

Fifteen Years of Operation with Inorganic Highly Selective Ion Exchange Materials

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ABSTRACT

During latest fifteen years three highly selective inorganic ion exchange materials, CsTreat[®], SrTreat[®], and CoTreat, have been in full scale commercial use. All these materials have high capacity, and they give high decontamination factor (DF) and remarkably good volume reduction factor for storage and final disposal. A new material for antimony removal is currently coming for demonstration phase.

Since 1991 only 160 liters (5.7 cu.ft) of cesium specific material, CsTreat[®], has been used to purify over 1,100 m³ (over 290,000 gal) of high salt evaporator concentrates in Fortum's Loviisa NPP in Finland (1-3). In Olkiluoto NPP about 240 m³ (63,400 gal) of pool water was purified by a single 12 liter (0.4 cu.ft) column.

First US application at Callaway NPP purified cesium from about 3,000 m³ (800,000 gallons) with about 250 liters (9 cu.ft) of CsTreat in their demin system. A demonstration project at SRS site showed possibilities to remove cesium and strontium from pool water by recirculation.

In Japan, reprocessing liquid was efficiently treated at JAERI site in Tokai-mura. Original cesium and strontium concentrations of about 7,4 GBq/liter (200 mCi/liter) were reduced by factors of well over 1,000. In UK, 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.

Because of slow kinetics of inorganic materials the use of these materials in powder form was developed. Powder form CoTreat was successfully tested for use as precoat to existing Funda filters in THOPR feed pond plant (Sellafield, UK). Based on the same chemistry, Graver

Technologies developed CsFloc and CoFloc materials for US market. CoFloc material has also demonstrated a secondary specificity for antimony removal, but this is still under testing.

Well over 200 different cases were tested by customers for these ion exchange materials. Many of those tests have led to real applications and there are still many cases to come. Best benefit for users come from high volume reduction of waste volume and from high decontamination of purified liquid.

INTRODUCTION

In 1979 a nuclear waste management program was started for the Loviisa NPP in Finland. Within first years a concept was created, where total system was optimized from collection of waste to its final disposal. In this concept each new phase had to increase safety and give economic savings. Thus, in any treatment of waste volume reduction was not the only criteria.

In this program selective removal of radionuclides from liquids, and release of inactive part of liquid, was found to be a most efficient method. In some storage tanks of the Loviisa NPP the only radionuclide, which limited the release of liquid, was cesium. After some innovations totally inorganic granular ion exchange material, CsTreat[®], based on ferrocyanides, was developed for cesium removal. This material was taken into full scale use in 1991, and since then it has been part of power plant's normal operation.

Parallel to the development of cesium removal strontium and cobalt removal was developed. SrTreat[®] and CoTreat are based on titanates, and they were taken for commercial use some years after CsTreat[®]. All these three materials are manufactured by Fortum Nuclear Services Ltd in Finland. New material for antimony removal is now in its demonstration phase.

HIGHLY SELECTIVE INORGANIC ION EXCHANGE MATERIALS

Highly selective inorganic ion exchange materials were originally developed by a research group in radiochemical laboratory of Helsinki University to remove radionuclides from evaporator concentrates at Fortum's Loviisa NPP. These waste liquids contained high amounts of sodium (3.0 mol/l) and potassium (0.2 mol/l), which compete with cesium in any ion exchange (3). CsTreat[®] was specifically developed for this purpose, and it was tailored to have highest possible selectivity for cesium, $k_{Cs/Na}=1,500,000$ and $k_{Cs/K}=50,000$, and very good ion exchange capacity, 0.35 meq/g, Fig. 1 (7).

CsTreat[®] is 100 % inorganic and its efficiency is based on hexacyanoferrate chemistry. Typical use of CsTreat[®] is in granular form in column operation. Column sizes from less than one liter to 250 liters have been used. Normal grain size is 0.30-0.85 mm, but smaller sizes 0.15-0.30 mm and 0.85-2 mm has been used in test operations. Latest development is the use of powder form material, <0.15 mm.

CsTreat[®] can be used either in granular or powder form. Use of this granular material as a once-through process in a column gives the highest decontamination factors with extremely high capacity. This type of use has been proven in several commercial projects in several countries.

The powder form can be used either in precoat systems or in tailor-made filters. Testing of this type of use has given very promising results. Better kinetics of the powder form makes it possible to use higher flow rates through the column.

