USE OF HIGHLY SELECTIVE ION EXCHANGERS FOR MINIMIZATION OF WASTE VOLUMES

E. Tusa
Fortum Engineering Ltd
Rajatorpantie 8, Vantaa, POB 10, FIN-00048 FORTUM, Finland

R.Harjula, J.Lehto
Helsinki University, Laboratory of Radiochemistry
POB 55, FIN-00014 HELSINKI UNIVERSITY, Finland

ABSTRACT

Treatment of liquid radwaste by highly selective ion exchangers separates essentially only the radioactive elements from the inactive substances for storage and disposal. Even in high salt solutions only the radioactive target nuclides are removed and concentrated to a very small volume, and the inactive elements are left in the liquid. After this kind of treatment the processed liquid can either be released or recategorized for easier treatment with less expensive system.

Conventional ion exchange materials, e.g. zeolites and organic resins, have been used for years for treatment of different liquids. Relatively low selectivity factors have limited their efficient use. Three new highly selective ion exchangers have been introduced to the market: CsTreat® for removal of cesium, SrTreat® for strontium, and CoTreat for cobalt and other corrosion products. Selectivity factors of these new materials are on much higher levels than for the conventional ones. Several industrial applications utilizing these new materials have already proven their efficiency. Typically decontamination factors of several thousands can be achieved. Because of high selectivity, large proportion of the ion exchange capacity of the media (from 0.35 meq/g to 5 meq/g) can be utilized for removal of radioactive elements to treat very large volume of liquid using a very small volume of the media.

Selective removal of radionuclides reduces the volume of wastes in storage and final disposal. The first application for CsTreat in the Loviisa NPP in Finland treated 700 m^3 of high-salt evaporator concentrates with 80 liters of CsTreat. After this several new processes, including mobile treatment units, were based on these ion exchangers both for low-salt and high-salt liquids. One application was constructed for treatment of reprocessing liquid to remove both cesium and strontium from highly acidic waste.

High volume reduction of waste leads to high concentrations of radioactive elements in the final waste. Highly selective ion exchangers can be utilized in many different ways. Most efficient way is to use compact columns with volume of 2-12 liters. Used ion exchange columns are very easy to dispose of in concrete containers. In the Loviisa NPP 12 pieces of columns with volume of 8 liters each are closed into one concrete container with inner diameter of one cubic meter.

Need of small volumes of ion exchange material makes it also possible to utilize columns which are integrated with a final disposal container. Small volume of ion exchanger and compact system together give remarkable savings in treatment and disposal costs.

INTRODUCTION

Radioactive waste liquids are commonly treated for final disposal by direct solidification with cement or bitumen. Pretreatment of the liquids may include evaporation, or they are purified with conventional ion exchangers, i.e. zeolites or organic resins, and these ion exchangers are finally solidified for final disposal. Low selectivity has limited the applications of the conventional ion exchangers to liquids that contain very low salt concentrations.

Highly selective ion exchange materials give new possibilities for the treatment of radioactive waste liquids. Even liquids that have a very high salt concentration can be treated with this technology. This 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. Also many liquids can be treated more economically, if original liquid effluent can be reclassified for easier treatment.

Large number of selective ion exchangers have been studied and developed in different countries during recent past decades. However, almost all of them have stayed in laboratory or pilot scale without any real industrial applications. Only 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[1]. These silicotitanates have found some test operations, but they still wait for larger applications.

During 1990's, three new highly selective ion exchangers have been introduced into the commercial market[2-5]. These materials are totally inorganic and they are available in different grain sizes for both column and precoat applications. Selectivity factors of these new ion exchangers are on much higher levels than for 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. Most importantly, these commercial products have already several full scale references to prove their performance.

NEW INORGANIC HIGHLY SELECTIVE ION EXCHANGERS

CsTreat®, SrTreat® and CoTreat are relatively new products for commercial market. These materials are manufactured in Finland by Fortum Engineering Ltd (until the end of 1999 the subsidiary company Selion Oy), and they have found several applications for different kind of waste around the world[2-5].

CsTreat® was originally developed for treatment of high salt (240 g/L $NaNO_3$) evaporator concentrates at the Loviisa NPP in Finland. CsTreat® has later found several applications for the treatment of other types of waste solutions, too. This ion exchanger is 100 % inorganic and its efficiency is based on the selective hexacyanoferrate compound. 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 0.25-0.85 mm, but other sizes, like 0.15-0.25 mm and 0.85-2 mm, have been used in test operations. The latest development is the use of powder, <0.15 mm, in precoat applications. CsTreat® has an extremely high selectivity coefficient for Cs, exceeding that of other commercial Cs-selective media (Table I), and because of that it can give very high decontamination factors (DF) even in high salt concentrations, typically thousands and in special cases even much higher values. CsTreat®'s operation pH range from 1 to 13 makes it also very attractive product for applications where stable pH is not easy to maintain.

