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Determination of ^{137}Cs and ^{85}Sr transport parameters in fucoidic sand columns and groundwater system

Invited Article

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Abstract: The determination is based on the evaluation of experimentally obtained breakthrough curves using the erfc-function. The first method is founded on the assumption of a reversible linear sorption/desorption isotherm of radionuclides on solid phase with constant distribution and retardation coefficients, whereas the second one is based on the assumption of a reversible non-linear sorption/desorption isotherm described with the Freundlich equation, *i.e.*, with non-constant distribution and retardation coefficients. Undisturbed cores of 5 cm in diameter and 10 cm long were embedded in the Eprosin-type cured epoxide resin column. In this study the so-called Cenomanian background groundwater was used as transport medium. The groundwater containing radionuclides was introduced at the bottom of the columns at about 4 mL h^{-1} constant flow-rate. The results have shown that in the investigated fucoidic sands: (i) the sorption was in principle characterized by linear isotherms and the corresponding retardation coefficients of ^{137}Cs and ^{85}Sr, depending on the type of sample, were approximately 13 or 44 and 5 or 15, respectively; (ii) the desorption was characterized by non-linear isotherms, and the retardation coefficients of the same radionuclides ranged between 23-50 and 5-25, respectively. The values of the hydrodynamic dispersion coefficients of these radionuclides varied between 0.43-1.2 cm^2 h^{-1}.

Keywords: *Sorption and desorption • Linear and non-linear isotherms • Dynamic flow • Breakthrough curves*

1. Introduction

Remediation of underground areas after acid leaching of uranium ore requires a in-depth knowledge about the transport of radionuclides in the surrounding rocks, which may affect negatively the quality of the groundwater. The chemical remediation processes also require information on the sorption properties of the affected rocks. One of the important rock constituents in the Stráž pod Ralskem site (Czech Republic) are fucoidic sands, which constitute a significant part of the Cenomanian aquifer [1,2]. Therefore, it is of great importance to determine, among others, their retardation properties with respect to univalent and divalent radionuclides dissolved in the groundwater [3,4]. The determination of sorption and desorption parameters in sand materials are carried out usually under static batch conditions, in which solid and liquid phases are contacted by mutual mixing or shaking a certain time period until equilibrium distribution of radionuclides. The transport parameter (*e.g.* the retardation coefficient) is determined indirectly by calculation from the value of a distribution coefficient [3-5]. More interesting methods were also used under dynamic conditions, in which the solid phase was placed into the column and the transport parameters of radionuclides were measured directly from the activity of aqueous phase passing through the column by using a breakthrough curve technique [6-12].

In this work, for determination of the most important transport parameters of $^{137}Cs^{+}$ and $^{85}Sr^{2+}$ (*i.e.*, retardation and hydrodynamic dispersion coefficients in fucoidic sands), a through-flow dynamic column method has been used. For column beds, intact undisturbed samples of drilled fucoidic sandstones were applied. The mobile phase was made by a background groundwater originating from the Cenomanian aquifer (CBW), in which

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the respective water-soluble salts $CsNO_3$ and $Sr(NO_3)_2$ were dissolved. Each experiment consisted of two parts: sorption of radionuclides in a given bed until saturation, followed by desorption of these radionuclides with CBW. The experimental data were evaluated by means of the erfc-function with incorporated equilibrium linear or non-linear sorption/desorption isotherms. The models of equilibrium sorption and/or desorption dynamics based on the erfc functions are commonly and extensively used for fitting experimental data obtained in advective and diffusive transport phenomena, among others of radionuclides in rock- or soil- groundwater systems [3-10]. Both linear and non-linear approaches were compared and assessed.

2. Experimental procedure

2.1. Column preparation

The borehole samples of fucoidic sandstones were taken from two localities of the former uranium underground (in-situ) leaching area in Stráž pod Ralskem (Czech Republic) [13]. Undisturbed cores of 5 cm in diameter and 10 cm height were embedded in the Eprosin-type cured epoxide resin column. The column ends were sealed with an acrylate resin and inlet and outlet tubes were mounted. The core sample and a part of the experimental setup are presented in Fig. 1. Results of the chemical bulk analysis of sands are given in Table 1. Some important physical parameters of fucoidic sand columns are summarized in Table 2. Before the experiments, the sands were saturated with a background groundwater originating from the Cenomanian aquifer (CBW) in MIPC-18 borehole. The chemical properties of CBW are given in Table 3. The preparation and mounting of fucoidic sand columns were made in DIAMO Technological Laboratories of Mining and Treatment of Uranium Department in Stráž pod Ralskem according to the contract with Nuclear Research Institute Řež plc [13]. The bulk analysis of fucoidic sand and cenomanian water was made by the same laboratories.

2.2. Procedure

Commercially available carrier-free $^{137}Cs^{+}$ and $^{85}Sr^{2+}$ of high radiochemical and radionuclidic purity were added into the CBW. To the CBW solution of radionuclides were added nitrate salts of cesium and strontium as isotopic carriers in a concentration of 10^{-6} mol L^{-1}. The water was spiked with radionuclides in order to reach a level of 10000 counts per min (cpm) (with RSD 1%) in 5 mL of sample aliquots.

