Influence of Distribution Coefficients on the Transfer of Radionuclides from Water to Geological Formation

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Abstract: The most likely process that can lead to the release of radionuclides from radioactive waste repository in a geological media is transport by groundwaters. Research in this field has lead to experimental determination of distribution coefficients. Influence of distribution coefficients was studied in detail for uranium and radium adsorbtion on clay. Therefore, with batch tests the influence of sorption and desorption coefficients in rock/groundwater systems of the Ciudanovita site was investigated. Results for corresponding studies with radium and uranium in clay-groundwater system are given which point to the possibility transfering laboratory batch data to field conditions by mathematical model. The present work is based mainly on this research direction: optimization and improvement of the performances obtained from the geo-chemical processes investigation methods in the waste dumps and the surrounding geological structures to isolate them, in order to reduce the negative environmental impact. Measurements of the two radionuclides concentrations in particles with different dimensions were made to supply accurate information regarding the selection of remediation strategies for the dumpsite in study.

Keywords: tailing dump, adsorption, desorption, radionuclides, distribution coefficients.

1. Introduction

Due to the singular importance of the physical and chemical reactions taking place inside the tailings deposit and the contamination potential, the present project allows the carrying out of a study regarding on one hand the chemistry and geochemistry of the uranium mill tailings deposits, respectively contamination of the surface water courses, by assessment of static and dynamic equilibrium between the soluble and insoluble forms, and, on the other hand, the accomplishment of a mathematical approach regarding the simulation of the natural radioactive elements migration in surface water courses [2].

The reversibility of an environmental reaction such as adsorption is of fundamental importance to the mobility of pollutants in the environment. If a contaminant which is dissolved in the aqueous phase can be isotopically distinguished from the same element bound by the solid, it is possible to simultaneously study the processes of uptake and release [9]. In order to describe the matter migration in the geosphere and biosphere, it is necessary to elaborate models considering on one hand the migration phenomena (seepage, diffusion, dispersion etc.), on the other hand the geochemical phenomena (speciation, dissolution/precipitation, adsorption/desorption, superficial complex formation) [1]. A combined chemistry-migration model shall be able to describe accurately (with certain simplifications) the evolution of a solution that contains radioactive elements in space and time [3].

Uranium is one of the radioelements whose mobility in soils may vary strongly depending on soil type and physico-chemical properties. Distribution coeficients, Kd, describe the mobility of elements in soils and rocks range in different environments from 0.03 in sandy soils to 20 000 in clayey soils [8]. The uncertainty associated with Kd values for several radionuclides results in a large variability of the predicted dose for humans after calculations, even when considering only site-specific soils.

Transport codes used for migration predictions usually include selected radionuclide Kd value stogether with hydrological parameters such as the rate of water movement. Several authors have compiled sets of Kd values for various radionuclides [5]. While these compilations indicate the likely range of environmental Kd values, they do not provide detailed information regarding the dependence of Kd on factors such as water chemistry or the mineralogy of the solid phase.

2. Material and methods

In many environmental systems, the measured elemental levels are extremely low, which requires large samples to be collected for analysis. It is rarely practical to use similar large volumes in the laboratory, which makes it

difficult to perform realistic laboratory experiments in a similar concentration range.

In this section, we summarize Kd data obtained in laboratory experiments with samples of Ciudanovita soils taken from field sites near waste dump.The distribution coefficient, or Kd value, is one of the simplest construct that describe contaminant sorption to sediment. It is the ratio of the contaminant concentration sorbed to the solid phase divided by the contaminant concentration in the liquid surrounding the solid phase:

$$Kd = C_{solid} / C_{liquid} \qquad (1)$$

where

C solid (M Kg^{-1}) and C_{liquid} (M l^{-1}) are the contaminant concentration in the solid and liquid phases, respectively.

The Kd value is commonly used to define the retardation factor, which is the ratio of the average linear velocity of water (ms^{-1}) divided by the average linear velocity of the contaminant (ms^{-1} [6].

For the second research cycle, where was studied the adsorption of radionuclides in the clay contaminated in groundwater, the expression to estimate the adsorption factor is [4]:

$$F_{des} = \frac{C_{f,f.l.des}}{C_{i,f.s.}} \times 100 \qquad (2)$$

where:

F_{des} = desorption factor (ml/g);

$C_{f,f.l.des.}$ = final concentration of radionuclides in the liquid stage after adsorption (mg/ml),

$C_{i,f.s.}$ = concentration of radionuclides during the solid stage at the beginning of the adsorption experience (mg/g).

The data reported here summarize sorption experiments for six samples, each representing a 5 cm interval within the top 15 cm of the two soil profiles.

Both the initial and final radionuclides content of radium 226 and natural uranium from the solid waste and clay samples were determined by means of the spectrometric gamma measurement chain HPGe-Oxford, with 40% efficiency.

Radium 226 present in liquid samples was determined by measurement of the alpha activity of the radium sulfate precipitate, chemically separated, together with barium and lead sulfates, measured with the system that measures the alpha and global beta radioactivity with FHT 1100 counter.

The concentration for natural uranium with chemical valence VI from the liquid samples, which is reduced to natural uranium with chemical valence IV by means of the zinc grains in hydrochloric acid environment 4.5 N, was compensated with arsenazo II and was spectophotometrically determined by measurement of complex U IV – Arsenazo III colour intensity, by means of a UV-VIS Analitik Jena AG spectro-photometer, Specord 205. The separation efficiency for for natural uranium is 83%. The typical radiochemical yields for radium 226 and natural uranium determinations were approximately 86% and 60%, respectively.

As the pH influences the migration of the two radionuclides, the pH of the eluted liquors was measured, by means of a Piccolo pH-meter with HI electrode.

