

THE POSSIBILITIES OF USE OF ZEOLITE AND HYDROXIDE CARRIER IN LIQUID RADIOACTIVE WASTE TREATMENT

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ABSTRACT

The processes for treatment of liquid radioactive waste (ion exchange by resins, evaporation), presently used in nuclear power plants exhibit some disadvantages, like low exchange efficiency, production of large volume of solidified waste and poor physical integrity of the solidified waste. On the other hand, zeolite as ionic exchanger were believed to have some advantage in the radioactive waste treatment: high exchange capacity, high selectivity of particular zeolite to particular radioisotopes, good solidification with cement, good physical integrity of solidified waste products (zeolite/cement) etc. Therefore, the possibility of using zeolite and hydroxide carriers (scavengers) in the technology of liquid radioactive waste treatment has been investigated on the laboratory scale. For this purpose, real samples of primary coolant, liquid radioactive waste from waste hold-up tank, and evaporator bottoms were treated in batch and/or continuously with zeolite and/or in different combinations with sorption on metallic hydroxides. Analysis of the experimental results has shown that using a combined method (continuous treatment with granulated zeolite and subsequent sorption of radioisotopes on freshly prepared iron (III) hydroxide) more than 99,9% of cesium radioisotopes, more than 99,8% of Mn-54 and about 90% of cobalt radioisotopes can be removed from the liquid radioactive waste. Solidification experiments have shown good quality of the concrete blocks and possibility of the volume reduction in comparison to ion exchange resins.

INTRODUCTION

The specific radioactivity of the liquid waste generated in nuclear power plants is usually higher than the values which can be discharged to the human environment (1) and volumes are such that the waste liquids cannot be stored for longer period. Therefore, the waste must be treated in order to immobilize radionuclides into a solid matrix and to minimize the volume to be stored and/or disposed in the repository (2). The operational experiences in the first Yugoslav Nuclear Power Plant Krsko (Westinghouse, PWR) have showed that the installed technology of radioactive waste processing is acceptable, but that it exhibits some significant deficiencies from the point of the operational efficiency, volume reduction and the quality of the solidified waste.

The goal of this work was to investigate the possibilities of using ion exchange by zeolite and sorption of radioisotopes on metallic hydroxides as an alternative or support process to evaporation and ion exchange by resins. The objectives were to achieve better availability of the waste treatment systems (longer continuous operation), better quality of solidified waste and eventually, the volume reduction of the solid waste.

EXPERIMENTAL METHODS

Real samples of radioactive liquids from the waste hold-up tank (WHT), the waste evaporator (EB) and from reactor cooling system (RC) of the Nuclear Power Plant Krsko have been treated under air-marked conditions with different types of zeolite; continuously in columns filled with granulated zeolite or the batch with powdered zeolite and, in some cases, in combination with the sorption of radionuclides on freshly precipitated iron (III) hydroxide. For this purpose zeolite 4A (NaA, KGK Karlovac), zeolite 13X (NaX, Union Carbide) and synthetic mordenite (NaSM, J.M.Huber Corp.) have been used. For the study of efficiency of radioisotope sorption on freshly precipitated Fe(OH)₃, precipitate has been prepared by adding determined amount of FeCl₃ into the waste solution in which pH is previously adjusted (pH 8) by adding NaOH solution. The treatment of radioactive liquids with powdered zeolite has been effected by suspending a certain quantity of zeolite in a determined volume of radioactive liquid, with or without addition on non-radioactive carriers, i.e. after adjusting the pH-value of solution. The suspension was stirred for a certain period of time (usually for 1 hour), and then the liquid phase was separated from zeolite by centrifuging. Clear liquid phase obtained after the separation of the solid phase

