90554

Journal of Radioanalytical and Nuclear Chemistry, Vol. 229, Nos 1–2 (1998) 57–60

(U)

Sorption and diffusion processes with ^{134}Cs and ^{85}Sr in natural sorbents

P. Jurček, V. Jedináková-Křížová

Institute of Chemical Technology, Department of Analytical Chemistry, Technická 5, 166 28 Praha 6, Czech Republic

(Received September 17, 1997)

Sorption and diffusion processes with ^{134}Cs and ^{85}Sr in natural bentonites have been investigated. The distribution coefficients (K_d) have been determined by a batch method. Various factors affecting the K_d value as water-to-bentonite ratio, concentration of the competitive cations in the aqueous phase or bentonite-to-sand ratio in the mixed sorbents have been evaluated. A comparison of the sorption and diffusion data has been made.

Introduction

For the assessment of the properties of bentonites as barrier materials it is necessary to specify the mechanism controlling the migration of radionuclides in the barrier materials and other factors affecting them. The most important ones are sorption and diffusion.

Sorption is generally any process leading to the removal of the dissolved compound from the solution and to its fixation on the surface of a solid phase. Sorption involves ion-exchange, formation of complexes on the sorbent surface, specific and physical adsorption and other mechanisms. Knowledge of values of the bulk density, porosity of studied rock together with the distribution coefficient describing the partition of each radionuclide is important for the prediction of the migration of radionuclides.

Diffusion can be characterised as the process which leads at different local concentrations to their equalising that means to an equilibrium state. Motivating force for this process is the concentration gradient and the characteristic parameter is the diffusion coefficient.

The diffusive movement of radionuclides through bentonites is difficult to analyse because it involves several physical and chemical processes as ion-exchange, physical and chemical sorption, filtration and precipitation. That means that the apparent diffusion coefficient D_a describing the diffusion of radionuclides through barrier materials is always lower than that in the aqueous phase. Many papers (e.g.[1]) shows the apparent diffusion coefficient D_a as a function of the distribution coefficient K_d

$$D_a = \frac{\varepsilon D_p}{\varepsilon + \rho K_d} = \frac{D_e}{\varepsilon + \rho K_d}, \qquad (1)$$

where D_p is the pore water diffusion coefficient, D_e is the effective diffusion coefficient, ρ is the bulk density and ε is the porosity of studied compacted bentonite.

Several methods are used for the determination of the apparent diffusion coefficient: in-diffusion,[2,3] through-diffusion,[2,4] back-to-back,[1,5–7] and impulse source.[3,8] Both the apparent (D_a) and the effective (D_e) coefficients can be determined simultaneously by the through-diffusion method. The modified through-diffusion method[9] can be mentioned as well. A different way of evaluation is used by this method giving a transient apparent diffusion coefficient D_a'.

Experimental

The distribution coefficient has been determined using the well known and simple batch method and was calculated from the initial (A_0) and equilibrium (A) specific gamma activity of the aqueous phase according to the equation

$$K_d = \frac{(A_0 - A)V}{mA}. \qquad (2)$$

More details about this method is given in Reference 10.

The through-diffusion method (see Fig.1) has been used for the determination of diffusion coefficients. This method is exactly described in Reference 3. Values of the cumulative amount of diffunded radionuclide per unit area Q/A have been plotted against the duration time of the experiment t. Effective diffusion coefficients have been calculated from the asymptote of the breakthrough curves according to the equation

$$D_e = \frac{\Delta Q}{A \Delta t} \cdot \frac{L}{c_0}, \qquad (3)$$

where L is the thickness of the bentonite sample and c_0 is the initial radionuclide concentration in the source reservoir. The apparent diffusion coefficient is then calculated from the intercept t_e on the time axis (lag-time) according to the equation

0236–5731/98/USD 17.00
© 1998 Akadémiai Kiadó, Budapest
All rights reserved

RECEIVED
NOV 0 8 2005
By Bw

Elsevier Science B. V., Amsterdam
Akadémiai Kiadó, Budapest

14577

$$D_a = \frac{L^2}{6t_e} \tag{4}$$

^{134}Cs and ^{85}Sr radionuclides declared by the producer as carrier free and bentonite from the Hroznětin mine in north-western Bohemia (particle size fraction 0.315–0.800 mm) have been used.

