Radioactive Wastewater Treatment Using a Cesium Selective Ion Exchanger and a Mixture of TANNIX™ Sorbent and VARION™ Mixed Bed Ion Exchange Resin

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Abstract
A wastewater treatment system has been developed by using a cesium selective inorganic ion exchanger. The selective separation of cesium ($^{137}$Cs, $^{134}$Cs) from high salt concentration and strongly alkaline evaporator bottom has a volume reduction factor about 1800-3500 at the value of the decontamination factor $DF>100$, for the samples of four tanks of the Hungarian PWR Paks.

Also an ion exchange treatment technology has been developed by using a mixture of ammonium-insoluble tannin and mixed ion exchange resin (MIX) for the selective separation of transuranium isotopes, including Pu, Am, Cm, and U, as well as fission and radioactive corrosion products from boric acid solution ($pH \sim 4.1$). The equilibrium and fixed bed sorption experiments resulted in $K_d$ values of $10^4$–$10^5$ ml/g, and decontamination factors of 1,000, with a breakthrough point between 1500 BV and 5000 BV of accumulated volume.

Key words: selective sorption; cesium; transuranium; fission products; fixed bed ion exchange.

1 Introduction
It is well known that in the Hungarian PWR Paks (PWR – Pressurized Water Reactor) the radioactive waste waters are collected in common tanks. These water streams contain radioactive isotopes in ultra-low concentration and inactive compounds as major components (borate 1.7 g/dm$^3$, sodium-nitrate 0.4 g/dm$^3$, sodium-hydroxide 0.16 g/dm$^3$, and oxalate 0.25 g/dm$^3$). Until now the low salinity solutions were evaporated by adding sodium-hydroxide, till 400 g/dm$^3$ salt content. There is about 6000 m$^3$ concentrated evaporator bottom in the tanks of the PWR. It is obvious that only the radioactive content of this waste should be embedded in concrete matrix and the radioactive components should be selectively removed before solidification. We have developed a complex technology for the selective separation of the long live radionuclides and for the partial recycle of boric acid from this evaporator bottom.
The separation of actinide elements from various waste materials is a significant problem facing developed countries. The chemical behavior of actinides is complex, and it is necessary to understand it more fully to be able to optimize separation processes under various conditions, as well as processes related to environmental clean-up. In general, tank wastes are either acidic or alkaline. Separation of actinides from acidic wastes is potentially much simpler than from neutralized wastes. This follows from the fact that actinides precipitate from alkaline media, and in some cases form colloids. For chemical separations to be effective the actinides must be solubilized, and in general, must be put into a separable ionic form. There are many techniques for treatment of transuranium (TRU) aqueous waste; solvent extraction and ion exchange are two of them. Though such techniques can decontaminate TRU aqueous waste, the production of secondary wastes is a serious problem to be solved. A special case is the treatment of PWR aqueous wastewater treatment, where the liquid contains boric acid or borates in a significant concentration (1–100 g/dm$^3$).

2 Experimental

2.1 Selective separation of cesium from concentrated evaporator bottom

The long-life radionuclides are present in very low concentration ($10^{-9}$ to $10^{-12}$ mol/dm$^3$) as ions, suspended, colloid particles and in complex form. The basics idea of the new technological scheme is the selective separation of these radionuclides with selective inorganic sorbent materials or reagents in very simple processes without any neutralization, dilution. The developed technology consists of the following parts:

- Firstly the high salt content, strongly alkaline ($pH$=13-14) evaporator bottom was microfiltered.
- Then the free EDTA, citrate, oxalate content was oxidized with underwater plasma torch and with Fenton oxidation.
- For the selective separation of the radioactive cesium isotopes ($^{137}$Cs, $^{134}$Cs) we developed a potassium-nickel-hexacianoferrate(II) cesium selective ion exchange material in granulated form.

