

# Impact of osmotic efficiency on contaminant transport parameters

## Effet d'efficacité osmotique sur des paramètres de transport de polluants

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### ABSTRACT

Contaminant flow parameters are commonly derived from experimental results using analytical solutions to the well-known advection-dispersion-reaction equation or ADRE. The authors have investigated the impact of several phenomena on flow parameters derived in this traditional analytical approach. These phenomena include electrostatic ionic interaction, competitive exchange and osmotic effects. Specifically, the effect of osmotic efficiency has been studied and presented in this paper. It has been shown that the presence of osmotic effects can lead to substantial underestimation of the contaminant flow rate.

### RÉSUMÉ

Des paramètres de transport de polluants sont généralement dérivés des résultats expérimentaux, en utilisant les solutions analytiques l'équation d'advection-dispersion-réaction. Les auteurs ont étudié l'effet de plusieurs phénomènes sur des paramètres d'écoulement dérivés dans cette approche analytique traditionnelle. Ces phénomènes incluent l'interaction ionique électrostatique, l'échange concurrentiel et les effets osmotiques. Spécifiquement, l'effet de l'efficacité osmotique a été étudié et présenté en cet article. On a montré que la présence des effets osmotiques peut mener sous-estimer sensiblement le débit de contaminant.

## 1 INTRODUCTION

A well-known mathematical description of contaminant flow is known as the advection-dispersion-reaction equation or ADRE. Numerous analytical solutions to this equation — each for very specific initial and boundary conditions — have been presented in literature. This makes it the preferred method for solving the inverse problem, i.e. deriving the basic flow parameters (in this case hydraulic conductivity  $k_h$ , diffusion coefficient  $D$  and retardation coefficient  $R_d$ ) from experimental data.

Over the last decade, several authors have been working on extending this “traditional” ADRE model to take into account phenomena as competitive exchange, coupling, osmotic effects, ionic interaction, . . . The authors have presented such extended model in several papers (Van Impe et al. (2003), Mazzieri et al. (2003)). The increased applicability of these models inherently gives rise to a certain increase in complexity on various levels as e.g. the shape of the mathematical expressions, the dependency and number of parameters. With increasing complexity, finding analytical solutions to these types of problems might prove to be difficult, not to say impossible. Therefore, solving the inverse problem will be far less transparent. The use of numerical solutions will be inevitable. Furthermore, one has to deal with a (much) larger number of parameters which will call for additional and/or new testing methods. In some cases even uniqueness of solution could be a problem.

Solving the inverse problem using the simplified analytical models however will result in a dependency of the flow parameters on the parameters governing the “new” phenomena. In certain cases, for instance, the diffusion coefficient of an ion will depend on the coefficients of all other ions present. Counter-diffusion of released ionic species could induce apparent retardation of — otherwise thought of as non-reactive — anionic species. Osmotic effects could impact a simple measurement of hydraulic

conductivity  $k_h$ .

In this paper we would like to discuss some of these interactions. In particular, the authors would like to present the preliminary results of parametric studies showing the impact of osmotic effects on the basic flow parameters.

## 2 ELECTROSTATIC IONIC INTERACTION

The measured diffusion coefficient  $D$  of an ionic species will depend on its partners in the solution. This is a result of the electro-neutrality requirement. The condition for electro-neutrality is correct only at a macroscopic level. The ions with greater diffusivity will tend to move across the medium at a faster rate than the ions with lower diffusivity. Such tendency for charge separation induces a local electric field among ions — on a microscopic scale — and in turn acts to slow down the faster ions and to accelerate the slower ions. The ADRE describes the movement of

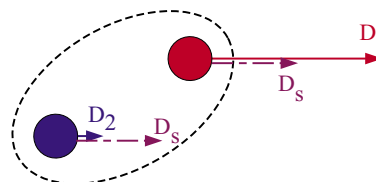


Figure 1: Impact of electrostatic interaction on ion-movement

an ionic species as if it were moving completely independently. It will not take into account this interaction between ions of different charge and solving the inverse problem in this situation could lead to — what would seem to be — illogical results. For instance, the derived diffusion coefficient for a certain ion would depend on its partner in the solution :  $\text{Cl}^-$  has a different diffusion coefficient  $D$  in a  $\text{HCl}$  solution as compared to a  $\text{NaCl}$

