

Modification of the Radioactive Wastewater Treatment Technology in the Hungarian Nuclear Power Plant Paks

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This paper describes the results of a joint research program of the Budapest University of Technology and Economics and the Paks Nuclear Power Plant (NPP) to modify the radioactive wastewater treatment technology for the evaporator bottom tanks in the NPP. The main characteristics of the modified technology were that we first removed all the long life radioactive isotopes with an underwater plasma torch reactor (UPTR), micro and ultrafiltration and a cesium selective ion exchanger stable at pH~12–13. After the separation of precipitated borate crystals, the remaining liquid was released as chemical waste.

Introduction

There are about 6000 m³ of concentrated evaporator bottom as liquid radioactive waste 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 (ethylene-diamine-tertaacetic acid (EDTA), citrate and oxalate). The treatment of this type of wastewater is complicated [1–4]. 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 then treated by a cesium selective ion exchanger CsTreat. The separated inorganic precipitation contains (~6–11%) radioactive isotopes and colloid iron from the original waste so unrestricted release of these solids as chemical waste is impossible without further washing.

To solve this problem we have developed a modified technology suitable to produce non-radioactive crystals and liquid for unrestricted release.

The modified technology

The main characteristics of the modification were, that after the destruction of the organic complex builders using UPTR, we removed all the long life radioactive isotopes from the evaporator bottom using micro and ultrafiltration and then a cesium selective ion exchanger, stable operating at pH~12–13. After these radioactivity separation steps we separated the

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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 tests the wastewater treatment system was built and started to work in the NPP. [1]

Laboratory Experiments

In our laboratory experiments we used evaporator bottom samples pre-treated in the NPP by UPTR. After this treatment the cobalt ions bound to EDTA and other organic complex builders were oxidized and the radioactive cobalt content was filtered out.

First we investigated the crystallization parameters of a non-radioactive model solution of the evaporator bottom. The model solution contained sodium borates, nitrate and free sodium hydroxide at a total dissolved solid, TDS~400 g/L. The thermostated crystallizer with stirrer, temperature and pH meter and acid dose system is shown in Picture 1. The thermostat, at 27°C 1 L model solution, was stirred at 300 rpm. After reaching a steady state condition we started the dose of 65 m/m% nitric acid with an average flow rate of 1.247 cm³/min and measured continuously the temperature and the pH values in the liquid phase. The acidification was stopped after reaching a pH value of 9.8. The crystallization experiments with simulated solutions were repeated three times. A typical acid volume-pH curve is shown in Figure 1.



a)



b)

Picture 1. The thermostated crystallizer with stirrer, pH-meter and acid dose system
a) at the starting time, b) at the end of crystallization (source: PÁTZAY Gy.)

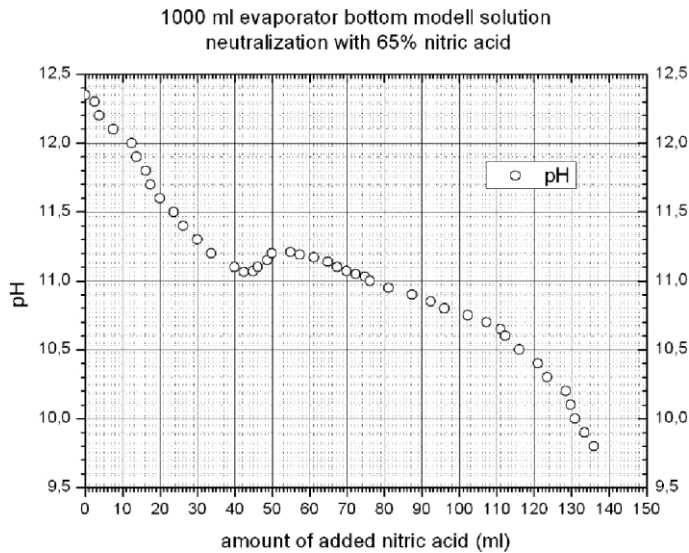
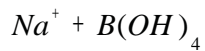


Figure 1. Neutralization of the evaporator bottom model solution
(source: PÁTZAY Gy.)

