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Abstract: The mechanism of molecular diffusion controls the migration of contaminants in very low-permeability porous media, like underground facilities for the storage of hazardous waste. Determining the relevant diffusion coefficients is therefore of prime importance. A few techniques exist for the *in situ* measurement of that quantity, but they suffer from many handicaps (duration, complexity and cost of the experiments). We propose here two innovative methods that have some potential to improve this situation. So far, we have found them feasible on the basis of design calculations and laboratory experiments. This work is presently protected by a patent.

1. SETTING THE SCENE: WHY DO WE NEED DIFFUSION COEFFICIENTS

In many situations, the movement of a fluid in the interstitial porous network of a material is controlled by two main parameters, permeability and porosity. A vast amount of literature describes techniques allowing *in situ* measurement of these quantities for such applications like the optimisation of oil production or the storage of gas in rock formations.

A large class of problems however concerns the migration of species over very long periods without any significant pressure gradient, or in low permeability material, and under the influence of a gradient in chemical composition. A typical example would be an underground storage of hazardous waste material, where there is at the same time a low permeability confinement barrier and concentration gradients acting as driving forces. Under these conditions, the relevant phenomenon is molecular diffusion and the parameters to be measured are the diffusion coefficient(s) and the accessible porosity.

One widely used approach consists in taking samples of the material of interest and performing experiments in the laboratory. Many techniques can be employed to measure diffusion coefficients in samples, as illustrated in the review by Shackelford [1]. This approach does not entirely solve the problem: on the one hand, samples may be difficult to extract, to condition or to store; on the other hand, to what extent do small scale laboratory experiments represent actual conditions, for example in a geological formation? This leaves ample room for the *in situ* measurement of diffusion coefficients in porous formations.

2. A FEW DEFINITIONS; A FEW CLASSICAL TECHNIQUES

A porous medium is composed of a solid matrix containing pores filled with some fluid. We shall suppose here that this fluid contains only one phase (liquid or gas – not both). The fluid may however contain different components; quite frequently there will be a main fluid (water for instance) in which diluted species migrate under the effect of concentration gradient. In many cases it is possible to use Fick's first law, which states that the flux of a given species is proportional to its concentration gradient (equation 1):

$$\bar{J} = -D_e \overline{\text{grad}(c)} \quad (1)$$

where \bar{J} is the flux density per unit area of porous medium ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$), c the concentration ($\text{mol}\cdot\text{m}^{-3}$) and D_e the effective diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$). Writing the balance equation for the species, it is possible to derive equation (2), which is often termed Fick's second law:

$$\frac{\partial c}{\partial t} = D_a \nabla^2 c \quad (2)$$

where the apparent diffusion coefficient D_a ($\text{m}^2\cdot\text{s}^{-1}$) is given by equation (3):

$$D_a = \frac{D_e}{R\varepsilon} \quad (3)$$

ε being the accessible porosity and R a retardation coefficient accounting for the physical or chemical interactions between the species and the solid matrix of the porous medium. If there are no such interactions, R is equal to 1 and $D_a = D_e / \varepsilon$ is commonly denoted D_p , the pore diffusion coefficient.

The prime objective is to measure D_e or D_a and if possible R and ε (they can be measured by other standard techniques).

To our knowledge, two classical methods can be considered for the *in situ* measurement of these quantities. The first one consists in drilling two boreholes in the porous formation. The species of interest is injected in the first borehole and its restitution is traced in the other one. This type of experiment is commonly performed to characterize the **flow** between two boreholes. When migration is driven by diffusion only, its velocity is reduced by several orders of magnitude and it may take a very large time period for the tracer to appear in the second one, possibly several years if the boreholes are a few metres apart.

The second method requires only one borehole. The species of interest is introduced in it and monitored as a function of time. The concentration gradient will make it diffuse into the porous formation and its concentration will decrease in the borehole (see Fig. 1 left). The diffusion coefficient can be estimated from the resulting $c(t)$ function. It is also possible to stop the experiment at some moment and to overcore the borehole (Fig. 1 right). The diffusion coefficient is then deduced from the concentration profile $c(r)$ in the overcored sample. Palut et al. [2] report an experiment at Mont Terri where concentration monitoring in the borehole and overcoring were used in combination.