Figure 1. Core sample of the fucoidic sand and a part of the experimental setup

Table 1. Chemical bulk analysis of fucoidic sands from two localities (SD = 2-20%)

Component	Locality	
%	VP10C7040	VP8C7095
Si	45.0 ± 0.9	44.0 ± 0.9
Al	1.25 ± 0.06	1.19 ± 0.05
Ca	0.053 ± 0.011	0.006 ± 0.013
Fe	0.207 ± 0.025	0.422 ± 0.044
Ti	0.142 ± 0.016	0.133 ± 0.017
K	0.030 ± 0.007	0.048 ± 0.009
MgO	-	-
O	53.30 ± 1.24	54.18 ± 1.36
C_{inorg}	0.951 ± 0.114	0.710 ± 0.099
C_{org}	0.561 ± 0.085	0.550 ± 0.083

The sorption experiments were carried out separately for ^{137}Cs or ^{85}Sr. The active CBW from a suitably large beaker (of several litres) was introduced at the bottom of columns (against gravity), by the use of a multi-head peristaltic pump, with flow-rate of 4.4 ± 0.2 mL h^{-1} (0.78 ± 0.01 cm h^{-1} water seepage velocity). From the beaker several 5 mL standards were taken for comparison with the outflow CBW from the column. After the input activity at the column outlet had been obtained, the

Table 2. Some important physical parameters of fucoidic sand columns

Characteristic parameters	**Locality**			
	VP10C7040		**VP8C7095**	
	Number of columns			
	48118Cs	**48118Sr**	**48562Cs**	**48562Sr**
G, g	368.6	381.8	362.3	359.0
D, cm	5.0	5.0	4.9	4.9
L, cm	10.1	10.1	10.1	10.2
S, cm²	18.8	19.8	19.8	18.6
V, cm³	199.1	187.0	193.3	193.0
ρ, g cm⁻³	1.849	1.918	1.923	1.857
θ, cm³ cm⁻³	0.307	0.282	0.280	0.304
PV, cm³	57.7	52.5	50.3	56.4
KF_v, m s⁻¹	3.21×10^{-7}	4.42×10^{-7}	6.44×10^{-7}	1.16×10^{-6}

footnotes:
G - mass of the dry sand monolith, SD < 2 g
D - diameter of inlet and outlet filtration area, RSD < 2%
L - length of sand monolith, RSD < 0.5%
V - volume of sand monolith, $V = 0.25\cdot D^2\cdot L$, SD < 1 cm³
ρ - volume mass of sand (bulk density), G/V, RSD < 2%
θ - porosity, 1- (G/(2.67·V)), RSD < 5%
PV - total pore volume, RSD < 3%
KF_v - hydraulic conductivity in the vertical orientation, RSD ≈ 10%

beaker was filled with inactive CBW, which was used for desorption of a given cation at the same flow-rate. During each experiment, 5 mL aliquots were taken from the column effluent at certain time intervals. The activity of aliquots and standards was measured by a gamma counter equipped with a NaI/Tl detector, an automatic sample changer and software for data acquisition and evaluation (1480 Automatic Gamma Counter WIZARD 3 Perkin Elmer Precision).

3. Theoretical procedure

3.1. Linear isotherm approach

Theoretical sorption breakthrough curves (BTC_S), expressed as a dependence of the theoretical relative activity of a given component outgoing from the column ($(A_{relS})_{theor}$) on the number of pore volumes (n_{PVS}), were calculated by Eqs. 1a and 1b. These equations were derived with assumption of reversible linear sorption isotherm type of $q = K_d\cdot C$, where q is the concentration of given component in solid phase, C is its concentration in liquid phase, and K_d is the distribution coefficient [14]. It holds for the theoretical relative output activity of the liquid phase from the column:

$$(A_{relS})_{theor} = (A_{tS})_{theor}/A_0 = 0.5\cdot \mathrm{erfc}[((R_S)_{theor} - n_{PVS})/ /(2\cdot((R_S)_{theor}\cdot n_{PVS}/Pe)^{0.5})] \qquad (1a)$$

$$(A_{relS})_{theor} = (A_{tS})_{theor}/A_0 = 1 - \{0.5\cdot \mathrm{erfc}\,[-((R_S)_{theor} - - n_{PVS})/(2\cdot((R_S)_{theor}\cdot n_{PVS}/Pe)^{0.5})]\}, \qquad (1b)$$

where: $(R_S)_{theor} = 1 + \rho\cdot(K_{dS})_{theor}/\theta,$ (2)

$q = (K_{dS})_{theor}\cdot C.$ (3)

