

Working report 97-63e

Model for diffusion and porewater chemistry in compacted bentonite

Preliminary results for the
ionic transport model

Jarmo Lehtikoinen
VTT Chemical Technology

December 1997

POSIVA OY

Mikonkatu 15 A, FIN-00100 HELSINKI, FINLAND

Tel. +358-9-2280 30

Fax +358-9-2280 3719

Working report 97-63e


Model for diffusion and porewater chemistry in compacted bentonite

**Preliminary results for the
ionic transport model**

Jarmo Lehtikoinen
VTT Chemical Technology

December 1997

Tilaaja Posiva Oy
Mikonkatu 15 A
00100 HELSINKI

Tilaus 9508/97/JPS 

Käsittelijä Tutkija Jarmo Lehikoinen, (09) 456 6371

Tehtävä Tutkimus diffuusiosta ja huokosvesikemiasta bentoniitissa (1997)

Tulokset Oheisessa raportissa "Model for diffusion and porewater chemistry in compacted bentonite - Preliminary results for the ionic transport model".

Espoo 31.12.1997

Ryhmäpäällikkö



Arto Muurinen

Tutkija



Jarmo Lehikoinen

JAKELU Posiva Oy
VTT Kemiantekniikka / arkisto

Working Reports contain information on work in progress or pending completion.

The conclusions and viewpoints presented in the report are those of author(s) and do not necessarily coincide with those of Posiva.

MODEL FOR DIFFUSION AND POREWATER CHEMISTRY IN
COMPACTED BENTONITE – PRELIMINARY RESULTS FOR
THE IONIC TRANSPORT MODEL

ABSTRACT

This report describes the progress of the computerized model for ionic transport in bentonite clay. The research is part of the project “Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency” (Contract No. FI4W-CT95-0012) within the European Commission Nuclear Fission Safety Program (1994-1998). The model will combine the local equilibrium of ions (Poisson-Boltzmann solver) with the modified Nernst-Planck equation for transport. This report presents some preliminary results, based on the modified Boltzmann statistics, for the equilibration module. These include, for example, the ionic concentration distributions in a clay sample submersed in Allard groundwater.

Keywords: Bentonite, montmorillonite, transport model, ionic equilibrium

MALLI DIFFUUSIOLLE JA HUOKOSVESIKEMIALLE KOMPAKTOIDUSSA BENTONITISSA - HUOKOSVESIKEMIAN TUTKIMUKSEN ALUSTAVAT TULOKSET

TIIVISTELMÄ

Tämä raportti on kuvaus ionien kuljetusmallin kehittämisen edistymisestä. Tutkimus on osa projektia "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency" (Contract No. FI4W-CT95-0012), joka kuuluu Euroopan komission organisoimaan Nuclear Fission Safety ohjelmaan (1994–1998). Malli yhdistää ionien paikallisen tasapainon (Poisson-Boltzmann ratkaisin) modifioituun Nernst-Planck'in kuljetusyhtälöön. Raportti tarjoaa alustavia tuloksia, jotka perustuvat modifioituun Boltzmann statistiikkaan, tasapainotusmoduulille. Näitä ovat mm. ionien pitoisuusprofiilit Allardin pohjaveden kanssa tasapainotetussa savessa.

Avainsanat: Bentoniitti, montmorilloniitti, kuljetusmalli, ionien tasapaino

FOREWORD

Within the European Commission Nuclear Fission Safety Program (1994–1998), the research project “Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency” (Contract No. FI4W-CT95-0012) has jointly been started by Clay Technology AB in Sweden, VTT Chemical Technology in Finland, Universität Hannover in Germany and Kungliga Tekniska Högskolan in Sweden. Professor Roland Pusch from Clay Technology AB is the co-ordinator of the project. The work in Finland is funded by The European Commission, Posiva Oy and VTT Chemical Technology. The contact person for Posiva Oy is Jukka-Pekka Salo. The work in Finland is concentrated on the development of a model for ionic transport and porewater chemistry in compacted bentonite.

