Final report TRIAS 835.80.033

1. **title**: Chemically and Electrically Coupled Transport in Clayey Soils and Sediments

2. **TRIAS project number**: 835.80.033

3. **research period**: 15/01/2001-15/04/2005

4. **names of researcher involved**: Sam Bader, R.J. Schotting
   for both: 15/01/2001-01/02/2004: TU Delft, Hydrology
   01/02/2004-15/04/2005: Utrecht University, Env.Hydrogeology

5. **research objective**: The main research objective is to develop the modeling capability to predict water and solute transport in clayey soils and sediments where chemical and electrical gradients are present, notably in situations with a serious threat of pollution and salinisation.
   research methods: The governing equations for coupled hydraulic and osmotic transport consist of a set of coupled nonlinear partial differential equations. The intricate nature of these equations implies that analytical, semi-analytical and numerical techniques have to be employed to fully understand properties and behaviour of solutions, both from the physical and the mathematical point of view. With respect to numerical code development, calibration and verification, it is extremely important to have insight in nature and properties of solutions . Numerical modeling studies of field and laboratory conditions have to be carried out in order to study the behaviour of the system of coupled flow processes. The so-called METROPOL is particularly suited for this work because it has a wide range of capabilities, has been extensively tested in comparative studies with similar codes and can easily be adapted.
   results: The aforementioned set of equations has been obtained from literature and have been improved, to comply with physical reality. The nature of these equations has been studied extensively and for simple situations of osmosis in groundwater, analytical solutions have been obtained. Furthermore, the equations have been applied to simulate buildup of osmotic pressure and simultaneous evolution of concentration and electrical potential in a range of laboratory and field experiments.

6. **popular summary**
   In problems of groundwater flow and solute transport in clayey soils subject to salt concentration gradients, chemical and electro-osmosis can be too important to neglect, as is commonly done in geohydrology. In this research, we have considered the quantification of these coupled effects to be able to simulate

experiments and natural situations involving possible chemically and electrically driven water flow. Using a model containing these effects, one should be able to address questions regarding anomalous pressure buildups or salinity profiles in compacted clayey environments, especially in coastal areas, or in any area where salt gradients may be expected to be present. Also, it can improve assessment of contaminant emissions from contaminated clay or assessment of leakage from waste disposal sites.

The building blocks of clay are negatively charged platelets that, when compacted in soil, impose electrical restrictions on charged particles that migrate through the clay. This means that the clay can be considered to be a semi-permeable membrane, and when a salt concentration gradient is present, all the conditions for chemical osmosis are met. Water flux, in these circumstances, is therefore dependent on the pressure gradient as well as the salt concentration gradient. It is shown that it can depend on gradients of electrical potential as well, in which case we speak of electro-osmosis. Assuming we may extend Darcy's law linearly with a salt concentration and an electrical potential gradient, the corresponding coupling parameters are called the reflection coefficient in the case of chemical osmosis and the electro-osmotic permeability in the case of electro-osmosis.

To obtain a full model for simulating osmosis in groundwater, the equations that follow from non-equilibrium thermodynamics have been derived; they are partly based on existing formulas. A number of aspects however, have been adapted because of serious shortcomings in equations appearing in literature. We have obtained analytical solutions for very simplified, general situations. These solutions clearly show the simultaneous development of pressure and concentration due to osmosis. The simplified setup was used to gain some insight in some matters that relate to osmosis. For example, we have presented the different timescales involved with modelling osmosis in groundwater, and we have justified some assumptions taken in this study. The influence of osmosis on molecular diffusion of a tracer was investigated, and the importance was shown of the choice of dependence of reflection coefficient on salt concentration. Also, we have shown how our model correctly describes limiting behaviour of the reflection coefficient.

Two chemical osmosis experiments from literature-one performed in the laboratory and one in a field situation, are modelled, where the emphasis is on the applicability of assumptions used to obtain (semi-)analytical solutions. It is shown by dimensional analysis how the storage parameters of the system determine this applicability. Furthermore, the frequently applied Boussinesq approximation was shown not too hold for problems involving osmosis in groundwater.

The influence of the membrane potential on the osmotic pressure and concentration development was studied. The value of the membrane

potential found in a particular experiment is derived from theoretical first principles. Furthermore, the membrane potential induces an electro-osmotic counter flow, that can be turned off by (virtual) short-circuiting the experimental setup. The derived model for chemical osmosis, extended with electro-osmosis, is shown to be able to simulate the transient buildup and decline of pressure, as well as the evolution of concentration and electrical potential. The effect of short-circuiting is shown to correspond with letting the electrical parameters pass to zero. Finally, an existing finite element groundwater code with chemical and electro-osmosis was adapted for osmosis. This code, called METROPOL, is used to model groundwater flow and solute transport in, for example, conditions of high salt concentration gradients. The existing, incorrect term for salt concentration driven water flow was adapted and electrical coefficients were added. To test the code, some sample problems were constructed, and METROPOL was shown, in most cases, to be very suitable for simulating osmosis in groundwater.