Here denotes:
A_0 - input activity of liquid phase on the top of the column (cpm),
$(A_{tS})_{theor}$ – theoretical value of output activity of liquid phase leaving the column in the course of sorption at time tS (cpm),
n_{PVS} ($= u\cdot tS/L$) - experimental value of number of bed pore volumes in the case of sorption at time tS,
tS – time of sorption experiment (*e.g.* h)
erfc - complementary error function,
$(R_S)_{theor}$ – theoretical sorption retardation coefficient,
Pe - Peclet number ($= u\cdot L/D_d$) of the column (from the point of view of experimental conditions, it is supposed that the value of Peclet number is the same for both sorption and desorption),
u – water seepage velocity (cm h^{-1}),
L – length of the bed in the column (cm),
D_d – hydrodynamic dispersion coefficient (cm^2 h^{-1}),
$(K_{dS})_{theor}$ – theoretical sorption distribution coefficient (mL g^{-1}),
q and C – total concentration of given component ($CsNO_3$ or $Sr(NO_3)_2$) in solid (mmol g^{-1}), and liquid (mmol mL^{-1}) phase, respectively,
ρ – bulk density (g cm^{-3}),
θ – porosity (cm^3 cm^{-3}).

It should be noted that for the calculation of $(A_{relS})_{theor}$, Eq. 1a can be used directly until

Table 3. Parameters of background groundwater originating from Cenomanian aquifer (CBW)[1] (SD = 5-20%)

Chemical composites	Concentration mg L^{-1}	Chemical composites	Concentration mg L^{-1}
sulfates	18 ± 2	Cr	< 0.002
nitrates	< 2	Fe total	0.06 ± 0.01
nitrites	< 0.005	K	1.3 ± 0.2
chlorides	3.0 ± 0.3	Mg	7.7 ± 0.8
carbonates	-	Mn	0.14 ± 0.03
fluorides	< 0.2	Na	3.8 ± 0.5
NH_3 and NH_4^+	< 0.05	Tl	< 0.01
Al	-	V	< 0.001
As	< 0.02	Zn	-
Be	< 0.001	Ni	-
Ca	40	Dissolved substances[2]	153 ± 9

[1] *Conductivity 27 mS m^{-1}, pH 8.2.*
[2] *Residue after evaporation of CBW at 105°C.*

$(A_{relS})_{theor} \leq 0.5$ (*i.e.*, until $((R_S)_{theor} - n_{PVS}) \geq 0$, but for the calculation of $(A_{relS})_{theor} > 0.5$). If $((R_S)_{theor} - n_{PVS}) < 0$, Eq. 1b should be used, which was derived from Eq. 1a according to [14-16] (because it holds: erfc $(-x) = 2 -$ erfc(x)).

For the calculation of the theoretical desorption breakthrough curve (BTC_D), which is centrally symmetric to the sorption BTC_S, the following Eqs. 4a (if $(A_{relD})_{theor} \geq 0.5$) and 4b (if $(A_{relD})_{theor} < 0.5$) were used, respectively:

$$(A_{relD})_{theor} = (A_{tD})_{theor}/A_0 = 1 - \{0.5\cdot \mathrm{erfc}[((R_D)_{theor} - - n_{PVD})/(2\cdot((R_D)_{theor}\cdot n_{PVD}/ Pe)^{0.5})]\}, \tag{4a}$$

$$(A_{relD})_{theor} = (A_{tD})_{theor}/A_0 = 1 - (1-\{0.5\cdot \mathrm{erfc}[- - ((R_D)_{theor} - n_{PVD})/(2\cdot((R_D)_{theor}\cdot n_{PVD}/ Pe)^{0.5})]\}), \tag{4b}$$

where: $$(R_D)_{theor} = 1 + \rho \cdot (K_{dD})_{theor}/\theta, \tag{5}$$

$$q = (K_{dD})_{theor} \cdot C. \tag{6}$$

The meaning of the symbols by analogy (*i.e.*, if index *S* (denotes sorption) is substituted by index *D* (denotes desorption)) is the same as in previous equations.

