

# COMBINED RADIOACTIVE LIQUID WASTE TREATMENT PROCESSES INVOLVING INORGANIC SORBENTS AND MICRO/ULTRAFILTRATION\*

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To check the influence of converting the sorbents to various cationic forms on their sorption properties, distribution coefficients of <sup>137</sup>Cs on natural zeolites from local deposits converted to NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup> or H<sup>+</sup> forms were determined. The results obtained show that the distribution coefficients of <sup>137</sup>Cs on the materials converted to H<sup>+</sup> form are higher than for the remaining forms studied, exceeding the value of  $9.8 \times 10^2$  ml/g.

The parameters of Langmuir and Freundlich adsorption isotherms have been determined using de sorption data. Both the Langmuir model and the Freundlich model indicate good correlation between the theoretical and experimental data, for the whole concentration range.

*Key words:* microfiltration, ultrafiltration, zeolites, decontamination, radioactive waste.

## 1. INTRODUCTION

Treatment of liquid radioactive waste quite often involves the application of several steps such as filtration, precipitation, sorption, ion exchange, evaporation and/or membrane separation to meet the requirements both for the release of decontaminated effluents into the environment and the conditioning of waste concentrates for disposal. New and improved materials and processes are under consideration and development in various countries [1].

Sorption combined with membrane filtration in a single stage process can provide efficient removal of both dissolved and suspended contaminants even in a colloidal form. This combination has not only the advantage of improved sorption kinetics on account of a very high surface area of the sorbents, but also provides for effective separation of the sorbents from the effluents [1].

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Zeolites are low-cost naturally occurring hydrated aluminosilicate minerals, with wide geographic distribution and large size of deposits [2, 3].

Experimental determinations concerning the treatment of liquid radioactive waste on semipermeable membranes were performed by using a filtration device.

Each membrane system will require some sort of feedwater pretreatment, either to protect the membrane's integrity and/or to optimize its performance [4]. The sorption of radionuclides on natural inorganic sorbents (zeolites) is an excellent pretreatment for membrane filtration. A variety of cations can be adsorbed on zeolites by the cation exchange mechanism and by modifying their surface, an increase in the ability to remove nonpolar and anion water pollutants can be obtained [5].

The treatment of simulated radwaste solutions like secondary waste from the decontamination process with modified CANDEREM (*CANadian DEcontamination and REMediation Process*) solution and with modified CANDECON (*CANadian DECONtamination Process*) solution by combining the sorption of radionuclides onto natural inorganic sorbents (zeolites) and then membrane filtration has been studied [6–8].

Numerous mathematical models with varying degrees of complexity have been developed for sorption in batch systems [3, 9, 10]. Use of these models to describe sorption by non-conventional adsorbents is somewhat cumbersome because most of these adsorbents, including the natural zeolite used in this study have an irregular shape [3].

The purpose of this work was to study the influence of converting the sorbents to various cationic forms on the  $^{137}\text{Cs}^+$  sorption from simulated CANDECON and CANDEREM solutions.

Combination of sorption with membrane treatment for solid/liquid phase separation was the next step of the research work.

## 2. EXPERIMENTAL

### 2.1. MATERIAL AND METHODS

#### 2.1.1. Sorbent

All the sorbents studied are natural zeolites from local deposits. The volcanic tuff from the area of Marsid (Romania) is of zeolitic type (zeolite content 20–80%) and altered (volcanic glass ~3.7%, quartz ~3.5%, feldspar ~2%). The major zeolite is of clinoptilolitic type (the *calcic potassic* variant). The associated mineral is heulandite. The degree of crystallinity is of 71.5% and the specific surface is 46.8 m<sup>2</sup>/g [11–13]. The zeolite samples are crushed and the fraction 0.5–1.0 mm is used during the experiments.

The chemical composition (wt%) of the mineral is listed in Table 1 [13]:

Table 1

The average chemical composition of the clinoptilolitic volcanic tuff, %

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	calcinating lost
69.98	12.60	1.04	4.80	0.80	2.20	0.40	0.18	9.31

### 2.1.2. Chemicals

For the main circuit of CANDU reactors which is made from carbon steel, the CANDECON decontamination procedure have been developed by the Canadian researchers from Chalk River Laboratory and Ontario Hydro, [14]. The Romanian researchers from ICN Pitesti developed a similar product which is the basis for the so called “modified CANDECON” procedure used for the decontamination of the primary circuit which is made from carbon steel SA-106. This product contains oxalic acid, citric acid, ascorbic acid, EDTA and phenylthiourea (corrosion inhibitor) [15].