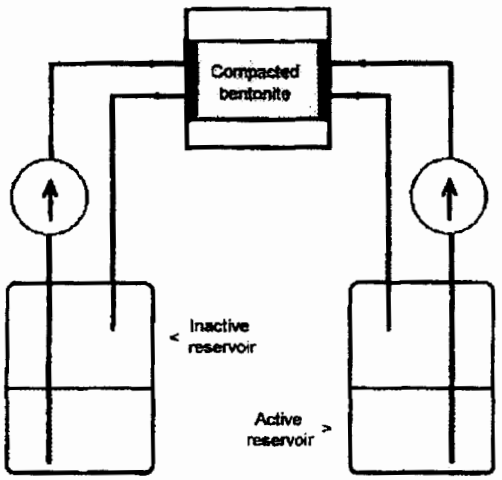

Fig. 1. Scheme of the apparatus used for through-diffusion experiments

Results and discussion

Sorption experiments

For the high precision measurement of nuclides in solution batch experiments it is necessary to work under conditions V/M>2.5 ml/g. Values of V/M«1 ml/g were found in the geological environment. Contrary to the fundamental distribution law, according to which sorption ratios should not be affected by liquid-solid ratios, sorption and desorption coefficient of radionuclides may change with decreasing liquid-solid ratios[11] according to the equation

$$K_d = \frac{m_T}{M\left[(m_T - c_0 M^{\gamma})\frac{M}{V}\right]^n} - \frac{V}{M}\left[(m_T - c_0 M^{\gamma})\frac{M}{V}\right]^{n-1}, \tag{5}$$

where m_T is the total mass of nuclides, M is the rock mass, V is the volume of the aqueous phase, c_0 is the specific sorbed concentration of nuclide per g, γ (<0) is the sorption exponent, n is the Freundlich constant of the system.

The exact mathematical description of this dependence is rather complicated that's why we have tried to find an empirical description (see Figs 2 and 3). It is evident from the figures that the K_d value depends linearly on the logarithm of liquid-solid ratio. This empirical relationship can be used for the estimation of K_d under conditions different from those during the sorption experiment.

Bentonite itself used in the deep repository has low heat conductivity that's why mixtures of bentonite with sand are used.[12] Mixtures of bentonite with pure silica sand have been studied to confirm whether sand has any influence on bentonite, e.g., grinding of bentonite particles.

Figures 4 and 5 show the dependence of K_d on the bentonite content (in % wt.) in the mixture. Linearity of the mentioned dependencies near to the direct proportion leads to the conclusion that sand acts only as a solid "solvent" and has no influence on the sorption properties of bentonite.

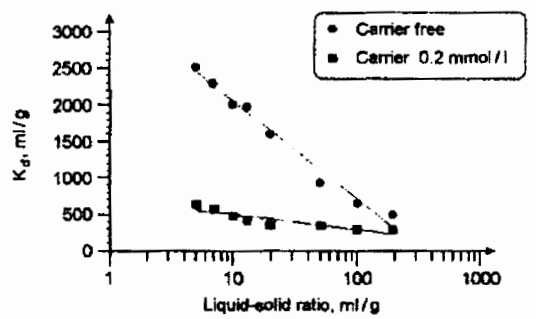

Fig. 2. Dependence of the distribution coefficient on the liquid-solid ratio for ^{134}Cs

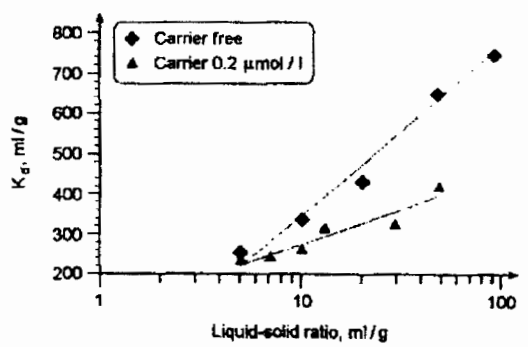

Fig. 3. Dependence of the distribution coefficient on the liquid-solid ratio for ^{85}Sr

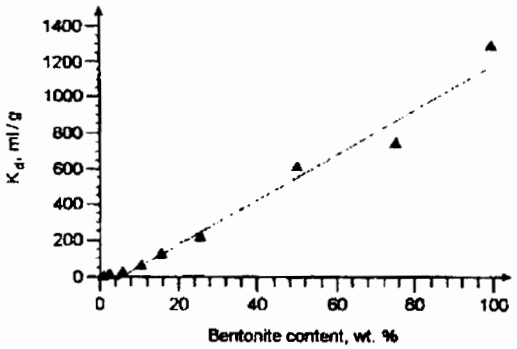

Fig. 4. Influence of the sand content in mixtures with bentonite on the distribution coefficient for ^{134}Cs