Table I. Selectivity coefficients for Cs/Na exchange in commercial ion exchangers [6]

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.

SrTreat® and CoTreat are 100 % inorganic ion exchangers based on titanium oxides. Typical use of SrTreat® and CoTreat is in granular form in column operation. Column sizes from less than one liter to 12 liters have been used. Normal grain size is 0.30-0.85 mm for both materials. Like in the case of CsTreat®, other grain sizes can be used according to treatment needs.

SrTreat®'s operation pH range is from neutral to alkaline conditions. As a rule the performance is improved when pH is increased. In high salt concentrations pH range above 9 is recommended. When the salt concentration is lower, reasonably good performance can be found in lower pH range, too. Calsium ions compete strongly with the strontium ion exchange, and like in the use of other ion exchangers high concentration of calsium will decrease the performance of SrTreat® in ^{90}Sr removal. The selectivity factor $k_{Sr/Na}$ is about 200,000 (for zeolites $K_{Sr/Na}$ is up to 100). Other cations have only very limited or no effect on strontium removal with SrTreat®. Typical DF is from several hundreds to several thousands.

CoTreat was developed for removal of radiocobalt, but it can also remove other corrosion product/activation products radionuclides such as ^{110m}Ag, ^{109}Cd, ^{54}Mn, ^{55,59}Fe, and ^{65}Zn. In low cobalt concentrations, i.e. <1,000 Bq/L, the operation pH is very narrow from 7 to 8. In higher concentrations, i.e. above 100 kBq/L, operation pH range from 5 to 10 is possible. Typically DF is from 100 to 1,000 for ionic cobalt.

APPLICATIONS OF NEW SELECTIVE ION EXCHANGERS

Loviisa NPP (PWR), Finland, was the first application of CsTreat®, and it has been in use since 1991 for the treatment of high salt (240 g/L $NaNO_3$) evaporator concentrates[7]. In these concentrates ionic cesium was the only radionuclide to prevent release of the liquid. Average processing capacity of the media has been about 14 700 L/kg (65,450 gal/cu.ft.) and the decontamination factor (DF) for ^{137}Cs has been above 1,000. Purified liquid could be released to the sea, which brought remarkable savings in the waste treatment costs.

At Olkiluoto NPP (BWR), Finland, low-salt floor drain wastewaters has been purified. 240 m^3 of waste water was purified with one 12 liter column. Processing capacity was over 33,000 L/kg (149,600 gal/cu.ft.), and there was no sign of exhausting of the media. The DF obtained for ^{137}Cs 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.

In July 1996, CsTreat® was installed at the Callaway NPP (PWR), Missouri, USA in the demineralizer system to replace evaporator [2]. The CsTreat® bed size was 250 liters and during three years about 3,000 m^3 of low salt waste water was treated with this bed. The activity of ^{137}Cs in the demineralizer effluent has been non-detectable after efficient filters were installed to remove particle-bound cesium from the influent. Processing capacity of the media was about 20,000 L/kg (90,000 gal/cu.ft.)

In 1996, a total of 760 m^3 of various waste waters, which originated from the operation of ex-Soviet naval training reactors were purified in Paldiskij, Estonia 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 100,000 L/kg (>473,000 gal/cu.ft.).

In 1996-97, a transportable NURES container, unit utilizing CsTreat® and SrTreat® beds, prefilters and a carbon filter, was used in Murmansk, Russia to treat 300 m^3 of different radioactive wastewaters originating from nuclear-powered icebreakers [8]. 24 liters of both ion exchange media were used. Maximum DF's for ^{137}Cs and ^{90}Sr have been 1,000 and 5,000, respectively. The NURES system appeared to be efficient for the removal of other radionuclides, e.g. ^{60}Co and ^{125}Sb, too. Processing capacity was about 20,800 L/kg for CsTreat® and about 15,600 L/kg for SrTreat® (93,500 gal/cu.ft.).

Table II summarizes the most essential data of these applications.

