

EFFICIENCY OF FORTUM'S CSTREAT[®] AND SRTREAT[®] IN CESIUM AND STRONTIUM REMOVAL IN FUKUSHIMA DAIICHI NPP

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ABSTRACT

After the accident of March 11th 2011, a huge amount of highly radioactive water accumulated in the buildings of the Fukushima Dai-ichi NPP. Quite soon in June 2011 a Circulating Water Cooling Water System was established. Within this system activity level is reduced by cesium removal systems. A reverse osmosis (RO) system is used to obtain clean water for reactor cooling. RO generates salt concentrates in the same rate as new groundwater is penetrating to the system.

When a treatment system for RO concentrates was needed, ALPS[™] (Advanced Liquid Processing System) was designed and installed by EnergySolutions and Toshiba. Within that system 62 radionuclides are removed to the set non-detectable levels. Within ALPS[™] cesium and strontium are removed with highly selective media, CsTreat[®] and SrTreat[®] correspondingly. In ALPS[™] cesium is removed with Decontamination Factor (DF) of over 8.3 million and strontium with DF about 165 million to reach required non-detectable levels.

1. Introduction

At 2:46pm, March 11th 2011 the Tohoku-Chihou-Taiheiyou-Oki Earthquake occurred. Due to this earthquake a large tsunami caused massive damage to the reactor cores of the Fukushima Dai-ichi NPP. At the early stage sea water was used for cooling, which brought a lot of salt into the buildings, and huge amount of highly radioactive water accumulated in the reactor and turbine buildings. Quite soon in June 2011 a Circulating Water Cooling Water System was established [1]. This system had also the first water treatment system, including the first cesium removal system and a reverse osmosis (RO) system. This system created clean water for reactor cooling. In August 2011 the second cesium removal system was taken into use within the Circulating Water Cooling System.

New water is accumulating all the time since groundwater penetrates through the broken structures into the buildings and mixes with the circulating radioactive water. RO system has to remove the same amount of concentrates into storage tanks as new water infiltrates into the system.

Cesium removal was very important from the beginning to reduce the radiation level within the Circulating Water Cooling System. The first cesium removal system was installed as soon as it was available. However, its capacity was not very high and it created a lot of secondary waste.

In order to produce less secondary waste and also for the back-up purposes the second cesium removal system was installed.

RO system had to remove salt from cooling water. It also created highly radioactive concentrate, which included all radionuclides, including the rest of cesium. These concentrates, about 400 m³/day, were led to a large tank storage farm. A new treatment system for treatment of these RO concentrates were needed, and for this purpose an ALPS™ (Advanced Liquid Processing System) was designed and installed by EnergySolutions and Toshiba. Within that system 62 radionuclides have to be treated to the levels which are below the set measuring limits. Within ALPS™ cesium and strontium are removed with highly selective media, CsTreat® and SrTreat® correspondingly.

2. Circulating Water Cooling System

2.1 Principle of the Circulating Water Cooling System

Figure 1 gives a system outline of the Circulating Water Cooling System and its connection to ALPS™.

Radioactive water is taken from the basement of the buildings into a radwaste building. After this water is taken into a cesium removal system and RO system. Water without salts is taken into a buffer tank, from where it can be used for cooling of the reactors.

Since about 400 m³/day of new groundwater is penetrating all the time into the basement of the buildings, the same amount of salt concentrate, with reduced amount of cesium, has to be taken out as RO concentrate. Concentrates are collected into a tank farm, from where it is treated further with ALPS™.