CONTENTS

ABSTRACT

TIIVISTELMÄ

FOREWORD

CONTENTS

1 INTRODUCTION	7
2 BASIS FOR THE MODEL	8
3 PRELIMINARY RESULTS.....	9
3.1 SIMPLE ELECTROLYTE.....	9
3.2 ALLARD GROUNDWATER.....	12
3.3 VOLUME EXCLUSION	14
4 SUMMARY AND FUTURE WORK	17
5 REFERENCES	18

1 INTRODUCTION

The computerized model is aimed to simulate and interpret equilibrium and transport experiments for bentonite clays containing different types of background electrolytes at various compactions. Specifically, emphasis is placed on quantifying the extent of co-ion exclusion and understanding the postulated surface diffusion mechanism on the basis of the well-established electric double-layer (EDL) theory.

At this point, the kernel of the model, the Poisson-Boltzmann (PB) solver, has been completed and is capable of calculating the equilibrium composition inside the slit-like pore for any combination of the surface charge density (or surface potential), slit opening and type of electrolyte in contact with the clay. Consequently, it qualitatively explains the experimentally observed cation-exchange selectivities to a clay surface, readily quantifies co-ion exclusion, and allows the calculation of the disjoining pressure, for example. Moreover, the enhanced version of the PB solver also accounts for the effect of finite ion sizes.

The incorporation of adsorption into the PB solver and, further, the integration of this extended PB solver with the transport module are currently underway and will be completed in the near future.

2 BASIS FOR THE MODEL

An attempt is made to decompose some quantities, most commonly integrated over the chemical composition, the structure of the pore network and the time scale, into their differential counterparts. Into this category typically fall, say, the apparent diffusivities of ionic species. To serve this objective, a two-dimensional unsteady molecular-level electrokinetic transport model for ionic species in bentonitic clays will be developed. The model incorporates additional features to the conventional Gouy-Chapman (GC) theory: ionic hydration, dielectric saturation, and the volume exclusion of ions.

Hydration effects for ionic species arise in a dielectric continuum, where the dielectric permittivity is treated as a local function of the electric field strength. The hydration of ions is considered in the framework of the Born solvation model. The modified PB equation, including hydration effects, accounts for the different adsorption selectivities of cations of like charge to the clay surface; a well-known phenomenon that cannot be distinguished by conventional treatment of the EDL theory. Moreover, a compact Stern layer for physisorbed counter-ions need not be introduced, since the hydration model simulates solvent co-ordination.

Contrary to the GC theory, which treats ions as point charges, the present modified EDL (MEDL) model considers ions as occupying a certain, ion-specific volume in the electrolyte. A practical aspect of this, together with the hydration effect, is that a cation cannot acquire an unphysically high concentration in close proximity to the negatively charged pore wall, which is a major drawback of the GC theory.

The governing equations for the flow of electrolyte solution through the pores are solved by an iterative numerical scheme to relate the characteristics of the flow to the characteristics of the pores and to the composition of the bulk solution in contact with the clay sample. In these pores, the equations governing the local chemical equilibrium are numerically integrated on a grid that dynamically adjusts according to the prevailing physico-chemical conditions. In practical terms, this means that the grid is refined in the proximity of the pore walls.

The pore geometry of the clay specimen is modelled as an array of non-interconnected tortuous slits with no parallel or serial type non-uniformities along the path. This roughly corresponds to the picture of clay particles of infinite extent aligned in parallel and spaced apart by a constant distance.

The theoretical basis and the mathematical preliminaries of the model can be found elsewhere (Lehikoinen, 1997) and will not be repeated here.

3 PRELIMINARY RESULTS

3.1 SIMPLE ELECTROLYTE

Figure 1 depicts the electrostatic potential as a function of the distance from the negatively charged clay surface ($\sigma = -0.125 \text{ C/m}^2$) for a sample immersed in 0.001 M, 0.01 M and 0.1 M NaCl electrolyte. The distance of 1 nm represents the half-opening of a slit-like pore¹. This would correspond to a clay dry density of $\sim 900 \text{ kg/m}^3$ in a perfectly oriented sample (Yong and Warkentin, 1975). As can be seen from this picture, the overlap of EDLs, and, consequently, the extent of anion exclusion, is reduced with the addition of the salt. Also, the model prediction according to the modified theory leads to a more negative potential over the entire opening. The resulting concentration profiles for the 0.001 M case are presented in Fig. 2. Here, the bending of the curve for the MEDL theory is to be noted. This is important in that the cations are not bound to attain unphysically high concentrations in close proximity to the surface with large values of $|\sigma|$, which is typical for the GC theory. The orientation of the solvent dipoles, induced by the varying electric field, gives rise to the relative dielectric permittivity profile in Fig. 3. It is clear from this figure (and intuitively) that the use of the "bulk" (or zero electric field strength) value of 78.46 for ϵ is far from being judicious. For overlapping double layers, it is valid *only* at the midpoint between clay platelets.

