The Influence of the Sludge Content on Transport Parameters of the Cemented based Radioactive Waste Form

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The paper describes the results obtained in the laboratory investigation on the transport parameters of the cement based radioactive waste form containing two kinds of sludge in different contents. One of them simulates the sludge obtained by treatment of liquid radioactive effluents using A PA-type anionic polyelectrolyte, *and the other one simulates the sludge obtained by decontamination of contaminated surfaces using a* pNaAc-type hydrogel. *The investigated transport parameters are: distribution coefficients and retardation factor for ^{60}Co, ^{137}Cs and ^{14}C.*

Keywords: waste form, transport parameters, radioactive sludge

The safety of a radioactive waste repository is related to its capacity to confine radioactivity and isolate it from the biosphere. The confinement of radioactivity and its isolation from biosphere is realised by solidification of radioactive waste in different forms. Cement based materials are widely used for solidification of low and intermediate level radioactive waste and as structural components of the waste repository. Typical concrete is a mixture of Portland cement, sand and water in various proportions. The concrete possesses many practical advantages: good mechanical properties, low cost, easy operation and thermal and radiation stability [1, 2]. One of the most important properties of cement is maintaining the waste form in alkaline conditions. Cement based materials show relatively high distribution coefficients for certain of these elements, particularly ^{60}Co or ^{14}C [3].

Recently it has been reported that the chemical degradation of organic polymers under alkaline, anaerobic conditions enhances the solubility of some elements due to the formation of water-soluble complexes. These findings suggest that the distribution coefficients of cement for these elements could be lowered by the presence of the sludge resulted from the decontamination of various kind of radioactive waste [4]. The sludge is a secondary radioactive waste resulted from treatment of aqueous radioactive waste as well as from decontamination of radioactive contaminated surfaces.

In Romania, techniques for the treatment of aqueous radioactive and for the decontamination of radioactive contaminated surfaces, using polymeric materials obtained through gamma irradiation, have been developed [6]. These techniques aim to obtaining a similar decontamination factor as those obtained through classical methods and to reducing the amount of radioactive sludge. The resulted sludge is characterized by a lower content of chemical compounds than the sludge resulted from the classical treatment and decontamination methods [5, 6].

The aim of this study is to experimentally examine the effect of the following two different kinds of sludge on the sorption parameters of ^{60}Co, ^{137}Cs and ^{14}C in cement waste form:

- sludge resulted from the treatment of aqueous radioactive waste using a PA-type anionic polyelectrolyte obtained through gamma-irradiation polymerization of an acrylamide and sodium-acrylate aqueous solution;
- sludge resulted from the decontamination of radioactive contaminated surfaces using a pNaAc-type hydrogel obtained through gamma-irradiation polymerization of a sodium-acrylate aqueous solution.

This paper presents the results of the experimentally study on the influence of the concentration of two different kinds of sludge on the distribution coefficients and on the retardation factor of ^{60}Co, ^{137}Cs and ^{14}C in cement based radioactive waste form.

Experimental part

Materials

Two kinds of sludge were simulated in order to prepare samples of cemented based waste form:

- the sludge hereinafter named CF is simulated by preparation of a dilute effluent obtained by dissolution in demineralised water of salts in the following concentrations: $Al_2(SO_4)_3$ 5 g.L^{-1}, PA - type polyelectrolyte 1 g.L^{-1}, NaCl 20%.
- the sludge hereinafter named HG is simulated by preparation of an effluent obtained by dissolution of 25 g of pNaAc type-hydrogel in 1 L of demineralised water.

The samples of waste form were prepared by mixing of cement, sand, water in a constant ratio, and CF and HG in different concentrations as presented in table 1. In order to compare the results, a reference sample with content of cement, sand and water was prepared (sample no.1, table 1).

The ratio of cement: sand: water was constantly maintained 1:1:0.4 in all samples.

