VÉDELEM TUDOMÁNY
KATASZTRÓFAVÉDELMI ONLINE TUDOMÁNYOS FOLYÓIRAT

György Pátzay, Emil Csonka , János Otterbein, Ferenc Feil, Gábor Patek, József Dobor

RADIOAKTÍV CÉZIUM IZOTÓPOK SZELEKTÍV ELVÁLASZTÁSA ATOMERŐMŰVI BEPÁRLÁSI KONCENTRÁTUMOKBÓL

Absztrakt

A Paksi Atomerőműben a keletkező radioaktív hulladékoldatokat összegyűjtik és nátronlúg hozzáadása mellett bepárlással mintegy kétszázadnyi térfogatra sűrítik. Az így keletkezett erősen lúgos radioaktív sűrítmény összes sótartalama ~400 g/l. Jelenleg mintegy 6500 m^3 sűrítményt tárolnak az erőmű tartályaiban. A sűrítmény cementezés előtti további térfogat csökkentésére dolgoztuk ki a folyékony radioaktív hulladék feldolgozó technológiát (FHFT). Ennek során a radioaktív cézium, kobalt és más izotópokat szelektíven elválasztjuk és ezek kerülnek cementezésre és temetésre a Nemzeti Radioaktív Hulladék Tárolóban. Így a10^4-10^6 Bq/l aktivitás koncentrációjú 10^{-9}-10^{-12} mol/dm3 kémiai koncentrációjú radioaktív izotópokat kis térfogatba tömörítve kapjuk meg. A visszamaradt inaktív csapadék közönséges vegyi hulladékként kerül ki az erőműből, az inaktív anyalúg pedig felhígítva a Dunába kerül.

A radioaktív cézium izotópok szelektív elválasztására három szorbenst, a finn CsTreat, a magyar CsFix és az orosz Termoxid-35 vizsgáltuk. Megállapítottuk, hogy a paksi radioaktív sűrítmények radioaktív cézium izotópjainak szelektív elválasztására a finn és magyar szorbens közel azonos minőségben alkalmazható, míg az orosz Termoxid-35 erre a feladatra nem alkalmas. A CsTreat és a CsFix cézium ioncserélő kapacitása függ a szorbens oszlopba töltésének módjától és szemben a magyar szorbenssel a CsTreat kapacitása függ az oldat kálium tartalmától is. A céziumszelektív ioncserélő oszlopok kapacitása sorba kapcsolt 2-3 oszlop esetén magasabb volt és a szorbenst tartalmazó fémoszlop be és kiömlő nyílásain található fémszűrő hálók méretét is növelni kellett 0,032mm-ről 0,18 mm-re.

Kulcsszavak: bepárlási maradék, szelektív cézium ioncsere, áttörési kapacitás, eloszlási koefficiens

VÉDELEM TUDOMÁNY
KATASZTRÓFAVÉDELMI ONLINE TUDOMÁNYOS FOLYÓIRAT

INVESTIGATION OF SELECTIVE SEPARATION OF RADIOACTIVE CESIUM FROM NPP EVAPORATOR BOTTOM RESIDUE

Abstract

In the Hungarian PWR-type (4 blocks of VVER-440/213) nuclear power plant of Paks the radioactive waste waters are collected in common tanks. Up to the present, the low salinity solutions were evaporated (by adding sodium-hydroxide) till 400 g/dm^3 salt content (pH~12-13) and stored for burial. Currently there is about 6500 m^3 concentrated evaporator bottom residue in the tanks of the NPP.

A Liquid Wastewater Treatment Technology (LWT) was developed to treat this wastewater before solidification and burial. The aim of this technology is selectíve separation of cesium and cobalt isotopes into small volume, then the remaining inactive chemicals could be treated as chemical waste. The radioactive liquids contain these radioactive isotopes with 10^4-10^6 Bq/L activity concentrations. The long-life radionuclides are present in very low concentration (10^{-9}-10^{-12} mol/dm^3) as ions, suspended, colloid particles and in complex (EDTA, oxalate, citrate) forms. In this treatment technology, two cesiumselective ion exchanger applied, the CsTreat and the CsFix.changer for the selective separation of radiocesium isotopes (^{134}Cs, ^{137}Cs). A third Russian selective sorbent Termoxid-35 was also tested.

