

**INFLUENCE OF THE MINERAL COMPOSITION AND THE
GROUNDWATER pH ON THE DIFFUSION OF ⁹⁹TcO₄⁻ AND H¹⁴CO₃⁻ ANIONS
THROUGH BORECORE SAMPLES OF BODA CLAYSTONE**K. Lázár^{1*}, J. Megyeri², Z. Máthé²¹ Institute of Isotopes, Budapest, P.O.B. 77, H-1525, Hungary² Mecsekérc Co., Esztergár L. 19., Pécs, H-7633, Hungary

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Abstract

Diffusion rates of TcO₄⁻ and H¹⁴CO₃⁻ anions are compared in break-through experiments performed on bore core samples with different mineral compositions. Measurements were carried out using synthetic ground water of different pH-s (8 and 12).

Significant increase of the apparent diffusivities was observed in samples containing smectite constituent for both anions in experiments performed at pH = 8. Rock capacity factors were also different in dependence of the composition in experiments with H¹⁴CO₃⁻ at pH = 8. The presence of smectite is assumed to result in formation of microcracks, providing additional free volume for diffusion. In the diffusion of H¹⁴CO₃⁻ the isotope exchange between the carbonate forms, CO₃²⁻_{solution} ↔ CO₃²⁻_{rock}, plays probably also a role in the migration process.



Introduction

Anionic species migrate faster in clays than cationic species do, due to the less expressed sorption of the former ones. Thus, to predict the expected rate of spreading the radionuclides around a repository, study of anionic species is preferred in the first stage. Adopting this approach, diffusion of characteristic anionic species was studied in samples originated from one of the geological formations perspective for a repository, namely from Boda Claystone. A preliminary account was already given on break-through experiments performed with $^{99}\text{TcO}_4^-$ and $\text{H}^{14}\text{CO}_3^-$ species with ground water of pH= 8. Similar values were obtained for both the effective diffusivities of $\text{H}^{14}\text{CO}_3^-$ and $^{99}\text{TcO}_4^-$ ($\sim 10^{-12} \text{ m}^2 \text{ s}^{-1}$ [Lázár et al.]).

Objectives

The present report provides an account on the extension of the previous studies. Namely, the influence of mineral composition on the migration rate has been studied recently by comparing samples with different composition, and in addition, experiments were performed with ground water at two different basicities. pH = 8 was selected as characterising the unperturbed original state of the geological environment, and pH = 12 was chosen to model the conditions of an arising cement plume in the neighbourhood of a concrete barrier of a repository.

Experimental

Samples

Samples are originated from a drill driven at c.a. ~1000 depth (below the ground level). The formation, diagenesis and post diagenetic processes for the Boda Claystone are described in [Árkay et al.].

Table 1.

The main mineral components of the studied samples (in %)

Sample	Quartz	Albite	Illite	Smectite	Kaolinite + chlorite	Hematite	Calcite
# 1	10	62	15	0	4	8	1
# 2	9	56	21	3	< 2	8	3

Ground water

The composition of the synthetic ground water is shown in Table 2. This composition corresponds to pH = 8. For the pH = 12 measurements NaOH was further added in appropriate amounts.



Table 2.

Main components in the ground water (mg / L):

Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻
323	< 5	10	< 10	18	37	21	729

Measurements

C.a. 8 mm thick discs were cut from the compact, dense borecores, and the break-through of radioisotopes was studied in two-compartment break-through cells, by recording the increase of the activity, i.e. the appearance of the radioisotope in the compartment, which was filled only with the inactive ground water at the start of the experiment. The break-through curves can be obtained by determining the increase of the activity in dependence of the elapsed time. The amount of H¹⁴CO₃⁻ used for spiking (3.7 MBq) is negligible in comparison to the original concentration of the HCO₃⁻ (1.2 x 10⁻² mol/ L). This small amount practically does not result in any change in the concentration, thus, the experiment is performed at a negligible concentration gradient of HCO₃⁻. Similar consideration holds for the ⁹⁹TcO₄⁻, its concentration is 5 x 10⁻⁴ mol / L in the „active” compartment of the measuring cell. Further, there is no pressure gradient during the measurement between the two compartments, either. Other details of the experimental conditions are described in [Lázár et al.]. For illustration, the break-through data obtained for the H¹⁴CO₃⁻ anionic species at pH = 12 are shown in Fig. 1 (bottom). The top part of the figure shows the relative activity in the „active” compartment.