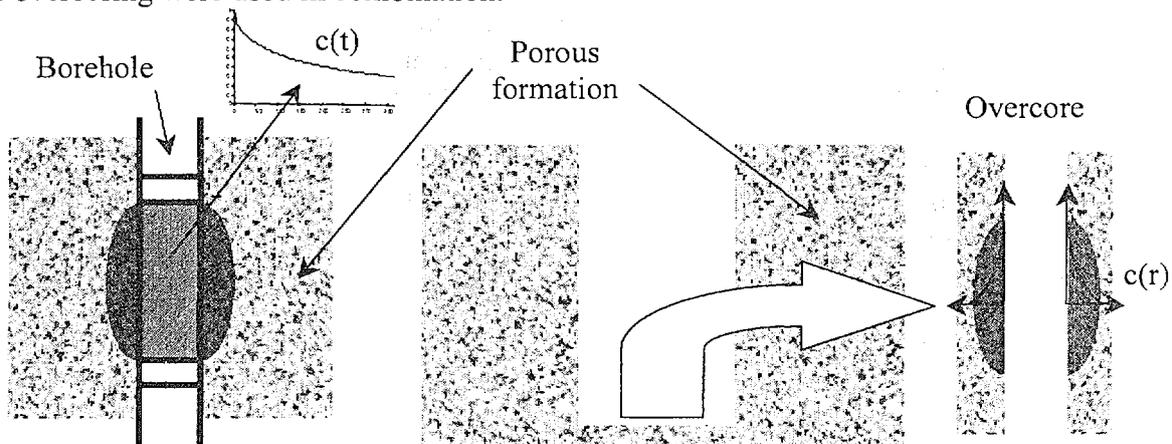


Fig. 1. A classical method for the *in situ* measurement of the diffusion coefficient (left: first stage – right: overcoring).

These techniques have proved very effective, but they may require observations over quite long time periods. In the case of the Mont Terri experiment, involving claystone as the porous medium and tritiated water (HTO) as the diffusing species (effective diffusion coefficient about $10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, accessible porosity approximately 0.15), several weeks were required before significant decrease of HTO activity in the injection chamber could be observed; overcoring was performed one year after the beginning of the experiment. This requires a lot of perseverance; overcoring was successful but nevertheless remains a complicated operation. Alternative methods allowing faster and simpler measurements would

obviously be very welcome. This paper presents two techniques. They have been tested at the laboratory scale so far and the principles and main findings have been patented.

3. A FIRST OPTION: THE “CONCENTRATION ECHO” METHOD

A first proposal consists in the procedure illustrated by Fig. 2: a measurement chamber is isolated in the borehole. The species of interest is introduced into the chamber, and left there for an adequate period of time to diffuse into the surrounding medium. If desired, the concentration can be kept constant in the chamber, for instance by connecting it to a large buffer tank. At the end of this stage, the tagged solution is flushed out of the chamber and replaced by non-marked fluid. Diffusion will now take place from the porous medium towards the chamber. The concentration will therefore rise from zero in this second stage and should be monitored as a function of time. This technique may be termed a “concentration echo” method (by reference to the work by Leroy et al. [3], with a pressure gradient as a driving force in their case), since what is measured is to some extent the “echo” of the injection into the medium.