Operation pH area 1-13 for CsTreat[®] in high salt liquids (2-11 in low salt liquids) is also unique for a hexacyanoferrate material. Historically, when these types of material were used in a precipitation process, the pH area was limited to about 8 or less. However, new synthesis of CsTreat[®] produced fine properties for this granular material. Wide pH area covers most of the needs to treat liquids both at the NPP and in other nuclear facilities.

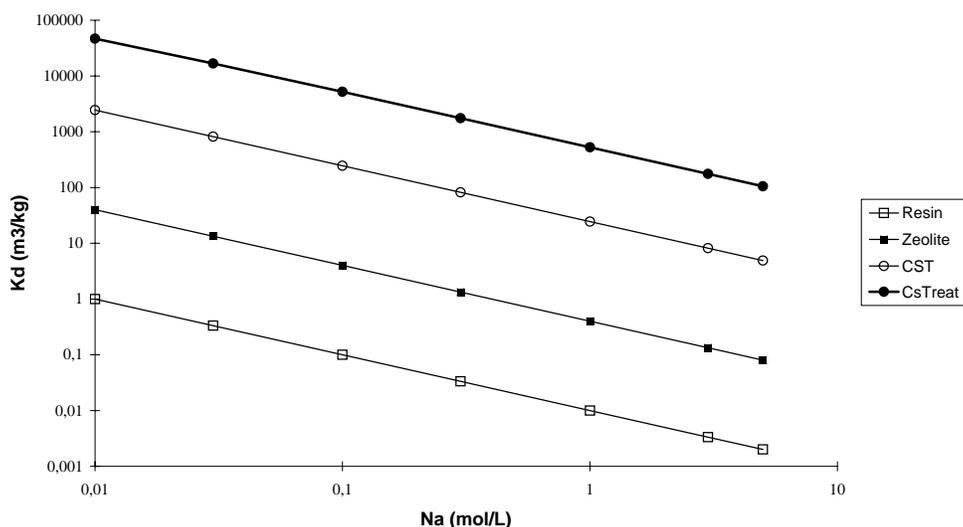


Fig. 1. Comparison of K_d -values for CsTreat[®] and other ion exchange materials as a function of sodium concentration in the liquid. K_d -value gives the maximum processing capacity.

In treatment of liquids use of granular material in once-through column was preferred. This made it possible to construct a simple treatment process. First there is a particle filtering phase to remove all possible particle bound activity and to protect the ion exchange bed from plugging, and after that there is an ion exchange bed to remove ionic radionuclides.

SrTreat[®] was developed for removal of radiostrontium (4) and CoTreat for radiocobalt and other corrosion products (5). New material for antimony removal is currently coming for demonstration phase.

Highly selective SrTreat[®] was developed for removal of strontium from alkaline solutions. It has high selectivity factor $k_{Sr/Na}=200,000$, but it is sensitive for calcium and pH. This material is based on titanium oxides, and it is also 100% inorganic material. It gives the best results in pH area 9 and higher, in some applications in neutral area, too. (4)

Typical use of SrTreat[®] is in granular form in column operation. Column sizes from less than one liter to 12 liters have been used. Normal grain size is 0.25-0.85 mm.

SrTreat[®] has been successfully used for treatment of reprocessing liquids, liquids from nuclear icebreakers, and it has been tested for pool waters and for example for liquids in Hanford and SRS tank farms.

SrTreat[®] and CoTreat are also effective for the removal of TRU nuclides, especially those of Pu.

Removal of cobalt has always been one of the most important questions in the nuclear power plants. Because of this, 100% inorganic CoTreat was developed. This material is based on titanium oxides. Its operation pH area is around neutral, giving best results from pH 6 to 8. Normal grain size is 0.25-0.85 mm.

CoTreat has efficiently removed cobalt and other corrosion products from NPP Floor Drain Waters in laboratory tests (8), being able to achieve decontamination factors (DF) as high as 1000 and processing capacities in excess of 50 m³/kg even in high-conductivity waters. CoTreat is usually used in granular form in a fixed-bed ion exchange column. Newest experience is emerging on a more efficient way of application as finely divided powders on precoated filters (8). Large volumes of pond water can be efficiently treated with small amount of ion exchange media.

Originally CoTreat was developed for removal of ionic cobalt. Soon it was noticed that several other corrosion products could be removed at the same time. Test results indicate that decontamination factors from 10 to around 1,000 can be achieved with CoTreat for different corrosion product nuclides.

