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Model for diffusion and porewater chemistry in compacted bentonite

Theoretical basis and the solution methodology for the transport model

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Nimeke – Title MODEL FOR DIFFUSION AND POREWATER CHEMISTRY IN COMPACTED BENTONITE – THEORETICAL BASIS AND THE SOLUTION METHODOLOGY FOR THE TRANSPORT MODEL	
Tiivistelmä – Abstract <p>This report describes the progress of the computer model for ionic transport in bentonite. The research is part of the project "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency" within the Nuclear Fission Safety Program organized by The Commission of the European Communities.</p> <p>The study was started by collecting a comprehensive body of available data on space-charge transport modelling and creating a conceptualization of the problem at hand. The numerical discretization of the governing equations by finite differences was also initiated.</p> <p>This report introduces the theoretical basis for the model, somewhat more elaborated than presented in "Progress Report 1/1996", and rectifies a few mistakes appearing in that report. It also gives a brief introduction to the solution methodology of the discretized governing equations.</p>	
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Nimeke – Title MALLI DIFFUUSIOLLE JA HUOKOSVESIKEMIALLE KOMPAKTOIDUSSA BENTONIITISSA – KULKEUTUMISMALLIN TEOREETTINEN PERUSTA JA RATKAISUMENETELMÄ	
Tiivistelmä – Abstract Tässä raportissa esitetään kuvaus ionien kulkeutumismallin kehittämisen edistymisestä. Tutkimus on osa projektia "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency", joka kuuluu Euroopan komission organisoimaan Nuclear Fission Safety ohjelmaan. Mallinkehitys aloitettiin keräämällä kattava, kulkeutumismallinnusta käsittelevä kirjallisuus sekä luomalla konseptuaalinen malli tämän materiaalin pohjalta. Myös mallinnettavaa systeemiä kuvaavien yhtälöiden numeerinen diskretointi differenssimenetelmällä aloitettiin. Raportti kuvaa mallin teoreettisen perustan raportissa "Progress Report 1/1996" esitettyä hieman kehittyneempänä ja korjaa joitakin em. raportissa esiintyneitä asiavirheitä. Raportti tarjoaa myös suppeahkon johdatuksen diskretoitujen yhtälöiden ratkaisumenetelmään.	
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FOREWORD

Within the Nuclear Fission Safety Program, organized by The Commission of the European Communities, the research project, "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency" 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 Commission of the European Communities, 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 diffusion and porewater chemistry in compacted bentonite.

CONTENTS

ABSTRACT

TIIVISTELMÄ

FOREWORD

CONTENTS

1 INTRODUCTION.....	1
2 THEORY.....	3
2.1 Modified Boltzmann equation	3
2.2 Poisson equation	6
2.3 Modified Nernst-Planck equation	7
2.4 Continuity equation.....	7
2.5 Navier-Stokes equation.....	8
2.6 Solution procedure.....	9
3 SUMMARY	10
4 REFERENCES	11
APPENDIX I Solution procedure.....	12

1 INTRODUCTION

A two-dimensional, transient molecular-level electrokinetic transport model that incorporates ionic hydration, orientation of solvent molecules by an applied electric field, solvent dipole-dipole interactions, dielectric saturation, and at a later stage, specific adsorption to the solid substrate (all of which are non-standard features of the theory), will be developed within the project.

The basic equations that govern the flow of electrolyte solution through the pore (i.e., momentum, convection-diffusion, and modified Poisson-Boltzmann equations) will be solved by an iterative numerical method to relate the characteristics of the flow (solute and solvent fluxes) to the characteristics of the pores (surface charge, and dimensions) and to the concentrations of the bulk solutions on both sides of the clay sample. The model is planned to be used to simulate and interpret equilibrium and transport experiments for bentonitic clays containing different types of background electrolyte solutions at various compactions. More 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 double-layer theory, which considers electrostatic interactions by means of the mean electrostatic field.

The pore geometry of the clay specimen is modelled as an array of tortuous negatively charged capillaries. Hydration forces arise from moving an ionic species in a dielectric continuum (pore space), where the dielectric permittivity is treated as a local function of the electric field strength. The modified Poisson-Boltzmann equation, including hydration effects, accounts for the different adsorption selectivities of cations of like charge to the clay surface, a well-known phenomenon which cannot be distinguished by conventional treatment of the double-layer theory. Moreover, a compact Stern layer for adsorbed counter-ions need not be introduced, since the hydration model simulates solvent co-ordination.

Since "Progress Report 1/96" we have further elaborated the theory behind the model and corrected a few mistakes that appeared in that report. The discretization of the governing equations as well as the coding of the first version of the model are practically at completion. We tried to adapt the model to the MATLAB[®] environment (also referred to in the Work Package description), but soon came to realize that the program execution would become extremely slow. Therefore, we had to seek for a more effective alternative to MATLAB[®]. We chose the Microsoft[®] Fortran Powerstation v. 4.0 compiler[†] (hereafter referred to as MS-FP) for that purpose. MS-FP is based on the newish Fortran 90 standard and so essentially offers the same array manipulation capabilities as MATLAB[®]. In addition, it enables the production of executable code, unlike MATLAB[®], and contains a large number of reliable and thoroughly tested IMSL[™] library routines to lighten our programming burden. However, we are currently still in the debugging phase of the code though expect to

[†] The professional edition.

get through this in the very near future. It is for the most part due to the readaptation of the code to the new computing environment that we are slightly behind schedule.

During the next reporting period, the code will be applied to a simple bentonite-electrolyte system. The model will also be advanced through the implementation of the specific adsorption of solutes to the charged pore wall.

2 THEORY

The following assumptions are made with regard to the theoretical basis of the transport model (Yeung, 1990):

- (a) the negative charge on the clay surface is homogeneously distributed,
- (b) the irreversible processes take place under isothermal conditions,
- (c) no hydraulic, electrical or concentration gradients exist within the external solutions,
- (d) local equilibrium of ionic species, and
- (e) the laws governing dilute electrolyte solutions apply.

