Successful Cesium Removal Campaign at the Loviisa NPP, Finland- 11002

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ABSTRACT

Selective removal of radionuclides from evaporator concentrates has been an essential part of waste management at the Loviisa nuclear power plant in Finland. During the period from 1991 to 2003 five purification campaigns had been carried out. About 1100 m^3 of evaporator concentrates had been purified with only 160 liters of CsTreat®. In 2009 the sixth campaign purified about 210 m^3 with 72 liters of CsTreat®. Cesium was removed during the whole period with a very high decontamination factor (DF). The DF value was up to almost 4800.

After these campaigns about 1310 m^3 of high salt evaporator concentrates have been released from radiological control and only 29 final waste columns, i.e. 232 liters of CsTreat® remains to be stored in three concrete containers. The initial plan at the Loviisa NPP for the evaporator concentrates was to solidify them directly into concrete. If 1310 m^3 of concentrates is directly cemented, about 2850 final waste concrete containers with a total net volume of 2850 m^3 is produced. Compared to this alternative the nuclide removal system (NURES™) has created a volume reduction from 2850 containers to less than 3 containers and there has been no need to solidify the waste. Thus, selective nuclide removal has created great savings in the waste management of the Loviisa NPP.

INTRODUCTION

Loviisa NPP is a power plant with two 488 MWe VVER-440-PWR reactors. Unit 1 was commissioned in 1977 and unit 2 in 1980. The power plant has a large liquid waste storage facility. Four tanks are used for evaporator concentrates, 300 m^3 each. Three similar tanks are used for spent resins.

A nuclear waste management program was started in 1979, and as a part of this program selective removal of radionuclides was found to be one of the most efficient ways to improve wet waste management. In 1991 a NUclide REmoval System (NURES™) was taken into use at the Loviisa nuclear power plant.

The original plan was to solidify all evaporator concentrates with cementation. However, the use of selective nuclide removal has made it possible to postpone the investment of the cementation system. Now a solidification plant has been constructed and it will be tested during 2011. The solidification plant will be used for solidification of all wet wastes like spent resins and sludge.

Typically for three operation years all evaporator concentrates, about 240 m^3, are collected into one tank. After that period the tank is isolated, which gives time for short lived radionuclides to decay. After the isolation time only cesium is evenly divided in the whole liquid volume and all corrosion products, including cobalt, have settled at the lowest level at the bottom of the tank. Thus, cesium is the only radionuclide, which limits the release of the liquid that fill the upper part of the tank.

Earliest after two years of storage the evaporator concentrate in the tank is treated with an existing nuclide removal system (NURES™) in a continually processing campaign. Cesium is removed by highly selective ion exchange material, CsTreat®, which is based on hexacyanoferrate. This special material is needed for the work, since the sodium and potassium nitrate salt content of the concentrate is from 200 to 300 grams/liter. After removal of cesium the purified liquid can be released into the sea. The use of cesium removal has historically decreased the Loviisa NPP's radioactive discharges. Corrosion products, which are included in the concentrates, are left on the bottom of the tanks to wait for cementation.

Until 2007 five purification campaigns were carried out and about 1100 m^3 of evaporator concentrates had been purified with only 160 liters of CsTreat®. Now in 2009 the sixth campaign purified about 210 m^3 with 72 liters of CsTreat®.

USE OF HIGHLY SELECTIVE ION EXCHANGE MATERIALS

Highly selective and fully inorganic ion exchange materials were developed in co-operation with a research group in the radiochemical laboratory of Helsinki University. CsTreat® with extremely high selectivity factor was needed to remove cesium from evaporator concentrates since cesium was the only limiting radionuclide for the release of these concentrates. Evaporator concentrates contain typically 3 mol/l of sodium (Na) and 0.2-0.3 mol/l of potassium (K). Because cesium removal is sensitive to potassium and sodium, CsTreat® was tailored to have the highest possible selectivity for cesium ($K_{Cs/K}$= 50,000 and $K_{Cs/Na}$= 1,500,000) with a good Cs exchange capacity of 0.35 meq/g /1, 2/.