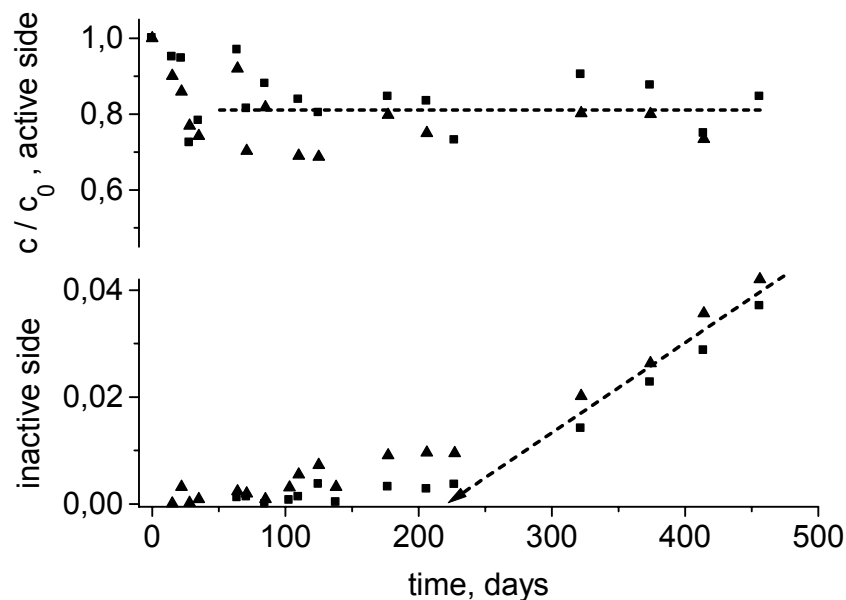


Fig 1. The relative activities in the active compartment ($t = 0$, $c_0 = 1$; top part), and the break-through data (bottom part) recorded with H¹⁴CO₃⁻ on samples 1 (■), and 2 (▲) at pH = 12.



Modelling

The results of the experiments are evaluated using the conventional approach described e.g. in [Mell et al.]:

$$C(t) / C_0 = (A D_e) t / (VL) - (\alpha A L) / 6V \quad , \quad (\text{Eq. 1})$$

where

C stands for the count rates, $C(t) / C_0$ is the relative activity change in the solution,

A : is the cross section of the sample disc,

D_e : is the effective diffusivity constant,

V : is the volume of the solution in the cell,

L : is the thickness of the bore core disc,

t : is the time elapsed,

α : is the so-called rock capacity factor.

The first part in Eq. 1 is the slope, the second is the intercept in the C_i/C_0 axis. Thus, D_e is calculated as:

$$D_e = C_i / C_0 \times (VL) / A \times 1 / \Delta t$$

The values of the effective diffusivities obtained with this approach the are shown in Table 3, and the α rock capacity factors in Table 4.

Table 3.

Values of the effective diffusion constants (D_e , $\text{m}^2 \text{s}^{-1} \times 10^{12}$)

Tracer	⁹⁹ TcO ₄ ⁻		H ¹⁴ CO ₃ ⁻	
	# 1	# 2	# 1	# 2
pH = 8	n.a.	1.16	0.39	1.57
pH = 12	n.a.	0.77	1.10	1.07

Table 4.

