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DEVELOPMENT FOR SELECTIVE CESIUM REMOVAL FROM THE EVAPORATION CONCENTRATES OF THE PWR PAKS

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At the Pressurized Water Reactor Paks the diluted radioactive wastewater is converted to concentrate by evaporation and the evaporator bottom is stored in tanks. The most important radionuclides in these solutions are ^{134}Cs, ^{137}Cs and ^{60}Co. The volume reduction technologies like selective ion exchange for cesium and the ultrafiltration for cobalt may reduce the volume of the liquid waste and the burial costs. In our research we studied our granular potassium nickel hexacyanoferrate(II) as a Cs-selective ion-exchanger. Its capacity was depending on the preparation method, temperature of pretreatment and age of the ion exchanger. We investigated also the effect of metal ions (Fe^{2+}, Fe^{3+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) on the Cs-capacity in the presence of complex forming compounds citrate, oxalate and EDTA. The cesium ion exchange capacity was increased in case of addition of inactive cobalt or nickel salts.

Additionally, we studied filtration, adsorption and ultrafiltration separation processes for cobalt removal. The results showed that only adsorption by active carbon could successfully be used for the cobalt removal from the evaporation concentrates. Experiments were also performed in our laboratory and at the PWR Paks.

Keywords: cesium and cobalt removal, ultrafiltration, potassium nickel hexacyanoferrate(II), selective ion exchange, adsorption, complex compounds

Introduction

Approximately 40000 m^3 diluted liquid radioactive wastewater is generated yearly in the Hungarian Pressurized Water Reactor (PWR) at Paks. At this time there is no selective waste collection. The collected liquid waste is the mixture of low or medium activity and/or salt content wastewater and often decontamination solution. The collected solutions are regularly concentrated by evaporation using NaOH for stabilization of the sodium borates in the evaporation bottom and are stored in common stainless steel tanks. The major component of the concentrate is sodium borate, and the solution is alkaline (pH=14). The final disposal of this waste is not solved. Sodium borates are incompatible with the embedding matrix material (concrete). In addition the direct cementation of the radioactive waste results a final volume two-three times larger then the volume of the evaporator bottom. Consequently it causes increasing burial cost.

The major ingredients of the evaporation concentrates are sodium borate, sodium nitrate and sodium hydroxide. They contain long-lived radioactive isotopes (^{134}Cs, ^{137}Cs and ^{60}Co) in ultra-low concentrations. Because 75-90% of the radioactivity is due to cesium isotopes its selective separation before solidification is the most important step. The selective removal and accumulation of these long-lived radionuclides in a small volume ion exchanger reduces the volume of the buried radioactive waste and the cost of the final disposal. [1]

It is well known that the heavy metal hexacyanoferrates (nickel-KNiFC, copper and cobalt-KCoFC) are selective cesium ion exchangers. The review of their properties and preparations can be found in [2]. Some methods are known to stabilize and improve their capacity e.g. KNiFC loaded zeolite [3], SiO_2-·KCoFC composite [4] etc.

The aim of the present work is the investigation of the possible improvement of the selective cesium removal using granulated potassium nickel hexacyanoferrate(II) ion exchangers and development of a suitable granular ion exchanger.

In this process we investigated various preparation methods, the effect of other factors, such as temperature, age of the exchanger, and other chemical components present in the solution.

The other important long-lived radionuclide in the evaporation concentrate is ^{60}Co. It is present as

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Table 1 Average chemical composition and radioisotope content of the evaporation concentrates of PWR Paks

	Concentration or specific activity	
pH	-	14
Na^+	g/dm^3	80
K^+	g/dm^3	24
NO_3^-	g/dm^3	45
H_3BO_3	g/dm^3	250
evaporated residue	g/dm^3	534
^{134}Cs	MBq/dm^3	7.2
^{137}Cs	MBq/dm^3	38.4
^{60}Co	MBq/dm^3	0.7

suspended matter, colloidal particles and in complex form. The dissolved cobalt can be removed by adsorption using for example charcoal [5] or montmorillonit [6]. In our research we investigated the removal of the suspended particulates of cobalt from the evaporation concentrate via filtration and ultrafiltration and the other forms via adsorption.