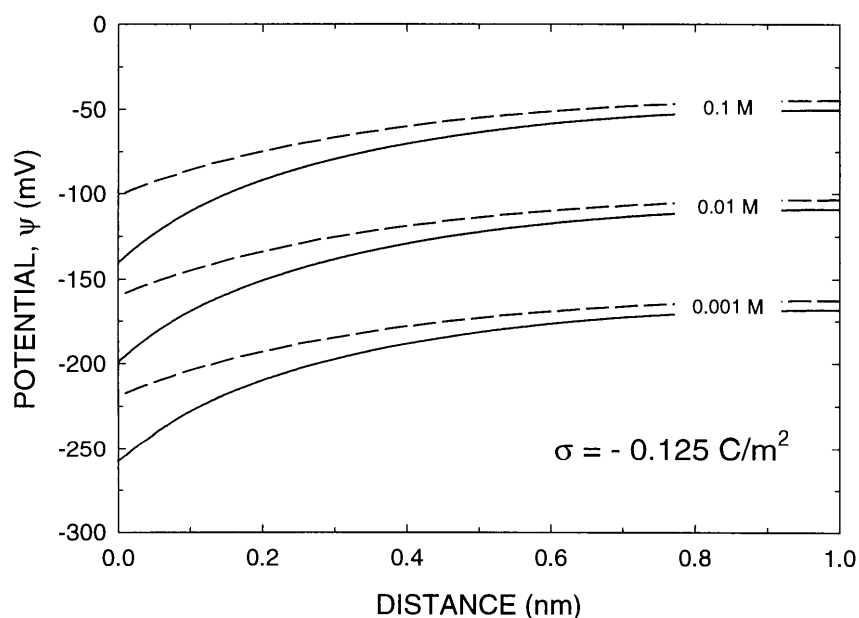


Fig. 1. Electrostatic potential as a function of the distance from the negatively charged surface in contact with a 0.001 M, 0.01 M and 0.1 M NaCl electrolyte. Broken line: GC theory, solid line: MEDL theory.

¹ This value is used in all calculations throughout the report.

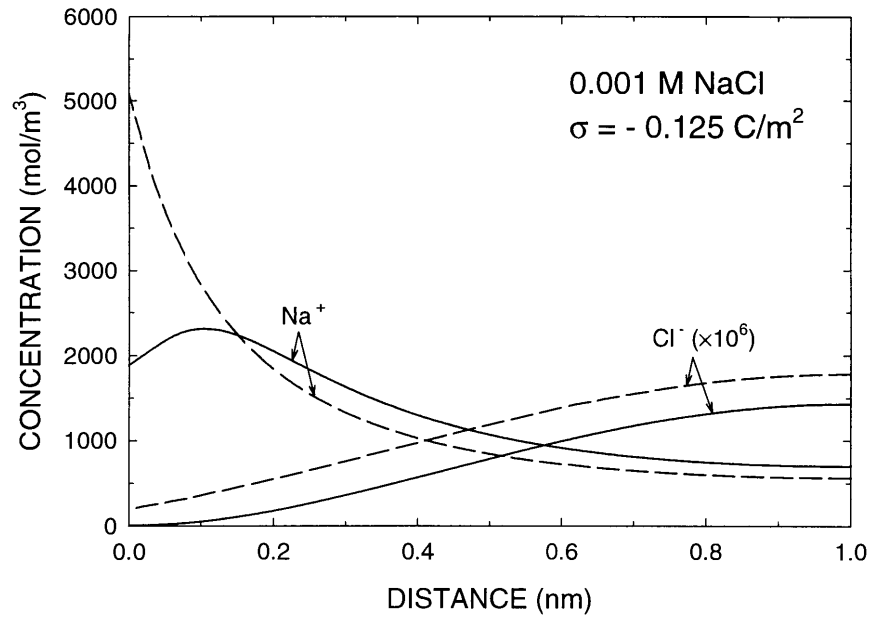


Fig. 2. Ionic concentrations as a function of the distance from the negatively charged surface in contact with a 0.001 M NaCl electrolyte. Broken line: GC theory, solid line: MEDL theory.

