USE OF NOVEL HIGHLY SELECTIVE ION EXCHANGE MEDIA FOR MINIMIZING
THE WASTE ARISINGS FROM DIFFERENT NPP AND OTHER LIQUIDS

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ABSTRACT

Highly selective inorganic ion exchangers give new possibilities to implement and operate new
innovative treatment systems for radioactive liquids. Because of high selectivity these ion
exchangers can be used even in liquids of high salt concentrations. Only selected target nuclides
will be separated and inactive salts are left in the liquid, which can be released or recategorized.
Thus, it is possible to reduce the volume of radioactive waste dramatically. On the other hand,
only a small volume of highly selective material is required in applications, which makes it
possible to design totally new types of compact treatment systems.

Three new highly selective inorganic ion exchangers have been introduced to the market:
CsTreat® for removal of cesium, SrTreat® for strontium, and CoTreat for cobalt and other
corrosion products. These ion exchangers have the highest selectivities and processing capacities
in commercial market, exceeding those of zeolites by several orders of magnitude. Typical
decontamination factors (DF) of several thousands can be obtained and because of high
selectivity, large proportion of the ion exchange capacity of the media (0.35 meq/g to 5 meq/g)
can be utilized for target nuclides and to treat very large volume of liquid with a small volume of
the media. In increasing number of applications there is a demand for total inorganity, which
makes these new materials even more interesting.

The first application with CsTreat, started in 1991 at Loviisa NPP in Finland, purified during
first 10 years about 900 m³ of high-salt (~ 240 g/L NaNO₃) evaporator concentrates with 112
liters of CsTreat (1). After this several new processes, even on mobile basis, were based on these
ion exchangers both for low-salt and high-salt liquids (2). There is also one application for
reprocessing liquid to remove both cesium and strontium from highly acidic waste (3). All these
systems are highly compact utilizing typically 2-12 L columns.

The major benefit of selective ion exchange media comes from the very large volume reduction
of radioactive waste in final disposal. It is also possible to save in investment costs, because
small ion exchanger volumes can be used and handled in a very small facility. This paper
describes different applications of these highly selective ion exchangers, both commercial full-
scale applications and laboratory tests, to give the idea of their efficiency for different liquids.
INTRODUCTION

Radioactive liquids have been treated in many cases only with proven but old-fashioned technology. Low level liquids have been concentrated and solidified with cement or bitumen for final disposal. Higher level of activity has often lead to very expensive solidification of large volumes of waste. Low selectivity of conventional ion exchangers, zeolites or organic resins, has limited the applications of these conventional ion exchangers only to liquids that contain very low salt concentrations. The use of conventional ion exchangers has also given remarkably high solidified waste volumes.

In recent years there has been an increasing pressure to minimize waste volumes. Highly selective ion exchange materials have given new possibilities for the treatment of radioactive liquids. Even liquids that have a very high salt concentration can be treated with new compact systems, based on these new highly selective ion exchangers. If radioactive elements can be removed from the liquid, very often the remaining low active liquid can be released. This technology can lead to good economical solutions, if more liquids can be released and at the same time radioactive releases and disposal volumes can be decreased.

For liquids, which contain high levels of radioactivity or chemicals, selective removal of radionuclides can give a high economical benefit. The original large liquid volume, which would need an expensive treatment, can be reclassified after selective nuclide removal. After this reclassification the biggest part of liquid can be treated more economically with an easier treatment method.

A large number of selective ion exchangers have been studied and developed during the past decades. However, very few of them are commercially available for column operations. Inorganic zeolites have been used a longer time for removal of cesium and strontium from low-salt liquids, but they are inefficient in liquids of higher salt content. In the USA, crystalline silicotitanates (CST) have been developed for selective removal of cesium and strontium and they have been available on semi-industrial scale in recent years. These silicotitanates have found some test operations, but they still wait for larger applications.