Laboratory Experiments

A mixture of the original evaporation concentrates of the PWR Paks was used in the laboratory experiments (*Table 1*). Three types of processes were examined, filtration (5 and 1 μm pore size filter), adsorption with active carbon and ultrafiltration (molecular weigh cut off 15000 Dalton) for its removal.

Development and testing of a Cs-selective ion-exchanger

Preparation of the ion-exchanger

Six different techniques were investigated for the preparation of a granular sorbent: freeze-thawing, boiling-gel and dehydration method using normal and reverse order of portioning of reagents (potassium hexacyanoferrate(II) and nickel sulfate solution). The capacity of the produced sorbents was tested by static method.

Ion exchange measurement technique in static method

100 mg of the granular ion-exchanger was added to 200 cm^3 of thermostated evaporation concentrate and stirred for an hour, then filtered with micropore filter paper. A NaI (Tl) detector and an 8000 channel EMG-8110 gamma-spectrum analyzer before and after the handling measured the Cs-content of a 100 cm^3 sample. The measurement time was 2000 seconds. The results are summarized in *Fig.1*. We found that the best Cs sorbent is the "ND" granular product.

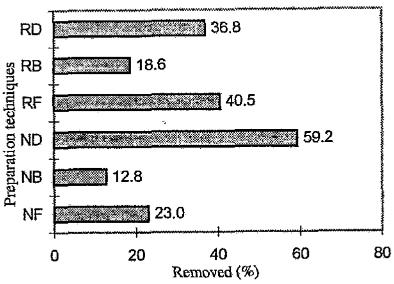

Fig.1 Effect of preparation techniques for Cs-137 removal (R: reverse order of portioning of reagents, N: normal order of portioning of reagents; D: dehydration method, B: boiling-gel method, F: freeze-thaw method)

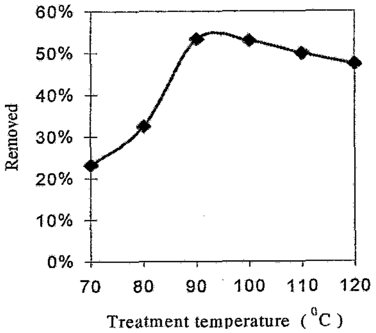

Fig.2 Cs-137 removal capacity for treatment temperature

The effects of other factors

Temperature

Because the best Cs-sorbent was prepared by drying (dehydration) we tried to optimize the treatment temperature of ND granular product. *Fig.2* shows the Cs removal capacity as a function of the dehydration temperature. The optimum is found between 80 and 100 °C.

Storage time (age of the exchanger)

The long-term stability of the product was depending on the temperature of dehydration. The sorbent that was handled at 90 °C was more stable than that at 80 °C. (see *Fig.3*)

Complexing agents

The evaporation concentrates contain complex forming compounds (oxalic acid, citric acid and EDTA) which decrease the sorbent ion exchange capacity. To minimize this effect by fixing these free complexing agents, in our next ion exchange experiments we applied as inactive reagents eight different metal salt (0.01 M salt concentration in every experiment). Two of them caused a significant increase in the cesium ion exchange capacity; namely the nickel sulfate and the cobalt nitrate (*Fig.4*).