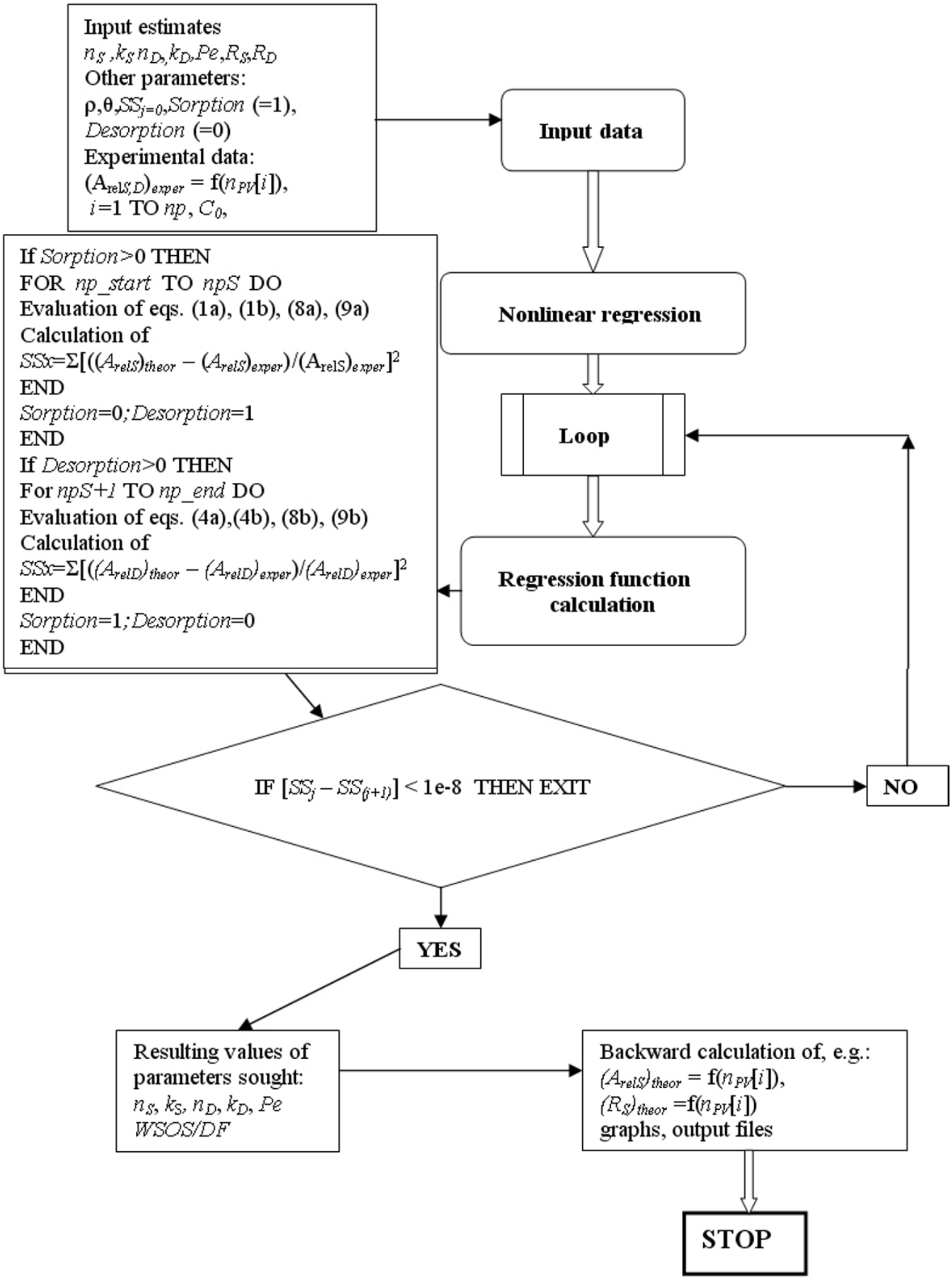
The obtained sorption BTC_S has a well-known S-shape; the desorption BTC_D has a reverse shape and is mirror-symmetric to the former, both of them with the inflexion point (see index *i*) at the position where for experimental values of retardation coefficients it holds: $(R_S)_{exper} = n_{PVSi}$ or $(R_D)_{exper} = n_{PVDi}$. This generally occurs at $A_{rel} = 0.5\cdot A_0$ [14-16]. It is evident that to the values of $(R_S)_{exper}$ or $(R_D)_{exper}$ correspond the values of $(K_{dS})_{exper}$ or $(K_{dD})_{exper}$, respectively, which can be calculated by means of Eq. 5, generally by relation $(K_d)_{exper} = ((R)_{exper} - 1)\cdot\theta))/\rho$. (These are the basic properties of breakthrough curves based on the error and/or complementary error functions.)

The evaluation of experimental data, (*i.e.*, $(A_{relS})_{exper} = (A_{tS})_{exper}/A_0 = f(n_{PVS})$ and $(A_{relD})_{exper} = (A_{tD})_{exper}/A_0 = f(n_{PVD})$), by means of Eqs. 1a, 1b, 2 and 3, and Eqs. 4a, 4b, 5 and 6, respectively, consisted of their simultaneous fitting in iteration cycle by the Newton-Raphson multidimensional method of non-linear regression (for the algorithm of fitting, see Fig. 2), in the course of which the values of three parameters, namely, K_{dS}, K_{dD} and *Pe* were sought [17]. ($(A_{tS})_{exper}$ and $(A_{tD})_{exper}$ are experimental values of the output activity of liquid phase leaving the column in the course of sorption and desorption at time *tS* and *tD*, respectively.)

As fitting criterion, the quantity of *WSOS/DF* [18] (Weighted Sum of Squares divided by the Degrees of Freedom) was calculated; the agreement (the goodness-of-fit) can be regarded as acceptable if $0.1 \leq WSOS/DF \leq 20$. The respective computational code PNLRPa11.fm (Code Package Stamb-2010) was constructed for FAMULUS software product [19], which was used for calculation.