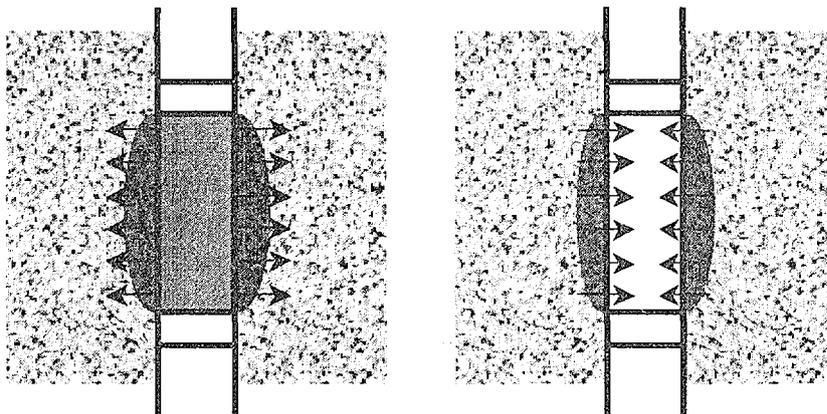


Fig. 2. The “concentration echo” method

(left: first stage, diffusion into the medium – right: second stage, diffusion into the chamber).

Fig. 3 shows a simulated concentration history, calculated with the same geometry as the Mont Terri experiment with typical values for the effective diffusion coefficient. The duration of the first stage was set to 10 hours.

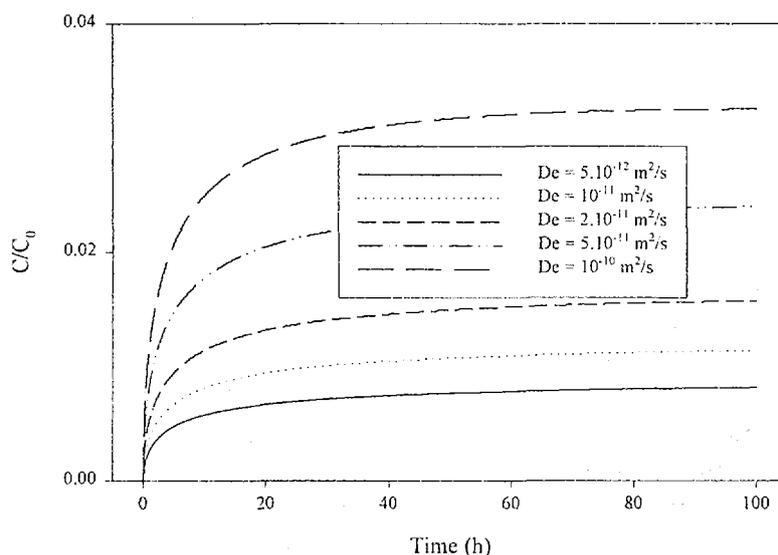


Fig. 3. Concentration histories as a function of the effective diffusion coefficient D_e .

Concentration reaches about 1 to 3 % of its value in the first stage (C_0 on Fig. 3), an unexpectedly high level. This value is reached within a few days only, a very important point when field monitoring has to be made. Correlation with D_e proves to be excellent. According to this simulation, fast response and good sensibility could be expected from this “echo” technique. The reason may be the high contrast in concentration achieved between the chamber and the medium (with the classical method, one has to detect a small decrease in a strong concentration; here, the concentration build-up may again be small compared to C_0 , but it is large to the zero value imposed at the beginning of the second stage). Another advantage is that the depth of penetration of the concentration profile can be controlled through the duration of the initial diffusion stage: varying this parameter it may be possible to measure the profile in D_e as a function of distance from the borehole.

On the other hand, several difficulties can be foreseen for the *in situ* applications. Good rinsing of the chamber may prove hard to achieve. If some of the initial solution remains in the chamber, the contrast in concentrations is lost; in the opposite, too strong rinsing may partly extract the diffusing species from the porous formation, which may again alter the measurements. Also, it may not be possible to determine D_e and ε (or $R\varepsilon$) at the same time with short-term experiments. Another weakness is that the porous formation does not return to its initial state at the end of the experiment since it will naturally retain some of the injected species. This problem however exists with the method of monitoring the concentration decay in the chamber - to say nothing of overcoring.

The “concentration echo method” has however been tested at the laboratory scale and found to be exploitable, as illustrated by the data on Fig. 4 obtained under presumably unfavourable conditions (sample with low and mainly unconnected pore volume).