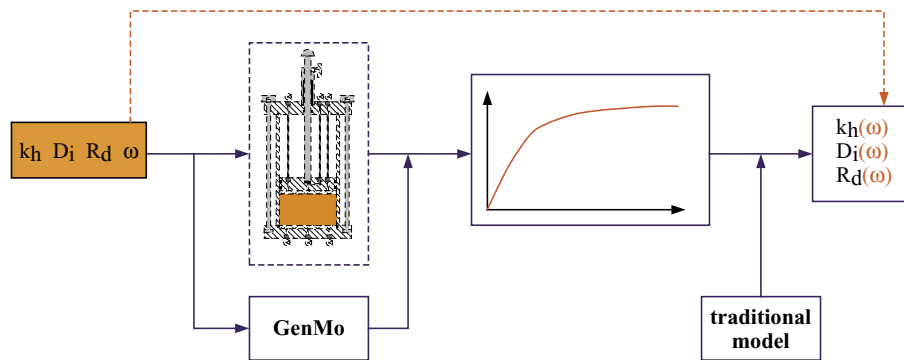


Figure 2: Principal of parametric study. The GenMo code acts as a generator of experimental results to allow to study the impact of osmotic efficiency on the flow parameters.

solution. This apparent change in diffusivity is usually attributed to changes in the tortuosity  $\tau$ . This is an acceptable solution but requires a different definition of  $\tau$ .

The use of the tortuosity factor  $\tau$  as a kind of correction factor would no longer be valid in more complex situations when chemical reactions take place. Consider the case of cationic exchange. The movement of the anionic species, which initially is considered to be non-reactive (e.g. based on results of batch tests), will be influenced by both the original cation and the released cation. Its actual diffusivity will change continuously during the exchange phase. In some cases, the released cation will move in the opposite direction of the anion. This counter-diffusion will slow down the movement of the anion. Solving the inverse problem using standard methods would reveal a reactive behaviour of the anions, in contradiction to the behaviour observed in sorption tests.

The authors are involved in several studies investigating the error on the flow parameters arising from methods ignoring this ionic interaction. The basis of the study is the GenMo code (Van Impe P.O. et al. (2003)). Results of similar research has very recently been published by Jungnickel et al. (2004).

### 3 OSMOTIC EFFECTS

Due to the charged nature of clay materials, these soils can act as electrostatic filters for movement of charged particles. This semi-permeable membrane behaviour gives rise to the well-known phenomenon of osmosis. The governing parameter in this process is the osmotic efficiency  $\omega$  which indicates the capacity of the material's selective behaviour when it comes to flow. The authors have presented mathematical descriptions for contaminant flow which includes osmotic effects in clays in several papers.

In highly active clays as bentonite (the main mineral component of a GCL), the osmotic effect can have a very strong impact on the transport behaviour of ionic pollutants. Analysis of this behaviour using standard methods will lead to system parameters which are strongly depending on the value of the (unknown) osmotic efficiency  $\omega$ .

Osmotic efficiency itself is very sensitive to changes in the system: pollutant concentration, temperature, void ratio, ... This could lead to a large discrepancy in behaviour between laboratory and in situ or even between identical laboratory tests with slightly different testing regime.

#### 3.1 Parametric study

To investigate the possible impact of osmotic efficiency on the flow parameters, the authors have performed both experimental

and theoretical studies. The experimental research is based on the so-called osmotic efficiency setup described by Malusis et al. (2001). Unfortunately, this type of testing requires a very long time (on average 4 to 6 months each) and did not yet allow the authors to state significant conclusions.

Alternatively, a parametric study based on the numerical model GenMo had been started. The aim is to generate data which would be analysed as if it were experimental results (figure 2). This analysis is performed using an analytical solution to the ADRE. Of course, both the GenMo code and the analytical results would be based on identical boundary conditions. It is the aim of the authors to repeat this study using actual experimental data in a following phase of the research.

The GenMo code has been used to simulate a simple column-test using a certain set of boundary conditions. Several parameters have been allowed to change: osmotic efficiency  $\omega$ , hydraulic permeability  $k_{h,init}$ , diffusion coefficient  $D_{init}$ , retardation coefficient  $R_{d,init}$  and initial concentration gradient. It has been assumed that no ionic interaction occurs and that the osmotic efficiency  $\omega$  can be considered constant.

