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NEW TECHNOLOGY SCHEME FOR HANDLING AND BURIAL FOR THE RADIOACTIVE EVAPORATOR BOTTOM OF THE PWR PAKS

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Abstract

At the Department of Chemical Technology we developed a complex technology for handling the radioactive evaporator bottom in Paks before burial. The basic concept of the technology is the primary selective separation of the long-lived radioisotopes and then the partial recovery of the boric acid content of the inactive solution. The selective separation is accomplished by using iom exchange and adsorption materials and reagents and the partial recovery of the boric acid content of the inactive solution. The selective separation is accomplished by using ion exchange and adsorption materials and reagents and the partial recovery of the boric acid is carried out by neutralisation with carbon dioxide combined with a purification step involving ammonium-ion exchange. The overall volume reduction factor is about 96.

Keywords: radioactive evaporator bottom, selective separation of cesium, cobalt and silver, volume reduction, recycling of the boric acid, neutralisation with carbon dioxide, ion exchange, thermal decomposition.

1. Introduction

It is well known that in the Hungarian pressurized water reactor (PWR) Paks the radioactive waters are collected in a common tank. These water streams contain radioactive isotopes in ultra-low concentrations and inactive compounds as major components (borate (as boric acid) 1.7 g/dm^3, sodium nitrate 0.4 g/dm^3, sodium hydroxide 0.16 g/dm^3, and oxalate (as sodium oxalate) 0.25 g/dm^3). Until now the low salinity solutions were evaporated to yield 400 g/dm^3 salt content after addition of sodium hydroxide. There is about 2000 m^3 concentrated evaporator bottom in the tanks of the PWR. This evaporator bottom may be solidified and buried directly but the effectiveness might be quite low for the volume reduction and the buried directly but the effectiveness might be quite low for the volume reduction and the buried solid phase consists of a lot of inactive inorganic material (macro components) and micro quantities of radioactive compounds (micro components). So it was necessary to develop a separation technology for the micro components and a technology for the partial recycling of the macro components.

We have developed a new technology for handling this evaporator bottom before burial. The handling technology consists of the selective separation of the long-lived radionuclides (^{137}Cs, ^{134}Cs, ^{90}Sr, ^{89}Sr, ^{60}Co, ^{58}Co, ^{110m}Ag) using sorption and filtration processes, and of the separation, purification and recycling of boric acid by neutralisation with carbon dioxide, ion exchange using a cation-exchange column in the NH_4^+-form, the thermal decomposition of ammonium borates and evaporation of the remaining salt solution to produce a dry salt.

2. Basic Parts of the Waste Water Handling Technology Scheme

2.1 Selective Separation of the Long-lived Radioactive Isotopes

The long-lived radionuclides are present in very low concentration (10^{-9} – 10^{-12} mol/dm^3) as ions, suspended and colloidal particles and in complex form.

The basic idea of the new technological scheme is the selective separation of these radionuclides with cheap sorbent materials or reagents in very simple processes without neutralisation or dilution. In the evaporator bottom of the Hungarian PWR in Paks, 75-90% of the radioactivity is due to cesium isotopes, so the separation of these nuclides is the most important step. For the selective separation of radioactive cesium isotopes (^{137}Cs, ^{134}Cs) we developed a potassium nickelhexacyanoferrate(II) cesium-selective ion exchange material in granulated form. During laboratory experiments and pilot-plant scale tests in the PWR we removed the radioactive cesium from about 200 dm^3 evaporator bottom without neutralisation, microfiltration or any additional process.

In the laboratory experiments we used glass ion-exchange columns (ID = 0.5 cm) filled with 2 cm^3 granulated (0.2–1 mm) ion-exchange material. The temperature was kept at 25 °C and the radioactive solution was passed through the column at a flow rate of 10 bed volumes per hour. Breakthrough curves were determined by collecting 100 ml fractions of the effluent and analysing their Cs-activity with a Ge(Li) semiconductor detector and an 8000 channel EMG NU-8110 gamma-spectrum analyser. The measurement time was 2000 sec. The cesium content in the effluent was determined using the ASPRO-NUC gamma-spectrum acquisition software. The actual and the average decontamination factors, the breakthrough values and the volume reduction factors were determined in each measurement . In the spectrum of the influent six significant gamma peaks were determined, namely those of the radionuclides Cs-143, Cs-137, Co-60, K-40. In the separation experiments three different samples were used from the radioactive evaporator bottom of the PWR, namely the samples from the tanks 01TW30B001, 02TW30B002 and 01TW30B003. The measured chemical compositions and radioisotope contents of these influents are shown in *Table 1.*

