Performance of Zeolite, Silicotitanate, CsTreat® and SrTreat® Ion Exchange Materials in Fukushima Clean-up — 17114

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ABSTRACT

The performance of the major facilities used in Fukushima for the treatment of ^{137}Cs-bearing waters is reviewed. The facilities include Kurion zeolite system, SARRY and the ALPS systems. These utilize chabazite zeolite, silicotitanate CST and hexacyanoferrate based CsTreat® materials, respectively. The average processing capacity of chabazite is 0.41 m^3/kg and that of silicotitanate 2.81 m^3/kg. CsTreat® material has shown a processing capacity > 38.6 m^3/kg during its initial operation.A theoretical analysis shows that the selectivity of the materials for cesium over sodium, measured in terms of selectivity coefficient $k_{Cs/Na}$, largely determines their processing capacities. There is a increasing linear relationship between the processing capacity and $k_{Cs/Na}$ in logarithmic scales. Also, the decontamination factors obtained with the material for ^{137}Cs increase with increasing $k_{Cs/Na}$.

INTRODUCTION

The use of sea water for the emergency cooling of damaged reactors at Fukushima nuclear power plant in 2011 has resulted in accumulation of well over 500 000 m^3 of radioactive water in the reactor buildings and in the specially constructed storage tank farms. Initially, after contact with the damaged reactors, the major radionuclides in the water were ^{137}Cs and ^{90}Sr at 10^9 Bq/l levels. In addition, more than sixty other radionuclides were present at lower activity concentrations.

Altogether, seven different water decontamination systems have been or are used for water treatment in Fukushima. Regarding processed water volumes and activities, three systems have carried out the majority of work. These include Kurion zeolite system [1] (Kurion system), Simplified Active Water Retrieve and Recovery System (SARRY) [2] and Advanced Liquid Processing System (ALPS). Three evolutionary variants of ALPS systems are in use [3]. All the systems above use selective inorganic sorbent materials for the ^{137}Cs removal.

Today, most of the radionuclides, except tritium, have been removed from the cooling water and they are retained by various sorbents and sludges used for the water decontamination. Also, considerable amounts of ^{90}Sr remains in the storage tanks as the purification systems initially targeted the gamma emitter ^{137}Cs. More recently contaminated ground water with low level of radioactivity entering the Fukushima site has become a major concern and needs further purification.

In this paper, we make a theoretical analysis of the Cs-processing capacity of the inorganic materials used in Fukushima and discuss factors that have effect on it. This should be helpful for assessing the continuing use inorganic ion exchange materials in Fukushima and for other future applications elsewhere.

WATER PUFIFICATION SYSTEMS AND SORBENTS

Purification Systems

The Kurion system started to remove ^{137}Cs from the sea water used for emergency cooling of damaged reactors in June 2011 to fulfill the urgent demand to recirculate the water for further cooling. The system uses four trains of fixed beds (four 1.2 m^3 Cs removal beds in each train) packed with a natural zeolite [1].

The SARRY systems utilizes 5-bed (bed volume ca. 2 m^3) trains. First 4 beds are packed with a natural zeolite and the fifth bed with a highly selective silicotitanate material [2].

After Kurion system and SARRY there is a reverse osmosis (RO) facility to remove chloride from the water. RO system is expected to remove also some radioactivity from water but there seems to be no data on its performance. The RO permeate is reused as cooling water while the RO reject is collected in storage tanks for further treatment.

The RO reject in the storage tanks is treated by three ALPS systems. While Kurion system and SARRY only removed most of ^{137}Cs form the water, ALPS systems are designed to remove residual ^{137}Cs, ^{90}Sr and 60 other radionuclides to non-detectable level.

ALPS1 system consist of iron and carbonate co-precipitation facilities and a train of 16 adsorption/ion exchange vessels [3]. The ion exchange vessels include two 1 m^3 beds packed with Cs-selective CsTreat® material and three 1 m^3 beds packed with Sr-selective SrTreat® material. Three trains operate in parallel each having an output of 250 m^3/day. ALPS 2 (also called improved ALSP) is similar to ALPS 1 except that there is only one precipitation system. ALPS 3, also known as High-Performance ALPS, has filtering as a pre-treatment method and contains 20 absorption towers [3].

Sorbents

Zeolites are natural or synthetic aluminosilicates that due to their nanoporous 2D and 3D structures can act as molecular or ion sieves. High silica zeolites such as chabazite and clinoptilolite are selective for cesium ions [4]. Natural chabazite is used in Fukushima in Kurion and SARRY systems. Clinoptilolite is used in Sellafield reprocessing plant to remove ^{137}Cs from pond waters.