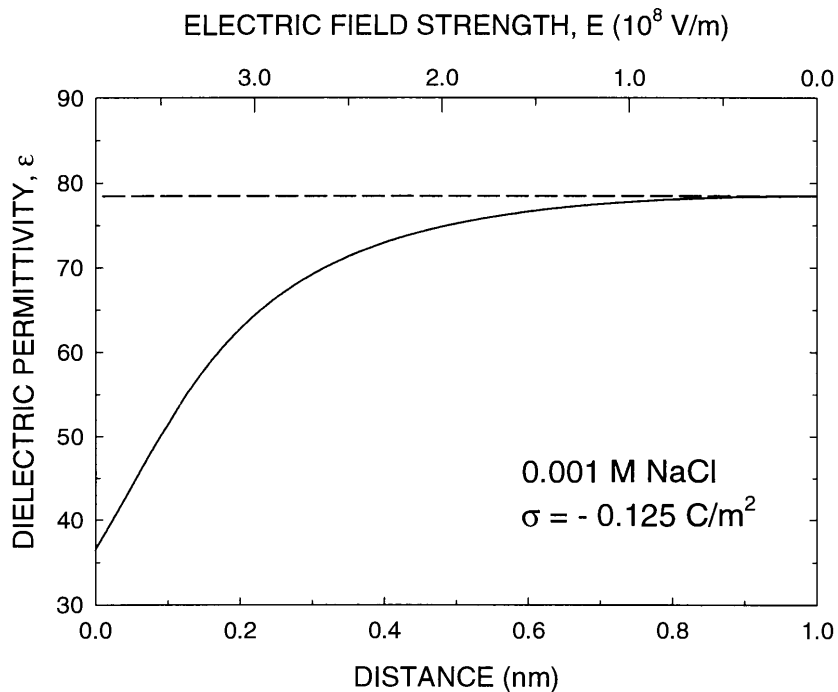


Fig. 3. Relation between the relative dielectric permittivity, the electric field strength and the distance from the negatively charged surface for a clay sample in contact with a 0.001 M NaCl electrolyte. Broken line: GC theory, solid line: MEDL theory. Notice the scale used for E .

Knowing the explicit form of the electrostatic potential from Fig. 1, it is now straightforward to calculate the electrostatic component of the disjoining pressure from the expression (e.g., Basu and Sharma, 1994)

$$\Pi_{el} = -\int_0^{\psi_m} \rho_m(\psi_m) d\psi_m = -\frac{kT}{e} \int_0^{\phi_m} \rho_m(\phi_m) d\phi_m \quad (1)$$

where ρ_m and $\phi_m = e\psi_m/(kT)$ are the charge density and the scaled potential at the midpoint between opposing surfaces. The integration can readily be carried out to yield

$$\Pi_{el} = kT \sum_{i=1}^M n_{i0} [\exp(-Z_i \phi_m) - 1] \quad (2)$$

where n_{i0} and Z_i are the number density in the bulk and the valence, respectively, of the i th ion. For the three molalities in Fig. 1, Π_{el} is (from top to bottom) for the MEDL theory 1.29, 1.69 and 1.73 MPa. The values of Π_{el} for the GC theory are somewhat less.

One important point to recognize in view of the diffusive movement of particles inside the clay is the extremely high viscosity of the pore fluid in the vicinity of the charged surface (Fig. 4). The increased viscosity acts to retard the diffusive transport.