3.2 Non-linear isotherm approach

The above mentioned Eqs. 1a, 1b, 4a and 4b hold as well, but with some differences resulting from the fact that it deals with non-linear equilibrium isotherm. This is described with two-parametric (k_S and n_S or k_D and n_D) Freundlich equations (*i.e.*, with Eq. 7a in the case of sorption, or Eq. 7b in the case of desorption). As for the retardation coefficients, the general relations (Eqs. 8a and 8b) were used. According to these equations, the retardation coefficients are the functions of the concentration, namely functions of the first derivative of the equilibrium isotherms ($q = f(C)$), $f'(C)_S$ (see Eq. 9a) in the point of $C(L,n_{PVS})$ or $f'(C)_D$ (see Eq. 9b) in the point of $C(L,n_{PVD})$.



```
If $Sorption>0$ THEN
FOR $np\_start$ TO $npS$ DO
Evaluation of eqs. (1a), (1b), (8a), (9a)
Calculation of
$SSx=\Sigma[((A_{relS})_{theor} - (A_{relS})_{exper})/(A_{relS})_{exper}]^2$
END
$Sorption=0; Desorption=1$
END
If $Desorption>0$ THEN
For $npS+1$ TO $np\_end$ DO
Evaluation of eqs. (4a),(4b), (8b), (9b)
Calculation of
$SSx=\Sigma[((A_{relD})_{theor} - (A_{relD})_{exper})/(A_{relD})_{exper}]^2$
END
$Sorption=1; Desorption=0$
END
```

Figure 2. Algorithm (flow sheet) of the PNLRPa11.fm code for non-linear isotherm approach. (The meaning of symbols – see chapter Theoretical: *np* – total number of experimental points, *np_start* – starting point for calculation of *Sorption*, *npS* – end point for calculation of *Sorption*, *npS+1* – starting point for calculation of *Desorption*, *np_end* – end point for calculation of *Desorption*; $(A_{rel})_{theor}$, $(A_{rel})_{exper}$, n_{PV}, n_S, k_S, n_D, k_D, Pe, $(R_S)_{theor}$, $(R_D)_{theor}$, ρ,θ, SS_j, C_0, *WSOS/DF*.)

$$q = k_S \cdot C^{nS} \quad \text{(for sorption)} \tag{7a}$$

$$q = k_D \cdot C^{nD} \quad \text{(for desorption)} \tag{7b}$$

$$(R_S)_{theor} = 1 + (\rho/\theta) \cdot f'(C)_S \tag{8a}$$

$$(R_D)_{theor} = 1 + (\rho/\theta) \cdot f'(C)_D, \tag{8b}$$

$$f'(C)_S = dq/dC = (n_S \cdot k_S \cdot ((A_{relS})_{theor} \cdot C_0)^{(nS-1)}), \tag{9a}$$

$$f'(C)_D = dq/dC = (n_D \cdot k_D \cdot ((A_{relD})_{theor} \cdot C_0)^{(nD-1)}), \tag{9b}$$

where C_0 is the total concentration of a given component (*i.e.*, $CsNO_3$ or $Sr(NO_3)_2$) in the liquid phase.

By analogy with our previous publication [11], it was supposed that the Freundlich equation parameters, by means of which the retardation coefficients can be calculated, were constant for all experimental points throughout the given experiment. As in the case of the linear isotherm approach, the Newton-Raphson multidimensional method of non-linear regression [17] was used for evaluation of experimental data also by the non-linear isotherm approach, *i.e.*, $(A_{relS})_{exper} = f(n_{PVS})$ and $(A_{relD})_{exper} = f(n_{PVD})$. The regression function, the incorporation of which into iteration cycle can be found in Fig. 2, consisted of Eqs. 1a, 1b, 4a, 4b, 8a, 8b, 9a and 9b. As a primary result of regression, five parameters were obtained: k_S, k_D, n_S, n_D and *Pe*. If parameter $n_S \approx 1$ or $n_D \approx 1$, the corresponding system (process) was characterized by linear isotherm and k_S or k_D was identical with $(K_{dS})_{theor}$ or $(K_{dD})_{theor}$, respectively. Also in this case, as fitting criterion, the quantity of *WSOS*/DF [18] and the code of PNLRPa11.fm were used.

4. Results and discussion

In spite of the fact that the individual groups of monoliths were cut from relatively short sandstone blocks of about 30 cm in length, they exhibit distinctive geological heterogeneity (Tables 1 and 2). Column experiments were preceded by orientation static (batch) tests to find the carrier concentration range of Cs (and Sr) ions suitable for determination of the transport parameters of their radionuclides in dependence on the sorption capacity [13]. Experiments with 1 g of fucoidic sands No. 48714 and 20 mL of CBW have shown that the most suitable concentration level is approx. 10^{-6} mol L^{-1} and therefore this carrier concentration was chosen for dynamic experiments with aqueous CBW solution of $CsNO_3$ or $Sr(NO_3)_2$ spiked with $^{137}Cs^+$ or $^{85}Sr^{2+}$, respectively. The flow-rates in the columns were close to each other (see chapter 2.2) and they appeared sufficient to reach sorption and/or desorption dynamic equilibrium (the residence time of the solution in a given bed was approx. 13 – 14 hours).

