Final report TRIAS

01

Chemically and Electrically Coupled Transport in Clayey Soils and Sediments (part 1)

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TRIAS project 835.80.031

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Background
Transport of water and solutes in clayey soils and sediments is important in groundwater and waste management, e.g. in seawater intrusion, in waste disposal sites with clay liners, in emissions from contaminated clayey sediments, and in radioactive waste storage in clay formations. Clay layers act as semipermeable membranes. Consequently, water transport can be induced not only by a gradient in hydraulic potential and solution density but also by gradients in salt concentration and electrical potential. These processes, termed chemical osmosis and electroosmosis, respectively, are significant at hydraulic conductivity less than $1 \cdot 10^{-9}$ m/s. As secondary effects, an electrical potential gradient can be induced by a hydraulic pressure gradient (streaming potential) and by a salt concentration gradient (membrane potential). They counteract hydraulic or osmotic water flow and solute diffusion.
Research objective
Chemical osmosis and electroosmosis are usually absent in transport models for soil and groundwater. Neglecting these transport phenomena is not justified in the situations

mentioned. The objective of this research is to substantiate this statement by demonstrating and quantifying the effect of induced electrical potential gradients on the transport of water and solutes in clay layers in laboratory experiments.

Research methods

Permeameters were constructed for bench-scale transport experiments on Wyoming bentonite, Oligocene Boom Clay from Belgium and Holocene Calais Clay from The Netherlands. Both flexible-wall and rigid-wall permeameters were constructed, with both gold and double-junction Ag/AgCl electrodes (Figure 1 and 2). Gradients of streaming potentials and membrane potentials, induced by hydraulic pressure gradients and salt concentration gradients, are measured and their effect on water and solute transport is quantified by experiments under both electrically shorted and non-shorted conditions.

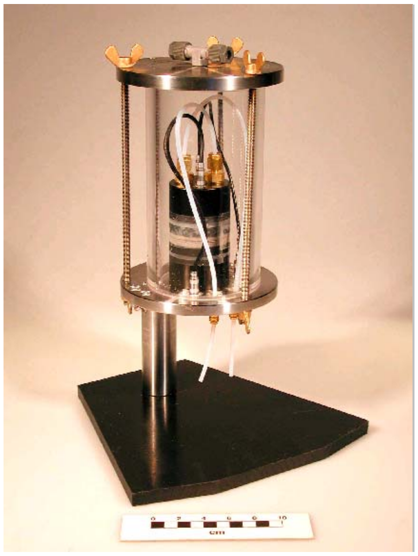

Figure 1: The flexible-wall permeameter cell for measurements of streaming potentials. The clay sample inside the permeameter can be connected to two fluid reservoirs.

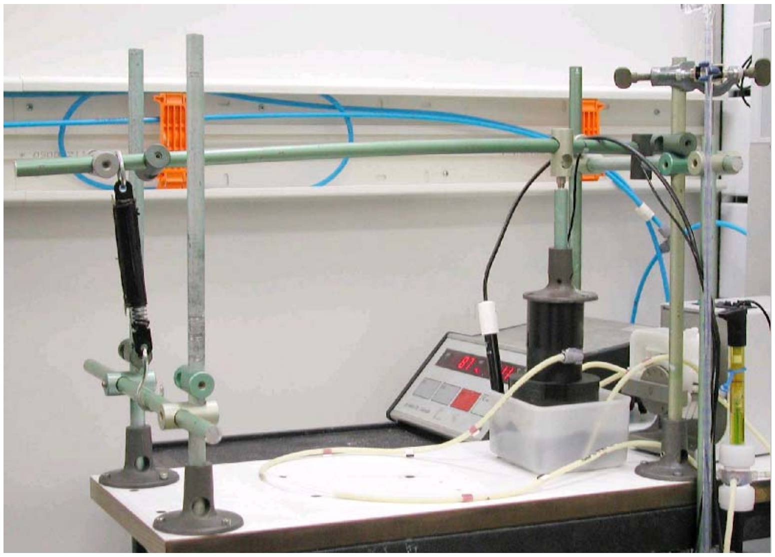

Figure 2: The rigid-wall permeameter set-up for measurements of membrane potentials.