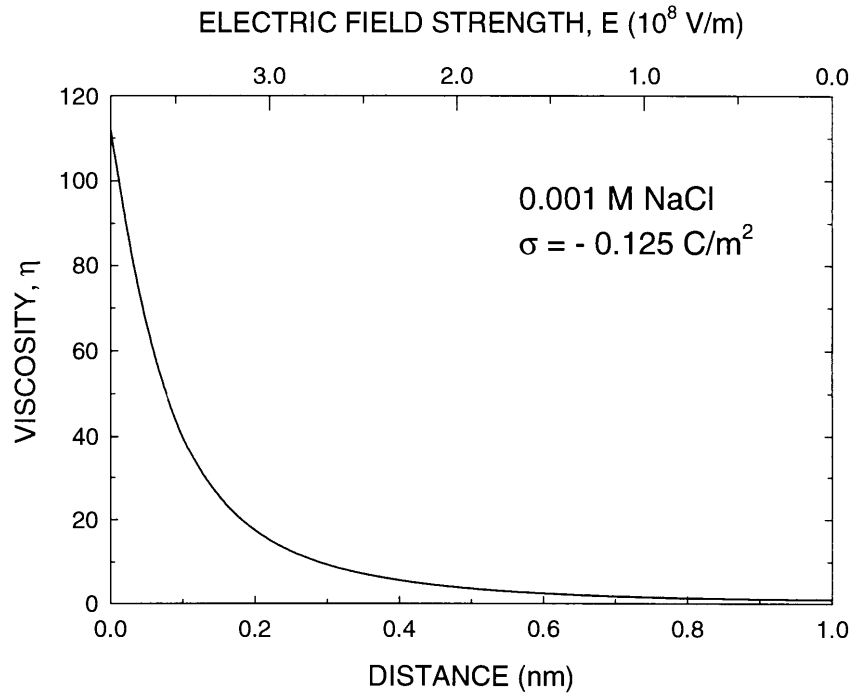


Fig. 4. Relation between the viscosity of the pore fluid, the electric field strength and the distance from the negatively charged surface for a clay sample in contact with a 0.001 M NaCl electrolyte. The calculated curve conforms to the MEDL theory and the expression due to Andrade and Dodd (1951) (cited from Hunter and Leyendekkers, 1978). The viscoelectric coefficient, f , was taken as $0.75 \times 10^{-15} \text{ m}^2/\text{V}^2$ (Hunter and Leyendekkers, 1978).

According to the GC theory, the behaviour of the EDL in a mixture of chlorides of the alkali metals is independent of the type of ions, that is, the profiles for all cations are identical (Fig. 5). However, when hydration forces are included in the PB equation, the concentration distributions are different for each type of ion. The physisorption of these cations can be found to increase according to the usual selectivity pattern: $\text{Li} < \text{Na} < \text{K} < \text{Cs}$.

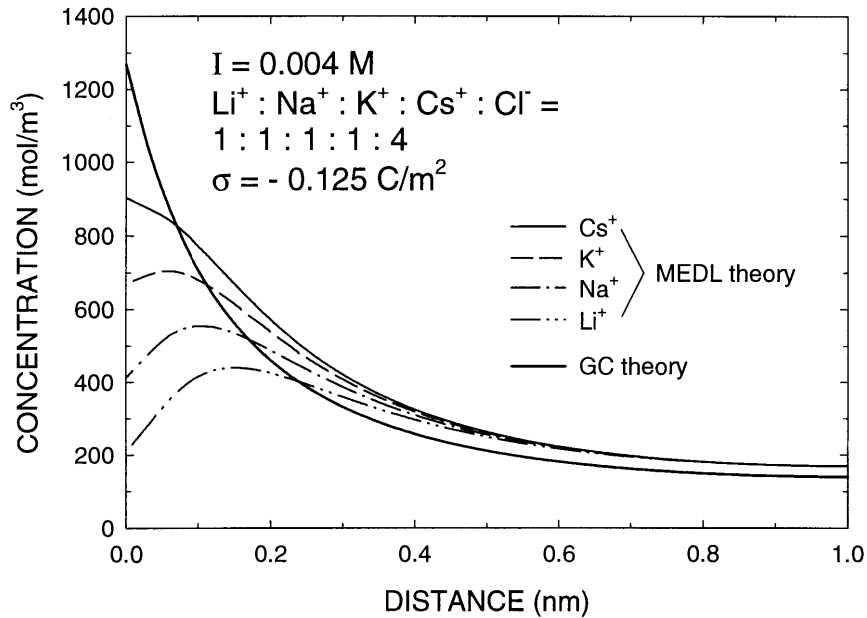


Fig. 5. Cationic concentrations as a function of the distance from the negatively charged surface in contact with a 0.004 M chloride background medium.

3.2 ALLARD GROUNDWATER

Next we wish to examine the effect of simulated Allard groundwater (composition given in the second column of Table I) on the equilibrium ionic concentrations inside the clay. The computed results are shown in Figs. 6 and 7 for the ionic concentration profiles. The surface excesses and deficits for the cations and anions, respectively, are clearly manifested. The second and third columns in Table I give two different measures of the extent of electrostatic adsorption for the ions. The fact that the ratio C_m/C_{Bulk} is the same for ions of like charge is due to vanishing dielectric saturation at the pore midplane.

Table I. Composition of the Allard groundwater (C_{Bulk}), the ratio of concentration averaged over the opening to that in the bulk ($C_{\text{Ave}}/C_{\text{Bulk}}$), and the ratio of concentration at the pore midpoint to that in the bulk ($C_{\text{m}}/C_{\text{Bulk}}$).