The use of CsTreat® is relatively easy, since it can operate over a large pH area in high-salt solutions (Fig.1). If very diluted water is treated (only less than some milligrams per liter of salts) the operation area ranges from pH 2 to 11.5.

CsTreat® has been used for many different liquids other than evaporator concentrates. For example, it was used at the Callaway NPP (Missouri, USA) to treat 3000 m^3 of floor drain waters. In Estonia CsTreat® was used to decontaminate 760 m^3 of reactor pool water. /3/ At the Japan Atomic Energy Research Institute's (JAERI) Tokai-mura site in Japan, CsTreat® together with a newer product SrTreat® were used for removal of Cs-137 and Sr-90 from alkaline reprocessing waste effluent. The effluent contained fairly high activities of Cs-137 and Sr-90 (7.4 GBq/l for both). /4/ At the Savannah River Site (SRS) CsTreat® was used in a demonstration project to decontaminate one old concrete walled pool. /2/ In UK, the United Kingdom Atomic Energy Authority (UKAEA) has used CsTreat® in their effluent treatment system to remove cesium from sodium coolant of their prototype fast reactor (PFR). 950 tons of sodium resulting in the generation of approximately 9000 tons of liquid effluent was treated. Cesium levels were reduced to below detection limit for release. /5/

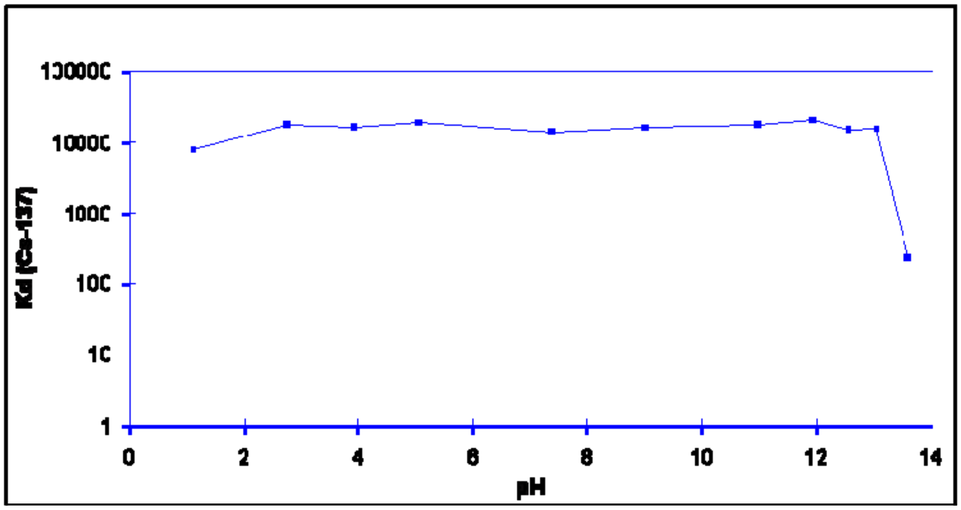

Fig. 1. Distribution coefficient K_d for Cs-137 as a function of pH. (Loviisa NPP evaporator concentrate B01, Na = 2.7 M, K = 0.3 M)

The later developed selective material, SrTreat®, was produced for removal of strontium, and it is most effective in neutral and alkaline solutions (Fig. 2). In a larger scale SrTreat® has been used in two published projects. The mentioned JAERI project used SrTreat® for purification of their reprocessing liquids. In a second project in Murmansk, Russia, different waters from nuclear powered icebreakers were purified with good results. /3/