(powdered zeolite or $\text{Fe}(\text{OH})_3$ precipitate) has been used for the determination of radioactivity $(A_n)_i$, of single radioisotopes in the mixture. The continuous treatment of radioactive liquids was performed by their passage, at determined flow rates, through columns filled with a determined quantity (5-20 g) of granules containing 50-70% of active exchanging substance (zeolite) and 30-50 wt% of binder. The granules were of a cylindrical shape, had an average length of 2 mm and an average diameter of 1 mm. The inflow of the radioactive liquids was at the bottom of the column, and the outflow was at the top of the column. A constant flow rate (1-12 cm^3/min) was ensured by the use of a laboratory metering piston pump or peristaltic pump. All experiments were performed at ambient temperature. After the passage through column, 20 ml aliquots of the treated solutions were collected in separate vials and were used for the measuring of the corresponding specific radioactivities $(A_n)_i$, or whole treated volume has been additionally treated by sorption on freshly prepared $\text{Fe}(\text{OH})_3$. From the measured specific radioactivities $(A_n)_i$ the decontamination factors (DF) of single radioisotopes in a mixture were measured as: $(\text{DF})_i = (A_p)_i / (A_n)_i$, where $(A_p)_i$ is the initial specific radioactivity of radioisotopes in mixture ($i = \text{Cs-134}, \text{Cs-137}, \text{Mn-54}, \text{Co-58}, \text{Co-60}$). For the measuring of specific radioactivities $(A_n)_i$ and $(A_p)_i$ is range of $3.7\text{E}5$ - $3.7\text{E}8$ Bq/m^3 ($1\text{E}-5$ to $1\text{E}-2$ Ci/m^3), gamma spectrometric system with Ge(Li) detector and 8K multi-channel analyzer connected to the DIGITAL PDP 11/04 computer (Canberra made QUANTA SYSTEM) were used. In some cases, the distribution of radioisotopes in the column has been determined in order to examine the influence of type of zeolite on the removal efficiency of single radioisotopes and the influence of the column fillings on the total effect of decontamination. For this purpose, after the treatment, the content of the column (granules) has been divided into a determined number of segments (layers) and the portion of radioactivity of single radioisotopes in each layer was measured by the Ge(Li) detector, using a special counting geometry.

RESULTS AND DISCUSSION

Because of limited space in this paper some results are given without the tabular or graphic support.

The Batch Treatment

Although the decontamination factors (DF), attained by the same treatment, differ considerably for various radioactive liquids (WHT,EB,RC), few general conclusions can be pointed out:

The removal efficiencies of radioisotopes of cesium, cobalt and Mn-54 from the radioactive liquids from Nuclear Power Plant Krsko were relatively low in comparison to the literature data (4-8). The addition of isotopic, non-radioac-

tive carriers did not show any considerable influence on the removal efficiency.

In accordance with the specific selectivity of zeolite (3-6), synthetic mordenite exhibited high affinity for Cs radioisotopes from solutions and zeolite A and X showed better affinity for radioisotopes of Co and Mn-54.

The removal efficiency of radioisotopes from radioactive liquids increases with the "purity" of the liquids, i.e. $\text{DF}(\text{RC}) > \text{DF}(\text{WHT}) > \text{DF}(\text{EB})$. For instance, $\text{DF}(\text{WHT})$ and $\text{DF}(\text{EB})$ for Co-60 and Mn-54 were between 2 and 3 and $\text{DF}(\text{RC}) > 317$ when the liquids were treated with powdered NaA. DF for radioisotopes of cesium were 2-18 when the solutions were treated with powdered zeolite NaA and NaX (lower values correspond to WHT and EB and higher values correspond to RC samples while $\text{DF}(\text{WHT}) = 27$ and $\text{DF}(\text{RC}) = 223$ for radioisotopes of cesium in the case when the liquids were treated with powdered synthetic mordenite.

Lower radioisotope removal efficiency from the liquids containing complexing agents and dispersed colloidal particles of corrosion products (WHR,EB) is caused by: (a) the formation of unexchangeable complexes of cobalt and manganese, (b) the partial sorption of radioisotopes of cobalt and Mn-54 on the colloidal particles of the corrosion products and (c) the blocking of surface of zeolite by the attachment of the corrosion products on zeolite particles.

