Eindrapportage-formulier TRIAS projecten
Final report format for TRIAS projects.

When a TRIAS project has finished, or is about to finish, a Final Report is required. This report serves several goals simultaneously:

- it enables the program commission to check whether the project has met its goals,
- it enables NWO-ALW to finalize the project administratively, e.g. pay the final part of the personnel costs of the project,
- it provides some of the information needed for evaluation purposes,
- it provides information which can be publicized, e.g. via a web site.

We have integrated the questionnaires from TRIAS and ALW into one, in order to prevent the need to fill in the same answers twice.

Please send in the filled out forms within a month after the project is completed to:

Netherlands Organisation for Scientific Research
Earth and Life Sciences
Carmen van Meerkerk and/or Theo Saat
P.O. Box 93510
2509 AM The Hague

Part I

General information, also intended for publication through the TRIAS website

01 Project Title.

Solubility and mobility of arsenic under changing redox conditions as affected by multi-component transport part II

02 TRIAS/ALW project number or file number

Trias project 835.80.006/DelftCluster 5.17

03 Research period, at what date did the project start, at what date did it end.

April 15th 2002 -March 1st 2006 extended to *****by Delft University of Technology.

04 Names of the researchers involved, the names and addresses of the institutes where the research work was carried out.

Part I Prof. Dr. W.H. van Riemsdijk, M. Stachowicz, Ir. T Hiemstra, Department of Soil Quality, Wageningen University. Dreijenplein 10 6700 HB Wageningen, The Netherlands.

Part II Dr J. Bruining, Dr. M.I.M Darwish, Faculty of Civil Engineering and Geosciences, Delft University, Mijnbouwstraat 120 2628 RX Delft, The Netherlands.

05 Short scientific summary (500 words) in English of: main research objective, research methods, results and conclusion.

Introduction

In recent years, the presence of dissolved arsenic in contaminated groundwater from both natural and anthropogenic sources has emerged as a major concern on a global scale. Arsenic (As) is a ubiquitous element present in various compounds through out the earth's crust. Disturbance of natural conditions led to mobilization of naturally occurring arsenic.

Adsorption/co-precipitation with iron oxyhydroxides is the most commonly adopted method for arsenic removal from contaminated water because the method is both effective and cheap compared with other methods.

Intermittent introduction of aerated water in extraction wells can in principle reduce the As load in the pumped water due to oxidation of Fe(II) and Mn(II) followed by formation of metal(hydr)oxides which will contain As through adsorption/ co-precipitation phenomena. These reactions occur at the transition zone between oxic and anoxic groundwater. The main idea of the in-situ treatment method of groundwater is to transfer the physical, chemical and biological processes of conventional above ground treatment plants into the aquifer. The aquifer carries the function of natural

subterranean reactor where oxidation and filtration processes for the removal of arsenic and other constituents take place.

Main Objectives

The main objectives of this research are:

1) A flow problem in porous media requires a description on a scale comprising at least half a million pore bodies as being representative of the core scale. This project (part II) uses the complex chemical understanding to construct models that describe the behavior in the soil on the core (cm-dm) scale.

2) To adapt a set of experiments to the specific requirements of this complex problem in collaboration with our part I. The experiments reciprocally help to validate the developed models.

Research methods

Experimentally, innovative experimental techniques were used to study and simulate the different stages of the redox alteration method for arsenic mitigation in drinking water. Visualization cell experiments were used for the determination of the Fe(II) oxidation rate constant. X-ray CT scanning, Nuclear Magnetic Resonance (NMR), dielectric constant and column experimental techniques were used to determine the adsorption of Fe(II) in porous media where the grains are coated with Ferric iron

Theoretically, up-scaled equations from pore-scale to core-scale were developed to predict the system behavior on the experimental scale.