Chemical osmosis and electroosmosis are coupled flow phenomena, described by irreversible thermodynamics, making use of the Onsager reciprocal relations. Thus, flows of fluid, electrical charge and solutes are linearly related to conjugated and non-conjugated driving forces. The semipermeability of clay is explained by diffuse double layer theory. However, a clay membrane is not ideal, i.e. part of the salt will pass the membrane by diffusion. The degree of ideality is expressed by the reflection coefficient. This, and the coefficients of hydraulic conductivity, electroosmotic conductivity, electrical conductivity and the diffusion coefficient are derived from the experiments by means of irreversible thermodynamics.

Results

Significant gradients of streaming potential and membrane potential, in the order of -20 V/m and -7 V/m, respectively, developed in the experiments. These driving forces induced significant counterflow of water and solutes during hydraulic and chemical osmotic flow in the Wyoming bentonite and Boom Clay. In the bentonite, 13 – 40% of the water flow was electrically induced in the streaming potential experiments and 5 – >90% was electrically induced in the membrane potential experiments depending on the experimental conditions. Of the solute flow, 47 – 92% was induced by electrical gradients in the bentonite in the membrane potential experiments. Figure 3 shows an example of the influence of membrane potential on the osmotic water flux through a bentonite membrane. The measured membrane potentials in the Boom Clay accounted for over 90% for the water flow and 20 – 73% for the solute flow. In the Calais Clay, electrokinetic effects were absent. This is due to the domination of multivalent cations in this acid sulphate soil (in Dutch: katteklei), since the Calais Clay was acidified during air-drying in the laboratory.

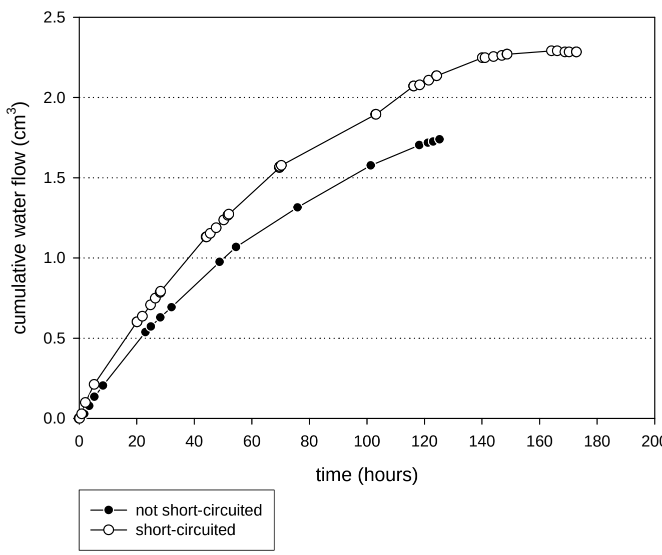

Figure 3: Cumulative water flow from the fresh-water into the salt-water reservoir through a bentonite membrane. Experimental conditions: 0.01 M NaCl – 0.1 M NaCl reservoir salt concentrations, 1 bar overburden load on the clay. In the non-shorted situation, the water flux is

less due to the existence of an electrically induced counterflow. In the shorted situation, the water flux is solely driven by the chemical concentration gradient.

Conclusions
Electroosmosis, both as secondary and primary process, is significant in compacted Wyoming bentonite and Boom Clay and should be included in transport models for water and solute. Therefore, the data and parameters from this laboratory study are presently being used to validate a model, developed by the Environmental Hydrogeology Group, Utrecht University, which includes chemical osmosis and electroosmosis in groundwater transport.