Table 1

Chemical compositions and radioisotope contents of various evaporator bottom samples

Concentration or Specific activity	Tank 01TW30B001 (550 m^3)	Tank 02TW30B002 (280 m^3)	Tank 01TW30B003 (470 m^3)
pH (-)	14	14	14
H_3BO_3 (g/kg)	248.0	248.0	263.6
Na^+ (g/kg)	71.2	78.0	91.3
K^+ (g/kg)	22.2	20.8	9.6
NO_3^- (g/kg)	38.0	65.3	28.7
oxidizable content (mg $KMnO_4$/kg)	3.34	2.10	1.61
Fe_{total} (mg/kg)	7.50	0.68	9.69
Ca^{2+} (mg/kg)	62.7	58.2	103.5
evaporated residue (g/kg)	437	430	461
total beta activity (kBq/kg)	11	18	92
^{134}Cs (MBq/kg)	5.81	10.36	163.10
^{137}Cs (MBq/kg)	30.9	34.6	230.7
^{110m}Ag (MBq/kg)	6.60	0.73	25.30
^{60}Co (MBq/kg)	0.56	7.80	29.63
^{58}Co (MBq/kg)	–	–	1.63
^{122}Sb (MBq/kg)	–	8.3	19.3

The breakthrough curve for the laboratory experiments with the 01TW30B002 sample is shown in *Fig. 1.* Using 2 cm^3 ion-exchange material the cesium radionuclides could be removed from 2950 cm^3 evaporator bottom with a decontamination factor greater than 1000, so the volume reduction factor was 1475.

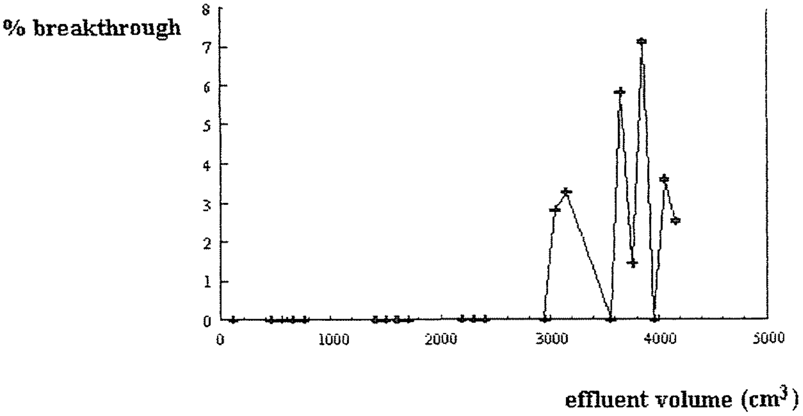

Fig. 1. Breakthrough curve of cesium for the laboratory experiments
2 cm^3 K-Ni-hexacyanoferrate(II), 01TW30B002 sample

The laboratory experiments were controlled in the PWR with a pilot plant scale column. In this separation experiment 75 cm^3 K-Ni-hexacyanoferrate(II) granulated (0.2–1 mm) ion exchanger was used in a glass column (ID = 3.3 cm) at a flow rate of 9 bed volumes per hour. The experiments were carried out at room temperature. Breakthrough curves were determined by collecting 100 ml fractions of the effluent and analysing their Cs-activity with a Ge(Li) semiconductor detector and an 8000 channel EMG NU-8110 gamma-spectrum analyser. The measurement time was 2000 sec. The cesium content in the effluent was determined using the ASPRO-NUC gamma-spectrum acquisition software. The actual and the average decontamination factors, the breakthrough values and the volume reduction factors were determined in each measurement. The average decontamination factor was computed using the following formula:

$$DF_{i,\text{average}} \equiv \frac{C_0}{C_{i,\text{average}}} \equiv \frac{C_0}{\sum_i C_i V_i / \sum_i V_i},$$

where

C_0 is the influent concentration

$C_{i,\text{average}}$ is the average concentration till the i-th sample

C_i is the concentration of the i-th sample

V_i is the effluent volume at the i-th sample.