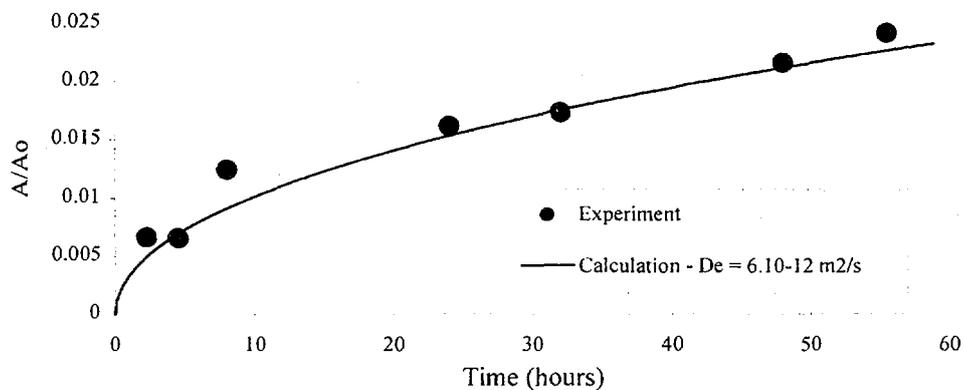


Fig. 4. Results from a small scale “concentration echo” experiment.

4. A SECOND OPTION: AN EXTENSION OF THE MACROPORE COLUMN

Young and Ball [4] describe the measurement of diffusion coefficients in what they name a “macropore column”: the material under investigation is shaped as an annulus, the core of which is filled with sand. The column is fed with a continuous flow of water; due to the large permeability difference between the materials, it will only flow in the sand core. If a pulse of tracer is injected at the inlet, it will i) move more or less like a plug in the core ii) diffuse into the surrounding material. After the plug has left the column, the tracer will diffuse back into the core and reach the outlet. Compared with a column containing only the sand packing, the tracer restitution curve has a lower peak and a larger tail. Fitting a suitable model allows to determine the diffusion coefficient.

The reason why Young and Ball used that particular technique was because it kept volatilisation and sorption losses to a minimum, an important factor since they were mainly interested in the migration of organic compounds. We however thought it might also apply to other materials and compounds, and therefore tested it on a rock core from a much studied rock formation. The result is presented on Fig. 5, which shows the restitution curve of the internal packing only and of the macropore column. Model parameters were fitted to simulate the latter. It resulted in an estimated diffusion coefficient of $4.10^{-11} \text{ m}^2.\text{s}^{-1}$, to be compared with a value of $7.10^{-11} \text{ m}^2.\text{s}^{-1}$ obtained from independent measurements. Another striking feature was the short duration of the experiment, about 5 hours. Several days might be necessary to achieve the same measurement with a classical set-up like a “through diffusion” cell (see Shackelford, [1]).

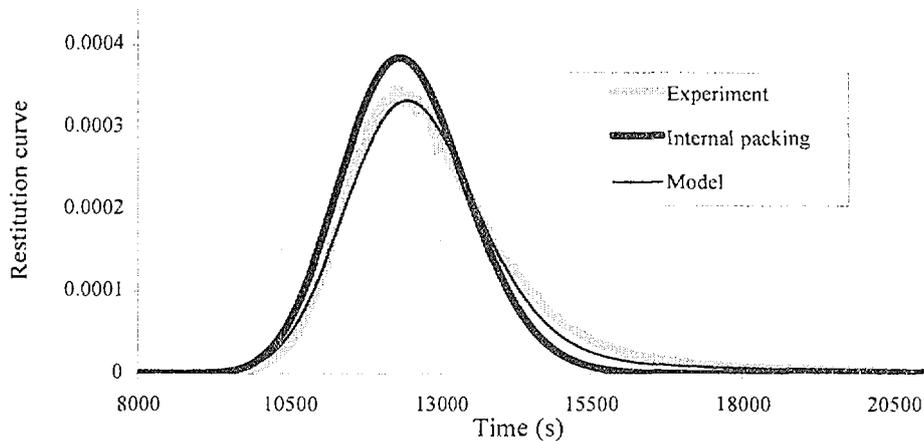


Fig. 5. Results from a “macropore column” experiment on a clay core.