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Transport van water en opgeloste stoffen door klei is van belang bij beheer van grondwater en afvalstoffen. Voorbeelden uit de praktijk zijn onder meer: indringing van zeewater in het grondwater van kustgebieden, kunstmatige kleischermen rondom afvalstortplaatsen, verspreiding van stoffen vanuit verontreinigde bagger en opslag van radioactief afval in diepe kleilagen. Dichte kleilagen gedragen zich als *semi-permeabele membranen* (te vergelijken met de wand van een biologische cel). Beweging van water in dichte kleilagen wordt daardoor niet alleen gedreven door hydraulische druk en de dichtheid van het water, maar ook door verschillen in zoutconcentratie en electrische spanning. Deze processen worden achtereenvolgens aangeduid als *chemische osmose* en *electro-osmose*. Behalve dat een electrisch spanningsverschil door de mens actief kan worden aangebracht over een kleilaag, kan het ook spontaan worden opgewekt in klei door een hydraulisch drukverschil en door een zoutconcentratieverschil. Deze spanningsverschillen worden, respectievelijk *stromingspotentiaal* en *membraanpotentiaal* genoemd. Ze werken de waterstroming en zoutdiffusie tegen.
In de transportmodellen voor bodem en grondwater, die in de praktijk gebruikt worden, wordt geen rekening gehouden met chemische osmose en electro-osmose. Het verwaarlozen van deze processen is niet gerechtvaardigd in de genoemde voorbeeld-situaties. De doelstelling van ons onderzoek is het onderbouwen van deze stelling door het effect van stromingspotentialen en membraanpotentialen op het transport van water en zouten in kleilagen te quantificeren middels laboratorium-experimenten. Hiertoe zijn twee opstellingen voor doorlatendheidsmeting geconstrueerd voor experimenten met Wyoming Bentoniet, Boomse Klei uit Mol, België en Calais Klei uit de Mijdrechtpolder, Nederland. Deze *permeameters* hebben een cylindrische wand, de één van flexibel materiaal, de ander van vast kunststofmateriaal (figuur 1 en 2). Ze bevatten een laag klei van 2 tot 3 mm dikte. De stromingspotentialen en membraanpotentialen die worden opgewekt door hydraulische of chemisch-osmotische stroming worden gemeten met verschillende soorten electroden. Het effect van deze electrische potentialen op het transport van water en zout wordt bepaald door de experimenten zowel onder electrisch-kortgesloten als niet-kortgesloten condities uit te voeren.

Figuur 1: Permeameter met flexibele wand voor het meten van stromingspotentialen. Het kleimonster in de permeameter is verbonden met de twee vloeistofreservoirs.

Figuur 2: Permeameter met vaste wand voor de meting van membraanpotentialen.

Chemische osmose en electro-osmose zijn gekoppelde transportprocessen, die beschreven kunnen worden met de thermodynamica van irreversibele processen. Bij de interpretatie van onze data maken we gebruik van de *Onsager Reciproke Relaties*. De semi-permeabiliteit van klei verklaren we met de diffuse dubbellaag theorie. Echter, een kleimembraan is niet ideaal, dat wil zeggen dat een deel van het zout het membraan zal passeren door diffusie. De mate van idealiteit wordt uitgedrukt door de *reflectie-coëfficiënt*. Deze, en de coëfficiënten voor hydraulische doorlatendheid, electro-osmotische doorlatendheid, electrische geleidbaarheid en de diffusiecoëfficiënt worden uit de experimenten afgeleid.
We hebben significante stromingspotentialen en membraanpotentialen gemeten, in de orde van -20 V/m en -7 V/m. Deze potentialen veroorzaakten significante tegenstroom van water en zout in de Wyoming Bentoniet en in de Boomse Klei. In de bentoniet werd 13 – 40% van de totale waterstroming veroorzaakt door de stromingspotentiaal en 5 – >90% werd veroorzaakt door de membraanpotentiaal (figuur 3), afhankelijk van de experimentele condities. Van het totale zouttransport in de bentoniet werd 47 – 92% veroorzaakt door de membraanpotentiaal. De gemeten membraanpotentialen in de Boomse Klei droegen meer dan 90% bij aan de totale waterstroming en 20 – 73% aan het totale zouttransport. In de Calais Klei werden geen electrokinetische effecten waargenomen. Dit wordt verklaard door de bezetting van deze klei met voornamelijk meerwaardige kationen, nadat ze door luchtdroging in het laboratorium in een zure katteklei is omgezet.

