DIFFUSION COEFFICIENTS OF CRITICAL RADIONUCLIDES FROM RADIOACTIVE WASTE IN GEOLOGICAL MEDIUM

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ABSTRACT:

Diffusion (D_s) and distribution coefficients (K_d) are needed to assess the migration of radionuclides through the geological medium proposed to locate the low and intermediate level radioactive waste disposal (an intermediate level radioactive waste is considered that waste who have an activity less than $10^4 Ci/m^3$).

This paper describes the geological medium and groundwater characteristics and the experimental methods used for D_s and K_d determination.

The analyzed samples were collected from the drilling of Saligny site (Saligny is proposed as host site for low and intermediate level radioactive waste disposal)

INTRODUCTION:

The objective of radioactive waste disposal is to isolate waste so that it does not exposure humans and environment at radiation.

The investigations for site selection covered the surroundings of the Cernavoda-NPP and Saligny site has been selected. A complete characterization from the point of view of physical, chemical, hydrological, geochemical and radionuclide migrations investigations are required as input data for disposal safety assessment program.

The near-surface disposal represents an option commonly used and demonstrated in several countries. In near-surface disposal, the disposal facility is located on or below the ground surface, where the protective covering is generally a few meters thick. These facilities are intended to contain low and intermediate level radioactive wastes without significant amounts of long lived radionuclides.

Experience has shown that the effective and safe isolation of waste depends on the performance of the overall disposal system, which is made up of three major components or barriers: the site, the disposal facility and the waste form.

The safety and environmental impact assessment of near-surface disposal facilities involves consideration of radiological impacts during both the operational and post-closure periods. Potential radiological impacts following closure of repository arise from natural processes that lead to the gradual release of radionuclides to the biosphere and from discrete events, which may have adverse impacts on the facility (such as human intrusion). The suitability of a site will depend largely on its capacity to confine radioactive wastes for required periods of time, and to limit release rates of radionuclides, and also on its capability to limit potential adverse impacts of the disposal system on humans and on the environment.

The long-term performance assessment of geological site as a host site for disposal is done based on the identification and evaluation of these factors controlling the release and transport of radionuclides in the environment.

The experimental data concerning the behavior of radionuclides were obtained on samples taken from the geological material drilled in the Saligny zone.

The experimental study of main radionuclides behavior (this paper deals with Cs-137 and Co-60) in geological material of the Saligny site is a first stage in evaluation of geological formation as natural barriers for the retarding of radionuclides migration.

The cationic exchange capacity, pH, the permeability, the density and the porosity are important characteristics for supporting the experimental results in the evaluation of migration parameters of Cs-137 and Co-60 in that particular geological material, specific for the site.

THE PHYSICAL-CHEMICAL CHARACTERISTICS OF GEOLOGICAL SAMPLES AND OF GROUNDWATER

The main feature of geological formation of Saligny site is the presence of four layers. The first layer (horizon A) is a loess (dusty loess), a soil having, in natural state, a large water sensitivity, a large porosity and, consequently, high permeability and weak foundation properties (see Fig. 5).

The second layer is horizon B, horizon what has two type of soil, a clayness loess and a brown clay (with a small loess content).

These two layers are disposed over a red clay formation (horizon C) with montmorillonit as predominant mineralogical component.

The horizon D is clay with sand and limestone insertions layer. [1]

The presence of clayness minerals, well-known for their higher cationic exchange capabilities, as well as the low porosity associated with the particles fineness, delay significantly the radionuclides migration so that the red clay layer can be considered a natural barrier against their movement.

The granulometric composition, pH and carbonate content of the Saligny drilling is shown in the Table I and Fig. 1, while the mineralogical content of clay is presented in Table II and Fig. 2.

