# Radiocarbon Sorption on Loess and Improved Loess Samples

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*[14]C sorption characteristics on the natural loess sampled from Saligny site and on mixtures of loess with different percents of Portland cement and Na type bentonite were determined performing batch sorption experiments. These experiments showed that while the bentonite added to the natural loess has a negligible effect on ^{14}C sorption, the low ^{14}C distribution coefficient on the natural loess is considerably improved by the Portland cement added to the loess. The values of ^{14}C distribution coefficient increased from 2.06L/Kg for natural loess to 42.40 L/kg by adding 9% of cement to the natural loess. This could have an important effect on the radiological impact due to the ^{14}C waste disposal on Saligny site.*

*Keywords: [14]C, sorption, loess, bentonite, cement*

The near surface repository for the low and intermediate level (LIL) radioactive waste from Cernavoda Nuclear Power Plant (NPP) operation and decommissioning will be built on Saligny site and will have dusty loess as foundation field. Loess is a foundation field with good mechanical properties only for reduced humidity, but its increased porosity determines a reduced resistance at higher humidity, when its structure is practically destroyed. Also, the bearing capacity and specific deformation of the natural loess do not recommend it as foundation field for objectives whose stability in time is absolutely necessary, as it is the case of the LIL waste disposal facility [1]. Consequently, the natural loess has to be improved to obtain a foundation ground able to guarantee the required resistance and stability in time.

In order to select the method for Saligny loess improvement, GEOTEC Bucharest have built at Cernavoda an experimental plot consisting of an embedded compacted loess and mixtures of loess with different percentage of cement and bentonite [2]. Besides the improvement of the geotechnical properties of the natural loess, the admixtures added to the natural loess will change its geochemistry and consequently the retention capacity of the radionuclides that will be potentially released from the repository.

Due to its high mobility in ground water systems, half-live (5730 years) and its inventory in LIL waste, ^{14}C is one of the radionuclides of concern for LIL waste disposal at Saligny site and it represents the major contributor to the total doze [3].

*Sorption experiments*

Sorption experiments were performed to test the effect of the mixtures added to improve the geotechnical properties of the natural loess on the ^{14}C retention.

Radionuclide sorption is usually described by the distribution coefficient ($K_d$), defined as the ratio of the quantity of contaminant sorbed per unit mass of solid to the equilibrium concentration of the contaminant in solution [4]:

$$K_d = \frac{A_{eq}}{C_{eq}} \qquad (1)$$

where:

$K_d$ represents the distribution coefficient (L/kg);

$A_{eq}$ - the contaminant concentration sorbed on solid matrix (Bq/kg);

$C_{eq}$ - the equilibrium contaminant concentration remained in solution (Bq/L).

Batch sorption experiments were performed contacting four grams of crushed material (loess and improved loess) with 40mL of ^{14}C solution. Four solutions with ^{14}C concentrations ranging between 4.2E+02Bq/L and 2.6E+04 Bq/L were used to estimate the radiotracers sorption isotherms at room temperature (21± 3°C). A standard of sodium acetate ($CH_3COONa . 4H_2O$) with ^{14}C specific activity of 4Ci/mol (9.61E+11 Bq/kg) was used to prepare the ^{14}C solutions.

Experiments were performed in 50 mL polycarbonate centrifuge tubes kipping constant the soil/solution ratio for all experiments (1/10) and the contacting time (7 days). All the samples were run in duplicate and one control sample with only the ^{14}C solution was run in the same conditions to check the possible sorption on the surfaces of the test tubes. Also, a blank sample was run for each sample to determine the ^{14}C background.

After the equilibration period solid-solution separation was attained by centrifugation (using a Universal 32 Type centrifuge) at 4.000 rpm for 30 min and 1mL aliquot of the supernatant was removed for radiotracers analysis. [14]C concentrations were determined using a 2100 Tri-Carb Packard liquid scintillation analyzer.

The improved loess samples were prepared in laboratory, using the same admixtures (cement and bentonite) percents as those used in the experimental plot [2]:

- Sample I - compacted loess without admixtures;
- Sample II - loess with 8% cement and 2% bentonite (II);
- Sample III - loess with 7% cement and 3% bentonite(III);
- Sample IV - loess with 5% cement and 2% bentonite (IV).

In addition, a mixture of loess with 9% of cement was prepared and used in the sorption experiments (sample V).

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The loess used in the laboratory preparation of the five samples was taken from one of the drills performed in Saligny site (FS 30) from 4m depth while the bentonite used was Na type.