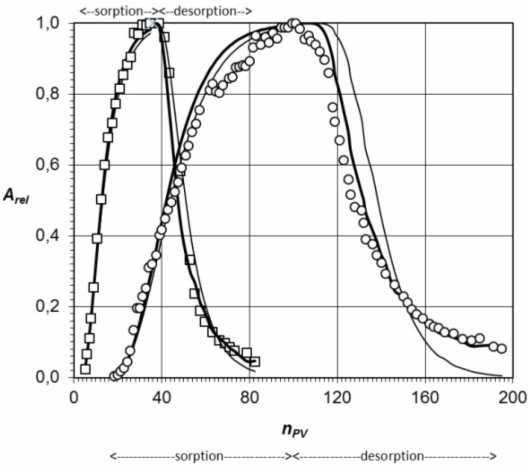


Figure 3. Fitting of the sorption and desorption BTCs of ^{137}Cs obtained in the columns with samples 48562Cs (□) and 48118Cs (○) (experimental values: symbols, and theoretical: thin curves – linear isotherm approach, thick curves – non-linear isotherm approach)

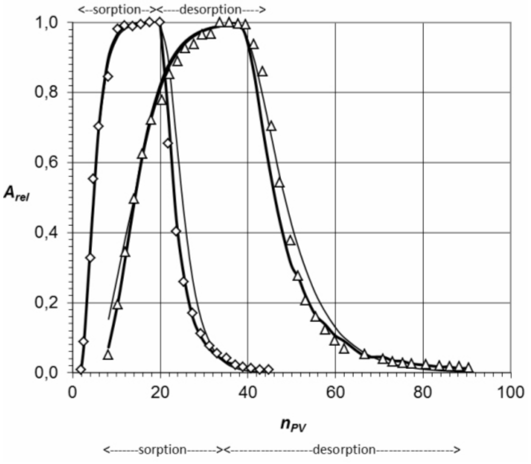


Figure 4. Fitting of the sorption and desorption BTCs of ^{85}Sr obtained in the columns with samples 48562Sr (◊) and 48118Sr (Δ) (experimental values: symbols and theoretical: thin curves – linear isotherm approach, thick curves – non-linear isotherm approach)

The course of dynamic experiments has been presented in Fig. 3 for $^{137}Cs^+$ and in Fig. 4 for $^{85}Sr^{2+}$. Both the experimental and theoretical breakthrough curves (BTCs) have been given. As it was explained above (in the theoretical chapter), linear and non-linear isotherm approaches were used for fitting both experimental sorption and desorption data. The resulting values of parameters obtained in the course of non-linear regression procedure are summarized in Table 4 (linear isotherm approach) and Table 5 (non-linear isotherm

Table 4. Values of the most important transport parameters of the sorption and desorption of ^{137}Cs and ^{85}Sr in fucoidic sand columns – linear isotherm approach

Radio-nuclide	Column	$(K_{dS})_{theor}$ or $(K_{dD})_{theor}$ mL g^{-1}	$(K_{dS})_{exper}$ or $(K_{dD})_{exper}$ mL g^{-1}	Pe	D_d cm^2 h^{-1}	$(R_S)_{theor}$ or $(R_D)_{theor}$	$(R_S)_{exper}$ or $(R_D)_{exper}$	WSOS/DF
				Sorption				
^{137}Cs	48118	6.41 ± 0.03	7.25	15.4± 0.20	0.45	44.1	44.7	12.3
^{137}Cs	48562	1.67 ± 0.01	1.67	6.84 ± 0,04	1.20	13.0	12.5	5.27
^{85}Sr	48118	1.90 ± 0.01	1.91	7.45 ± 0.07	1.11	14.8	14.0	16.6
^{85}Sr	48562	0.58 ± 0.01	0.57	9.47 ± 0.10	0.87	4.72	4.5	20.9
				Desorption				
^{137}Cs	48118	5.61 ± 0.04	4.10	15.4 ± 0.20	0.45	38.7	25.7	12.3
^{137}Cs	48562	2.11 ± 0.00642	1.49	6.84 ± 0.04	1.20	16.1	11.2	5.27
^{85}Sr	48118	1.90 ± 0.01	1.68	7.45 ± 0.07	1.11	14.9	12.4	16.6
^{85}Sr	48562	1.00 ± 0.01	0.64 ?	9.47 ± 0.10	0.87	7.83	4.9 ?	20.9

Table 5. Values of the most important transport parameters of the sorption and desorption of ^{137}Cs and ^{85}Sr in fucoidic sand columns – non-linear isotherm approach