Three new highly selective ion exchangers, CsTreat®, SrTreat® and CoTreat, have been introduced into the market recently, and they are manufactured in Finland by Fortum Nuclear Services Ltd. (until the end of 1999 the subsidiary company Selion Oy). These materials are totally inorganic and they are available in different grain sizes for both column and precoat applications. The selectivity of these new ion exchangers is on much higher levels than for the other commercially available materials. Unlike conventional resins and some new inorganic/organic composite resins or membranes, these ion exchangers can also be used in the expanding area of applications where there is the requirement for totally inorganic ion exchangers.

Typically these all-inorganic ion exchange materials are used in columns or packed bed in granular form. Typical grain size is 0.25-0.85 mm. However, different tests in a laboratory and in a full-scale system have proven the idea to use them also in a precoat system (4). In some applications the tailored columns, where material with smaller particle size is used, make it
possible to utilize the capacity of the ion exchange material even more efficiently than in a column operation.

**SELECTIVE ION EXCHANGERS**

**CsTreat**

CsTreat® was originally developed for treatment of liquids, where high salt concentrations made it impossible to use conventional ion exchange. When this material was developed, its extremely high selectivity factors, $k_{\text{Cs/Na}}=1,500,000$ and $k_{\text{Cs/K}}=50,000$, made it ideal for treatment of almost any cesium bearing liquids. Over ten years' continuous use in treatment of evaporator concentrates (1) has proved its efficiency.

CsTreat® has been used for treatment of evaporator concentrates, floor drain waters, reactor coolant, liquids from nuclear ice-breakers, spent fuel pool water in SRS, and reprocessing liquids. It has been successfully tested for decontamination liquids and resin regeneration solutions. New applications are coming for full-scale use. Typical decontamination factors are well above 1,000.

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, <0.15 mm, in precoat applications (5).

CsTreat®'s total ion exchange capacity is only 0.35 meq/g, but its selectivity for cesium makes its performance extremely interesting. Table I shows CsTreat®'s selectivity factor $k_{\text{Cs/Na}}$ for ion exchange in sodium solutions compared to the selectivity factors of other ion exchange materials (6).

Fig. 1 gives the comparison of the distribution coefficients $K_d$, which give an idea of the total processing capacities in column operation, of different ion exchangers as a function of sodium concentration in solution. Sodium is the most common and abundant ion present in nuclear waste solutions and most interfering element for cesium. The data shows that already in moderate sodium concentration only highly selective ion exchangers can give good processing capacity.

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.

TABLE I. Selectivity coefficients for Cs/Na exchange in commercial ion exchangers

<table>
<thead>
<tr>
<th>Ion Exchange Material</th>
<th>Concentration of Na (mol/l)</th>
<th>Selectivity coefficient, k_{Cs/Na}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphonic acid resin</td>
<td>not known</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Resorcinol-formaldehyde resin</td>
<td>6.0</td>
<td>11,400(^a))</td>
</tr>
<tr>
<td>Zeolite (mordenite)</td>
<td>0.1</td>
<td>450</td>
</tr>
<tr>
<td>Silicotitanate (CST)</td>
<td>5.7</td>
<td>18,000</td>
</tr>
<tr>
<td>CsTreat®</td>
<td>5.0</td>
<td>1,500,000</td>
</tr>
</tbody>
</table>

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

Fig.1. Comparison of CsTreat® K\(_d\)-values

SrTreat

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. (7)

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.

CoTreat

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 recent 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 (5). Large volumes of pond water can be efficiently treated with small amount of ion exchanger.

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.

TREATMENT SYSTEM FOR HIGH SALT EVAPORATOR CONCENTRATES

Since 1991, the first NUclide REmoval System (NURES) utilizing CsTreat® has been in use in the Loviisa NPP (PWR) in Finland for treatment of high salt (240 g/L) evaporator concentrates (1). Table II gives the results from purification of the four tanks in the Loviisa NPP.