CsTreat and Csfix have near the same Cs ion exchange capacity, sorbent Termoxid-35 was not effective for these residues. Capacity of CsTreat and CsFix depends on the sorbent charging technique into column and for CsTreat on the potassium content. Ion exchange properties of sorbent CsFix were independent of potassium concentration. Columns were more effective in serial coupling (2-3 columns). The screen size for inlet and outlet should be increased from 0.032mm to→0.18mm to avoid plugging. Further research is required to increase the slope of breakthrough curves.

Key words: Evaporator bottom residue, selective cesium ion exchange, breakthrough capacity, distribution coefficient

1. INTRODUCTION

In the Hungarian PWR-type (4 blocks of VVER-440/213) nuclear power plant Paks 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).

Up to the present the low salinity solutions were evaporated (by adding sodium-hydroxide) till 400 g/dm^3 salt-content (pH~13) and stored for burial. There is about 6500 m^3 concentrated evaporator bottom residue in the tanks of the NPP.

A Liquid Wastewater Treatment Technology (LWT see Figure 1.) was developed to treat this wastewater before solidification and burial. The radioactive liquids contain these radioactive isotopes (^{134}Cs, ^{137}Cs, ^{60}Co) with 10^4-10^6 Bq/L activity concentrations. The long-life radionuclides are present in very low concentration (10^{-9}-10^{-12} mol/dm^3) as ions, suspended, colloid particles and in complex (EDTA, oxalate, citrate) forms.

In this technology the CsTreat and CsFix cesium selective ion exchangers are used after the oxidation treatment of organic complex builders and cobalt removal for the selectice separation of radiocesium isotopes (^{134}Cs, ^{137}Cs) [1].