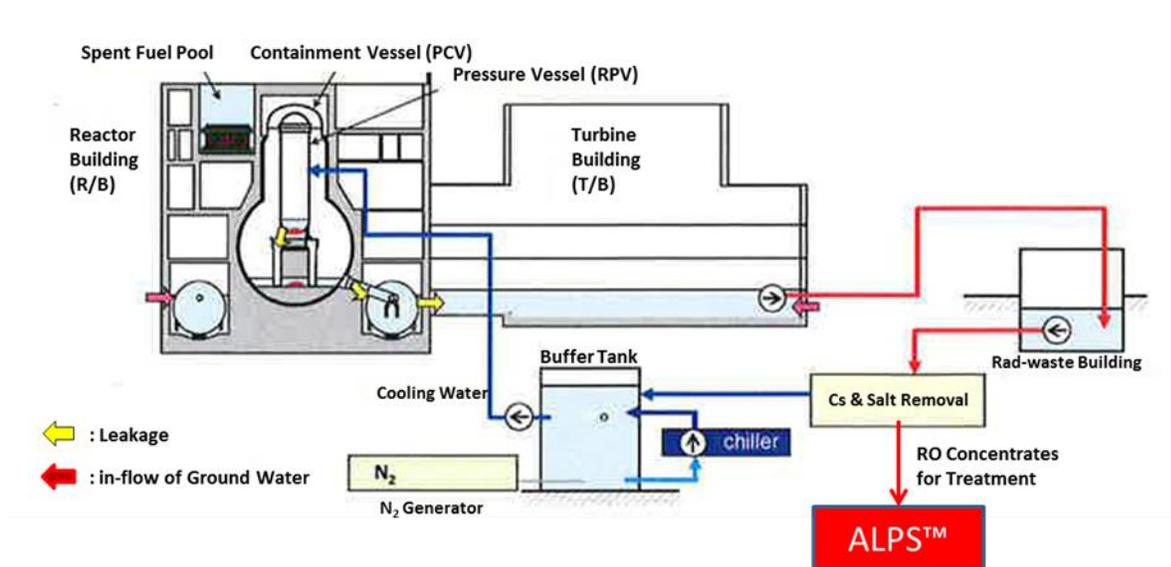


Fig. 1. System outline of the Circulating Water Cooling System in Fukushima Daiichi and its connection to ALPS™

2.2 Efficiency of cesium removal in the Circulating Water Cooling System

The first cesium removal system started its operation in June 17, 2011 [1]. This system was based on the use of engineered zeolites, and until the end of 2013 it had treated 203 740 m³ of water [2]. This system was in continuous operation until 26 April 2012. After this the system has been only temporarily in operation.

The second cesium removal system SARRY started its operation in Aug 19, 2011 [1]. This system uses silicotitanate to remove cesium. Until the end of 2013 this system has treated 636220 m³ of water [2].

In both these treatment systems the goal is to reduce the activity concentration of the water inside the Circulating Water Cooling System. Within this system it is not very essential, which level of decontamination is achieved. Purified liquid is recirculated back to the system. Thus, almost any DF is good for reduction of activity levels.

When the original cesium concentration within the Circulating Water Cooling System was about 5E+9 Bq/l [3], a good decontamination factor (DF) could be expected. The first cesium removal system with engineered zeolite gave as an average DF around 10 000, and the second system with silicotitanate gave typically DF around 100 000 [2].

The capacities, which could be achieved for cesium removal systems in the Circulating Water Cooling System, were about 0,4 m³/kg (364 BV) for engineered zeolite and about 3,22 m³/kg (over 3300 BV) for silicotitanate [2].

3. ALPS™ (Advanced Liquid Processing System)

For treatment of RO concentrates a new system, ALPS™ was constructed. The goal of this system is to reduce totally 62 radionuclides to the non-detectable level, and this was confirmed quite early by testing [4]. For cesium and strontium removal in ALPS™ the highly selective materials CsTreat® and SrTreat® were selected.

ALPS™ is a multiple phase system to remove all those required radionuclides [5]. There are two precipitation phases in a pretreatment facility and after these 14 ion exchange vessels plus 2 ion exchange towers as an Absorption Tower [5]. Ion exchange materials are used in vessels with 1 m³ net volume. The system includes three parallel lines, A, B and C line, each with a nominal capacity of 250 m³/h. Two operational lines can start to reduce the amount of highly active concentrates in the tank farm.

ALPS™ started its operation with the first line on March 30, 2013. On April 2, 2013 totally 68 m³ was already reported as treated [6]. The second line of ALPS™ started its operation at 9:49 on June 13, 2013 [7]. Until January 21, 2014 totally 40 369 m³ had been treated to non-detectable level [8].

The figure 2 gives a schematic picture of one line of ALPS™.