Ion	C_{Bulk} (mol/m ³)	$C_{\text{Ave}}/C_{\text{Bulk}}$ (%)	$C_{\text{m}}/C_{\text{Bulk}}$ (%)
Na	2.25	6 257	2 539
K	0.10	7 787	2 539
Ca	0.45	98 389	64 455
Mg	0.19	70 637	64 455
Cl	1.48	1.8	3.9
HCO ₃	1.94	1.8	3.9
SO ₄	0.10	0.05	0.16

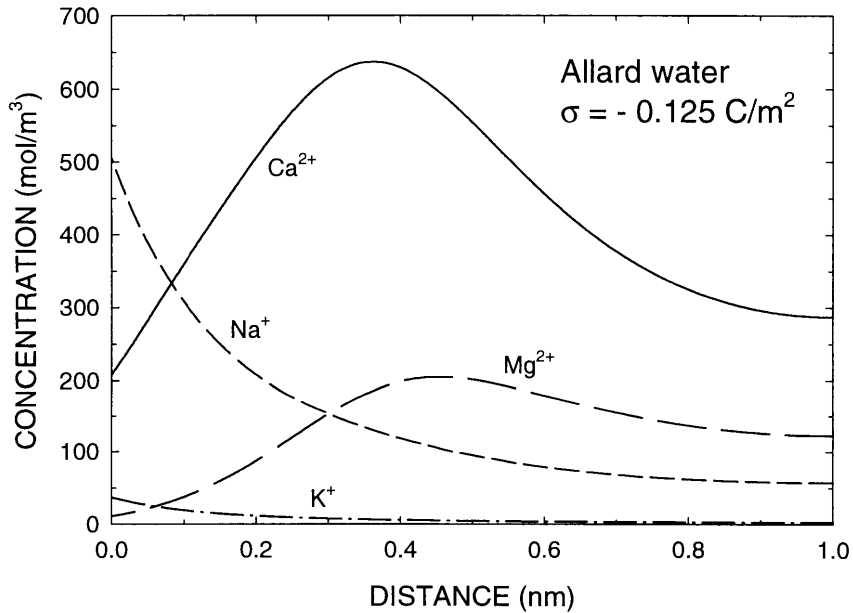


Fig. 6. Cationic concentrations as a function of the distance from the negatively charged surface in contact with the Allard groundwater simulant.

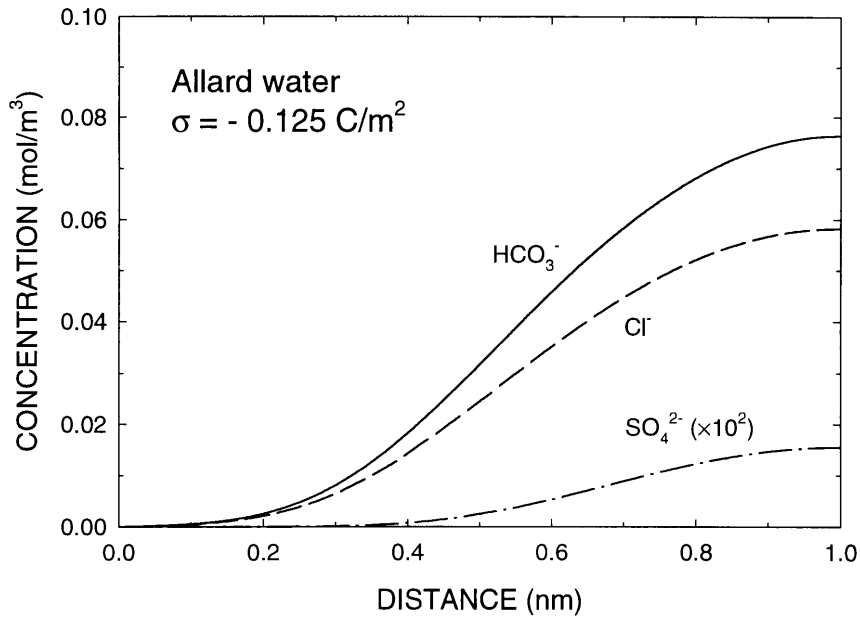


Fig. 7. Anionic concentrations as a function of the distance from the negatively charged surface in contact with the Allard groundwater simulant.

