

Selective Separation of Radionuclides from NPP Evaporator Bottom Residue – 14091

György Pátzay *, Emil Csonka *, Csilla Tonkó *, János Otterbein **, Ferenc Feil **, Gábor Patek **

* Budapest University of Technology and Economics

** Paks Nuclear Power Plant Ltd P.O.Box 71, Paks 7031 Hungary

ABSTRACT

There is about 6500 m³ concentrated evaporator bottom residues in the tanks of the Hungarian PWR Paks. 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 residue. A wastewater treatment system has been developed by using a cesium selective inorganic ion exchangers. The selective separation of cesium (¹³⁷Cs, ¹³⁴Cs) from high salt concentration and strongly alkaline evaporator bottom residue in Paks Nuclear Power Plant has a volume reduction factor about 3000 /at the value of the decontamination factor $DF > 100$, for the samples of four tanks of the Hungarian PWR Paks. We investigated the Fortum CsTreat, the Russian Termoxid-35 and at the Technical University of Budapest developed CsFix cesium selective ion exchanger columns capacity and selectivity. The 12 dm³ cesium selective ion exchangers purified with the underwater plasma torch oxidized and ultrafiltered evaporator bottom residue with a 10 BV/hour feed rate. According to our experiments in the NPP and in the laboratory of the university the CsTreat and CsFix sorbents has nearly the same capacity (1% breakthrough at 3000 BV treated waste), except one charge, where one CsTreat column has a breakthrough at 7000 BV, while Termoxid-35 capacity was significantly lower (1% breakthrough at 400 BV treated waste).

INTRODUCTION

There are about 6500 m³ concentrated evaporator bottom in the tanks of the Hungarian NPP Paks. A liquid waste treatment technology was developed for the separation of the long life radioactive isotopes (¹³⁴Cs, ¹³⁷Cs, ⁶⁰Co etc.) from the inorganic chemicals borates and nitrates. The radioactive liquids contain these radioactive isotopes with 10⁴-10⁶ Bq/L activity concentrations, dissolved salts with about 400 g/L and organic complex builders (EDTA, citrate and oxalate). The original treatment technology starts with the underwater plasma torch reactor (UPTR) destruction of the organic complex builders followed by crystallization of inorganic borates using nitric acid acidification. The resulting liquid is the treated by a cesium selective ion exchanger CsTreat. The separated inorganic precipitation contained (~6-11%) radioactive isotopes and colloid iron so unrestricted release of these solids as chemical waste was impossible without further washing.

THE MODIFIED TECHNOLOGY

The main characteristics of the modification [1] were, that after the destruction of the organic complex builders using UPTR, we removed all the long life radioactive isotopes form the evaporator bottom using

micro and ultrafiltration and then a cesium selective ion exchanger, stable operating at pH~11-12. After these radioactivity separation steps we separated the alkali borates by crystallization using nitric acid acidification. The radioactivity of the separated inorganic borates was at unrestricted release level and the radioactivity of the liquid was lower than 290 Bq/L. We tested the modified technology steps under laboratory conditions using 1 L batches and followed testing at the NPP using 20 L batches. After successful test full scale technology was constructed and started in 2012. the scheme of the modified technology is shown in Figure 1.