WHY TO USE GRANULAR OR POWDER FORM MATERIAL

All inorganic materials have typically relatively slow kinetics. Because of this the typical flow rate for all these three materials is from 10 to 20 bed volumes per hour (BV/h). In high salt concentrations even much slower flow rates have been used. Slow flow rates make it difficult to use granular materials in applications, where big volumes have to be treated quickly. For example, if four parallel 12 liter columns are used, only from 480 to 1,000 l/h can be treated.

Because of slow kinetics new applications for powder form materials have been developed. When powder with grains of <0.15 mm is used, the flow rate can be even hundreds of bed volumes per hour. Applications, where about 20 liter (0.7 cu.ft) of powder form material is used in one filter unit, could successfully treat about 6.8 m³/h (30 gpm). Parallel use of this kind of filter units can treat remarkably high liquid volumes.

In applications, where use of granular material with slow flow rate meets the requirements, ion exchange bed can be dimensioned according to the flow rate. The volume of ion exchange material can have very high ion exchange capacity, and if the total volume of liquid is not very big, some part of this ion exchange capacity is left over.

In the use of powder form material the filter unit has relatively small amount of ion exchange material, and the number of filter units is dimensioned according to the total flow rate. During operation total ion exchange capacity of the ion exchange material can normally be utilized. This can be more economical way to use selective ion exchange materials, if high liquid volumes have to be treated.

FULL SCALE APPLICATIONS FOR Cs/Sr/Co REMOVAL

Granular Material in Column Operation

Since 1991 only 20 ion exchange columns, 8 liters each, totaling to 160 liters (5.7 cu.ft) of cesium specific material, CsTreat[®], has been used to purify about 1,100 m³ (over 290,000 gal) of high salt evaporator concentrates in Loviisa NPP (VVER-type) in Finland (1-3). These highly alkaline liquid wastes contained high amounts of sodium and potassium, cations that compete with cesium in any ion exchange media, Table I (3).

Table I. Main Chemical and Radiochemical Constituents in a Typical Evaporator Concentrate (aged for several years) from the Loviisa NPP

Constituent	Concentration (mol/l)	Activity (kBq/l)
Na ⁺	3.0	
K ⁺	0.2	
BO ₂ ⁻	0.7	
NO ₃ ⁻	0.7	
pH	>13.5	
Cs-137		400
Cs-134		100
Co-60		6

Table II gives the results for the purification of five tanks of evaporator concentrate in the Loviisa NPP since 1991. After treatment of fourth tank the average processing capacity for about 900 m³ was about 12,200 L/kg (7). After the fifth tank about 1,100 m³ has been treated, and the average processing capacity is about 10,400 L/kg. Processing capacity for the fifth tank was much lower than that for the previous tanks. Probable reason for this was noticed to be higher amount of solids in the waste liquid. In the case of fifth tank there was about 3.4 mg/L of solid material with very small particle size. 0.1 µm particle filter probably could not remove enough solid particles, which led to plugging of part of ion exchange capacity. Because of this more columns were used for purification of this tank than for other corresponding tanks.

In treatment of about 1,100 m³ of evaporator concentrates in Loviisa NPP the average decontamination factors have been well over 1,000 (3). Figure 2 gives a typical performance curve for one 8 liter (about 0.28 cu.ft) column. DF is relatively low in the beginning of treatment of high salt liquids, but it rather soon reaches good decontamination levels (DF = 10,000 or above). After some time, in the case of Fig. 2 after about 40 m³, DF starts to decrease, because

exhaustion of the ion exchange capacity starts to take place. At any level the operator can decide, which level he accepts for final shut-down of the column.

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

	Treated in	Volume treated, m ³	IX mass used, liters	Total salt conc., g/l	DF	Processing capacity, l/kg	VRF
Tank 1	1991-92	253	24	240	>2,000	16,000	2000
Tank 2	1993	210	32	176	>2,000 max 30,000	10,000	1260
Tank 3	1995	230	24	228	>1,000	15,000	1840
Tank 4	2000	202.6	32	220	>1,000 max 28,571	9,600	1200
Tank 5	2002 -03	200.7	48	>220	>1,000 max 16,129	6,400	800

Total volume reduction factor in final disposal was calculated for packed waste. 1 m³ of concentrate would produce about 3.4 m³ of cemented waste, including the volume of concrete containers. Thus, 1,100 m³ of liquid would yield 3,740 m³ of cemented waste for final disposal. When ion exchange columns are packed for final disposal, 12 columns can be packed into one container having a volume of 1.7 m³. Thus, when 20 columns or 160 liters of CsTreat[®], is packed in concrete containers, a volume of about 2.83 m³ is produced for final disposal. Volume reduction of 1320 in final disposal was achieved for this amount of waste.