Results

One of the important aspirations that we tried to achieve was to mimic the real field processes with our experiments as much as we could, while balancing simplifications of the complex system that we are dealing with. Therefore, we tried to implement non-destructive measurements techniques as to obtain the values of the targeted parameters. An innovative visualization technique was designed to evaluate the Fe(II) oxidation rate constant (ORC) under well-defined flow and transport conditions. The average value of the ORC was quite close to that in literature measured otherwise. However, the ORC values were time dependant which was attributed to the passivation phenomena.

Column experiments were carried out to determine the Fe(II) adsorption rate constant (ARC) onto ferric iron coated grains. Experiments gave ARC values which are comparable to literature values.

X-ray CT Scanner and NMR methods were used to detect the Fe(II) concentration profiles while injecting Fe(II) solution into short columns backed with ferric iron coated grains. In the case of CT scanner measurements, Fe(II) concentration profiles were detected

but the resolution and sensitivity for the small concentrations was not satisfactory. Thus, much higher concentrations were needed in order to get more reliable profiles which is not the case in the field. For the NMR experiments, the idea was to measure the Fe(II) concentration profiles indirectly through its effect on the water relaxation behavior. But due to other effects in the porous media (e.g. bulk and surface relaxations) it was not possible to extract concentration profiles from the measured water relaxation data.

Dielectric measurements used to determine Fe(II) concentration profiles, gave very weak response (i.e. little sensitivity) which means that solutions with much more Fe(II) concentration are needed.

We applied homogenization, a mathematical method to derive the up-scaled reactive transport equations for the Fe(II) and As precipitation on metal hydroxides-coated soil grains. In the derivation, we used a physically oriented approach for homogenization and arrived at the same result as obtained from the purely mathematical approach.

Homogenization is a well established methodology that can be used for upscaling. The advantage of homogenization over other upscaling methods is that it only requires the choice of a periodic unit cell to overcome the closure problem. The choice of the unit cell is completely flexible and only limited by computer capacity. Our interest is in the upscaling of reactive diffusion convection flows in connection with arsenic contaminated water remediation. We have re-derived the homogenized equations with emphasis on the physical aspects. By considering a simple two-dimensional example we cover all computational aspects linked to the actual application of the method. However, the method can be easily extended to more complicated configurations in 3-D. The computed dispersion coefficient shows a similar (qualitative) dependency on the Peclet number as literature data, albeit that the values for this 2-D example are considerably smaller. Moreover in the case of non-linear adsorption the dispersion coefficient depends on the concentration. However, application of the procedure to convection/ diffusion of free iron ions in equilibrium with adsorbed ions on the grain surface lead to an up-scaled convection/ diffusion equation that includes a retardation factor. The procedure also gives an auxiliary equation to compute the dispersion coefficient. We expect that an extension to 3-D leads to a confirmation of using this technique for upscaling reactive diffusion processes in porous media. Moreover, we able to make the method accessible to engineers.

Conclusions

- **Visualization techniques make it possible to determine the in-situ Fe(II) profiles and oxidation rates as a function of space and time**
- **Homogenization is a powerful mathematical technique to derive up-scaled equations for reactive transport models in porous media starting from the micro-scale equations..**
- **The physically oriented approach makes it easy to use homogenization for problems of engineering interest.**
- **The computed dispersion coefficient shows the typical dependence on the Peclet number, but is smaller than typical literature data.**
- **The dispersion coefficient increases if adsorption behavior is taken into account, showing that the dispersion coefficient in cases of equilibrium adsorption is concentration dependent.**