At pH=11.3 the colour of the solution changed to yellow, at pH=11.07 the crystallization started and white crystals accumulated at the lower part of the reactor. The pH and the temperature of the solution increased slightly after a 40 cm³ nitric acid dose, because during the dilution sodium borate dissociated and sodium hydroxide generated [2] according to the following equation:



Finishing the acid dose we stirred the solution and the crystals for an additional 30 minutes. Then we filtered the crystals and dried them at 96°C for 12 hours. According to the material balance we introduced into the reactor 366.1 g dissolved salt and 848.89 g water, then added 121.84 g nitric acid and 65.60 g water (altogether 1402.43 g materials) and separated

206 g dry crystals and 1042.5 g liquid (altogether 1402.3 g materials).

Based on the nonradioactive experiments with simulated solutions, the second step was we investigated the selective separation of cesium radioactive isotopes from the evaporator bottom samples pre-treated in the NPP by underwater plasma torch.

6 L of evaporator bottom solution was treated by 1.5 cm³ cesium selective ion exchanger with 10 bed volume/hour (BV/hour) fluid flow and the effluent solution was controlled by an ORTEC GMX25P4-76C Gamma-X HPGe coaxial detector with a 25% relative efficiency and an ORTEC DSPEC-jr-2.0 pro and DigiDart MCA (multichannel analyzer). The gamma-spectra were evaluated by a Gamma Vision – 32 software. The measured ¹³⁷Cs breakthrough curve is shown in Figure 2 as the breakthrough in percent and as the function of ion exchanged solution in bed volumes unit. The cesium breakthrough (0.1%) is reached after 3800 BV.

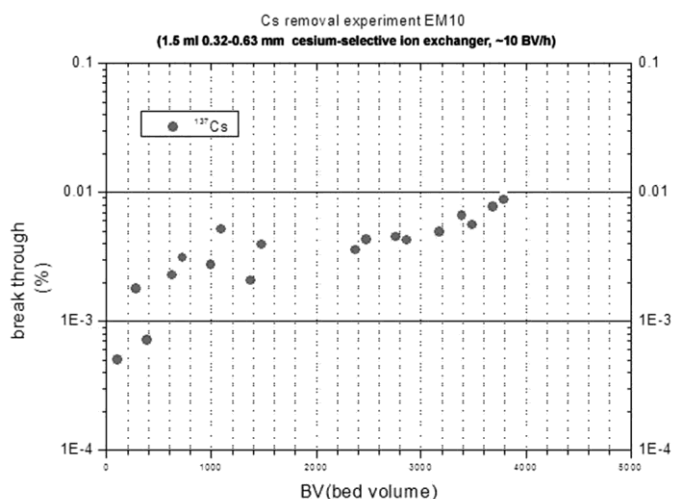


Figure 2. The ion exchange breakthrough curve for the pre-treated evaporator bottom (source: PÁTZAY Gy.)

1 L of ion exchanged solution was then stirred at 300 rpm and thermostated at 27°C. We used this operating temperature, because at the NPP the conditions are similar. After reaching steady state condition we started the dose of 65 m/m% nitric acid with an average flow rate 1.0 cm³/min and measured continuously the temperature and the pH values in the liquid phase. The acidification was stopped when a pH value of 9.7 was reached. The crystallization experiments with radioactive evaporator bottom solutions were repeated three times. The measured acid volume–pH curves were similar to Figure 2.

Finishing the acid dose we stirred the solution and the crystals for an additional 30 minutes, then we filtered the crystals and dried them at 96°C for 12 hours. In this experiment we separated as on an average 206 g dry crystals and 1042.5 g of liquid. The radioactivity of the liquid and the dry crystals was at the background level.

We repeated the crystallization with the original technology too, i.e. without preliminary cesium selective separation, but the resulting borate precipitate contained about 6–11% of the original radioactivity (in the case of ¹³⁷Cs ~8700–10240 Bq/kg) and the precipitation had a yellowish–brown colour, caused by colloid iron precipitation. Washing the radioactive crystals with ~50% by volume water, the crystals were suitable for unrestricted release.

We also investigated the mass balance of separated crystals at different drying temperatures [3]. Starting with 288 g of wet mass, drying at 35°C for 48 hours we got 194 g dry crystals and part of the crystals were further dried at 65°C, 80°C and 105°C for 48 hours resulting in 126.93 g, 123.319 g and 120.19 g dry crystals respectively. Plotting the mass decrease as a function of temperature together with an exponential curve fit the results and are shown in Figure 3.