- Standard treatment capacity per line : 250 m³/24h/line
- Number of Line : 3 lines (2 lines for regular operation)
- 2 lines for regular operation (100 % operation is possible at maintenance for 1 line)

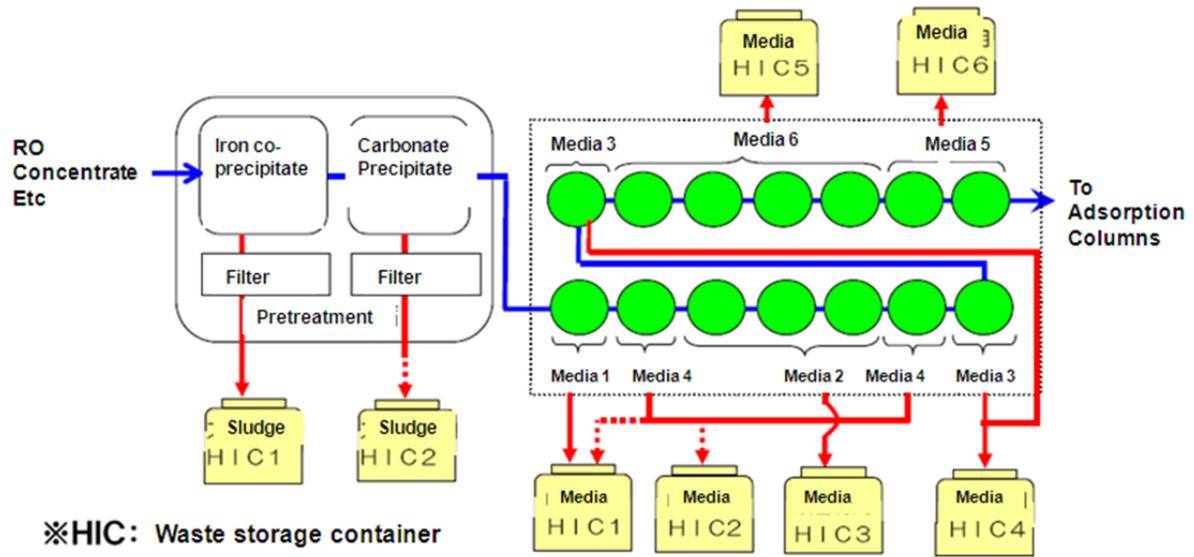


Fig 2. System outline of one line in ALPS™

4. Efficiency of CsTreat® and SrTreat® in ALPS™

Within the Circulating Water Cooling System a good part of cesium is removed in the first and second cesium removal system, but only minor part of strontium is removed. In RO concentrate the cesium concentration is about 3E+06 Bq/l, and that of strontium is about 1,6E+07 Bq/l.

A measuring limit for cesium concentration was set to 0,36 Bq/l, and a measuring limit for strontium concentration to 0,097 Bq/l [9]. The operation of the ALPS™ has met these non-detectable values. Because of this CsTreat® has given huge DF of over 8 330 000.

Strontium is removed in two phases. First precipitation takes some part of strontium into precipitate. After this SrTreat takes the rest. There is no exact data how much these two phases take individually, but typically precipitation gives DF of some tens. Strontium is altogether removed with huge DF of over 165 000 000. SrTreat®'s part of this millions.

Table 1 gives decontamination data for cesium removal and table 2 for strontium removal.

| Cs-137 in RO reject, Bq/l | Measuring limit for Cs-137, Bq/l [9] | Cs-137 measured, Bq/l | DF (CsTreat®) |
|---------------------------|--------------------------------------|-----------------------|---------------|
| 3E+06 | 3.6E-01 | <3.6E-01 | >8,330,000 |

Table 1. Decontamination factor (DF) for cesium in ALPS™

| Sr-90 in RO reject, Bq/l | Measuring limit for Sr-90, Bq/l [9] | Sr-90 measured, Bq/l | DF (precipitation plus SrTreat [®]) |
|--------------------------|-------------------------------------|----------------------|---|
| 1.6E+07 | 9.7E-02 | <9.7E-02 | ~165,000,000 |

Table 2. Decontamination factor (DF) for strontium in ALPS™

The capacity of CsTreat[®] and SrTreat[®] cannot be calculated in detail, since until January 21, 2014 and 40 369 m³ no vessel was changed. If total treatment is estimated for one 1 m³ vessel only, the capacities are 60,2 m³/kg (40 369 BV) for CsTreat[®] and 45,9 m³/kg (40 369 BV) for SrTreat[®]. When longer operation history exists, exact capacities can be calculated, but due to high capacities this will take long time.

5. Comparison of cesium removal efficiencies

From different tests and projects comparison of removal efficient has been calculated. Already long time ago the capacity data of the figure 3 as K_d has been presented [10]. From this comparison one can read that capacity of zeolite is about ten times less than capacity of silicotitanate. From results of cesium removal in Circulating Water Cooling System, as presented in Chapter 2.2. above, one can see that the difference between engineered zeolite and silicotitanate is about the same. The capacity of CsTreat[®] is well over ten times higher than capacity of silicotitanate and altogether about 1000 times higher than capacity of zeolite.

