

Cesium and Strontium Removal with Highly Selective Ion Exchange Media in Fukushima and Cesium Removal with Less Selective Media - 14018

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ABSTRACT

After the Fukushima accident on March 11th 2011 huge amount of highly radioactive salt water accumulated in the buildings. Quite soon in June 2011 a Circulating Water Cooling Water System was established. This system included also the first cesium removal system and a reverse osmosis (RO) system, and it 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 circulating radioactive water. RO system has to remove the same amount of concentrates into storage tanks as new water infiltrates into the system.

Capacity of the first cesium removal system reached just over 350 bed volumes (BV), and the second one reached values of over 3,000 BV.

Since the activity of liquid was above 1 GBq/l, high decontamination factors (DF) could be expected. The first cesium removal system reached typically DF less than 20,000. The second cesium removal system reached DF values typically from tens of thousands to over hundred thousand, and even higher than 2 million value was reported.

When a new treatment system for treatment of RO concentrates were needed, an ALPS™ (Advanced Liquid Processing System) was installed. Within ALPS™ cesium and strontium are removed with highly selective media, CsTreat® and SrTreat® correspondingly, and cesium is removed with DF of over 8.3 million and strontium with DF about 165 million to reach required non-detectable levels.

INTRODUCTION

When the Tohoku-Chihou-Taiheiyu-Oki Earthquake occurred at 2:46pm, March 11th 2011, quite soon started the work to construct the first treatment system for radioactive waters. Immediately after the accident sea water was used for cooling. Soon after this a Circulating Water Cooling System was established, and this system needed a treatment system to produce clean water for cooling of the reactors [1]. When this treatment system was taken into operation, water was taken from basements of the buildings, cleaned and used for cooling. The system was both to reduce the activity content of the liquid and to remove salts. Because of these requirements the system included both decontamination system and a reverse osmosis plant. Concentrate from reverse osmosis plant was taken out for storage. The amount of this concentrate was determined by the inflow of groundwater into the buildings.

The first system to reduce the amount of radioactivity inside the Circulating Water Cooling System included a decontamination system and a first cesium removal system. This water processing facility started its operation in June 17, 2011 [1]. The decontamination system was based on co-precipitation and it formed sludge, which removed radioactivity [2]. The first cesium removal was based on the use of engineered zeolites, and its continuous operation stopped on 26 April 2012. It had treated 168,170 m³ until 3 October 2012. After this the system has been temporarily in operation, and as of October 29, 2013 this system has treated 193,560 m³ of water [3]. Only 25,390 m³ was treated within about thirteen months.

The second cesium removal system SARRY started its operation in Aug 19, 2011 [1]. This system uses silicotitanate to remove cesium. Until October 29, 2013 this system has treated 587,530 m³ of water [3].

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.

Since all the time about 400 m³/day of additional water has been flowing into the system from groundwater, water has been treated by reverse osmosis (RO) system and 400 m³/day has been taken out from circulating water as RO concentrate. Since this much concentrate is led daily into the tank storages, there was a need to have a treatment system to treat RO concentrates to the activity levels which are below detection levels. For this purpose 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]. Until October 29, 2013 totally 25,888 m³ were treated to non-detectable level [3]. Until that time no ion exchange bed was changed.

The second Line of ALPS™ started its operation at 9:49 on June 13, 2013 [7].

The Figure 1 shows the system outline of the Circulating Water Cooling System and connection of ALPS™ to it [8].