<table>
<thead>
<tr>
<th>Treated in</th>
<th>Volume treated, m³</th>
<th>IX mass used, liters</th>
<th>Total salt conc., g/l</th>
<th>DF</th>
<th>Processing capacity, l/kg</th>
<th>VRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank 1</td>
<td>1991-92</td>
<td>253</td>
<td>24</td>
<td>240</td>
<td>&gt;2,000</td>
<td>16,000</td>
</tr>
<tr>
<td>Tank 2</td>
<td>1993</td>
<td>210</td>
<td>32</td>
<td>176</td>
<td>&gt;2,000 max 30,000</td>
<td>10,000</td>
</tr>
<tr>
<td>Tank 3</td>
<td>1995</td>
<td>230</td>
<td>24</td>
<td>228</td>
<td>&gt;1,000 max 28,571</td>
<td>9,600</td>
</tr>
<tr>
<td>Tank 4</td>
<td>2000</td>
<td>202,6</td>
<td>32</td>
<td>220</td>
<td>&gt;1,000 max 28,571</td>
<td>9,600</td>
</tr>
</tbody>
</table>

Average processing capacity of the media for the whole volume in four tanks has been about 12,200 L/kg. Treatment of this liquid has given remarkably high decontamination factors (DF). Typically DF is pretty low in the beginning of the treatment of high salt liquids, but rather soon it reaches good values. Figure 3 shows this DF behavior for the first column in the treatment of
the fourth tank in Loviisa.

![Graph showing decontamination factor (DF) for one column during its operation time.](image)

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

Volume reduction factor (VRF) in final disposal can be calculated from the basic alternative for treatment of the evaporator concentrates. Cementation of evaporator concentrates would produce 2 m$^3$ of cement product in the final disposal containers. As the net volume of one container is 1 m$^3$ and outer volume 1.7 m$^3$, total outer volume for the final product from 1 m$^3$ of waste would be 3.4 m$^3$. At present the spent CsTreat$^\text{®}$ columns, 8 liters each, are placed in concrete containers so that 12 columns are placed in one container with a volume of 1.7 m$^3$, which outside disposal volume is similar to the ones for cemented products. VRF for the whole volume treated was over 1,500, which means high economical savings in final disposal.

One new tank, including 262 m$^3$ of evaporator concentrates, is waiting for treatment. This purification work will start late 2002.

The second NURES system for treatment of evaporator concentrates is under construction in the Paks NPP in Hungary. Fortum Nuclear Services Ltd. has implemented this system together with Paks NPP (9). The system treats evaporator concentrates and other radioactive liquids. The purpose of the system is to remove target radionuclides (Cs and corrosion products) and to recover boron for reuse and to allow release of purified liquid.

This liquid waste treatment system in the Paks NPP consists of three subsystems: a boron recovery system, an ultrafiltration system and a cesium removal system. Compared to conventional treatment methods the new system minimizes the volume of waste in interim storage and in final disposal. Depending on the quality of original waste the overall volume reduction factor for evaporator concentrates varies in the range of 40 to 90.

The installation of the system started in late 2001 and the commissioning is scheduled to start in the shift of years 2002 and 2003. Fig 3 shows the layout of the cesium removal and boron recovery system.
TREATMENT OF FLOOR DRAIN WATERS

Two applications of CsTreat® have been used for treatment of floor drain waters. In Olkiluoto NPP (BWR), Finland, low salt (conductivity = 670 µS/cm) floor drain wastewaters have been purified. 240 m³ of floor drain waters was purified with one column, including 12 liters of CsTreat.

In Olkiluoto, the DF obtained for Cs-137 was dependable on the flow rate (2). Purification was started at a flow rate of 20 BV/h and DF’s above 1,000 were obtained. Later on, the flow rate was stepwise increased to 50 BV/h, which resulted in a gradual decrease of DF. At 50 BV/h, the DF stabilized to a value of about 100.

Another application for removal of cesium from floor drain waters was installed in July 1996 at the Callaway NPP (PWR), Missouri, USA. CsTreat was taken into use in the existing filter/demineralizer system to replace the evaporator (2). The CsTreat® bed size was 250 liters. During three years about 3,000 m³ of medium-salt floor drain water (Na 100-300 ppm, Ca 20-60 ppm, and K 8-23 ppm) was treated with this bed.