Table II. Results from selected CsTreat® and SrTreat® references

site	type of waste	treated, m^3 (gallons)	ion exchanger used, liters (cu.ft.)	processing capacity, L/kg (gal/cu.ft.)	DF	media
Loviisa NPP, Finland	evaporator concentrate	700 (185,000)	80 (48 kg) (2.8)	14,700 (>65,000)	>1,000	CsTreat®
Olkiluoto NPP, Finland	floor drains	240 (63,400)	12 (7.2 kg) (0.42)	>33,000 (149,600)	100 - 1,000	CsTreat®
Callaway NPP, MI, USA	floor drains	>3,000 (>800,000)	250 (150 kg) (8.8)	>20,000 (90,000)	up to 1,000	CsTreat®
Paldiskij, Estonia	training reactor waters	760 (>200,000)	12 (7.2 kg) (0.42 cu.ft.)	>100,000 (473,000)	3,000	CsTreat®
Murmansk, Russia	different waters from nuclear ice-breaker	300 (>79,000)	24 (0.85 cu.ft) (14.4 kg Cs 19.2 kg Sr)	20,800 Cs 15,600 Sr (93,500 gal/cu.ft.)	1,000 Cs 5,000 Sr	CsTreat® SrTreat®

In the summer of 1992, a different type of application for CsTreat® and SrTreat® was taken into use at Japan Atomic Energy Research Institute's (JAERI) Tokai site in Japan for the removal of Cs-137 and Sr-90 from alkaline reprocessing waste effluent. The original concentrations of 74 MBq/L of both Cs-137 and Sr-90 were reduced by DFs of over 1000 [9]. The project has succesfully ended in the year 2000. The goal of the system was to reclassify the original liquid for easier further treatment.

A new liquid waste treatment system, including utilization of CsTreat® , has been designed and licensed and is now in implementation phase for the Paks NPP, Hungary (PWR, VVER-440). The operation, which will start in 2001, will be very similar to that at Loviisa NPP. Close to 2000 m^3 (about 530,000 gallons) of evaporator concentrates and other liquids have been accumulated in the storage tanks at Paks NPP for treatment. According to the estimate a very remarkable part of this waste volume can be released after treatment.

In 2000, the first appplication at the USDOE's site with CsTreat® and SrTreat® was started at Savannah River Site. About 20 000 m^3 of contaminated water of the old disassembly pool will be decontaminated to demonstrate the efficiency of these materials.

VOLUME REDUCTION BY SELECTIVE ION EXCHANGERS

In Loviisa, Finland, 700 m^3 of high-salt (240 g/L) evaporator concentrate was treated with ten pieces of 8 liter columns. 700 m^3 of original waste was reduced to 80 liters of selective ion exchanger. The original plan of the NPP was to solidify evaporator concentrates with cement. Cementation would have produced about 1400 m^3 on concrete from this original 700 m^3.

Used ion exchange columns will be disposed of in concrete containers. Fig. 1 shows the final disposal container, which can store up to 12 used ion exchange columns. The inner volume of this container is 1 m^3. Compared to the original volume, if cemented, utilization of CsTreat® has caused the volume reduction factor of 1400.

At the Olkiluoto NPP, 240 m^3 of water in storage tanks was purified using a single 12 L column of CsTreat® with no sign of bed exhaustion. Direct reduction of unpacked waste volume was about 20 000.

As an example of low-salt waste processing the project in Paldiskij, Estonia, caused the waste volume reduction from 760 m^3 to 12 liters, and there was no sign of media exhaustion. Volume reduction factor for unpacked waste was over 63 000.

Table III summarizes volume reduction factors from some selected references.

Table III. Examples of volume reduction factors (VRF)

site	original waste volume (m^3)	used ion exchange media (Liters)	waste for final disposal, original plan, (m^3)	waste for final disposal, with ion exchange (m^3)	**VRF** Orig.waste/ ion exchange media	**VRF** ratio of final disposal forms
Loviisa NPP, Finland	700	80	1,400	1	8,750	1,400
Olkiluoto NPP, Finalnd	240	12	N/A	N/A	20,000	N/A
Paldiskij site, Estonia	760	12	N/A	N/A	63,000	N/A

Fig. 1. Used ion exchange columns are disposed of in concrete containers. One container can have cesium from about 1000 m^3 of high-salt evaporator concentrate.

ECONOMIC BENEFITS FROM SELECTIVE REMOVAL OF RADIONUCLIDES

Selective removal of radionuclides can bring remarkable savings for the treatment costs of different liquids. After treatment with selective ion exchange liquids can typically be released or they can be for example reclassified for easier treatment with less expensive system.

In power plant operations, savings are often obtained when smaller amount of liquid is coming for solidification and less final disposal containers are coming into final repository. As an example, cementation costs of 700 m^3 of evaporator concentrates at the Loviisa NPP would have cost close to 6 million USD. Invest in and operation of the new selective nuclide removal system was only a fraction of these costs.

In some systems, like in demineralizer, the savings may come from reduction of the volume of the ion exchanger. For example, if zeolite is used instead of CsTreat® for removal of cesium, even in moderately low salt concentration the amount of zeolite can be thousands times bigger than the amount of CsTreat®. The demineralizer system itself can be very advantageous compared to evaporation and cementation. In Callaway NPP in USA, the use of CsTreat® in the demineralizer system has reduced the liquid radwaste processing costs by 50 %, and in this saving both the ion exchanger and the system modification contributed [10].