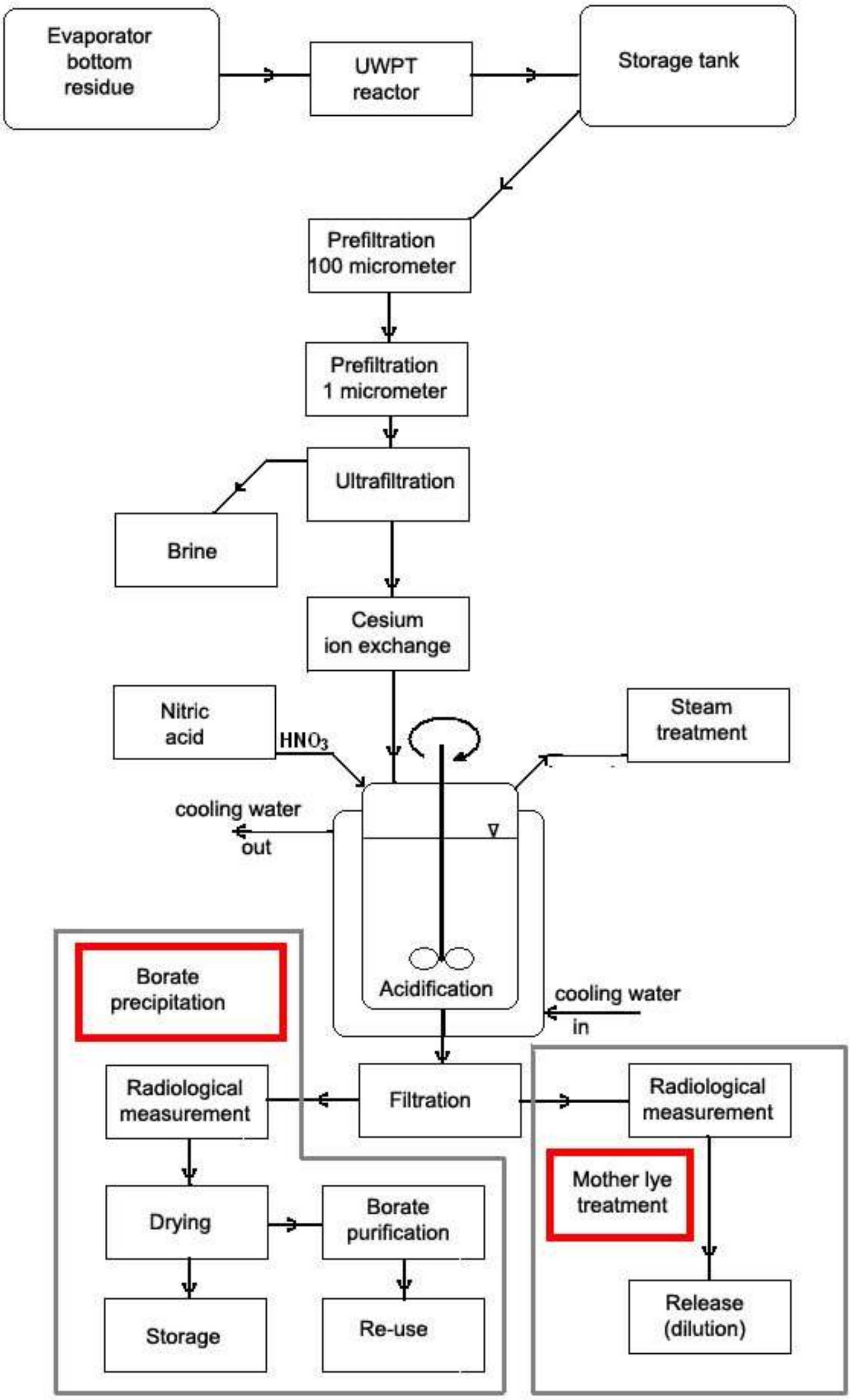

Figure 1. The LWT process in Paks

Presently the underwater plasma treating is substituted by a permanganate oxidation and the resulted fluid is filtered by MF and UF before selective caesium separation. For the selective caesium separation three different sorbents were tested, the Finnish CsTreat, the Hungarian CsFix and the Russian Termoxid-35. The tests were evaluated in laboratory scale at Budapest University of Technology and Economics and in industrial scale at NPP Paks.

2. EXPERIMENTAL

Laboratory scale tests were performed with a 1,5 ml ion exchanger, at 10 BV/h flow rate, fed with oxidation treated, ultrafiltered evaporator bottom residue from NPP Paks. Separation efficiency was determined by regular sampling and HPGe analysis. The CsTreat and CsFix sorbents had good caesium breaktrough (1%, DF>100) with 3500-4500 bed volume treated while Termoxid-35 had an early breakthrough at ~400 bed volume (see Figures 2. and 3.).

Figure 2. The laboratory ion exchange column

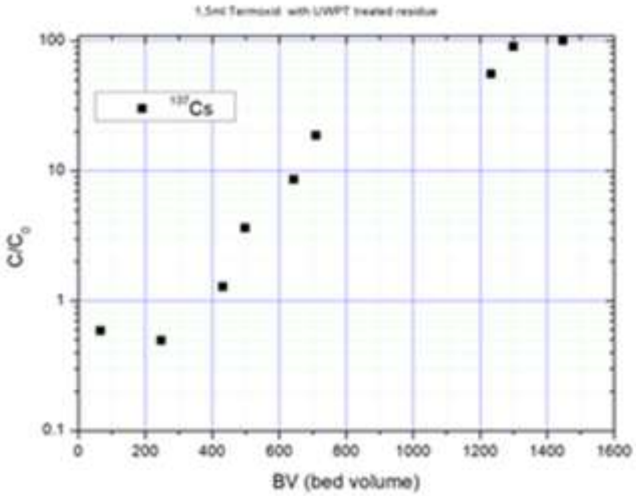

Figure 3. The Termoxid-35 breakthrough curve

According to the laboratory test results we concluded that the Termoxid-35 was not suitable for selective caesium separation from evaporator residue of NPP Paks.

3. COMPARISON OF THE TWO CAESIUM SELECTIVE SORBENTS CAPACITY AT THE NPP PAKS

Using the two efficient sorbent types (CsTreat and CsFix), first one, later two independent filter columns 12 liter sorbent in each was operated in serial or in parallel connection depending on the cesium activity of liquid waste. Filters in lead shield (radiation protection, transportation) are shown in Figure 4.

Figure 4. The 12L sorbent columns in lead shield

Experiments at the NPP

According to results of the caesium selective ion exchange at the NPP we got slightly fluctuating breakthrough for both types of sorbents. Depending on the inflow composition (potassium content, residual oxidative compounds) the breakthrough bed volumes (BV) at DF>100 were between 2200-2600 BV, except of one CsTreat breakthrough measured several years ago (7300 BV) as seen in Figure 5.