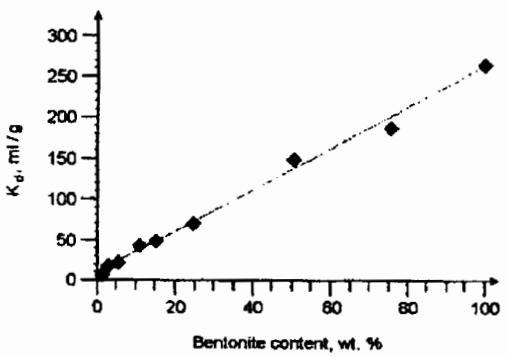

Fig. 5. Influence of the sand content in mixtures with bentonite on the distribution coefficient for ^{85}Sr

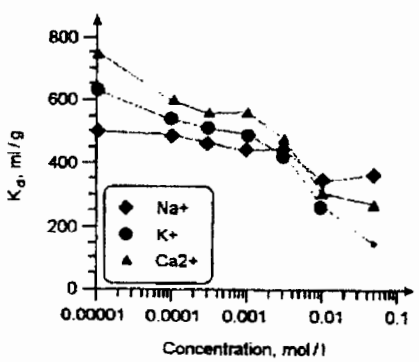

Fig. 6. Influence of the concentration of the competitive cations on the sorption of ^{134}Cs

Ion exchange as one of the most important mechanisms taking part in sorption processes on bentonites has been studied by the assessment of the influence of the competitive cations. It was necessary to study how the concentration of the competitive cations affects the distribution coefficient.

The K_d values have been determined for several concentrations of calcium, potassium and sodium added to the aqueous phase (see Fig. 6). The distribution coefficient decreases approximately linearly with the logarithm of the molar concentration of cations as a result of the competitive cation exchange equilibria.

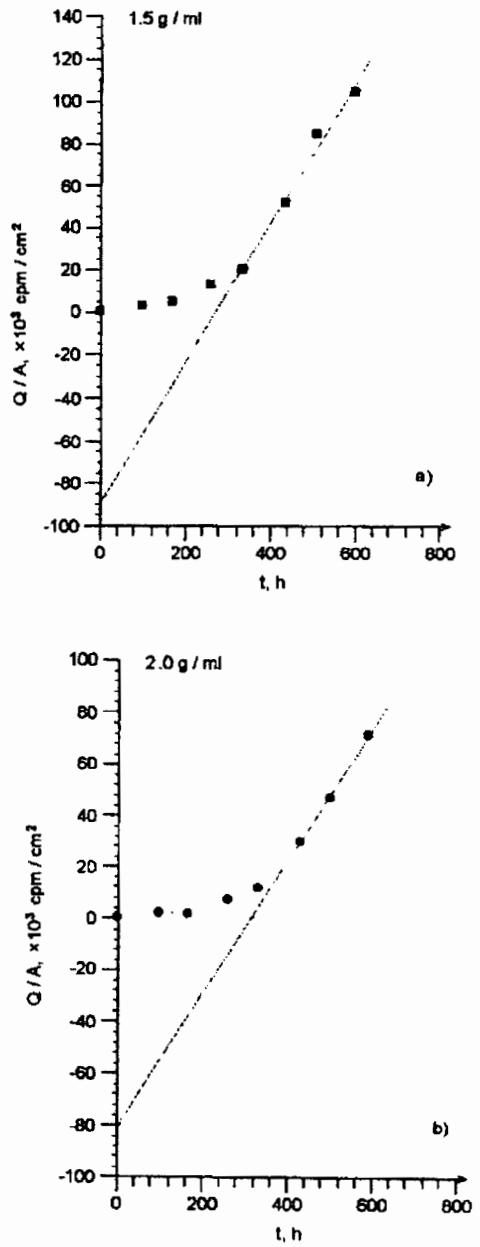

Fig. 7. Breakthrough curves of ^{85}Sr (carrier 1 μmol/l) for two dry bulk densities of compacted bentonite

Diffusion experiments

Effective (D_e) and apparent (D_a) diffusion coefficients have been determined using the through-diffusion method. The breakthrough curves show the dependence of the cumulative amount of diffunded radionuclide per unit area on the duration time. Resulting curves for two values of the dry bulk density of compacted bentonite and radionuclide ^{85}Sr with inactive carrier (1 μmol/l) are shown in Fig. 7.