CANDECON method consists in recirculating a solution, which contains a mixture of oxalic acid, citric acid and EDTA, through the circuit or on surface of the component, which is being decontaminated. The process takes place at 85–90°C. A corrosion inhibitor can be added most probably phenylthiourea with a concentration of 0.1–0.5 g/l [8].

We performed experiments using simulated waste solutions like secondary waste from the decontamination processes with modified CANDECON solution and modified CANDEREM solution.

Because the lab testing suggested that the oxalic acid could cause the metal attack, the oxalic acid was removed, thus being created the CANDEREM process by using citric acid and EDTA as active ingredients [8].

The simulated CANDECON solutions composition is:

- oxalic acid 0.3 g/l
- citric acid 0.2 g/l
- EDTA 0.5 g/l
- radionuclides content: four solutions with <sup>137</sup>Cs in the range between 71.06 kBq/l and 282.33 kBq/l for the sorption isotherm and one solution with 2.9 kBq/l <sup>60</sup>Co, 25.5 kBq/l <sup>137</sup>Cs for pilot scale tests.

The simulated CANDEREM solutions composition is:

- citric acid 0.27 g/l
- EDTA 0.4 g/l
- radionuclides content: four solutions with <sup>137</sup>Cs in the range between 70.95 kBq/l and 268.08 kBq/l for the sorption isotherm.

For experimental determination of ion exchange capacity we used a 0.1 N solution of cesium or cobalt nitrate, labeled with <sup>137</sup>Cs, respectively <sup>57</sup>Co.

The microfiltration and ultrafiltration experimental tests have been done with cellulose acetate (CA) membranes manufactured at Research Center for Macromolecular Materials and Membranes Bucharest.

### 2.1.3. Ion Exchange Capacity

The batch ion exchange capacity is obtained using following procedure: 1 gram sorbent with particle size range 0.5–1.0 mm is equilibrated for 5 days with 100 ml of 0.1 N solution of cesium or cobalt nitrate, labeled with  $^{137}\text{Cs}$ , respectively  $^{57}\text{Co}$ . Each portion of 1 gram of zeolite was weight accurately, and transferred into a 250 ml polyethylene vial equipped with a polyethylene screw top. The reaction mixture was subject to periodically shaking. After reaching the equilibrium (5 days) the solid-liquid suspension was filtrated and the filtrates were than radioactive characterized. The exchange capacity (meq/g), is calculated according to the equation:

$$K = \frac{(C_0 - C_{eq}) \cdot V_{sol}}{M_{solid}} \quad (1)$$

where  $C_0$  and  $C_{eq}$  are the initial and equilibrium concentration (meq/ml),  $V_{sol}$  is the volume of the solution (ml) and  $M_{solid}$  is the weight of the sorbent (g) [1].

### 2.1.4. Measurement of Distribution Coefficient

For the determination of the distribution coefficient, the batch method was employed [16, 17]. The experimental conditions for measurement of the distribution coefficient are the same as the above (see exchange capacity), but the contacted solutions are simulated CANDEREM, respectively CANDECON solutions, spiked with  $^{137}\text{Cs}$  in the concentration range of 71–282 kBq.l<sup>-1</sup>.

The distribution coefficients (ml/g), are calculated according to the equation:

$$K_d = \frac{(A_0 - A_{eq}) \cdot V_{sol}}{A_{eq} \cdot M_{solid}} \quad (2)$$

where  $A_0$  and  $A_{eq}$  are the activities of the radionuclide in the solution at the start of the experiment and in equilibrium (Bq/l),  $V_{sol}$  is the volume of the solution (ml) and  $M_{solid}$  is the weight of the sorbent (g) [1].

The adsorption equilibrium of  $^{137}\text{Cs}$  on natural zeolite and sorbents converted to various cationic forms was determined at 25°C. Sorption equilibrium experiments were performed in batch mode. The pH solutions were adjusted in range 5.5–6. The batch tests were similar, except for the concentration of the dissolved contaminant. The  $K_d$  for the resulting isotherm is

typically calculated from the slope of the plot of  $C_i$  (remaining concentration of the contaminant in the filtrate) *versus*  $A_i$  (concentration of adsorbate sorbed on the solid phase) [18].