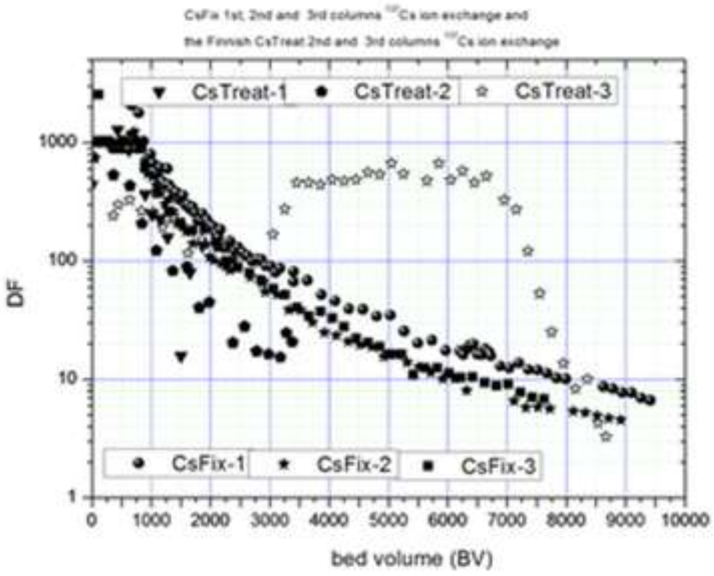

Figure 5. Breakthrough curves of CsTreat and CsFix sorbents

In the second half of 2017 due to increased filling conditions of CsTreat and CsFix sorbents into columns the breakthrogh results showed better results:

- CsTreat: 5000-7300 BV till 1% breakthrough
- CsFix: 4500-6000 BV till 1% breakthrough (Figure 6.)

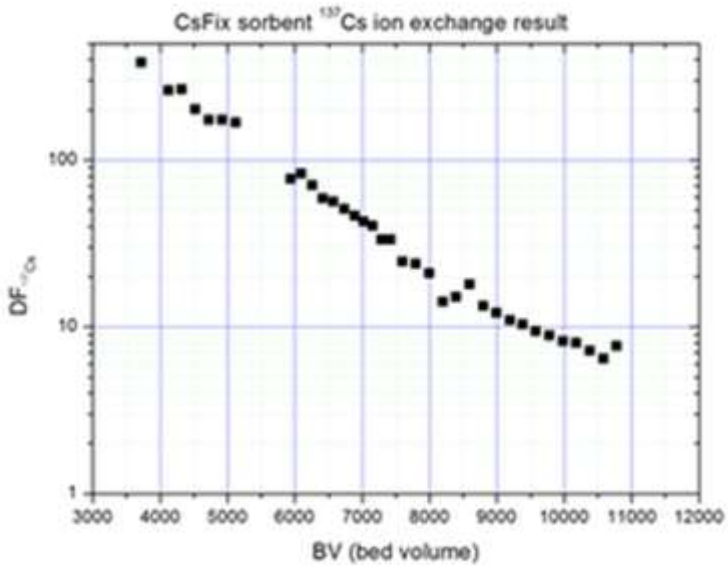

Figure 6. Breakthrough curve of CsFix in 2017

Problems with the ion exchange columns

During the separation processes some problems were detected:

- partial change of flow direction from down top
- too fine screen at the in and outflow
- too small distributing and collecting area

To investigate these problems, we performed some laboratory experiments with a 12 L column and the two sorbents using evaporator residue model solutions. Our results indicated the possible negative effects of pressure drop, channeling and plugging (Figures 7-9.).

Figure 7. Experimental setup for column

Figure 8. Channelling during high flow rate

Figure 9. Pugging of the outlet by 0.032 mm size screen

According to the results we suggested to increase the outlet screen size from 0.032 mm to 0.18 mm to avoid the plugging problems.

4. EFFECT OF POTASSIUM CATION CONCENTRATION ON THE BREAKTHROUGH

From the Finnish experimental results [2] it is known that the breakthrough capacity of sorbent

CsTreat depends strongly on potassium concentration. According to their results the distribution coefficient decreases with

$$\lg(K_d) \approx \frac{1}{\left[K^+\right]^{0,89}} \qquad (1)$$

We tested also the sorbent CsFix breakthrough capacity as the function of potassium concentration (8-20 g/l) in the influent. The calculated K_d values for CsTreat and the measured K_d values for CsFix are shown in Figure 10.