In the subsequent discussion we give a concise description of the governing equations and outline their solution procedure.

2.1 MODIFIED BOLTZMANN EQUATION

The electrochemical potential for an ionic species j can be written

$$\mu_j = \mu_j^S + RT \ln c_j + \delta W_j \quad (1)$$

where the superscript "S" refers to the Standard State value of a given quantity, R and T have their usual meanings, c_j is the concentration, and δW_j is the free energy required to bring a species with charge z_j from the Reference State (superscript "R") potential to the given potential, ϕ , and relative dielectric permittivity of the solvent, ϵ (78.46 at 25 °C and 1 atm (Marcus, 1985)), and is given by (Gur *et al.*, 1978)

$$\delta W_j = z_j F(\phi - \phi^R) + A_j \left(\frac{1}{\epsilon} - \frac{1}{\epsilon^R} \right) + RT \ln \left(\frac{p_j^R}{p_j} \right) \quad (p_j^R \rightarrow 1) \quad (2)$$

where A_j is the hydration coefficient being equal to

$$A_j = -\Delta H_{j \text{ hydr}} \frac{\epsilon_b}{\epsilon_b - 1} \quad (3)$$

$\Delta H_{j \text{ hydr}}$ is the hydration enthalpy and the superscript "b" denotes the bulk solution. Values for $\Delta H_{j \text{ hydr}}$ and A_j can be found in Table I.

In Eqn. (2), ϵ is treated as a function of electric field strength, E ($\mathbf{E} = -\nabla\phi$). For field strengths greater than $2.0 \times 10^7 \text{ V}\cdot\text{m}^{-1}$ (Booth, 1951)

$$\epsilon(E) = n^2 + \frac{3(\epsilon_b - n^2)}{\beta E} \mathcal{L}(\beta E) \quad (4a)$$

$\mathcal{L}(x) = \coth(x) - 1/x$ is the Langevin function, n is the refractive index of water (1.3325 at 25 °C (Marcus, 1985)), and

$$\beta \equiv \frac{5\mu}{2kT}(n^2 + 2) \quad (4a')$$

where μ is the dipole moment of water (1.834 D (Marcus, 1985)) and k is the Boltzmann number. For electric fields smaller than $2.0 \times 10^7 \text{ V}\cdot\text{m}^{-1}$ (Booth, 1951)

$$\varepsilon(E) = \frac{\varepsilon_b}{\sqrt{qE}} \arctan(\sqrt{qE}) \simeq \varepsilon_b \left(1 - \frac{1}{3} qE^2\right) \quad (4b)$$

where $q \simeq 3.853 \times 10^{-17} \text{ m}^2 \cdot \text{V}^{-2}$.

Table I. Size exclusion and hydration parameters for various ions.

Ion	$V_h^{\infty \dagger}$ ($\text{cm}^3 \text{ mol}^{-1}$)	τ^\ddagger	$-\Delta H_{\text{hydr}}^0 \text{ ¶}$ (kJ mol^{-1})	A (kJ mol^{-1})	A (kcal mol^{-1})
H ⁺		27.0 [ⓔ]	1103	1117.2	266.6
Li ⁺	125.9	7.0	531	537.9	128.4
Na ⁺	109.0	6.0	416	421.4	100.6
K ⁺	94.4	5.2	334	338.3	80.7
Rb ⁺	92.8	5.1	308	312.0	74.5
Cs ⁺	92.8	5.1	283	286.7	68.4
Ca ²⁺	156.7	8.7	1602	1622.7	387.3
Mg ²⁺	176.9	9.8	1949	1974.2	471.2
Sr ²⁺	156.7	8.7	1470	1489.0	355.4
Cl ⁻	93.6	5.2	367	371.7	88.7
NO ₃ ⁻	95.3	5.3	325	329.2	78.6
SO ₄ ²⁻	123.0	6.8	1018	1031.1	246.1

[†] Partial molar hydrated volume (Marcus, 1985).

[‡] Calculated from $V_h^{\infty} / \bar{V}_{\text{H}_2\text{O}}$, where $\bar{V}_{\text{H}_2\text{O}}$ ($\simeq 18.069 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 25 °C and 1 atm (Marcus, 1985)) is the partial molar volume of water.

[¶] Marcus, 1987.

[ⓔ] The radius of a solvated proton equals three times the radius of a water molecule (Marcus, 1985).

In Eqn. (2), p_j represents the probability of finding τ_j available neighbouring vacant sites on which to introduce an ion of species j and generate a hydrated ion (Fig. 1). This means that upon dividing the volume of the water pool (here porewater) into layers, and each layer into identical sites (the volume of each site being equal to the volume of a water molecule), τ_j sites are allocated to species j (Table I). The probability p_j is given by

$$p_j = (1 - f)^{\tau_j}, \quad \text{where } f = \Omega^{-1} \sum_j \tau_j c_j \quad (\Omega = c_w + \sum_j \tau_j c_j) \quad (5)$$

where c_w and c_j are the concentration of water and the j th species respectively. Ω is the water constant, being equal to about $55.51 \text{ mol}\cdot\text{L}^{-1}$. Introducing size exclusion through Eqn. (5) is analogous to treating ions as occupying a certain, ion-specific volume in the electrolyte[†]. A practical aspect of this is that a cation cannot acquire an unrealistically high concentration in close proximity to the negatively charged pore wall, which is typical for the standard theory.

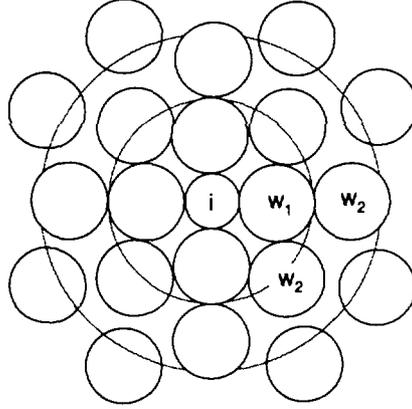


Fig. 1. The concentric shell model for the hydration of an ion. w_1 and w_2 constitute the primary and secondary solvation sheaths of the ion respectively (after Marcus, 1985).