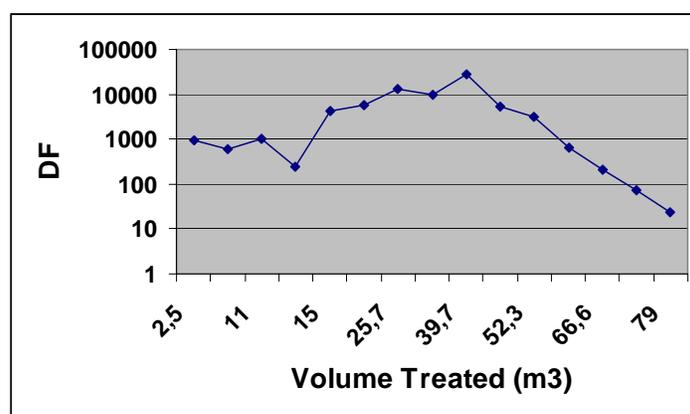


Fig. 2. Decontamination factor (DF) for one eight liter column during its operation time

Applications for pool waters showed very high capacities in low salt liquids. In Olkiluoto NPP (BWR) in Finland about 240 m³ (63,400 gal) of pool water was purified by a single 12 liter (0.4 cu.ft) column. Very high volume reduction for direct waste volume was achieved. Purified liquid could be released to the sea.

First US application at Callaway NPP purified cesium from about 3,000 m³ (800,000 gallons) of floor drain water. About 250 liters (9 cu.ft) of CsTreat was used in their demin system (9). A demonstration project at Savannah River Site (SRS) site was carried out to show possibilities to remove cesium and strontium from old R-basin disassembly pool water by recirculation. Although CsTreat[®]'s performance suffered from relatively high flow rate (~50 BV/hr), operators concluded that the efficiency was completely satisfactory for the recycle mode of operation (10).

In Japan, reprocessing liquid was efficiently treated at JAERI site in Tokai-mura. Original cesium and strontium concentrations of about 7.4 GBq/l (200 mCi/liter) were reduced by factors of well over 1,000. Operators found very good performance for treatment of this liquid (11). This liquid waste from reprocessing research was recategorized with this treatment for later easier treatment.

In UK, 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. (12)

In Paks NPP in Hungary a combined nuclide removal system and boron recovery system was installed to treat all types of liquid wastes from the power plant, Fig 3., (13) Use of granular CsTreat and CoTreat is planned.



Fig. 3. The new liquid waste treatment system of Paks NPP

Use of Material in Powder Form

In the applications mentioned above ion exchange materials were used in granular form. Because inorganic materials have slow kinetics, there has been great interest and requirement to develop new ways of using these materials, where higher flow rates can be used. Use of fine powder of the same materials can be an answer to this requirement.

In column operation, when granular material is used, normal flow rate is only from 10 to 20 BV/hr. This means that for a flow of 1 m³/hr a bed size from 50 to 100 liters is needed. When fine powder is used, the flow rate can be from some hundreds to some thousands of bed volumes per hour (BV/hr). In this case the needed bed volume could be only on the range of one liter. Thus, much less material is needed inside the system, and the bed size can be dimensioned according to the ion exchange capacity and not to the flow rate. Laboratory tests with simulated waste waters have given promising results (14).

Powder form CoTreat was successfully tested for use as precoat to existing Funda filters in THORP feed pond plant (Sellafield, UK). On the feed level 200 Bq/l the exhausting capacity was 513,300 l/kg (about 3,000,000 gal/cu.ft) and with the feed level of 600 Bq/l CoTreat was finally exhausted at 1,200,000 l/kg (over 27,000,000 gal/cu.ft) (15).

Graver Technologies, LLC developed Radex™ CsFloc and Radex™ CoFloc powdered media utilizing the same chemistries as the CsTreat® and CoTreat sold by Fortum. These media consist of flocculated particles similar to traditional ion exchange resin precoats. Consequently, they can be used in traditional precoat applications and are compatible with a variety of filter and septum configurations. The CoFloc and CsFloc media were developed specifically for treatment of nuclear plant radwaste. CoFloc and CsFloc exhibit high selectivity for radiocesium (¹³⁴Cs and ¹³⁷Cs) and radionickel (⁵⁸Co and ⁶⁰Co) ions, respectively.