Table I – Granulometric composition, carbonate content and pH

Horizon	Depth [m]	Granulometric composition [%]			Carbonate [%]	pH
		Sand	Dust	Clay		
A	0 - 21	51.2	25.3	23.9	16.9	9.3
B	21 - 33.6	38.0	30.5	31.5	20.3	9.6
C	33.6 - 41.2	42.3	17.3	40.4	3.6	9.2
D	41.2 – 50	56.9	17.5	25.6	34.5	9.4

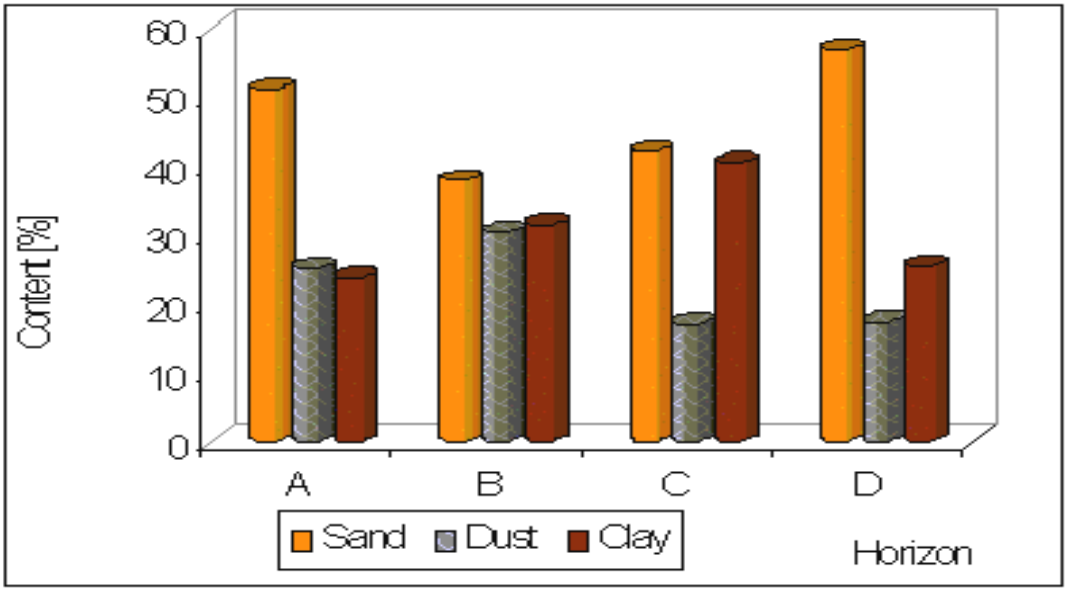


Fig. 1 – Granulometric composition of drilling

Table II – Mineralogical composition of the clay

Horizon	Mineralogical composition [%]		
	Montmorillonit	Illit	Kaolin
A	14.5	9.0	1.9
B	20.9	8.5	2.1
C	27.6	10.6	2.2
D	13.7	8.7	3.2