06 Popular summary to inform the general public (1/2 to 2 pages of text)

The funding organisations of TRIAS (SKB, NWO-ALW and Delft Cluster) want to inform a more general audience about the results of the TRIAS Research projects. That is why we ask you to give an executive summary of the project in a popularising way and written in the Dutch language. **Wat betreft grondwaterkwaliteit op wereldschaal zijn volgens British Geological Survey (BGS) arseen en fluoride veruit de belangrijkste probleemstoffen. Arseen komen van nature vooral in verhoogde concentraties voor in anoxische grondwaterpakketten. Arseen komt voor als arseniet en arsenaat. Naast arseen komt in dit type grondwater ook veel hogere concentraties fosfaat voor alsmede Fe(II), Mn(II), Ca, DOC, bicarbonaat en silicaat. Arseen adsorbeert sterk aan ijzer(hydr)oxiden waarbij de mate van adsorptie meer of minder sterk afhangt van de interactie met de overige componenten in de oplossing. De meest gangbare behandeling om het As gehalte te reduceren is beluchten van het water bovengronds of ondergronds. De verhouding waarin de verschillende chemische stoffen voorkomen in het grondwater blijkt heel sterk van plaats tot plaats te kunnen variëren waardoor het effect van beluchting op As verwijdering zeer variabel is en vaak teleurstellend.**

Dit onderzoek is een stap op weg om een opgeschaald transport model af te leiden. Dit model richt zich op aspecten reactief transport van ijzer ionsn en is gericht op in situ remediatie d.w.z. het beschrijven en optimaliseren van het effect van injectie van zuurstofhoudend water. Het model is voor een belangrijk deel gebaseerd op het vereenvoudigde proces model dat het adsorptie- en co-precipitatie gedrag van Arseen kan kwantificeren. Opschaling is gebaseerd op homogenisatie. Experimentele validatie is gerealiseerd middels de in het Dietz laboratorium (Delft) opgebouwde infrastructuur. De trits (a) opschaling, (b) analyse en

(c) experimenten blijken in staat gesteld complexe processen in de ondergrond te analyseren.

Onze contacten met de Universiteit in Dhaka (Kazi Matin) en J. Boes die een sociaal implementatie plan heeft ingediend met het doel de bevindingen hun weg te laten vinden naar de gebruikers in Bangladesh, kon niet worden gerealsieerd, door problemen met de subsidiering van een spiegelproject waarbij de sociale context meer aandacht kreeg. Dit blijkt echter in de nabij toekomst wel mogelijk zodat een vervolg van dit project zeer waarschijnlijk is. Hierbij kan de methode dan in het veld worden getoetst.

07 What impact and relevance has this project's outcome for practicing soil protection and/or soil remediation? Again, please motivate.

The project outcome has two folds:

Experimental:

The experimental work in this project determined a *useful set of parameters* (i.e. soil) that are needed for the design of remediation systems by practitioners. As an example, of these parameters, the heterogeneous ferrous iron oxidation rate constant and the ferrous iron adsorption rate constant in a porous medium were evaluated experimentally under changing pH conditions. In fact these parameters are not only useful for soil remediation practitioners but also for drinking water treatment practitioners as well.

Theoretical:

Since the values of the parameters that we measured on the laboratory scale needed to be up-scaled to the field scale in order to use it for field application, up-scaled equations and their corresponding parameters were derived in this project, using mathematical homogenization as up-scaling technique. Originally, the method was developed by mathematicians and was difficult to understand by practitioners. That is why it was not popular in the engineering environment. In this project we clarified the method and made it more appealing for engineers by including as much physical understanding as we can during the derivation of the up-scaled equations.

08 Please list the presentations held in connection to this project (refereed abstracts and conference papers)

- **Oral presentation, in 'Soil & Water' Netherlands Scientific Symposium 'Injection of oxygen-rich water as an arsenic remediation technique' TRIAS and SSEO, Zeist, 1-2 June 2005, Netherlands.**
- **Poster presentation + conference contribution in 7th International Symposium on the Geochemistry of the Earth's Surface (GES-7). Aix-en-Provence, France August 23-27, 2005.**

- **Poster presentation + conference contribution in the 5th International Congress on Environmental Geotechnics, Cardiff, Wales, UK, June 2006**
- **Oral presentation + conference contribution in the 10th European Conference on the Mathematics of Oil Recovery, Amsterdam, Netherlands. 24-27 Sep 2006.**

09 Please list publications (published and submitted) in connection to this project. Please indicate publication took place in either a refereed journal, a non-refereed journal (incl. conference proceedings); whether it was published as a chapter of a book, as a monography or as a dissertation.

