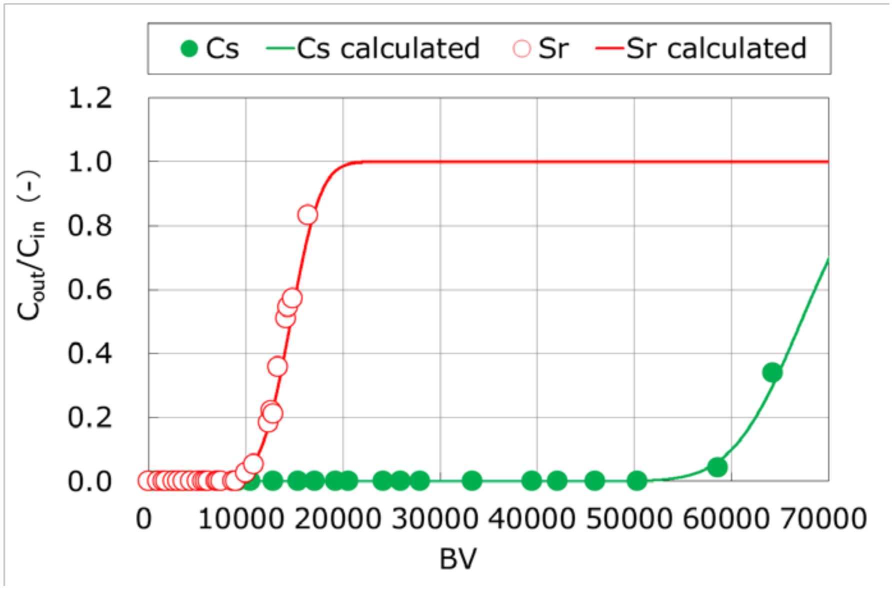


Fig. 5. Comparison of test results and calculation results

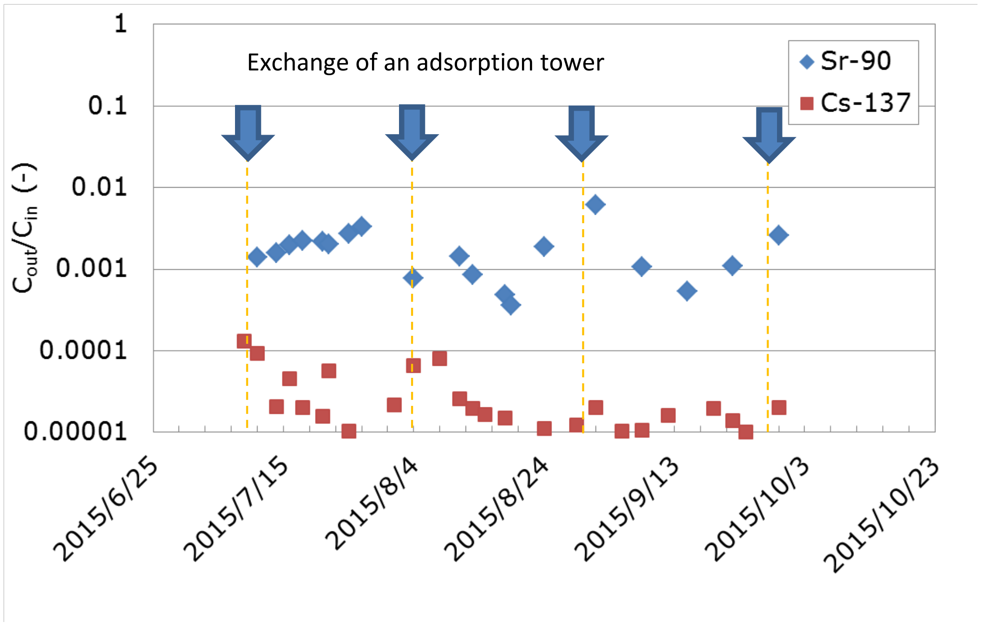


Fig. 6. Trend of relative concentration of Cs and Sr treated by SARRY^{TM}

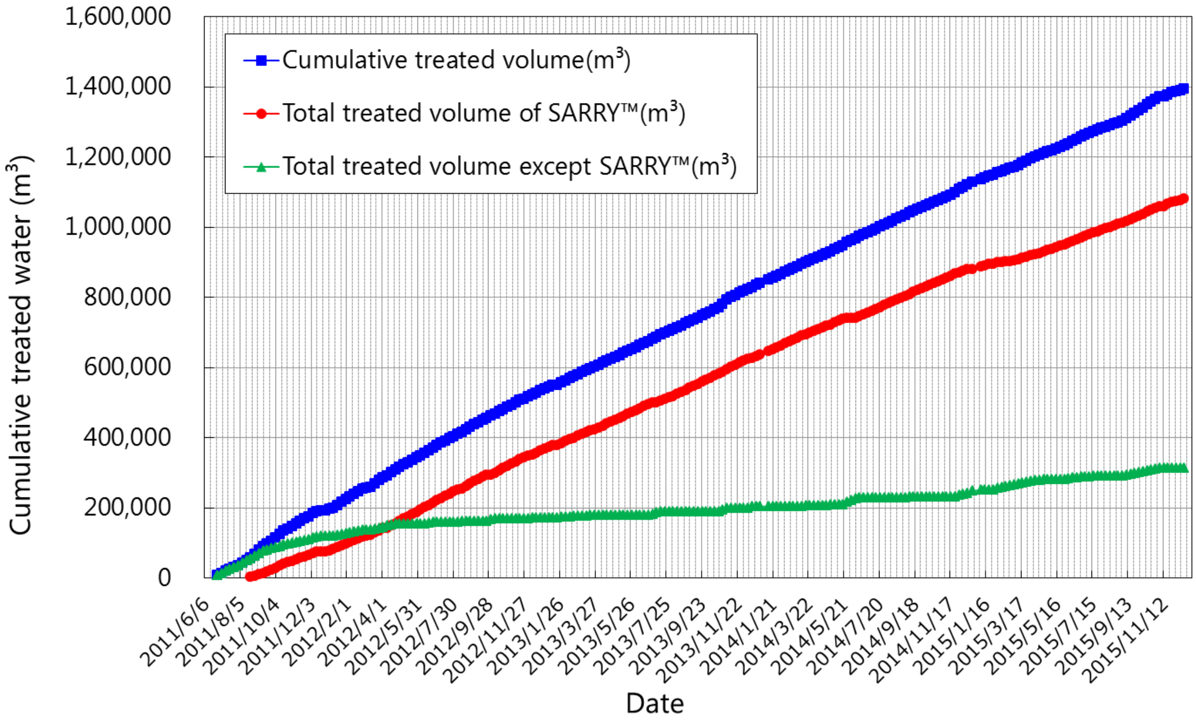


Fig. 7. Total volume of contaminated water treated by SARRY^{TM}.

CONCLUSIONS

We selected CST for removing both Cs and Sr simultaneously by using an adsorbent. The selected CST had a K_d value of over 10^4 ml/g for both Cs and Sr. The highest-selectivity CST had a lifetime of more than 125000 BV for Cs and 18000 BV for Sr, when the test was conducted at 10BV/h. Calculation code was also developed for estimating the lifetime from the relationship between BV and DF using an adsorption rate model for diffusion and adsorption. The calculation results of the Cs and Sr adsorption behavior agreed well with the experimental results. The evaluation showed that the selected CST has sufficient performance for practical usage. Toshiba proposed loading the CST in SARRY^{TM}, and SARRY^{TM} loaded with this CST started removing both Cs and Sr since December 2014, resulting in decreased contaminated water. It has been continuously working since then.

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