Radio-nuclide	Sample (column)	k_S or k_D mL g^{-1}	n_S or n_D	Pe	D_d cm^2 h^{-1}	* $(R_S)_{theor}$ or $(R_D)_{theor}$	$(R_S)_{exper}$ or $(R_D)_{exper}$	WSOS/DF
				Sorption				
^{137}Cs	48118	5.24 ± 0.12	0.990 ± 0.001	16.1 ± 0.10	0.43	41.8 44.1	44.7	2.16
^{137}Cs	48562	1.72 ± 0.10	1.000 ± 0.003	7.94 ± 0.08	1.03	12.5 12.7	12.5	0.97
^{85}Sr	48118	1.80 ± 0.16	1.000 ± 0.006	13.5 ± 0.2	0.61	14.2	14.0	1.67
^{85}Sr	48562	0.78 ± 0.05	1.020 ± 0.004	11.4 ± 0.1	0.72	4.49 4.83	4.5	1.34
				Desorption				
^{137}Cs	48118	0.17 ± 0.01	0.750 ± 0.002	16.1 ± 0.10	0.43	27.9 49.2	25.7	2.16
^{137}Cs	48562	0.13 ± 0.01	0.800 ± 0.004	7.94 ± 0.08	1.03	12.0 21.0	11.2	0.97
^{85}Sr	48118	0.14 ± 0.01	0.810 ± 0.002	13.5 ± 0.20	0.61	11.7 24.9	12.4	1.67
^{85}Sr	48562	0.0936 ± 0.0032	0.840 ± 0.002	11.4 ± 0.10	0.72	5.45 10.6	4.9 ?	1.34

** It deals with the interval from – to, e.g., from 41.8 to 44.1*

approach). It results from the *WSOS/DF* values that the non-linear isotherm approach is better than the linear isotherm approach, especially for the more accurate fitting of desorption part of BTCs.

On the other hand, the sorption of both radionuclides on fucoidic samples is unambiguously characterized with linear isotherms (compare the values of $(K_{dS})_{theor}$ – $(K_{dS})_{exper}$ – k_S – n_S in Tables 4 and 5), and therefore it can be evaluated satisfactorily with the linear isotherm approach. From this point of view, the similarity between $(K_{dS})_{theor}$ and $(K_{dS})_{exper}$ is as expected. These corroborate the dependences of retardation coefficients on n_{PV}, obtained in the course of fitting procedure, presented in Figs. 5 and 6. It is evident that the sorption retardation coefficients, $(R_S)_{theor}$, are – because the isotherms are linear – in all cases practically constant, whereas the values of $(R_D)_{theor}$ – because the isotherms are non-linear – strongly depend on the n_{PV} flow parameter. As for the experimental values of $(R_S)_{exper}$ and $(R_D)_{exper}$ assessed for experimental BTCs, their agreement with theoretical values can be found only in a case of systems characterized with linear isotherms, it means that only the values of $(R_S)_{exper}$ and $(R_S)_{theor}$ are comparable, which can be regarded as a result of above mentioned similarity of $(K_{dS})_{theor}$ and $(K_{dS})_{exper}$ (see Table 4).

If individual fucoidic samples and both cations are to be compared, then it is better to take into account the results of the non-linear isotherm approach (Table 5), because it also implicates the linear isotherm approach, especially for sorption. The sorption parameters (k_S, and K_{dS}, too) are higher for Cs$^+$ than for Sr^{2+} by about 3-times in the same type of samples; the same relation holds approximately for both types of fucoidic samples. In other words: (i) the sorption capacity for cesium is significantly

Table 6. Estimated values of the mass balance parameters of ^{137}Cs and ^{85}Sr sorption and desorption in fucoidic sand columns (RSD ≈ 5%)

Radio-nuclide	Column	Total sorption mol	Sorption capacity mol kg^{-1}	Desorption %
^{137}Cs	48118	4.78E-5	1.30E-4	94
^{137}Cs	48562	1.41E-5	3.89E-5	81
^{85}Sr	48118	1.55E-5	4.06E-5	64
^{85}Sr	48562	5.24E-6	1.46E-5	58

higher than for strontium for both types of samples; (ii) the sample No. 48118 has significantly higher sorption capacity than sample No. 48562. The effect of heterogeneity of the solid phase is quite evident, not only for the values of transport parameters (retardation coefficients), but also for the values of Peclet numbers and dispersion coefficients that differ from each other (see Table 5). The heterogeneity also demonstrated itself in the former sorption capacity studies carried out under static conditions [13], according to which the sorption capacities of both cations are higher than in the dynamic experiments.

As it was mentioned above, the column experiments were preceded by some preliminary static (batch) tests. Unfortunately, the direct comparison of K_d for the investigated cations under static and dynamic conditions is difficult as different sand types were used [13], but it is confirmed that the distribution coefficient for Cs$^+$ is higher under static conditions, as well. In comparison of these two procedures one may keep in mind that in static shaking technique, using the crushed and ground fucoidic sand-core, practically the bulk of active centers are open to sorption and desorption of cations; this is in contrast to the dynamic flow technique, where only a part of the solid phase is involved into the sorption/desorption cycle due to geometrical barriers, and the fucoidic sand comes into contact with the groundwater through the so-called preferential flow only [20].