2.2 Separation of the transuranium and fission product radioactive isotopes

During the chemical cleaning of corrosion products on the surface of the fuel cladding, some 30 fuel assemblies from the Paks-2 VVER-440 reactor (Hungary) overheated and were severely damaged. The event has been rated 3 on the International Nuclear Event Scale. The generated waste water (~100 m$^3$) contained ~20 g/dm$^3$ boric acid and gamma-, beta- and alpha-emitting radionuclides ($^{134}$Cs, $^{137}$Cs, $^{144}$Ce, $^{141}$Ce, $^{60}$Co, $^{125}$Sb, $^{110m}$Ag, $^{106}$Rh, $^{103}$Ru, $^{90}$Sr, $^{242}$Cm, $^{244}$Am, $^{239,240}$Pu, $^{238}$Pu, $^{238}$U, $^{234}$U etc.). Most of the radionuclides at $pH$=4.2 are in ionic form and TRUs are in suspended and dissolved form. To separate selectively the long-life transuranium and actinide radionuclides we have developed a new TRU waste treatment ion exchange technique by using the TANNIX insoluble tannin gel sorbent of the Mitsubishi Nuclear Fuel Co. Ltd. [1], combined with the conventional Hungarian VARION strong acid/base mixed bed ion exchange resin in fixed bed columns. The mixed sorbent system, called TMIX, was suitable for the selective separation of the transuranium and actinide isotopes as well as for the removal of fission and corrosion products.
The radioactive wastewater contained TRU isotopes with $10^3$–$10^4$ Bq/dm³ activity concentration. Filtration and batch contact experiments were performed to evaluate the selectivity of radionuclide removal from the wastewater generated during the event from the overheated and damaged fuel elements. The radioactive composition of this water changed continuously due to the regular cleaning using the ion exchange columns and filtration devices of the nuclear power plant (NPP).

A 10 dm³ sample was used taken from the NPP spent fuel basin. The pH of this sample was 4.1 and the boric acid concentration was 21 g/dm³. Firstly we filtered the radioactive solution with a fine pore size filtration paper.

Following the filtration we determined the distribution coefficients ($K_d$) for various radioactive isotopes on TANNIX and on a mixed TMIX (TANNIX + strong base/strong acid mixed bed ion exchange resin) sorbent at 25°C. In order to obtain distribution coefficients of fission and corrosion products as well as of transuranium and actinide isotopes at pH~4.1 for TANNIX and TMIX (50% TANNIX + 50% MIX) sorbents, batch contact experiments were carried out at 25°C with batches of the sorbents. In all experiments, three parallel measurements were carried out and the sorbent to solution phase ratio was 1 g to 120 cm³. The known volumes of the wastewater (120 cm³) were contacted with sorbent samples (1.0 g) in screw cap High-Density Polyethylene (HDPE) bottles. The bottles were shaken in an incubator-shaker at 25 rpm and 25°C for 24 h (repeated 48 h experiments gave the same results within experimental error). At the end of the contact period, the liquid was separated from the resin by filtration using individual Sartorius 0.2-micron filter units. Aliquots of the original waste (120 cm³) were treated the same manner as the samples without contacting the sorbent. Samples (100 cm³) were taken from the filtered solutions and analyzed by the NPP analytical laboratory. The isotopes $^{238}$Pu and $^{241}$Am were measured as a sum because of the alpha energy peak overlap.

After the equilibrium experiments ultrafiltration and sorption experiments were performed to evaluate the selectivity of radionuclide removal from the waste water generated during the event from the overheated and damaged fuel elements. The radioactive composition of this water changed continuously due to the regular cleaning using ion exchange columns and filtration. A 10 dm³ sample was used taken from the nuclear power plant (NPP) spent fuel basin. The pH of this sample was 4.1 and the boric acid concentration was 21 g/dm³. The radioactive waste water was first ultrafiltered with a TECH-SEP MICRO-CARBOSEP 20-40-60 laboratory scale ceramic type ultrafiltration device having molecular weight cutoff MWC~ 15 kDa.