Figuur 3: Cumulatief watertransport vanuit zoet- naar zoutwater reservoir via het bentoniet membraan. Experimentele omstandigheden: zoutconcentraties in de reservoirs 0.01 M NaCl – 0.1 M NaCl, externe belasting op de klei 1 bar. Bij afwezigheid van electrische kortsluiting is het watertransport langzamer door een electrisch geïnduceerde tegenstroming. In de kortgesloten situatie wordt watertransport alleen door chemische osmose bepaald.

We concluderen dat electro-osmose, zowel actief toegepast, als geïnduceerd door waterstroming, significant bijdraagt aan transport in dichte Wyoming Bentoniet en Boomse Klei, en dient te worden ingebouwd in transport modellen voor water en opgeloste stoffen. De data en coëfficiënten, verkregen in ons onderzoek, zijn geschikt voor validatie van zulke modellen.

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The outcome of this project points at the need to include coupled flow, like chemical osmosis and electroosmosis, and streaming and membrane potentials as driving forces for water and solutes, in transport models for water and solutes in clayey materials. These driving forces are significant in dense clays. Thus, assessments of the retention capacity of clays and clay layers for salts and contaminants will be improved. At present, these processes are absent in groundwater models.

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- ‘Flocculation and gelation of bentonite. Dependency on the clay concentration’. Poster presentation by K. Richter. Nationaal Symposium BodemBreed, Lunteren, The Netherlands, 26 – 27 November 2001.
- ‘Stability of clay membranes in chemical osmotic processes’. Oral presentation by K. Richter. Geochimica Actie seminar series, Utrecht University, 2 May 2002.
- ‘Stability of clay membranes in chemical osmotic processes’. Oral presentation by K. Richter. 1st National Scientific Soil Symposium BodemDiep, Zeist, The Netherlands, 5 – 6 June 2002.
- ‘Stability of clay membranes in chemical osmotic processes’. Oral presentation by K. Richter. The Clay Minerals Society 39th Annual Meeting, Boulder, Colorado, 8 – 13 June 2002.
- ‘Numerical modeling of chemical osmosis and ultrafiltration across clay membranes’. Co-author of oral presentation by S. Bader. 14th International Conference on Computational Methods in Water Resources (CMWR), Delft, The Netherlands, 23 – 28 June 2002.
- ‘A new laboratory set-up for measurements of electrical, hydraulic, and osmotic fluxes in clays’. Oral presentation by K. Richter. 4th Symposium on Electrokinetic Remediation (EREM 2003), Mol, Belgium, 14 – 16 May 2003.
- ‘Coupling between chemical and electrical osmosis in clays’. Oral presentation by J.P.G. Loch. Symposium on the Mechanics of Physicochemical and Electromechanical Interactions in Porous Media of the International Union of Theoretical and Applied Mechanics, Kerkrade, The Netherlands, 18 – 23 May 2003.
- ‘Measurements of streaming potentials in bentonite with a flexible-wall permeameter”. Poster presentation by K. Richter. 2nd National Scientific Soil Symposium BodemDiep, Zeist, The Netherlands, 4 – 5 June 2003.
- ‘Coupling between solute flow and electrical osmosis in clays’. Oral presentation by J.P.G. Loch. Geochimica Actie seminar series, Utrecht University, 12 June 2003.
- ‘Outwitting membrane potentials in clays. An attempt to eliminate their effect in chemical osmosis’. Poster presentation by K. Heister. Netherlands Scientific Symposium Soil & Water, Zeist, The Netherlands, 2 – 3 June 2004.
- ‘Coupling of hydraulic, chemical and electrical fluxes in bentonite clay’. Poster presentation by J.P.G. Loch. Gordon Research Conference on Flow and Transport in Permeable Media, Oxford, UK, 11 – 16 July 2004.
- ‘Virtual short-circuiting of a clay membrane to quantify the effects of membrane potential in chemical osmosis processes’. Oral presentation by K. Heister. 55th Annual Meeting of the International Society of Electrochemistry, Thessaloniki, Greece, 19 – 24 September 2004.
- ‘Quantifying the effects of membrane potential in chemical osmosis across clay membranes’. Oral presentation by K. Heister. Geochimica Actie seminar series, Utrecht University, 12 October 2004.