α rock capacity factors in Eq. 1 estimated from plots of H¹⁴CO₃⁻ data

Sample	# 1	# 2
pH = 8	0.08	0.51
pH = 12	1.15	0.96



Conclusions

Conclusions can be drawn by comparing the experimental results in dependences on the radioisotope, on the pH, and on the composition of samples as well.

First, it is worth comparing samples # 1 and # 2 when using $^{99}\text{TcO}_4^-$ tracer. On sample # 1 no break-through has taken place during ~ 500 days, whereas noticeable breakthrough is detected on sample # 2. As an apparent possibility the difference can probably be attributed to the presence or absence of the smectite component: sample # 1 does not contain smectite, whereas sample # 2 contains it in 3 %. Most probably swelling in the interlayers of smectite results in formation of additional pores or even cracks, providing larger pore volume available for diffusion.

In general, $^{99}\text{TcO}_4^-$ data indicate limited interactions between the rock and the tracer anion. The observed $\sim 10^{-12} \text{ m}^2 \text{ s}^{-1}$ value for the effective diffusion constant can be interpreted as characteristic for non-interacting ions in aqueous solutions, since in a neutral rock with 0.5 – 2.3 % porosity similar data can be obtained using the self-diffusion constants of ions in electrolytes ($\sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

For the interpretation of data obtained from the measurements with $\text{H}^{14}\text{CO}_3^-$ three further conditions should be considered. First, in spite of the low amount of the applied $\text{H}^{14}\text{CO}_3^-$ tracer, the concentration of the HCO_3^- anion is large, the ground water is practically saturated with this anion, since the rock contains calcite in 1 to 3 per cent. Considering this condition, only limited interaction might be expected between the rock and the tracer anion. Secondly, the pH dependence of the equilibria between the different forms of the hydrocarbonate/carbonate ions should also be considered. In particular, the $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-}$ equilibrium is shifted from the hydrocarbonate to carbonate form at pH 10.3. The third point is that exchange of active $^{14}\text{CO}_3^{2-}$ may proceed from the aqueous solution to the solid phase, since the rock contains calcite.

The data obtained from the $\text{H}^{14}\text{CO}_3^-$ measurements can be interpreted in correspondence with the mentioned three aspects. For instance, if we compare the D_e values calculated from pH = 8 data the difference between samples # 1 and # 2 is almost similar as in the case of $^{99}\text{TcO}_4^-$. Namely, the effective diffusion in sample # 2 is considerably larger than in sample # 1, the difference can similarly be attributed to the presence of smectite in sample # 2 and absence in sample # 1. In a modest variation, D_e is measurable in sample # 1, in contrast with $^{99}\text{TcO}_4^-$, where D_e was not detectable. This variance can probably be attributed to the two orders of magnitude difference in the concentration, in favour of the HCO_3^- vs. $^{99}\text{TcO}_4^-$ ($\sim 10^{-2}$ vs. $5 \cdot 10^{-4} \text{ mol L}^{-1}$, respectively).

In the case of pH = 12 samples, similar D_e values were obtained for samples # 1 and # 2. Most probably the change in pH from 8 to 12 resulted in the $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-}$ conversion, and the latter form got into equilibrium with the solid carbonate of the rock via exchange. This may be reflected in a slight decrease of the D_e found in sample # 2 (from 1.6 to $1.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$). In correspondence, the enhanced



interaction at pH = 12 with the rock is clearly reflected in the large values of rock capacity factors shown in Table 4.

The results of measurements can be summarized in short as follows:

- The mineral composition influences the value of apparent diffusion, in particular the presence of smectite has a characteristic influence.
- The effect of the change of the pH of the ground water is also demonstrated. Namely, the $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-}$ equilibrium is shifted to the right direction upon increasing the pH, and, at the pH = 12 case where the carbonate form is stabilized the distribution of $^{14}\text{CO}_3^{2-}$ between the liquid and solid phases can be suggested via isotope exchange.

References

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