

Radioactive wastewater treatment using selective ion exchangers

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Abstract

It is well known that in the Hungarian PWR-type 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/dm³, sodium-nitrate 0.4 g/dm³, sodium-hydroxide 0.16 g/dm³, and oxalate 0.25 g/dm³). These low salinity solutions were evaporated by adding sodium-hydroxide, until 400 g/dm³ salt content is reached. There is about 6000 m³ concentrated evaporator bottom residues in the tanks of the PWR. 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 exchanger. 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 1800-3500 at the value of the decontamination factor DF > 100, for the samples of four tanks of the Hungarian PWR Paks.

Keywords

Radioactive · wastewater · ion exchange · crystallization

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1 Introduction

In the Hungarian PWR-type 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/dm³, sodium-nitrate 0.4 g/dm³, sodium-hydroxide 0.16 g/dm³, and oxalate 0.25 g/dm³).

Up to the present the low salinity solutions were evaporated (by adding sodium-hydroxide) till 400 g/dm³ salt content (pH~13) and buried. There is about 6000 m³ concentrated evaporator bottom residue in the tanks of the PWR. A Liquid Wastewater Treatment Technology (LWT see Fig. 1) was developed to treat this wastewater before solidification and burial.

The long-life radionuclides are present in very low concentration (10⁻⁹-10⁻¹² mol/dm³) as ions, suspended, colloid particles and in complex (EDTA, oxalate, citrate) form. In this technology the SELION CsTreat cesium selective ion exchanger is used for the selective separation of radiocesium isotopes (¹³⁴Cs, ¹³⁷Cs). The SELION CsTreat cyanoferrate-based cesium-selective ion exchanger is not stable at pH > 11 (see reaction equation below), so the use of CsTreat needs partial neutralisation of the evaporator bottom residue to pH~9-11, and during neutralisation sodium-borate crystals precipitate with about 15-30% of the cesium radioactivity.



The contaminated crystals should be washed to remove the radioactive isotopes from the crystals.

To eliminate the generation of radioactive borate crystals we have developed a M₂Ni[Fe(CN)₆] type cesium selective granulated ion exchanger (where M is an alkali ion) which has good stability at pH > 11.

Based on this new cesium selective ion exchanger stable at pH > 11 we have modified the radioactive evaporator bottom residue treatment technology at the nuclear power plant. The basic idea of the new technological scheme is the selective separation of all radionuclides with inorganic sorbent materials or reagents in very simple processes without any prior neutralization, dilution. After the separation of all radionuclides the in-

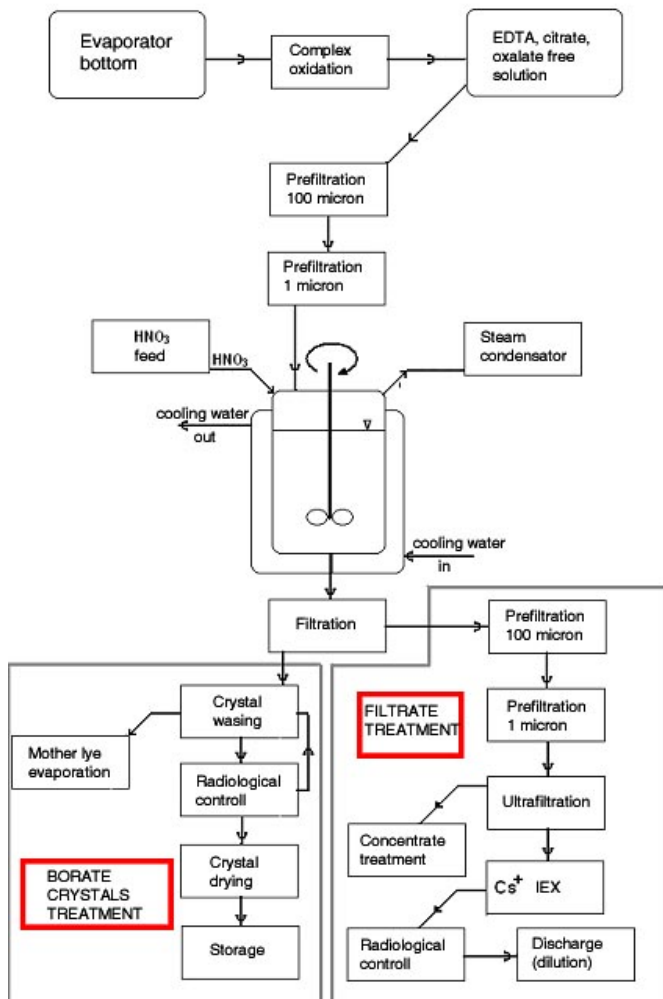


Fig. 1. The Liquid Wastewater Treatment Technology

organic salt content (borates, nitrates) could be separated with crystallization using nitric acid neutralization and the inactive crystals could be treated as chemical waste. The developed modified technology consists of the following parts:

- Firstly the high salt content, strongly alkaline ($pH \sim 13-14$) evaporator bottom residue is *microfiltered*.
- Then the free EDTA, citrate, oxalate content is *oxidized* with underwater plasma torch and with Fenton oxidation (Co isotopes removed by precipitation as oxide-hydroxide).
- Selective separation of the radioactive cesium isotopes (^{137}Cs , ^{134}Cs) using ion exchange material stable at alkaline pH.
- Crystallization of borates from the mother lye.