- ‘Laboratory investigation on the effect of induced membrane potentials in chemical osmosis across clay membranes’. Oral presentation by K. Heister. UCG colloquium, Utrecht University, 28 February 2005.

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Refereed journals:

- Bader, S. and Heister, K., submitted. The effect of membrane potential on development of chemical osmotic pressure in compacted clay.
- Heister, K., Kleingeld, P.J. and Loch, J.P.G., submitted. Induced membrane potentials in chemical osmosis across clay membranes.
- Heister, K., Kleingeld, P.J. and Loch, J.P.G., 2005. Quantifying the effect of membrane potential in chemical osmosis across bentonite membranes by virtual short-circuiting. Journal of Colloid and Interface Science 286 (1): 294 – 302.
- Heister, K., Kleingeld, P.J., Keijzer, T.J.S. and Loch, J.P.G., 2005. A new laboratory set-up for measurements of electrical, hydraulic, and osmotic fluxes in clays. Engineering Geology 77 (3-4): 295 – 303.
- Heister, K., Keijzer, T.J.S. and Loch, J.P.G., 2004. Stability of clay membranes in chemical osmosis. Soil Science 169 (9): 632 – 639.

Conference proceedings:

- Loch, J.P.G., Richter, K. and Keijzer, T.J.S., 2005. Coupling between chemical and electrical osmosis in clays. In: Huyghe, J.M., Raats, P.A.C. and Cowin, S.C. (Eds.) IUTAM-Proceedings on Physicochemical and Electromechanical Interactions in Porous Media. Kluwer, Boston, Dordrecht, London, pp. 283 – 288.
- Garavito, A.M., Bader, S., Kooi, H., Richter, K. and Keijzer, T.J.S., 2002. Numerical modeling of chemical osmosis and ultrafiltration across clay membranes. In: 14th International Conference on Computational Methods in Water Resources (CMWR), 23 - 28 June 2002, Delft, The Netherlands, pp. 647 – 653.
- Richter, K., 2002. Stability of clay membranes in chemical osmotic processes. In: 1st National Scientific Soil Symposium BodemDiep, 5 - 6 June 2002, Zeist, The Netherlands, pp. 19 – 21.

Dissertation:

- Heister, K., 2005. Coupled transport in clayey materials with emphasis on induced electrokinetic phenomena. Ph.D. thesis. Universiteit Utrecht, Utrecht, The Netherlands, 120 pp.

10

Not applicable.

11a

The original research objectives of the larger, cooperative project (TRIAS project number 835.80.003), as indicated in the project application are:

- to demonstrate osmotic transport in clayey soils and sediments and its relevance for the distribution and emission of contaminants, salt and water,
- to develop a numerical model from the data to be obtained in laboratory and field experiments to predict water and solute transport in these media, when chemical and electrical potential gradients are present.

The sub-project reported here concerns the laboratory studies, for which the research objectives are:

- to modify the permeameter set-up developed by Keijzer et al. (1999) in order to measure osmotic pressures, induced streaming potentials and streaming currents during hydraulic and osmotic water flow in bentonite, harbour sludge and clay samples associated with the field experiments,
- to subject these materials in separate experiments directly to electrical gradients to measure electroosmotic water transport.