The original pH values for the exchange processes (pH 3 for the exchange of cesium radioisotopes and pH = 6 for the exchange of Mn-54 and radioisotopes of cobalt) are comparable with the published data (4,5,9).

Continuous Treatment

In contradiction to the published data (4,10-12) it was found that the flow rate of the samples through the columns does not influence the decontamination efficiency in the range, $uv = 1$ -12 cm^3/min . This contradiction can be explained by the higher ratio between the mass of zeolite(s) in the column and the chemical concentration of radioisotopes (traces) in the liquids, so that breakthrough has not been reached even at high flow rates ($uv = 12$ cm^3/min). Decontamination factors $\text{DF} = 6$ -9 for Mn-54, $\text{DF} = 4$ -6 for Co-58/60 and $\text{DF}250$ for Cs-134/137 were reached after 200 cm^3 of EB sample has been passed, with the flow rates $uv = 1$ -12 cm^3/min , through the columns filled with the mixtures of granulated zeolite (6.7 g of zeolite A, 6.7 g of zeolite X and 6.7 g of synthetic mordenite). The results presented in Table I show that the addition of nonradioactive isotopic carriers ($10\text{E}-4$ meq/dm^3) in EB increases the efficiency of decontamination, but the justification of their use should be evaluated in each particular operational use.

The dependence of the decontamination factor on the volume of the treated liquid radioactive waste has been

TABLE I

Average DF-s for Elements in the Radioactive Waste for Eight Successive Samples With or Without Carrier in Continuous Treatment

ELEMENT	Average Df-s		
	without carrier	with carrier	percentage for which are DF-s with carrier higher than for those without carrier
Cs	150	219	46
Co	44,2	4,8	14
Mn	7,6	10,7	41

examined by passing 17260 cm³ of the WHT sample through the column filled with 20 g of granulated zeolite A. The liquid radioactive waste was passed through the column at a constant flow rate of 10 cm³/min, except at the end of treatment (after 16000 cm³ has been treated) when flow rate was reduced at 5 cm³/min. During the passage of WHT sample through the column a strong sedimentation of particles of the corrosion products on the granules was observed, so that after a certain volumes of WHT samples were passed through the column, granules were rinsed with double-distilled water. It is noticeable that the decontamination factors for all radioisotopes increase considerably after the rinsing of the column, i.e. after the removal of the corrosion products sedimented on the granules (see Fig. 1). After passage of the whole sample through the column, zeolite was divided in three layers and radioactivity of the each layer was measured. The results are shown on the Table II.

The "inverse" distribution of radioactivity in the column confirms conclusion of corrosion products sedimentation. In normal conditions (without the presence of corrosion products) the radioactivity of granules should be reduced in the direction of the flow (4,10,13). Since the quantity of corrosion products sedimented on the granules is reduced in the direction of the flow the surface of granules which are near to the top of the column is blocked in a smaller degree and thus, more "open" to the exchange, the consequence of which is the "inverse" distribution of radioactivity. The results presented in the Table III shows that the radioactivities, actually removed from 17600 cm³ of WHT samples are higher than the values measured in granules. The differences are due to retention of some liquids in macropores

TABLE II

Distribution of Radioactivity on the Granules of Zeolite in the Column

Radio - isotope	Radioactivity k Bq/layer (layer 6,7 g)			TOTAL
	Lower layer	Middle layer	Upper layer	
Cs-134	45	59	90	95
Cs-137	67	88	136	290
Co-58	40	42	53	135
Co-60	34	36	52	122
Mn-54	26	20	34	87

direction of the fluid flow →

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of granules (for Cs-134/137) as well as to sorption of Co-58/60 and Mn-54 on the colloidal particles of corrosion products, removed from the granules by rinsing. The results presented in Table III are in accordance with the DF values of radioisotopes of cobalt and Mn-54 reached by the removal of corrosion products from WHT and EB samples by centrifugation (see Table IV.)