From the assumption “d” one has $\mu_j^A = \mu_j^B$, where “A” and “B” refer to two different locations in the direction perpendicular to the pore wall (for a given axial position). Eqn. (5) leads to the Boltzmann distribution of ions in the pore

$$c_j^A = c_j^B \exp\left(\frac{\delta W_j^B - \delta W_j^A}{RT}\right) \quad (6)$$

If, for example, “B” denotes the pore centreline (superscript “0”), Eqn. (6) is expanded as (superscript “A” dropped)

$$c_j = c_j^0 \left(\frac{p}{p^0}\right) \exp\left[-\frac{z_j F \psi}{RT} - \frac{A_j}{RT} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_b}\right)\right] \quad (7)$$

where $\psi = \phi - \phi^0$. If the double layers of two opposing plates overlap, c_j^0 refers to a “fictitious” external solution with $\psi = 0$ which is thought to be in equilibrium with the pore solution at position x . These concentrations therefore obey $\sum z_j c_j^0 = 0$ (i.e., the potential ψ is measured relative to an electrically neutral electrolyte).

[†] The standard theory considers ions as point charges.

The second term on the right side of Eqn. (2), representing the free energy of solvation, can also be viewed as an activity coefficient for ionic species. The selectivity pattern of cations of like charge, similar to that found in cation-exchange studies, arises from this term (Fig. 2). Moreover, a compact Stern layer for adsorbed counter-ions need not be introduced, since the hydration model simulates solvent coordination.

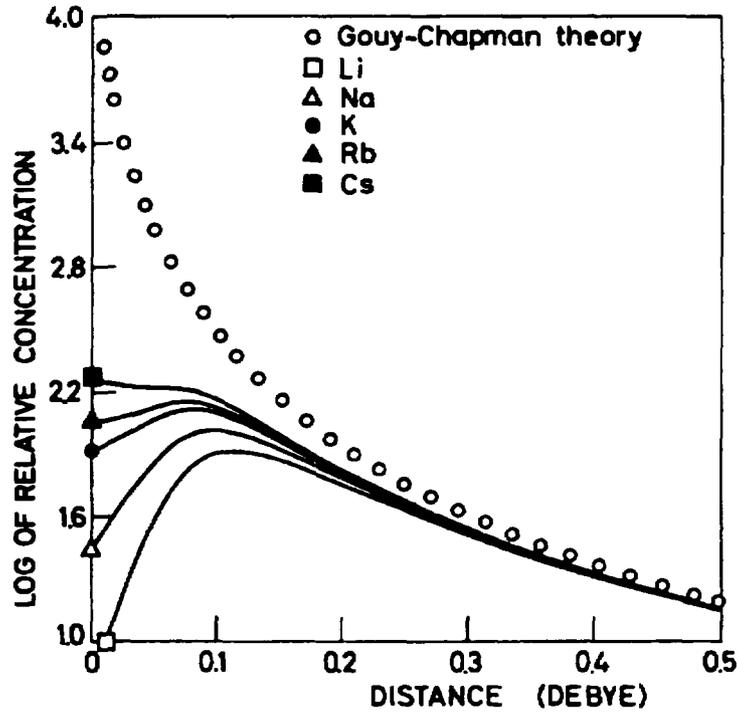


Fig. 2. Computational cation distributions in the double layer (surface potential -250 mV, bulk concentration of each cation 0.01 N) (Gur et al., 1978). The empty circles conform to the conventional treatment of the double layer; no selectivity differences between cations of like charge can be observed. The unit of the abscissa, "Debye", is widely used in conjunction with double-layer studies.

2.2 POISSON EQUATION

Another relation between the ionic concentrations and the potential is provided by the Poisson equation

$$\nabla \cdot (\epsilon \mathbf{E}) = \frac{\rho_e}{\epsilon_0} \quad (8)$$

where ϵ_0 is the permittivity of vacuum ($8.8542 \times 10^{-12} \text{ C} \cdot \text{V}^{-1} \cdot \text{m}^{-1}$) and the space charge density, ρ_e , is given by

$$\rho_e = F \sum_j z_j c_j \quad (9)$$

Together, Eqns. (6) and (8) constitute the modified Poisson-Boltzmann equation to give the weighted equilibrium distribution of ions across the pore cross-section.

2.3 MODIFIED NERNST-PLANCK EQUATION

For the characterization of ion transport, we need an expression for the ionic flux, \mathbf{N}_j ,

$$\mathbf{N}_j = c_j u_j (-\nabla \mu_j) \quad (10)$$

where u_j is the ionic mobility. The assumption “e” justifies the use of the Nernst-Einstein equation, $u_j = D_j/RT$, where D_j is the molecular diffusivity. Substituting Eqn. (1) into (10) and taking into account the flux of water results in the Nernst-Planck equation (Babchin and Masliyah, 1993)

$$\mathbf{N}_j = c_j \mathbf{v} - D_j \nabla c_j + \frac{z_j c_j D_j F}{RT} \mathbf{E} - \frac{c_j D_j F}{eRT} A_j \nabla \left(\frac{1}{\epsilon} \right) \quad (11)$$

where the terms one to five represent contributions from advection, molecular diffusion, electromigration, and hydration. In Eqn. (11), $\mathbf{v} = (u, v)$ is the barycentric velocity of the solvent.