3.3 VOLUME EXCLUSION

In addition to the conventional treatment of the EDL theory, the above model results account for the ionic hydration to give rise to a modified (MEDL) theory. When the finite size of ions is also taken into consideration, we arrive at the electrostatic potential profile in Fig. 8 for a clay sample in contact with 0.001 M KCl. The effect of volume exclusion is to increase the double-layer overlap (and anion exclusion). This leads to a substantially smoothed concentration distribution for potassium (Fig. 9) and somewhat lower dielectric permittivity over the opening (Fig. 10). The electrostatic component of the disjoining pressure, as calculated from Eqn. (1) is considerably higher than that obtained from the plain MEDL model (this can be deduced from the difference in their electrostatic potentials in the midplane of the slit - Fig. 8). In fact, volume exclusion now becomes the governing contribution to Π_{el} (see also Leodidis and Hatton, 1989).

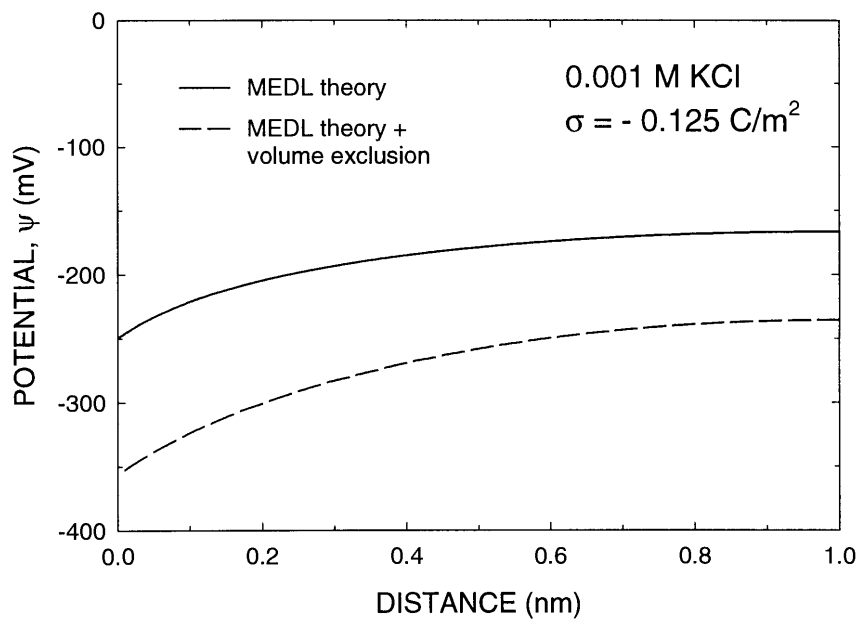


Fig. 8. Electrostatic potential as a function of the distance from the negatively charged surface in contact with a 0.001 M KCl electrolyte.

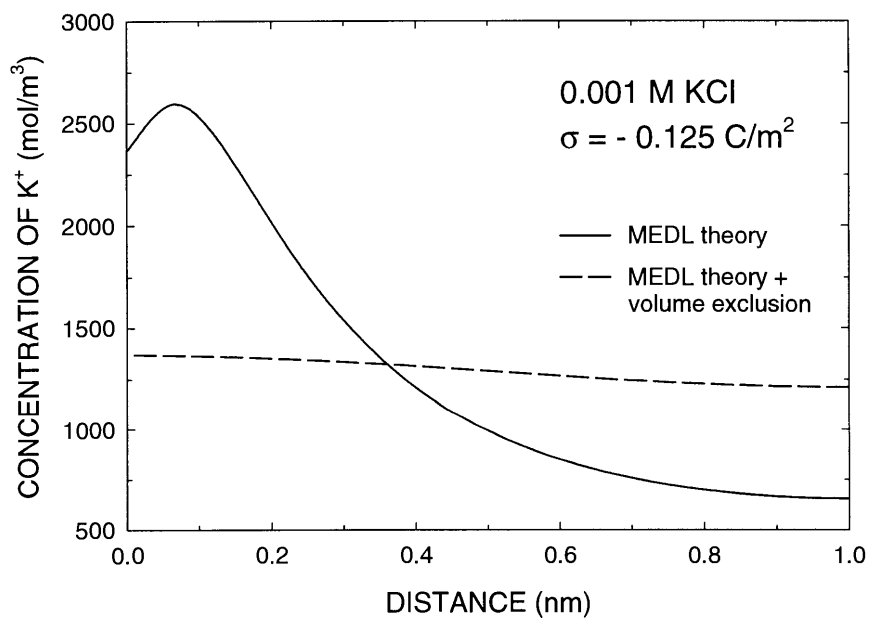


Fig. 9. Potassium concentration as a function of the distance from the negatively charged surface in contact with a 0.001 M KCl electrolyte.