## 2.2. APPARATUS AND INSTRUMENTS

Characterization of the solutions as concerns the radioactive composition was performed by measurement of gamma emitting radionuclides concentrations with a high resolution spectrometer comprising: a HPGe detector with 25% relative efficiency, a low background shielding and a Canberra spectrometric analyzer, model InSpector. The analysis software was GENIE-PC from Canberra. The spectrometer was energy and efficiency calibrated in the range 60 keV – 1500 KeV, by considering all counting geometries used in the experiments. The nuclear properties values used for data reduction were gathered from the original generic library of the software GENIE PC v. 1.4.

The pH measurement was done by use of Mettler Toledo pH meter.

## 3. EXPERIMENTAL TESTS

### 3.1. EXPERIMENTAL SORPTION CAPACITY AND SORPTION ISOTHERMS

The experimental sorption capacity for cobalt and cesium is given in Table 2. The values show that the sorption capacity of the sorbent converted to  $\text{Na}^+$  is higher than for the remaining forms studied. Therefore, it can be concluded that the type of the cationic form of the sorbents has an important effect on its sorption properties.

Table 2

Influence of cationic form of the sorbent on sorption capacity

Zeolite type	$K_{\text{Co}}$ , [mEq/ g]	$K_{\text{Cs}}$ , [mEq/ g]
ZN	0.75	1.16
ZH	1.18	0.58
$\text{ZNH}_4$	1.03	1.46
ZNa	2.07	1.77

The comparison of experimental and calculated data by Langmuir [3, 19] equilibrium isotherms for the system  $^{137}\text{Cs}$  from simulated CANDEREM, respectively CANDECON solution, and natural zeolite or in -H,  $-\text{NH}_4$ , -Na forms is presented in Fig. 1 and Fig. 2.

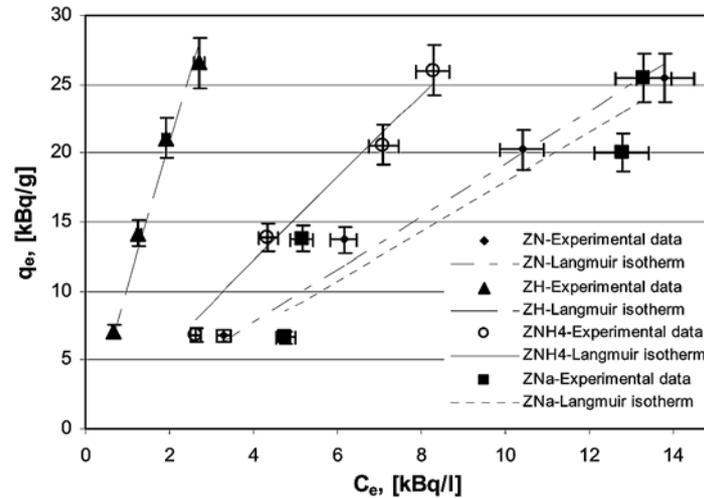


Fig. 1 – Comparison of experimental and calculated data by Langmuir equilibrium isotherms for sorption of  $^{137}\text{Cs}$  from simulated CANDEREM solution on different sorbent forms.

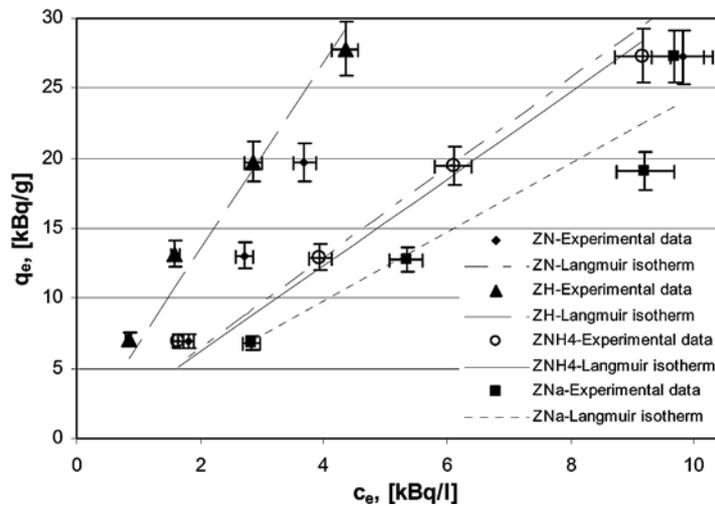


Fig. 2 – Comparison of experimental and calculated data by Langmuir equilibrium isotherms for sorption of  $^{137}\text{Cs}$  from simulated CANDECON solution on different sorbent forms.