The Radex™ CsFloc and Radex™ CoFloc materials are most commonly utilized in Functionalized Liquid Ion Polisher (FLIP™) filters also manufactured by Graver Technologies. These FLIP™ filters combine the standard unit processes of filtration and ion exchange within a single cartridge. Filtration is controlled by inner (core) or outer (cage) wraps of flat, molded, porous polymeric materials with specific micron ratings. Either the CsFloc or the CoFloc media is contained within an annulus created between the core and cage components. The FLIP™ filter cartridges (typically an array of six 2.625 in {6.67 cm} X 30 in {76.2 cm} filters) are utilized within existing, standard filter housings as final polishers in radwaste systems in nuclear power plants.

Ameren UE Callaway Station in Missouri (USA) evaluated the CsFloc FLIP™ filters starting in August 2004. Robert Mitchell from Callaway discussed the results of these evaluations in a paper given at the EPRI Low Level Waste Conference in June 2005 [17]. He concluded that these filter were effective at selectively removing radiocesium in both the high and low activity regimes with moderate differential pressure and extended throughput (>245,000 gallons / > 925,000 L).

Even greater success has been achieved with the CoFloc FLIP™ filters at American Electric Power D.C. Cook Station in Michigan (USA). This plant first installed these filters in February 2004. The initial filters reduced radionickel (typically ⁵⁸Co) from activities of 1.0·10⁴ Bq/L (2.9·10⁻⁴ μCi/mL) to activities of 6.6·10⁰ Bq/L (2.0·10⁻⁷ μCi/mL) or less. This corresponds to a typical decontamination factor (DF) in excess of 1500. In many cases, no measurable radionickel (⁵⁸Co and ⁶⁰Co) was present in the processed effluent (MDA). Each set of CoFloc FLIP™ filters at D.C. Cook processes 250,000 gallons (ca. 950,000 L) of radwaste before being

taken out of service based on this administrative end point. Under these conditions, the CoFloc FLIP™ filters operate for 6 – 9 months.

An unanticipated side benefit of the CoFloc FLIP™ filters at D.C. Cook plant is substantial reduction of radioantimony (¹²⁵Sb). Influent radioantimony activity levels typically have been approximately 2.0·10² Bq/L (5.8·10⁻⁶ μCi/mL) while effluent activities most commonly drop below MDA levels. This drop corresponds to DF's of 100 or more.

DEVELOPMENT OF NEW MATERIAL FOR ANTIMONY REMOVAL

Novel proprietary metal oxide materials (MOM) have been tested for the removal of Sb-125 from simulated Floor Drain Waters of BWR (18). Antimony was present in the solutions as oxidized anionic form. Long term column experiment with simulated liquid showed high Sb-125 removal at least up to 8000 bed volumes. One column experiment was carried out using non-radioactive Sb to exhaust the column. Leaching tests with 1000 ppm boric acid showed that 100 % of absorbed Sb remains in the sorbent material. Column experiments with real Fuel Pond Water from Olkiluoto NPP (BWR) showed reduction of Sb-125 (feed level 400 Bq/L, 1·10⁻⁵ μCi/mL) below detection limit (MDA = 1.7 Bq/L, 5·10⁻⁸ μCi/mL) (Table III).

Table III. Column Removal of Radionuclides from the Fuel Pond Water.

No. of BV treated	DF		
	Sb-125	Cs-137	Co-60
360	>230	1.7	2.7
861	>230	1.5	1.7
1354	>230	1.4	1.4
1831	>230	1.3	1.0

BV = bed volumes, DF = decontamination factor

CONCLUSIONS

During the past fifteen years, good experience has been gained in the full-scale use of three highly selective inorganic ion exchange medias, CsTreat[®], SrTreat[®], and CoTreat, for the treatment of liquid radwaste. Major lessons learned by the experience include:

- Unlike conventional demineralizer resins, highly selective materials can be used for the treatment of high-salt (high-conductivity) effluents with good efficiency (high decontamination factor and volume reduction factor).
- In low- and medium salt solutions extremely high processing capacities can be obtained, providing very high volume reduction. Often the exhaustion of the medias cannot be detected and the operation is limited by the radiation build-up in the media.
- In many cases decontamination proceeds below minimum detectable activity so that treated liquids can be discharged.
- Column operation with granular materials is most favorable when throughput rates and liquid volumes are relatively low.

- When high throughput rates and high liquid volumes are involved it is better to use powdered materials in various filter configurations.

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