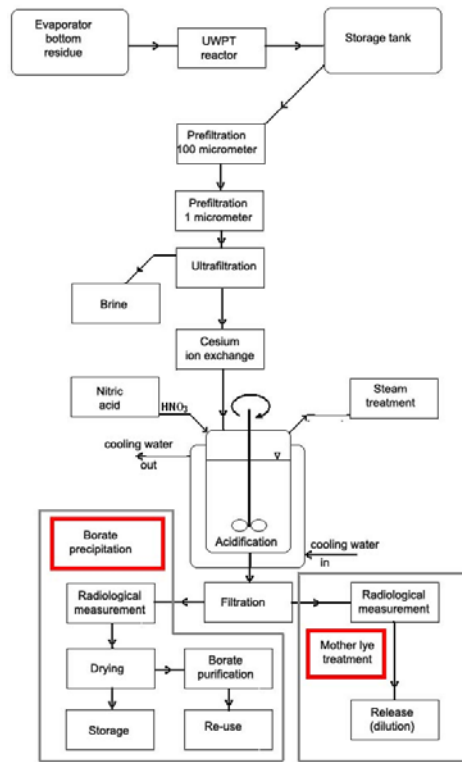


Fig1. The modified liquid radioactive waste treatment technology scheme

INVESTIGATION OF DIFFERENT CESIUM SELECTIVE ION EXCHANGERS

The modified wastewater treatment system uses a cesium selective inorganic ion exchangers. The selective separation of cesium (^{137}Cs , ^{134}Cs) from high salt concentration and strongly alkaline evaporator bottom residue treated with UPTR and ultrafiltration in Paks Nuclear Power Plant has a volume reduction factor about 3000 /at the value of the decontamination factor $DF > 100$, for the samples of four tanks of the Hungarian PWR Paks.

In the next step we investigated various commercial cesium selective ion exchanger materials. We investigated the Fortum CsTreat, the Russian Termoxid-35 [2] and at the Technical University of Budapest developed CsFix cesium selective ion exchanger columns capacity and selectivity.

In our experiments we used 12 dm³ cesium selective ion exchangers columns. During the selective ion exchange experiments we purified evaporator bottom residue solutions, treated previously with the underwater plasma torch and ultrafiltration. The flow rates were always 10 BV/hour, which was 120 L/hour feed rate. The ion exchange column and the shielding system is shown in Figure 2.



Fig. 2. The ion exchange column and the shielding system

CsTreat-cesium Selective Sorbent (Finland, Fortum)

The Fortum **CsTreat** (Figure 3.) cyanoferrate based cesium-selective ion exchanger is stable at $\text{pH} < 13$. It is a high efficiency cesium selective sorbent, suitable to treat pretreated evaporator bottom residue solutions. It was already used in Loviisa NPP and also in NPP Paks. We used it in 12L columns with 10 BV/hour flow rate.



Fig.3. CsTreat cesium selective sorbent

CsFix-cesium Selective Sorbent (Hungary, Technical University of Budapest)

The Hungarian **CsFix** (Figure 4.) cyanoferrate based cesium-selective ion exchanger is stable at $\text{pH} < 13$. It is a high efficiency cesium selective sorbent, suitable to treat pretreated evaporator bottom residue solutions. It was already tested in in NPP Paks. We used it in 12L columns with 10 BV/hour flow rate.



Fig.4. CsFix cesium selective sorbent

Termoxid-35 Cesium Selective Sorbent (Russia, Termoxid)

Termoxid-35 (Figure 5.) is a zirconium-oxide based potassium-nickel-hexacyanoferrate type cesium selective ion exchanger. It was successfully used in South-Ukrainian NPP (Ukraine), Kalinin NPP (Russia)

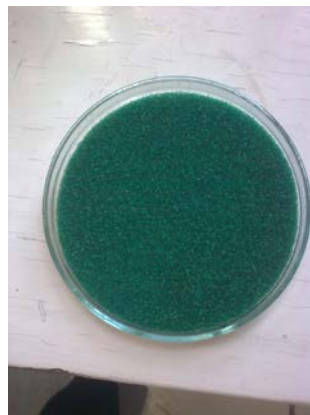


Fig.5. Termoxid-35 cesium selective sorbent

Cesium Selective Ion Exchange with the Three Different Ion Exchange Materials

According to experimental setup we used evaporator bottom residue solution from five different tanks of the NPP Paks. The UPTR treated and ultrafiltered solutions contained 137-200 g/L sodium- borates, 6-60 g/L sodium-nitrates, 97-131 g/L free sodium-hydroxide with a pH=12-13. The cesium content was 10^5 - 10^6 Bq/L ^{137}Cs and 10 - 10^3 Bq/L ^{134}Cs . Since 2012 686m³ solution was treated with CsTreat, 457m³ with CsFix and 16m³ with Termoxid-35.