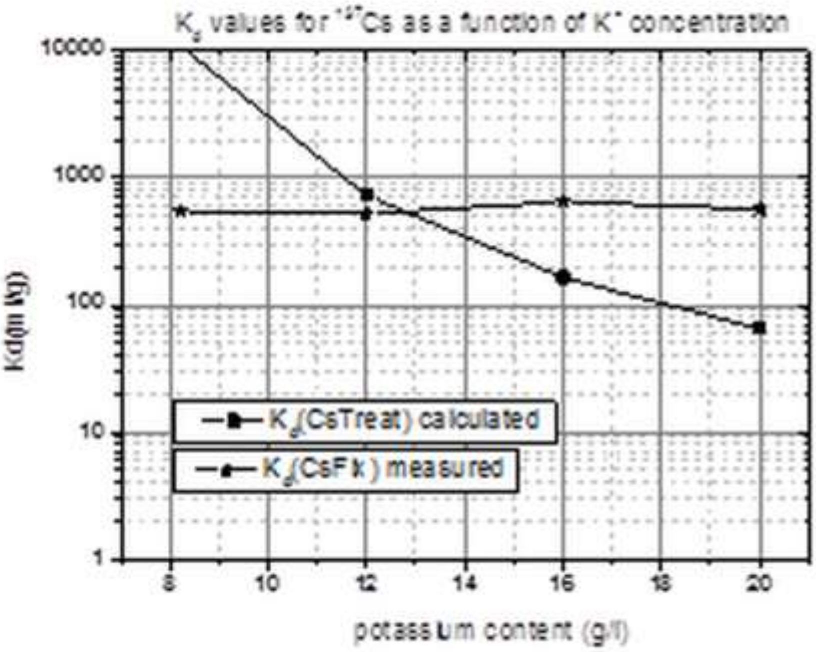

Figure 10. K_d values of ^{137}Cs for CsTreat and CsFix

It is seen that while K_d of CsTreat depends strongly on potassium concentration between 8-20g/l, in case of CsFix does not.

5. CONCLUSION

Sorbents CsTreat, CsFix and Termoxid-35 were tested for cesium removal from evaporator bottom residue of NPP Paks. CsTreat and Csfix have near the same Cs ion exchange capacity, while Termoxid-35 is not effective for such treatment. Capacity of CsTreat and CsFix depends on the sorbent charging technique and for CsTreat on the potassium content. Columns are more effective in serial coupling (2-3 columns). The screen size for inlet and outlet should be increased from 0.032mm to 0.18mm. Further research is required to increase the slope of breakthrough curves.

REFERENCES

[1] György Pátzay, László Weiser, Ferenc Feil, János Schunk, Gábor Patek, Radioactive wastewater treatment using selective ion exchangers, Periodica Polytechnica, Chemical Engineering, 53/2, 2009, 67-69

[2] J. Lehto, R. Harjula, J. Wallace, Absorption of Cesium on Potassium cobalt Hexacyanoferrate(II), Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 111, No 2 (1987) 297-304

Prof. Dr. Pátzay György, egyetemi tanár, Nemzeti Közszolgálati Egyetem Katasztrófavédelmi Intézet

patzay.gyorgy@uni-nke.hu

Prof. György Pátzay, professor, Institute of Disaster Management, National University for Public Service

https://orcid.org/0000-0002-5541-8012

Csonka Emil, mérnök, tanszéki mérnök, Budapesti Műszaki és Gazdaságtudományi Egyetem, Kémiai és Környezeti Folyamatmérnöki Tanszék,

csonka.e@eik.bme.hu

Emil Csonka, engineer, Budapest University Of Technology And Economics, Department of Chemical and Environmental Process Engineering,

csonka.e@eik.bme.hu

Otterbein János, mérnök, Paksi Atomerőmű Zrt.,

otterbeinj@npp.hu

János Otterbein, engineer, Paks Nuclear Power Plant Company,

otterbeinj@npp.hu

Feil Ferenc, mérnök, Paksi Atomerőmű Zrt.,

feilf@npp.hu

Ferenc Feil, engineer, Paks Nuclear Power Plant Company,

feilf@npp.hu

Patek Gábor mérnök, Paks II. Zrt.

patek.hu@gmail.com

Gábor Patek mérnök, Paks II Nuclear Power Plant Company

patek.hu@gmail.com

Dr. habil. Dobor József, egyetemi adjunktus, Nemzeti Közszolgálati Egyetem Katasztrófavédelmi Intézet
dobor.jozsef@uni-nke.hu

Dr. József Dobor, Institute of Disaster Management, National University for Public Service

https://orcid.org/0000-0003-0191-4261