This encourages us to propose an extension of the “macropore column” to *in situ* experiments. The simplest possible configuration, shown on Fig. 6, could consist in isolating a portion of borehole with two packers and placing in this chamber an inner cylinder fitted with piping for the circulation of the fluid. The annular space between the inner cylinder and the porous formation should be filled with a high-permeability packing material (polymer foam, sintered material, glass beads ...).

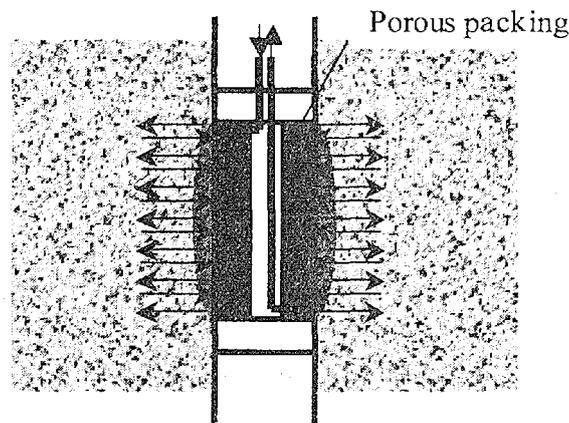


Fig. 6. A proposal for the transposition of the “macropore column” to field conditions.

Numerical simulations in the same conditions as in Fig. 3 again showed short response time and reasonable sensitivity to the value of D_e (see Fig. 7). As in the “concentration echo”, it seems possible to probe variable distances into the porous formation. The control parameter would be here the flow rate into the column. An additional advantage is that no significant amount of tracer is left after the experiment, which allows, at least in theory, to perform several successive injections in the same location.

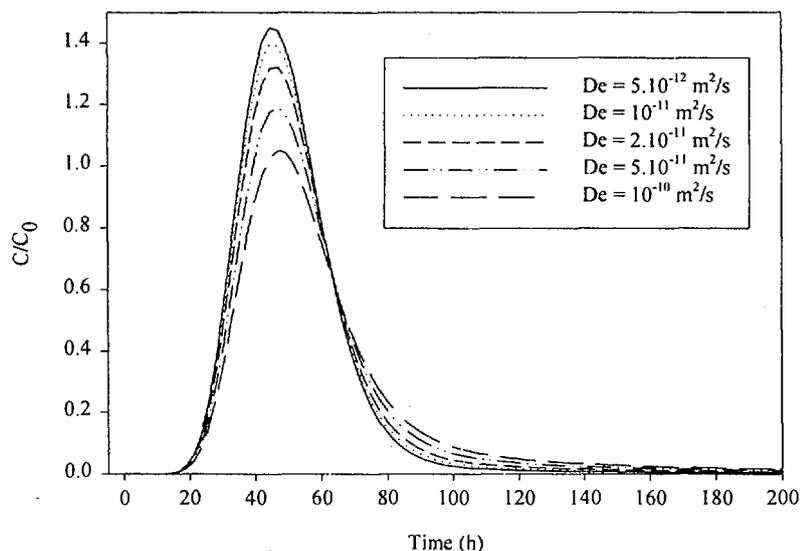


Fig. 7. Restitution curves as a function of the effective diffusion coefficient D_e .

Among predictable problems, the main one can be the difficulty to obtain a homogeneous packing in the borehole; also, suitable flow rates may be very low and hard to sustain for a long time; lastly, it is possible that D_e and ε (or $R\varepsilon$) may not be accessible independently with those experiments – in which case the measurement of $\varepsilon/R\varepsilon$ has to be made with available standard techniques.

As a whole, we believe that the two methods proposed here (“concentration echo” and “macropore column”) offer good potential for the *in situ* measurement of diffusion coefficients with i) little intrusion into the porous formation ii) good representativity and iii) reasonably fast experiments, hence fully compatible with the conditions of field work.

References

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