TABLE III

Comparison of the Radioactivity Removed From the Sample and Measured on the Granule

Radioisotope	Removed radioactivity from 1726 cm ³ of the sample (K Bq)	Percentage for which the removed radioactivity is higher than measured
Cs-134	310	57
Cs-137	400	37
Co-58	300	121
Co-60	290	137
Mn-54	150	73

The Combination of Continuous Treatment and Sorption on Iron(III) Hydroxide

In the last 30 years extensive research has been done in the field of radioisotopes sorption on metallic hydroxides (15-18). Based on these results it was expected that radioisotopes of cobalt and manganese could be removed from radioactive liquids by their sorption on Fe(OH)₃, precipitated at higher pH. For this reason, in the samples of

TABLE IV

Decontamination Factors After Centrifuging Samples From EB and WHT

Radioisotope	Sample from the EB		Sample from the WHT	
	Ap (Bq/m ³)	DF	Ap (Bq/m ³)	DF
Cs-134	1,9E8	1.1	2,6E7	1.1
Cs-137	3,7E8	1.0	5,2E7	1.0
Co-58	2,1E8	2.0	2,7E8	14.0
Co-60	2,0E8	2.3	2,5E7	2.5
Mn-54	6,7E7	3.2	1,7E7	1.7

EB in which pH was previously adjusted to desired values (7,8,9 and 10) Fe(OH)₃ (5 x 10E-3 mol dm³) was precipitated by the addition of the needed volume of FeCl₃ solution. DF values, measured after the solid/liquid separation are presented in Fig. 2 as function of pH on which sorption process was done. As expected, radioisotopes of cesium remain in the liquid phase (no sorption) while, in accordance with the literature data (15-18), radioisotopes of cobalt and Mn-54 reached maximal sorption at pH > 9 as the consequence of the formation of hydroxycomplexes of cobalt and manganese in alkaline solutions, which can be sorbed on Fe(OH)₃. In the case when continuous treatment (passing of 250 cm³ of WB sample, with uv = 5 cm³/min, trough three columns filled with 15 g of granulated zeolite A) preceded the sorption on Fe(OH)₃ (5 x 10E-3 mol dm³) precipitated at pH = 10, more than 99,9% of Cs-134/137 (DF=1700), more than 99,8% of Mn-54 (DF=600) and about 90% of Co-58/60 (DF = 7) can be removed from the EB, as shown in Fig. 3. Here, most of Cs-134/137 and quite a portion of Co-58/60 (5%) and Mn-54 (85%) were exchanged with Na⁺ ions from zeolite A, and the rest of Co-58/60 and Mn-54 were sorbed on Fe(OH)₃ precipitate.

The difference between the yields of sorbed radioisotopes of cobalt and Mn-54 is possibly consequence of the differences in the stability of hydroxycomplexes of cobalt and manganese and the formation of Co-complexes with complexing agents, which cannot be sorbed on Fe(OH)₃.

Cement Solidification Tests

For the balance of materials calculation it is important to have data about conditioning of waste. It is of particular interest to find the proper cement/zeolite ratio and strength of the cement blocks what together with leachability gives parameters for evaluation of the conditioned waste. Preliminary tests with Na form of zeolite A granule show the good strength and C/Z ratio and are presented in the Table V.

CONCLUSION

The laboratory tests were designed to simulate realistic operational situations and several technological possibilities. The radioactive effluent from Nuclear Power

TABLE V

Results of Preliminary Tests of Cement Solidification of Zeolite A Granule

Sample	Zeolite g	Cement g	Sands g	Water g	Aditiv ml	Strength MPa	C/Z
1	937,5	500	125,0	53,1	3	12,8	0,53
2	909,1	727,3	181,8	88,2	4	18,1	0,80
3	1153,8	692,3	-	40,0	7	14,7	0,80