Methods

The radionuclides sorption was studied by "in batch" technique through the static method. All experiments were

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Table 1
CHEMICAL COMPOSITION OF CEMENT BASED WASTE FORM SAMPLES

Identification code of sample	Portland cement [g]	Sand [g]	Water [mL]	HG [g]	CF [mL]
1	-	-	120	0	0
2	-	-	120	30	0
3	-	-	120	60	0
4	-	-	80	0	40
5	300	300	0	0	120
6	-	- -	80	60	40
7	-	-	80	30	40
8	-	-	40	30	80
9	-	-	0	30	120

performed at room temperature. The *p*H of the solution was adjusted with nitric acid or with sodium hydroxide solution. The solid liquid phase ratio was maintained at 1:25 throughout the experiments, 25 mL of solution were mixed with 1 g of crushed solid in 50 cm^3 polyethylene bottles with screw cap. The mixture was shaken for 1 hour. The separation of solid from the liquid phase was performed by centrifugation. The activity of the liquid phase before and after the solid separation was measured. ^{137}Cs as well as ^{60}Co activities in solution were counted using a CANBERRA gamma multi-channel spectrometer with a Ge(Li) detector while ^{14}C concentration was measured in a 2100 TRI-CARB Packard model Liquid Scintillation Analyzer. The sorption process is determined by the retardation factor which, in case of a linear reversible sorption, is defined by the following relation:

$$R = 1 + \frac{\rho_b}{\eta_e} K_d \qquad (1)$$

The distribution coefficient is defined as the ratio of activity of radionuclide per mass unit of solid (1 g in this case) to the equilibrium radionuclide activity in liquid phase and it is calculated through the following relation:

$$K_d = \frac{A_s}{A_{eq}} = \frac{A_0 - A_{eq}}{A_{eq}} \cdot \frac{V}{m} \qquad (2)$$

Due to a linear dependence of the amount of radionuclide sorbed on the solid phase with the equilibrium concentration of radionuclide in liquid phase, the K_d values are obtained by sorption isotherms where amount of radionuclide sorbed on solid phase as function of equilibrium concentration in liquid phase are plotted for five different values of initial concentration.

The range of activity varied as follows: ^{60}Co between 5.10^6Bq/L and 10^4, ^{137}Cs between 2.5×10^5Bq/L and 10^5, and ^{14}C between 6×10^6 and 10^2 Bq/L.

The solid density, ρ_g, is the ratio of the mass of the solid phase of the sample and its total volume (solid and pore volumes together). The solid density (ρ_g) of a sample is evaluated on the basis of two measured values: (1) M_f, the oven-dried mass of the sample and (2) *Vt*, the total volume of the sample.

The effective porosity, η_e, of the waste form sample is defined as the ratio of the part of the pore volume, where the water can circulate, and the total volume of the sample. The definition of effective porosity is linked to the concept of pore fluid displacement rather than to the percentage of the volume occupied by the pore spaces.

The effective porosity is related to the total porosity, η, and the volumetric water content, θ, according to the following expression:

$$\eta_e = \eta - \theta \qquad (3)$$

The total porosity, η, is calculated on the basis of two measured quantities: (1) ρ_b the bulk density of the sample, and (2) the solid density ρ_g of the sample according to the expression:

$$\eta = 1 - \frac{\rho_b}{\rho_g} \qquad (4)$$

The volumetric water content, θ, is defined as the ratio of the volume of water V_l retained in the sample, after all downward gravity drainage has ceased, and the total volume of the sample. The volumetric water content θ of a sample is evaluated on the basis of three measured quantities: (1) M*w*, the wet mass of the sample; (2) M_d, the oven-dried mass of the sample; and, (3) V_t the total volume of the sample, according to the following expression:

$$\theta = \frac{V_l}{V_t} = \frac{M_w - M_d}{V_t \cdot \rho_b} \qquad (5)$$

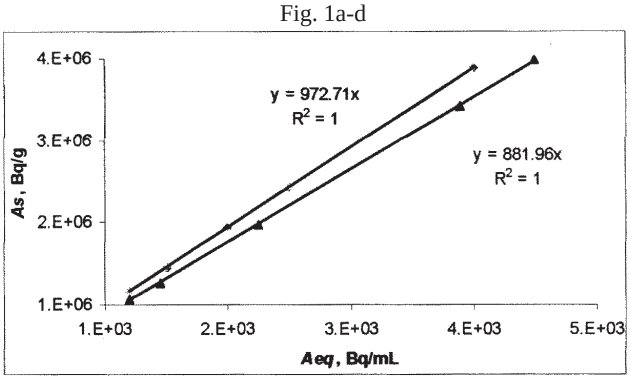
Results and discussions

The values of the distribution coefficients for ^{60}Co, ^{137}Cs and ^{14}C for the reference sample have the same range as the values reported for Portland cement [7, 8].