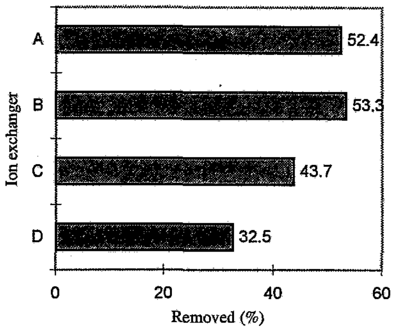

Fig.3 Effect of storage time on Cs-137 removal (A: handling at 90 °C two weeks later; B: handling at 90 °C; C: handling at 80 °C two weeks later; D: handling at 80 °C)

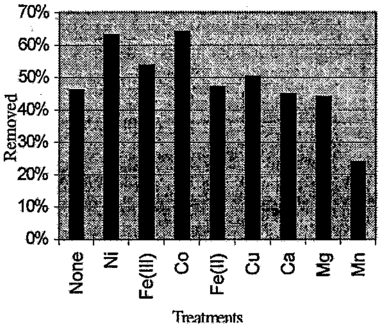

Fig.4 Effect of metal ions on the Cs-137 capacity

Based on the static experiment results we concluded that the Cs-removal capacity depended on the preparation method of the sorbent, the temperature of pretreatment, the storage time and the amount of complexing agents (EDTA, citric acid etc.) and the free complexing agents could be "deactivated" by reacting with added nickel and cobalt compounds.

Column tests (dynamic tests)

In the column experiments we used a glass ion-exchange column (ID = 5 mm) filled with 2 cm^3 granulated (0.125-0.2 mm) potassium nickel hexacyanoferrate(II) prepared by dehydration method (ND). The initial flow rate was 50 cm^3 (25 BV) per hour. The effluent concentrate was collected in 100 cm^3 plastic flasks. The measurement technique was similar to the static test. 100 cm^3 of solution was measured during 2000 seconds by NaI(Tl) detector and an 8000 channel EMG-8110 gamma-spectrum analyzer.

In our dynamic experiments we compared the efficiency of the cesium removal from the concentrate and from the pretreated (with cobalt-nitrate) concentrate. We found that the pretreatment increased the Cs-capacity of the exchanger. The breakthrough curves are shown in *Fig.5*.

Fig.5 shows that the Cs$^+$ breakthrough is smaller in case of the pretreated concentrate. This result means that the dosed cobalt compound reacted with the aggressive complex compounds and the decomposition of the exchanger was smaller.

Table 2 Summary of filtration processes

Isotope	Microfiltration (5 μm pore size) removed	Microfiltration (1 μm pore size) removed	Activated carbon filter (with $Co(NO_3)_2$) removed	Ultrafiltration (1 μm prefiltered solution) removed
^{134}Cs	0.18%	6.3%	30.2%	1.9%
^{137}Cs	0.21%	7.2%	30.4%	2.4%
^{60}Co	0%	6.2%	78.4%	5.0%

% Removed = 100·[1-(solution activity after the treatment/ solution activity before the treatment)]

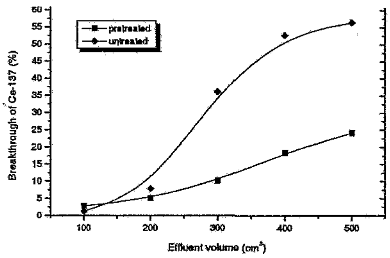

Fig.5 Cesium ion exchange breakthrough curves of un- and pretreated concentrates

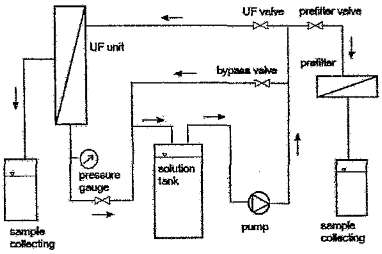

Fig.6 Filtration and ultrafiltration setup

Filtration, adsorption and ultrafiltration experiments

The effective removal of the various forms of the long-lived radionuclides from evaporation concentrate was also investigated using filtration, ultrafiltration and adsorption processes.