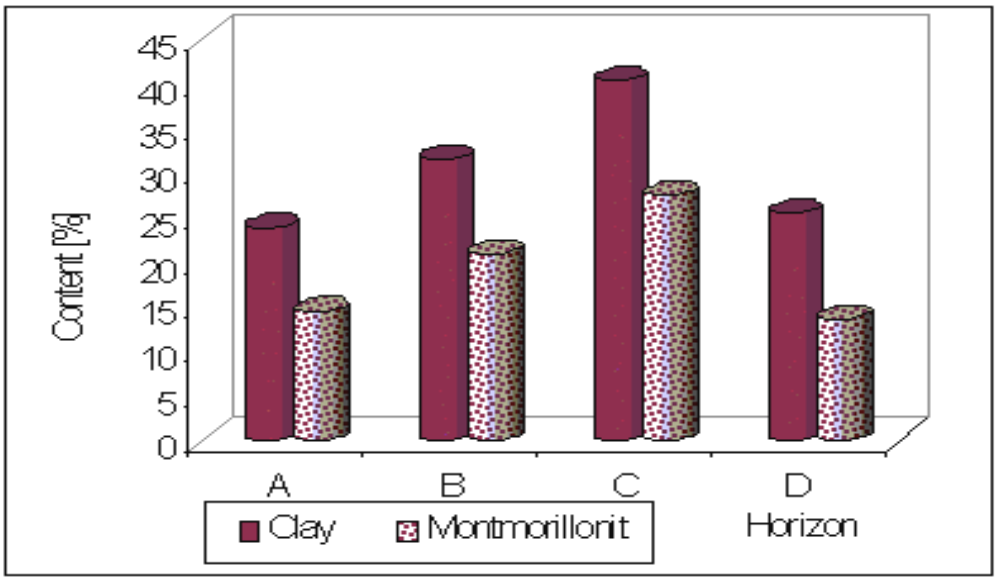


Fig. 2 – Clay and montmorillonit content

The water table is located approximately 30-35 m below the soils surface.

Water samples were collected from 8 drillings at monthly intervals, March-October, between 1995-1999 years.

The water samples were analyzed for Cl^-, SO_4^{2-}, HCO_3^- concentrations using volumetric techniques, and Ca^{2+} Na^+ Mg^{2+}, K^+ concentrations were measured by atomic absorption spectrophotometers. The dominant cations and anions in groundwater are Na^+, Ca^{2+} (the ratio $Ca^{2+}/Na^+ <1$) and Cl^-, HCO_3^-. The pH values for groundwater from the 8 drilling are range 7.6 - 8.6. The TDS (total dissolved solids) groundwater's contents is between 0,4 – 2.5g/l and consequently a higher electroconductibility.

The average values of these parameters on 8 samples analyzed since the period which have been considered (1995-1999) is presented in the Table III

The radioactive waste was a liquid radioactive waste from TRIGA reactor consists in a neutral (pH=6.8) mixture containing in principal radionuclides Cs-137 and Co-60. Typical activity of radionuclides was in the range of a low-level radioactive waste and the major ions of this solution were Na^+, SO_4^{2-} and OH^-.

Table III The characteristic physical-chemical of groundwater Saligny site

Sample	pH	TDS [mg/l]x10^3	Concentration [ppm]				
			Ca^{2+}	Na^{+}	SO_4^{2-}	Cl^{-}	HCO_3^{-}
1	7.4	2.5	144	156	805	433	339
2	7.4	1.9	127	199	174	382	254
3	8.4	0.9	57	161	84	163	508
4	7.4	0.8	64	112	175	145	575
5	7.6	1.6	63	148	215	253	419
6	8.7	0.8	32	124	64	137	295
7	8.3	0.5	34	160	73	169	174
8	8.6	0.7	29	143	108	245	245

The groundwater is a slight alkaline water type NaCl-$NaHCO_3$–Na_2SO_4– $CaCl_2$. [2]

EXPERIMENTAL METHODS

Diffusion experiments:

Studies of radionuclide transport in porous media have shown that there are many situations where molecular diffusion is the dominant migration mechanism. In these situations the transport characteristics can be described by the diffusion coefficient of the radionuclides in the medium.

The transient diffusion transport of radionuclide in a porous medium is described by Fick's second low:

$$\frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where: c is the concentration of radionuclide [μg/g]
D_s is diffusion coefficients, [cm^2/s]

For a porous medium of length L, the applicable initial and boundary conditions are:

$c(x,0) = c_0$ for $0 < x < x_0$
$c(x,0) = 0$ for $x_0 < x < L$, and
$\frac{\partial c}{\partial x} = 0$, at x = 0 and x = L

In this case solution to equation (1) is (Carslaw and Jaeger 1959):

$$c / c_0 = (x_0 / L) + (2/\pi)\sum_{i=1}^{\infty}\left[\exp\left(-D_a i^2 \pi^2 t / L^2 / i\right)\right]\cos(i\pi x / l)\sin(i\pi x_0 / L) \qquad (2)$$

In equation (2), the interface is at $x = x_0$, the radioactive end of the cell is at x = 0 and, while the initial non-radioactive end is at x = L.