2.4 CONTINUITY EQUATION

The temporal evolution of ionic species j is given by the continuity equation, which accounts for the conservation of material in the system

$$\frac{\partial c_j}{\partial t} = -\nabla \cdot \mathbf{N}_j \quad (12)$$

The continuity equation, Eqn. (12), and the Nernst-Planck equation, Eqn. (11), can be combined to give

$$\begin{aligned} \frac{\partial c_j}{\partial t} = & -\mathbf{v} \cdot \nabla c_j + D_j \nabla^2 c_j - \frac{z_j D_j F}{RT} (c_j \nabla \cdot \mathbf{E} + \nabla c_j \cdot \mathbf{E}) + \\ & + \frac{D_j F}{eRT} A_j \left\{ c_j \nabla^2 \left(\frac{1}{\epsilon} \right) + \nabla c_j \cdot \nabla \left(\frac{1}{\epsilon} \right) \right\} \end{aligned} \quad (13)$$

In deriving Eqn. (13) we have taken account of the incompressibility of the fluid

$$\nabla \cdot \mathbf{v} = 0 \quad (14)$$

The first three terms in Eqn. (13) yield the more familiar advection-diffusion equation.

2.5 NAVIER-STOKES EQUATION

To integrate Eqn. (13), we need an expression for \mathbf{v} , the fluid mass average velocity. This is provided by the non-stationary Navier-Stokes equation for the incompressible viscous flow (e.g. Verbrugge and Pintauro, 1989; Fletcher, 1991)

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla P - \frac{2}{3}\nabla(\eta\nabla\cdot\mathbf{v}) + 2\nabla\cdot(\eta \text{ def } \mathbf{v}) + \rho_e \mathbf{E} - \frac{1}{2}(\mathbf{E}\cdot\mathbf{E})\nabla\epsilon \quad (15)$$

where ρ is the density of water ($0.997045 \text{ g}\cdot\text{cm}^{-3}$ at $25 \text{ }^\circ\text{C}$ (Marcus, 1985)), D/Dt ($=\partial/\partial t + \mathbf{v}\cdot\nabla$) is the substantive derivative, η is the dynamic viscosity ($0.890\times 10^{-3} \text{ Pa}\cdot\text{s}$ at $25 \text{ }^\circ\text{C}$ and 1 atm (Marcus, 1985)), and $\text{def } \mathbf{v} \equiv \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)$. The differential forms of the x_1 and x_2 momentum equations in cylindrical co-ordinates ($(x_1, x_2) = (x, r)$) thus read (after having made use of Eqn. (14))

$$\begin{aligned} \rho \frac{Du}{Dt} = & -\frac{\partial P}{\partial x} + 2\frac{\partial}{\partial x}\left(\eta\frac{\partial u}{\partial x}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left[r\eta\left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial x}\right)\right] + \rho_e E_x - \\ & -\frac{1}{2}(E_x^2 + E_r^2)\frac{\partial\epsilon}{\partial x}, \end{aligned} \quad (16a)$$

$$\begin{aligned} \rho \frac{Dv}{Dt} = & -\frac{\partial P}{\partial r} + \frac{2}{r}\frac{\partial}{\partial r}\left(r\eta\frac{\partial v}{\partial r}\right) + \frac{\partial}{\partial x}\left[\eta\left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial x}\right)\right] + \rho_e E_r - \\ & -\frac{1}{2}(E_x^2 + E_r^2)\frac{\partial\epsilon}{\partial r}, \end{aligned} \quad (16b)$$

Assuming $\partial v/\partial x \simeq 0$, $\partial v/\partial r \simeq 0$, $v \ll u$, $\partial u/\partial x \simeq 0$ (by Eqn. (14)), Eqns. (16) simplify to

$$\rho \frac{\partial u}{\partial t} = -\frac{\partial P}{\partial x} - \rho_e \frac{\partial\phi}{\partial x} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\eta\frac{\partial u}{\partial r}\right) - \frac{1}{2}\left[\left(\frac{\partial\phi}{\partial x}\right)^2 + \left(\frac{\partial\phi}{\partial r}\right)^2\right]\frac{\partial\epsilon}{\partial x} \quad (17a)$$

$$0 \simeq -\frac{\partial P}{\partial r} - \rho_e \frac{\partial\phi}{\partial r} + \frac{\partial\eta}{\partial x}\frac{\partial u}{\partial r} - \frac{1}{2}\left[\left(\frac{\partial\phi}{\partial x}\right)^2 + \left(\frac{\partial\phi}{\partial r}\right)^2\right]\frac{\partial\epsilon}{\partial r} \quad (17b)$$

To solve for P , the pressure equation must be called for. This is obtained from $\partial[\text{Eqn. (17a)}]/\partial x + \partial[\text{Eqn. (17b)}]/\partial r$.

For η , we use the form suggested by Andrade and Dodd (1951)

$$\frac{\eta - \eta_0}{\eta_0} = f E^2 \quad (18)$$

where η_0 is the bulk viscosity, and f is the viscoelectric coefficient, estimated to have a value of $(0.5-1.0) \times 10^{-15} \text{ V}^{-2} \cdot \text{m}^2$ (Hunter and Leyendekkers, 1978).

2.6 SOLUTION PROCEDURE

One conceivable solution method for the set of equations (6, 8, 9), (13) and (15) is obtained through discretization by finite differences (Appendix I). This leads to a set of non-linear differential algebraic equations subject to suitably chosen boundary conditions and some simplifying presumptions (Fair and Osterle, 1971; Sasidhar and Ruckenstein, 1981). The time dependence appearing in Eqn. (13) will be handled in an explicit manner, that is, the concentrations for every species at a given time are calculated explicitly from previously determined values. This means that the solution is a two-step procedure in which each time step is separated into a transport and equilibration phase.

3 SUMMARY

This study is part of a project where a computer model for ionic transport in bentonite will be developed. The model will be based on the micro- and macro-scale material properties of bentonite and surrounding conditions.

A two-dimensional, transient molecular-level electrokinetic transport model that incorporates ionic hydration, orientation of solvent molecules by an applied electric field, solvent dipole-dipole interactions, dielectric saturation, and at a later stage, specific adsorption to the solid substrate (all of which are non-standard features of the theory), will be developed. The model is planned to be used to simulate and interpret equilibrium and transport experiments for bentonitic clays containing different types of background electrolyte solutions at various compactions. More 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 double-layer theory.