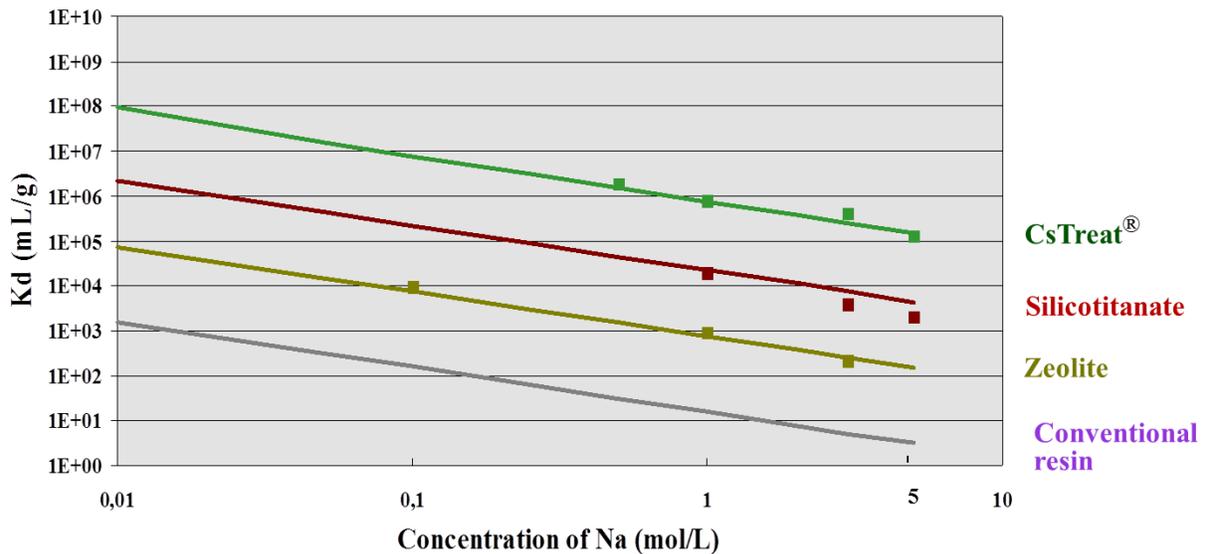


Fig. 3. Comparison of CsTreat[®]'s K_d values to others

Decontamination factor of different selective ion exchangers is related to the selectivity coefficient. Table 3 gives data for selectivity coefficient of different materials, including CsTreat[®], silicotitanate and natural zeolite [10]. This table includes also decontamination factors, which were achieved in Fukushima. The data indicate clearly that increase of selectivity coefficient by about two orders of magnitude, increases decontamination factor (DF) by about one order of magnitude, and in the case of CsTreat[®] with a greater factor.

| Ion Exchange Material | Concentration of Na (mol/l) | Selectivity coefficient, $k_{Cs/Na}$ | DF in Fukushima |
|-------------------------------|-----------------------------|--------------------------------------|-----------------------|
| Sulphonic acid resin | not known | <10 | |
| Resorcinol-formaldehyde resin | 6.0 | 11,400 ^{a)} | |
| Zeolite (mordenite) | 0.1 | 450 | ~10 000 ^{b)} |
| Silicotitanate (CST) | 5.7 | 18,000 | ~100 000 |
| CsTreat [®] | 5.0 | 1,500,000 | >8 330 000 |

a) selectivity coefficient calculated from measured distribution coefficient of 5450 ml/g.

b) data obtained with engineered zeolite

Table 3. Selectivity coefficient for Cs/Na exchange in commercial ion exchangers and DF obtained in Fukushima

6. Conclusions

In Fukushima Dai-ichi NPP the ALPS™ was constructed to treat salt concentrates which comes from a reverse osmosis system. CsTreat[®] and SrTreat[®] were selected for removal of cesium and strontium cesium in this ALPS™. During operation cesium is removed with DF of over 8,3 million and strontium with DF about 165 million to reach required non-detectable levels. These values are among highest performances ever.

Both CsTreat[®] and SrTreat[®] has shown very high capacity, and real values can be shown only after long time when ion exchange vessels has been changed.

When the performance of these highly selective ion exchangers is compared to the performance of other material, we can conclude that highest selectivity coefficients and high capacities have led to the best performance ever.

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