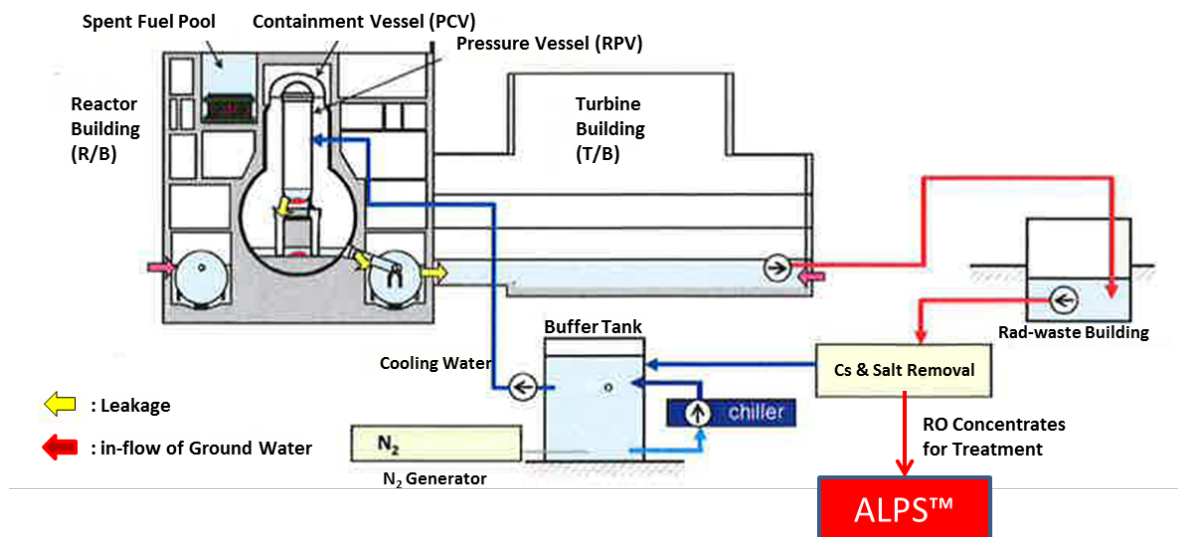


Fig. 1. System outline of the Circulating Water Cooling System in Fukushima Daiichi and connection of ALPS™

TREATMENT CAPACITIES

Cesium Removal System 1&2

In the first cesium removal system engineered zeolite is used, and its K_d in sea water is about 2000 ml/g (2 m³/kg) [9]. In the second cesium removal system (SARRY) crystalline silicotitanate has K_d over 20 000 ml/g (over 20 m³/kg) in sea water [9]. Sea water contains typically 10.7 g/l of sodium.

In the first cesium removal system the engineered zeolite is used in a 1.2 m³ bed [10]. If the density of that material is about 0.9 kg/l, one vessel contains about 1080 kg of ion exchange media. The performance of this system in its early days of operation and in its latest phases is presented in Table 1 [11]. This system has treated totally about 193,560 m³, from which about 118,000 m³ in 2011, about 50,170 m³ in 2012 (since its continuous operation was stopped on April 26, 2012) and about 25,390 m³ during some weeks in 2013 until October 29, 2013.

On October 29, 2013 the first cesium removal system had reached a cumulative capacity of 0.41 m³/kg. This value is only about 20% of the capacity, which was shown by K_d as maximum capacity in sea water.

In the second cesium removal system (SARRY) silicotitanate is used in 1.95 m³ beds, and until beginning of 2013 it has given throughputs of over 1800 bed volumes [9]. Silicotitanate's bulk density is 1.041 g/cm³ [12]. Thus, one bed contains about 2030 kg of media.

According to the published press releases the performance of the SARRY system in its early days of operation and in its latest phases is presented in Table 2 [13]. Until October 29, 2013 this system has treated totally about 587,530 m³. From the figures of Table 2 one can see that

cumulated capacity (m^3 treated/ m^3 of bed) has improved when operation experience has improved. This capacity improvement is probably caused by reduction of salt concentrations. This system has treated close to 70,000 m^3 in 2011, about 342,000 m^3 in 2012, and until October 29, 2013, about 240,000 m^3 in 2013.

On October 29, 2013 the second cesium removal system reached a cumulated capacity of 3.22 m^3/kg . This value is only about 16% of the capacity, which was shown by K_d as maximum capacity in sea water.