Refereed Journals:

Darwish, M.I.M., V. van Beek, J. Bruining, 2005, In situ Arsenic removal using redox condition alteration: Visualization experiments, Journal of Geochemical Exploration, Vol. 88, January-March, 2006.

Refereed Conferences:

Darwish, M.I.M., J. Bruining, 2006, Upscaling of iron adsorption during arsenic remediation using homogenization, presented at the 5th international congress on environmental geotechnics, Cardiff, Wales, UK.

Bruining, J., Darwish, M.I.M., 2006, Homogenization for Fe^{2+} deposition near drink water tube wells during arsenic remediation, presented at the 10th European Conference on the Mathematics of Oil Recovery, Amsterdam, Netherlands.

10 Please list Patent applications or other professional products (including contracts, articles in the popular media, contributions to documentaries or scientific television or radio programs, CD-ROMS, DVD or other (electronic) media).

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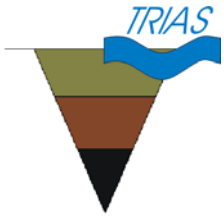


Part II

Detailed information, primarily intended for administrative and statistical use by NWO-ALW

11a Under item 5 you have filled in the main research objectives. Please list all the original research objectives as indicated in the project's application and both indicate as well as motivate, to what extent these goals were realised, and/or whether the original research objectives had to be adapted.

Due to unplanned change of researchers in the course of the project the main original objectives were somewhat changed.
The main original objectives of the project as formulated under 5) are:
1) This project (part II) uses the complex chemical understanding to construct models that describe the behavior of ….. in the soil on the core (cm-dm) scale.

This objective was met. Equations at core scale (i.e. scale of experimental measurements) were derived from the equations at pore scale (i.e. scale of grains). This was done utilizing the homogenization up-scaling method instead of the network modeling that was initially planned. This method was initially developed in the field of mathematics which makes it difficult to be understood by engineers. Therefore the mathematical homogenization method was not used intensively by engineers. During the derivation of the equations we tried, as much as we could, to include our physical understanding of the system and make the developments more systematic. We believe that we made the method accessible for engineers Initially, the plan was to use Network modeling in up-scaling pore scale equations to core scale equations but during the development of the project the decision was made to use the homogenization method instead. This is because the homogenization leads to model equations, instead of "numerical results", which still need to be translated into model equations. Another disadvantage of network models is that they require to impose intuitive rules at the node points. Our efforts led to a derivation and quantification of the dispersion coefficient and the influence of adsorption on the dispersion coefficient. We are presently extending the findings to a 3-D geometry and converting the ECMOR conference paper to a journal paper.

2) To adapt a set of experiments to the specific requirements of this complex problem in collaboration with our part I. The experiments reciprocally help to validate the developed models.

This objective was partially met. Initially, column experiments were performed as was planned. Later we realized that the amount of information that we can get out of these experiments is not sufficient to validate the developed model due to technical difficulties, keeping in mind the fact that we need to work under reduced conditions (i.e. oxygen free). Thus, innovative visualization cell experiments were designed in order to get more information and better control of experimental conditions. In these experiments it was possible to get information about the temporal and spatial ferrous iron concentration in a porous medium, pH and oxygen while injecting oxygenated water by monitoring the change of the color of iron compound with digital optical and image analysis techniques. The developed model was validated with the data obtained from the visualization cell.

11b Did the project also include objectives which were not scientific? For instance, did the project also intend to apply research results, or strengthen the economic position of certain businesses?

The knowledge acquired in this project is relevant for the development of subsurface aeration and cleaning technology for drinking water production. This perspective was a driving force to provide tools that may be used in order to develop technological solutions.