RESULTS

The breakthrough curves, measured with CsTreat, CsFix and Termoxid-35 cesium selective ion exchangers are shown in Figures 6-8 . as a function decontamination factor (DF) of treated fluids in bed volume (BV) unit. We measured 100ml effluent samples regularly collected and the ^{137}Cs activity concentration were determined with HPGe gamma-spectrometry. We calculated the breakthrough volume at $DF \leq 100$.

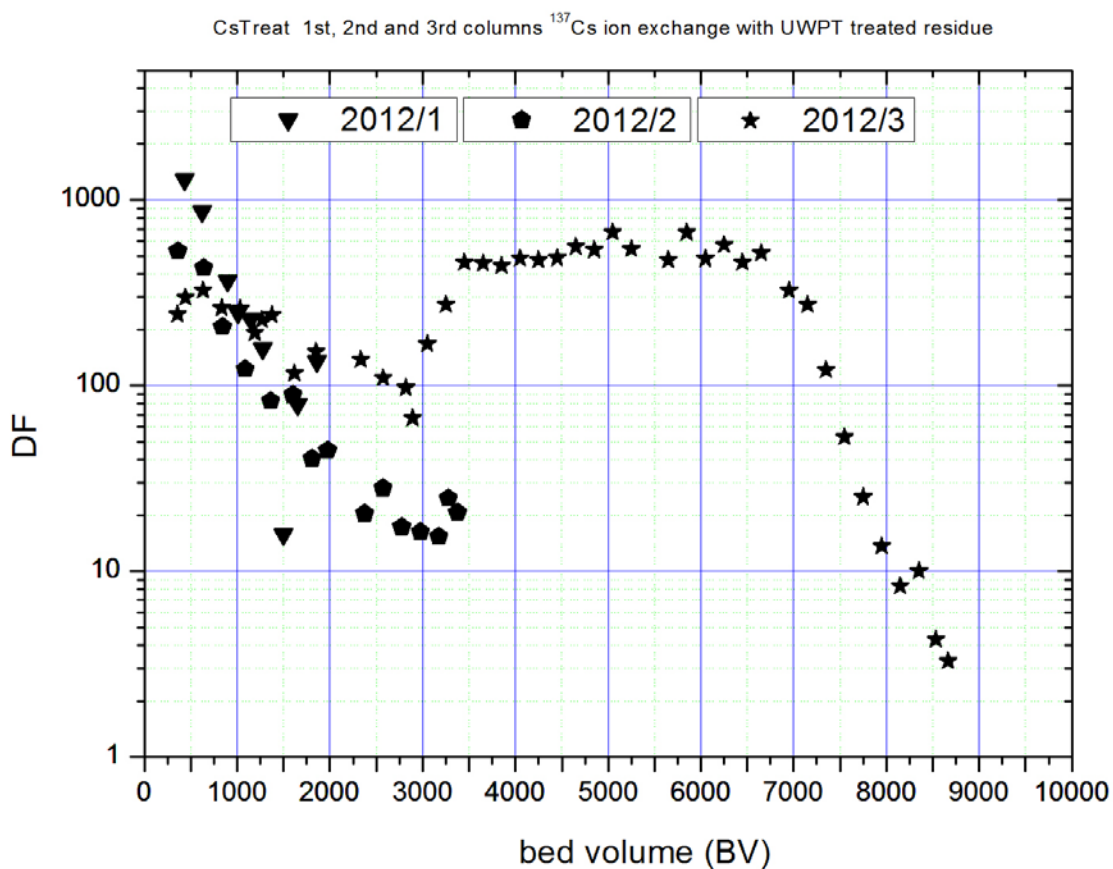


Fig. 6. CsTreat breakthrough curves for three different columns

According to our measured data the CsTreat sorbent could treat 2000-7500 bed volume evaporator bottom residue solution till breakthrough. The sever fluctuation is due to chemical composition differences (potassium and sodium content, pH) and to channeling in from down to up flow direction regime.