## Results and discussions

The cement introduced in the sorption sistem (solid sample with the liquid containing the radionuclide) increase the pH of the solid/liquid mixtures from 7.5 for the natural loess sample to 11.5 - 12 in the test tubes containing samples II to V.

After the determination of the $^{14}C$ content in the aliquots sampled from the centrifuged tubes, the quantity of $^{14}C$ sorbed on the solid matrix was calculated using the following relation:

$$A_{eq} = \left(C_0 - C_{eq}\right) \cdot \frac{V}{m} \qquad (2)$$

where:

$A_{eq}$ is the radionuclide concentration sorbed on solid matrix (Bg/kg);

$C_0$ - the initial aqueous concentration of radionuclide (Bq/L);

$C_{eq}$ - equilibrium contaminant concentration in solution (Bq/L);

V - solution volume (mL);

M - the mass of crushed solid phase present in the batch experiments (g).

Linear [5], Freundlich [6, 5] and Langmuir [7, 5] sorption models were used to fit experimentally data but reasonably coefficients of correlation were obtained only for Linear and Freundlich models suggesting that the $^{14}C$ sorption on the investigated samples was not a monolayer sorption since the Langmuir sorption model usually fits well the experimental data in the case of a monolayer adsorption [5].

The linear sorption isotherms obtained for the $^{14}C$ sorption on the 5 samples are presented in figure 1 and the values for distribution coefficients, determined from the slope of these isotherms, are presented in table 1. In table 1 are also presented the correlation coefficients of experimental data with this sorption model.
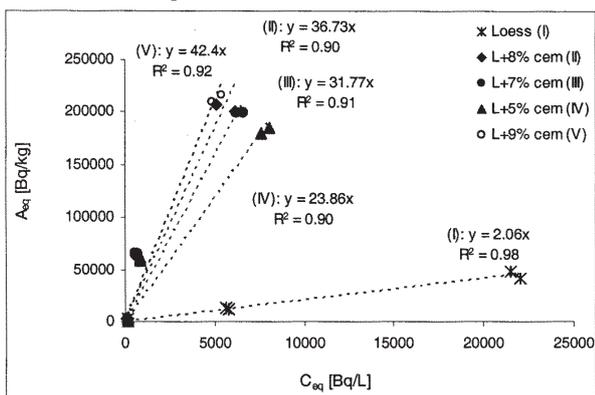


Fig. 1. Linear sorption isotherms for $^{14}C$ on natural and improved loess samples

Experimental data were also plotted logarithmically and the following Freundlich linearized form was used to obtain the Freundlich sorption characteristics (sorption constant and the dimensionless exponential constant):

$$log\,A_{eq} = log\,K_F + N\,log\,C_{eq} \qquad (3)$$

where:

$K_F$ is Freundlich adsorption constant [L/kg];

N - a dimensionless constant related both to the relative magnitude and diversity of energies associated with a particular sorption process.

The Freundlich sorption characteristics ($K_F$ and N) were estimated from the slopes and intercepts of the isotherms (fig.2) and are presented in table 1. The coefficients of correlation between experimental data and this sorption model are also presented in table 1.
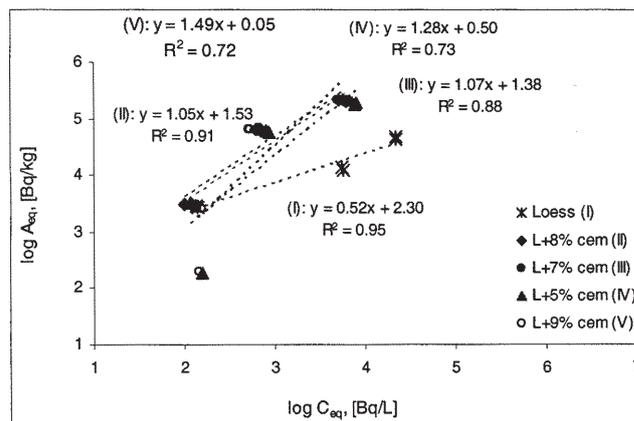


Fig. 2. Linearized Freundlich sorption isotherms for $^{14}C$ on natural and improved loess samples

The best fit were obtained for linear sorption model (table 1); values of correlation coefficients ($R^2$) range between 0.98 for natural loess and 0.90 for loess mixed with 5% of cement and 2% of bentonite (IV). Even the fits with the Freundlich model were not as good as those obtained with the linear model, fitting data with the Freundlich model brings additional information regarding the sorption mechanism.