Plant Krsko have been treated at laboratory scale using powdered and granulated zeolite as ionic exchanger and Fe(OH)₃ precipitate as sorbent. In all cases, decontamination efficiencies were higher in continuous treatment with granulated zeolite than in batch treatment with powdered zeolite. Presence of colloidal dispersed corrosion products and the complexing agents from the decontamination and washing chemicals considerably decreases the yield of Co-58/60 and Mn-54 exchanged with Na⁺ ions from zeolite, because of partial sorption of the radioisotopes on the corrosion products and the formation of unexchangeable complexes. Additionally, the particles of corrosion products inhibit the exchange process due to their sedimentation on

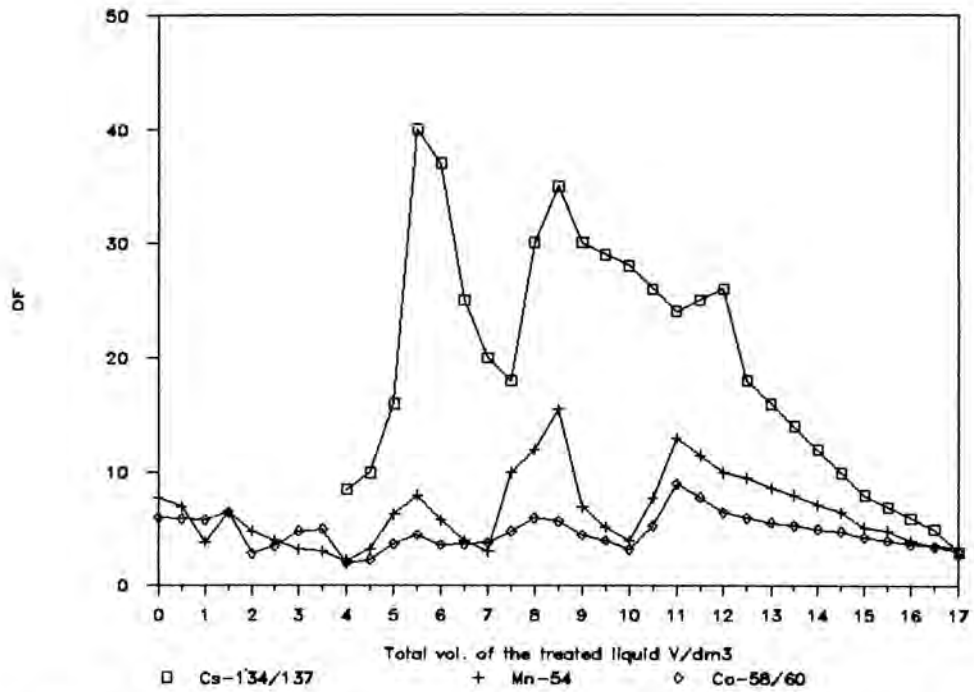


Fig. 1. Dependence of DF on the Volume of the Continuously Treated Liquid Waste.