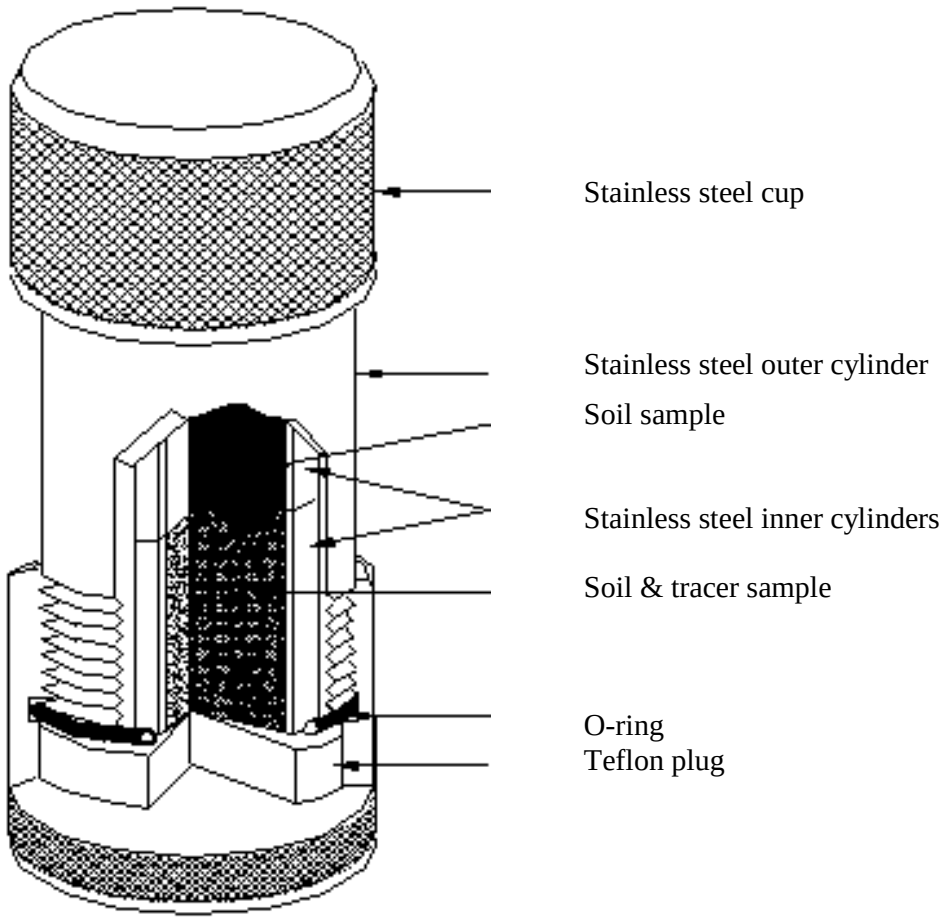


Fig. 3 – Diffusion closed-cell

Diffusion coefficients were determinate by transient method using diffusion closed-cell (see Fig. 3). [4]

Experiments have been conducted by using average samples for each horizon (A, B, C and D) of the drilling made on Saligny site.

The two soil samples for each horizon were prepared, one of these is the radioactive and one is the non-radioactive sample. The radioactive samples were prepared by mixing liquid radioactive waste from TRIGA reactor (with known radionuclides activity, for Cs-137=1.2×10^5, Cs-134=9.8×10^3, Co-60=4.9×10^3 and Mn-54=4.6×10^3 Bq/l) with soil. The non-radioactive samples were prepared by adding a known volume of deionised water sufficient to saturate the soil.

Before the diffusion experiment, the soil samples (half-cells) are kept to equilibrate for a minimum one week, which allows the water and radionuclides in the case of radioactive sample, to become evenly distributed throughout the soil.

Following the equilibration period, the half-cells are switched so that each cell has one radioactive and one non-radioactive sample.