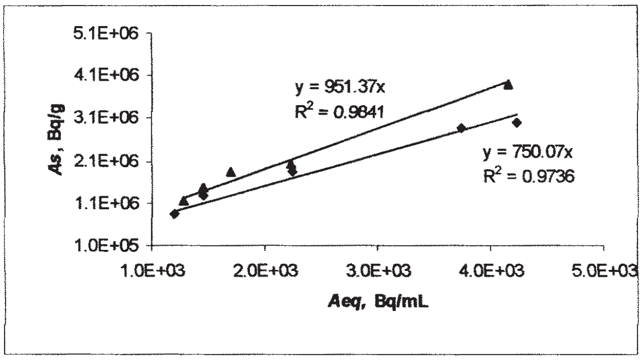
The sorption isotherms of ^{60}Co on the waste form samples with different content of HG as well as CF are presented in figures 1a-d.

The samples with content of HG show a high affinity of ^{60}Co, the values of distribution coefficients are 10 times higher than the value obtained for the reference sample. Due to a low content of organic polymers in CF, the distribution coefficients are not influenced, the obtained values are in the same range as the ordinary Portland cement.

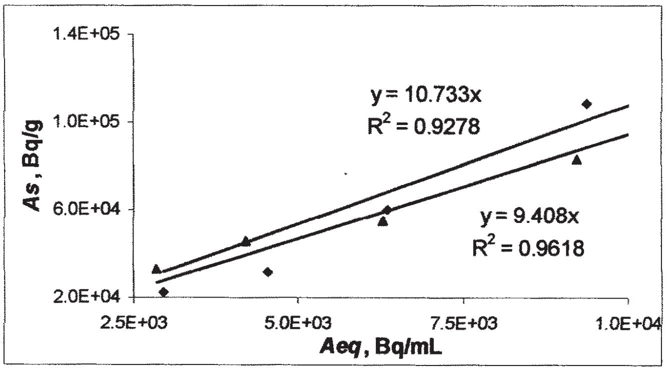
Fig. 1a-d



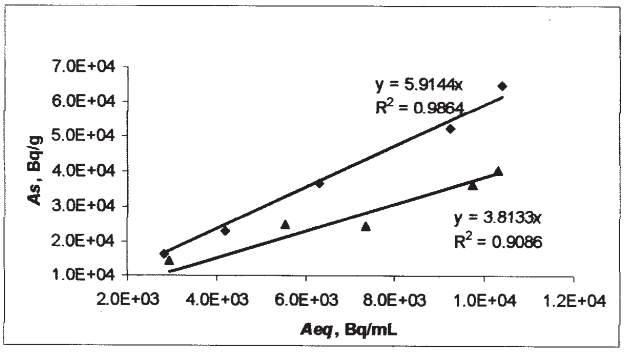
a) HG 30g
HG 30g+CF 40mL



b) HG 60g
HG 60g+CF 40mL



c) CF 40mL
CF40mL + HG 30g

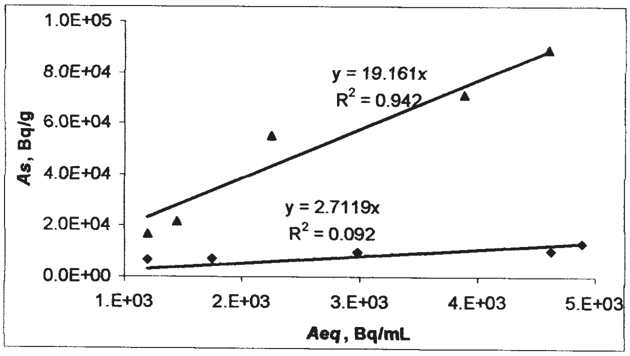


d) CF 120mL
CF 120mL + HG 30g

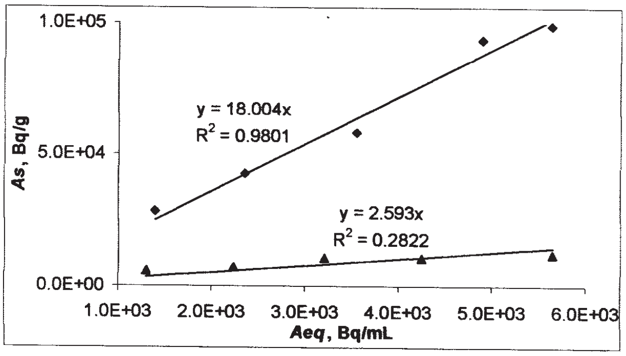
Fig. 1a-d. Sorption isotherms for ^{60}Co

The sorption isotherms of ^{137}Cs on the waste form samples with different contents of HG as well as CF are presented in figures 2a-d.