The study was started by collecting a comprehensive body of available data on space-charge transport modelling and creating a conceptualization of the problem at hand. The numerical discretization of the governing equations by finite differences was also initiated.

Since "Progress Report 1/96" we have further elaborated the theoretical basis for the model and corrected a few mistakes that appeared in that report. The discretization of the governing equations as well as the coding of the first version of the model are now practically at completion. The outline of the solution procedure for the equilibration part of the model is described in this report.

4 REFERENCES

- Andrade, E. N. da C., and Dodd, C. 1951. *Proc. Royal Soc. (London), Ser. A*, **204**, 449.
- Babchin, A. J., and Masliyah, J. 1993. Modified Nernst-Planck equation for hydration effects. *J. Colloid Interface Sci.*, **160**, 258-259.
- Booth, F. 1951. The dielectric constant of water and the saturation effect. *J. Chem. Phys.*, **19**, 391-394, 1327-1328, 1615.
- Fair, J. C., and Osterle, J. F. 1971. Reverse electro dialysis in charged capillary membranes. *J. Chem. Phys.*, **54**, 3307-3316.
- Fletcher, C. A. J. 1991. Computational techniques for fluid dynamics 2: Specific techniques for different flow categories. 2nd ed. Springer-Verlag, Berlin Heidelberg, chapter 11.
- Gur, Y., Ravina, I., and Babchin, A. J. 1978. On the electrical double layer theory. II. The Poisson-Boltzmann equation including hydration forces. *J. Colloid Interface Sci.*, **64**, 333-341.
- Hunter, R. J., and Leyendekkers, J. V. 1978. Viscoelectric coefficient for water. *J. Chem. Soc., Faraday Trans. 1*, **74**, 450-455.
- Marcus, Y. 1985. Ion solvation. John Wiley and Sons Ltd., Chichester, 306 p.
- Marcus, Y. 1987. The thermodynamics of solvation of ions. Part 2. - The enthalpy of hydration at 298.15 K. *J. Chem. Soc., Faraday Trans. 1*, **83**, 339-349.
- Sasidhar, V., and Ruckenstein, E. 1981. Electrolyte osmosis through capillaries. *J. Colloid Interface Sci.*, **82**, 439-457.
- Verbrugge, M. W., and Pintauro, P. N. 1989. Transport models for ion-exchange membranes. In: Conway, B. E., Bockris, J. O'M., and White, R. E. (eds.), *Modern aspects of electrochemistry*, **19**, Plenum Press, New York. Pp. 1-67.
- Yeung, A. T. 1990. Coupled flow equations for water, electricity and ionic contaminants through clayey soils under hydraulic, electrical and chemical gradients. *J. Non-Equilib. Thermodyn.*, **15**, 247-267.

SOLUTION PROCEDURE

1 EQUILIBRATION

1.1 Differential equation

Whenever solving differential equations (DEs), it is a good idea to scale them first. In fact, scaling may even turn out to be a prerequisite for finding a solution to the problem. Here we start by defining a non-dimensional spatial co-ordinate in the radial direction

$$\tilde{r} \equiv [\exp(\kappa r) - 1] \xi; \quad \xi = \frac{1}{\exp(\kappa a) - 1} \quad (\text{A.1})$$

where κ is the reciprocal of the so-called Debye screening length, obtained from

$$\kappa^2 = \frac{F^2}{\epsilon_0 RT} \sum_{j=1}^m z_j^2 c_j(0) \quad (\text{A.2})$$

The mapping in Eqn. (A.1) produces a dynamically adjusting co-ordinate system in the physical r -space, which exhibits enhanced resolution where most badly needed, that is, in the proximity of the pore walls where the solution of the DE experiences rapid fluctuations. Apart from having the property of giving a non-dimensional quantity, \tilde{r} , the mappings such as that of Eqn. (A.1) are very desirable in the sense that they may speed up the convergence of the solution procedure enormously.

The electrostatic potential, ϕ , is cast to a non-dimensional form through

$$\psi \equiv \frac{F\phi}{RT} \quad (\text{A.3})$$

ψ being the non-dimensional potential.

To evaluate the spatial derivatives appearing in the Poisson equation, Eqn. (8), we apply the chain rule of differentiation to obtain the following useful identities

$$\frac{\partial}{\partial r} = \left(\frac{d\tilde{r}}{dr} \right) \frac{\partial}{\partial \tilde{r}} = \kappa(\tilde{r} + \xi) \frac{\partial}{\partial \tilde{r}} \quad (\text{A.4a})$$

$$\frac{1}{r} \frac{\partial}{\partial r} = \kappa^2 \frac{(\tilde{r} + \xi)}{\ln\left(\frac{\tilde{r} + \xi}{\xi}\right)} \frac{\partial}{\partial \tilde{r}} \quad (\text{A.4b})$$

$$\frac{\partial^2}{\partial r^2} = \kappa^2 (\tilde{r} + \xi) \left[\frac{\partial}{\partial \tilde{r}} + (\tilde{r} + \xi) \frac{\partial^2}{\partial \tilde{r}^2} \right] \quad (\text{A.4c})$$

The electric field strength, E , is given by

$$E = \text{sgn}(\sigma) \frac{\partial \phi}{\partial r} = \frac{\text{sgn}(\sigma) RT}{F} \kappa (\tilde{r} + \xi) \frac{\partial \psi}{\partial \tilde{r}} = \frac{RT}{F} \kappa (\tilde{r} + \xi) \tilde{E} \quad (\text{A.5})$$

where

$$\tilde{E} = \frac{F}{RT} \frac{E}{\kappa (\tilde{r} + \xi)} \quad (\text{A.6})$$

is the non-dimensional counterpart of E .