After an appropriate diffusion time each cell is disassembled, the two-soil plugs are separated, and one plug at a time is sliced.

The masses of the slices are determined, and then they are analyzed for radioactivity by gamma spectroscopy; the concentration of radionuclides in each slice being determined.

The computer program to calculate D_s values from the experimentally determinate c/c_0 and x values uses equation (2).

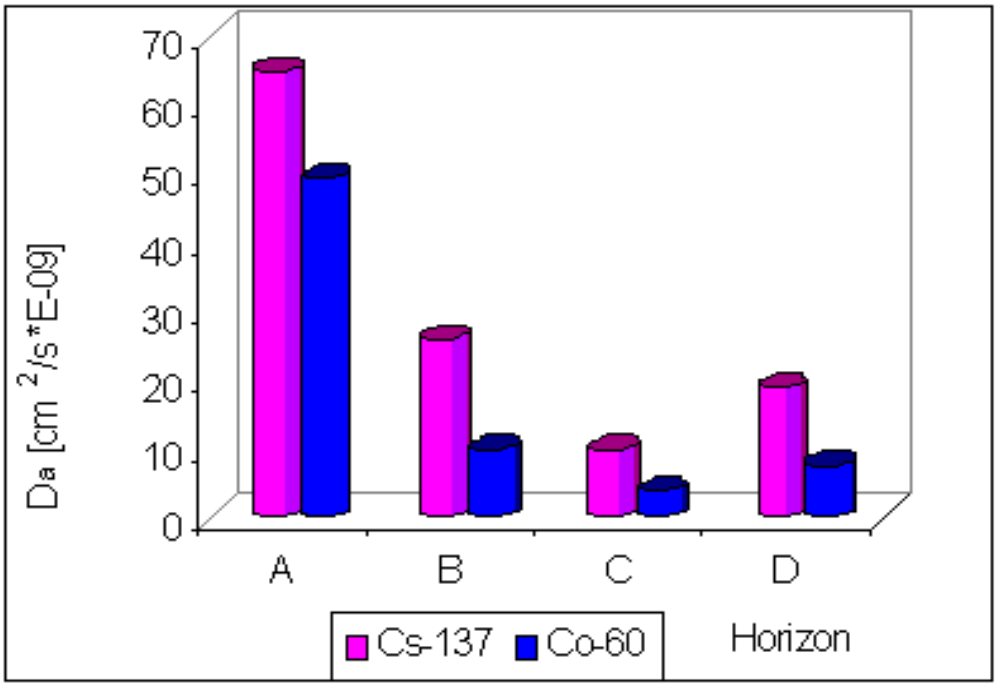
The diffusion coefficients for Cs-137 and Co-60 were determinate, and D_s values were presented in Table III and in Fig. 4. [3]

The greatest value of diffusion coefficient has been obtained for C-horizon, which is red clay layer with a higher montmorillonit content.

Table III Values of diffusion coefficients

Horizon	**D_s [cm^2 / s]**	
	Cs-137	**Co-60**
A	6.50E-08	4.94E-08
B	2.60E-08	9.92E-09
C	9.89E-09	3,84E-09
D	1.89E-08	7,57E-09

Fig. 4 – Diffusion coefficients variation



Experimental "in batch" method:
The radionuclides transport through geosphere is a function of several factors, an important role being played by sorption and retardation. The process and values of migration parameters influence upon the radionuclide release.

These are:
- geochemical interactions between groundwater and waste solidification matrix;
- interactions among the chemical speciations of the water and the components of host soil

The distribution coefficient is the ratio between the mass concentration of radionuclide on the solid phase (expressed on an oven-dried basis) and the concentration in the liquid phase, at the equilibrium.