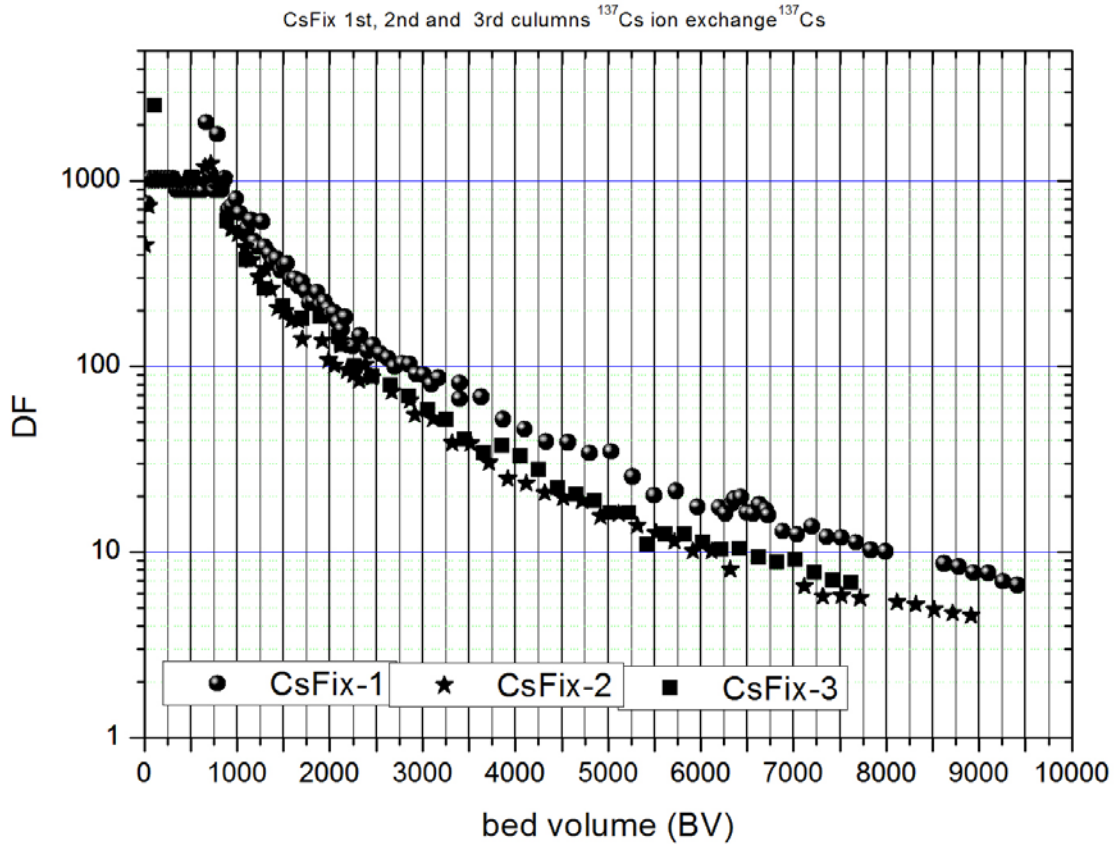


Fig. 7. CsFix breakthrough curves for three different columns

According to our measured data the CsFixt sorbent could treat 2500-3200 bed volume evaporator bottom residue solution till breakthrough. The fluctuation is due to chemical composition differences (potassium and sodium content, pH) and to channeling in from down to up flow direction regime.