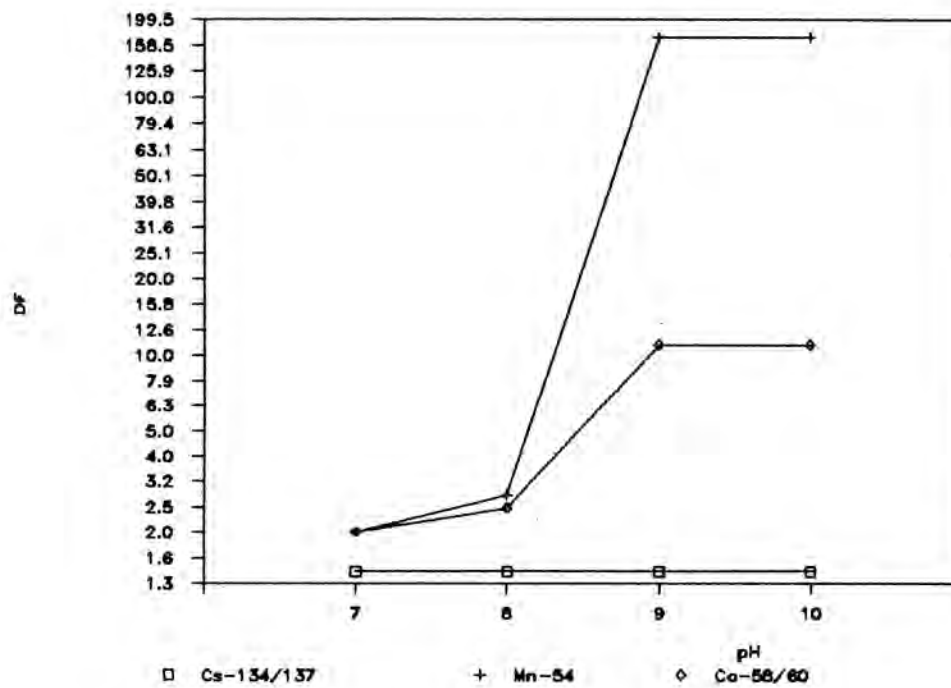


Fig. 2. Dependence of DFs on the pH.

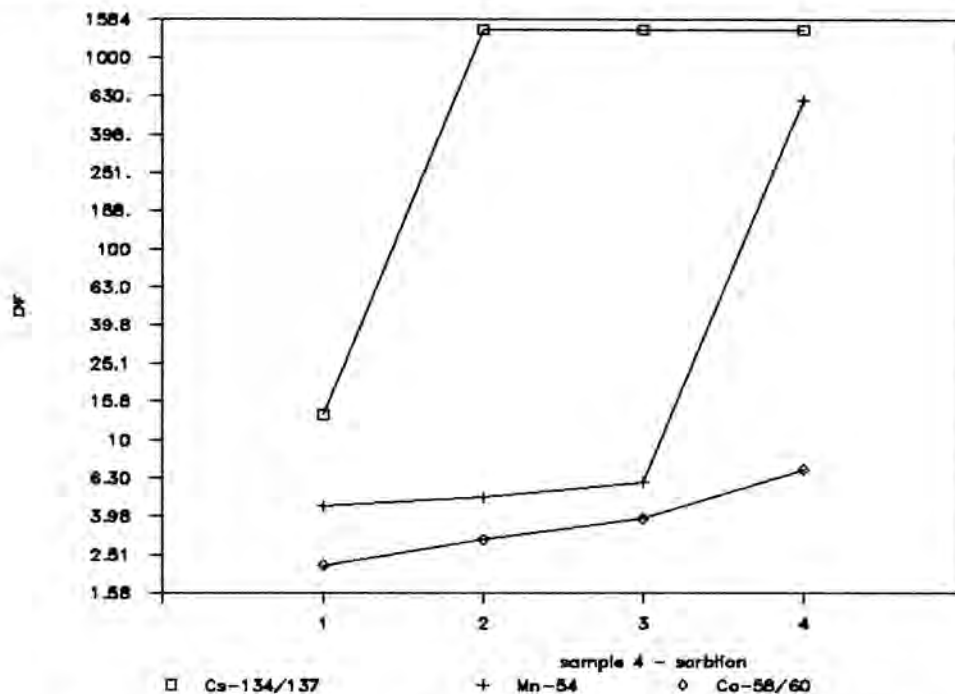


Fig. 3.DFs for Triple Passage Through the Column and Sorbtion at the End.

the granules and thus, by blocking the surface of granules at which the exchange process takes place. Therefore, the removal of corrosion products by centrifuging or filtration is necessary prior to further treatment (ion exchange, sorption).

Using combined method (continuous treatment with granulated zeolite + sorption on Fe(OH)₃), more than 99,9% of Cs-143/177, more than 99,8 of Mn-54 and about 90% of Co-58/60 can be removed from the liquid radioactive waste from Nuclear Power Plant Krsko.

Preliminary tests of the solidification of granulated zeolite A with cement show good strength for cement zeolite ratios 0.53-0.6. It was calculated that when zeolite are solidified with cement a volume reduction between 3 and 5.7 times can be achieved in comparison to encapsulation method.

Generally a further laboratory testing and eventually on semi pilot plant scale is justified.

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