Sorption isotherms are plotted for sorption of  $^{137}\text{Cs}$  from simulated radioactive waste solution on different sorbents. The isotherm, given in Figs. 1 and 2, are linear showing constant distribution coefficients in the studied concentration range ( $\sim 10^{-7}$ – $10^{-8}$  meq/l).

The  $K_d$  values calculated from the slope are shown in Table 3.

Table 3

Distribution coefficients for  $^{137}\text{Cs}$  from simulated CANDEREM and CANDECON radioactive waste on the studied sorbents,  $\text{ml g}^{-1}$

Zeolite form \ Simulated waste	ZN	ZH	ZNa	ZNH <sub>4</sub>
CANDEREM	946.1	989.8	949.5	970.1
CANDECON	963.4	983.1	965.8	964.7

### 3.2. REMOVAL OF $^{134,137}\text{Cs}$ AND $^{60}\text{Co}$ FROM SIMULATED RADIOACTIVE WASTE BY SORPTION AND MEMBRANE FILTRATION

The method developed was tested in an experiment with CANDECON simulated radioactive liquid waste on 20 L batch scale.

For the treatment, 200 g of the zeolite in  $\text{Na}^+$  form (0.5–1 mm) was added to 20 L of CANDECON simulated radioactive liquid waste. After mixing and 7 days of standing, phase separation was achieved by microfiltration and ultrafiltration. For the separation, pH of samples was adjusted to 8.0–8.5.

Following the filtrate will be passed through a reverse osmosis module.

After each of the stages, the activity of the solution was measured. The results of this treatment process are summarized in Table 4.

Table 4

The result of the combined sorption – ultrafiltration treatment of a CAN-DECON simulated radioactive waste

Radionuclide	Initial specific activity of the waste ( $\text{Bq}\cdot\text{l}^{-1}$ )	Activity of the solution after sorption ( $\text{Bq}\cdot\text{l}^{-1}$ )	Activity of the solution after micro and ultrafiltration ( $\text{Bq}\cdot\text{l}^{-1}$ )
$^{60}\text{Co}$	$2993 \pm 46$	$2534 \pm 51$	$2136 \pm 31$
$^{134}\text{Cs}$	$141 \pm 10$	< DL*	< DL*
$^{137}\text{Cs}$	$25532 \pm 50$	$5892 \pm 104$	$3526 \pm 52$
global	$28666 \pm 106$	$8426 \pm 155$	$5662 \pm 83$

\* detection limit ( $\text{DL} = 40 \text{ Bq}\cdot\text{l}^{-1}$ ).

The microfiltration and ultrafiltration experimental tests have been done with cellulose acetate (CA) membranes manufactured at Research Center for Macromolecular Materials and Membranes Bucharest.

## 4. CONCLUSIONS

The sorption capacity of Co and Cs on volcanic tuff from the area of Marsid (Romania), converted to  $\text{NH}_4^+$ ,  $\text{Na}^+$  or  $\text{H}^+$  form was determined. This

was done to check the influence of converting the sorbents to various cationic forms on their sorption properties. The results obtained show that the sorbent converted to Na<sup>+</sup> form is more efficient than the remaining forms studied. Therefore, it can be concluded that the type of the cationic form of the sorbents has an important effect on its sorption properties.

The experimental values of the sorbent capacity and distribution coefficients obtained for the radionuclide of concern on volcanic tuff from the area of Marsid (Romania) are similar with the same parameters obtained by other authors for zeolite deposits located in Northeast Rhodope Mountain (Bulgaria) [1].

The sorption isotherms in the studied concentration range are linear. The equilibrium studies shown that both the Langmuir model and the Freundlich model indicate good correlation between the theoretical and experimental data, for the whole concentration range.

Generally, it can be concluded that the results obtained show the applicability of natural zeolite from the area of Marsid (Romania) for treatment of liquid with radionuclide inventory governed mainly by <sup>137</sup>Cs.

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