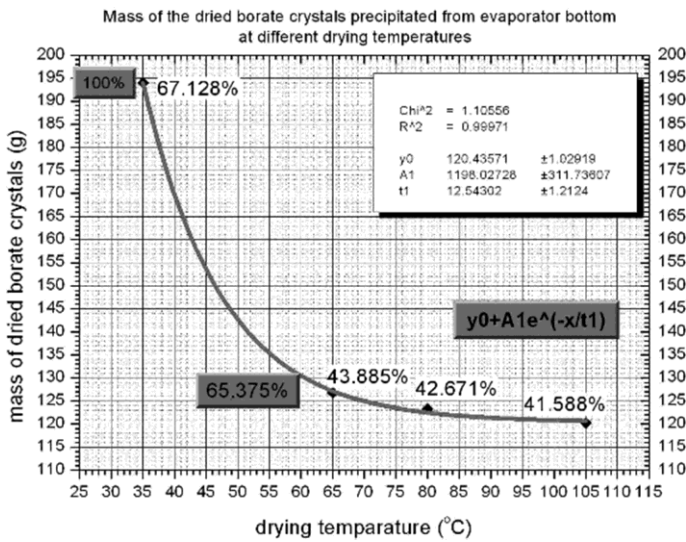


Figure 3. Mass of dried sodium borate crystals as a function of temperature (source: PÁTZAY Gy.)

According to our drying experiments we found that drying at 35°C results in a mass with 67.13% of the original wet precipitation, drying at 65°C the remaining mass is 43.89%. According to the solubility of sodium metaborate ($\text{NaBO}_2 \cdot 8\text{H}_2\text{O}$) as a function of temperature (Figure 4.) above ~55°C $\text{NaBO}_2 \cdot 8\text{H}_2\text{O}$ releases four water molecules, which results in $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, whose mass is 65.675% of the octahydrate compound. This mass decrease is in coincidence with the observed value at 65°C. Drying the sodium metaborate crystals below 55°C does not release bounded water [4].

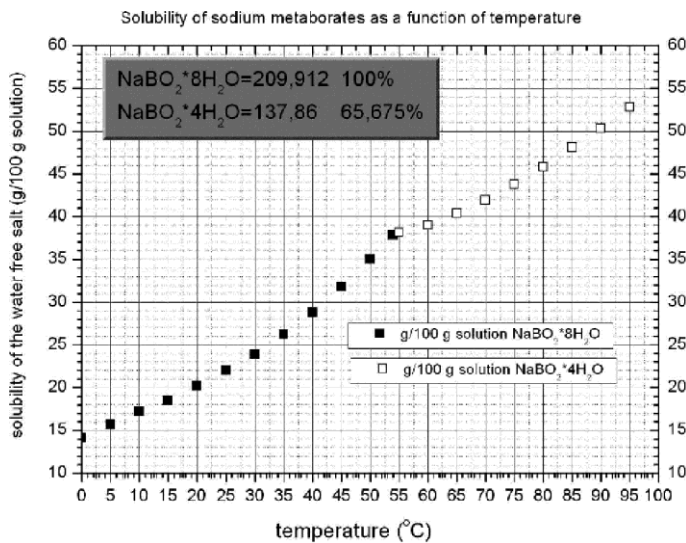


Figure 4. Solubility of sodium metaborates as a function of temperature (source: PÁTZAY Gy.)

Experiments in the NPP Paks

In the third step we repeated the investigation of the NPP using 20 L batches of evaporator bottom samples pretreated by UPTR. First the solution was microfiltered by 100 mm and 1 mm filters then ultrafiltered by a 20 kDa molecular weight cutoff (MWC) membrane filter with a 50–50 L/h permeate flow rate. According to our gamma spectrometry measurements we found that microfiltration removes only 10–20% of the remaining cobalt content. The results of the ultrafiltration experiment are shown at Table 1.

Table 1. Ultrafiltration of the evaporator bottom pretreated by UPTR and microfiltration (source: PÁTZAY Gy.)

Fluid flow	⁶⁰ Co activity concentration (Bq/kg)	%	¹³⁴ Cs activity concentration (Bq/kg)	%	¹³⁷ Cs activity concentration (Bq/kg)	%
Feed	294*	100	1330	100	180000	100
Permeate	260	88.4	1300	97.7	176000	97.7

Following the ultrafiltration, 60 L ultrafiltered evaporator bottom solution was treated by 60 cm³ cesium selective ion exchanger, stable at pH>12, with 10 BV/hour fluid flow. The effluent solution was controlled by the same ORTEC GMX25P4–76C Gamma–X HPGe coaxial detector, jr–2.0 pro and DigiDart MCA and the gamma–spectra were evaluated by a Gamma Vision – 32 software too. After passing 1000 bed volume solution we could not reach breakthrough.