Eqn. (8) is expressed in terms of ψ as

$$(\tilde{r} + \xi) \frac{\partial^2 \psi}{\partial \tilde{r}^2} [\alpha(E)E + \varepsilon] + \frac{\partial \psi}{\partial \tilde{r}} [\alpha(E)E + \varepsilon \delta(\tilde{r})] = -\frac{F}{\varepsilon_0 RT} \frac{\rho_e}{\kappa^2 (\tilde{r} + \xi)} \quad (\text{A.7})$$

where

$$\alpha(E) = \left(\frac{d\varepsilon}{dE} \right) \quad (\text{A.8})$$

and

$$\delta(\tilde{r}) = 1 + \frac{1}{\ln\left(\frac{\tilde{r} + \xi}{\xi}\right)} \quad (\text{A.9})$$

Taking account of $\alpha(E)E = \alpha(\tilde{E})\tilde{E}$ we arrive at a slightly modified form for Eqn. (A.7)

$$(\tilde{r} + \xi) \frac{\partial^2 \psi}{\partial \tilde{r}^2} [\alpha(\tilde{E})\tilde{E} + \varepsilon] + \frac{\partial \psi}{\partial \tilde{r}} [\alpha(\tilde{E})\tilde{E} + \varepsilon \delta(\tilde{r})] = -\frac{F}{\varepsilon_0 RT} \frac{\rho_e}{\kappa^2 (\tilde{r} + \xi)} \quad (\text{A.10a})$$

To tackle the singularity at $r = 0$ ($\tilde{r} = 0$), we utilize the fact that

$$\lim_{r \rightarrow 0} \frac{1}{r} \frac{\partial}{\partial r} = \frac{\partial^2}{\partial r^2} \quad (\text{A.11})$$

so that Eqn. (A.10a) simplifies to

$$\left[\frac{\partial \Psi}{\partial \tilde{r}} + (\tilde{r} + \xi) \frac{\partial^2 \Psi}{\partial \tilde{r}^2} \right] [\alpha(\tilde{E})\tilde{E} + 2\varepsilon] = -\frac{F}{\varepsilon_0 RT} \frac{\rho_e}{\kappa^2(\tilde{r} + \xi)} \quad (\text{A.10b})$$

For $E \geq E_t$ ($= 2.0 \times 10^7 \text{ V} \cdot \text{m}^{-1}$) ($\tilde{E} \geq \tilde{E}_t$, where $\tilde{E}_t = \frac{FE_t}{RT} \frac{1}{\kappa(\tilde{r} + \xi)}$), ε and α are given by

$$\varepsilon(\tilde{E}) = n^2 + \frac{3(\varepsilon_b - n^2)}{\tilde{\beta}\tilde{E}} \left[\coth(\tilde{\beta}\tilde{E}) - \frac{1}{\tilde{\beta}\tilde{E}} \right] \quad (\text{A.12a})$$

and

$$\alpha(\tilde{E}) = \frac{3(\varepsilon_b - n^2)\tilde{\beta}}{(\tilde{\beta}\tilde{E})^3} \left\{ 2 + (\tilde{\beta}\tilde{E})^2 - (\tilde{\beta}\tilde{E}) \coth(\tilde{\beta}\tilde{E}) \left[(\tilde{\beta}\tilde{E}) \coth(\tilde{\beta}\tilde{E}) + 1 \right] \right\} \quad (\text{A.13a})$$

respectively. In Eqns. (A.12a) and (A.13a), $\tilde{\beta} = \beta \frac{RT}{F} \kappa(\tilde{r} + \xi)$.

For $\tilde{E} < \tilde{E}_t$,

$$\varepsilon(\tilde{E}) = \varepsilon_b \left[1 - \frac{q}{3\beta^2} (\tilde{\beta}\tilde{E})^2 \right] \quad (\text{A.12b})$$

and

$$\alpha(\tilde{E}) = -\frac{2q\varepsilon_b}{3\beta} (\tilde{\beta}\tilde{E}) \quad (\text{A.13b})$$

The assumption “d” in Chapter 2 means that the electrochemical potential, μ_j , in the radial direction be constant at a given axial position. Thus, we may write $\mu_j(\tilde{r}) = \mu_j(0)$ (with x fixed), which leads to the radial concentration distribution

$$c_j(\tilde{r}) = c_j(0) \left[\frac{p_j(\tilde{r})}{p_j(0)} \right] \exp \left[-z_j(\psi(\tilde{r}) - \psi(0)) - \tilde{A}_j \left(\frac{1}{\varepsilon(\tilde{r})} - \frac{1}{\varepsilon_b} \right) \right] \quad (\text{A.14})$$

1.2 Boundary conditions

Radial symmetry about the pore centreline, $\tilde{r} = 0$ ($r = 0$), results in

$$E|_{\tilde{r}=0} = \tilde{E}|_{\tilde{r}=0} = 0 \quad (\text{A.15})$$

while the radial direction boundary condition at the pore wall, $\tilde{r} = 1$ ($r = a$), reads

$$E|_{r=a} = \text{sgn}(\sigma) \frac{\partial \phi}{\partial r} \Big|_{r=a} = \frac{\text{sgn}(\sigma) \sigma}{\epsilon_0 \epsilon} \quad (\text{A.16})$$

and is written in a dimensionless form as

$$\tilde{E}|_{\tilde{r}=1} = \text{sgn}(\sigma) \frac{\partial \psi}{\partial \tilde{r}} \Big|_{\tilde{r}=1} = \frac{\text{sgn}(\sigma) F \sigma}{\epsilon_0 RT \kappa (\xi + 1) \epsilon} \quad (\text{A.17})$$

σ is the surface charge density (subject to specific adsorption at a later stage).

1.3 Mass balance constraints

Pore:

The concentration in Eqn. (A.14) must satisfy the following mass balance equation

$$c_{jT} = \frac{\pi}{a^2} \int_0^a c_j(r) r dr = \frac{\pi}{(a\kappa)^2} \int_0^1 c_j(\tilde{r}) \frac{\ln\left(\frac{\tilde{r} + \xi}{\xi}\right)}{(\tilde{r} + \xi)} d\tilde{r} \quad (\text{A.18})$$

where c_{jT} is the total concentration of the j th species. Eqn. (A.18) is really nothing more but an average concentration taken over the pore cross-section.