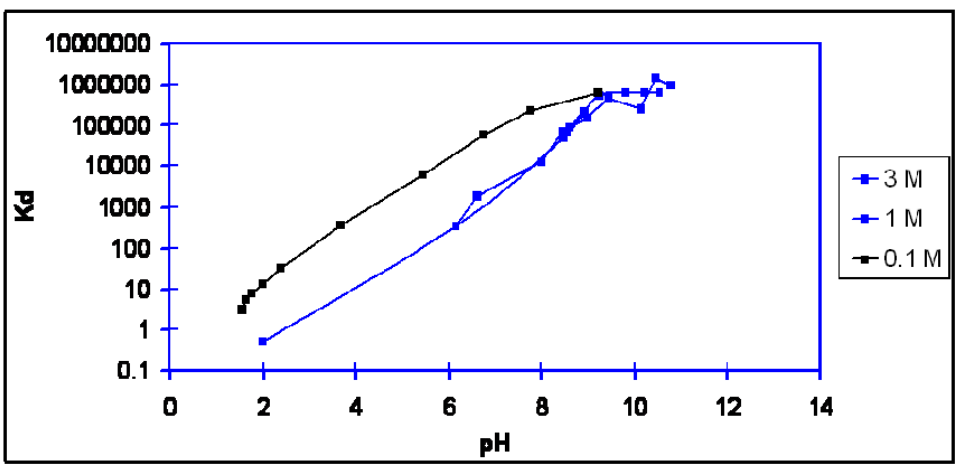

Fig. 2. SrTreat, K_d as a function of pH (3 M, 1 M and 0.1 M $NaNO_3$)

Also a titanium oxide-based material, CoTreat®, was developed for removal of cobalt and other activated corrosion products. It is most effective in neutral solutions such as pond waters and floor drain waters of nuclear power plants (Fig. 3). This material has been tested for example for different floor drain waters /6/, and for removal of cobalt from THORP pond water in Sellafield, UK /7/.

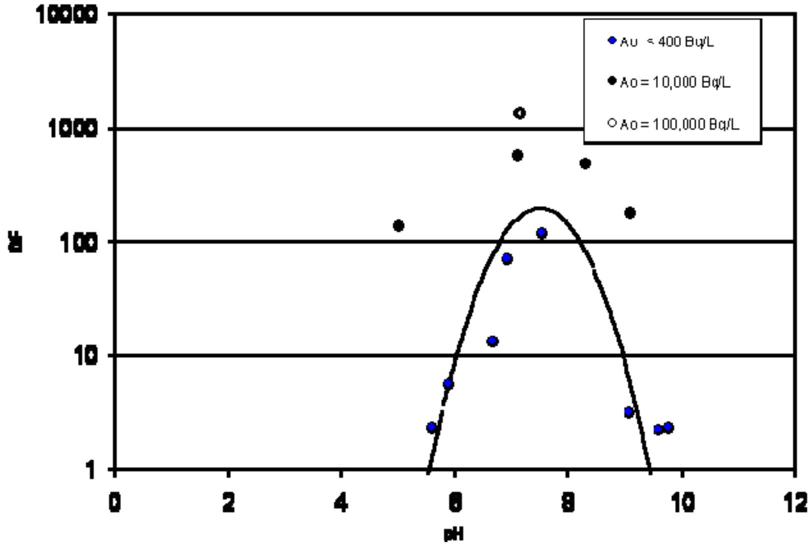

Fig. 3. Effect of pH and Co-57 feed activity on the decontamination factor (DF) (Base solution 100 ppm Na)

Recently, a new material has been developed for removal of antimony, and it is soon coming to the commercial use /8/.

The inorganic CsTreat®, SrTreat® and CoTreat® can typically be used in granular form in columns or in packed beds. The flow rate is limited to 10 or up to 20 bed volumes per hour (BV/h). Since this property limits the use of materials in several cases, special cartridges have been developed, where these materials can be used in flow rates up to hundreds of BV/h /2/.

HISTORY OF WET WASTE TREATMENT IN THE LOVIISA NPP

From 1991 to 2000 four tanks were purified in four campaigns with excellent results. Altogether, close to 900 m^3 of concentrates were purified with only 112 liters of CsTreat®. In all campaigns the settled sludge was left on the bottom of the tank. When this practice was used, more and more sludge accumulated on bottom of the tanks. /1/ During the fifth campaign it was anticipated that the accumulated amount of sludge started to affect the performance of the ion exchange columns. When previous tanks were purified with three or four columns, 8 liter each, 6 columns were needed for the fifth tank /2/. Since the amount of competing ions were on the same level as in the previous tanks the poorer performance resulted most probably from very fine suspended particles, which adhere on the surface of CsTreat® material and block partly the access of Cs ions into the ion exchange positions in the material. However, after this fifth campaign totally about 1,100 m^3 of concentrates had been purified with only 20 columns containing 160 liters of CsTreat®.