Following the cesium separation, 60 L of ion exchanged solution was then stirred at 300 rpm and thermostated at 30°C. After reaching a steady state condition we started the dose of 65 m/m% nitric acid with an average flow rate 21 cm³/min and measured continuously the temperature and the pH values in the liquid phase. The acidification was stopped at a pH value 9.0–9.7 adding 1800–2200 cm³ concentrated nitric acid to the stirred solution. The measured acid volume–pH curves were similar to Figure 2.

Finishing the acid dose we stirred the solution and the crystals for 30 additional minutes, then we filtered the crystals and dried at 96°C for 12 hours. In this experiment we separated on an average 3800 g dry crystals. The radioactivity of the liquid and the dry crystals was at the background level.

We repeated the crystallization in the NPP according to the original technology, with- out preliminary caesium selective separation, but the resulting borate precipitate contained about 6–11% of the original radioactivity (in the case of ¹³⁷Cs ~8700–10240 Bq/kg) and the precipitation had yellowish–brown colour, caused by colloid iron precipitation. Washing the radioactive crystals with ~50% volume by water, the crystals were suitable for unrestricted release. In Table 2. we compare the analytical compositions of the liquid after crystallization.

Table 2. Analytical composition of the mother lyes from the original and the modified technology (source: PÁTZAY Gy.)

Parameter	Unit	Liquid modified technology	Liquid original technology	Remark
Boric acid	g/dm ³	19.5	21.2	Nearly the same
Chloride	mg/dm ³	67.8	164.2	Original higher
Nitrate	g/dm ³	86.5	85.9	Nearly the same
pH		9.6	9.9	Nearly the same
ICP ² -analysis				
Ag	mg/dm ³	<0.01	<0.01	Nearly the same
Ba	mg/dm ³	<0.01	<0.01	Nearly the same
Cd	mg/dm ³	<0.01	<0.01	Nearly the same
Co	mg/dm ³	3	6.4	Original higher
Cr	mg/dm ³	32.8	33.7	Nearly the same
Cu	mg/dm ³	0.5	0.5	Nearly the same
Fe	mg/dm ³	27.3	0.58	Modified higher
Mn	mg/dm ³	<0.01	<0.01	Nearly the same
Na	g/dm ³	27	30	Nearly the same
Ni	mg/dm ³	5.53	5.68	Nearly the same
Pb	mg/dm ³	1.05	2.08	Original higher
Zn	mg/dm ³	0.23	0.11	Modified higher
As	mg/dm ³	0.10	0.10	Nearly the same
Mo	mg/dm ³	2.23	2.39	Nearly the same
Sn	mg/dm ³	0.35	0.08	Modified higher
Hg	mg/dm ³	0.1	0.08	Nearly the same

It can be seen that the iron content remains in the liquid in the modified technology while precipitates together with the borates in the original technology caused a yellowish–brown colour of the precipitated crystals. The measured average activity concentrations in the liquid and the separated dry crystals are summarized in Table 3.

Table 3. Measured average activity concentrations in the mother lyes and in the separated dry crystals in the original and in the modified technology (source: PÁTZAY Gy.)

Experiment	Activity concentration in the liquid (Bq/g)	Activity concentration in the dry crystals (Bq/g)
1 L original technology	170 000	102 000
1 L modified technology	0.250	~0
20 L original technology	175 000	105 000
20 L modified technology	0.290	~0

2 ICP– inductively coupled plasma

More detailed radioactivity analysis results are seen at Table 4.

Table 4. The measured activity concentrations in the dry separated crystals in the modified technology (source: PÁTZAY Gy.)

Radionuclide	Measured specific activity (Bq/g)	Unrestricted re-lease 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

Summary

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

1. The use of the new cesium selective ion exchanger stable at $\text{pH} > 12$ eliminates the acidification of the evaporator bottom before the cesium removal by ion exchange.
2. We can thus avoid the formation of borate crystals contaminated with radionuclides of cesium etc. and the additional washing of the separated crystals for the radioactivity removal.
3. According to measured specific activity data we could release the dried solid crystals from the NPP and could be used as non-radioactive borate chemical. For a practical aspect we compared the activity-concentrations of borax with the valid unrestricted release levels of general solid radioactive waste.

References

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