2 Experimental

About 500 dm^3 evaporator bottom residue was oxidized with underwater plasma torch for the EDTA, citrate and oxalate removal. The oxidized evaporator bottom residue was then microfiltered and ultrafiltered to remove suspended matter from the solution having a $pH \sim 12.3$.

The resulting solution was then passed batchwise through fixed bed ion exchange columns filled with 60 cm^3 0.2-0.32

Tab. 1. Ultrafiltration of the waste water after oxidation of the complex compounds

	^{60}Co activity concentration (Bq/kg)	%	^{134}Cs activity concentration (Bq/kg)	%	^{137}Cs activity concentration (Bq/kg)	%
Feed	2310*	100	1350	100	181000	100
Permeat	258	11.2	1210	89.6	164000	90.6

mm size cesium selective ion exchanger, stable at this pH. The columns were running until 1% breakthrough, which were at about 2500 bed volumes. The flow velocity was about 10 BV/hour and we did not detect the dissolution or destruction of the new ion exchange material at the very alkaline solution during the 2-3 weeks service of the columns. A typical breakthrough curve is shown in Fig. 2. The breakthrough (1%) is at about 2500 BV.

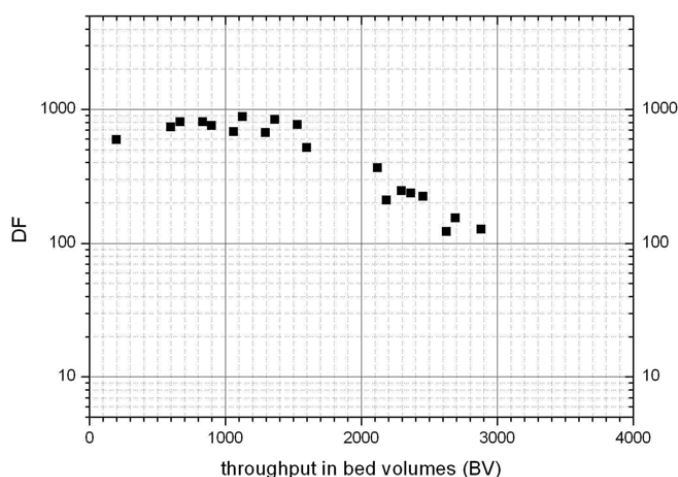


Fig. 2. Breakthrough curve of ^{137}Cs (BV-bed volume)

The solution purified from radioactive cesium was then acidified with concentrated nitric acid in 20 dm^3 batches in a cooled mixed reactor till $pH \sim 9.0$. The crystallization reactor is shown in Fig. 3.

The crystals were separated by filtration, dried at $50 \text{ }^\circ\text{C}$ and weighted. The crystalline product contained mainly sodium-metaborate ($\text{NaBO}_2 \cdot 8\text{H}_2\text{O}$). Heating the product above $55 \text{ }^\circ\text{C}$ the crystalline phase released four water molecules and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ formed. Fig. 4 shows the separated wet crystals.

3 Results

The measured specific radioactivity of the separated, dried crystals and the unconditional clearance limit values are summarized in Table 2.

4 Conclusion

Based on our modification of the original wastewater treatment technology in the Hungarian Nuclear Power Plant we get beneficial results summarized as follows:



Fig. 3. The crystallization reactor



Fig. 4. The separated wet crystals

Tab. 2. The measured specific radioactivity of the crystals and the release limits

Radionuclide	Measured specific activity (Bq/g)	*Unconditional clearance *limit (Bq/g)
⁵¹ Cr	1.42E-02	30
⁵⁴ Mn	1.19E-03	1
⁵⁸ Co	1.01E-03	1
⁵⁹ Fe	1.93E-03	0.9
⁶⁰ Co	1.17E-03	0.9
⁶⁵ Zn	2.66E-03	2
⁹⁵ Nb	1.10E-03	0.9
⁹⁵ Zr	1.81E-03	3
¹⁰⁶ Ru	1.15E-02	1
^{110m} Ag	1.83E-03	0.9
¹²⁴ Sb	1.83E-03	0.9
¹²⁵ Sb	7.63E-03	1
¹³⁴ Cs	1.66E-03	0.9
¹³⁷ Cs	1.11E-01	2
¹⁴⁴ Ce	1.02E-02	30
¹⁵⁴ Eu	2.59E-02	0.9
³ H	2.94E-02	2000
¹⁴ C	1.91E-05	200
⁵⁵ Fe	3.01E-05	100
⁵⁹ Ni	6.20E-06	800
⁶³ Ni	2.72E-04	300
⁹⁰ Sr	3.19E-02	1
⁹⁹ Tc	7.19E-05	1
¹²⁹ I	1.24E-09	0.9
²³⁴ U	4.69E-07	0.9
²³⁵ U	1.71E-07	0.9
²³⁸ U	1.09E-07	0.9
²³⁸ Pu	4.83E-07	0.9
^{239,240} Pu	3.62E-07	0.9
²⁴¹ Am	5.48E-08	0.9
²⁴² Cm	4.01E-07	0.9
²⁴⁴ Cm	4.26E-07	0.9

* valid values for the nuclear power plant wastes

- The use of the new cesium selective ion exchanger eliminates the acidification of the evaporator bottom residue before the cesium removal by ion exchange.
- Hence we can avoid the formation of borate crystals contaminated with radionuclides of cesium etc. and the additional washing of the separated crystals for the radioactivity removal.
- According to measured specific activity data we are able to release the dried solid crystals from the NPP and they could be used as non-radioactive borate chemical.