The breakthrough curve and the average decontamination factor curve for the pilot plant experiments are shown in *Figs. 2–3.*

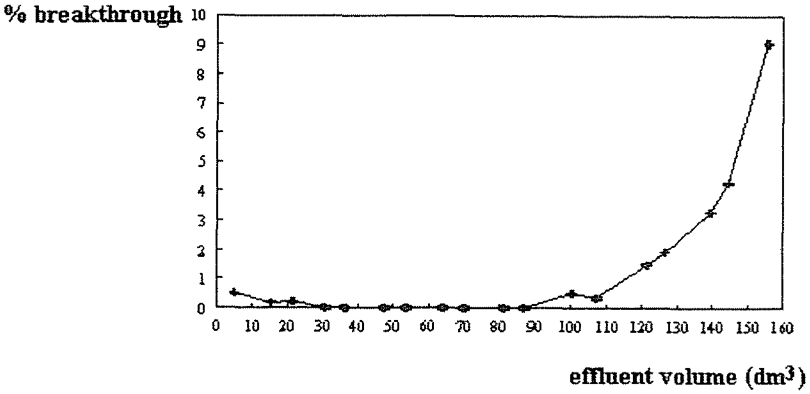

Fig. 2. Breakthrough curve of cesium for the pilot plant experiments
75 cm^3 K-Ni-hexacyanoferrate(II), 01TW30B002 sample

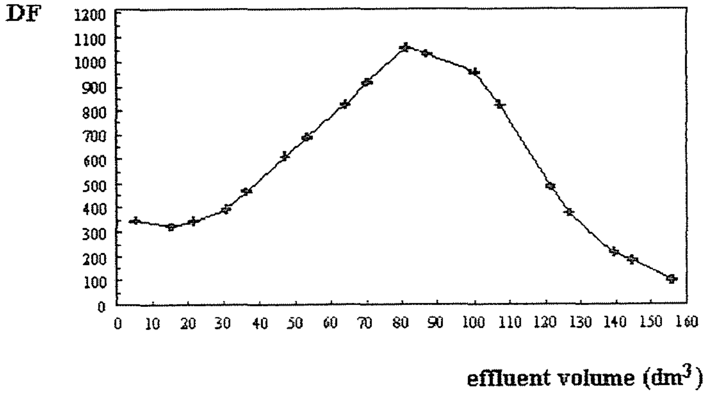

Fig. 3. Average decontamin factor
75 cm^3 K-Ni-hexacyanoferrate(II), 01TW30B002 sample

Using 75 cm^3 ion-exchange material the cesium radionuclides could be removed from 100.4 dm^3 evaporator bottom with an average decontamination factor greater than 958, so the volume reduction factor was 1339.

In the developed cesium separation technology, at a value of the decontamination factor of 1000 the volume reduction factor was about 1400 for the samples of the three above-mentioned tanks of PWR Paks, while for the tank 01TW30B003 it was lower (between 200–500) because of the oxidising effect of this waste. During the separation experiments no dissolution or destruction of the ion exchange material was detected at very alkaline pH (pH = 14) during the 2–3 week service of the columns.

In the technology scheme selective separation of the silver and cobalt radionuclides (^{60}Co, ^{58}Co, ^{110m}Ag) can be achieved by combination of filtration and complex destruction with sulphide reagents. Using precoat filtration or microfiltration one can remove all the radioactive silver and most of the cobalt (50–85%), but part of the cobalt content is in complex form (cobalt(III)oxalate or EDTA complex) which can be removed only after destruction of these very stable compounds. In our technology scheme a short heating was combined with addition of sulphide reagent, and the resulting small particle size cobalt sulphide and the silver were removed by microfiltration or precoat filtration with activated carbon. At a decontamination factor of 1000 the volume reduction was about 120.

In a laboratory scale experiment selective separation of the abovementioned radionuclides was achieved from 500 cm^3 evaporator bottom samples from the tank 02TW30B002. The cesium, cobalt and silver isotopes were fixed on 5.1 cm^3 of sorbent (ion exchanger and activated carbon) which means that the general volume reduction factor is 96. The gamma-spectrum of the final solution contained only the ^{40}K peak (i.e. the background). Using these technology steps one can achieve selective separation of the cesium, cobalt and silver isotopes from the evaporator bottom without neutralisation or dilution. The measured gamma-spectrum after all the separation steps is shown in *Fig. 4*.