Bentonite-water interface:

The concentrations should meet two conditions. The first of these stems from the equality of electrochemical potential in the bulk and at the pore mouth (a zone, thickness (Δx) , which is thought to be in equilibrium with the bulk at all times) (e.g. Sasidhar and Ruckenstein, 1981)

$$c_j(\tilde{r}) = c_{jb} \left[\frac{p_j(\tilde{r})}{p_{jb}} \right] \exp \left[-z_j \psi(\tilde{r}) - \tilde{A}_j \left(\frac{1}{\epsilon(\tilde{r})} - \frac{1}{\epsilon_b} \right) \right] \quad (\text{A.19})$$

where $\tilde{A}_j = A_j / (RT)$. The second condition is the mass conservation for the combination of the equilibrium zone and the bulk

$$\begin{aligned}
M_{jT} &= 2\pi(\Delta x)N_p \int_0^a c_j(r) r dr + V_b c_{jb} = \\
&= \frac{2\pi(\Delta x)N_p}{\kappa^2} \int_0^1 c_j(\tilde{r}) \frac{\ln\left(\frac{\tilde{r} + \xi}{\xi}\right)}{(\tilde{r} + \xi)} d\tilde{r} + V_b c_{jb}
\end{aligned} \tag{A.20}$$

where M_{jT} is the total mass of the j th species, V_b is the volume of the bulk reservoir and N_p is the number of pores, calculable from

$$N_p = \frac{n}{T} \left(\frac{S}{\pi a^2} \right) \tag{A.21}$$

n and S being the porosity and the cross-sectional area of the bentonite sample respectively. T is the tortuosity of the pore network (see p. 19). The above conditions (Eqn. (A.19) and (A.20)) account for the fact that the bulk concentration should also be iterated on. At first glance, it would be tempting to apply Eqn. (A.19) alone and determine the concentration at the pore mouth explicitly from the bulk concentration. However, a severe contradiction arises if the bulk phase does not contain the species of interest but the pore mouth does. Using Eqn. (A.19) solely would then lead to a situation where the mass for that species is not conserved, i.e., the concentration becomes zero irrespective of the species' concentration in the sample. This might occur, for example, when a montmorillonite sample saturated with sodium is brought into contact with a bulk electrolyte containing, say, KCl.

1.4 Method of solution

Since Eqn. (8) cannot be solved analytically, we must integrate it by means of a numerical technique. Our candidate for that technique is the finite difference method (Smith, 1978), which gives a number of non-linear algebraic equations along with an equal number of unknowns. The discretization comprises the division of the spatial domain, \tilde{r} , into a sequence of abscissas, denoted $\tilde{r}_0, \tilde{r}_1, \dots, \tilde{r}_N$ which are spaced apart by a constant step $(\Delta\tilde{r})$, $\tilde{r}_i = \tilde{r}_0 + i(\Delta\tilde{r})$ ($i = 0, 1, \dots, N$). Here, $\tilde{r}_0 = 0$, $\tilde{r}_N = 1$, and $(\Delta\tilde{r}) = (\tilde{r}_N - \tilde{r}_0)/N = 1/N$. A function $F(\tilde{r})$ has known values at the \tilde{r}_i 's, $F(\tilde{r}_i) \equiv F_i$. For example, Eqn. (A.4) is discretized as

$$\left. \frac{\partial F}{\partial \tilde{r}} \right|_i = \kappa(\tilde{r}_i + \xi) \frac{F_{i+1} - F_{i-1}}{2(\Delta\tilde{r})} + O[(\Delta\tilde{r})^2] \tag{A.22a}$$

$$\left. \frac{1}{r} \frac{\partial F}{\partial r} \right|_i = \kappa^2 \frac{(\tilde{r}_i + \xi)}{\ln\left(\frac{\tilde{r}_i + \xi}{\xi}\right)} \frac{F_{i+1} - F_{i-1}}{2(\Delta\tilde{r})} + O[(\Delta\tilde{r})^2] \tag{A.22b}$$

$$\left. \frac{\partial^2 F}{\partial r^2} \right|_i = \kappa^2 (\tilde{r}_i + \xi) \left[\frac{F_{i+1} - F_{i-1}}{2(\Delta\tilde{r})} + (\tilde{r}_i + \xi) \frac{F_{i+1} - 2F_i + F_{i-1}}{(\Delta\tilde{r})^2} \right] + O[(\Delta\tilde{r})^2] \tag{A.22c}$$

After some manipulation we arrive at the discretized governing equations:

1.4.1 DE

$$\begin{aligned} & (\psi_{i+1} - 2\psi_i + \psi_{i-1})(\alpha_i \tilde{E}_i + \gamma_i \varepsilon_i) + \frac{(\Delta \tilde{r})}{2(\tilde{r}_i + \xi)} (\psi_{i+1} - \psi_{i-1}) \times \\ & \times (\alpha_i \tilde{E}_i + \delta_i \varepsilon_i) = -\frac{F\rho_{e,i}}{\varepsilon_0 RT} \frac{(\Delta \tilde{r})^2}{[\kappa(\tilde{r}_i + \xi)]^2} \end{aligned} \quad (\text{A.23})$$

$$\gamma_0 = 2, \quad \delta_0 = 2$$

$$\gamma_i = 1, \quad \delta_i = 1 + \frac{1}{\ln\left(\frac{\tilde{r}_i + \xi}{\xi}\right)} \quad (i \neq 0) \quad (\text{A.24})$$

$$\tilde{E}_i = \frac{\text{sgn}(\sigma)}{2(\Delta \tilde{r})} (\psi_{i+1} - \psi_{i-1}) \quad (\text{A.25})$$