The efficiency of purification is measured with decontamination factor (DF), which is the ratio of cesium concentration in the inlet to that in the outlet. For purified liquids the DF have been well over 1,000 on an average. Maximum DF values have been beyond the measuring limit, which means that the DF has been tens of thousands. Table I give data for all of the five purification campaigns performed at the Loviisa NPP /2/.

Table I. Results from the Purification of Five Evaporator Tanks in the Loviisa NPP

Campaign No.	Treated in years	Purified volume, m^3	Spent amount of CsTreat®, liters	DF	Processing capacity, l/kg
1	1991 - 1992	253	24	>2,000	16,000
2	1993	210	32	>2,000 max 30,000	10,000
3	1995	230	24	>1,000	15,000
4	2000	202.6	32	>1,000 max 28,571	9,600
5	2002 - 2003	200.7	48	>1,000 max 16,129	6,400

NEW TREATMENT CAMPAIGN

Sixth cesium removal campaign was successfully carried out in the Loviisa NPP in 2009. The target was to purify 200 m^3 of evaporator concentrates from one tank. The target was exceeded since in practice slightly over 210 m^3 was purified.

The pH value of this tank was controlled to the about 11.5 on 27 October 2008, and purification started on 12 February 2009. The campaign was finished four months later on 18 June 2009. The flow rate in the Loviisa NPP's system is 10 bed volumes per hour, i.e. 80 liters/h. With continuous processing 1.92 m^3/day can be purified. Since there was no hurry in the treatment work, about 210 m^3 was purified in 126 days and the average realized capacity was about 1.7 m^3/day, which is about 87 % of the nominal capacity. About 13 % of time was used for changing new columns.

In the Loviisa NPP CsTreat® is used in 8 liter columns, and in the sixth campaign totally 9 ion exchange columns were collected as final waste. During purification one of these columns was blocked almost immediately after start of operation, and 9 columns, i.e. 72 liters of CsTreat®, purified the liquid with an average capacity of about 25 m^3/column. The first column was lost as a conventional waste since one of the pipelines included precipitation from earlier works and release of this precipitated material blocked the column. The following Table II gives the data of this sixth purification campaign.

Table II. Results from the Purification of Sixth Evaporator Tank in the Loviisa NPP

Campaign No	Treated in	Purified volume, m^3	Spent amount of CsTreat®, liters	DF	Processing capacity, l/kg
6	2009	210,2	72	>1,000 max 4,800	4,400

Cesium was removed with high decontamination factor (DF). Maximum DF value was close to 4800. During this campaign totally about 0.25 GBq of Cs-134, about 0.07 MBq of Cs-135, and about 14.6 GBq of Cs-137 was removed from the concentrates.

One special and new feature was found out during this purification campaign. Two efficient particle filters with pore size 1 µm and 0.1 µm are used in series in front of the ion exchange columns. In earlier purification campaigns particle filters were changed more often than the ion exchange columns. During this latest campaign only one set of particle filters was needed for the whole waste volume. The reason comes from the history of tank content.

As described in the previous chapter a decrease of capacity was noticed in the fifth campaign. In the fifth campaign tank there were many particles with the grain size over 0.1 µm. Because of this particle filters had to be changed often. In the sixth campaign tank the amount of particles with the particle size much less than 0.1 µm was probably much bigger than in previous tanks resulting in the large number of ion exchange columns used. However, there is no real reason, why the amount of particles with the grain size over 0.1 µm was so small. This only indicates that the contents of the tanks can be different during different years even if the operation practice at the power plant seems to have remained the same.