The simulations result in graphs of hydraulic flux vs. time and effluent ionic flux vs. time, as would be the case in an actual experimental setup. Based on the hydraulic flux, a value for the hydraulic conductivity  $k_h$  can be calculated and will be compared to the initial "real" value  $k_{h,init}$ . Using a suitable analytical solution to the ADRE (such as described by van Genuchten and Alves (1982) or van Genuchten and Parker (1984)), values of the diffusion  $D$  and retardation coefficient  $R_d$  can be found. The ratio with their correct values  $D_{init}$  and  $R_{d,init}$  can be related to the value of the osmotic efficiency  $\omega$ .

#### 3.2 Results

The filtering effect of a membrane can have a serious impact on the contaminant flow behaviour. This can be seen looking at some simulation results which give the effluent curve for a column-test for different values of the osmotic efficiency (figure 3).

Figure 4 shows the change of the hydraulic flux as a function of time for different values of the osmotic efficiency. After an initial transient phase, the flux will reach a constant value which is lower for increasing value of osmotic efficiency: the normal flow resulting from the hydraulic gradient will be counteracted by the flow induced by the osmotic behaviour. The downward peak is a result of the high initial concentration gradients existing at the boundaries. For high values of the osmotic efficiency this could even lead to a temporary reversal of the advective flow. One should take care to assure that the total contaminant flow is always positive. A total negative concentration flux would be in contradiction with the entropy condition and cannot be a realistic

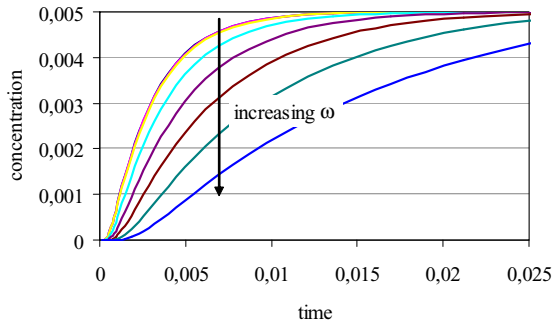


Figure 3: Impact of osmotic efficiency on effluent curves in column-test

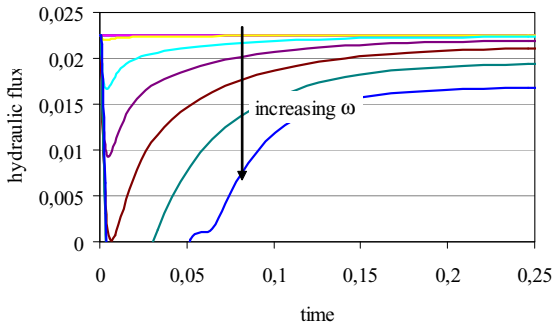


Figure 4: Impact of osmotic efficiency on hydraulic fluxes in column-test

result.

Based on the values of the flux, a value for the hydraulic conductivity can be calculated. The dependency of the conductivity on the osmotic efficiency is shown in figure 5. Clearly the osmotic efficiency can have a large impact even on a “simple” parameter as hydraulic conductivity. The results are grouped based on the original Peclet number, i.e. the Peclet number based on the initial parameters  $k_{h,init}$  and  $D_{init}$ .

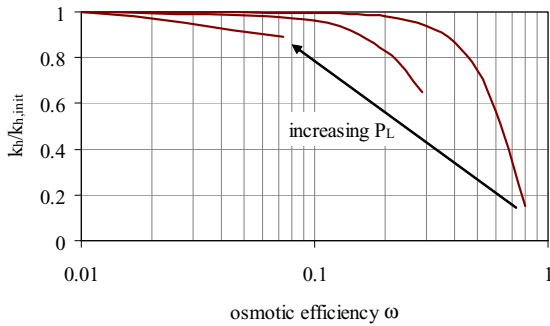


Figure 5: Impact of osmotic efficiency on measured hydraulic conductivity

Based on the calculated values of  $k_h$ , values of the diffusion  $D$  and retardation coefficient  $R_d$  can be determined using an analytical solution of the ADRE. Figures 6 and 7 give the relative change of these parameters as a function of osmotic efficiency for different Peclet numbers.