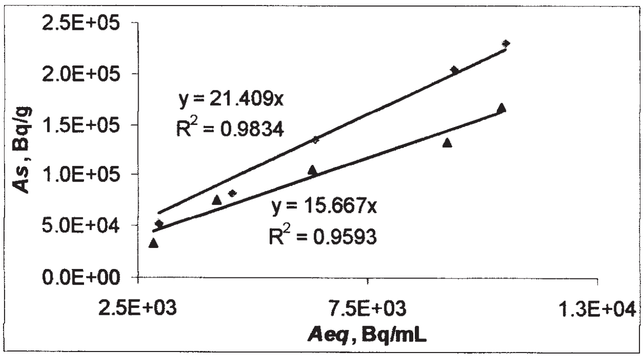
Fig. 2a-d



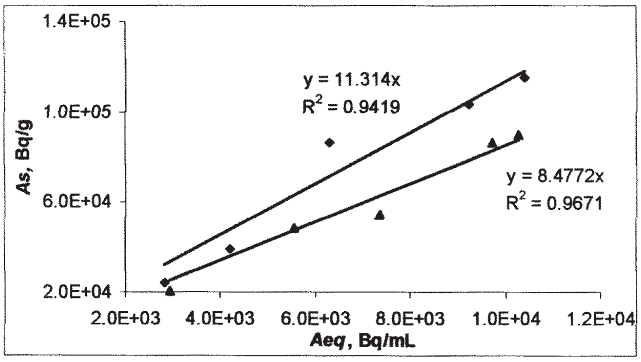
a) HG 30g
HG 30g+CF 40mL



b) HG 60g
HG 60g+CF 40mL



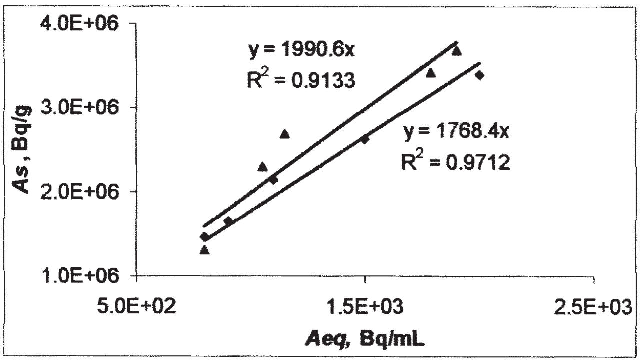
c) CF 40mL
CF40mL + HG 30g



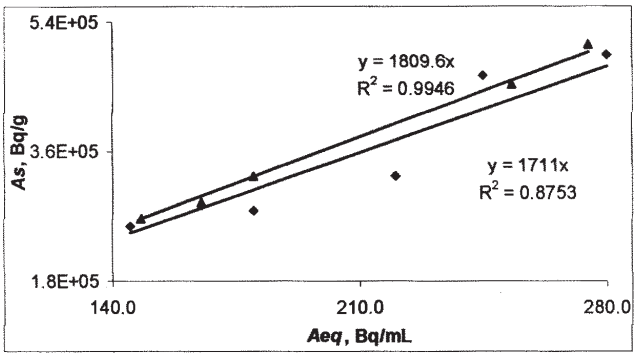
d) CF 120mL
CF 120mL + HG 30g

Fig. 2a-d. Sorption isotherms for ^{137}Cs

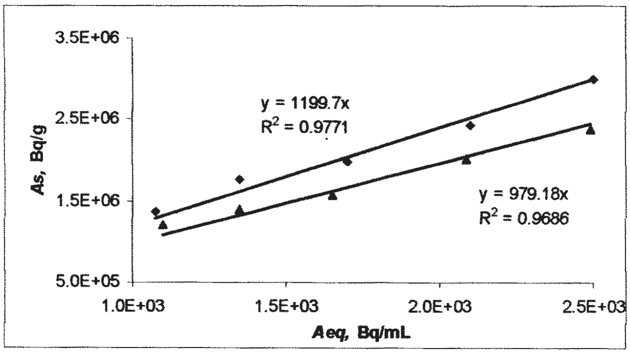
Fig. 3a-d



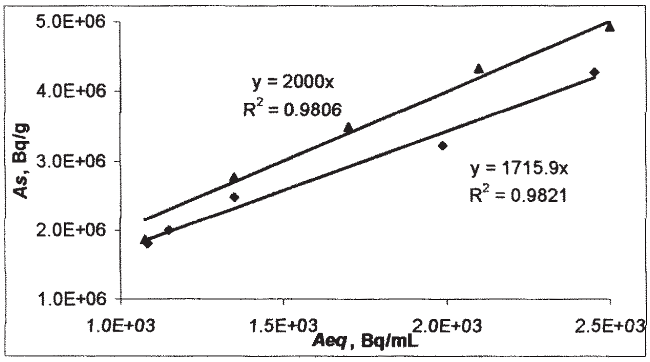
a) HG 30g
HG 30g+CF 40mL



b) HG 60g
HG 60g+CF 40mL



d) CF 120mL
CF 120mL + HG 30g



c) CF 40mL
CF40mL + HG 30g

Fig 3a-d. Sorption isotherms for ^{14}C

Table 2
PHYSICAL PARAMETERS OF THE SAMPLES

ID samples	R ^{60}Co	R ^{137}Cs	R ^{14}C	ρ_g [g/]	ρ_b [g/cm^3]	θ	η [cm^3/cm^3]	η_e [cm^3/cm^3]
1	153	20	2000	3.29	2.3	0.15	0.3	0.18
2	7472	21	1768	3.21	2.15	0.05	0.33	0.28
3	6690	19	1809	3.29	2.04	0.09	0.38	0.29
4	128	212	2000	3.29	2.3	0.13	0.3	0.17
5	109	207	1200	3.05	2.38	0.09	0.22	0.13
6	10121	32	1990	3.29	2.3	0.10	0.3	0.20
7	6635	160	1711	3.43	2.3	0.07	0.33	0.26
8	124	98	1715	3.43	2.3	0.13	0.33	0.20
9	51	286	979	3.20	2.4	0.07	0.25	0.18

The content of HG as well as of CF has a low influence on the sorption of ^{14}C. The reported values of the distribution coefficients for ^{14}C in concrete are in the range of 2000 mL/g depending on the investigated method [8]. The samples with high content of HG (60g) as well as CF(120mL) show the lowest values of the distribution coefficients.

In table 2 the values obtained for retardation factor, solid density, bulk density volumetric content of water, total porosity and the effective porosity of the samples are presented.

The retardation factor is calculated using the equation (1). The solid density, the bulk density and the volumetric water content of the samples were determined by laboratory measures. The total porosity is calculated using equation (4).

Conclusions

The content of HG leads to the increasing of ^{60}Co affinity for cement based waste form to up 10 times. Recently, has been reported that the HG content influences the mechanical strength in sense of diminishing of it [9]. Therefore, it is recommended to establish an optimum content of HG based both on the effect of sorbtion and the effect of mechanical strength of the cemented based waste form.