TABLE 1. Capacities of the first cesium removal system in the Circulating Water Cooling System during different time periods

Treated volume, m^3	Cumulative, m^3	Vessels used, cumul. #	Media used, cumul. m^3	Capacity, m^3/kg	Cumul. capacity, m^3/kg	Cumul. capacity, BV
7230	7230	23	27.6	0.29	0.29	262
6380	13610	43	51.6	0.35	0.29	264
6130	19740	57	68.4	0.49	0.32	289
4510	24250	71	85.2	0.36	0.32	285
Ref [7]	172740	406	487.2		0,39	355
Ref [8]	179610	424	508.8		0,39	353
Ref [3]	193560	438	525.6		0.41	368

TABLE 2. Capacities of the second cesium removal system (SARRY) in the Circulating Water Cooling System during different time periods

Treated volume, m^3	Cumulative, m^3	Vessels used, cumul. #	Media used, cumul. m^3	Capacity, m^3/kg	Cumul. capacity, m^3/kg	Cumul. capacity, BV
1760	1760					
3480	5240	3	5.85	0.86	0.86	896
3480	9080	5	9.75	0.86	0.89	931
3870	12950	7	13.65	0.95	0.91	949
Ref [14]	389020	68	132.6		2.92	2934
Ref [15]	494740	80	156		3.05	3171
Ref [3]	587570	90	175.5		3.22	3348

Cesium And Strontium Removal Capacities In ALPS™

When we study the performance of ALPS™, we have the performance of the Table 3 and of Table 4. The tables give the situation on October 29, 2013 [3], and since there has been no change of vessel until that date, the capacity is calculated until that date for the first vessel.

Table 3 gives the performance of CsTreat® and Table 4 the performance of SrTreat®. Both materials are used in a 1 m^3 bed. The density of CsTreat® is 0.67 kg/l and density of SrTreat® is 0.88 kg/l .

TABLE 3. Capacity of CsTreat[®] in ALPS[™]

Treated volume, m ³	Cumulative, m ³	Vessels used, cumul. #	CsTreat [®] used, cumul. m ³	CsTreat [®] capacity, m ³ /kg	Cumul. capacity, m ³ /kg	Cumul. capacity, BV
	25888	0	0		38.6	25888

TABLE 4. Capacity of SrTreat[®] in ALPS[™]

Treated volume, m ³	Cumulative, m ³	Vessels used, cumul. #	SrTreat [®] used, cumul. m ³	SrTreat [®] capacity, m ³ /kg	Cumul. capacity, m ³ /kg	Cumul. capacity, BV
	25888	0	0		29.4	25888

When the performance of CsTreat[®] for cesium removal is compared to the performance of engineered zeolite and silicotitanate, a good match for our old comparison of Figure 2 can be seen. [16]