It can be seen that the counteraction of the osmotic effect induces a general reduction in the contaminant flow velocity. This is translated into a decrease in hydraulic conductivity and diffusion coefficient and an increase in the retardation coefficient. This

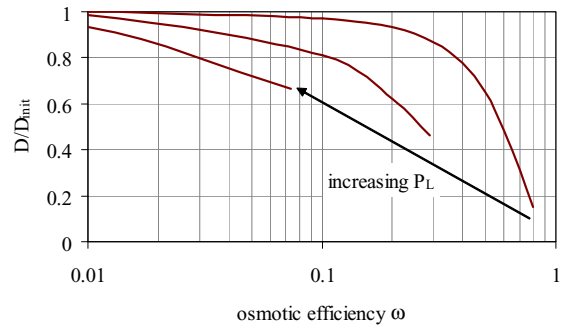


Figure 6: Impact of osmotic efficiency on measured diffusion coefficient

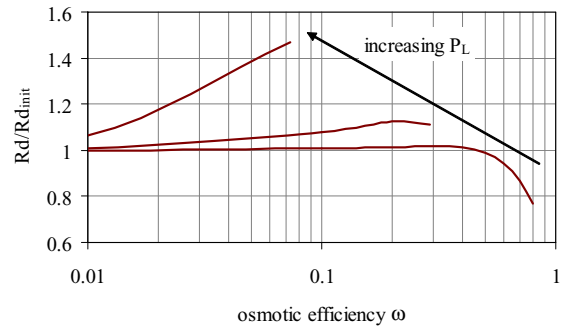


Figure 7: Impact of osmotic efficiency on measured retardation coefficient

means that the analytical solutions provide an unsafe guess of the flow parameters.

The decrease of  $R_d$  for small Peclet numbers and large osmotic efficiencies is probably a result of problems with solving the inverse problem. For small  $P_L$  and large  $\omega$ , the shape of the breakthrough curve is very different from what can be established using the ADRE. This leads to a fitting problem and a problem of uniqueness of solution (multiple minima). Least-square fitting probably overestimates the drop in diffusion coefficient which leads to a drop in  $R_d$  as well.

The impact of osmotic efficiency increases as the original Peclet number increases, but this is limited as also the ultimate value of osmotic efficiency drops when  $P_L$  increases. This limitation is a requirement for the stability of the equations. The system should always remain parabolic, i.e. no integration ever occurs “backwards in time”. The following matrix expresses how the time derivatives of  $c_a$ , etc., depend on their second space derivatives:

$$\frac{\partial}{\partial t} \begin{pmatrix} c_a \\ c_c \\ c_{cs} \end{pmatrix} = M \frac{\partial^2}{\partial \zeta^2} \begin{pmatrix} c_a \\ c_c \\ c_{cs} \end{pmatrix} + [\text{expr. involving lower space derivatives}] \quad (1)$$

Stability will be ensured if the eigenvalues of  $M$  all have non-negative real parts. These eigenvalues can be expressed as functions of  $\omega$ . Limitations will be imposed on the value of  $\omega$  if all eigenvalues are to be positive. This numerical stability is equivalent to the entropy condition which guarantees the existence of a net diffusive flow.

## 4 CONCLUSIONS

We have investigated the impact of certain phenomena on flow parameters determined by traditional methods. More specifically, it has been shown that analytical solutions to the ADRE tend to underestimate the hydraulic conductivity and the diffusion coefficient in the presence of an osmotic effect. Furthermore, the osmotic effect could give rise to an artificial retardation phenomenon. The deviation on the parameters increases with increasing Peclet number and increasing osmotic efficiency  $\omega$ . The largest values of the osmotic efficiency however can be found only in case of low Peclet number.

A fitting problem occurs in cases with high osmotic efficiency where the breakthrough curve (effluent concentration) has a shape which is very different from the one that can be generated by the ADRE. In this situation, the determination of the flow parameters is strongly depending on the type of fitting procedure. It should be investigated if the leastsquare-fitting is the best option.

The selection of the fitting method is an area of research which is also of interest in cases where no osmotic effects are present. Very different solutions (pairs of diffusion and retardation coefficients) can be found when adopting different fitting-schemes. In this field, the authors are investigating the impact of statistical error on the formation of multiple minima.

Finally, research is planned to validate these results using different approaches: different types of boundary conditions, variable value of osmotic efficiency, . . . . An experimental study is ongoing to validate the numerical study.

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