The content of CF has a low influence on the distribution coefficients for all the investigated radionuclides.

The affinity of the ^{137}Cs on the waste forms with content of HG and CF is similar to the cemented based waste forms.

The cement based waste forms with content of HG and CF show a slight decreasing of the affinity of ^{14}C but in the same range as the reported values for cemented based waste form.

The porosity as well as the density is affected mainly by the HG content, due to the release of the water in the hardening process of the cement. These show higher values for the samples with HG content, respectively lower values for the samples with CF content, than the reported values for the cemented based waste forms.

For the radioactive waste with mainly content of ^{14}C and ^{137}Cs, due to the fact that the sorbtion is not highly affected by HG and CF content, it is recommended that for preparation of cemented based radioactive waste form, the content of HG and CF to be determined only by the effect they have on th mechanical strength of the cemented based radioactive waste form.

Notation

Symbol

A_0 - initial concentration of radionuclide in liquid phase, Bq/L
A_{eq} - equilibrium concentration of radionuclide in liquid phase, Bq/L
A_s - amount of radionuclide sorbed on the mass unit of solid, Bq/g
^{14}C - isotope of Carbon
^{60}Co – isotope of Cobalt
^{137}Cs - isotope of Caesium
K_d - distribution coefficient, mL/g
m - mass of solid, g
M_d - mass of the oven-dried sample, g
M_w -mass of the wet sample, g
R - retardation factor
V - volume of liquid phase, mL
V_l - volume of water retained in the sample, mL
V_t - total volume of the sample, mL

Greek

η_e - total porosity, mL/mL
η_e - effective porosity, mL/mL
θ - volumetric water content
ρ_b - bulk density, g/mL
ρ_g - solid density, g/mL

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