VOLUME REDUCTION OF WET WASTES AT THE LOVIISA NPP

In the Loviisa NPP a concrete container is used for all solidified liquid wastes. This container has a diameter of 1.3 m and height of 1.3 m. The net volume for cemented waste in a container is 1 m^3. For disposal of spent ion exchange columns this same container type is used. Fig. 4 shows the container, where there are 12 positions for spent ion exchange columns and the remaining space is filled with concrete.

Before this sixth nuclide removal campaign about 1100 m^3 of evaporator concentrates had been purified by 20 columns, i.e. with 160 liters of CsTreat®. After this sixth campaign there are 29 columns, i.e. 232 liters of CsTreat® stored in three concrete containers as final waste and about 1310 m^3 of high salt evaporator concentrates have been released from radiological control. Totally 12 columns can be loaded into one concrete container. There are two containers full of columns, and in the third container 5 positions out of 12 has been used.

Fig. 4. Ion exchange column loaded into a concrete container at the Loviisa NPP

As an alternative for treatment and release of evaporator concentrates there is cementation used for solidification of liquid wastes at the Loviisa NPP. If 1310 m^3 of concentrates is cemented, about 2850 concrete containers are produced as final waste. Compared to this alternative, NURES™ has created a volume reduction from 2850 containers to 3 containers, and volume reduction factor from 2850 containers to the capacity used from 3 containers is close to 1200.

BIG SAVINGS IN TREATMENT AND DISPOSAL COSTS

Release of purified evaporator concentrates has created big savings. Spent ion exchange columns can be directly disposed of without any further processing. Because of this the cost of nuclide removal consists only of the costs of the columns, particle filters, disposal containers, and some man-hours. For the treated concentrates there has been no need for solidification. If 1310 m^3 of concentrates had been cemented, its cost had been some tens of million of Euros. Compared to this figure the operation cost with NURES™ is very small.

There has been good savings in disposal costs in addition to the savings in treatment costs. Final repository, which has been constructed into the bedrock of the Loviisa NPP, includes one cavern for solidified waste. Thanks to the waste volume reduction gained be the selective ion exchangers it has been possible to make this cavern only half of the originally planned volume.

Altogether selective nuclide removal has created great savings to the Loviisa NPP.

EFFECT OF NUCLIDE REMOVAL ON SAFETY OF FINAL DISPOSAL

At the Loviisa NPP CsTreat® columns will be disposed of in concrete containers and in the underground repository where they will stay within a multi barrier system about 110 meters below the sea level.

Cesium is very tightly bound in the ion exchange material. The elution rate of cesium was measured in an early study with hexacyanoferrates /9/. When hexacyanoferrate was loaded with cesium, the elution rate was one part per 10^6 in a month. When CsTreat® in ion exchange column is disposed of in concrete containers, there are close to similar conditions as in a referred study, and no measurable amounts of cesium will leach out from the containers.

An alternative treatment for evaporator concentrates would be direct cementation and disposal in concrete containers. Cesium has known leaching rates from cement products, which can be in the range of 1 to 5 parts per 10^3 in a month. If the use of CsTreat® is compared to this performance, it can be concluded that use of selective ion exchange material improves the safety of final disposal.

EFFECT OF NUCLIDE REMOVAL ON RADIOACTIVE RELEASES

During first operation years of the Loviisa NPP the releases of radionuclides into the sea were around 15 GBq/a. This was still a small fraction, about 1.7 %, of the annual release limit of 888 GBq/a.

When nuclide removal system was taken into use in 1991, annual releases were decreased (see Fig. 5). A more strict practice was applied after 1991 and during later years the amount of released radionuclides has further been decreased.