Both diffusion coefficients have been calculated from the slope of the asymptote and from the lag-time using Eqs (3) and (4), respectively. The K_d value has been evaluated from the D_e and D_a according to Eq. (1). Porosities necessary for the evaluation have been determined from the grain and dry bulk densities. All results are summarised in Table 1. This table contains also the values of the liquid-solid ratios which have been determined from the weight loss during drying of the water saturated sample of the compacted bentonite.

Comparison of the sorption and diffusion data

K_d values determined by the batch sorption method (with the same concentration of ^{85}Sr as in the diffusion experiments) and calculated from the diffusion data and hydrodynamic parameters have been plotted on the same graph. All data points have been fitted by the above described dependence (see Fig. 8). The very good agreement of data points with the regression line indicates that sorption and diffusion processes are coherent and the diffusion and sorption data are useful in the assessment of the properties of natural bentonites.

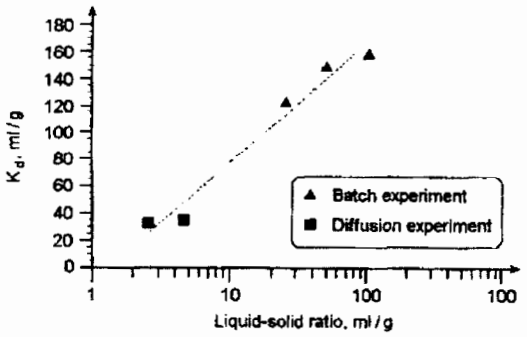

Fig. 8. Comparison of K_d for ^{85}Sr (carrier 1 μmol/l) determined by the batch method with those calculated from the diffusion data

Table 1. Diffusion coefficients determined by the through-diffusion method and calculated K_d values

Dry bulk density, g/ml	1.5	2.0
D_e, m²/s	$8.86 \cdot 10^{-10}$	$9.11 \cdot 10^{-10}$
D_a, m²/s	$1.68 \cdot 10^{-11}$	$1.44 \cdot 10^{-11}$
K_d, ml/g	34.9	31.5
V/m, ml/g	0.47	0.26

Conclusions

The influence of the competitive cations on the K_d value (and in this way the iron exchange machanism of the sorption as well) has been confirmed. The distribution coefficient decreases approximately linearly with the logarithm of the molar concentration of the cation.

The K_d value depends linearly on the logarithm of the liquid-solid ratio. This empirical relationship can be used for the estimation of K_d under conditions different from those during the sorption experiment.

The experimental results show that sand acts only as a solid "solvent" and has no influence on sorption properties of bentonite.

K_d values have been determined by the batch sorption method and calculated from the diffusion coefficients determined by the through-diffusion method and hydrodynamic parameters. The very good agreement of data points indicates that sorption and diffusion processes are coherent and diffusion and sorption data are in the assessment of properties of natural bentonites.

References

1. H. T. KIM, W. T. SUK, S. H. PARK, C. S. LEE, Waste Managem., 13 (1993) 303.
2. J. A. BERRY, P. J. BOURKE, H. A. COATES, A. GREEN, A. K. JEFFERIES, A. K. LITTLEBOY, A. J. HOOPER, Radiochim. Acta, 44/45 (1988) 135.
3. S. C. H. CHEUNG, Canadian J. Civil Eng., 16 (1989) 434.
4. J. W. CHOI, D. W. OSCARSON, J. Contam. Hydrol. 22 (1996) 189.
5. B. TORSTENFELT, B. ALLARD, H. KIPATSI, Soil Sci., 139 (1985) 512.
6. B. CHRISTIANSEN, B. TORSTENFELT, Radiochim Acta, 44/45 (1988) 219.
7. K. MIYAHARA, T. ASHIDA, Y. KOHARA, Y. YUSA, N. SASAKI, Radiochim. Acta, 52/53 (1991) 293.
8. M. J. L. ROBIN, R. W. GILLHAM, D. W. OSCARSON, Soil Sci. Soc. Am. J. 51 (1987) 1102.
9. C. WOLFRUM, H. LANG, H. MOSER, W. JORDAN, Radiochim. Acta, 44/45 (1988) 245.
10. P. JURČEK, V. JEDINÁKOVÁ-KŘÍŽOVÁ, P. IVANOVÁ, J. Radioanal. Nucl. Chem., 208 (1996) 519.
11. H. MEIER, E. ZIMMERHACKL, G. ZEITLER, P. MENGE, Radiochim. Acta, 66/67 (1994) 277.
12. V. JEDINÁKOVÁ-KŘÍŽOVÁ, P. VAŇURA, P. JURČEK, Návrh základních metod charakterizace bariérových materiálu, MPO 94-26/A, Praha, 1994 (in Czech).