Reclassification of liquids can give high savings, if vitrification or even construction of new system can be avoided by selective removal of radionuclides. In the project in JAERI, relatively high concentrations of Cs-137 and Sr-90 did not allow direct removal of this 11 m^3 batch of liquid for normal waste treatment at the Tokai-mura site. When this amount of liquid was treated with 20 columns, each containing 0.8 liters of CsTreat® and 0.8 liters of SrTreat®, purified liquid could be treated with the normal waste liquid treatment at the site.

CONCLUSION

The use of highly selective ion exchangers makes it possible to optimize treatment of different liquid effluents in a new way. Conventionally, part of the liquids are purified only with moderate or low efficiency, and the liquids are then discharged, even if they cause remarkable radioactive releases into the environment. The rest of the liquids are solidified for final disposal, giving considerable amount of solid waste. The new type of treatment with highly selective ion exchangers gives a possibility to change this practise. 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. This is possible even for liquids with high salt concentrations. Thus, many of the liquids that nowadays are solidified directly 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. Economic benefit from this kind of system modification can be large, as experience obtained with the new systems has shown. The additional advantage of the new highly selective 100%-inorganic ion exchangers is the applicability in the growing number of cases where no organics are allowed.

REFERENCES

[1] R.Braun, T.J.Dangieri, D.J.Fennelly, J.D.Sherman, W.C.Schwerin, R.R.Willis, L.A.Bray, G.N.Brawn, N.E.Brown, J.E.Miller, D.D.Lee, R.G.Anthony, C.V.Philip, T.T.Borek and W.J.Connors, "Crystalline Silicotitanates - Novel Commercial Cesium Ion Exchangers", Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management Spectrum '96, Vol 1, 1996, p.204.

[2] R.Harjula, J.Lehto, L.Brodkin and E.Tusa: CsTreat - Highly Efficient Ion Exchanger for the Treatment of Cs-Bearing Waste Waters, Proceedings of EPRI International Low Level Waste Conference, Providence, RI, USA, July 21-23, 1997.

[3] R.Harjula, J.Lehto, L.Brodkin, E.Tusa and J.Rautakallio: Treatment of Nuclear Waste Effluents by Highly Selective Inorganic Ion Exchange Medias - Experiences gained and new developments, Proceedings of Waste Management '98, Tucson, AZ, USA, March 1-3, 1998.

[4] R.Harjula, J.Lehto, A.Paajanen, L.Brodkin and E.Tusa: Testing of Highly Selective CoTreat Ion Exchange Media for the Removal of Radiocobalt and Other Activated Corrosion Product Nuclides from NPP Waste Waters, Proceedings of Waste Management '99, Tucson, AZ, USA, February 28-March 4, 1999.

[5] J.Lehto, L.Brodkin, R.Harjula and E.Tusa: Separation of Radioactive Strontium from Alkaline Nuclear Waste Solutions with Highly Effective ion Exchanger SrTreat, Nucl.Tech., 127(1999)81.

[6] R.Harjula, J.Lehto, A.Paajanen, L.Brodkin and E.Tusa: Removal of Radioactive Cesium from Nuclear Waste Solutions with the Transition Metal Hexacyanoferrate Ion Exchanger CsTreat®, submitted for publication

[7] E.H.Tusa, A.Paavola, R.Harjula and J.Lehto: Industrial Scale Removal of Cesium with Hexacyanoferrate Exchanger - Process Realization and Test Run, Nuclear Technology vol.107, Sept. 1994, pp.279-284.

[8] J.Lehto, L.Brodkin and R.Harjula: SrTreat - A Highly Effective Ion Exchanger for the Removal of Radioactive Strontium frrom Nuclear Waste Solutions, Proceedings of 6th International Low Level Waste Conference on Radioactive Waste Management and Environmental Remediation, Singapore, October 12-16, 1997, p.245.

[9] H. Tajiri, T. Mimori, K. Miyajima, T. Uchikosi, H. Mizubayashi and E.Tusa: Experience of Test Operation for Removal of Fission Product Nuclides in TRU-Liquid Waste and Concentrated Nitric Acid Using Inorganic Ion-Exchangers, Proceedings of Waste Mangement 2000, Tucson, AZ, USA, February 27-March 2, 2000.

[10] B.Miller and P.Tucker: Evaps to Demins - The Sponge is Working at Callaway, Proceedings of EPRI International Low Level Waste Conference, July 21-23, 1997, Providence, RI, USA.