Titanosilicates are nanoporous structures consisting of silica tetrahedra and titanium octahedra and having molecular sieve properties. Crystalline silicotitanate CST was developed by Sandia laboratories and Texas A&M [5] and has been tested extensively for radionuclide removal. In SARRY system, the CST manufactured by UOP is used.

CsTreat® and SrTreat® are highly selective inorganic ion exchange materials for ^{137}Cs and ^{90}Sr removal, respectively [6,7]. SrTreat® material can also be used for the removal of key TRU nuclides. CsTreat® and SrTreat® were developed by University of Helsinki, Finland in the early 1990's. Both Treat-materials have been used in Fukushima since 2012 in the ALPS system. CsTreat® functionalily is based on hexacyanoferrate chemistry and SrTreat® on sodium titanates.

System performances
As of October 2013, the Kurion system had treated 193 560 m^3 and SARRY 587 570 m^3 of Cs-contaminated water (Table 1). ALPS 1 system had treated 25 888 m^3 of RO reject with no CsTreat bed change. Considering the amounts of sorbents used, the cumulative (average) processing capacities were 0.41 m^3/kg, 3.22 m^3/kg and 38.6 m^3/kg for Kurion, SARRY and ALPS1 systems, respectively (Table 1).
By October 20, 2016 ALPS systems had treated totally 688 649 m^3 [8], and as an estimate from this volume   ALPS 3 had treated well over 100 000 m^3.   Kurion system has not operated much since 2013, and by October 20,2016 it has treated totally 366 130 m3. The amount of water treated by SARRY was   1 281 670 m^3 in late October 20, 2016 [8].

Table 1. Amounts of water treated and cumulative processing capacity of sorbents of the Fukushima purification systems by October, 2013 [9].

System	Water treated (m^3)	Cumulative capacity m^3/kg sorbent
Kurion	193 560	0.41
Sarry	587 570	3.22
APLS-CsTreat	25 888	38.6

The zeolite in the Kurion system provided decontamination factors DF for ^{137}Cs in the range of few 1 000s to 200 000, typical values were a few 10 000s (Table 2). The DFs provided by the SARRY were about an order of magnitude higher with typical values of several 10 000s. Working independently in parallel, the Kurion and SARRY systems did not decrease the level of ^{137}Cs below the detection limit that is the requirement for release.

[137]Cs activity in ALPS 1 after the CsTreat beds was below the detection limit which means that the DF was well over 8 000 000 (Table 2).

Table 2.Decontamination factors provided by the Fukushima purification systems [9].

System	DF for [137]Cs
Kurion/zeolite	4 400-23 200
Sarry/silicotitanate	40 000- 2 000 000
APLS-CsTreat	> 8 300 000

THEORETICAL ANALYSIS

The sea water used for the emergency cooling of reactors at Fukushima has a considerable dissolved salt content (3.5 %) which will interfere with the ion exchange uptake of radionuclides. Among cationic ions, Na^+ (10.5 g/L) and K^+ (0.40 g/L) interferes the Cs^+ removal. Strontium removal is often hindered by Ca^{2+} (0.38 g/L) and in some cases also by K^+. We based our first analysis on the selectivity coefficient $k_{Cs/Na}$ for Cs/Na exchange considering that Na^+ was the most abundant cation in the sea water. The selectivity coefficient $k_{Cs/Na}$ for Cs/Na exchange was defined as

$$k_{Cs/Na} = \frac{[Cs]_S [Na]_L}{[Cs]_L [Na]_S} \qquad \textbf{Eq.} 1$$

where subscripts s and l refer to the ion concentrations in the solid and liquid phases, respectively. The processing capacity (L/kg) at full exhaustion is given by the value of the distribution coefficient k_d:

$$k_d = \frac{[Cs]_S}{[Cs]_L} \qquad \textbf{Eq.} 2$$

By combining Eqs. 1 and 2, and inserting $[Na]_S = Q - [Cs]_S$ it is obtained after some manipulation for k_d (and maximum processing capacity):

$$k_d = \frac{Q}{\dfrac{[Na]_L}{k_{Cs/Na}} + [Cs]_L} \qquad \textbf{Eq.} 3$$

where Q is the total ion exchange capacity (mol/kg) of the material.