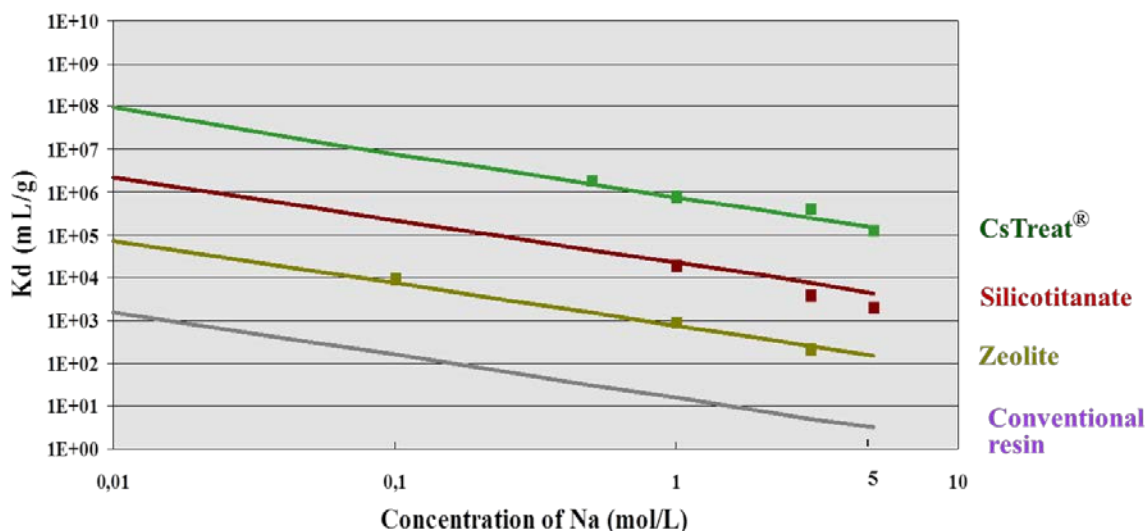


Fig. 2. Comparison of CsTreat[®]'s K_d values to others

DECONTAMINATION FACTORS (DF)

Decontamination factors are closely linked to the selectivity of the ion exchanger. The higher selectivity factor the better uptake of target radionuclide from the solution of salts. Previously the comparison of selectivity coefficients of different cesium selective materials have been published as in Table 5 [16]. These figures gives the idea what can be expected for the decontamination factors for different media.

DF In Cesium Removal System 1&2 In The Circulating Water Cooling System

When a combined system with the first cesium removal system and decontamination system as of Aug 9, 2011, were in operation total DF for cesium was $1E+06$. The first cesium removal system had as of Aug. 9, 2011 a DF of $6E+03$ [1].

TABLE 5. Selectivity coefficient for Cs/Na exchange in commercial ion exchangers.

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

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

The SARRY system was reported to have DF over 2 million for cesium [9]. Table 6 gives the DF for different operation periods according to the published press releases [17]. As of Nov 29, 2011 the DF of $5E+05$ was reported [1].

From the figures of Table 6 can be concluded that typically the first cesium removal system with engineered zeolite in the Circulating Water Cooling System gives DF <20,000. In the same way typical DF for the second cesium removal system (SARRY) in the Circulating Water Cooling System is from tens of thousands to about hundred thousand.

By using published data about ingoing activities and calculated DF values we can conclude that the first cesium removal system has removed about $1.3E+17$ Bq of cesium into 525.6 m^3 of ion exchange material resulting in the activity concentration of about 0.275 TBq/kg. In the second system correspondingly about $8.7E+16$ Bq was removed into 175.5 m^3 of ion exchange material resulting in the cesium concentration of about 0.476 TBq/kg.

As an estimate, at the time of accident there was about $2.9E+18$ Bq of Cs-134 and about $1.6E+18$ Bq of Cs-137 in the three cores of damaged reactors. If we compare the removed activity into the original activity concentration, it is about 4.9 % of the Cs activity in the cores. Taking into account decay of Cs-134 the percentage in reality is somewhat higher.

TABLE 6. Decontamination factor of first and second (SARRY) cesium removal system during different time periods

Press Release #	Before treatment (1), Bq/cm ³	Exit cesium removal system 1	Before treatment (2), Bq/cm ³	Exit of cesium removal system 2	DF (1)	DF (2)
10	1.3E+06	1.2E+04	1.3E+06	2.3E+01	108	56,522
15	1.1E+06	6.7E+01	8.3E+05	<3.6E-01	16,418	2,305,555
21	7.2E+05	7.4E+01	4.3E+05	<4.7E-01	9,730	914,894
30	3.8E+05	2.8E+01	2.4E+04	<6.0E-01	13,571	40,000
46	1.3E+05	8.0E+00	8.9E+04	8.6E-01	16,250	103,488
65	1.1E+05	3.4E-01	4.8E+04	1.2E+00	323,529	40,000
85	5.3E+04	1.2E+01	6.2E+04	1.9E+00	4,417	32,632
95	6.4E+04	6.9E+00	3.5E+04	6.9E-01	9,275	50,725
105			3.3E+04	3.5E-01		94,286
108	5.5E+04	5.2E+00	2.8E+04	3.4E-01	10,577	82,353
119			3.6E+04	3.0E-01		120,000

Cesium And Strontium DF in ALPS™

Original cesium concentration in the Circulating Water Cooling system was about 5E+6 Bq/cm³ [9], and it was reduced by the cesium removal system to such a level that in RO reject it is about 3E+3 Bq/cm³ [18].