3. Results and discussion

The two radionuclides concentration values, measured following the sorption and adsorption processes on the clay with various granularity in stationary regime are presented in tables 1-2.

TABLE 1. Radionuclide concentrations (in μg/g) of the whole < 0,5 mm clay fractions

	^{226}Ra [μg/g]	U$_{nat}$ [μg/g]
Uncontamined clay	0.57	0.91
Contamined clay	24.6	75.7

TABLE 2. Radionuclide concentrations (in μg/g) of the whole > 5mm clay fractions

	^{226}Ra [μg/g]	U$_{nat}$ [μg/g]
Uncontamined clay	0.68	1.20
Contamined clay	48.9	103

Measurements of radionuclide concentrations in various soils fractions were made to provide ancillary information pertinent to the selection of remediation strategies at the study site. The fact that radionuclide from smaller size fraction was inconsistent, suggests that soil washing, which removes contamined smaller particles and returns to the remediation site less contamined larger particles, would not be a viable option at this site.

Soil washing is especially effective when a majority of contaminants are associated with a small, well-defined, size fraction.

Kd values are presented in table 3 and 4.

The variability of the measured Kd values was extremely high. Among the more plausibile causes for this variability is that the samples appeared to differ greatly in texture, color and organic matter content, hence they had different sorption properties.

The ioni of radium of water infiltration are in balance with reversible adsorbed cations and their relationship is expressed through constant distribution Kd. The ion of radium falling in these two forms (in solution and reversible adsorbed) is always alimentation. It is recognized that the places where the adsorption radium are covered initial warehouse sulphate.

After disappear the places of soluble sulphate, the radium ions are still blocked by barium sulphate difficult soluble. It can lead to a strong growth rate of distribution Kd.

Kd is a parameter that is potentially a very large impact on the migration of constituents at the top of waste dump. The Kd increase in the order Unat <^{226}Ra. It is noted that the values Kd increase invaribil with decrees concentrations ^{226}Ra and Unat. This phenomenon can be explained by the ability to retain radionuclides on the clay. Then, appears the inverse relationship between Kd and concentration.

The Kd obtained shows a solubilisation low ^{226}Ra, so a slowing in migration, while uranium is more mobile.

TABLE 3. Sorption Kd values for U_{nat} [in mL/g, Eq (1)]

Kd for U_{nat}, clay > 5mm	Kd for U_{nat}, clay<0,5mm	Time [days]
0,011	0,006	2
0,023	0,014	4
0,034	0,018	6
0,041	0,031	8
0,056	0,055	10
0,079	0,067	12
0,094	0,094	14
0,108	0,108	16
0,123	0,123	18
0,136	0,136	20

TABLE 4. Sorption Kd values for ^{226}Ra [in mL/g, Eq (1)]

Kd for ^{226}Ra clay > 5mm	Kd for ^{226}Ra clay<0,5mm	Time [days]
0,015	0,015	2
0,031	0,030	4
0,047	0,046	6
0,063	0,063	8
0,080	0,078	10
0,097	0,097	12
0,114	0,112	14
0,130	0,130	16
0,147	0,146	18
0,164	0,164	20

Kd values are correlated with the ability cationic exchange. Ra^{2+} exists as cation in pH 5-8, and U (VI) at a pH greater than 7 are as anion. Therefore, the ability of cationic exchange ^{226}Ra is greater than the U.

Hydrodinamic dispersion allow gradual expansion of a contaminant to the front channels with laminar flow, during the process, the peak of contaminant decrease thanks dilution.

Water underground is nourished by rain and infiltration of surface water in the centre, parent portions of the land mass. Directorate of underground water is the end date hydraulic degree. The water is moving underground in regions with large hydropower capacity, to the waters with small hydropower capacity.

The values of the adsorption coefficients calculated based on the experimental data with formula 1 are presented in table 5.

TABLE 5. Desorption Factor values [in mL/g, Eq (2)]

F_{des}	^{226}Ra	U_{nat}
Argilă <0,05 mm	1,172	0,107
Argilă >5mm	0,152	0,123

The values obtained for the adsorption factor on clay proves that even though clay can slow down the rate of flow, almost none of the underground element component is permeable. If the groundwater has enough time, it will cross the clay; then the contaminants can be diffused through clay even when their content of water is reduced.

4. Conclusions

These results have important implications for remediation strategies. To traditional sorption Kd values, desorption Kd values are conditional in nature, and therefore, dependent on the environmental conditions under which they were collected. Thus, if conditions change at the field site, it is expected that the Kd values for the radionuclides may change, especially for sensitive elements like U. Uranium sorption properties require careful attention when defining site-specific values of Kd for biosphere safety assessments of nuclear waste disposal programs or mine drainage remedial measures.

Since the Kd value is a ratio of the concentration of the element in the solid phase to its concentration in the soil solution, this parameter is highly sensitive to small changes in the concentration in the liquid phase. Soil variability within a specific area is sometimes large enough to have Kd values ranging over five orders of magnitude [7].

Also, desorption Kd are expected to change slightly as a function on time. For example, if a desorption Kd values measured shortly after a radionuclide comes in contact with a soil, the Kd value would be expected to be smaller than if it had been measured after the radionuclide had "aged" with the soil. Finally, one important advantage of desorption Kd values that can not be over emphasized is that do not require that the experimenter make any assumption about the species existing in the system. In case of sorption experiments, the experimenter must select a specie(s) to spike into the solid/liquid system. Given the inherent difficulties in estimating particulate-sorbed fractions of radionuclides, and resuspension and transport, it is not clear, however, that further research would necessarily reduce the uncertainties.

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