Two different size columns made of glass tube (7.22 mm and 45 mm i.d.) were used in the separation experiments. The columns contained 2 cm³ and 300 cm³ of ammonium-form TMIX (mixture of TANNIX and VARION KSN/ATN type mixed bed conventional ion exchange resin) sorbent. A known quantity of TMIX was put in to into the column as slurry using 21 g/dm³ boric acid solution. The outside walls of the column were tapped while the sorbent was being placed to ensure uniform packing of the resin bed. The sorbent particles had a size of 0.1-1.0 mm. After the column was packed, the resin was conditioned with 12 bed volumes (BVs) of 21 g/dm³ boric acid solution. The loading of the column started at the moment the waste water contacted the sorbent. The solution was passed downward through the column at constant flow rates of 5, 10 and 20 BV/h. Effluent samples were then collected from the column outlet and the activity concentrations in the effluent fractions were determined by alpha- and gamma-spectroscopy.
3 Results and discussion

3.1 Selective cesium removal

During laboratory and pilot-plant scale tests we removed the radioactive cesium from about 500 dm³ evaporator bottom without neutralization, or any additional processes. At the value of the decontamination factor (DF=\(C_0/C\)) \(DF>100\), the volume reduction factor was about 1800-3500 for the samples of four tanks of PWR Paks. The flow velocity was about 10 BV/hour and we didn't detect the dissolution or destruction of the ion exchange material at the very alkaline pH (pH=13-14) solution during the 2-3 weeks service of the columns. Typical breakthrough curve (breakthrough=\(C/C_0\times 100\)) is shown in Fig.1. The breakthrough is at \(\sim 3800\) bed volume (BV).

![Cs removal experiment EM10](image)

Fig. 1 The measured cesium breakthrough curve

3.2 Separation of the transuranium and fission product

According to our early experiments we draw the conclusions that the \(^{95}\)Nb and the \(^{134}\)Cs and \(^{137}\)Cs activity concentrations are nearly independent of the investigated \(pH\) range and could not be filtered with filter paper, while the \(^{144}\)Ce and \(^{141}\)Ce activity concentrations are diminishing at alkaline \(pH\) and they are partially filterable. Similarly the gross-alpha activity concentration has a minimum at \(pH=6\), and about 63% is filterable. The \(^{239,240}\)Pu and \(^{238}\)Pu (\(^{241}\)Am) activity concentrations are nearly constant and could not be filtered with filter paper, while the \(^{244}\)Cm and \(^{242}\)Cm activity concentrations have a minimum at \(pH=6\) and 65–72% is filterable. These conclusions are in agreement with our model calculation results using the equilibrium calculation software VMINTEQ 2.3. Based on these results we concluded that at \(pH=4.1\) the boron compounds and the TRUs are mainly in soluble ionic form.
The distribution coefficients were calculated from the initial and final equilibrium concentrations of isotopes. Typically, the distribution coefficients are measured at equilibrium so the data represents one point on the equilibrium isotherm. The results are shown in Table 1.

Table 1 Equilibrium data on TANNIX and TMIX sorbents at 25 °C (pH=4.1)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_d$ ($^{95}$Nb)</th>
<th>$K_d$ ($^{134}$Cs)</th>
<th>$K_d$ ($^{137}$Cs)</th>
<th>$K_d$ ($^{144}$Ce)</th>
<th>$K_d$ ($^{141}$Ce)</th>
<th>$K_d$ ($^{239}$Pu$^{240}$Pu)</th>
<th>$K_d$ ($^{238}$Pu$^{241}$Am)</th>
<th>$K_d$ ($^{244}$Cm)</th>
<th>$K_d$ ($^{242}$Cm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>cm$^3$/g</td>
<td>cm$^3$/g</td>
<td>cm$^3$/g</td>
<td>cm$^3$/g</td>
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<td>cm$^3$/g</td>
<td>cm$^3$/g</td>
</tr>
<tr>
<td>TANNIX</td>
<td>1.53E+04</td>
<td>2.82E+02</td>
<td>2.70E+02</td>
<td>1.86E+05</td>
<td>2.35E+05</td>
<td>7.01E+03</td>
<td>1.22E+04</td>
<td>3.13E+04</td>
<td>3.61E+04</td>
</tr>
<tr>
<td>TMIX</td>
<td>-</td>
<td>1.58E+04</td>
<td>1.59E+04</td>
<td>2.77E+05</td>
<td>2.92E+05</td>
<td>5.24E+04</td>
<td>6.00E+04</td>
<td>1.51E+05</td>
<td>2.60E+05</td>
</tr>
</tbody>
</table>