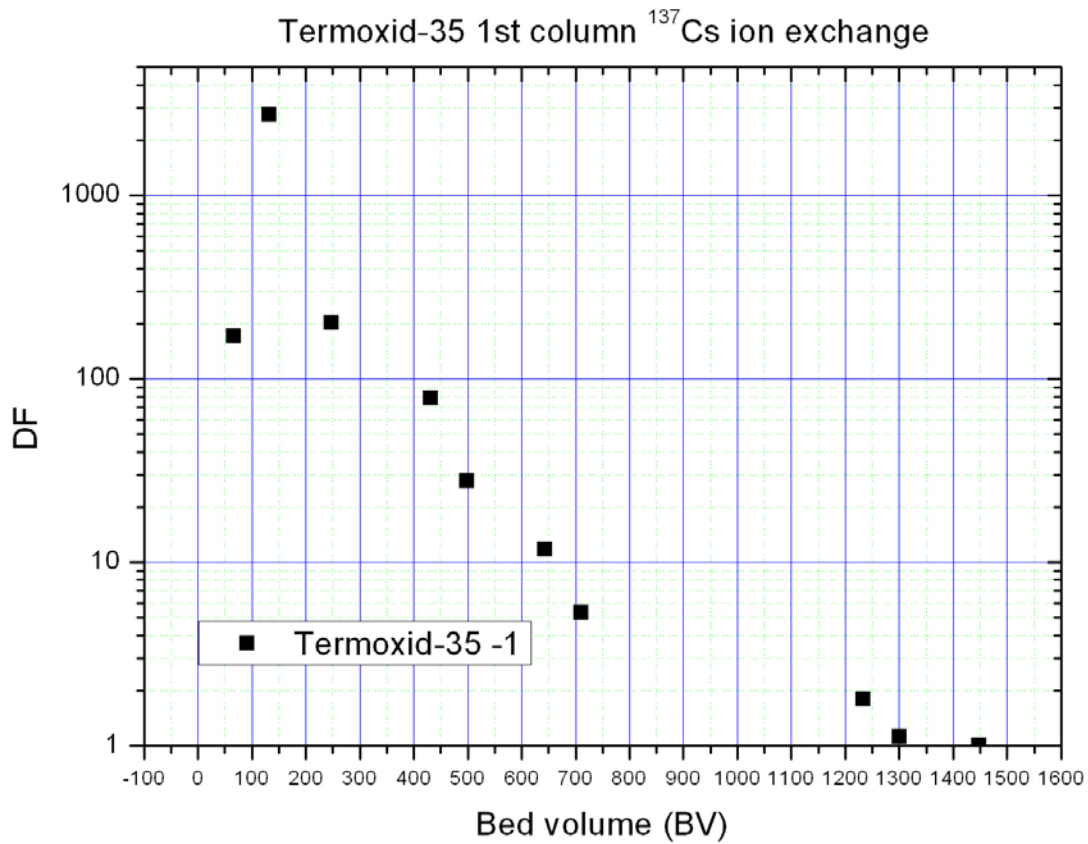


Fig.8. Termoxid-35 breakthrough curves for three different columns

According to our measured data the Termoxid-35t sorbent could treat 350-400 bed volume evaporator bottom residue solution till breakthrough.

CONCLUSIONS

According to our experiments in the NPP and in the laboratory of the university the best breakthrough result were measured with CsTreat, the CsFix sorbents had somewhat lower breakthrough capacity, while Termoxid-35 capacity was significantly lower (1% breakthrough at 400 BV treated waste). The observed severe fluctuations of the breakthrough in case of CsTreat and somewhat lower extent of CsFix is due to differences in chemical compositions (potassium, sodium, pH) and the probable channeling. So we suggested to feed the columns from up to down flow direction.

REFERENCES

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- [2] Dmitriev S.A., Lifanov F.A., Savkin A.E., Lachenov S.M., Baldov A.N., Slastennikov U.T., Sinyakin O.G., Arustamov A.E., TECHNICAL PROPOSALS ON PROCESSING EVAPORATOR CONCENTRATES, ACCUMULATED AT THE BN-350 REACTOR IN KAZAKHSTAN, WM'01 Conference, February 25-March 1, 2001, Tucson, AZ