Using the Freundlich model different behavior of $^{14}C$ on the two types of loess samples (natural and improved loess) were observed. The exponential constant (N) is less than one for the natural loess but it is higher than one for samples that have cement in their composition. Values of N less than one could suggest that significant sorption takes place at low contaminant concentration but the increase in the amount contaminant sorbed with concentration becomes less significant at higher concentrations. In this situation, the $^{14}C$ mobility in natural loess could be significantly greater for the higher initial concentrations.

Values for N higher than one could suggest that significant sorption may take place even at high ion concentration, in

**Table 1**
$^{14}C$ SORPTION CHARACTERISTICS

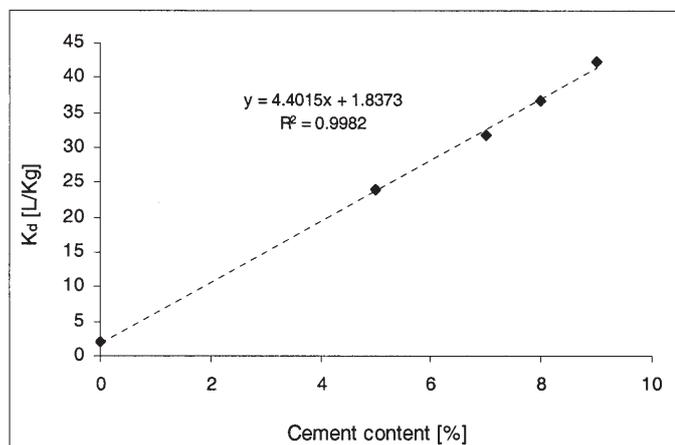| Sample ID | Sorption characteristics | | | | |
|---|---|---|---|---|---|
| | Linear model: $A_{eq} = K_d \cdot C_{eq}$ | | Freundlich model: $A_{eq} = K_F \cdot C_{eq}{}^N$ | | |
| | $K_d$ [L/kg] | $R^2$ | $K_F$ [L/kg] | N | $R^2$ |
| I | 2.06 | 0.98 | 200.31 | 0.52 | 0.95 |
| II | 36.74 | 0.90 | 33.88 | 1.05 | 0.91 |
| III | 31.77 | 0.91 | 24.09 | 1.07 | 0.88 |
| IV | 23.86 | 0.90 | 3.20 | 1.28 | 0.73 |
| V | 42.40 | 0.92 | 1.01 | 1.49 | 0.72 |

Fig. 3 Correlation between $^{14}$C distribution coefficients and the percentage of the Portland cement added to the Saligny natural loess

other words $^{14}$C distribution coefficient on loess samples having cement in their composition could be higher if $^{14}$C concentration increases over the range used for these experiments. Typically, values for N higher than one describe the precipitation process [8].

Analyzing the experimental data, no correlation between the bentonite content and $^{14}$C distribution coefficients were evidenced, but a direct correlation was observed between the distribution coefficients and the cement content of the samples. $^{14}$C distribution coefficients obtained as the slope of the linear sorption isotherm increase with the increase of the cement content (fig. 3). Previous studies performed for radionuclide sorption on cement matrices showed that $^{14}$C is one of the radionuclides presented in the radioactive waste that is highly sorbed on cement matrices [9]; the processes involved in $^{14}$C partitioning between solution and solid matrix are precipitation and izotopic exchange with inactive $^{12}CO_3^{2-}$ from the $CaCO_3$ presented in the cement [10]. Since these two proceses can not be separated, the distribution coefficients experimentaly determined for $^{14}$C on the investigated samples reflect the global efect of the two processes.

## Conclusions

$^{14}$C is one of the radionuclide presented in the LIL waste generated from Cernavoda NPP operation that has the half-life ($T_{1/2}$ = 5730 years) long enough to be potentially released from a surface repository after the operational control period (usually 300 years after the repository closure). Since it is negligible retarded by the natural environments, any engineered barrier that could improve its confining in the repository zone has an important impact on repository safety assessment.

Significant improvement of the $^{14}$C distribution coefficient was achieved by adding Portland cement to the natural loess. Batch sorption experiments showed that the $^{14}$C distribution coefficient was more that one order of magnitude higher on the loess with 9% of cement than that obtained in the same experimental conditions for the natural loess: ~ 40 L/kg for loess with 9% of cement compared with ~ 2 L/kg for natural loess.

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