In the filtration and ultrafitration experiments we used a WATTENTECHNIK microfiltration module and a MICRO CARBOSEP 40 M5 ultrafiltration membrane (the operating pressure was 2 bar). The experimental setup is shown in *Fig.6*. According to our previous experiments the cesium and cobalt radionuclides may be present in the concentrate as ions, suspended and colloidal particles and in complex forms. The results of our filtration and ultrafiltration experiments showed that a small part of the cobalt content could be removed by filtration (6%) and the ultrafiltration had also low efficiency (5%). Although the adsorption of cobalt by an active carbon filter seemed effective means of separation, unfortunately the capacity of the carbon filter is very low. Our filtration experiments showed that the long-lived radionuclides definitely occur in non-filterable (ionic or complex) form (*Table 2*).

Table 3 Summary of filtration processes from the mother lye

Isotope	Microfiltration (1 µm) removed	Ultrafiltration (1 µm prefiltered solution) removed
^{134}Cs	0.3%	1.6%
^{137}Cs	0%	3.5%
^{60}Co	0%	0%

On-site experiments at the PWR Paks

The results of the dynamic experiments obtained in our laboratories were controlled and tested at Paks NPP on site. In the experiment we used a freshly "produced" and an "older" evaporation concentrate solutions. One was the mother lye (partially neutralized evaporator concentrate) of an old stored concentrate (pH=9.5, H_3BO_3 16.1 g/cm^3) the other a freshly evaporated concentrate (pH=14, H_3BO_3 109 g/cm^3). The fresh concentrate contained medium-lived radionuclides such as ^{54}Mn, ^{58}Co, ^{57}Co and the long-lived isotopes (^{134}Cs, ^{137}Cs and ^{60}Co). All the measurements were performed at the isotope laboratory of the PWR using a calibrated HPGe semiconductor detector (1000 seconds measurement time; 100 cm^3 sample in plastic flasks).

Selective ion exchange

In this method we used wider.column (ID=8 mm) filled with 2 cm^3 granulated (0.2-0.3 mm) potassium nickel hexacyanoferrate(II) prepared by our preparation technique. The flow rate was 100 cm^3 (50 BV) per hour. The ion-exchange separation efficiency from the "fresh" concentrate was very low, because manganese dioxide precipitated continuously from the concentrate onto the surface of the exchanger. In the case of the mother lye the efficiency was excellent, the average decontamination factor was 250 and the volume reduction factor more than 1700. We could not determine the breakthrough point because of lack of the limited experimental time. The breakthrough curve is shown in the *Fig.7*.

Filtration and ultrafiltration

The same laboratory filtration and UF equipment were used in these experiments. Only 20% of the cobalt could be removed from the fresh concentrate by a 1 µm pore size filter and consecutive ultrafiltration. In the case of the mother lye the filtration processes were unsuccessful (*Table 3* and *4*).

Conclusion

According to the laboratory and on-site experiments we conclude that the cobalt content of the evaporation concentrates at the PWR Paks is mostly not in suspended and colloidal forms but is rather present in complexes. The only applied technique that could reduce the quantity of complex form radiocobalt is adsorption on activated carbon. We prepared a granular Cs-selective ion exchanger, determined its optimum parameter of preparation, drying and storage. We successfully tested its selective cesium separation efficiency in laboratory and on-site at the PWR Paks.

Table 4 Summary of filtration processes from the fresh concentrate

Isotope	Microfiltration(1 µm pore size filter) removed	Ultrafiltration (1 µm prefiltered solution) removed
^{54}Mn	1.1%	9.0%
^{57}Co	8.7%	3.7%
^{58}Co	4.4%	15.4%
^{134}Cs	6.5%	11.7%
^{137}Cs	1.3%	10.6%
^{60}Co	0.2%	15.8%

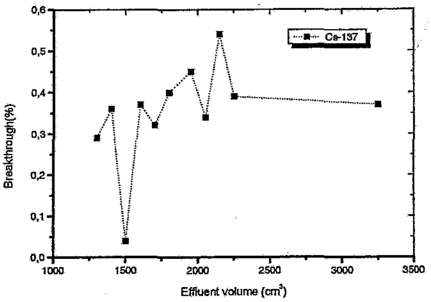

Fig.7 Cesium ion exchange breakthrough curve of the mother lye

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