TREATMENT OF REACTOR WASTE WATER WITH MOBILE NUCLIDE REMOVAL SYSTEM

Fortum Nuclear Services Ltd. has constructed also a mobile NURES facility into a standard 20" container. This NURES container includes different treatment possibilities, and its efficiency is based on highly selective ion exchange materials.

The NURES container is an independent unit, which can treat different liquids with automatic control. The container has connections for electricity and incoming liquid. With an in-built control system the process can be operated automatically. The system can operate 24 hours a day. Depending on the waste properties some inspection and sampling is needed. Otherwise the system can control itself or close itself if the column capacity has become full. This container is
ideal for treatment of the wastes at the sites, where there are no possibilities to install a fixed system.

In 1996, a total of 760 m³ of various very low-salt waste waters, which originated from the operation of ex-Soviet naval training reactors were purified in Paldiskij, Estonia with the NURES container using a single 12 L CsTreat® column. No sign of bed exhaustion was observed when the treatment campaign was completed, which means that the processing capacity of CsTreat® exceeded 100 m³/kg.

TREATMENT OF WASTE WATERS FROM NUCLEAR-POWERED ICE-BREAKERS

In 1996-97, the NURES container, utilizing CsTreat® and SrTreat® beds (12 L), prefilters and a carbon filter, was used in Murmansk, Russia to treat radioactive wastewaters originating from nuclear-powered icebreakers (10). These waters had low to medium salt contents (NaCl 400-4000 ppm, Ca 7 ppm, and Mg ppm). The major radionuclides to be removed from the water were Cs-137 (0.4-1.1 MBq/l) and Sr-90 (0.02 – 0.8 MBq/l). Maximum DF's for Cs-137 and Sr-90 have been 1,000 and 5,000, respectively. The NURES system appeared to be efficient for the removal of other radionuclides, e.g. Co-60 and Sb-125, too.

TREATMENT OF REPROCESSING LIQUIDS

At the Japan Atomic Energy Research Institute's (JAERI) Tokai-mura site in Japan, CsTreat® and SrTreat® were taken into use for the removal of Cs-137 and Sr-90 from alkaline reprocessing waste effluent in the summer of 1997. The effluent contained fairly high activities of Cs-137 and Sr-90 (7.4 GBq/l for both). The system utilized columns packed with CsTreat® and SrTreat®, 0.8 l each. The original concentrations of both Cs-137 and Sr-90 were reduced by DFs of well over 1000 (3). The project has ended successfully in the year 2000.

In this JAERI's application the original acidic waste liquid contained so high content of activity, that reclassification of this liquid was needed. After treatment this liquid could be removed for the treatment system of very low level liquids. The system was constructed into a very small area. Lack of room volume made it necessary to have very small columns and other components in use.

TREATMENT OF POOL WATER WITH RECIRCULATION

In 2000, the first application at the USDOE's site with CsTreat® and SrTreat® was started at Savannah River Site. About 20,000 m³ (5 Mgal) of contaminated water is stored in the old disassembly pool, and a demonstration system was installed to remove radionuclides from this pool. The system utilized about 85 liters of CsTreat and about 45 liters of SrTreat in columns. Treated liquid was recirculated back to the same pool.

By 30 November 2000, about 4,500 m³ was treated with CsTreat® (1,189,000 gallons), and from 97% to 99% of Cs-137 was removed. The result of this test was completely satisfactory for the recycle mode of operation (11).
TREATMENT OF DECONTAMINATION AND RESIN REGENERATION SOLUTIONS

Minicolumn experiments (bed volume 1 ml) have been carried out using a simulated decontamination liquid that contained detergents and complexing agents and with simulated resin regeneration solution (Na 6.7 g/l, K 3.3 g/l, pH = 6.0) indicating excellent results for cesium removal.

A test carried out at the Diablo Canyon NPP in USA using CsTreat®, silicotitanate, zeolites and other hexacyanoferrate ion exchangers for the decontamination of high conductivity (14,000 µS/cm) resin regenerant solution showed that CsTreat had a superior performance compared to the other exchangers (12).