The equation used for distribution coefficient calculation is equations 3.

$$Kd = \left(\frac{Co - C}{C}\right) \cdot \frac{V}{m} \qquad \text{or} \qquad K_d = \left(\frac{A_0 - A}{A}\right)\frac{V}{m} \tag{3}$$

where:
K_d - distribution coefficient, [ml/g]
C_o, A_0 - initial concentration, radioactivity of contaminant, [μg/l], [Bq/l]
C, A - final concentration, radioactivity of contaminant, [μg/l], [Bq/l].

For retardate factor calculation we use equation 4.

$$R=1+K_d \cdot \rho/\eta \tag{4}$$

where:
R – retardate factor;
ρ - density [g/cm^3];
η - porosity [cm^3/cm^3]
K_d - distribution coefficient, [ml/g]

If the radionuclides have affinity on the soil surface and they are adsorbed, they will be released from water and moved slower then groundwater. Consequently, the time of movement will be shorter. This fact led to the concept of retardation factor, defined by Relyea in 1982 from relation:

$$R=V_a/V_r$$

where:
V_a - the rate of moved a groundwater [cm/year] or [cm/s];
V_r - the rate of transport a radionuclides [cm/year] or [cm/s].

With this relation we can deduce the rate of transport a radionuclides V_r using the values of retardate factors from equation (4) which include same specific proprieties of sample. (in this paper aren't calculated)

Soil samples were collected, prepared and analyzed in the laboratory.

Distribution coefficients (K_d) were determinate both for the stabile elements Cs, Co and Sr and for radionuclides Cs-137, Co-60 using laboratory technique "in batch".

K_d for stabile elements Cs, Co and Sr, were determinate using contacting water, which was obtained by equilibrating the solid sample with deionised water. In this contacting water were added Cs, Sr and Co in the 10^{-3}-10^{-4}M concentration at the pH 7.5.

For radionuclides Cs-137, Co-60 K_d were determinate using a liquid radioactive waste from TRIGA reactor with some composition of those used in the diffusion experiment. In both experiments were used ratio solid-liquid 1:4.

The filtrate samples was analyzed for Cs, Sr and Co by atomic absorption spectrometry and for Cs-137 and Co-60 by gamma spectrometry.

Determinations for stable elements were done on the 20 perturbed samples on the depth interval 0-50 m of the drilling, and those for radionuclides were made on the average samples of horizons (A, B, C and D) from same drilling.

The density of the samples was 1.40 – 1.95 g/cm^3 and the porosity were 0.30 – 0.45[cm^3/cm^3]

The correlation between mineralogical composition and the experimental K_d values for Cs, Sr, and Co on the 20 soil samples of study drilling are showed in Fig. 5.

The great values of distribution coefficients and retardate factors for Cs, Sr, Co (on the individual samples) have been obtained for C-horizon, which is red clay layer with a higher montmorillonit content. Same variation of distribution coefficients and retardate factors it was obtained for the Cs-137 and Co-60 on the average samples on horizons of this drilling.

The experimental values for distribution coefficients and retardate factors for radionuclides Cs-137 and Co-60 are given in Table IV and in Fig. 6 [4]

Table IV – values of distribution coefficients and retardate factors:

Horizon	**Cs –137**		**Co - 60**	
	K_d [ml/g]	**R**	**K_d[ml/g]**	**R**
A	65	227	55	193
B	90	448	35	186
C	120	700	70	407
D	70	442	63	397