The concentration of Sr-90 (half-life about 29 years) in RO reject is about 1.6E+4 Bq/cm³ and Sr-89 (half-life about 51 days) late 2011 about 1.1E+4 Bq/cm³ [18].

RO reject has about 10 000 mg/l of chloride and about 7 000 mg/l of sodium [18], which means that its salt content is about 70% of the ionic content of sea water.

As long as cesium and strontium removal goes until the measuring limit, DF within ALPS™ can be calculated directly from incoming activity concentration to the measuring limit. For cesium removal this figure represent almost fully the performance of highly selective CsTreat®. For strontium removal this figure represents the effect of both the preceding precipitation phase and the highly selective SrTreat®. Tables 7 and 8 give the corresponding decontamination factors.

For the performance of CsTreat® almost this high decontamination factors have been measured before, but for strontium removal this DF is extraordinary high.

TABLE 7. Decontamination factor (DF) for cesium in ALPS™

Cs-137 in RO reject, Bq/cm ³	Measuring limit for Cs-137, Bq/cm ³ [8]	Cs-137 measured, Bq/cm ³	DF (CsTreat®)
3000	3.6E-04	<3.6E-04	>8,330,000

TABLE 8. Decontamination factor (DF) for strontium in ALPS™

Sr-90 in RO reject, Bq/cm ³	Measuring limit for Sr-90, Bq/cm ³ [8]	Sr-90 measured, Bq/cm ³	DF (precipitation plus SrTreat®)
1.6E+04	9.7E-05	<9.7E-05	~165,000,000

When DF for cesium in ALPS™ is compared to those of cesium removal systems 1 & 2 in the Circulating Cooling Water System, one can find that they are in good correlation with the selectivity coefficients of Table 5. Since the first cesium removal system utilizes engineered zeolites and not only mordenite type material, its DF is closer to that of silicotitanate than expected by the figures of Table 5. Maximum available DF with CsTreat® cannot be defined since it always gives DF until measuring limit, but it is remarkably higher than with the compared materials, and the value of over 8.3 million to the non-detectable level is extremely high.

Until October 29, 2013, in the ALPS™ totally about 7.77E+13 Bq of cesium and about 4.14E+14 Bq of strontium has been removed. If we estimate that these amounts were removed into the first column only, they were removed into 1 m³ both. This results in the concentration of about 0.12 TBq/kg of cesium and about 0.47 TBq/kg for strontium. In both cases only the future will show how high total capacity can be reached.

CONCLUSIONS

After the Fukushima accident there was urgent need to reduce the level of activity in the Circulating Water Cooling System. Soon after that there was a need to start to reduce the amount of highly active RO condensate in the tank farm, and this could be done by treating the concentrate with new ALPS™.

In recirculating system less selective ion exchangers, engineered zeolite and silicotitanate, have done good job in reducing radiation levels. In the Circulation Water Cooling System the requirement of DF is not so important. DF levels from thousands to tens of thousands has been good from zeolite. DF level from tens of thousands to over hundred thousand has been excellent from silicotitanate.

In ALPS™ system, where the requirement is to reduce the concentrations of radionuclides to the non-detectable level, cesium is removed with highly selective CsTreat®, which has given DF above 8.3 million. For strontium removal SrTreat® with preceding precipitation section gives huge DF of about 165 million.

ALPS™ system has demonstrated excellent removal efficiency both for cesium and strontium. Overall decontamination factors are something which can be achieved only together with the highest selectivity of ion exchangers.

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