Three different solution composition domains can be envisaged in Eq. 3:

- $[Cs]_L >> [Na]_L/k_{Cs/Na}$ (solution contains mostly Cs or $k_{Cs/Na}$ is very high). In this case total ion exchange capacity Q determines maximum processing capacity at given $[Cs]_L$.
- $[Cs]_L \approx [Na]_L/k_{Cs/Na}$. In this case, at given [Na] and [Cs] both Q and $k_{Cs/Na}$ determine maximum processing capacity
- $[Cs]_L << [Na]_L/k_{Cs/Na}$. In this case Cs-concentration in solution has no effect on the maximum processing capacity. At given [Na] both Q and $k_{Cs/Na}$ determine maximum processing capacity

Regarding the two latter cases, the total ion exchange capacities of ion exchange material typically top at about 1-5 mmol/g and cannot be increased higher for practical or theoretical reasons. Selectivity coefficient on the other hand has no

"maximum" values and is thus the key in developing high processing capacity materials. For the analysis, we plotted Eq.3 in logarithmic form

$$log k_d = log \frac{Q}{[Na]_L} + \; log(k_{Cs/Na}) \hspace{4cm} \text{Eq.4}$$

The k_d-values in Eq. 4 were replaced by processing capacities from Table 1. In the case of SARRY and silicotitanate, the contribution of zeolite 0.41 m^3/kg was subtracted giving a value of 2.81 m^3/kg for silicotitanate only. The values of $k_{Cs/Na}$ were literature values taken from Table 3. We also assumed that all sorbents had an ion exchange capacity of 1 meq/g and that the Na content of the water was constant and same for all sorbents. In this case the first term on the right had side of Eq. 4 is constant.

Table 3. Selectivity coefficients $k_{Cs/Na}$ and processing capacities for zeolite, silicotitanate and CsTreat [10].

Sorbent	Selectivity coefficient $k_{Cs/Na}$
Zeolite (mordenite)	450
Silicotitanate	18000
CsTreat	1500000

The processing capacity of the sorbents as a function of $k_{Cs/Na}$ (Fig. 1) was linear in the logarithmic scales (Fig. 1). Selectivity for Cs over Na is thus the key factor in determining the processing capacity. Also the decontamination factors obtained for ^{137}Cs seem to increase with the increase in $k_{Cs/Na}$ although there is not such a clear trend as for the processing capacity.

CONCLUSIONS
The theoretical analysis of chabazite zeolite, silicotitanate CST and CsTreat indicated that the selectivity for Cs/Na exchange, expressed as the selectivity coefficient $k_{Cs/Na}$ was the a key factor in determining the processing capacity of the materials in the ^{137}Cs removal from contaminated sea water. Also decontamination factors for ^{137}Cs increased with increasing selectivity.

Chabazite zeolite was ideal to remove high levels of ^{137}Cs from the Fukushima water. High selectivity was not needed as processing capacity was controlled by the radioactivity loading. However, zeolites were not able to reduce ^{137}Cs below detection limit required for water discharge.

Silicotitanate CST provided much higher processing capacity than chabazite producing far less spent media. It also gave much higher decontamination factors than chabazite but not high enough for the release of treated water.

Highly selective CsTreat was optimal material to polish the pretreated water being able to reduce ^{137}Cs below detection limit from $1\text{-}10 \cdot 10^6$ Bq/L levels.

High selectivity could be fully utilized to provide a high processing capacity and decontamination factor for [137]Cs.
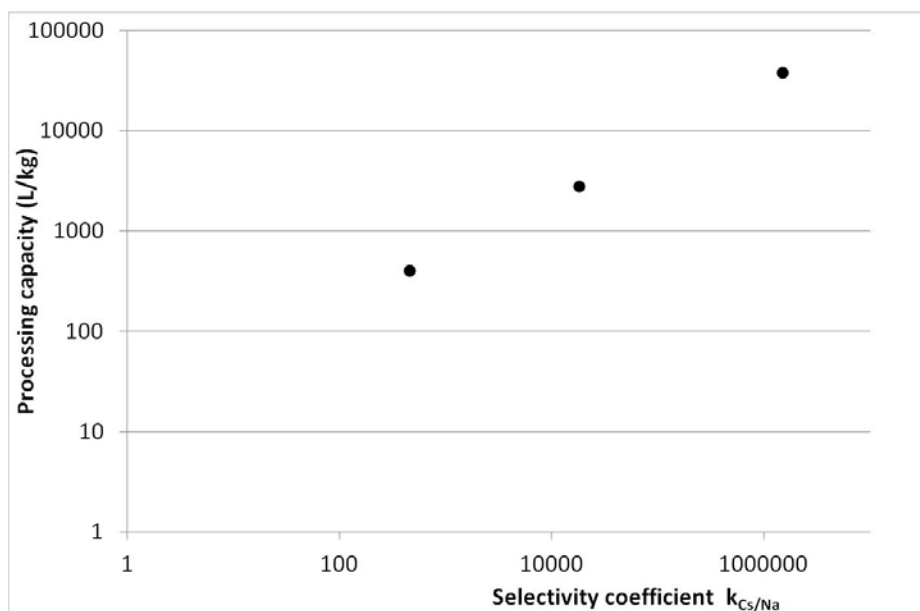

Figure 1. Processing capacity of zeolite, silicotitanate and CsTreat as a function of selectivity coefficient $k_{Cs/Na}$.

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