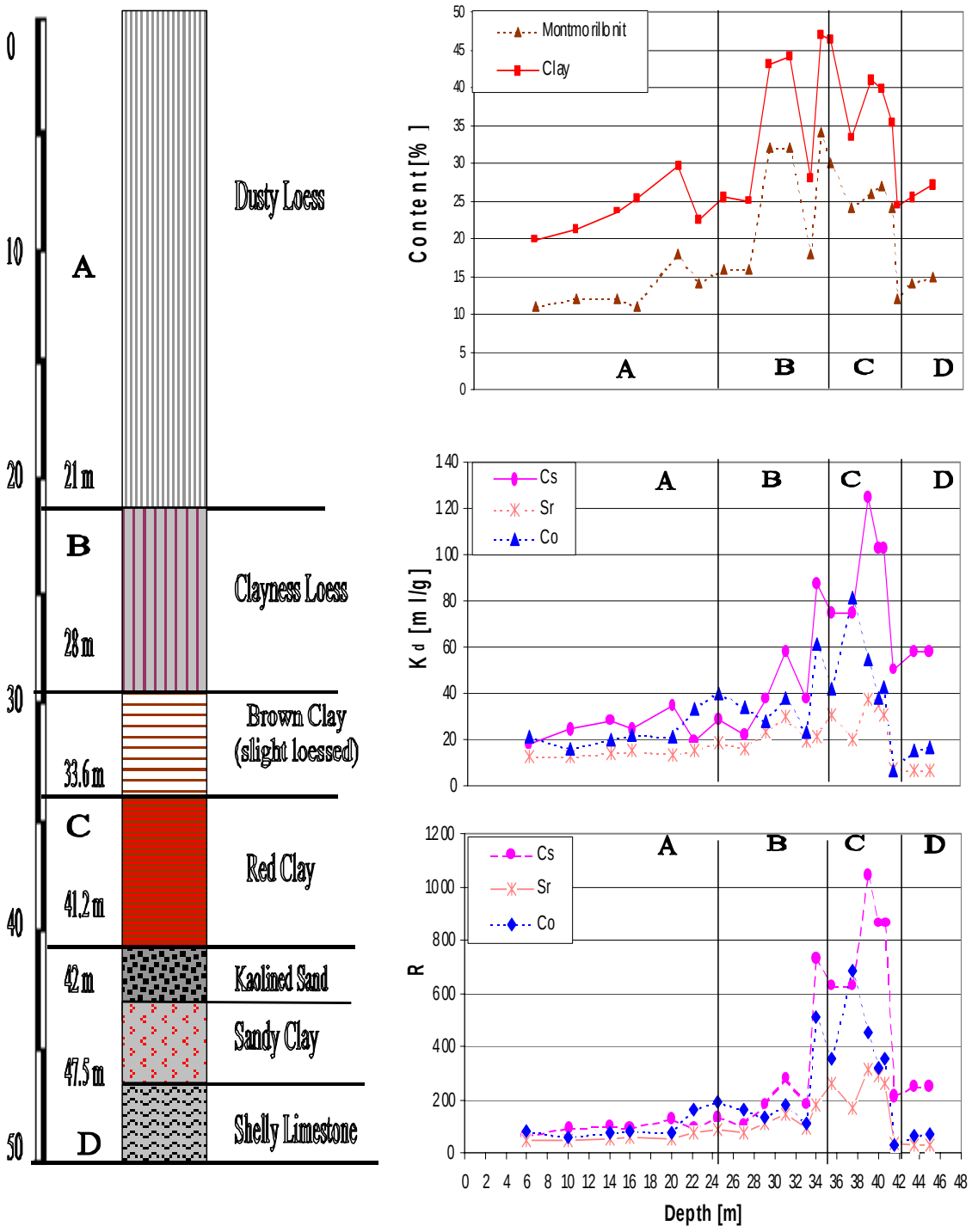


Fig. 5 - Lithographic section from Saligny drilling and K_d, R and clay content variation with depth