For $\tilde{E}_i \geq \tilde{E}_i$,

$$\varepsilon_i = n^2 + \frac{3(\varepsilon_b - n^2)}{\tilde{\beta}\tilde{E}_i} \left[\coth(\tilde{\beta}\tilde{E}_i) - \frac{1}{\tilde{\beta}\tilde{E}_i} \right] \quad (\text{A.26a})$$

and

$$\alpha_i = \frac{3(\varepsilon_b - n^2)\tilde{\beta}}{(\tilde{\beta}\tilde{E}_i)^3} \left\{ 2 + (\tilde{\beta}\tilde{E}_i)^2 - (\tilde{\beta}\tilde{E}_i) \coth(\tilde{\beta}\tilde{E}_i) \left[(\tilde{\beta}\tilde{E}_i) \coth(\tilde{\beta}\tilde{E}_i) + 1 \right] \right\} \quad (\text{A.27a})$$

For $\tilde{E}_i < \tilde{E}_i$,

$$\varepsilon_i = \varepsilon_b \left[1 - \frac{q}{3\beta^2} (\tilde{\beta}\tilde{E}_i)^2 \right] \quad (\text{A.26b})$$

and

$$\alpha_i = -\frac{2q\varepsilon_b}{3\beta} (\tilde{\beta}\tilde{E}_i) \quad (\text{A.27b})$$

1.4.2 Boundary conditions

Eqn. (A.15) suggests

$$\Psi_{-1} = \Psi_1 \quad (\text{A.28})$$

From Eqn. (A.17) we have

$$\tilde{E}_N = \frac{\text{sgn}(\sigma)F\sigma}{\epsilon_0 RT\kappa(\xi + 1)\epsilon_N} \quad (\text{A.29})$$

while Eqn. (A.5) proposes

$$\Psi_{N+1} = \Psi_{N-1} + 2\text{sgn}(\sigma)(\Delta\tilde{r})\tilde{E}_N \quad (\text{A.30})$$

Ψ_{-1} and Ψ_{N+1} are fictitious potentials outside the actual spatial domain. They can be imagined as the endpoints for a domain extended one layer, $\Delta\tilde{r}$. This extension has been done to preserve the formal second-order accuracy in the discretization.

1.4.3 Mass balance constraints

Pore (Eqn. (A.18)):

$$c_{jT} \equiv \frac{\pi(\Delta\tilde{r})}{(a\kappa)^2} \sum_{i=0}^N w_i c_{ji} \frac{\ln\left(\frac{\tilde{r}_i + \xi}{\xi}\right)}{(\tilde{r}_i + \xi)} \quad (\text{A.31})$$

where w_i are the Newton-Cotes integration[†] weights (calculated up to $N = 20$ by the author).

Bentonite-water interface (Eqns. (A.19) and (A.20)):

$$c_{ji} = c_{jb} \left(\frac{p_{ji}}{p_{jb}} \right) \exp \left[-z_j \Psi_i - \tilde{A}_j \left(\frac{1}{\epsilon_i} - \frac{1}{\epsilon_b} \right) \right] \quad (\text{A.32})$$

$$M_{jT} \equiv \frac{2\pi(\Delta\tilde{r})(\Delta\tilde{r})N_p}{\kappa^2} \sum_{i=0}^N w_i c_{ji} \frac{\ln\left(\frac{\tilde{r}_i + \xi}{\xi}\right)}{(\tilde{r}_i + \xi)} + V_b c_{jb} \quad (\text{A.33})$$

The set of non-linear algebraic equations arising from the DE (Eqn. (A.23)), boundary conditions (Eqns. (A.28-30)) and mass balance constraints (Eqns. (A.31) or (A.32-33)) are to be solved iteratively using the IMSL MATH/LIBRARY[®] routine DNEQBF, which is seamlessly integrated into the MS-FP compiler.

[†] Also known as Bode's rule (Abramowitz and Stegun, 1970), which is exact for polynomials of degree N .

2 TRANSPORT

As a first approximation we assume that the advective component of the flux in Eqn. (11) is negligibly small so we can drop it. This simplifies the solution procedure considerably since we need not solve for the fluid velocity, \mathbf{v} , from the Navier-Stokes equation, Eqn. (15). For the axial co-ordinate we employ a transformation which maps the computational domain ($\tilde{x} \in [0,1]$) onto a physical one ($x \in [0, L_s]$) with enhanced resolution near its ends

$$\tilde{x}(x) = \frac{1}{2} + \frac{1}{2} \frac{\ln\{(\beta + 2x/L_s - 1)/(\beta - 2x/L_s + 1)\}}{\ln\{(\beta + 1)/(\beta - 1)\}} \quad (\text{A.34})$$

where the stretching parameter β determines the extent of refining near $x = 0$ and $x = L_s$ (L_s is the sample length). For $\beta \rightarrow 1+$, very high resolution near the ends is achieved. The spatial derivatives in Eqn. (12) for the transformed domain are obtained by applying the chain rule of differentiation to yield $\frac{\partial}{\partial x} = \left(\frac{d\tilde{x}}{dx}\right) \frac{\partial}{\partial \tilde{x}} = \tilde{x}' \frac{\partial}{\partial \tilde{x}}$ and $\frac{\partial^2}{\partial x^2} = \tilde{x}'' \frac{\partial}{\partial \tilde{x}} + \tilde{x}'^2 \frac{\partial^2}{\partial \tilde{x}^2}$. To account for the irregular pore geometry, we have to introduce a quantity called tortuosity, T , defined as

$$\frac{dx}{dX} = \frac{1}{T} \quad (\text{A.35})$$

where $X (\in [0, L])$ is the actual capillary co-ordinate (L being the length of a pore). Eqn. (A.35) also implies the more familiar form for the tortuosity, $T = L/L_s$.

We feel that it is not necessary to introduce the discretization for the transport part of the model. We merely state that it is much more straightforward to realize than that of the equilibration part, the very kernel of the model, introduced in the previous chapter.

3 REFERENCES

Smith, G. D. 1978. Numerical solution of partial differential equations. Finite difference methods. 2nd ed. Clarendon Press, Oxford. 304 p.

LIST OF POSIVA REPORTS PUBLISHED IN 1997

POSIVA-97-01 Model for diffusion and porewater chemistry in compacted bentonite
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