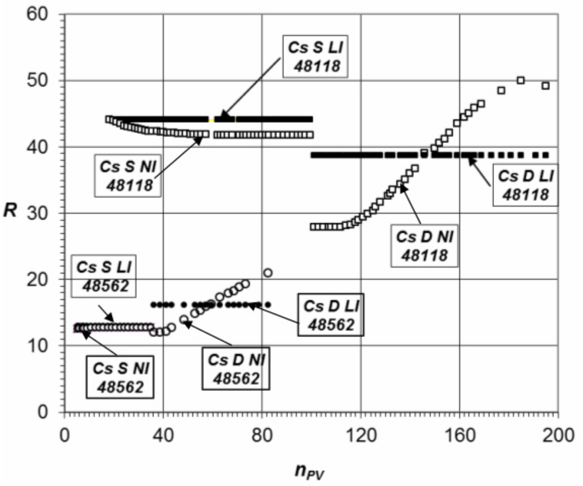


Figure 5. Calculated values of $(R_{S,D})_{theor}$ for ^{137}Cs as a function of $n_{PVS,D}$. $(R_{S,D})_{theor}$ values result from the fitting of sorption (S) and desorption (D) BTCs (see Fig. 3) obtained in the columns with samples 48562Cs and 48118Cs using non-linear isotherm (NI) or linear isotherm (LI) approach.

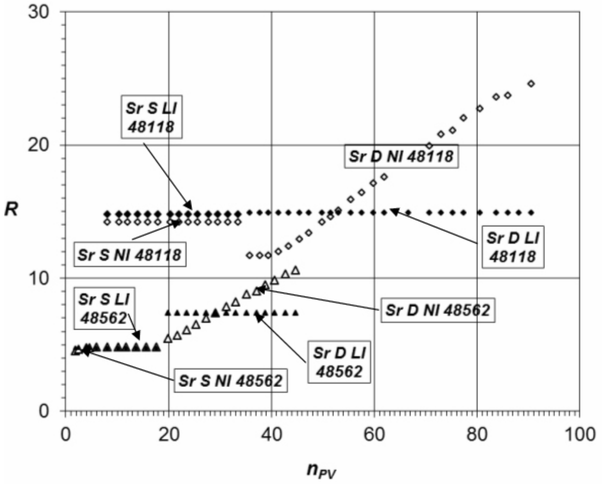


Figure 6. Calculated values of $(R_{S,D})_{theor}$ for ^{85}Sr as a function of $n_{PVS,D}$. $(R_{S,D})_{theor}$ values result from the fitting of sorption (S) and desorption (D) BTCs (see Fig. 4) obtained in the columns with samples 48562Sr and 48118Sr using non-linear isotherm (NI) or linear isotherm (LI) approach.

The obtained experimental BTC$_S$ and BTC$_D$ can be also used to the rough estimation of mass balance of sorbed and desorbed Cs or Sr. For this purpose, the numerical integration of the surfaces below the sorption (BTC$_S$) and desorption (BTC$_D$) curves, based on application of library code [19] of iterated cubic splines method, was used. The results can be found in Table 6 (*i.e.*, the moles of Cs and Sr sorbed on given fucoidic samples and the approximate values of percentage of desorbed Cs and Sr in the course of the same experiment). It is necessary to add, that in this case, the relative standard deviation (RSD) of obtained values was estimated on the basis of overall experimental error of individual points which amounts approx. to 5-10%. In agreement with the results discussed above, the amount of sorbed moles of cesium is approx. 3 times higher than that of strontium, but Cs is desorbed with higher efficiency than Sr. It can be probably regarded as a result of the composition of CGW, *i.e.*, of relatively high concentration of Ca^{2+} cation having higher sorption selectivity than Cs$^+$, and of cation-exchange mechanism of sorption/desorption taking part on the deprotonated surface groups of type >SiOH , >TiOH, >AlOH and >FeOH (on the basis of their protolytic constant values [21], it can be supposed that at least partially deprotonation exists, namely due to the alkaline value of pH in CGW – see Table 3).

5. Conclusions

A fairly good agreement has been found between experimental and theoretical sorption/desorption breakthrough curves and transport parameters of Cs^+ and Sr^{2+} in systems consisted of fucoidic sand-cores and groundwater originating from Cenomanian aquifer, especially if the non-linear isotherm approach is used. Of course, if only the sorption part of BTCs should be described, then the linear isotherm approach can be found as the best solution. This fact, including the results of balance parameters estimation, confirms that the ion-exchange mechanism of the sorption/desorption cycle for both radionuclides can be supposed. The resulted values show that the sorption capacity of cesium is about 3 times higher than the sorption capacity of strontium in the same fucoidic samples at 10^{-6} mol L^{-1} carrier concentration. However, desorption with groundwater originating from the Cenomanian aquifer is more effective in the case of cesium than that of strontium, probably due to the relatively high concentration of Ca^{2+} in CGW and to the above mentioned ion-exchange mechanism. The non-homogeneity of the fucoidic sand core plays an important role in the sorption/desorption cycle, as the retardation coefficients and Peclet numbers differ somewhat from each other. The obtained data confirm our previous results concerning the low sorption capacity of these radionuclides in fucoidic sands.

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