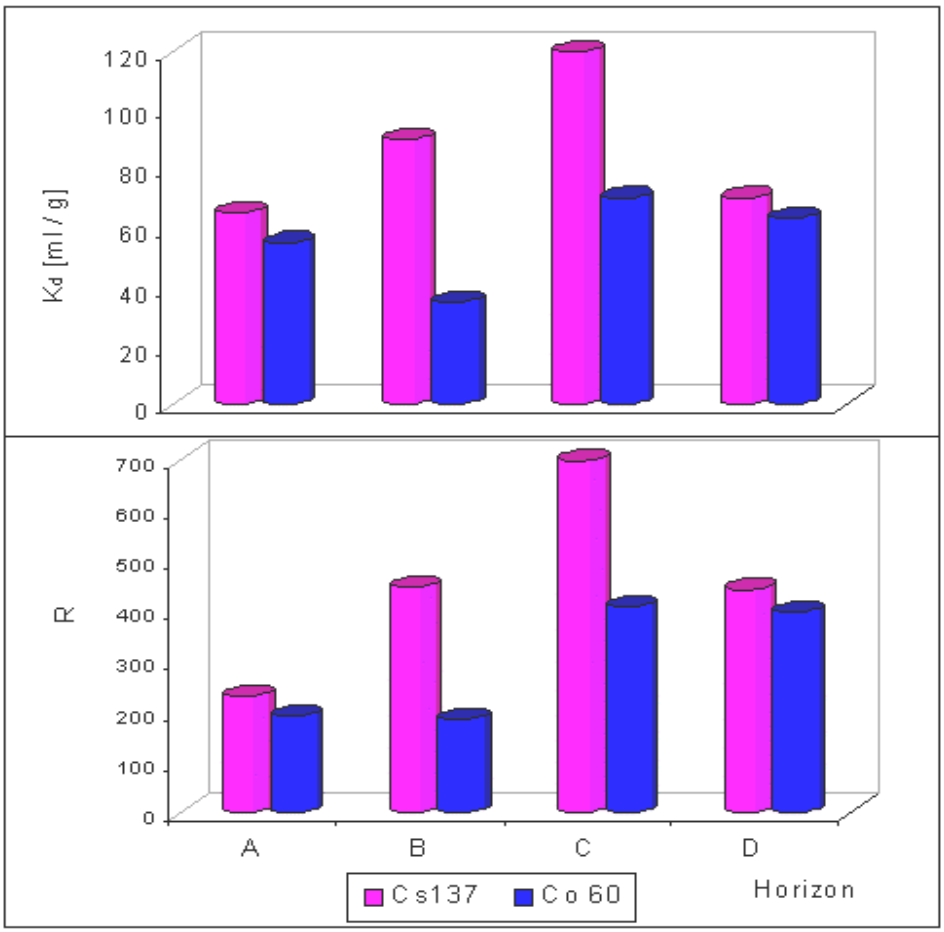


Fig. 6 – Distribution coefficients and retardate factors variation

CONCLUSION;

The goal of this paper was to determine the transport parameters (D_s, K_d, and R) of critical radionuclides (Cs-137, Co-60) from low level radioactive waste.

These parameters were determinate on the characteristic geological material of the Saligny site (Saligny was proposed as host site for low and intermediate level radioactive waste disposal).

A complete characterization of the site is required as input data for disposal safety assessment program.

The drilling lithography consists in four horizons: horizon A (a loess formation), horizon B (formation with two type of layer, clayness loess and brown clay), horizon C (red clay formation) and horizon D (clay with sand and limestone insertions formation).

On each of these horizons clay content was determinate, horizon C being the horizon with the highest clay content (~ 40%). The predominant mineralogical component of the clay is the montmorillonit what influences the radionuclide sorption (especially cesium)

The analyzed samples have a higher pH (9.2-9.6) because of high carbonates content of the samples.

The cationic exchange capacity varies between 8 and 20 meq/100g, the highest value reaching in horizon C.

The analyze of results, show that the distribution coefficient values in the loess layers are smaller for Cs-137 with an order of magnitude than these for clay layers and for Co-60 a order of magnitude is same in all type of soil.

The values of diffusion coefficients for Cs-137 and Co-60 in the loess layers are bigger with an order of magnitude than for clay layers.

Maximum of clay content corresponds with the maximum of retardation factor and with the minimum of diffusion coefficient.

The experimental results obtained of us are comparable with those form specialized literature for same type of soil and range of concentration.[6]

From analyses of experimental results we find a good behavior of clay formation in the sorption process of radionuclides, consequently the clay can play the roll of natural barrier in the radionuclide migration from disposal.

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