The following conclusions can be drawn from the equilibrium experimental results. The equilibrium separation of $^{134}$Cs isotopes is not very efficient at pH=4.1 ($K_d=2.82 \times 10^2$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has better separation efficiency ($K_d=1.58 \times 10^4$ cm$^3$/g). The equilibrium separation of $^{137}$Cs isotopes is not very efficient ($K_d=2.70 \times 10^2$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has better separation efficiency ($K_d=1.59 \times 10^4$ cm$^3$/g). The equilibrium separation of $^{144}$Ce isotopes is efficient ($K_d=1.86 \times 10^5$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has even better separation efficiency ($K_d=2.77 \times 10^5$ cm$^3$/g). The equilibrium separation of $^{141}$Ce isotopes is efficient ($K_d=2.77 \times 10^5$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has slightly better separation efficiency ($K_d=2.92 \times 10^5$ cm$^3$/g).

The equilibrium separation of $^{239,240}$Pu isotopes is efficient ($K_d=7.7 \times 10^3$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has even better separation efficiency ($K_d=5.25 \times 10^4$ cm$^3$/g). The equilibrium separation of $^{238}$Pu$^{241}$Am isotopes is efficient ($K_d=1.22 \times 10^4$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has even better separation efficiency ($K_d=1.10 \times 10^4$ cm$^3$/g). The equilibrium separation of $^{244}$Cm isotopes is efficient ($K_d=3.13 \times 10^4$ cm$^3$/g) with TANNIX while the TMIX mixed sorbent has even better separation efficiency ($K_d=1.51 \times 10^5$ cm$^3$/g). The differences between the separation efficiencies of the curium isotopes are due to different generation processes of these two nuclides and due to different phase distribution between solid (colloid) and dissolved ionic form.

According to ultrafiltration experiments the following conclusions could be drawn. Using 15 kDA MWC ultrafiltration 67-90% of the radionuclides $^{60}$Co, $^{95}$Zr, $^{95}$Nb, $^{144}$Ce and $^{141}$Ce could be separated. The ultrafiltration is ineffective in the separation of cesium isotopes. About 90% of the gross-alpha activity could be separated using ultrafiltration. This is mainly due to the good filterability of the curium isotopes.

Using the determined activity concentrations in the ion exchange separation with TMIX the average decontamination factors of three repeated experiments as a function of treated bed volumes at two flow rates are shown in Fig. 2.
According to results the following conclusions could be drawn. Increasing the flow velocity the separation efficiency will be decreased. The gross-alpha $DF$ will diminish from $DF=600-700$ to $DF=150-250$ at an increased flow velocity from 10 BV/h to 20 BV/h. The gross-alpha separation efficiency strongly depends on the separation efficiency of $^{242}$Cm. The initial fluctuation at low velocity is due to the initial ammonia leaking from the TANNIX component. The separation efficiency of the most important cesium isotopes depends less on the flow velocity and the cesium removal is mainly due to organic mixed bed resin component of the TMIX sorbent mixture. On contrary the separation efficiency of the important cerium isotopes decreases from $DF=700-800$ to $DF=100$ at increasing velocity from 10 BV/h to 20 BV/h. The cerium removal is mainly due to TANNIX component of the TMIX sorbent mixture. The TMIX sorbent has also good separation efficiency for the $^{90}$Sr removal. The activity concentrations in the effluent and the related decontamination factors fluctuate at lower throughput at lower velocities.

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**References**