7. **impact for soil protection:**
   The model for describing osmosis in groundwater, which is the quintessential result of this research, has proven to be able to simulate real physical behaviour in laboratory and field situations. A large water flow induced by chemical or electro-osmosis was shown to be present in such setups. This water flow was previously disregarded in all studies regarding simulating groundwater flow and solute transport in clayey soils. Using our model, we expect more accurate results in assessing flow in clayey aquifers, where considerable salt concentration gradient are present. This can be rather important when investigating emissions from waste disposal sites where clay is used as an impermeable liner, or, for instance, in clay containing sludge. In coastal areas, where clay is abundant, and salt concentration gradients are present, we can expect rather large deviations in flow data.

8. **oral presentations**:
   2001: INTAS meeting Kazan, Russia
   Hydrology group meeting: Delft
   2002: CMWR: Delft
   2003: IUTAM: Kerkrade
   Bodemdiep: Zeist
   INTAS meeting Moscow
   Hydrology group meeting
   2004: Soil and Water, Zeist
   2005: Environmental Hydrogeology Colloquium

   poster presentations:
   2002: Bodemdiep: Zeist
   2003: EGS: Nice
   AGU meeting, San Francisco

2004: Gordon Research Conference, Oxford

9. **publications**:

Bader, S. 2005 Osmosis in groundwater: chemical and electrical extensions to Darcy's law, Ph.D. thesis, defense in September 2005 (Ph.D. thesis)

Bader, S. 2005 A review paper on the reflection coefficient (to be submitted to a refereed journal)

Bader, S., Heister, K. The effect of short-circuiting on membrane potential in bentonite; modelling and experimental results submitted to Transport in Porous Media (refereed journal)

Bader, S., Kooi, H. 2004 Modelling of solute and water transport in semi-permeable clay membranes: comparison with experiments. Advances in Water Resources 28 203-214 (refereed journal)

Bader, S. 2003 Modelling of chemical osmosis in clay Proceedings 2nd National Scientific Symposium Bodem Diep, Zeist, The Netherlands (conference proceedings)

Bader, S., Schotting, R.J. 2003 Modelling of chemical osmosis in groundwater Proceedings of the IUTAM Symposium on Mechanics of Physicochemical and Electromechanical Interactions in Porous Media (refereed conference proceedings)

Kooi, H., Garavito, A.M., Bader, S. 2003 Numerical modelling of chemical osmosis and ultrafiltration across clay formations} Journal of Geochemical Exploration 78-79 333-336 (conference proceedings)

Garavito, A.M., Bader, S., Kooi, H., Richter, K., Keijzer, T.J.S. 2002 Numerical modelling of chemical osmosis and ultrafiltration across clay membranes Developments in Water Sciences. Proceedings of the International Conference in Computational Methods in Water Resources 1 647-653 (conference proceedings)

10. none

11.

a. All goals as laid down in the original research objectives were met. The modelling capability for osmosis in groundwater was obtained and results of experiments from other subprojects were successfully modelled. The numerical code METROPOL was successfully adapted but it was shown that the particular nature of the solver of the code does not allow for large deviations from linearity. Hence, our advice would be that, for general situations, other numerical codes instead of METROPOL will have to be used for modelling of osmosis in groundwater.

b. no

c. Yes: during the project, many contacts were made, both nationally as internationally.

12. As all objectives were research objectives, we refer to the answer to question 11a.

13. The subproject is part of a larger project in which, from the onset, results of the subprojects were meant to be integrated in the other subprojects.

14. Adapting existing models for coupled groundwater flow and solute transport has shown to be quite successful. Other extensions of known transport laws could therefore be contemplated. For instance, temperature or volume change effects, research on which was beyond the scope of the project, could well be studied to improve even more the predictive qualities of the relevant models. Furthermore, in the answer to question 17 some additional research questions are presented that reached the surface in this project.

15. There is quite some activity on the subject of coupled effects in hydrogeology, especially because of field evidence for chemical osmosis in clay obtained in the last couple of years. We believe that the results of this project deliver a significant contribution to this research. Other scientists may well profit from the modelling and theoretical results obtained in this project.

16. The research has led to an improved model for describing osmotic transport in groundwater and can be readily applied to practical situations.

17. **new research questions**:

    What theories exist for the relevant coefficients, how do they compare and what is the influence of different corresponding expression on the physical results? (addressed in the study)

    What is the influence of the cation occupation of clay on specific properties of the soil?

    How can the observed values of the streaming potential be explained?

    These last two questions have been combined (i.e. the cation occupation may be the cause of anomalous streaming potential) and this is the basis for a new project proposal by a member of an alternate subproject.

18. This particular subproject was a part of a larger project, where we collaborated with researchers from the Vrije Universiteit Amsterdam and Utrecht University. The aim in this larger project was to perform experiments that were to be

modelled within this particular subproject. Cooperation was quite fruitful and resulted, among other things, in a number of joint publications and presentations

19. The research in this project has greatly increased the knowledge on the subject of transport of contaminants and flow of ground water. The improved model can lead to adaptations of policies on, for instance, assessment of contaminant emissions, or contaminant leakage from waste disposal sites.

20. none

21. n/a