In the developed technology selective separation of the ^{90}Sr radioisotopes may be completed using an Al_2O_3-based gypsum coprecipitation and sorbent material. This radionucleide is absent from most of the evaporator bottom samples.

2.2 Separation and Recycling of Boric Acid from the 'Inactive' Solution after Isotope Separation

The final solution obtained after isotope separation is very alkaline (pH = 14) and highly concentrated (about 400 g/dm^3 salt content). In our scheme boric acid separation is carried out by neutralisation of the solution in a gas-fluid reactor using carbon dioxide gas as neutralising agent. During the neutralisation till pH = 11 most of the borate content and sodium carbonate precipitated from the solution and it was less dangerous for the environment than the nitrate compounds after the usual nitric acid neutralisation. The precipitated crystals were dissolved in water and the sodium ions were exchanged in a cation-exchange column in the ammonium form. The resulting ammonium borates and ammonium carbonate were destroyed by

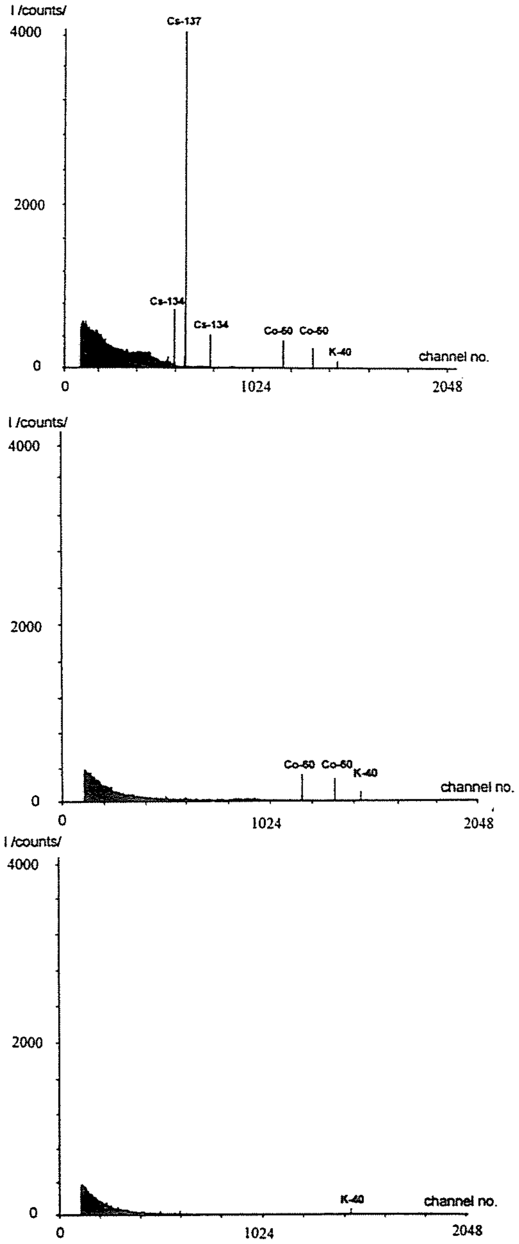

Fig. 4. Gamma-spectra of the nuclide separation steps
(time of measurement: 2000 sec)
a) Gamma-spectrum of the influent
b) Gamma-spectrum after cesium removal
c) Gamma-spectrum after complete nuclide separation

thermal decomposition yielding high-purity boric acid as final product. The yield was about 70%. The solution obtained after neutralisation contained a considerable amount of inactive salts like sodium carbonate, sodium nitrate, sodium borates, and was evaporated to dryness and the resulting dry salts were packed in metal drums (TÓTH and PÁTZAY, 1993).

3. Summary and Conclusion

At the Department of Chemical Technology a complex technology was developed for handling the radioactive evaporator bottom in Paks nuclear power station before burial. The basic concept of the technology is selective separation of the long-lived radioisotopes followed by partial recovery of boric acid from the inactive solution. The selective separation was accomplished by using ion exchange and adsorption materials and reagents, and the partial recovery of boric acid was achieved by carbon dioxide neutralisation combined with an ammonium-ion exchange purification step. The overall volume reduction factor was about 96.

References

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