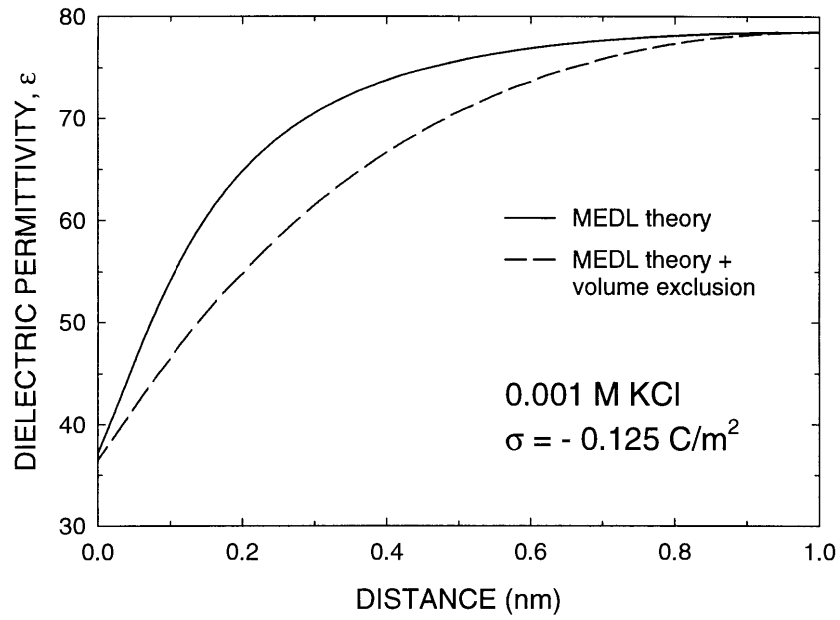


Fig. 10. Relative dielectric permittivity as a function of the distance from the negatively charged surface in contact with a 0.001 M KCl electrolyte.

4 SUMMARY AND FUTURE WORK

The core of the equilibration module, the PB solver, being also the most computer-intensive component of the electrokinetic transport model to be developed within the project, has now been completed. It is able to qualitatively explain the experimentally observed cation-exchange selectivities (Fig. 8) and to readily quantify co-ion exclusion (Table I) in terms of the MEDL theory. The equilibration module will be coupled with the modified Nernst-Planck equation for ionic transport, which is a special case² of the more general Maxwell-Stefan approach (Krishna and Wesselingh, 1997). For specifically adsorbing solutes, the PB solver will be adjusted to conform either to the adsorption isotherm (e.g., Langmuir, Frumkin or Tóth isotherm) or the charge regulation approach (e.g., Basu and Sharma, 1994), whichever is better suited to the present purpose.

² Ion-ion friction is ignored.

5 REFERENCES

- Andrade, E. N. da C. and Dodd, C. 1951. *Proc. Royal Soc. (London)*, **A204**, 449.
- Basu, S. and Sharma, M. M. 1994. Effect of dielectric saturation on disjoining pressure in thin films of aqueous electrolyte. *J. Colloid Interface Sci.*, **165**, 355-366.
- Hunter, R. J. and Leyendekkers, J. V. 1978. Viscoelectric coefficient for water. *J. Chem. Soc., Faraday Trans. 1*, **74**, 450-455.
- Krishna, R. and Wesselingh, J. A. 1997. The Maxwell-Stefan approach to mass transfer. *Chem. Engng. Sci.*, **52**, 861-911.
- Lehikoinen, J. 1997. Model for diffusion and porewater chemistry in compacted bentonite: Theoretical basis and the solution methodology for the transport model. Report POSIVA-97-01, 19 p.
- Leodidis, E. B. and Hatton, T. A. 1989. Specific ion effects in electrical double layers: Selective solubilization of cations in aerosol-OT reversed micelles. *Langmuir*, **5**, 741-753.
- Yong, R. N. and Warkentin, B. P. 1975. *Soil Properties and Behaviour*. Elsevier, Amsterdam. 449 p.