The primary goal to demonstrate osmotic transport in clayey soils and sediments and its relevance for the distribution and emission of water and solutes was satisfactorily realized. The results of the laboratory experiments were made available to the Environmental Hydrogeology Group of the Department of Earth Sciences, Utrecht University, partner in the larger project, to develop and validate their model for water and solute transport in the presence of chemical and electrical potential gradients. Regarding the goals of the laboratory studies, parts of the research objectives had to be adapted. From a technical point of view, it was not possible to directly modify the permeameter set-up developed by Keijzer et al. (1999) to measure osmotic pressures, induced streaming potentials and streaming currents during hydraulic and osmotic water flow. Accordingly, a new flexible-wall permeameter set-up was designed to realize the intended measurements. It turned out that the type of electrodes plays a crucial role in the measurements. Therefore, a more detailed study regarding the mode of functioning and feasibility of different types of electrodes had to be carried out. This study, which was not part of the original research objectives, led to the realization of a rigid-wall permeameter in which the required electrodes could be employed. With these two set-ups, it was possible to measure streaming potentials (during hydraulic water flow) in bentonite and membrane potentials (during osmotic water flow) in bentonite and two field clays. The field clays were obtained from two field sites studied by the Department of Hydrology and Geoenvironmental Sciences, Vrije Universiteit Amsterdam (TRIAS project number 835.80.032), the third partner in the larger project. Harbour sludge samples were not studied in the laboratory, since a corresponding field site was not selected. Instead, upon the initiation of a cooperation within the project with SCK·CEN in Mol, Belgium, Boom

Clay was chosen as field site and consequently as laboratory testing material. Based on the conclusions obtained in the electrode study, no active application of electroosmosis was performed within the course of the project. Using the knowledge obtained in this project, this research objective should be addressed in a new research project.

11b

No.

11c

The project's aims did not explicitly include the expansion of the (international) network of contacts. However, contacts were definitely expanded. Although this project is not part of an international research program, a cooperative agreement was signed with SCK·CEN, Mol, Belgium during the course of the project. In addition, a long-term contact was strengthened with Prof. P.H. Groenevelt, University of Guelph, Canada, who is an expert in modeling transport in soils by irreversible thermodynamics. Furthermore, the project indirectly led to a four months sabbatical visit of the project leader to Prof. S.J. Fritz, at Purdue University, IN, USA, who is an expert of membrane behaviour of clays.

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The results obtained match for the most part the original objectives.
The effect of electrical potential gradients on the transport of water and solutes in clays was clearly demonstrated and quantified in laboratory experiments. Permeameter set-ups capable to measure the required parameters were realized and the data obtained from experiments on bentonite and two field clays were made available to the Environmental Hydrogeology Group of the Department of Earth Sciences, Utrecht University for development and validation of their model.
Due to lack of time, experiments on harbour sludge samples were not performed, neither in the laboratory nor in the field. It was intended to perform the laboratory experiments on samples coming from the field sites, integrating the sub-projects.
The objective to perform experiments with active application of electroosmosis was not fulfilled due to technical difficulties with the measurement of electrical potentials with the electrodes used. Since little was known about the feasibility of electrodes to be used for our purposes, a study of this subject had to be performed, which was not considered initially.

13

Together with the results of the sub-project on field research of chemical osmosis in clay (sub-project 835.80.032), the results of this sub-project are of particular use as input to a transport model. This model is developed by the Environmental Hydrogeology Group of the Department of Earth Sciences, Utrecht University, as was intended in the third sub-project of TRIAS 835.80.033.
In addition, laboratory experience and data were provided to the sub-project on field research for improving their measuring devices and for model input.
All mentioned collaborations were intended and optimized from the beginning of the project.