11c Did the project's aims include the expanding the (international) network of contacts (at what level), providing education, improve communication, serve as input for policy drafting or policy decisions, etc.? Please motivate.

The project formed a basis for participating in a international summerschool, where the results of the homogenization technique were presented. The summerschool was attended by European and American leading experts in groundwtare contamination.

12 Do the results obtained match the original objectives?
Please provide a short motivation why they do or don't.

Yes, to some extent, as motivated in 11a

13 Will the results of this project serve as input for an initiative integrating/and or generalizing input from several projects, for instance into a (numerical) model, or into more understanding at the higher/system level? If so, was this intended and optimised from the beginning or did it occur by chance/ spontaneous? Please elaborate.

To some extent the results of this project can be used as input for other projects since we tried to mimic the field conditions as much as we can and the up-scaled equations added more understanding at higher system level. Experimental difficulties and a change of researchers involved gave that project a new direction which has been focusing mainly on the in-situ (trans)formation of iron oxides due to injection of oxygen rich water. It has not been possible to study the corresponding interaction with As. Implementation of the surface chemical approach of the counter part group at Wageningen university is therefore premature at this moment.

14 To what extent has this research project pointed the way in which further research has to be undertaken? Please motivate the guiding role perceived.

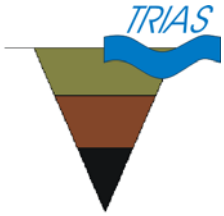
This research work pointed out that innovative experimental techniques, where non-destructive measurements methods and more control are used, are needed to maximize the amount of reliable data gained. Experimental techniques such as X-ray CT scanner, NMR and Dielectric measurements, can be used to detect the iron concentration in porous media but the methods should be optimized in order to improve the sensitivities of these techniques. These optimizations require parametric and sensitivity studies. The homogenization up-scaling method has a big potential in engineering application by incorporating the physical understanding of the system under consideration while developing the equations. Based on the results of the visualization cell experiments, local pH values changes will affect the oxidation and adsorption behavior of ferrous iron in porous medium and needs to be considered.

15 In what way, and to what extent, are the results reached of importance to research done by others? Please motivate or elaborate.

see 11a-2, this project has generated fundamental knowledge which is of great interest for geochemistry and geo-hydrology

16 Are you aware of any essential gaps or obstacles standing in the way of applying the results from your research project? Please elaborate.

See 14



Part II - continued

Detailed information, primarily intended for administrative and statistical use by NWO-ALW

17 Which new research questions were generated through this project?
Were these new questions addressed within this research project itself?
Or will these new questions, or the results from your research project lead to new research projects (to be) funded by either 1st , 2nd,or 3rd category funding or funding through international funding agencies? Please elaborate.

See 11a-2 and 14

18 In what way did you link this project to other projects within the TRIAS-program or link it to projects outside TRIAS? Did you cooperate within the TRIAS-program and did this cooperation lead to integrated results?

No explicit linkages with projects other than that of our counterparts have been made.

19 Can you elaborate on the impact on society as a whole of your results (e.g. societal organisations, NGO's, businesses, schools, municipal authorities, etc.)

The project has a rather fundamental approach that has achieved its scientific goals and is of direct relevance for other researches (see 15). The theoretical developments will contribute to valuable practical applications, but cannot be pointed out explicitly.

20 What actions were taken to disseminate the results in the direction of the general public, besides the usual scientific channels?

21 Have the researchers involved obtained a new position or employment after the project came to an end? Please specify and elaborate!