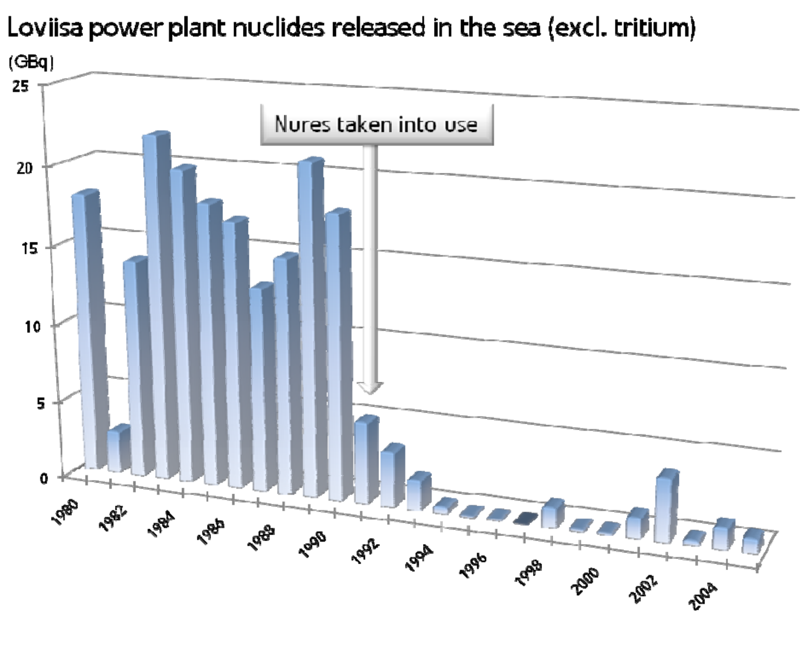

Fig. 5. Nuclides released into the sea from the Loviisa NPP

LESSONS LEARNED FROM THE LATEST PURIFICATION CAMPAIGN

One special and new feature was found out during the latest purification campaign. Normally when efficient particle filters are used in front of ion exchange columns particle filters are changed more often than the ion exchange columns. During this campaign the same set of particle filters were used for the whole waste volume. The reason comes from old history of the storage tanks. Sludge is always left on bottom of the tank, when liquid is taken for purification. According to this practice more sludge is accumulated in the tanks. When the previous tank was treated, bigger amount of fine particles caused high consumption of particle filters. In this latest campaign the same feature was not observed. Even if the practice has been the same during the operation years at the power plant, the content of each tank has been a bit different. Because of this the amount of filters is not so easy to estimate before purification.

In order to decrease costs of filtering a modification of the filtering system is realized at the Loviisa NPP. In the original configuration cartridge type filters have been used. A new modification makes it possible to utilize less expensive bag filters for the tanks with higher concentrations of fine particles. As part of the same modification also a pumping system is renovated for more simple operation.

When using small ion exchange columns with highly sensitive material there is always a risk that small amount of impurities can block the column. This was realized in the beginning of the latest campaign when one column was blocked almost immediately after the start of the campaign. The reason was the accumulation of precipitation in a pipeline that was not used in the previous campaign. In order to eliminate accumulation of precipitation the system has to be carefully flushed after each campaign.

CONCLUSION

In the Loviisa NPP selective nuclide removal has been a normal practice since 1991. Five purification campaigns were realized from 1991 to 2003. In these campaigns totally about 1,100 m^3 of evaporator concentrates was purified with only 160 liters of CsTreat®. In 2009 the sixth campaign purified an additional about 210 m^3 of evaporator concentrates with 72 liters of CsTreat®. Highly selective ion exchange material made it possible to separate cesium with high decontamination factor from the concentrates eve though the concentrates included 200 to 300 grams/liter of salts. Up to now about 1310 m^3 of concentrates have been purified with only 232 liters of CsTreat®.

If selective ion exchange would not be used, all evaporator concentrates would be cemented in a solidification system. If 1310 m^3 of concentrates is cemented, about 2850 concrete containers with about 2850 m^3 of solidified waste product are produced as final waste. When this 1310 m^3 was treated with NURES™, only 29 columns with 232 liters of CsTreat® was left as waste, and 29 columns fill less than three concrete containers. Hence a volume reduction from 2850 containers to less than 3 containers is achieved when comparing cementation to the use of NURES™ which gives a volume reduction factor close to 1200.

Large amounts of cementation, storage and final disposal costs are avoided as a result from the release of a big volume of evaporator concentrates,. Selective nuclide removal has created great economical savings at the Loviisa NPP. At the same time the use of CsTreat® has decreased the radioactive releases into the environment and improved the safety of the final disposal.

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