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The results of this project clearly underline the importance of electrically induced fluxes in clays. During the course of the project, laboratory devices were developed to measure and to quantify the effects of induced electrical potential gradients on the flow of water and solutes in clay. Until now, only the effect of induced electrical potential gradients was studied, but of course, it is of great practical and scientific interest to actively apply electrical potential gradients to clayey soils and sediments, in order to determine the effects of electroosmosis on the transport of water and solutes, including contaminants. The consequences for contaminant transport, clay consolidation and dewatering are of practical interest. Active electroosmosis is of great scientific interest because it would enable us to verify cross-coupling effects according to the Onsager reciprocal relations (Onsager 1931a, b), a central theme in irreversible thermodynamics. This is possible with the capacities and the knowledge obtained in our laboratory.
The induced electrical gradients observed in the laboratory should be detectable in the field. They may play a role in e.g. hyperfiltration by clay layers during salt (sea) water intrusion. A cooperative research including geophysical expertise could shed more light on their presence and effects in the field.
The developed model that includes the effects of chemical osmosis and electroosmosis is still elementary. To predict solute transport in field situations, effects arising from reaction of the solutes with the soil particles are expected to influence the fluxes and the electrical potential gradient. Especially the effect of ion exchange is considered to be important because cation exchange could influence the diffusivity of the salt and additional electrical potential gradients could be induced. To enhance the model, more experimental data obtained in laboratory studies will be needed and more field sites should be investigated.

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The results of this research project are of importance to hydrologists developing transport models for water and/ or solutes in sediments and groundwater. In this respect, they are of particular interest in modeling contaminant transport and in modeling seawater intrusion and related hyperfiltration. In addition, they are of importance to geotechnical engineering interested in application of electroosmosis for consolidation and dewatering of clay structures, clayey sediments and sludges.

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A major obstacle for applying the results will be financial support for the required elaborate field testing of the processes investigated.

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In general, three new research questions arose in this project:

1.) Which types of electrodes are suitable for applying and/ or measuring electrical potential gradients?
2.) How does actively applied electroosmosis influences the fluxes of water and solutes in clay?
3.) How does ion exchange as occurring in natural clays influence coupled transport processes?

Firstly, during the laboratory experiments, it turned out that not all types of electrodes are feasible to measure and/ or to apply electrical potential gradients. Therefore, it had to be investigated which types of electrodes were suitable for our purposes, although this was not considered in the project proposal. For the success of the project, it was essential to solve this problem. So, it had to be addressed within the course of the project.
Secondly, no active electroosmosis experiments were performed until now, partly due to the problems with the electrodes as mentioned above. As already pointed out under 14, quantification of the effects of electroosmosis on the fluxes of water and solutes in clay is of practical and scientific interest. Consequently, this new research question will be addressed in a new research project to be funded by 2nd (and possibly 3rd) category sources.
Thirdly, as also mentioned under 14, effects due to ion exchange in natural clays are expected to influence coupled transport processes. This new research question will be addressed in a new research project. A VENI proposal will be sent to NWO (application deadline May 2005).

18

This project was not linked to other projects within the TRIAS program. It was of course very closely linked with the two other sub-projects (TRIAS project numbers 835.80.032 and 835.80.033) within the larger project 835.80.003. This cooperation lead to the integrated result of a groundwater transport model, in which the studied processes were included.
As mentioned under 11a, it was linked with the research by SCK·CEN in Mol, Belgium, through a cooperative research contract.

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The results present a stimulus for policy makers, and consequently for consulting firms and applied research institutes, to improve their assessments of groundwater flow and water balance on the one hand, and of contaminant distribution on the other hand, in coastal areas, like The Netherlands.

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Within the framework of the larger project, a modeling workshop is intended to present the processes and the resulting model to potential users. This workshop is entitled ‘Modelleren: Verpakt bedrog of waardevol instrument’ and is organized by SKB. It will take place on 12 May 2005 in Gouda.

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No, until today, the Ph.D. student mentioned under 4 did not obtain a new position yet. Since she favours to continue work in this specific field of interest, suitable vacancies are scare as far as we know. Currently, we work on a proposal to NWO to obtain a VENI-grant, which would assure a postdoctoral position for three years at Utrecht University, Department of Earth Sciences – Geochemistry.

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Onsager, L., 1931b. Reciprocal relations in irreversible processes II. Physical Review, 38: 2265 - 2279.