Not yet

Delft, October 2006

Our answers to the comments are:

Timo Heimovaara (oral):
- the report could be drawn up more positively, especially parts of section 05; many things have been tried, some failed. But it should be explained why it failed and what was learned from it. Not all the experiments have been mentioned and discussed in section 11a (no 2). Remind, a negative result is also a result!
Answ: We have added text to emphasize the positive findings of the project
- more attention should be paid to the chances of homogenization as an innovative and promising technique (see section 11a, no 1);
Answ: This is also done
- not has been proved if the system of in situ treatment of the groundwater by alternative pumping and injection would work in field conditions; in the small-scale experiment done it worked; next step should be a semi-field scale experiment like the sandbox experiment of Marian Langevoort in Utrecht or a real aquifer treatment;

Answ: It is the intention to extend the project in collaboration with the Faculty of Policy, Technology and management, where also Wageningen remains to be involved. Also there is now collaboration (Delft-Eindhoven-Utrecht) with Stutgart (Vegas facility) , which would make such a sandbox experiment possible. Possibly it is preferred to test method in the field.

Kees van Beek (translated):
In the Introduction of paragraph 05 is spoken about "Natural geochemical contamination through soil ..." This is somewhat strange, because is it possible to speak about "natural contamination" ? My suggestion is: "Disturbance of natural conditions led to mobilization of naturally occurring arsenic".
Furthermore, some editorial slipshods.
Kees would like to receive a copy of the publications!

Answ: We made the changes and sent the papers to Kees van Beek.

Jasper Griffioen (summarized and translated):
The report is not very clear. The project clearly suffered of a changing crew and a lack of tradition in environmental chemical research. On the one hand this led to charming non-traditional experimental and modelling approaches, but at the same time because of the necessary trial and error approach to a limited output. It is difficult to read from the report which knowledge has been achieved and can be used by others. But over all, Jasper can agree with it.

Answ: We tried to improve the quality of the report. We disagree that there is limited output. There are three conference papers and one journal paper. We are presently extending the ECMOR contribution to 3-D and then submit it for publication. This has been taken longer than we hoped, and for this reason we were not yet able to combine the results of Wageningen with the results of Delft.
We, however, believe that we made to major contributions: (1) the experimental methodology (which is published and can be used by the readers as is evidenced that many people have contacted us to get a copy of the paper. (2) We have made a important contribution by showing that homogenization is readily accessible for engineers and also given a computational procedure and example to calculate the dispersion coefficient and its dependence on adsorption.

Nico de Rooij will unfortunatelly not comment on the report, because he feels too remote. Sorry for this, but I can not change it!

Personally, I can agree with the report. I think it is a clear statements of what has been done, the difficulties met and the findings. But indeed, I agree with Timo that more could be said about the experiments and modelling approaches that failed and why. A summary in Dutch for the general public should still be added (paragraph 06). The textual slipshods should be corrected. I will add a copy with my corrections (in red).

Answ: We have made the corresponding corrections

About the project as a whole, personally I am somewhat disappointed that it has appeared not to be possible to come up with some common research or modelling approach with the counterparts in Wageningen. It is understandable because of the changes that were necessary and the experimentally difficulties met and I don't blame you for this, but still I feel it as a shortcoming of the common effort in the past five years.

Answ: The reason for this is not as much that the collaboration was achieved. The development of the theory of homogenization took longer than anticipated (as always). We think that we are able to wrap up the results and write a journal paper about this. We have submitted a proposal with Wageningen and Technical Policy and Management (TUD) to extend the project. The project gives he opportunity of a complete field application. A jioint paper delaing with homogenization including the findings of Wageningen can be expected.
In summary the project has led to excellent collaboration with Wageningen and joint publications in the near future are to be expected.

I would propose that you revise and complete the report according to the comments given and then dispatch it to Theo Saat (with a copy to me) for finalization of the project, scientifically and financially. I apologize for the delay in the handling-off.

Answ: Done

Finally, I would be happy to hear about any further research efforts in this field or that Mohamed will finish his commitment with this research and his future work.

Answ: See above. We have very much appreciated the way you have handled the supervision of this joint project and the open-mindedness with which we could always discuss and find solutions to problems that hampered the progress of the research.