USE OF HIGHLY SELECTIVE ION EXCHANGERS IN PRECOAT APPLICATIONS

The present industrial applications involve column operations utilizing granular ion exchange material. The rate of ion diffusion in the crystalline inorganic material is relatively low – hence the ion exchange rate is low and the flow rates in columns packed with granular material need to be low, typically 10-50 bed volumes per hour (BV/h), to obtain a good decontamination factor. Hence, large beds, with high excess of ion exchange capacity, are needed for large throughput rates. Decreasing the exchanger particle size can increase the rate of radionuclide uptake.

Process development work has been carried out to utilize the inorganic ion exchange materials as fine powders on a support matrix (precoat operation). Pilot scale test carried out for CsTreat® indicate that utilization of fine powders is highly efficient compared to conventional column operation: the throughput rates can be increased 100-fold (1,000-5,000 BV/h) compared to column operation while the degree of purification still remains at a very high level (4).

Recently, laboratory tests have been carried out to support the application of CoTreat to existing pre-coated Funda filter operations at BNFL Sellafield (UK) THORP Head End Feed Pond (HEFP) plant. The aim of the tests was to optimize the operating conditions (e.g. quantity applied and formulation) of CoTreat for application to a pre-coated 30m² Funda filter and to provide a framework for assessing the performance of CoTreat under HEFP operating conditions (13). DF’s in the range of 10-1000, depending on the feed activity, have been measured for $^{57}$Co tracer in these tests.

VOLUME REDUCTION BY SELECTIVE ION EXCHANGERS

In reduction of the total waste management costs the reduction of waste volumes can be an essential factor. Use of highly selective ion exchangers, especially due to a small treatment system needed, can in many cases fit to the total system to reduce the total costs. Table III gives some examples of volume reduction factors achieved. These results indicate the possibility for very high VRFs even for high-salt liquids.
Table III. Volume reduction factors (VRF) achieved for different waste types

<table>
<thead>
<tr>
<th>waste type</th>
<th>salt concentration</th>
<th>VRF achieved</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loviisa NPP</td>
<td>evaporator concentrates</td>
<td>high</td>
<td>1,535 8,000</td>
</tr>
<tr>
<td>Olkiluoto NPP</td>
<td>floor drain water</td>
<td>medium</td>
<td>20,000</td>
</tr>
<tr>
<td>Paldiski-project</td>
<td>reactor water</td>
<td>low</td>
<td>63,000</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Highly selective ion exchange materials have made it possible to implement and operate totally new types of compact liquid waste treatment systems. A NUclide REmoval System (NURES), utilizing these new inorganic materials, has proven its efficiency in treatment of many types of radioactive liquids, and an oldest system has now operated for over ten years.

Due to high selectivity of new ion exchange materials target radionuclides can be separated into a small waste volume. Present experience has shown that even in high-salt evaporator concentrates well over 10 m³ of waste can be treated with one single kilogram of ion exchange material (about 60,000 gal/ft³). In low salt liquids this processing capacity can be orders of magnitude higher. This high processing capacity can cause interesting volume reduction factors, in the order of thousands or even in tens of thousands, for storage and final disposal.

When major part of radionuclides is separated, largest part of the liquid can be either released or recategorized. In many cases the amount of water to be released can be increased at the same time as the activity release is decreased and the amount of final waste to be disposed of is also decreased. Thus, many of the liquids that nowadays are solidified without further treatment can be purified for release, provided that the chemical character of these liquids does not limit the release. Liquids that contain high levels of radioactivity can be purified with selective ion exchangers to lower level for reclassification.

The amounts of highly selective ion exchange materials, which are needed for the treatment of even large waste volumes, are small. Use of small amounts of materials makes it possible to design, install and operate new types of compact liquid waste treatment systems. A new system can be installed in a relatively small floor area, or even as different kind of mobile units, either in a container or in skids. Economic savings from using this kind of new treatment system can be remarkably high.
REFERENCES


